VALERIU FILIP

INTRODUCTORY THERMAL PHYSICS

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Preface

Thermal Physics is one of the basic fields of study in the curricula of any sound training in Physical Sciences. Many of the concepts operating in this branch of Physics have also everyday homonyms. Therefore, it is always tempting for beginning students to overuse intuitive shortcuts in dealing with practical problems and to think with vulgar arguments. However, while intuition is definitely a basic tool for a physicist, it should clearly rely on a solid conceptual background.

The present set of lectures aims to develop the basic ideas and concepts of Thermal Physics for a beginning reader, starting from the intuitive counterparts of terms and adding the necessary amount of rigor needed for both an effective use in solving the practical work and in preparing for more advanced approaches of the field. The presented material assumes some basic knowledge of elementary physics and mathematics, at the usual level of high-school curricula. Nevertheless, it is essentially self-contained and includes some mathematical interludes on basic calculus, linear differential forms and elementary probability theory. At the end of every chapter a specialized bibliography and a set of exercises are offered. The exercises are intended for immediate practice on the topics treated in the corresponding chapter and are of various degrees of difficulty. Answers are provided to all of them. The most difficult problems are fully solved and hints are offered for the ones of intermediate difficulty.

The lectures, which are currently followed by the first year of English-speaking students at the Faculty of Physics of the University of Bucharest, can be profitably used by those studying any related technical field and even by interested terminal high-school students.

The Author

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1. Introduction

1.1 Macroscopic and microscopic theories

Physics is a science dealing with **experimental facts** that is with events which can be systematically reproduced by preparing each time analogous environmental conditions. The experimental facts are further organized in various theories attempting to fit our mental reasoning on the obtained experimental results.

Physical theories can belong essentially to two important categories: **microscopic** or **macroscopic**. Generally speaking, a macroscopic theory makes use of a restraint set of parameters, namely the ones which are more or less available to our direct senses. On the contrary, a microscopic theory may involve quite abstract representations (never met in our current sensitive experience) and therefore needs a much higher number of physical parameters.

Usually it is useful to attach both a macroscopic and a microscopic point of view to every field of physics. One particularly striking example in this sense is **The Physics of Thermal Phenomena**: it can be described both macroscopically, in the so-called field of **Thermodynamics**, and microscopically in **Statistical Physics**. Those two different theories are actually not completely distinct since they share the same starting points and the same purposes. There are also several shared physical parameters and concepts, which allow a close interaction between the two "thermal" theories.

1.2 Measurable and hidden parameters

It is now a very well established fact that every **macroscopic body** (that is a body whose presence may be evidenced through usual senses) is actually a system of a huge number (of the order of 10^{23}) of interactive **microscopic units** or **particles** (upon the case, these may be atoms, molecules, electrons, even virtual particles like phonons, which result from the quantization of the atomic lattice vibrations in a crystal lattice, or photons, that is confined electromagnetic field particles). These units are far from being still: they are in a permanent, rapid and apparently disordered motion. **The phenomena emerging from the motion and reciprocal interaction of the microscopic units of physical bodies are usually termed as thermal phenomena**.

It is almost obvious that the microscopic description of a macroscopic body would imply a gigantic number of parameters (for example the Cartesian components of the position and velocity of every microscopic unit). On the other hand, the direct study of such a system can be performed only by macroscopic instruments. Being essentially macroscopic entities, these instruments (even the most sensitive of them) are certainly unable to resolve the enormous complexity of the microscopic structure macroscopic bodies. **Any physical apparatus is a relatively macroscopic entity, whose operation is usually hindered by certain inertia during the measuring act**.

For example a membrane pressure sensor plunged in a gas cannot feel the individual collisions of the molecules with its membrane. Every molecular collision results in a momentum transfer towards the membrane, but those events repeat so rapidly that they cannot be followed by deformations of the membrane. In the same way, the molecular collisions are very "localized" events, so that the momentum transfer to the membrane is not at all homogeneous on all the microscopic regions of its surface. But the elastic properties of the membrane are never ideal and it cannot follow the spatial inhomogeneities of the forces applied by the gas molecules. Consequently, the membrane will undergo a constant and uniform average deformation.

Another possible example may be a temperature sensor plunged in a certain amount fluid. The molecules of the fluid hit the sensor's surface in a rapid sequence, transferring each time a certain amount of energy to it. But, usually, the collision frequency is so high and its spatial variations so localized that the sensor can catch only a space and time average of its energetic income.

One can thus conclude that the physical instruments can measure only certain (temporal and/or spatial) averages for the values of the parameters of the microscopic motion. This is a direct consequence of the gigantic number of the microscopic units of each macroscopic body and of their apparently disordered incessant motion. **Thus, the key idea is that any measurement replaces a great number of microscopic parameters by a representative mean value** (which may be looked at as a **macroscopic parameter** of the system). This observation is essentially the basis of the connection between the microscopic and the macroscopic description of thermal phenomena.

At this point we may distinguish two types of microscopic parameters. For one kind of such parameters, the values of the averages obtained through the measurement process strictly depend on the external conditions to which the system is subjected. These parameters are called **measurable parameters**. Their representative mean values are **not identically zero**. For the other type of microscopic parameters, the measurements give **always zero values** of the averages. They are termed as **hidden parameters** since they don't sow-up in a usual measurement process and no macroscopic parameter can be associated with them.

As an example of measurable parameter one may take the kinetic energy of the molecular translation in a certain macroscopic amount of gas. The corresponding macroscopic parameter will be the internal energy. Another example of macroscopic parameter resulting from an average on a microscopic measurable parameter is the gas pressure. Its measured values always result from an average of the projection of the translation molecular momentum on the direction normal to a certain wall, when only molecules running towards the wall are considered. Neither the value of the gas pressure nor the one of its internal energy can be identically zero. Also, both of them strongly depend on the external conditions imposed to the gas.

Examples of hidden parameters may be the momentum of gas molecules or the orientation of poliatomic molecules of a gas in the absence of any electric or magnetic external field and at high temperatures. For the first case, given the enormous number of molecules in permanent disordered motion, with a very high probability, each molecular momentum can be paired with the momentum of another molecule, which is equal in absolute value and opposite to the first. In this way the average momentum measured by a hypothetic macroscopic apparatus would always vanish. Obviously, the same can be said about the angular orientation of the poliatomic molecules of the aforementioned gas.

It must be stressed here that, despite the fact that hidden parameters don't show up in macroscopic measurements, their simple existence brings a decisive influence on the macroscopic behavior of the considered system.

1.3 The main purpose of Thermal Physics

The Physics of Thermal Phenomena (or shortly Thermal Physics) is mainly concerned with the macroscopic consequences of the existence of hidden parameters of systems. This statement is essentially correct, but it should not be taken as exhaustive. It is sufficient for a beginner, but the more advanced student may easily find many other useful targets of this field of study. Generally, in **Thermodynamics** one tries to take into account the influence of the hidden parameters by defining some specific **thermodynamic state functions** and by establishing their relation with the other state functions of the given system. On the contrary, **Statistical Physics** starts from a microscopic description of the system, into the frame of some suitable dynamics (classical or quantum) and, making use of the **concept of probability**, computes various averages which can be compared with the results of some macroscopic measurements.

Both the starting points and the interpretation of the results of Statistical Physics imply the use of some fundamental thermodynamic concepts. This is the reason for which a study of Thermal Physics should begin with the macroscopic point of view, namely with Thermodynamics. Nevertheless, the microscopic point of view proves frequently essential for a thorough understanding of thermal phenomena. Thus, the ideas of Statistical Physics will be introduced as soon as possible in order to allow the treatment of the main applications from both points of view.

1.4 Some fundamental concepts of Thermodynamics

a) **A <u>thermodynamic system</u> is a set of macroscopic entities (including possibly radiation fields) that can exchange energy among them even if they don't interact either by some ordered (macroscopic) way or by mass exchange**.

This definition needs some supplementary explanations. First, by **macroscopic entity** we mean a region of space that contains a very large number (of the order of the Avogadro's number: $N_A = 6.0221 \cdot 10^{23}$ mol^{-1}) of identical microscopic units. Then the **interaction by some ordered (macroscopic) way** includes mechanical interactions (resulting in macroscopic deformations of the system), or interactions with some external fields (electric, magnetic, gravitational, …) acting systematically on all the microscopic units of the system.

One may already observe that the interactions between the components of a thermodynamic system and (as it will be further discussed) between the thermodynamic systems themselves, **reduce uniquely to energy exchanges**. This special role of the energy is really fundamental both in Thermodynamics and in Statistical Physics and is a consequence of the tacit hypothesis that thermodynamic systems are considered to be fixed in the reference frame of the laboratory. Thus, the various interactions of the thermodynamic system can change only its energetic content. Nevertheless, there are important generalizations (which are useful mainly at an astronomic scale) which take into account the variations of all the integrals of motion of the system (including the total momentum or the total angular momentum). No such generalizations will be considered in this introductory set of lectures.

The definition of the thermodynamic system includes another fundamental idea: the possibility of the energy exchange between systems through some special mechanism, different from both macroscopic and mass exchange interaction types. This new type of interaction uses the disordered motion of the microscopic units as an energy exchange mechanism. Tiny amounts of energy are exchanged during each interaction between microscopic units. They result in a macroscopic energy transfer which may take place only at the interface between the two systems (and thus imply their direct physical contact). This type of energy exchange is called **thermal interaction**. It occurs significantly (and should be taken into account) only in thermal phenomena. **Therefore a thermodynamic system may be defined as a collection of macroscopic entities which are able to exchange energy through thermal interaction**.

The exterior (or environment) of a thermodynamic system is the rest of bodies not included in the system (and with which it is supposed to interact). The reunion between the system and its exterior represents the **thermodynamic universe**.

Very often the necessity dividing the studied thermodynamic system into two or more parts occurs. This operation is called **thermodynamic decomposition**. Since the thermal interaction is supposed to exist in the initial system, all the other parts resulted from the division should have the same property and have to be considered automatically as thermodynamic systems. As opposed to the thermodynamic decomposition, one may also consider the **thermodynamic reunion** of two or several thermodynamic systems. However, **the thermodynamic reunion is possible uniquely if the initial systems are able to interact thermally with one another**. Otherwise the obtained system will not be thermodynamic. The thermodynamic reunion of two such systems A and B will be denoted by A∪B.

b) **A <u>simple thermodynamic system</u> is a thermodynamic system consisting of homogeneous and isotropic macroscopic parts, which are neutral from both the electrical and chemical point of view**. While this definition does not explicitly exclude the influence of external fields on the system, the requested homogeneity and isotropy properties imply the **absence of strong external force fields** which could produce preferred directions or bunches of matter into the system. This would make some properties of the system position dependent (*the definition actually requires that the homogeneity and isotropy properties hold at least over macroscopic parts of the system*). For example, if a uniform gravitational field is being acting on the system, the mass density may vary along the vertical axis and thus the homogeneity of the system would be destroyed along this axis. Therefore, the vertical axis becomes a privileged one and the system will cease to be isotropic. Nevertheless, it is obvious that it is impossible to literally wipe out the inhomogeneities induced by external fields acting on a system. One can only hope to make setups leading to negligible action of these fields (for example by taking conveniently small macroscopic pieces of a given system in an external field, so that the ordering action of the field to be neglected). From this point of view, the concept of simple thermodynamic system is merely an ideal one which helps reasoning in thermodynamics (since the number of thermodynamic quantities needed to describe a simple system is very reduced). Usually, a small amount of normal fluid best matches the requests for being a simple system and, for this reason, when speaking of a simple system we'll think about **an amount of fluid** in what follows. The characteristics of such a simple system may be thus described by its pressure (P), volume (V), temperature (T) and mass (m). More complicated systems, like those acted upon by external fields may be treated as composed of several interacting simple systems.

c) In order to analyze a given thermodynamic system, one has to choose a set of physical quantities (macroscopic parameters), which may completely describe its properties. This is a purely heuristic step, for which no recipe can be given. Among the characteristic parameters of a system, one can always find a minimal set which are independent of each other. This minimal set has to provide all the thermodynamic information on the system. By giving a compatible value for each parameter from the minimal set, one says that a **<u>thermodynamic state</u>** of the system was established. The macroscopic parameters of any system can take different values in different states. They are thus called **state parameters**. The obtained values of the state parameters come from averages over some microscopic parameters of the system, whose values establish the **microscopic state** of the system. As several different sets of numbers may give the same average, **to each macroscopic (thermodynamic) state it usually corresponds several (ordinarily a very high number!) of microscopic states**.

d) If the values of the state parameters of a thermodynamic system are constant in time, then the corresponding state of the system is an **equilibrium state**. For a simple system, *the parameters should also take definite values at equilibrium* that is *they have to be homogeneous and isotropic properties of the system*.

e) Any change of the thermodynamic state of a system is called a **thermodynamic transformation** or a **process** of the system. The thermodynamic processes can be classified in three categories: natural, unnatural (or abnormal, or anomalous) and reversible [1, 2]. A **natural process** begins and ends always in equilibrium states of the system. A process during which the system leaves spontaneously an equilibrium state for some other states which are not of equilibrium is called **unnatural** (or **abnormal**, or **anomalous**). During a **reversible process** the system passes only by equilibrium states (not only the initial and final ones are equilibrium states). The reversible process is actually an **ideal limit of a natural process**. If such a reversible process is followed in one sense and then in the reverse sense, then no change occurs in the thermodynamic universe. By opposition to the reversible processes, the natural processes are often termed as **irreversible**.

A process whose initial and final states coincide is a **cyclic process** or a **thermodynamic cycle**.

***Comments*:**

1) For a thermodynamic system to undergo a process it is necessary that at two different times at least one macroscopic quantity of the system have different values. Take for example the case of two amounts of ideal gas separated by a removable wall. When the separation is removed, the gases began to mix through the chaotic motion of molecules (diffusion). This may be looked at as a process as long as the two initial gases differ at least by one macroscopic parameter or by the nature of the molecules (even if this difference in nature is very weak, as is the case of two isotopes). However, if the two gases are not initially distinguishable, then no thermodynamic process occurs when the separation wall is removed.

2) The natural and unnatural processes are the only one that a thermodynamic system can really undergo. For example, the unnatural processes can be produced by random fluctuations of the parameters of an equilibrium state. On the contrary, the reversible processes may never be real. For

certain real processes, the reversibility can be approached with great accuracy, but the intermediary states are never perfectly equilibrium ones. From this point of view, the concept of reversible process is of the same nature as the one of simple thermodynamic system. They play a formal role in Thermodynamics, analogous to the role of the mass point concept in Mechanics.

3) A reversible process has necessarily to be conceived as a very slow one, in order to allow the macroscopic parameters of the system to attain the definite values of each intermediary equilibrium state. A process proceeding slowly is called **quasi-static**. But a general quasi-static process should be clearly distinguished from a reversible one: **a quasi-static process is not necessarily a reversible one**. As a typical example, take the diffusive mixing of two ideal gases. Making the temperatures and the pressures of the two gases to coincide, the overall temperature can be lowered as much as possible so as the diffusion process can proceed as slowly as desired. But, as it will be further demonstrated through the Second Law of Thermodynamics, the diffusion process is essentially an irreversible one. This is a consequence of the fact that, even if almost all the parameters are always well defined in the system, the chemical composition will permanently depend on the position until the mixing is completed.

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2. Zeroth Law of Thermodynamics. The concept of empirical temperature.

2.1 Zeroth Law

The possibility of thermal interaction between different thermodynamic systems allows the flow of energy from one system to another, even in the absence of other types of interaction. In order to describe and control the energy flow during the thermal interaction between different bodies, one has to classify them upon some characteristic feature (parameter). For example, the warm and cold physiological sensations during some thermal interaction (contact) of one's hand with a foreign body are obviously connected with the flow of energy towards and, respectively, outwards the human skin. Thus, in everyday life, one can classify bodies upon the intensity of the sensation produced by the thermal contact between the skin and each of the studied bodies: one can readily distinguish between hotter and colder. The term "temperature" is normally used to make this distinction clearer. While the concept can be readily extended to non-physiological purposes, its use in Physics should be preceded by a sound definition. The necessary logical framework for this enterprise is offered in Thermodynamics by the so-called Zeroth Law. This law consists essentially of a couple of sentences representing the synthesis of an enormous amount of experimental data. To analyze all the way by which these experimental data became Zeroth Law needs a lot of space and may deviate the reader's attention from our main target: the operational presentation of the main frame of Thermodynamics. For this reason we content here to only state the Zeroth Law and to discuss its consequences. Before doing this we shall first introduce two more very useful concepts.

We already stated in the introductory lesson that, given two thermodynamic systems A and B which are allowed to interact thermally, their reunion $A\cup B$ is also a thermodynamic system. If the united system $A\cup B$ is in an equilibrium state then we say that A and B are in a **relative thermodynamic equilibrium**. [1,2]. Further suppose that the two systems can interact *through the thermal way only* (that is the mass exchange or any ordered macroscopic interactions are turned off). In this case, the relative thermodynamic equilibrium of the systems A and B is called **thermal equilibrium**. The concept of thermal equilibrium is usually extended to couples of systems which are not necessarily in contact. *If two thermodynamic systems would be in thermal equilibrium when placed in thermal interaction, then, even if they have no actual physical contact, they are still considered as being in thermal equilibrium.*

The two parts of the Zeroth Law are the following:

a) **<u>The uniqueness of the thermodynamic equilibrium state of a system placed in some fixed external conditions</u>: if a thermodynamic system is placed in a given fixed environment then, after some characteristic time, its characteristic macroscopic state parameters reach a unique set of values which define a unique equilibrium state.**

b) **<u>The transitivity of the thermal equilibrium</u>: Let A, B and C be three thermodynamic systems. If A and B are in thermal equilibrium and if the same is true for B and C, then A and C should be also in thermal equilibrium. Moreover, a real function τ(A,B) can always be defined on the set of ordered couples of states of thermodynamic systems so that τ(A,B) = 0 if and only if A and B are in thermal equilibrium.**

Comments:

1) In the notation τ(A,B) *each argument actually represents the set of values of the characteristic state parameters of the system in the given state*. The symbols A and B are used here for convenience and thus the systems they represent *need not be distinct: A and B can represent two different states of the same system*. From the same point of view, the condition τ(A,B) = 0 does not mean that A and B are in some effective thermal interaction. It should merely be interpreted as *the possible thermal equilibrium of A and B if they were placed in thermal contact*.

2) The second part of the Zeroth Law actually introduces an equivalence relation among the set of all possible thermodynamic sates of the thermodynamic systems. The transitivity of the relation is postulated in this statement while its reflexivity (τ(A,A) = 0) and its commutativity (τ(A,B) = 0 $\Rightarrow$ τ(B,A) = 0) follow from the previous comment and from the definition of the thermal equilibrium.

2.2 The empirical temperature

Let us take consider a certain thermodynamic system (denoted for example by X) to be fixed. One can always choose for this role a conveniently constrained simple system so that its equilibrium states may be described by the values of only one significant macroscopic parameter. Let's denote by θ_X a generic value of this parameter. As examples one may consider a liquid closed in a small glass bulb continued with a (closed) capillary glass pipe or a fixed end bimetallic strip (that is a couple of tightly bonded strips made of different metals, with different expansion coefficients, allowing the bending of the system upon heating). In the first case, the liquid can change only the distance over which it penetrates the capillary pipe and in the second case only the orientation of the bimetallic strip can change. So, the proper state parameters for the two considered examples are the length of the liquid column into the capillary and the orientation of the bimetallic blade, respectively.

For every state θ_X of the system X and for some other system A one can find a set of states of A (namely A', A'', A''',…) that are "in thermal equilibrium" with θ_X, that is $\tau(\theta_X$,A') = 0, $\tau(\theta_X$,A'') = 0, $\tau(\theta_X$,A''') = 0,… Similar considerations can be made for any other thermodynamic systems B, C,…: for each one of them a collection of states exists there (B', B'', B''',… for B, C', C'', C''',… for C, etc) so that one may write $\tau(\theta_X$,A') = $\tau(\theta_X$,A'') = $\tau(\theta_X$,A''') = … = $\tau(\theta_X$,B') = $\tau(\theta_X$,B'') = $\tau(\theta_X$,B''') = … $\tau(\theta_X$,C') = $\tau(\theta_X$,C'') = $\tau(\theta_X$,C''') = … = 0. In other words the state θ_X defines a *class of states* of different thermodynamic systems which are (or may be) in thermal equilibrium with it. Each possible value of θ_X defines one such class of states. Taking into account the comments of the preceding section, one can see that the defined sets are actually equivalence classes (since they are generated by an equivalence relation). In this way **the set of all possible thermodynamic states can be spanned into equivalence classes determined by the values of the real parameter θ_X**.

The obtained equivalent classes are disjoint. Indeed, suppose that a given state A belongs to two different classes θ'_X and θ''_X ($\theta'_X \neq \theta''_X$). It follows that $\tau(\theta'_X, \mathrm{A}) = 0$ and $\tau(\theta''_X, \mathrm{A}) = 0$. From the Zeroth Law, this imply that $\tau(\theta'_X, \theta''_X) = 0$. Since θ_X is the only parameter that describe the macroscopic state of X, it follows that the states θ'_X and θ''_X are identical and thus $\theta'_X = \theta''_X$, which contradicts the hypothesis.

The value of θ_X corresponding to each equivalence class of thermodynamic states is termed as **the empirical temperature of the class**. The thermodynamic system X, taken as a "reference", is called a **thermometer**.

A practical problem arises from the preceding definition of the empirical temperature: since the value of the empirical temperature is essentially the value of the unique macroscopic state parameter of the thermometer, it follows that the concept of empirical temperature strongly depends on the very nature of the thermometer. Different numerical values will correspond to the same temperature if one uses different kinds of thermometers: some length of a liquid column in a liquid expansion thermometer, some deviation angle in a bimetallic strip thermometer, some value of the gas pressure in a constant volume gas thermometer, or some voltage in a thermocouple-based thermometer. In order to remove the uncertainties brought in by the previous definition of the empirical temperature the scientific community agreed with a specific convention in 1954 [3]. The empirical temperature was then defined as (the so-called **ideal gas temperature**):

$$T_X = \frac{\theta_X}{\theta_{X3}} \cdot 273.16\,K, \tag{2.1}$$

where 273.16 is the value associated with the temperature of the state of **the triple point of pure water**. The unit K of the empirical temperature was chosen after the name of Lord Kelvin and **represents 1/100 of the temperature interval between the melting point of pure ice at normal atmospheric pressure and the boiling point of pure water at normal atmospheric pressure**. θ_{X3} is the value of the state parameter of the thermometer X, taken at the triple point of pure water. The reference state of the triple point of pure water represents the state where the solid, liquid and gaseous states of pure water coexist in thermodynamic equilibrium. It will be further demonstrated that for a pure substance **such a state is unique**. Moreover, from the practical point of view, this state is easily and perfectly reproducible.

The index X of T defined by Eq. (2.1) shows that this temperature still depends on the nature of the thermometer. Indeed, if the temperature defined by Eq. (2.1) were universal (thermometer independent), then it would follow that only linear and homogeneous relations might be possible between all the conceivable thermometer state parameters θ_X. This is definitely not the case as readily becomes clear if one takes only the example of the thermistor and thermocouple-based thermometers (for another example see also Exercise 2.1). Nevertheless, as it will be further demonstrated, a universal (thermometer independent) temperature can be defined in connection with the Second Law of Thermodynamics. Thus, the ideal gas temperature may be looked at as a practical approximation of this universal temperature.

The value of 273.16 K for the empirical temperature of the triple point of pure water has historical roots. Before using the standard Kelvin temperature scale the Celsius scale was defined (and is still in frequent use). The relation between the two scales is the following (as defined by the International Committee of Weights and Measures):

$$t_X = T_X - 273.15 \tag{2.2}$$

and this gives **equal units** for them. Only the notation is different: ^{0}C for the Celsius scale. The Celsius scale was based on two fixed points (states): the melting point of pure ice at normal atmospheric pressure (for which the 0 ^{0}C value was associated) and the boiling point of pure water at normal atmospheric pressure (for which the 100 ^{0}C value was associated). Equation (2.2) resulted from the researches on perfect gases. For example, the study of a constant volume process of a given amount of gas showed a linear behavior of the gas pressure as a function of Celsius temperature, around the standard conditions of a perfect gas. The extrapolation of the linear diagrams thus obtained gave the same intercept on the temperature axis at zero value of the pressure, irrespective of the nature of the gas under study: - 273.15 ^{0}C. Thus, the idea of a universal temperature scale appeared and the value of - 273.15 was taken as its origin. Further researches revealed that this scale is far from being universal and a new fixed point was adopted in the much better reproducible triple point state of pure water, at 0.01 ^{0}C. The scale defined by Eq. (2.2) works now as a unitary empirical temperature, but with T_X defined by (2.1). Eq. (2.2) serves only as a relation between the ideal gas scale and the Celsius scale. Nevertheless, to the universal (thermodynamic) temperature (that will be further defined in connection with the Second Law of thermodynamics) the same Kelvin scale is attached.

Bibliography

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Exercises

2.1 Find what would be assigned to the temperature of boiling water if one used CO_2 in a constant volume thermometer instead of an ideal gas, assuming that CO_2 ($\upsilon = 500\ \text{cm}^3\text{g}^{-1}$) obeys the van der Waals equation (p in atmospheres, υ in cm^3g^{-1}):

$$P = \frac{1.8654 \cdot T}{\upsilon - 0.973} - \frac{1861}{\upsilon^2}.$$

Hint/Answer: The pressure in a constant volume ideal gas thermometer is the empirical temperature, so that (2.1) holds rigorously. By using this relation when the pressure is given by the van der Waals equation, one would obtain: $T_{bp} = \frac{P(\upsilon,373.15)}{P(\upsilon,273.16)} \cdot 273.16K = 373.88$ K = 100.73 ^{0}C.

2.2 When the ice point and the steam point are chosen as fixed points with 100 degrees between them, we have for their Kelvin temperatures T_i and T_s

$$r_s = \frac{T_s}{T_i} = \lim_{P \to 0} \frac{P_s}{P_i},$$

where P_s and P_i are the pressures read on a constant volume thermometer at the steam point and at the ice point respectively; thus

$$\frac{T_s - T_i}{T_i} = \lim_{P \to 0} \frac{P_s}{P_i} - 1; \quad T_i = \frac{100}{\lim\limits_{P \to 0} \frac{P_s}{P_i} - 1}.$$

Suppose that the limit r_s can be determined only with an accuracy dr_s:

(a) Show that the fractional error in T_i produced by an error dr_s in r_s is very nearly

$$\left|\frac{dT_i}{T_i}\right| = 3.73 \left|\frac{dr_s}{r_s}\right|.$$

(b) Any ideal gas temperature can be written $T = T_i \cdot r$, where $r = \lim\limits_{P \to 0} \frac{P}{P_i}$ at constant volume. Show that the maximum fractional error in T is $\left(\frac{dT}{T}\right)_{max} = \frac{dr}{r} + 3.73 \frac{dr_s}{r_s}$.

(c) Now that there is only one fixed point, show that the fractional error is $\frac{dT}{T} = \frac{dr}{r}$, where $r = \lim\limits_{P \to 0} \frac{P}{P_3}$, P_3 being the pressure read on the constant volume thermometer at the triple point of water.

Hint/Answer: (a) Since we have $T_i = \frac{100}{r_s - 1}$, it follows that $dT_i = -\frac{100}{(r_s - 1)^2} dr_s$, so that $\frac{dT_i}{T_i} = -\frac{dr_s}{r_s - 1} = -\frac{r_s}{r_s - 1}\frac{dr_s}{r_s}$. As $r_s \cong \frac{373}{273}$, it follows that $\left|\frac{dT_i}{T_i}\right| = 3.73\left|\frac{dr_s}{r_s}\right|$. (b) $dT = r\,dT_i + T_i\,dr$; then $\frac{dT}{T} = \frac{dT_i}{T_i} + \frac{dr}{r}$ and $\left(\frac{dT}{T}\right)_{max} = \frac{dr}{r} + 3.73\frac{dr_s}{r_s}$. When the ice and steam points are used as fixed points, the error in r_s, that is the error in the determination of the Kelvin temperature of the ice point, comes into any measurement of the Kelvin temperature. (c) With one fixed point, T is defined as $T = 273.16 \cdot r$, thus $\frac{dT}{T} = \frac{dr}{r}$.

2.3 A platinum resistance thermometer is calibrated at the ice ant steam points. The values of resistance found were $R_i = 105.2\ \Omega$ and $R_s = 146.4\ \Omega$.

(a) What would be the value of the resistance at 50 ^{0}C on the linear platinum centigrade scale $R = R_0(1 + a\,t)$?

The temperature variation of the resistance of platinum is better represented by the quadratic formula

$$R = R_0\left(1 + a\,t + b\,t^2\right)$$

where R_0 is a constant, t is (Celsius) temperature and a and b have the values $a = 3.98 \cdot 10^{-3}$ K^{-1} and $b = -6.04 \cdot 10^{-7}$ K^{-2}.

(b) What would the value of R be at 50 ^{0}C?

(c) Roughly what error is involved near 50 ^{0}C in taking the resistance to vary linearly with the temperature?

(d) In view of the accuracy of the measurements, is it worth using the more accurate formula?

Answers: (a) 125.8 Ω; (b) 126.0 Ω; (c) 0.5 K

3. The concept of internal energy and the First Law of Thermodynamics.

3.1 Extensive and intensive parameters.

Let π be a thermodynamic parameter and $\pi(A)$, $\pi(B)$ its values for some equilibrium states of two thermodynamic systems A and B, **which are in relative thermodynamic equilibrium** (their thermodynamic reunion, A∪B, is thus implicitly supposed as possible). If one may write $\pi(A) + \pi(B) = \pi(A \cup B)$, then the π is termed as an **extensive parameter**. The typical example is the *mass of the system* or (except for some special situations arising in connection with quantum gases) *the number of particles in the system*. Very frequently *the volume* is also taken as an extensive parameter but this is actually true only for specific conditions. For systems which are able to keep their distinct volume following the reunion, the affirmation is correct. Nevertheless, for a mixture of two ideal different gases, for example, the volume is no longer an extensive parameter. For this case one gets $V(A) = V(B) = V(A \cup B)$, since both gases occupy the same recipient and are not hindering each other.

If, for some thermodynamic parameter π one gets $\pi(A \cup B) = \pi(A) = \pi(B)$, then the π is termed as an **intensive parameter**. As most noticeable examples one may take the temperature in a fluid. The pressure in a fluid is also frequently considered as an intensive parameter. But if one takes again the previous example with the gas mixture, the pressure in the unite system will be obviously the sum of the "partial" pressures of the components (Dalton's Law) and thus pressure actually appears here as an extensive parameter. In conclusion, the extensivity or intensivity of a thermodynamic parameter should be carefully verified in each particular case.

3.2 Variations of state parameters

Let π_1 and π_2 be two values that a thermodynamic parameter π take in two equilibrium states of a given system, at the beginning and at the end of a certain process, respectively. Then the difference $\Delta\pi = \pi_2 - \pi_1$ is called **the variation of the parameter π** during the specified process. If one has $|\Delta\pi| << |\pi_{1,2}|$ so that the quantities $\left|\frac{\Delta\pi}{\pi_{1,2}}\right|^2$ be negligible in the computations, then the variation of the parameter π is termed as an **infinitesimal** one. Usually the notation $\Delta\pi$ is replaced by $d\pi$ in such cases. A process during which the parameters of a thermodynamic system undergo infinitesimal variations is an **infinitesimal process**.

3.3 *The concept of internal energy*

By **internal energy** of a **simple** thermodynamic system we understands **an extensive parameter of state that equals the sum of the individual energies of all the microscopic units (particles) as measured in the center of mass referential, including the reciprocal interaction of the particles**. The typical notation for this parameter is *U*.

It is already known from Mechanics that the general concept of energy can be defined only up to a undetermined additive constant. Thus, by defining the internal energy of a thermodynamic system one implicitly admits the same constraint: **only the variations of the internal energy are actually measurable quantities**.

As was already stated in the introductory lecture, the interactions between thermodynamic systems are supposed to reduce essentially to energy exchanges. Thus, only energy flows can take place between systems during thermodynamic processes. Actually this hypothesis works well only when the involved processes connect equilibrium states of the systems. The theory developed on this fundamental statement is called **Equilibrium Thermodynamics**. Nevertheless, non-equilibrium states for a system and processes connecting this kind of states can be defined. Beside energy, the interacting systems can exchange other integrals of movement (like momentum or angular momentum) during such processes. This kind of phenomena belongs to the field of **Non-equilibrium Thermodynamics**. Since their study is generally more involved it will be avoided in the present beginner's addressed lecture course.

Only energy interactions will be allowed between systems during thermodynamic processes. As was already noticed several different mechanisms for energy exchange are possible. Each such mechanism defines what we shall call an **interaction (or communication) channel**. One may first distinguish the **work type channel** through which a system exchanges energy in some ordered macroscopic manner: by some macroscopic deformation or by a uniform thorough action of an external field. The work type channel can thus be further divided into a **mechanical work channel**, an **electrical work channel**, a **magnetic work channel** and so on, upon the nature of the macroscopic action on the system. When a volume variation of the system occurs then we speak about a mechanical work and when the system undergoes a global electrical or magnetic action, then an electrical or magnetic work measures the corresponding energy exchange. For simple thermodynamic systems only the mechanical work channel will be considered and the energy exchange through it will be termed shortly as work.

As was also stated in the definition of thermodynamic systems, energy can be exchanged through the specialized disordered (or thermal) interaction. This kind of interaction defines the **thermal channel** for energy exchange. The energy exchanged through this channel is called **heat**.

Finally, since every particle (microscopic unit) of a thermodynamic system wears a certain amount of energy with which it contributes to the total energy of the system, exchange of energy is also possible through particle exchange (or mass exchange) between systems. This kind of interaction defines the so-called **chemical channel** and the energy exchanged through it is correspondingly denoted as **chemical work**.

The most frequently used notations for the amounts of energy exchanged through each type of channel are W for the mechanical work, M for the chemical work and Q for heat. It should always be remembered that the amounts of energy flowing through each channel are essentially *variations* of the internal energy of the considered system and consequently should wear positive or negative signs. The convention used in the following lectures is that each work or heat has *positive values* only if the corresponding energy flow is *directed towards the system*, that is if it determines the increase of its internal energy. *Outwardly directed energy flows* will result in *negative values* for the corresponding work or heat.

***Important remark*:** As was already defined, the extensivity of the internal energy means that, if A and B are two thermodynamic systems which are (or could be) placed in thermal contact, then $U(\mathrm{A} \cup \mathrm{B}) = U(\mathrm{A}) + U(\mathrm{B})$. Strictly speaking, this equality cannot be applied for two interacting systems A and B (irrespective of their nature: thermodynamic, mechanical, nuclear, electric etc.). One should always include in the total energy of the reunion some amount of **interaction energy**. As a general rule, when the interaction is strong energy amounts comparable with the energies of the interacting systems can be exchanged in very short time. Such systems cannot be treated as separate entities: they should be looked at as a unique indivisible system. Thus, **the extensivity of the internal energy in thermodynamics actually implies that all possible interactions between two different systems should be supposed as sufficiently weak**. The interaction energy between systems is usually termed as a **perturbation** and one can safely neglect it with respect to the systems' internal energies. This by no way means that the total amount of energy exchange between interacting systems is small. On the contrary, during various processes, the energy exchanges may be very often of the order of magnitude of the internal energies. The possibility of such consistent energy exchanges during such weak interactions can be assured only if **the processes are sufficiently slow**. So, when dividing a thermodynamic system into subsystems, one should make sure that their interaction is weak enough to allow them to be treated as separate entities. This hypothesis frequently works when the systems interact only through some definite boundary (like two pieces of metal placed in thermal contact). Usually the number of boundary particles are several orders of magnitude fewer than the number of particles in the bulk and their relative fraction should be comparable to the ratio of the energy exchanged at the boundary to the energy of the bulk. The same can be said in some boundary-less interactions, as is the case of two amounts of ideal gas mixed together in the same vessel: the molecular interactions are so weak and un-frequent that the interaction energy between the two gases can be completely neglected as compared o their internal energies. Imagine now that one of the two gases is positively ionized and the other consists in free electrons only (that kind of mixture is called plasma). Keeping this mixture at some high pressure, the interaction between the two gases is far from being weak. Consequently, no separate treatment is possible for the two components. Only for low pressure plasmas it may be possible a separate study of the electron and ion gases.

3.4 The mechanical work

Several operational expressions for the mechanical work will be obtained in this section. It has to be stressed from the beginning that there is no universal expression for it, which could fit all the possible situations. The forms that will be obtained here refer to some frequent experimental setups and each of them has to be adopted as a postulate: only heuristic motivations can be constructed to obtain these forms. Moreover, every expression for mechanical or chemical work refers only to **reversible processes**. Indeed, these expressions imply state parameters of the system whose values are well defined only in equilibrium states. Thus the referred process should be a sequence of only equilibrium states, that is a reversible process.

The origin of the concept of mechanical work is certainly placed in Mechanics where the work of a certain force during an infinitesimal displacement of its application point is defined as the scalar product of the force by the infinitesimal displacement. Since such an infinitesimal work means an infinitesimal energy transfer (which is an additive quantity by definition), the work along a certain trajectory will be a sum (integral) over all the infinitesimal works along the trajectory:

$$W_{mech} = \int_{trajectory} \vec{F}(\vec{r}) \cdot d\vec{r} \, .$$

Among the large variety of practical cases, some particular situation may be of interest for the following lectures or may arise in problems. We shall thus consider them in some detail.

a) The first and very important example is that of **the work on a certain amount of fluid** during an infinitesimal process. Obviously, in this case it is not possible to punctually apply a force on the system. Instead the external force should be spread on a certain rigid surface that we usually call **piston**. It follows that the tangential component of the force have no relevance for the action on the fluid and all that matters is the component of the force normal to the piston surface. The reaction of the system should always balance the external action in order to maintain the equilibrium (that is to perform a reversible process; see Figure 3.1). If the action of the force is an infinitesimal outward displacement *dx* of the piston then the internal force produces a positive work on the exterior of the system. Thus our system transfers some amount of energy towards its exterior and **the**

corresponding energy flow has to be negative: $\delta W = -|F|\cdot|dx|$. The volume of the fluid undergoes a positive variation from V to $V + dV$, where $dV = S\cdot|dx|$ and S is the piston area. By multiplying the expression of δW by $S/S = 1$ and by taking into account that $|F|/S$ is the pressure P in the system, one obtains:

$$\delta W = -P\,dV\,. \tag{3.1}$$

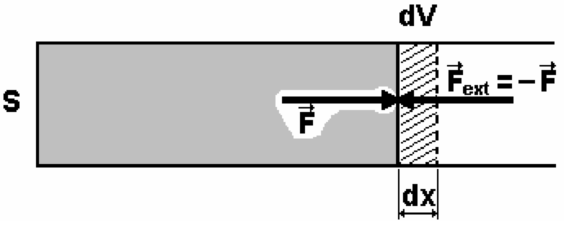

Figure 3.1

If the displacement of the piston would be towards the interior of the system then this one should receive a **positive** amount of energy equal to $\delta W = +|F|\cdot|dx|$. But the volume variation $dV = -S\cdot|dx|$ would be negative and this actually leads to the same expression for δW. In Eq. (3.1) the pressure plays quite the same role as the force in the expression of the mechanical infinitesimal work of a force. *The pressure actually measures the reaction of the system to the external tendency of modifying its volume*. **The pressure is thus an intensive parameter of the system**. As is the case in mechanics, the value of the pressure in Eq. (3.1) is conveniently taken at the beginning of the interval $[V, V + dV]$, that is P means $P(V)$. It is obviously possible to change this convention for any value of the pressure in the aforementioned interval, but the integration process that leads to the total work in a macroscopic process will certainly give the same result: for an integrable function, the value of the integral on a certain interval does not depend on the division procedure of the interval.

b) A second example is **the elastic wire**. Taking an infinitesimal elongation dl of the wire, the elastic stress produces a negative work (since it opposes the elongation). The external force makes thus a positive work providing the system with a certain amount of energy. Consequently, if ***F*** **is the absolute value of the elastic force**,

$$\delta W = F\,dl\,. \tag{3.2}$$

The absolute value of the elastic force represents here the measure of the reaction of the system to the external tendencies of deformation and is an intensive parameter. Indeed, if a couple of wires are bounded together to form a longer one and if the system is stretched by an external force, then the mechanical equilibrium condition requires that the same elastic force arise in each of the wires.

c) Another example is the **work of torsion** on a torsionally elastic rod. This situation resembles the preceding one in the sense that if the external torque produces a torsion with an angle $d\theta$, then the system **receives from the exterior** a certain amount of energy. The corresponding work will be thus given by:

$$\delta W = M_{el}\, d\theta\,. \tag{3.3}$$

where M_{el} represents the absolute value of the elastic torque of the rod. This quantity, which is also an intensive parameter, represents here the measure of the reaction of the rod to the external tendencies to increase its energy by torsional deformations.

d) When the thermodynamic system wears some electric charge its electric interactions with the environment should be taken into account. Suppose first that the system is some piece of conductor charged with some amount of positive electricity. If a tiny charge increase dq occurs as a result of the external interactions, then the energy of the system increases by the amount $\Phi \cdot dq$, where Φ is the electric potential of the conductor. Thus the electrical work should be given by:

$$\delta W = \Phi\, dq\,. \tag{3.4}$$

A simple analysis shows that Eq. (3.4) works equally well for a decrease of the positive charge or for the case of a conducting (that is equipotential) system charged with negative electricity. The electric potential Φ is obviously an intensive parameter since it is uniform in a conductor. Eq. (3.4) can be readily extended for non-conductive systems by allowing the electric potential to depend on the position inside the system. Then dq represents the *local* variation of the charge and the actual value of the electric work should imply a volume integration of Eq. (3.4). In any case the electric potential represents the measure of the electric response of the system to the tendency of changing its charge.

3.5 The chemical work

In what follows we shall adopt the convention to measure the amount of substance (the mass) of a system by the number of moles ν. As was already outlined, since any microscopic unit of a certain thermodynamic system bears some amount of energy, the exchange of particles (that is the exchange of mass) between different systems results in energy exchange. Thus, if some infinitesimal amount of substance $d\nu$ is added to a system, which otherwise is supposed as completely isolated from any external influence, its internal energy is expected to "increase" with a correspondingly infinitesimal amount $dU = U(\nu + d\nu) - U(\nu)$. The functional dependence of U on the number of moles is supposed to be analytic and can thus be expressed by a power series expansion: $U(\nu + d\nu) = U(\nu) + U'(\nu)\cdot d\nu + U''(\nu)\cdot(d\nu)^2/2 + \ldots$ Since the mass variation is supposed infinitesimal, the terms of degree higher than unity in $d\nu$ can be safely neglected in the expansion. Thus, by identifying the internal energy variation with the corresponding "work" δM done by the system in order to accommodate the new amount of mass $d\nu$, one may write:

$$\delta M = \mu\, d\nu \quad ; \quad \mu \equiv U'(\nu)\,. \tag{3.5}$$

On the same line as the previous examples of mechanical work, the quantity μ, termed as **chemical potential**, should be an **intensive parameter. It measures the reaction of the system to the tendency of its mass variation**. The quantity δM is the corresponding **chemical work**. The values of the chemical potential may be positive as well as negative. For example, if a new particle (of, say, zero initial energy) is to be accommodated in a certain system where the overall potential energy is negative for any individual particle inside, then the new particle would bring a positive amount of energy and $\mu > 0$. The system actually *attracts* the new particle inside it. On the contrary, the new particle should be *rejected* if the overall potential energy would be positive for any individual particle inside the system and one would have then $\mu < 0$.

The fact that the chemical potential is an intensive parameter may result from its very definition as a derivative of the internal energy with respect to its number of moles. Since the derivative is essentially a ratio and since in this ratio both the internal energy and the mass are extensive parameters, it follows that the result should be mass independent, that is an intensive quantity.

If the system consists in several types of microscopic units (particles) which are not in reciprocal interaction (that is, for example, they cannot transform in one another) then for each type a separate chemical potential and a separate chemical channel can be defined. The total chemical work takes thus the form of a sum over all these channels:

$$\delta M = \sum_i \mu_i \, d\nu_i \ . \tag{3.6}$$

As a general observation, one may note that all the expressions (3.1)-(3.6) contain products between certain intensive parameters taken in the original state and a small variation of corresponding extensive parameters. By analogy with Mechanics, the intensive parameters (which generally measure the reaction of the system to the corresponding infinitesimal process) are called **generalized forces** and the extensive ones **generalized configurations**.

Finally, it should be stressed again that, since the generalized forces are supposed to be well defined, the relations (3.1)-(3.6) correspond to **reversible infinitesimal processes**.

3.6 Constraints, envelopes and walls

Defining some particular system in Physics always imply the specification of its boundary conditions, that is the system's behavior at its boundary, the way it interacts with the exterior. Thus, the definition of thermodynamic systems in the introductory lecture may serve only as a general guide for this concept. For a particular system to be completely defined, the boundary conditions are needed and they always result from a set of **constraints** imposed to the system by its environment. Asking for the constraints is equivalent to specifying the nature of the **envelope** of the system. The envelope can further be divided into different **walls**, each one with some specific feature. The walls can be classified in various types upon the interactions that they forbid (or after the implied constraints). Here are some useful examples:

a) The **rigid wall** is that part of the envelope obstructing the mechanical channel. The opposite concept is the mobile wall that is usually called a **piston**.

b) The **impermeable wall** is the one that closes the chemical channel, that is the one that forbids the mass exchange. If the system has several chemical channels then one may have specifically impermeable walls for each channel: the **partially permeable walls**.

c) The **adiabatic wall** is the one that closes the thermal channel, that is it forbids the energy exchange through the microscopic movement of particles between the system and its environment. The opposite of the adiabatic wall is the **diathermal** one.

One should first observe that the walls of a certain type could never be perfect. For example, a practical rigid wall will always show some flexibility. So, it will never keep invariable its shape under a sufficiently large range of pressure values. Also, a piston will always experience some friction during its motion and it will never be able to make an energy transfer purely through the mechanical channel. Similarly there can be no perfectly impermeable or perfectly adiabatic walls in practice.

Another observation is that a certain wall may simultaneously serve several purposes. For example one may have rigid adiabatic walls as well as partially permeable pistons. Sometimes the envelope of a thermodynamic system may be purely formal, as a conventional limit of its environment.

From the point of view of the constraints which are imposed to them the simple thermodynamic systems may be classified in three categories: **isolated systems** (those with rigid, impermeable and adiabatic envelope), **closed systems** (those with rigid and impermeable envelope) and **open systems** (whose envelope allows the energy exchange through all the interaction channels).

In Thermodynamics, helpful schematic diagrams frequently accompany abstract reasoning. To properly read such diagrams one should be familiar with some graphic conventions. For example, a solid double line always represents an adiabatic wall, while a diathermic wall is drawn as a simple solid line. Partially permeable walls are represented as dotted lines if they are also diathermic. If dotted lines are doubled then they represent adiabatic partially permeable walls.

3.7 The First Law of Thermodynamics

In Physics, the law that has the broadest area of application is the principle of energy conservation. In all the field of Physics no physical phenomenon was found to contradict this principle: during any process that takes place in an isolated system, the total energy of the system is constant. For this reason, the principle of energy conservation was extended to the whole Universe. The generalization is obviously questionable, but at small scale this principle works perfectly. An important restriction of this general law exists in Thermodynamics too. It is known as **The First Law of Thermodynamics**: **the internal energy is invariable in the thermodynamic universe**. In other words, the internal energy can only be exchanged between a given thermodynamic system and its exterior, but it can never disappear or be created in the thermodynamic universe. From the mathematical point of view, it means that any variation of the internal energy of a given system have to equal the sum of all the amounts of energy which the system is exchanging with its exterior through the various interaction channels:

$$\boxed{\Delta U = W + Q + M + \ldots}. \tag{3.7}$$

The sum in the right hand side of Eq. (3.7) contains as many terms as are necessary to describe all the interaction channels.

***Important remark*:**

In a famous treatise of Thermodynamics E. A. Guggenheim [1] points out a very subtle and useful ***complement to The First Law***: **the interaction channels of a thermodynamic system are independent**.

In order to make this affirmation clearer we'll take a simple example. Let A and B be two thermodynamic systems for which a thermodynamic reunion, A∪B, exists. The extensivity of the internal energy ($U(A \cup B) = U(A) + U(B)$) implies that during a certain process one should have:

$$\Delta U(A \cup B) = \Delta U(A) + \Delta U(B), \tag{3.8}$$

where in parenthesis is indicated the system to which the symbol refers. By applying The First Law to each term of Eq. (3.8), one gets:

$$\begin{aligned} & W(A \cup B) + Q(A \cup B) + M(A \cup B) + \ldots = \\ & = W(A) + Q(A) + M(A) + \ldots + W(B) + Q(B) + M(B) + \ldots = \\ & = [W(A) + W(B)] + [Q(A) + Q(B)] + [M(A) + M(B)] + \ldots \quad . \end{aligned} \tag{3.9}$$

Obviously, Eq. (3.9) *does not* imply by itself that:

$$\begin{aligned}&W(A\cup B)=W(A)+W(B),\\&Q(A\cup B)=Q(A)+Q(B),\\&M(A\cup B)=M(A)+M(B),\\&\ldots,\end{aligned}\tag{3.10}$$

but the previously added complement to The First Law *grants* these very important relations. Indeed, if the interaction channels are independent, it follows that the system always performs a separate energy transfer through each interaction channel. Equations (3.7) and (3.10) constitute together the most general and complete form of The First Law of Thermodynamics.

Even if very general, the form (3.7) of the First Law is of little utility in practical computations. Instead, its "local" (or differential) form is much more important from this point of view. In infinitesimal processes the following equality holds:

$$\boxed{dU=\delta W+\delta Q+\delta M\ldots}.\tag{3.11}$$

For a **simple fluid** (that eventually contains several independent constituents), this relation takes the following more precise form [1, 2]:

$$dU=\delta Q-P\,dV+\sum_i \mu_i\,dv_i\ .\tag{3.12}$$

For other kinds of simple systems the term describing the mechanical work should be suitably modified.

It is worth to stress again here that, by explicitly using values of the intensive state parameters in Eq. (3.12), it is admitted implicitly that this form of The First Law corresponds to **infinitesimal <u>reversible</u> processes** (since the values of the state parameters should always be well defined). On the contrary, the forms (3.7) and (3.11) could be applied to any kind of natural processes.

Comment:

For purely historical reasons [1] heat or work are sometimes termed as "parameters". However is quite clear that one cannot speak about the "heat of a state" or about the "work of another state". Heat and work are simply amounts of energy exchanged by the system during certain processes. Different transformations connecting the same couple of states can produce different heat or work values. On the contrary, the variations of the true parameters are always the same between a given couple of states. In order to make a clear distinction, the true parameters are called **state parameters** (the temperature, the volume, the internal energy, etc.) and the false ones (heat, work, chemical work, etc.) are termed as **process (or transformation) parameters**. Nevertheless, it is much more convenient to reserve the term "parameter" for state variables only. The infinitesimal variations of the state parameters will always be designed by adding the symbol *d* before the symbol of the parameter (like for dP, dV, dU, etc.). For the infinitesimal values of energy exchange we'll use the symbol δ preceding the one for heat, work etc. (δQ, δW, δM, ...). As the reader already may have noted, these symbols have been used several times in this chapter. Therefore, the present observation provides the explanation for their use.

Bibliography

[1] E. A. Guggenheim, *Thermodynamics*, North-Holland, 1957.

[2] M. W. Zemansky, *Heat and Thermodynamics*, McGraw-Hill, 1968.

Exercises

3.1 Two thermally insulated equal globes, one filled with one mole of a light ideal gas, and the other with one mole of a heavy ideal gas at the same temperature and pressure, are placed one above the other with the light gas uppermost. When communication is open between the globes, the gases are completely mixed in a short time. Assuming the gases to be monatomic, find an expression for the change of temperature. Calculate this change when the light gas is helium (density $\rho_1 = 0.18\cdot10^{-3}$ g cm^{-3}) and the heavy gas is xenon (density $\rho_2 = 5.85\cdot10^{-3}$ g cm^{-3}), at standard temperature and pressure, for a distance h between the centers of the globes = 100 cm.

Answer: $\Delta T = -(\rho_2 - \rho_1)\dfrac{g h T}{3P} = -0.050\ {}^\circ C$.

3.2 5 kg of O_2 occupy a volume of 10 m^3 at 300 K. Find the work necessary to halve the volume (a) at constant pressure, (b) at constant temperature. What is the temperature at the end of process (a)? What is the pressure at the end of process (b)? Find also the energy exchanged as heat and the change of internal energy in both cases.

Answer: $W_a = -1.95\cdot10^5$ J; the final temperature in (a) is 150 K; $\Delta U_a = -4.87\cdot10^5$ J; $Q_a = -6.82\cdot10^5$ J; $W_b = Q_b = -2.70\cdot10^5$ J; the final pressure in (b) is $7.79\cdot10^6$ Nm^{-2}; $\Delta U_b = 0$.

3.3 Demonstrate that the internal energy of the air in a room is independent of temperature provided the outside pressure is constant.

3.4 How much energy should be transferred as heat to the air in a 40 m^3 room in order to rise its temperature from 0 ^{0}C to 20 ^{0}C. The outside pressure is supposed constant at the normal value (10^5 Nm^{-2}). The heat needed to rise the temperature of one mole of air with 1 K at constant pressure is supposed to be $7R/2$, where $R = 8.3145$ J·K^{-1}·mol^{-1}.

Answer: approx. 1 MJ.

4. Mathematical interlude

It is very unfortunate that, in the usual Physics curricula of the universities, the study of higher mathematics begins almost simultaneously with the study of the introductory branches of Physics. Even if elementary, these presentations of Physics concepts need a certain mathematical apparatus that the beginners generally are not yet acquainted with. Thermal Physics makes no exception and such a lecture course should therefore necessarily contain short introductions into the use of the main mathematical tools. Obviously, no rigor or completeness could be claimed for such introductions. One can only hope in an operational presentation of the mathematical concepts and techniques, which are strictly necessary for the student to understand the next lectures.

Presently, the reader is considered as being familiar with the concept of function of several real variables and with those of differentiability and partial differentiation. Since a general treatment would possibly confuse the beginners, the discussions will be made with functions of three real variables only. Almost no mathematical proofs will be provided in what follows.

One important point concerning the notations should always be remembered: it is customary in Thermodynamics to indicate, at each partial differentiation, the variables that are kept constant. This is intended for the unambiguous indication of the complete set of variables of the function to be differentiated. This in turn is necessary since in Thermodynamics there exist the quite unfortunate habit to use the same symbol for different functions, only because they take values in the same range. For example, one can have the internal energy as a function of temperature and volume, $U(T_X,V)$, or as a function of temperature and pressure as well $U(T_X,P)$. These are obviously *different functions* (since they are defined on *different sets*), but having both of them the values in the energy range, they are denoted with the *same letter*. It turns thus to be essential to indicate which one of these functions is subjected to the differentiation operation. We shall then write $\left(\frac{\partial U}{\partial T_X}\right)_V$, for the first function and $\left(\frac{\partial U}{\partial T_X}\right)_P$, for the second one.

4.1 Linear differential forms

An example will be considered first. As was discussed in the preceding lecture, the infinitesimal mechanical work done by a fluid has the form of Eq. (3.1). If the volume is not chosen as an independent parameter, then its variation dV could be written, for example, as a function of infinitesimal variations of the temperature and pressure (the mass is supposed constant):

$$dV = \left(\frac{\partial V}{\partial T_X} \right)_P dT_X + \left(\frac{\partial V}{\partial P} \right)_{T_X} dP . \tag{4.1}$$

If one replaces this expression in Eq. (3.1) then the infinitesimal work is obtained in the following form:

$$\delta W = -P\left(\frac{\partial V}{\partial T_X} \right)_P dT_X - P\left(\frac{\partial V}{\partial P} \right)_{T_X} dP . \tag{4.2}$$

In the right hand side of Eq. (4.2) there is a linear combination of infinitesimal variations of the temperature and pressure. These variations are actually **independent variables**, just like the "macroscopic" ones T_X or P, with the only restriction of being "very small" with respect to them. The coefficients of the linear combination are functions of T_X and P. So, the right member of Eq. (4.2) is actually a function of **four** independent arguments. It is an example of what is usually called a **linear differential form**.

More generally, consider three scalar functions $a(x,y,z)$, $b(x,y,z)$ and $c(x,y,z)$, of the **real variables** x, y and z, supposed as continuos and differentiable over all the set of definition. Let dx, dy and dz three **infinitesimal variations** of those variables. They are still independent variables: on the condition of being "very small" ($|dx/x|$, $|dy/y|$, $|dz/z| << 1$), dx, dy and dz take arbitrary values. The **linear homogeneous combination**

$$\delta w(x,y,z) = a(x,y,z)dx + b(x,y,z)dy + c(x,y,z)dz \tag{4.3}$$

is termed as a **linear differential form (LDF)** in the variables x, y and z. The homogeneity of the linear combination refers to the absence of "macroscopic" terms, without infinitesimal factors.

The typical example of a LDF is the very differential of some scalar function $f(x,y,z)$:

$$df(x,y,z) = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz . \tag{4.4}$$

The partial derivatives are actually functions of x, y and z. The thermodynamical notation was not used for them since no confusion can arise about the variables used. Nevertheless, if it is true that any differential of a scalar function is a LDF, **it can by no means be said that any LDF is the differential of some scalar function**. This is why the symbol of a differential of a scalar function will contain a d in front of the function's symbol while a LDF will be denoted by a symbol containing the Greek δ.

A LDF that can be written as the differential of a certain scalar function will be called **integrable linear differential form** or an **exact differential (ED)**. A LDF of only one real variable is always integrable since it can be written as the derivative of some of its primitives. The integrability of more general LDFs can be investigated by using the following **theorem** (sated here for only three independent variables) [1, 2]: **The LDF of Eq. (4.3) is integrable if and only if the following equalities**

$$\frac{\partial a}{\partial y} = \frac{\partial b}{\partial x} \quad ; \quad \frac{\partial b}{\partial z} = \frac{\partial c}{\partial y} \quad ; \quad \frac{\partial a}{\partial z} = \frac{\partial c}{\partial x} \tag{4.5}$$

are simultaneously fulfilled.

Since the partial differentiation order is immaterial, one can readily verify that these conditions are fulfilled in the case of Eq. (4.4):

$$\frac{\partial^2 f}{\partial y \, \partial x} = \frac{\partial^2 f}{\partial x \, \partial y} \quad ; \quad \frac{\partial^2 f}{\partial z \, \partial y} = \frac{\partial^2 f}{\partial y \, \partial z} \quad ; \quad \frac{\partial^2 f}{\partial z \, \partial x} = \frac{\partial^2 f}{\partial x \, \partial z} . \tag{4.6}$$

The conditions of Eq. (4.5) could take a shorter form if a vectorial notation would be used: the coefficients of the LDF could be considered as the Cartesian components of a vectorial function denoted by $\vec{w}(x, y, z)$:

$$\vec{w}(x, y, z) \equiv \left(a(x, y, z), b(x, y, z), c(x, y, z)\right). \tag{4.7}$$

If the infinitesimal variations of the arguments, *dx*, *dy* and *dz* are also taken as the Cartesian components of an infinitesimal vector:

$$d\vec{r} \equiv (dx, dy, dz), \tag{4.8}$$

then one may write Eq. (4.3) as a scalar product:

$$\delta w = \vec{w}(x, y, z) \cdot d\vec{r} \ . \tag{4.9}$$

The vectorial function defined by Eq. (4.7) may be called the **vector of the LDF *δw(x,y,z)***. One may then readily see that the conditions (4.5) are equivalent to the nullity of the components of Cartesian form of the curl of the LDF's vector. That is to say, the integrability of the LDF $\delta w(x,y,z)$ is equivalent to the relation:

$$rot\, \vec{w}(x, y, z) = \vec{0} \, . \tag{4.10}$$

4.2 Holonomic LDFs

Lets take a concrete example of LDF:

$$\delta w(x, y, z) = x\, y\, dx + x^2\, dy + x\, dz \ . \tag{4.11}$$

This form is not integrable since, for example, the derivative of xy with respect to y gives x and the derivative of x^2 with respect to x gives $2x$. Thus, at least one of the conditions (4.5) is not fulfilled.

Nevertheless, if one multiplies all the coefficients of δw by the function $1/x$, then a new LDF is obtained which fulfills all the conditions (4.5) and is therefore integrable:

$$\delta u(x,y,z) = y\,dx + x\,dy + dz\,. \tag{4.12}$$

If for some LDF $\delta w(x,y,z) = \vec{w}(x,y,z)\cdot d\vec{r}$ a differentiable function $\lambda(x,y,z)$ exists so that, the new LDF $\delta u(x,y,z) = \vec{u}(x,y,z)\cdot d\vec{r}$ with $\vec{u}(x,y,z) = \lambda(x,y,z)\vec{w}(x,y,z)$ is integrable then the LDF δw is called **holonomic linear differential form (HLDF)**. The $\lambda(x,y,z)$ function is termed as an **integrand factor**.

Now, one may obviously suspect that not all non-integrable LDFs actually do enjoy the existence of such an integrand factor. Indeed, an important theorem of Calculus [2] demonstrates that **a LDF is holonomic if and only if the LDF vector is always orthogonal to its Cartesian curl**:

$$\vec{w}(x,y,z)\cdot rot\,\vec{w}(x,y,z) = 0\,. \tag{4.13}$$

The necessity of this condition results quite easily from the following vector identity:

$$rot\left[f(x,y,z)\vec{v}(x,y,z)\right] = f(x,y,z)rot\,\vec{v}(x,y,z) - \vec{v}(x,y,z)\times grad\,f(x,y,z)\,, \tag{4.14}$$

where $f(x,y,z)$ is a scalar function and $\vec{v}(x,y,z)$ is a vectorial differentiable function. Indeed, if one assumes that δw is holonomic, then it should exist a function $\lambda(x,y,z)$ so that $rot\left[\lambda\,\vec{w}\right] = \vec{0}$. By using the identity (4.14), one gets the following equality:

$$rot\,\vec{w}(x,y,z) = \vec{w}(x,y,z)\times grad\left[ln\left|\lambda(x,y,z)\right|\right]. \tag{4.15}$$

As the right hand side of Eq. (4.15) is a vectorial product, it should be orthogonal on both its factors. Eq. (4.13) follows then directly. The proof of the reverse sense of the equivalence stated by the preceding theorem is much more complicated since it should imply the effective construction of an integrand factor using (4.13) as the hypothesis. Eq. (4.15) provides us with a systematic possibility to find out an integrand factor for the HLDF by solving the system of partial differential equations that results if (4.15) is written by components. However we shall not enter into any further detail. We content here only to observe that, since the solution of such a system is not unique, **each HLDF can have several different integrand factors**.

One should also observe that the condition (4.10) triggers automatically Eq. (4.13), so that the EDs are a subset of the set of HLDF's. An LDF that is not holonomic is simply termed as **non-holonomic**.

As an application of the theorem on the holonomy, it can be observed that any LDF of two real variables is holonomic. Indeed, if $\delta v(x,y) = a(x,y)dx + b(x,y)dy$ is such a form, then the curl of its vector $\vec{v}(x,y)=(a(x,y),b(x,y),0)$ can be readily found as $rot\,\vec{v}(x,y)=\left(0,0,\frac{\partial b}{\partial x}-\frac{\partial a}{\partial y}\right)$. So, the scalar product between the vector of the LDF and its curl becomes: $\vec{v}(x,y)\cdot rot\,\vec{v}(x,y)=(a(x,y),b(x,y),0)\cdot\left(0,0,\frac{\partial b}{\partial x}-\frac{\partial a}{\partial y}\right)=0$, showing the holonomy of $\delta v(x,y)$.

4.3 Integration of LDFs

In analytical geometry one may represent a three-dimensional curve as an ordered triple of scalar functions of the same real argument (**coordinate functions**): ($x(s)$, $y(s)$, $z(s)$). For every value of the argument s one obtains an ordered triple of coordinate values that correspond to a certain point on the curve. This representation of the curve is called **parametric** and the corresponding argument is the **parameter**. Sometimes, one of the coordinates (say x) may be taken as a parameter and the corresponding representation becomes: (x, $y(x)$, $z(x)$). In Mechanics this method is frequently used for working out problems related to trajectories. The most useful parameter in these cases is the time, t. In what follows we shall use the symbol t for the parameter of the analytical representation of a space curve (in order to keep with the analogy with Mechanics and to let the discussion more intuitive). If **the coordinate functions of some curve are continuous and almost everywhere differentiable** (that is they are differentiable everywhere except for a finite number of points), then we call this curve a **path**.

In a LDF (like that defined by Eq. (4.3)) one may imagine that x, y and z are the coordinates of the points of a certain path. In this case their variations dx, dy and dz will be no more arbitrary and can be written as functions of a unique variation of the parameter t of the respective path:

$$dx = x'(t)dt\ ;\ dy = y'(t)dt\ ;\ dz = z'(t)dt. \tag{4.16}$$

It thus follows that the restriction of the LDF to the set of points on the path becomes a one-argument LDF which could be integrated in the usual Riemann way between any two points of the path. So, one may define [2] **the integral of the LDF $\delta w(x,y,z)$ between two points $A = (x(t_A), y(t_A), z(t_A))$ and $B = (x(t_B), y(t_B), z(t_B))$, along the path $C = (x(t), y(t), z(t))$, by**:

$$\begin{aligned}\int_{(C)}^{A\to B}\delta w \equiv \int_{t_A}^{t_B}\Big\{&a\big[x(t),y(t),z(t)\big]x'(t)+b\big[x(t),y(t),z(t)\big]y'(t)+\\ &+c\big[x(t),y(t),z(t)\big]z'(t)\Big\}dt\end{aligned}. \tag{4.17}$$

Note. It should be observed that the previous definition of the integral of a LDF implies no metric into the space of points (x,y,z). In fact, in the most cases the set of the thermodynamic states of a system cannot be organized as a metric space with a usual Euclidean metric because of the dimensional conflicts induced by the definition of such a metric.

The following useful properties can be readily obtained from the corresponding theorems of the Riemann integration of functions of one variable:

$$\int_{(C)}^{A\to B}\delta w=-\int_{(C)}^{B\to A}\delta w\,, \tag{4.18'}$$

$$\int_{(C)}^{A\to B}\delta w+\int_{(C)}^{B\to D}\delta w=\int_{(C)}^{A\to D}\delta w\,, \tag{4.18''}$$

$$\int_{(C)}^{A\to B}\left(\delta w+\delta u\right)=\int_{(C)}^{A\to B}\delta w+\int_{(C)}^{A\to B}\delta u\,. \tag{4.18'''}$$

A **closed path** is a differentiable curve for which it exists two points A and B with $t_A \neq t_B$ and $(x(t_A), y(t_A), z(t_A)) = (x(t_B), y(t_B), z(t_B))$. The usual notation for an integral over a closed path is $\oint_{(C)}\delta w$.

In Calculus one may demonstrate the following important theorem [2, 3]: **δw is an ED if and only if the integral of δw along any closed path is zero**. It can be thus concluded that, if δw is integrable, then its integral taken between any two points do not depend on the path along which it is performed. Let C and C' be two of these possible paths. If one integrates along C from A to B and along C' from B to A, then the reunion of these two paths is a closed path. So, by taking into account the definition (4.17), one may write:

$$\oint_{(C\cup C')}\delta w=0=\int_{(C)}^{A\to B}\delta w+\int_{(C')}^{B\to A}\delta w=\int_{(C)}^{A\to B}\delta w-\int_{(C')}^{A\to B}\delta w\Rightarrow\int_{(C)}^{A\to B}\delta w=\int_{(C')}^{A\to B}\delta w. \tag{4.19}$$

A function can always be constructed through the integration process if starting from an ED. The differential of the obtained function will be the given ED. Indeed, if δw is such an ED and if we take a fixed point A, then the following function can be defined:

$$F\left(x,y,z\right)=\int^{A\to(x,y,z)}\delta w. \tag{4.20}$$

In accordance with the property (4.19) the integration path is immaterial. The differential of F may be written as the difference of its values between two infinitely closed points:

$$\begin{aligned} dF(x,y,z) &= F(x+dx,y+dy,z+dz) - F(x,y,z) = \\ &= \int^{A\to(x+dx,y+dy,z+dz)} \delta w - \int^{A\to(x,y,z)} \delta w = \int^{(x,y,z)\to(x+dx,y+dy,z+dz)} \delta w \end{aligned} , \tag{4.21}$$

where the integration path has to include these two points but otherwise may be arbitrary. The last integral of Eq. (4.21) may easily be transformed, by way of Eq. (4.17), in a real interval integral over *t*, from *t* to *t* + *dt*. The value of this integral may be written, by using the mean value theorem, as the value of the integrand (taken at the point *t*) times the length of the integration interval, *dt*. It can thus be obtained:

$$\begin{aligned} dF(x,y,z) = \{ & a[x(t),y(t),z(t)]x'(t) + b[x(t),y(t),z(t)]y'(t) + \\ & + c[x(t),y(t),z(t)]z'(t) \} dt \end{aligned} \tag{4.22}$$

and, as the integration path in (4.21) is arbitrary, is follows that:

$$dF(x,y,z) = a(x,y,z)dx + b(x,y,z)dy + c(x,y,z)dz = \delta w(x,y,z). \tag{4.23}$$

4.4 Implicit dependence

If a differentiable function *f* of three variables exists so that:

$$f(x,y,z) = 0, \tag{4.24}$$

then *x*, *y* and *z* are called **implicitly dependent**. It follows from Eq. (4.24) that *df* = 0, that is:

$$\frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0. \tag{4.25}$$

The equation (4.24) can provide, at least in principle, the variable *z* as a function of *x* and *y*. It thus defines what is usually called an **implicit dependence** among the three variables. Eq. (4.25) can also be looked at as a linear relation between *dx*, *dy* and *dz*. Moreover, by stressing the supplementary condition *x* = *constant* (that is *dx* = 0 in Eq. (4.25)), Eq. (4.24) becomes a simple functional relation between *z* and *y*. It thus follows:

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} (dy)_{x,f} = -\left(\frac{\partial f}{\partial z}\right)_{x,y} (dz)_{x,f} \quad and \quad (dy)_{x,f} = \left(\frac{\partial y}{\partial z}\right)_{x,f} (dz)_{x,f}. \tag{4.26}$$

By replacing $(dy)_{x,f}$ in the first part of Eq. (4.26), one obtains (after simplification with $(dz)_{x,f}$):

$$\left(\frac{\partial f}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial z}\right)_{x,f} = -\left(\frac{\partial f}{\partial z}\right)_{x,y}. \tag{4.27}$$

Similarly, if one combines Eqs. (4.24) and (4.25) with *y* = *constant*, it results:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial x}\right)_{y,f}=-\left(\frac{\partial f}{\partial x}\right)_{y,z}. \tag{4.28}$$

Finally, by using Eqs. (4.24) and (4.25) together with the condition $z = constant$ it can be shown that:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z}\left(\frac{\partial x}{\partial y}\right)_{z,f}=-\left(\frac{\partial f}{\partial y}\right)_{x,z}. \tag{4.29}$$

By multiplying the equalities (4.27)-(4.29) one obtains the following identity:

$$\left(\frac{\partial x}{\partial y}\right)_{z,f}\left(\frac{\partial y}{\partial z}\right)_{x,f}\left(\frac{\partial z}{\partial x}\right)_{y,f}=-1 \tag{4.30}$$

which is of major importance in Thermodynamics.

Considering Eq. (4.26) again, if one replaces $(dz)_{x,f}$:

$$(dz)_{x,f}=\left(\frac{\partial z}{\partial y}\right)_{x,f}(dy)_{x,f}, \tag{4.31}$$

then it follows that:

$$\left(\frac{\partial f}{\partial z}\right)_{x,y}\left(\frac{\partial z}{\partial y}\right)_{x,f}=-\left(\frac{\partial f}{\partial y}\right)_{x,z}. \tag{4.32}$$

Now, by multiplying the relations (4.27) and (4.32) one gets:

$$\left(\frac{\partial y}{\partial z}\right)_{x,f}\left(\frac{\partial z}{\partial y}\right)_{x,f}=1, \tag{4.33}$$

which represents an expression of the one-argument inverse function theorem. In order to legitimate the simplifications, the validity of Eqs. (4.30) and (4.33) obviously restricts on the ranges where the factors are not zero, that is on the bijectivity ranges of the various one-argument functions generated by the imposed conditions.

We close this section with another important relation. Let's write Eq. (4.25) along a path included in a "plane" parallel to (x,y), $C = (x(t), y(t), z = constant)$:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z}\left(\frac{dx}{dt}\right)_{(C)}+\left(\frac{\partial f}{\partial y}\right)_{x,z}\left(\frac{dy}{dt}\right)_{(C)}=0. \tag{4.34}$$

By comparing Eq. (4.34) with the restriction of Eq. (4.29) to the points of the path C, one obtains:

$$\left(\frac{\partial x}{\partial y}\right)_{z,f,(C)} = -\frac{\left(\frac{\partial f}{\partial y}\right)_{x,z}}{\left(\frac{\partial f}{\partial x}\right)_{y,z}} = \frac{\left(\frac{dx}{dt}\right)_{(C)}}{\left(\frac{dy}{dt}\right)_{(C)}} . \tag{4.35}$$

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Exercises

4.1 Prove that the following LDF:

$$\delta w = (y+z)dx + (x+z)dy + (x+y)dz$$

is integrable and compute its integral between a reference point (x_0,y_0,z_0) and a current point (x,y,z).

Answer: $\int_{(x_0,y_0,z_0)}^{(x,y,z)} \delta w = (yz + zx + xy) - (y_0 z_0 + z_0 x_0 + x_0 y_0)$.

4.2 Check the integrability of the following LDF:

$$\delta w = 3\,y\,z\,dx + x\,z\,dy + x\,y\,dz .$$

If it is holonomic, find an integrand factor of it.

Answer: The LDF is holonomic; a possible integrand factor is $\lambda(x,y,z) = x^2$.

4.3 Check the integrability of the following LDF:

$$\delta w = x^2\,y\,dx + x\,z\,dy + (x+y+z)dz$$

and compute its integral along the following path: $C = (t,t,t)$ between the points (1,1,1) and (3,3,3).

Answer: 40.667.

5. The restraint statement of The Second Law of Thermodynamics. The concept of entropy

5.1 Preliminary concepts

a) A thermodynamic system interacting with its exterior through the thermal channel only and whose temperature keeps a constant value during the interaction with any other thermodynamic system is what we call a **thermostat** or **thermal reservoir**. Such a thermodynamic system **is characterized uniquely by its temperature**.

Obviously, no perfect thermostat can be found in practice. Only bodies with high amount mass can be considered to satisfactorily approximate a thermostat.

b) A transformation of a thermodynamic system during which its temperature keeps a constant value is called **isothermal process**. Such processes can be performed by letting the system interact and being in equilibrium with a thermostat.

c) Any ***closed simple thermodynamic system*** performing a cyclic process is usually called a **thermal engine** (**TE**). If the corresponding cycle is reversible then we have a **reversible thermal engine** (**RTE**).

d) A **monothermal cycle** (**MC**) is ***a thermodynamic cycle during which a simple closed system interacts with only one thermostat***. A general MC *is not restricted of being a reversible process*: one may have reversible as well as irreversible MCs. The system subject to a MC is called a **monothermal engine** (**ME**).

e) A **Carnot cycle** (**CC**) is ***a reversible thermodynamic cycle of a simple closed system during which it interacts with only two thermostats***. The system subject to a CC is called **Carnot engine** (**CE**).

In applying The First Law to TEs one should note that, given the fact that their processes are cyclic, the total variation of the internal energy is zero. Moreover, since TEs are defined as *simple closed systems*, their chemical channel is considered ***as closed*** during the corresponding processes and thus their corresponding chemical work is zero valued. Consequently, for a complete cycle The First Law gives:

$$W + Q = 0 \quad \Leftrightarrow \quad W = -Q. \tag{5.1}$$

5.2 The restraint statement of The Second Law of Thermodynamics

For accessibility reasons, only *simple closed thermodynamic* systems will be considered in the present chapter. It is much more convenient for beginners to use the TEs approach in order to become familiar with the relatively abstract concept of entropy introduced by The Second Law of

Thermodynamics. Obviously this is not the most general approach (since it refers to only simple closed systems), but it is certainly the most accessible for intuition. The formal generalization for any kind of thermodynamic system to be presented in the next chapter will seem thus more natural. Some remarkable authors [1] prefer direct axiomatic constructions of the concept of entropy. While more rigorous, such approaches may seem less meaningful for Thermodynamics beginners.

A reasonable starting point may be the following statement also known as the restraint form of The Second Law of Thermodynamics [2, 3]: **during a MC a system can only receive energy through the mechanical channel and give off energy through the thermal channel; the total work will be zero if and only if the MC is reversible**. There are still other equivalent statements of this kind, but we shall content ourselves with only this one. The restraint form of The Second Law can be stated more formally by using Eq. (5.1), as follows: **during a MC the two following relations**

$$\boxed{W \geq 0 \quad ; \quad Q \leq 0} \tag{5.2}$$

are the only ones that can be simultaneously satisfied; the equalities hold if and only if the MC is reversible.

If the previous statement would not hold then the possibility of building an engine that could produce work from the simple contact with a thermostat (e.g. with the environmental air or with the water of a lake) would be implied. As such an energy source would be practically inexhaustible, the corresponding engine would be termed as a **perpetuum mobile of the second kind**. The restraint form of The Second Law then simply states that **it is impossible to construct a perpetuum mobile of the second kind**.

5.3 The theorem of Carnot

Let A be a CE interacting only with the thermostats of temperatures T_{X1} and T_{X2}. Let Q_1, Q_2 be the corresponding heat amounts reversibly exchanged by A with the two thermostats during a complete cycle. [Obviously our language is slightly abusive here: one should not say "the heat (or work) exchanged by the system", but instead "the energy exchanged by the system as heat (or work)". Nevertheless, brief expressions of this kind are frequently used for convenience in Thermodynamics owing to its traditional roots in the ancient Caloric Theory. One should therefore always remember the strict sense of such an expression in order to avoid any confusion.] If the cycle of A is performed n times (n being a positive integer) then it is obvious that the total amount of heat exchanged with the thermostats will be nQ_1 and nQ_2, respectively. If the cycle is reversed then all the dilations become contractions and vice versa. Consequently, the total work performed will have an opposite sign and, taking into account Eq. (5.1), the corresponding exchanged heat amounts will be $-Q_1$ and $-Q_2$. If the reversed cycle is then performed m times (m natural), then the heat exchanges will be $-mQ_1$ and $-mQ_2$. From this point of view, instead of saying that the cycle is performed m times in the reverse, it is usual (and more convenient) to say that the cycle is performed $-m$ times ahead.

Let now another TE (reversible or not), denoted by B, which shares one of the thermostats, say T_{X2}, with A (the engine B may otherwise interact with any number of thermostats). Let Q'_2 be the heat amount exchanged by B with the thermostat T_{X2} in a complete cycle. Since the possibility of the thermal interaction between A and B exists, the thermodynamic reunion A∪B may be taken as a new thermal engine. When running this engine so that B performs m complete cycles (m being a **positive integer**) and A performs n cycles (n being an **arbitrary integer**), the total heat exchanged by the united engine A∪B with the thermostat T_{X2} will be $nQ_2 + mQ'_2$. As is supposed to be known from elementary Calculus, the real number Q'_2/Q_2 can be approximated with an arbitrary precision by a rational number, that is by a ratio of two integers. Consequently, one can always find integers n and m ($m > 0$) so that the fraction $-n/m$ be arbitrarily close to the real number Q'_2/Q_2 or, equivalently, so that the number $nQ_2 + mQ'_2$ be arbitrarily close to zero. It may be concluded that, **by conveniently running the two engines A and B, one can arrive at a practically zero heat exchange between the united engine A∪B and the thermostat T_{X2}**. In other words, **the engine A∪B can always be run in such a way so as to essentially prevent the interaction with the thermostat T_{X2}**.

This very important result will be frequently used in this chapter where the German **method of "Gedanken" (thought) experiments** will be extensively used.

<u>Theorem 5.1 (Carnot).</u> Let T_{X1} and T_{X2} be the thermostats of a CE and let Q_1 and Q_2 be the corresponding amounts of heat exchanged by the engine during a complete cycle. In these conditions a real function f exists which is independent of the nature of the system used in the CE, such that

$$\boxed{\frac{Q_1}{Q_2} = -f\left(T_{X1}, T_{X2}\right)}. \tag{5.3}$$

As may be readily noted, ***the function f takes the same value (namely Q_1/Q_2) for any kind of empirical temperature scale***. From this point of view, the function *f* is **universal**. The minus sign in Eq. (5.3) was chosen for pure convenience, as it will be seen in what follows.

<u>Proof</u>. Let A be a certain CE working with the thermostats T_{X1} and T_{X2} and exchanging the corresponding amounts of heat Q_1 and Q_2. Consider then another CE, B, using the same thermostats and correspondingly exchanging the amounts of heat Q'_1 and Q'_2 in a complete cycle. From the previous general result we may conclude that the two engines could be operated in such a way that the united engine A∪B behave as a ME. In other words integers n and m can always be found so that, for example, the total heat exchanged with the thermostat T_{X2} be essentially zero: $nQ_2 + mQ'_2 = 0$. Since both A and B run over reversible cycles, the united engine A∪B becomes thus a reversible ME (shortly a RME). It should be stressed here that one complete cycle of A∪B as a RME would consist of n cycles of A and m cycles of B. By applying the restraint statement of The Second Law of Thermodynamics to this new engine it follows that the total heat it exchanges in its complete cycle, namely the heat $nQ_1 + mQ'_1$ exchanged with T_{X1}, should equally vanish. Stated shortly, one may say that:

$$nQ_2 + mQ'_2 = 0 \quad \Rightarrow \quad nQ_1 + mQ'_1 = 0 . \tag{5.4}$$

It then follows that:

$$\frac{Q'_2}{Q_2} = \frac{Q'_1}{Q_1}\left(= -\frac{n}{m} \right) \tag{5.5}$$

and then:

$$\frac{Q'_1}{Q'_2} = \frac{Q_1}{Q_2} . \tag{5.6}$$

It was thus demonstrated that the ratios of the amounts of heat exchanged by two ***arbitrarily different*** CEs are equal. It follows that the corresponding ratio is independent of the nature of the thermodynamic system working as a CE with the two fixed thermostats. This ratio should then depend only on the temperatures of the used thermostats:

$$\frac{Q'_1}{Q'_2} = \frac{Q_1}{Q_2} = -f\left(T_{X1}, T_{X2}\right). \tag{5.7}$$

5.4 Some properties of the function f(T$_{X1}$,T$_{X2}$)

a) If in the demonstration of the Carnot's Theorem one reverses the roles of the thermostats, which actually reduces to interchanging their indexes 1 and 2, then one gets similarly:

$$\frac{Q_2}{Q_1} = -f\left(T_{X2}, T_{X1}\right). \tag{5.8}$$

By comparing Eq. (5.3) with (5.8) it readily follows that:

$$f\left(T_{X2}, T_{X1}\right) f\left(T_{X1}, T_{X2}\right) = 1 \quad \Leftrightarrow \quad f\left(T_{X2}, T_{X1}\right) = \frac{1}{f\left(T_{X1}, T_{X2}\right)} . \tag{5.9}$$

b) No couple of thermostats can produce zero values for the function *f*. Indeed, by taking $f(T_{X1},T_{X2}) = 0$ for a certain couple of thermostats T_{X1} and T_{X2} then, following Eq. (5.3), one should admit that $Q_1 = 0$ and $Q_2 \neq 0$. But in this case the engine would become a RME since it interacts with T_{X2} only. By using again The Second Law in its restrained form, it turns out that, Q_2 being the total heat exchanged in the reversible monothermal cycle (RMC), it should also worth zero, which clearly contradicts the hypothesis. It thus follows that:

$$f(T_{X1},T_{X2}) \neq 0, \quad (\forall) T_{X1},T_{X2}. \tag{5.10}$$

c) The properties expressed by (5.9) and (5.10) readily imply that *f* should be a bounded function:

$$f(T_{X1},T_{X2}) \neq \pm\infty, \quad (\forall) T_{X1},T_{X2}. \tag{5.11}$$

If the function *f* is bounded and nonzero everywhere on its domain of definition, then it should keep the same sign over its entire domain.

d) We also have:

$$f(T_X,T_X) = 1. \tag{5.12}$$

Indeed, if one would take $T_{X1} = T_{X2} = T_X$, then the corresponding cycle would become monothermal and reversible which would imply $Q_1 + Q_2 = 0$. So we should have:

$$f(T_X,T_X) = f(T_{X1},T_{X2}) = -\frac{Q_1}{Q_2} = 1. \tag{5.13}$$

e) From the preceding property of *f* and from the fact that it keeps a constant sign throughout its domain of definition it follows that *f* takes always strictly positive values:

$$f(T_{X1},T_{X2}) > 0, \quad (\forall) T_{X1},T_{X2}. \tag{5.14}$$

f) Let T_{X1}, T_{X2} and T_{X0} three different thermostats. The following relation holds:

$$f(T_{X1},T_{X2}) = \frac{f(T_{X1},T_{X0})}{f(T_{X2},T_{X0})}. \tag{5.15}$$

Proof. Let A be a CE working with the thermostats T_{X1} and T_{X2}. Let B_1 be another CE that performs its cycle with the thermostats T_{X1} and T_{X0} and B_2 a CE operating with the thermostats T_{X2} and T_{X0}. Let Q_1 and Q_2 be the one-cycle amounts of heat exchanged by the engine A with the thermostats T_{X1} and T_{X2}. Also, let q_1, q'_0 and q_2, q''_0 be the one-cycle heat amounts exchanged with the corresponding thermostats by B_1 and B_2 respectively. From the discussion at the beginning of the preceding section it is clear that, if the engine A would run *n* times, the engines B_1 and B_2 could be always conveniently run *m*' and *m*" times, respectively, so as the heat exchanges with the thermostats T_{X1} and T_{X2} to essentially vanish: $nQ_1 + m'q_1 \cong 0$ and $nQ_2 + m''q_2 \cong 0$. [Strictly speaking, a different couple of integers, n_1, m_1 and n_2, m_2, is proven to exist for each such relation: $n_1Q_1 + m_1q_1 \cong 0$ and $n_2Q_2 + m_2q_2 \cong 0$. The integer n may be defined as a common multiple of n_1 and n_2. Then one should put $m' = m_1n/n_1$ and $m'' = m_2n/n_2$.] If one looks now at the united (reversible) thermal engine A∪B$_1$∪B$_2$, which is driven in such a way that A performs n cycles, B$_1$ performs m' cycles and B$_2$ performs m'' cycles, then it should actually behave as RME interacting with the thermostat T_{X0} only. The heat exchanged with this thermostat should be $m'q'_0 + m''q''_0$. In this case, the restraint statement of The Second Law implies that the total heat exchanged by A∪B$_1$∪B$_2$ should be zero, so that actually $m'q'_0 + m''q''_0 = 0$. This implies of course that $m'/m'' = -q''_0/q'_0$. The following relations can then be arranged to hold simultaneously:

$$\begin{gathered} \frac{m'}{n} = -\frac{Q_1}{q_1} \\ \frac{m''}{n} = -\frac{Q_2}{q_2} \\ \frac{m'}{m''} = -\frac{q''_0}{q'_0} \end{gathered} . \tag{5.16}$$

By dividing the first two of these relations and by using the last one it follows that:

$$\frac{Q_1}{Q_2}\frac{q_2}{q_1} = -\frac{q''_0}{q'_0} \quad \Leftrightarrow \quad \frac{Q_1}{Q_2} = -\frac{q''_0}{q_2}\frac{q_1}{q'_0} . \tag{5.17}$$

But, by separately applying the Carnot's theorem to the engine A and to the two parts of the cycle of B, one gets:

$$\frac{Q_1}{Q_2} = -f(T_{X1},T_{X2}) \quad ; \quad \frac{q''_0}{q_2} = -f(T_{X0},T_{X2}) \quad ; \quad \frac{q_1}{q'_0} = -f(T_{X1},T_{X0}). \tag{5.18}$$

Consequently, Eq. (5.17) can be written as:

$$f(T_{X1},T_{X2}) = f(T_{X0},T_{X2})f(T_{X1},T_{X0}), \tag{5.19}$$

which, by use of Eq. (5.9), gives the result (5.15).

An important consequence of the existence of the universal function f is the following.

<u>Theorem 5.2</u>. Let a BE working with the thermostats T_{X1} and T_{X2} in an irreversible cycle. Denoting the corresponding heat exchanges by Q_1 and Q_2, respectively, the following relation holds:

$$Q_1 + Q_2\, f(T_{X1},T_{X2}) < 0 . \tag{5.20}$$

Proof. Let A be the irreversible engine and let B a CE working with the same thermostats as A. Let Q_1, Q_2 and Q'_1, Q'_2 be the one-cycle heat amounts exchanged with the thermostats by A and B, respectively. As was several times remarked before in this chapter, the engines A and B can always be united in a complex A∪B. Moreover, A could be run in convenient way *n* times (*n* integer > 0) and B could be run *m* times (*m* integer), so that in the complex cycle of A∪B the heat exchange with one of the thermostats, say T_{X2}, could be made as small as desired:

$$nQ_2 + mQ'_2 = 0 \quad (n > 0). \tag{5.21}$$

Once Eq. (5.21) is fulfilled, the compound system A∪B behaves as a monothermal irreversible engine and, according to the restraint statement of The Second Law, the total heat exchanged by this engine should be strictly negative:

$$nQ_1 + mQ'_1 < 0. \tag{5.22}$$

By combining Carnot's theorem with Eq. (5.21) for the engine B one gets:

$$mQ'_1 = -mQ'_2\, f(T_{X1}, T_{X2}) = nQ_2\, f(T_{X1}, T_{X2}). \tag{5.23}$$

It is thus possible to replace mQ'_1 in Eq. (5.22), wherefrom the relation (5.20) results, after simplification with the positive integer *n*.

5.5 The absolute thermodynamic temperature

Consider a fixed thermostat of temperature T_{X0}. For any other thermostat T_X a CE can be imagined as operating with only T_X and T_{X0} and a unique value for the real function *f* can be obtained. The numbers $f(T_X,T_{X0})$ can thus be considered as the values of a real function of T_X only:

$$\varphi(T_X) \equiv f(T_X, T_{X0}). \tag{5.24}$$

The choice of the temperature T_{X0} is termed as the **scaling** of the function φ. By using the properties of the function *f*, it is a simple matter to prove that ***any change of scaling can modify φ by a factor independent of T_X only***. Indeed, let T_{X0} and T'_{X0} be two fixed temperatures and let φ and φ' the functions corresponding to these scaling values. Then one may write:

$$\frac{\varphi'(T_X)}{\varphi(T_X)} = \frac{f(T_X, T'_{X0})}{f(T_X, T_{X0})} = \frac{f(T_{X0}, T_X)}{f(T'_{X0}, T_X)} = f(T_{X0}, T'_{X0}), \tag{5.25}$$

where the properties (5.9) and (5.15) were successively used. It thus follows that the ratio of the values which the two functions φ and φ' take for an arbitrary temperature T_X is independent of T_X. In other words any change of the scaling of φ multiplies it by a constant factor.

One may also readily conclude from the properties of the function *f* that ***φ is a bounded strictly positive function***.

Also, by using the theorem 5.2, it can be demonstrated that ***φ is a strictly increasing function of T_X***. Indeed let T_{X1} and T_{X2} be the temperatures of two thermostats such that $T_{X1} < T_{X2}$. Let A be a thermodynamic system which **can communicate with its environment by the thermal channel only**. Suppose that, in the initial state, A is in thermal equilibrium with the lower temperature thermostat T_{X1}. Starting from this state, the system is put in thermal contact with the higher temperature thermostat T_{X2}. Let Q_2 (> 0) be the heat received by A during the process towards the state of thermal equilibrium with T_{X2}. From this new state the system A is then put back in thermal contact with T_{X1}. During the cooling process it will lose the heat Q_1 (< 0) and will actually reach its initial equilibrium state. A bithermal cycle was thus completed for the system A, by using thermal interactions only. Since the work channel was closed during this process, The First Law of Thermodynamics gives:

$$Q_1 = -Q_2 . \tag{5.26}$$

Now, ***the previously described bithermal cycle is irreversible***. Indeed, suppose that the cycle were reversible. In this case A would be a CE, for which Carnot's theorem combined with Eq. (5.26) give $-\frac{Q_1}{Q_2} = f\left(T_{X1}, T_{X2}\right) = 1$. According to the property *d*) of the function *f* this would imply that $T_{X1} = T_{X2}$, which obviously contradicts the previous assumption.

From the previous result it follows that the theorem 5.2 can be applied to A and one may write:

$$Q_1 + Q_2\, f\left(T_{X1}, T_{X2}\right) < 0 \quad \Rightarrow \quad Q_1 + Q_2 \frac{f\left(T_{X1}, T_{X0}\right)}{f\left(T_{X2}, T_{X0}\right)} = Q_1 + Q_2 \frac{\varphi\left(T_{X1}\right)}{\varphi\left(T_{X2}\right)} < 0 , \tag{5.27}$$

where the property (5.15) of the function *f* and the definition (5.24) of the function φ have also been considered. If Eq. (5.26) is now replaced in Eq. (5.27), one arrives at:

$$Q_2 \left[\frac{\varphi\left(T_{X1}\right)}{\varphi\left(T_{X2}\right)} - 1 \right] < 0 \quad \Leftrightarrow \quad \frac{\varphi\left(T_{X1}\right)}{\varphi\left(T_{X2}\right)} - 1 < 0 \quad \Leftrightarrow \quad \varphi\left(T_{X1}\right) < \varphi\left(T_{X2}\right), \tag{5.28}$$

since the heat Q_2 was supposed to be positive. The last inequality proves that **φ is a strictly increasing real function**.

In summary, we have defined (up to a constant factor) ***a real, strictly positive, strictly increasing and bounded function φ, which is universal*** (not dependent on the nature of the some thermodynamic system). These properties allow the construction of a φ-based temperature scale. This temperature scale is no more linked to any kind of specific thermometer and is therefore a truly

universal temperature. Following the custom notation of Thermodynamics, the symbol T will be used for the function φ (with no thermometer index). This universal temperature is called ***the absolute thermodynamic temperature***, or shortly, ***the absolute temperature***:

$$T = \varphi(T_X). \tag{5.29}$$

By an international agreement, the scale of the absolute temperature has been identified with the ideal gas temperature scale defined by Eq. (2.1). Thus, the unit of the absolute temperature is one Kelvin (K) and, in order to remove the indeterminacy brought in by Eq. (5.25), the absolute temperature of the triple point of pure water is taken as:

$$T_0 = 273.16 K . \tag{5.30}$$

5.6 The relation of Clausius

The concept of absolute temperature allows more useful forms for the relations (5.3) and (5.20). For example, by (5.3), (5.15), (5.24) and (5.29), one may write for a CC:

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2} \quad \Rightarrow \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 . \tag{5.31}$$

Similarly, for an ***irreversible BE***, one has (since the absolute temperatures are always strictly positive):

$$Q_1 + Q_2 \frac{T_1}{T_2} < 0 \quad \Rightarrow \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} < 0. \tag{5.32}$$

where use was made of (5.20), (5.15), (5.24) and (5.29). In Eqs. (5.31) and (5.32) T_1 and T_2 may be thought of as absolute temperatures of the used thermostats. Eq. (5.31) is called the **Clausius equality** for a CE, while Eq. (5.32) is the **Clausius inequality** for an irreversible BE. As will be shown below, those two relations can be generalized for any type of thermodynamic cycles of closed systems.

To this purpose, let A be a system undergoing a cyclic process (reversible or not) during which it interacts with only N different thermostats. We shall denote these thermostats by T_i, i =1, 2, …, N (N-thermal cycle). The process contains therefore N isothermal transformations of the system. Between these isotherms, the system is supposed as thermally isolated by an adiabatic wall. That is to say, between any two isotherms, the system A performs an **adiabatic process**.

Let Q_i, i = 1, 2. …, N, be the heat exchanges of A with the thermostats T_i, during one complete cycle. Let T_0 be a thermostat which is different of the others and let B$_i$, i = 1, 2. …, N, be N thermodynamic systems performing Carnot cycles by means of the thermostats T_0 and T_i, i = 1, 2.

…, N, respectively. Let q_{0i} and q_i be the one-cycle heat exchanges of B_i with T_0 and T_i, respectively. For each $i = 1, 2. …, N$ a couple of integers n_i, m'_i ($n_i > 0$), may be found so that the united engine $A \cup B_i$ almost vanishes its heat exchange with the thermostat T_i: $n_iQ_i + m'_iq_i \cong 0$. By defining n as a common multiple of all n_i-s ($n > 0$) and $m_i = m'_i\, n/n_i$, one may obviously still write: $nQ_i + m_iq_i \cong 0$, $i = 1, 2. …, N$. Now, consider the reunion of the systems, $A \cup B_1 \cup B_2 \cup \ldots \cup B_N$. Suppose that A performs n complete cycles and that B_i performs m_i times its CC cycle between T_0 and T_i, $i = 1, 2. …, N$. Then the total heat exchanges of $A \cup B_1 \cup B_2 \cup \ldots \cup B_N$ during the united complex cycle would be:

$$\begin{aligned} & n\,Q_i + m_i\, q_i \;\; with\; T_i, \quad i = 1, \ldots, N \\ & \sum_{i=1}^{N} m_i\, q_{0i} \;\; with\; T_0 \end{aligned} \quad . \tag{5.33}$$

According to the previous choice of the numbers, one may further write:

$$n\,Q_i + m_i\, q_i = 0, \quad i = 1, \ldots, N \quad (n > 0). \tag{5.34}$$

Thus the engine $A \cup B_1 \cup B_2 \cup \ldots \cup B_N$ becomes monothermal (since it exchanges heat only with T_0). The cycle of the united engine $A \cup B_1 \cup B_2 \cup \ldots \cup B_N$ may also be assigned as reversible or as irreversible upon the type of processes that A undergoes during its own cycle (since the B_i-s are supposed to be reversible engines). By applying the restraint statement of The Second Law to the engine $A \cup B_1 \cup B_2 \cup \ldots \cup B_N$, one may write:

$$\sum_{i=1}^{N} m_i\, q_{0i} \le 0\,, \tag{5.35}$$

the equality being satisfied if and only if the cycle of A were reversible. Moreover, during the CC performed by each B_i, the Clausius equality (5.31) can be applied:

$$\frac{q_i}{T_i} + \frac{q_{0i}}{T_0} = 0 \quad \Rightarrow \quad q_{0i} = -T_0 \frac{q_i}{T_i}\,. \tag{5.36}$$

By replacing q_{0i} in (5.35), one gets:

$$-T_0 \sum_{i=1}^{N} \frac{m_i\, q_i}{T_i} \le 0\,. \tag{5.37}$$

The products m_iq_i may be replaced from Eq. (5.34), so that Eq. (5.37) becomes (remember that n and T_0 are positive numbers):

$$n\,T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} \le 0 \quad \Rightarrow \quad \sum_{i=1}^{N} \frac{Q_i}{T_i} \le 0\,. \tag{5.38}$$

The equal sign in the relation (5.38) holds if and only of the N-thermal cycle of A is reversible.

For each i, the heat Q_i may be written as an integral over the path defined by the given isothermal process: $Q_i = \int_{T_i} \delta Q$. By taking into account that, during each such process, the thermostat temperature T_i is a constant, Eq. (5.38) becomes:

$$\sum_{i=1}^{N} \frac{1}{T_i} \int_{T_i} \delta Q = \sum_{i=1}^{N} \int_{T_i} \frac{\delta Q}{T_i} = \sum_{i=1}^{N} \int_{T_i} \frac{\delta Q}{T} \le 0 . \tag{5.39}$$

On the other hand, for each adiabatic process contained in the cycle of A, we get $\delta Q = 0$, which vanishes the integral of $\delta Q/T$ over every such an adiabatic process. As every couple of consecutive isothermal processes have to be separated by an adiabatic one, the N-thermal cycle of A must contain exactly N adiabatic "segments" for which we may write:

$$\sum_{i=1}^{N} \int_{(adiabatic)_i} \frac{\delta Q}{T} = 0 . \tag{5.40}$$

Therefore, by adding Eqs. (5.39) and (5.40), one obtains:

$$\sum_{i=1}^{N} \left[\int_{T_i} \frac{\delta Q}{T} + \int_{(adiabatic)_i} \frac{\delta Q}{T} \right] \le 0 . \tag{5.41}$$

The reunion of all the considered isothermal and adiabatic processes gives exactly the N-thermal cycle of A. All the isothermal and adiabatic "segments" of this cycle are obviously disjoint (since the thermostats have all different temperatures). Thus, by taking into account the additivity property of path integrals over disjoint path segments, Eq. (5.41) may be written as:

$$\boxed{\oint \frac{\delta Q}{T} \le 0}, \tag{5.42}$$

the equality being satisfied if and only if the cycle is reversible.

The explicit appearance of the number of thermostats is no more present into the left side of the relation (5.42). This relation may thus be considered as true for an indefinite number of thermostats with which the system interacts during a certain cyclic process. Actually, it can be demonstrated that Eq. (5.42) holds even for cycles where the temperature varies continuously when the system passes through the individual states of the cycle. This inequality, which is thus satisfied *for any thermodynamic cycle* constitutes **the general relation of Clausius**.

Note. On the possibly irreversible parts of a cycle one may question the definiteness of the system's temperature to be entered into the integral of (5.42). In fact, as is actually clear from the proof of Eq. (5.42) for a cycle containing a finite number of isotherms, in this relation, T does not represent the system's temperature, but the temperatures of the thermostats with which the system interacts during the process.

5.7 The efficiency of a Carnot motor

Generally, we speak of a thermal engine of being a **thermal motor** if **the total work performed by the system during a complete cycle is negative**, that is if

$$W = -Q\left(<0\right). \tag{5.43}$$

The efficiency of a thermal motor is defined as **the ratio of the absolute value of the total work produced in a complete cycle to the corresponding total absorbed heat**:

$$\eta \equiv -\frac{W}{Q_{abs}}. \tag{5.44}$$

If the motor is a CE, then it will be called a **Carnot motor**. Let us denote by T_1 and T_2 the temperatures of its corresponding thermostats and suppose that $T_1 < T_2$. Then, obviously, $Q_{abs} = Q_2$ and $Q = Q_1 + Q_2$. By using these observations and Eqs. (5.43) and (5.31) in the definition (5.44), one obtains:

$$\eta_C = \frac{Q_1 + Q_2}{Q_2} = 1 + \frac{Q_1}{Q_2} \quad \Rightarrow \quad \boxed{\eta_C = 1 - \frac{T_1}{T_2}}. \tag{5.45}$$

It is important to note here that, given the universal character of the absolute temperature, the expression (5.45) of **the efficiency of a Carnot motor holds for *any* particular thermodynamic system that performs such a cycle**.

Moreover it can be proven that, **if certain thermodynamic system performs a motor cycle (reversible or not!), the efficiency of such an engine could never exceed the efficiency of a Carnot motor working with the thermostats of the extreme temperatures reached by the given system during its cycle**. Indeed, the infinitesimal heat exchange, δQ, of the given system during the cyclic process can always be written as an algebraic sum between the corresponding absorbed ($\delta Q_{abs} > 0$) and released ($\delta Q_{rel} < 0$) heat amounts: $\delta Q = \delta Q_{abs} + \delta Q_{rel}$. By using the property (4.18''') of the integrals of LDFs, the Clausius relation (5.42) can be written as:

$$\oint \frac{\delta Q}{T} = \oint \frac{\delta Q_{abs}}{T} + \oint \frac{\delta Q_{rel}}{T} = \oint \frac{\delta Q_{abs}}{T} - \oint \frac{\left|\delta Q_{rel}\right|}{T} \leq 0. \tag{5.46}$$

If T_{min} and T_{max} are, respectively, the minimum and maximum temperatures of the thermostats with which the system interacts during its cyclic process, then we obviously have:

$$\oint \frac{\delta Q_{abs}}{T} \geq \oint \frac{\delta Q_{abs}}{T_{max}} = \frac{1}{T_{max}} \oint \delta Q_{abs} = \frac{Q_{abs}}{T_{max}} \tag{5.47}$$

and

$$-\oint \frac{\left|\delta Q_{rel}\right|}{T} \geq -\oint \frac{\left|\delta Q_{rel}\right|}{T_{min}} = \frac{1}{T_{min}} \oint \delta Q_{rel} = \frac{Q_{rel}}{T_{min}}. \tag{5.48}$$

By adding the inequalities (5.47) and (5,48) and by using the relations (5.46), one obtains:

$$\frac{Q_{abs}}{T_{max}} + \frac{Q_{rel}}{T_{min}} \leq \oint \frac{\delta Q_{abs}}{T} - \oint \frac{\left|\delta Q_{rel}\right|}{T} = \oint \frac{\delta Q}{T} \leq 0. \tag{5.49}$$

It then follows that:

$$Q_{rel} \leq -Q_{abs} \frac{T_{min}}{T_{max}} \quad \Rightarrow \quad Q = -W = Q_{abs} + Q_{rel} \leq Q_{abs}\left(1 - \frac{T_{min}}{T_{max}}\right), \tag{5.50}$$

where use was made of Eq. (5.43). Now, if the definition (5.44) and the result (5.45) are applied, the final inequality of (5.50) leads to the desired result:

$$\eta = -\frac{W}{Q_{abs}} \leq 1 - \frac{T_{min}}{T_{max}} = \eta_C. \tag{5.51}$$

Note. The previous result holds as an inequality even for reversible motor cycles. Equal sign might appear in (5.51) only if the same were true for (5.47), (5.48) and if the given cycle were reversible. That is to say, **equality in the relation (5.51) might hold only for a Carnot motor**.

5.8 The concept of entropy

The most important result of this chapter is the fact that, at least for closed systems, equality holds in (5.42) for any reversible cyclic process. Recalling a theorem stated in Chapter 4, it follows that, if δQ is the heat exchange in an infinitesimal reversible process, then **the differential form $\delta Q/T$ should be an ED** (at least as far as closed systems are involved). In other words, for reversible infinitesimal processes of closed systems, δQ is a HLDF for which $1/T$ is an integrand factor. The ED $\delta Q/T$ could thus be considered as the total differential of some state function (which will be denoted by S):

$$dS = \frac{\delta Q}{T}. \tag{5.52}$$

The variation of this function between some initial (i) and final (f) equilibrium states could then be expressed as the integral of $\delta Q/T$ taken along any reversible process connecting the two states:

$$S_f - S_i = \int_{rev.}^{i\to f} \frac{1}{T}\delta Q . \tag{5.53}$$

This new state function is known under the name of ***entropy*** and plays the keystone role in thermodynamics. In order to specify the value of the entropy in some equilibrium state a scaling is needed, that is a value of the entropy should be defined in an **equilibrium state of reference** (which will be denoted as the state 0). Thus the value of the entropy in some other (variable) equilibrium state (*a*) will be:

$$S_a = S_0 + \int_{rev.}^{0\to a} \frac{1}{T}\delta Q . \tag{5.54}$$

The definition of the entropy through Eq. (5.54) is obviously based on the supposition that **any two equilibrium states of a thermodynamic system can be connected by a reversible process**. This is actually **a fundamental hypothesis** that must be included in a general statement of The Second Law. The usefulness of the ideal concept of a reversible process is perhaps most prominently manifested in this context.

Therefore, by taking an irreversible process between the two previously considered states of a thermodynamic system, *i* and *f*, one can always complete a cycle by a reversible process *f* → *i*. For the obtained cycle the strict inequality of Clausius should hold:

$$\oint_{irrev.} \frac{1}{T}\delta Q = \int_{irrev.}^{i\to f} \frac{1}{T}\delta Q + \int_{rev.}^{f\to i} \frac{1}{T}\delta Q = \int_{irrev.}^{i\to f} \frac{1}{T}\delta Q + S_i - S_f < 0 . \tag{5.55}$$

Otherwise stated, this means that:

$$S_f - S_i > \int_{irrev.}^{i\to f} \frac{1}{T}\delta Q . \tag{5.56}$$

As stressed before, the temperature under the integral of (5.56) should be interpreted as the temperature of some thermostat with which the system is interacting in a given infinitesimal stage of its irreversible process. If this transformation takes place in a totally isolated system then, obviously, δQ vanishes everywhere and the integral in (5.56) should be replaced by zero. This would lead to:

$$S_f > S_i , \tag{5.57}$$

which means that **during an irreversible process taking place in an isolated system, the entropy always increases with respect to the initial state**. Besides the introduction of a specified direction of the behavior of irreversible transformations of thermodynamic systems, this conclusion shows that the entropy cannot be a conservative quantity of a system (like the internal energy is). **Entropy sources** should exist that enhance its value during an irreversible process, despite the total isolation of the system.

From the thermodynamic standpoint, the existence of the entropy in the states i and f appearing in the relations (5.56) and (5.57) implies that these states are conceived as equilibrium thermodynamic states of the system. The process $i \rightarrow f$ should thus be a **natural** one (see the section 1.4). Therefore, for the case of total isolation where inequality (5.57) holds, the system cannot leave spontaneously its initial state. The process can proceed only if some internal constraints are changed and the system should accommodate to the new conditions. For example, one may consider the removal of a separation wall between two internal compartments containing different gases, which therefore begin to mix. Since the entropy of the system is strictly increased in the final state, it follows that it reaches the maximum possible value under the new conditions (if an intermediary equilibrium state would exist for which the entropy would take a higher value, then the process directed ***from*** this state ***towards*** the final one f would contradict The Second Law through the reversion of the inequality (5.57)). Obviously, every equilibrium state of an isolated system can be imagined as a final state of a certain natural process. It thus follows that **the entropy of an isolated system in an equilibrium state should attain its maximum value compatible with the actual constraints of the system**. This conclusion is of essential importance for the characterization of equilibrium states of thermodynamic systems. If some **anomalous process** occurs (see again the section 1.4), starting from some equilibrium state of an isolated system, then it cannot end in an equilibrium state. Therefore such processes do not involve any changes of the constraints of the system. Anomalous processes are produced spontaneously and can lead only do **decreases of the entropy** (as far as this concept could be extended to the final non-equilibrium states). **The condition of negative variation of the entropy of an isolated system becomes thus the necessary and sufficient condition for the *stability* of its state against fluctuations (or anomalous processes)**.

5.9 Example of a non-thermodynamic system

In section 1.4, when the definition of a thermodynamic system was given, the **necessity of a thermal interaction between different parts of the system** was stressed. This central thermodynamic idea will be reinforced in this section by an example [4].

Consider an adiabatically insulated cylinder containing an adiabatic piston inside (Figure 5.1). The two ends of the cylinder are closed by two diathermal pistons, which thus enclose equal masses of two **different** ideal gases (that is with different constant-volume molar heat capacities). For simplicity, one mole of each will be considered.

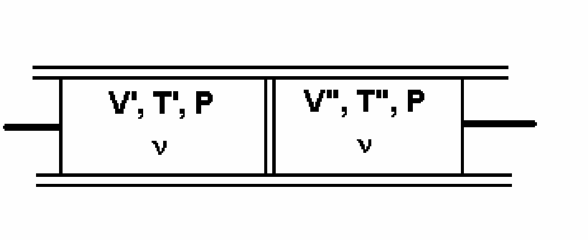

Figure 5.1

Suppose now that the two considered amounts of gas form a thermodynamic reunion, that is a thermodynamic system. Then the total heat exchanged by this system during a reversible infinitesimal process should be written as the sum of the separate heat exchanges (see Eqs. (3.10)):

$$\delta Q = \delta Q' + \delta Q'' = (dU' + P\,dV') + (dU'' + P\,dV''), \tag{5.58}$$

where it should be remembered that the two gases keep constant masses and that the pressure is the same in both compartments. As known from the high-school textbooks of physics, for perfect gases, the internal energy is a function of the absolute temperature only ($U = C_V\,T$) and the pressure is given by the perfect gas law, $P = RT/V$, where R is the perfect gas constant. By using these relations in Eq. (5.658, the total heat exchange can be written as a LDF:

$$\delta Q = C_V'\,dT' + C_V''\,dT'' + R\frac{T'}{V'}dV' + R\frac{T''}{V''}dV''. \tag{5.59}$$

As the internal piston is supposed frictionless, the pressure in both compartments should be equal and the volume variations should not be independent, but connected through a linear relation:

$$P = R\frac{T'}{V'} = R\frac{T''}{V''} \;\Rightarrow\; V'' = V'\frac{T''}{T'} \;\Rightarrow\; dV'' = \frac{T''}{T'}dV' - \frac{V'T''}{T'^2}dT' + \frac{V'}{T'}dT''. \tag{5.60}$$

Hence the LDF (5.59) takes the form:

$$\delta Q(T',T'',V') = \left(C_V' - R\frac{T''}{T'}\right)dT' + (C_V'' + R)dT'' + R\frac{T' + T''}{V'}dV'. \tag{5.61}$$

If the reunion of the two amounts of gas would be a thermodynamic system, then it should fulfil the requirements of The Second Law. As we have already seen, one major consequence of this Law is that the differential heat exchange of the total system be a HLDF. A temperature could thus be defined for the system, which would be the integrand factor for δQ. In other words, the LDF (5.61) should satisfy the condition (4.13). The vector of our LDF is obviously the following:

$$\vec{Q}(T',T'',V') = \left(C_V' - R\frac{T''}{T'},\, C_V'' + R,\, R\frac{T'+T''}{V'} \right) \tag{5.62}$$

and its curl follows immediately as:

$$rot\,\vec{Q}(T',T'',V') = \left(\frac{R}{V'}, -\frac{R}{V'}, \frac{R}{T'} \right). \tag{5.63}$$

By replacing the last two relations in the criterion (4.13), one obtains:

$$\vec{Q}(T',T'',V') \cdot rot\,\vec{Q}(T',T'',V') = \frac{R}{V'}\left(C_V' - C_V''\right) \neq 0\,, \tag{5.64}$$

since the molar heat capacities of the two gases are different by hypothesis.

Eq. (5.64) shows that **the LDF (5.61) does not satisfy the necessary and sufficient condition for holonomy** and thus that **there is no integrand factor for this LDF**. It follows that **a temperature cannot be defined for the considered two-gas system** and that **this system is not thermodynamic**. The key element of this non-thermodynamic configuration is obviously the fact that the internal piston is adiabatic and that the temperatures of the two compartments have independent variations. Thus, the thermal interaction (either direct or indirect, through some common thermostat) between the two parts of the system is cut off. If the internal piston were diathermal then the two gases could succeed in reaching the same temperature, which could be defined as the thermodynamic temperature of their system. A system whose parts are allowed to interact thermally (and which is thus thermodynamic) is sometimes labeled as a **thermal system**.

One may observe in passing that if the external pistons were fixed then the total volume of the system would be constant:

$$V' + V'' = constant\,, \tag{5.65}$$

and the number of independent variables would be reduced. This new condition together with (5.60) would bring the LDF of the total heat exchange to the form:

$$\delta Q(T',T'') = C_V'\,dT' + C_V''\,dT''\,, \tag{5.66}$$

which is an **integrable LDF**. This is still not conformal with The Second Law since **no temperature could be defined for the system as an integrand factor of *δQ***. Thus, even if the system becomes "simpler", it is still non-thermodynamic in the absence of the thermal interactions between its parts.

One more question may arise in the situation when the two gases of the preceding example were identical. Then, the scalar product of Eq. (5.64) vanishes and the differential form of (5.61) would become holonomic. A temperature, for example $(T' + T'')/2$, could be defined for this system in the present case. Nevertheless, for such a non-thermal system, the essential feature of extensivity (see the next chapter for a thorough discussion) cannot hold for the entropy. This also contradicts The Second Law in its general form (see the next chapter) and the system still keeps out of being thermodynamic.

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Exercises

5.1 A heat pump (that is a CE working in a reverse-motor regime) is to be used to maintain a building at an average temperature of 22 ^{0}C. How much power will be required to do this when the outside temperature is 3 ^{0}C and the average total heat loss is 10^9 cal per day? The efficiency of the pump is reduced by half owing to mechanical and other losses. How much power would be required if direct heating, say by means of electric fires, would be used instead?
Hint/Answer: The ideal heat pump should be a CE operating between the outside temperature (T_1) and the inside one (T_2). The heat delivered to the building should compensate the total loss per day. The pump efficiency should be thus expressed as the ratio between the heat delivered at the hot thermostat and the work provided from outside. The needed power for indirect heating is thus 6.24 kW. For the direct heating one would need 48.4 kW.

5.2 A building is maintained at a temperature t_2 = 20 ^{0}C by a reversible heat pump driven by a Carnot motor. The highest temperature available for the motor is t_3 = 100 ^{0}C and it releases heat at the temperature of the building. The heat pump is taking heat from a cold reservoir at the temperature t_1 = 3 ^{0}C. If the total heat delivered to the building is Q_2 and the heat absorbed by the motor is Q_3, find the ratio Q_2/Q_3.
Answer: $\frac{Q_2}{Q_3} = \frac{T_2}{T_3} \cdot \frac{T_3 - T_1}{T_2 - T_1} = 4.48$.

5.3 A simple closed thermodynamic system, whose isobaric and isochoric heat capacities are constants, performs a reversible cyclic process consisting in the following transformations: adiabate

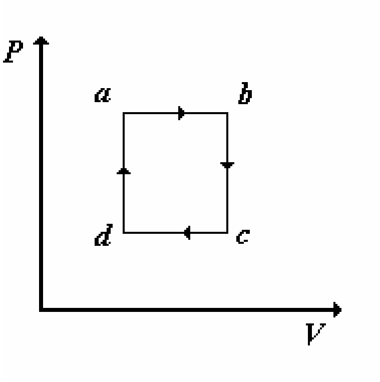
(1 → 2), isobare (2 → 3) and isochore (3 → 1). The temperatures correspondent to the intersection points are: $T_3 > T_2 > T_1$.

a) Prove the following relation: $\frac{T_3}{T_1} = \left(\frac{T_3}{T_2}\right)^{\gamma}$; $\gamma = \frac{C_P}{C_V}$.

b) Find the efficiency of the previously described thermal engine when running it as a motor. It is known that $\gamma = 3/2$ and $T_3/T_2 = 4$.

Hint/Answer: For a), the zero variation condition of the entropy in a complete cycle should be written down explicitly. b) $\eta = 2/9 = 22.22$ %.

5.4 A simple closed thermodynamic system containing one mole of substance whose isobaric and isochoric molar heat capacities are constants, performs a reversible cyclic process consisting in two isobares and two isochores. The temperatures correspondent to the intersection points are: $T_b > T_a > T_c > T_d$ (see the attached illustration).



a) Prove the following relation: $T_a T_c = T_b T_d$.

b) Given the values of T_a, $T_b/T_a = n$, $T_a/T_d = m$ and that of the total work produced per cycle, $-W$, find the difference $C_P - C_V$ for the considered substance.

Hint/Answer: For a), the zero variation condition of the entropy in a complete cycle should be written down explicitly. b) $C_P - C_V = \frac{mW}{T_a(n-1)(m-1)}$.

5.5 50 grams of milk at the temperature T_1 is poured slowly into 250 grams of coffee at the temperature T_2. Assuming the specific heat of milk and coffee to be equal to the corresponding value for water, find the equilibrium value of the temperature, T_f. Find also the variation of the total entropy and prove that it is strictly positive if the temperatures of the two liquids are different. What general conclusion could be drawn from this result?

Hint/Answer: Assume that the system "milk + coffee" is isolated from the outside world and use The First Law.

It follows that $T_f = \frac{m_1 T_1 + m_2 T_2}{m_1 + m_2} = \frac{T_1 + 5T_2}{6}$; $\Delta S = m_2 c\left[(\mu+1) ln\frac{\mu+\theta}{\mu+1} - ln\,\theta\right]$, where μ = m_1/m_2 and $\theta = T_2/T_1$. If $f(\mu,\theta) = (\mu+1) ln\frac{\mu+\theta}{\mu+1} - ln\,\theta$, it can be seen that $f(\mu,1) = 0$ and that

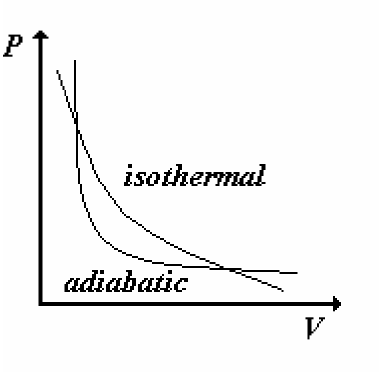
$\frac{\partial f}{\partial \theta} = \frac{\mu(\theta - 1)}{\theta(\mu + \theta)}$. So, $f(\mu,\theta) > 0$, whether $\theta > 1$ or $\theta < 1$. Thus the thermal mixing of two fluids should be an irreversible process.

5.6 Two *rigid* bodies whose initial temperatures are T_1 and T_2 ($> T_1$) have constant heat capacities C_1 and C_2, respectively. They are to be used as "thermostats" for a "bithermal motor". Assuming that the heat capacity of the working system (C) is very much smaller than C_1 and C_2, find the maximum amount of work that can be obtained from this motor and the final temperatures of the two bodies.

Hint/Answer: First it should be observed that, since the temperatures of the "thermostats" are not constant during the operation, no cyclic process could be really imagined for the considered three-component system. Secondly, it should be noted that the maximum efficiency could be reached if the engine would be run in a succession of Carnot motor cycles. This could be achieved if infinitesimal amounts of work would be exchanged during each Carnot cycle, in order to consider that the temperatures of the thermostats would be invariable when completing such a cycle. To this limit, all the processes of heat transfer should be supposed as reversible and thus the overall process of the ***isolated*** three-component system might be taken as reversible: $\Delta S = \Delta S_{C_1} + \Delta S_{C_2} + \Delta S_C = 0$ (the extensivity of the entropy is taken here as granted; this subject will be thoroughly discussed in the next chapter and in some following others, after the presentation of the statistical point of view in Thermal Physics). Since C performs a succession of Carnot cycles we also have $\Delta S_C = 0$, so that $\Delta S_{C_1} + \Delta S_{C_2} = 0$. According to the restraint form of The Second Law, the process of work producing terminates when the (reversible) motor becomes monothermal, that is when the temperatures of the two "thermostats" coincide. Thus, the entropy variations of the two bodies could be written as functions of their final common temperature (T), which gives: $C_1 \int_{T_1}^{T} \frac{d\theta}{\theta} + C_2 \int_{T_2}^{T} \frac{d\theta}{\theta} = ln \frac{T^{C_1 + C_2}}{T_1^{C_1} T_2^{C_2}} = 0 \Leftrightarrow T = T_1^{\frac{C_1}{C_1 + C_2}} T_2^{\frac{C_2}{C_1 + C_2}}$. On the other hand, the total system $C_1 \cup C_2 \cup C$ is assumed as isolated. Thus, the variation of its internal energy should also vanish and the total produced work ($-W$) should equal the total heat exchange $Q = Q_1 + Q_2$ (the heat retained by the working system C was neglected since its heat capacity is considered as much smaller as compared to those of the "thermostats"). It follows that $|W| = Q_1 + Q_2 = C_1(T - T_1) + C_2(T - T_2) = (C_1 + C_2)T - C_1 T_1 - C_2 T_2$. For the special case when only one of the bodies (say 1) have a finite heat capacity, the final temperature tends obviously to T_2 and the total work obtained from the system becomes $|W| = C_1(T_2 - T_1)$.

5.7 Show that two reversible processes, one isothermal and the other adiabatic of a closed simple system, cannot intersect twice.

Hint: Assuming a double intersection of the two curves plotted in the *V-P* representation (see the attached figure), a *reversible monothermal* cycle could be performed during which a non-vanishing work would be exchanged with the environment. This would contradict the restrained form of The Second Law.



5.8 By taking the model of a Carnot motor find out the temperature modification of which thermostat should induce the most important absolute change in the efficiency of the motor. What practical conclusions could be drawn from this result?

Hint: $\left(d\eta_C\right)_{T_1} = \frac{T_1}{T_2^2}dT_2$; $\left(d\eta_C\right)_{T_2} = -\frac{1}{T_2}dT_1$. It follows that both the increase of the temperature of the "hot" reservoir and the decrease of the temperature of the "cold" reservoir lead to the increase of the motor efficiency. If equal absolute variations of the temperatures are assumed for the two reservoirs then we find out that $\left|\frac{\left(d\eta_C\right)_{T_1}}{\left(d\eta_C\right)_{T_2}}\right| = \frac{T_1}{T_2} < 1$, so that the most sensitive temperature change is at the "cold" thermostat. Thus, improving the motor efficiency implies lower minimum temperatures for the working system.

6. The general statement of The Second Law of Thermodynamics. The fundamental equation of Thermodynamics. The Third Law of Thermodynamics and the scaling of the entropy

The entropy as a state function and the absolute thermodynamic temperature were introduced in the preceding chapter. The starting point was the restraint form of The Second Law and the results were restricted to the closed thermodynamic system only. By extensively using the concepts of Carnot and monothermal engines it was concluded that the LDF of the heat exchange in an infinitesimal reversible process, $(\delta Q)_{rev}$, is holonomic and the absolute temperature, T, was defined as the inverse of an integrand factor of it. Furthermore, the entropy was defined as "the primitive" of the ED thus obtained: $dS = (\delta Q)_{rev}/T$.

According to the wide experimental evidence in Thermal Physics, all these results may be generalized for any kind of thermodynamic system. **In fact, the entire content of the previous chapter may be reconstructed for open thermodynamic systems too, by simply replacing everywhere the mechanical work *W* by the sum between *W* and the chemical work *M*.**

In the next section a collection of statements will be prescribed, which together constitute the general form of The Second Law of Thermodynamics. Nevertheless, it should be observed that, even if other equivalent forms of this fundamental law of Thermodynamics may be stated [1, 2], the practical conclusions derived therefrom are always the same.

The crucial role of the entropy in Thermal Physics was recognized more than one century ago by Clausius, Kelvin, Maxwell, Boltzmann, and many others. Therefore it may appear quite astonishing to note that most of the main features of entropy are widely unknown to physicists and that many problems in connection with entropy are still open or have been solved only in the last few years.

There may be two reasons for this. The first is that physicists are more interested in determining the entropy of a given specific system as a function of some parameters such as temperature, density, etc., rather than in considering general properties of entropy. The second is that the proofs of many of those properties are generally rather tricky and involved, requiring some, so-to-say, unusual mathematics, at least in the quantum mechanical case.

The name "entropy" is due to Clausius (1865) [3] and means transformation (τροπη). The prefix "en" was chosen to have a resemblance to the word "energy". Sometimes, mainly in the mathematical literature, one uses the letter H (first introduced by Burbury in 1890 [4]) instead of S for entropy, whereas Boltzmann originally used "E". In physics, H and E are both not very good notations because of the risk of confusion with the Hamiltonian or with the energy.

6.1 The general statement of The Second Law of Thermodynamics

This fundamental law consists of three complementary statements:

a) **Any couple of equilibrium states of a thermodynamic system can be connected by a reversible process.**

b) **The infinitesimal amount of heat, $(\delta Q)_{rev}$ exchanged by a thermodynamic system during an infinitesimal reversible process can be expressed as a holonomic differential form with respect to the independent state parameters of the system. An integrand factor of this form, denoted by $1/T$, defines a universal temperature scale, namely the absolute thermodynamic temperature.**

c) **A state function, the entropy, can be defined through the integration of the exact differential $dS = (1/T)\cdot(\delta Q)_{rev}$ over a reversible process. *The entropy is an extensive state function* whose variation between two equilibrium states, *i* and *f*, satisfies the following relation:**

$$\boxed{\Delta S = S_f - S_i \geq \int_{(process)}^{i \to f} \frac{1}{T}\,\delta Q}, \tag{6.1}$$

where the equality may hold if and only if the integration is performed over a reversible process.

Notes.

a) When the process $i \to f$ indicated in (6.1) is ***irreversible***, the parameter T should be interpreted as the temperature of the thermostats with which the system instantaneously interacts.

b) The property of ***extensivity of the entropy***, should also be conditioned, as it was for the case of the internal energy, by the weak interaction between the considered macroscopic parts of a thermodynamic system. Nevertheless, there is another condition that must be stressed, from the thermodynamics point of view, in order that the extensivity property to hold for the entropy. This condition is that the temperature should be a homogeneous parameter over the considered thermodynamic system. Indeed, by taking into account the second of the equations (3.10), the heat exchange of a thermodynamic system should equal the algebraic sum of the heat amounts exchanged by all its subsystems. When this condition of The First Law is imposed to an infinitesimal process, one may write: $\delta Q(A \cup B \cup \ldots) = \delta Q(A) + \delta Q(B) + \ldots$. This means that, if the temperatures of the subsystems A, B, …, and that of the reunion A∪B∪… are not the same, then one ***may not*** write $dS(\mathrm{A}\cup\mathrm{B}\cup\ldots) = dS(\mathrm{A}) + dS(\mathrm{B}) + \ldots$, which is demanded by the stated extensivity of the entropy. Thus, from the standpoint of Thermodynamics, the extensivity of the entropy should be interpreted as follows: the entropy of a thermodynamic system, whose temperature is a homogeneous (i.e. position independent) parameter, is the sum of the entropies of its subsystems. In an equivalent statement, one may say that the concept of entropy makes no sense in Thermodynamics in the absence of the thermal equilibrium. This feature brings another contrast between entropy and internal energy, whose extensivity is not conditioned by the thermal equilibrium.

6.2 The fundamental equation of Thermodynamics

Consider a reversible process connecting two infinitely close equilibrium states of a thermodynamic system. The Second Law applied to this case leads to:

$$dS = \frac{1}{T}(\delta Q)_{(rev.)} . \tag{6.2}$$

The infinitesimal heat exchange in this process may be obtained from the local form of The First Law (Eq. (3.11)) and, when replaced in (6.2), one obtains:

$$dU = T\,dS + (\delta W)_{(rev.)} + (\delta M)_{(rev.)} . \tag{6.3}$$

Due to its very important role in practical computations, this relation is sometimes called the ***fundamental equation of Thermodynamics***. It essentially combines in only one expression the two main laws of Thermodynamics. For a ***simple thermodynamic system (a fluid)***, the equation (6.3) takes a more concrete form:

$$dU = T\,dS - P\,dV + \sum_i \mu_i\,dv_i . \tag{6.4}$$

It should always be remembered that relations of the type (6.4) are written for **infinitesimal reversible processes**. The parameters T, P and μ_i actually cannot be defined if the process were irreversible. Owing to The Second Law, for irreversible transformations one may write only the following inequality:

$$dU < T\,dS + (\delta W)_{(irrev.)} + (\delta M)_{(irrev.)} . \tag{6.5}$$

Equation (6.4) is far from being purely formal. In fact, by integrating an exact differential, it can be used to effectively obtain the entropy variations as a function of the extensive parameters U, V and v_i:

$$dS(U,V,\{\mu_i\}) = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dv_i . \tag{6.6}$$

Moreover, Eq. (6.6) allows a more precise definition of the chemical potential of some component (i) of the system (once the entropy is obtained through the integration procedure):

$$\mu_i = -T\left(\frac{\partial S}{\partial \nu_i}\right)_{U,V,\{\nu_j,\, j\neq i\}} . \tag{6.7}$$

Note. In order to have a more intuitive idea of the concept of entropy, consider Eq. (6.3) for a closed system ($\delta M = 0$). Suppose that the system undergoes some infinitesimal process during which outgoing energy fluxes through both mechanical and thermal channels produce a decrease of its internal energy. Then, the absolute value of the work that may be obtained from the system in the given process may be written as: $|(\delta W)_{rev}| = |dU| - |T\cdot dS|$. The variation of the entropy might be thus interpreted as **the measure of the unavailability of a system's thermal energy for conversion into mechanical work**.

In some contexts, the entropy may also be interpreted as a measure of **the degree of disorder or randomness in the system**. This is actually the statistical point of view on this state function, which will be detailed in the next chapters. For the moment we shall content to note that, for example, according to (6.1), the entropy of a certain **system has to increase** when passing from an ordered crystalline state to a (less ordered) liquid state through a fusion process performed with absorption of heat at constant temperature. So, the increase of entropy is here related to a decrease of order into the considered system.

On the same line could be interpreted the so-called **relaxation processes** that take place in adiabatically closed systems when some internal constraints are removed (see an example in the exercise (6.4)). On one hand, removing constraints implies a decrease of the order in the system. On the other hand, as was already revealed, the processes that take place in such conditions may only lead to an increase of the entropy of the system.

6.3 The entropy variation in a heating or cooling process through a pure thermal contact

Consider a **fixed volume closed simple system**. The thermodynamic states of such systems may be characterized by temperature only. All other state quantities may be expressed as functions of this unique state parameter. The interaction of this system with its exterior is allowed only through the thermal channel and the heat exchange during an infinitesimal reversible process should be proportional to the corresponding infinitesimal temperature variation: $(\delta Q)_{rev} = C(T)\cdot dT$, where $C(T)$ is a state quantity known as **heat capacity** of the system. We shall deal in more detail with such state quantities in the next chapters.

In practical problems the following question arises quite frequently: **what is the entropy variation of such a fixed volume closed simple system when its temperature changes (reversibly or not) from T_i to T_f?** The most common situation is when the heat capacity is a

positive constant (at least over the working temperature range): C. To answer this problem we must remember that at least one reversible process should exist between the states T_i and T_f. So, we may compute the entropy variation following such a reversible process:

$$S_f - S_i = \int_{rev.}^{i\to f} \frac{1}{T} \delta Q = C \int_{T_i}^{T_f} \frac{dT}{T} = C\, ln \frac{T_f}{T_i} . \tag{6.8}$$

The same trick may be used to compute the internal energy variation between the two states. Since the internal energy is a state quantity, by applying The First Law to our *fixed volume closed simple system*, one gets:

$$U_f - U_i = \int_{rev.}^{i\to f} \delta Q = C \int_{T_i}^{T_f} dT = C\left(T_f - T_i\right). \tag{6.9}$$

Another frequent question in problems is: **when a fixed volume closed simple system with constant heat capacity *C* and initial temperature *T_i* interacts with a thermostat at the temperature *T_f*, what is the entropy variation of the thermostat**? To answer this second problem we must observe that a thermostat may be looked at as a **fixed volume closed simple system with infinite heat capacity**. So, we'll consider first a fixed volume closed simple system of heat capacity C_0 and initial temperature T_f, which thermally interacts with our given system inside of some adiabatic closure. Then, in order to approach the thermostat condition, we'll consider the result in the limit $C_0 \to \infty$. The two-body system is clearly isolated and therefore The First Law implies a vanishing total internal energy variation: $\Delta U + \Delta U_0 = 0$. By applying Eq. (6.9) to both bodies, one may find their final temperature, T:

$$C\left(T - T_i\right) + C_0\left(T - T_f\right) = 0 \quad \Rightarrow \quad T = \frac{C T_i + C_0 T_f}{C + C_0} . \tag{6.10}$$

According to Eq. (6.8), the entropy variation of the thermostat may therefore be written as:

$$S_{0f} - S_{0i} = \lim_{C_0\to\infty} C_0\, ln \frac{T}{T_f} = C \lim_{C_0\to\infty} ln \left(1 - \frac{C}{C + C_0} \frac{T_f - T_i}{T_f}\right)^{\frac{C_0}{C}} = -C\left(1 - \frac{T_i}{T_f}\right). \tag{6.11}$$

The entropy variation of the thermodynamic universe in this interaction will then be:

$$S_{uf} - S_{ui} = C\left(\frac{T_i}{T_f} - 1 - ln\frac{T_i}{T_f}\right). \tag{6.12}$$

By defining $x \equiv \frac{T_i}{T_f} - 1$, one may consider the function $f(x) = x - ln(1 + x)$ in order to study

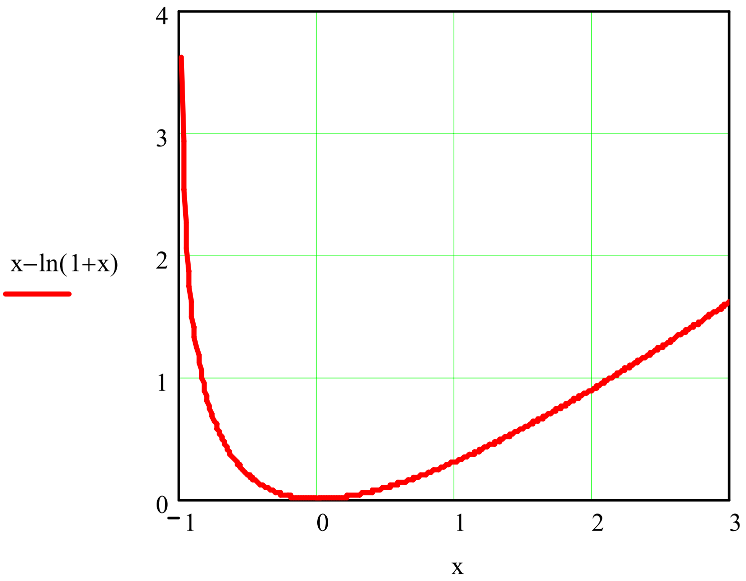


Figure 6.1

the sign of the entropy variation of the universe. Since the temperatures are positive it is obvious that $x > -1$. We have also $f(0) = 0$, $f'(x) = x/(1 + x)$ and $f''(x) = (1 + x)^{-2}$. It follows that $f(x) > 0$ for any $x > (-1, 0)\cup(0, \infty)$. We have a (double) root of f at $x = 0$ only (see also the graph of Figure 6.1), which corresponds to $T_i = T_f$. As C was taken as a positive constant, it may be concluded that **the entropy variation in this purely thermal interaction inside the isolated system formed by the thermostat and the body with heat capacity *C* is strictly positive**. In other words, the **considered heating or cooling process is always irreversible**.

6.4 The Third Law of Thermodynamics and the entropy scaling

The Third Law of Thermodynamics (also referred as ***the Nernst theorem***) was established by the German physicist Walter Hermann Nernst in 1906 [5]: *when a thermodynamic system is cooled, so that its absolute temperature tends to zero, its entropy tends towards a constant value (S_0), which is independent of any of the state variables of the system.*

The original statement of Nernst was later completed by Max Plank who proposed $S_0 = 0$ as an absolute normalization of the entropy "*for any pure substance*". Presently, The Third Law is stated as follows [5]:

When the absolute temperature of a thermodynamic system tends to zero by no matter what process, the entropy of the system tends towards the value of zero.

Notes.

a) Based on this Law, one may conclude that **the limit values of the first derivatives of the entropy with respect to some state parameters, when $T \to 0$, are also zero** [6-8]. As an example one may consider $\lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_{U,\{v_i\}} = \lim_{T\to 0}\frac{\partial}{\partial V}S(U,V,\{v_i\})$. The partial derivative is itself defined through a limit procedure. As a consequence of the assumed derivability of the entropy, this limit exists everywhere in its domain of definition:

$$\lim_{T\to 0}\frac{\partial}{\partial V}S(U,V,\{v_i\}) = \lim_{T\to 0}\lim_{V'\to V}\frac{S(U,V',\{v_i\}) - S(U,V,\{v_i\})}{V'-V}. \tag{6.13}$$

The volume is always supposed as finite and the two limits in the right hand side of Eq. (6.13) exist separately. Their order could thus be changed, so that one could obtain:

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_{U,\{v_i\}} = \lim_{V'\to V}\frac{\lim\limits_{T\to 0} S(U,V',\{v_i\}) - \lim\limits_{T\to 0} S(U,V,\{v_i\})}{V'-V} = 0, \tag{6.14}$$

since, following The Third Law, the two limits of the entropy vanish. In a perfectly analogous manner one can also prove that:

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial v_j}\right)_{U,\{v_i,i\neq j\}} = 0. \tag{6.15}$$

By comparing these results with Eq. (6.6) for a simple fluid, one may readily conclude that:

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial V}\right)_{U,\{v_i\}} = \lim_{T\to 0}\frac{P}{T} = 0 \tag{6.16}$$

and

$$\lim_{T\to 0}\left(\frac{\partial S}{\partial v_j}\right)_{U,\{v_i,i\neq j\}} = -\lim_{T\to 0}\frac{\mu_j}{T} = 0. \tag{6.17}$$

Eqs. (6.16) and (6.17) imply the fact that **both the pressures and the chemical potentials tend to zero values at zero absolute temperature**.

No such conclusion may be drawn for the derivative of the entropy with respect to the internal energy, which, from Eq. (6.6), equals $1/T$. Its limit when T tends to zero is obviously infinite. Physically, this result could be explained as follows. The internal energy is essentially an average of the energies of the microscopic states of the system. As $T \to 0$, the system is brought near its unique fundamental quantum state. Thus, it turns out that no variations are possible in the internal energy of the system near the absolute zero and, if one tries to compute the derivative upon the pattern of Eq. (6.14), then, near $T = 0$, the fraction should be divided by $U' - U = 0$.

Nevertheless, there are other derivatives of the entropy which go to zero when $T \rightarrow 0$, but each case should be carefully considered in order to avoid evaluation errors.

b) As a consequence of The Third Law, it can be proven that **it is impossible to attain the zero absolute temperature through a finite succession of reversible processes**. Due to this conclusion (whose proof will not be included here), it is frequently stated that The Third Law establishes the impossibility of reaching the absolute zero for a thermodynamic system. Actually, from this point of view, this conclusion is quite redundant since the fact that $T \neq 0$ ($T > 0$) was already established through the consequences of The Second Law. Thus, one may say that **The Second and Third Laws of Thermodynamics concurrently establish the impossibility of reaching the temperature $T = 0$**.

c) The Third Law is particularly important for the study of the very low temperature phenomena. For an introductory lecture course, the importance of this law resides mainly in establishing a reference value for the entropy. From this point of view, The Third Law is complementary to The Second Law (which defines only the entropy variations), allowing for an unambiguous definition of the entropy. It is thus usually stated that **The Third Law establishes a scaling for the entropy** as a state function.

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Exercises [9]

6.1 One kilogram of water at 273 K (specific heat c = 4186.8 J/(Kg·K)) is brought into contact with a heat reservoir at 373 K. When the water has reached 373 K, what is the entropy change of the water? Of the reservoir? Of the thermodynamic universe?

If the water had been heated from 273 K to 373 K by first bringing it into contact with a reservoir at 323 K and then with a reservoir at 373 K, what would have been the entropy changes? How could one heat the water so that the change of entropy of the universe is less than a prefixed quantity?

Answer/Hint: Apply Eqs. (6.8), (6.11) and (6.12). For the first part, ΔS = 1306.73 J/K; $\Delta S_{reservoir}$ = -1122.47 J/K; $\Delta S_{universe}$ = 184.26 J/K (> 0 ⇒ irreversible process). For the second part, ΔS = 1306.73 J/K; $\Delta S_{reservoir\ 1}$ = -648.95 J/K; $\Delta S_{reservoir\ 2}$ = -561.03 J/K; $\Delta S_{universe}$ = 96.30 J/K. The increase of the entropy of the universe can be made as small as desired by increasing the number of the reservoirs at intermediate temperatures, that is by approaching the conditions for a reversible process.

6.2 One fixed-volume body of heat capacity C is heated from an initial temperature T_i to a final one T by placing it in thermal contact with a series of N thermostats of increasing temperatures: T_1, T_2, …, $T_N = T$ so that $T_k = T_i + k\cdot\Delta T$, where $\Delta T = (T - T_i)/N$. Compute the entropy variations of the body and of the thermodynamic universe and show that, while the first is independent of N, the second tends to zero as N increases to infinity.

Answer/Hint: The entropy variation of the body may be calculated by Eq. (6.8): $\Delta S_{body} = C\,ln\dfrac{T}{T_i}$.

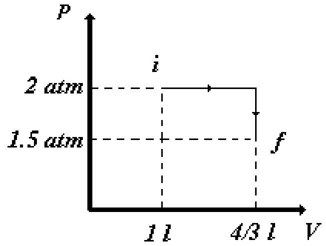
The entropy variation of the k-th thermostat follows from Eq. (6.11): $\Delta S_k = -C\left(1-\dfrac{T_{k-1}}{T_k}\right) = -C\dfrac{\Delta T}{T_k} = -\dfrac{C}{N}\dfrac{T-T_i}{T_i}\dfrac{1}{1+\dfrac{T-T_i}{T_i}\dfrac{k}{N}}$, so that the entropy variation of the thermodynamic universe becomes: $\Delta S_u = C\,ln\dfrac{T}{T_i} - \dfrac{C}{N}\dfrac{T-T_i}{T_i}\sum_{k=1}^{N}\dfrac{1}{1+\dfrac{T-T_i}{T_i}\dfrac{k}{N}}$. For high values of N, one may approximate the sum by using the following limit (a > 0): $\lim_{N\to\infty}\dfrac{1}{N}\sum_{k=1}^{N}\dfrac{1}{1+a\dfrac{k}{N}} = \int_0^1\dfrac{dx}{1+a\,x} = \dfrac{1}{a}ln(1+a)$. Therefore $\lim_{N\to\infty}\Delta S_u = 0$.

6.3 Calculate the entropy change when a piece of copper weighing 21 g is removed from a steam chamber at 100 ^{0}C and placed quickly in a copper calorimeter weighing 120 g containing 46 g of water at 15 ^{0}C. The average specific heat of copper between 15 ^{0}C and 100 ^{0}C is C_P = 389.79 J/(Kg·K).

Answer: ΔS = 2.323 J/K

6.4 A thermally insulated cylinder closed at both ends is fitted with a frictionless heat conducting piston which divides the cylinder into two parts. Initially, the piston is clamped at the center with one liter of air at 300 K and 2 atm on one side, and one liter of air and 1 atm on the other. The piston is released and reaches equilibrium at a new position. Compute the final pressure and temperature of the gas and the total increase of entropy. For air, a good approximation for the constant volume molar heat capacity is $C_V = (5/2)R$.

Hint/Answer: The temperature of the system does not change during the process since the total internal energy is kept constant by the rigid adiabatic enclosure. The final pressure can be found from mechanical equilibrium arguments and gives 1.5 atm. The final volumes will be 4/3 liter for the first compartment and 2/3 liter for the second. Although no heat entered the system, there is no reason to consider the process as reversible. Take, for example, the gas of the first compartment: it evolves from the state of temperature 300 K and pressure P_1 = 2 atm towards the state of temperature 300 K and pressure P = 1.5 atm. One may choose a reversible way between these two states consisting in a reversible isobaric transformation followed by a reversible isochore (see the attached figure). The corresponding entropy variation would be concentrated on the isochore: $\Delta S_1 = \int\limits_{isobare}^{V\to 4V/3} \frac{\delta Q}{T} + \int\limits_{isochore}^{P_1\to P} \frac{\delta Q}{T} = \nu_1 C_P \int\limits_{V}^{4V/3} \frac{dT}{T} + \nu_1 C_V \int\limits_{P_1}^{P} \frac{dT}{T}$. But, on the isobare we have dT/T = dV/V and on the isochore, dT/T = dP/P. Therefore, $\Delta S_1 = \nu_1 C_P \int\limits_{V}^{4V/3} \frac{dV'}{V'} + \nu_1 C_V \int\limits_{P_1}^{P} \frac{dP'}{P'} = \nu_1 \left(C_P - C_V\right) ln\frac{4}{3} = \nu_1 R\, ln\frac{4}{3}$. In an analogous way one finds: $\Delta S_2 = -\nu_2 R\, ln\frac{3}{2}$. Since $P_1 = 2 \cdot P_2$, it follows that $\nu_1 = 2 \cdot \nu_2 = 2 \cdot P_2 V/(RT)$. Finally one gets $\Delta S = \Delta S_1 + \Delta S_2$ = 0.0573 J/K.



7. Statistical description of thermal phenomena

The general macroscopic point of view in Thermal Physics is built up from the Laws of Thermodynamics. This framework offers an effective possibility of description and interpretation of thermal phenomena by using a restraint number of state parameters for the given system. Nevertheless, some related concepts (e. g. the entropy) may have no immediate physical significance. Therefore, a deeper understanding of the thermodynamic concepts certainly needs microscopic investigation. Moreover, as it will become clear in the next chapters, beside the Laws, the thermodynamic study of a certain system needs some *specific* data embedded in a set of relations between its state parameters (the so-called equations of state). These relations cannot be established within the general framework of The Laws of Thermodynamics. They are usually established through specific experimental research. Nevertheless, deducing (or, at least, verifying) such relation from the microscopic viewpoint may often prove a very helpful and clarifying task.

The microscopic description of a thermodynamic system should necessarily start from the ***dynamics of the microscopic units of the system***. This dynamics is necessarily a ***quantum*** one (if one takes into account the small sizes and the interactions of the microscopic units). There are however plenty of cases when the behavior of the units can be approximated by a ***classical dynamics***. Anyway, whether quantum or classical, the dynamics of the microscopic units needs information of two different kinds: a detailed knowledge of their reciprocal interactions and the complete description of an initial state. Obviously there is no practical way to provide any of these types of information for a macroscopic system containing usually a number of the order of 10^{26} units. Thus, it can be easily concluded that no purely dynamical description of such a system could be performed. One should necessarily content with an ***approximate description***, based on the concept of ***probability***. This kind of description is termed as ***statistical***. Before starting to use the statistical viewpoint in Thermal Physics it may be useful for the beginning student to have a mathematical introduction of the concept of probability and of its properties.

7.1 Elements of the probability theory and mathematical statistics

7.1.1 The idea of probability

As everyone knows, scientific discovery is essentially made through ***experiments***. To a certain extent, this is also true for any cognitive action of humans. In order to make reliable connections between various outcomes of an experiment it is frequently needed to repeat it a great number of times. Thus, an experiment usually consists of several ***trials***. The possible outcomes of each trial are called ***events***. In everyday life the concept of probability measures the degree of belief in the possibility of occurrence of a certain event that is not yet produced. Despite its essential subjectivity, this concept has steeply promoted in science and lies presently at the foundation of the very effective ***statistical method***. Originally, the mathematical study of this concept begun in connection with the games of chance: when a couple of dices are thrown on a table, the result is not known for certain. Step by step, the old philosophic (and almost mystic) idea of causality that dominated the scientific world up to the nineteenth century was replaced by that of a statistic behavior of phenomena. The mathematical tools of this new point of view are grouped in what is called the Theory of Probability.

The basic concept in the Theory of Probability is that of ***event***. A given event can be generally divided in simpler events. The decomposition follows a heuristic procedure, which follows the peculiarities of the phenomenon under study. An event that cannot be reasonably decomposed through such a procedure is termed as a ***simple event***. An event that is not simple is a ***compound event***. A compound event is an aggregate of simple events. Thus, to each experiment a ***set of all related events*** can be attached, which is called the ***sample space*** of the given experiment (we shall usually denote such a space in this chapter by E). In a geometrical language, simple events are also called ***points***. Compound events consist of sets of such points and all these sets are the elements of the sample space. ***The void set*** of events represents the image of ***the impossible event*** (denoted by $\varnothing$) related to the experiment under study. On the contrary, ***the set of all the simple events*** represents ***the certain event*** that may appear in the experiment. Both the impossible and the certain events are members of the sample space. In the following discussions, ***we shall denote the certain event of a sample space by*** $\boldsymbol{\sigma}$.

For example, in order to discover the fine imperfections of a dice, one may design an experiment consisting of throwing it a great number of times. Each throw of the dice is a trial and the outcomes of trials are the related events. Obviously, the apparition of anyone of the six faces constitutes a simple event and, altogether, those six simple events are points of the sample space of our experiment. The event of the apparition of a number less than five, for example, will be a compound event, since it consists in the apparition of anyone of the numbers from one to four (it is therefore a set of four points). The event of no apparition is the impossible event and the event of apparition of any of the numbers inscribed on the dice’s faces is the related certain event.

As another example, consider an experiment of measuring the radioactivity of a source with a Geiger counter. By making one recording of the number of impulses produced say during ten seconds, one makes a trial of this experiment. Each such possible number is a distinct event: a specific event is obtaining five impulses and another event is obtaining of six impulses. These are both ***simple events***. Obtaining a number of impulses between five and nine, during a working time of ten seconds of the Geiger counter, is a compound event, since it is composed from the simple events of obtaining six, seven, or eight impulses.

Let two events of the sample space of a given experiment be *e* and *f*. The compound event consisting in the occurrence of either *e* or *f*, or of both of them is called the ***reunion*** of the two events and is denoted by $e \cup f$. Reunions of several events of the same sample space can be defined in a similar way.

Generally, different compound events can occur simultaneously. Consider a set of simple or compound events, *a*, *b*, *c*, …, of a sample space. The compound event consisting in the simultaneous occurrence of all of them is called the ***intersection*** of the these events and is denoted by $a \cap b \cap c \cap \ldots$ If the outcome of one of them precludes the outcome of everyone else of this set, then these events are called ***mutually exclusive*** (or ***incompatible***). For example the events (connected with the radioactivity measurement with the Geiger counter) consisting of "recording a number of impulses between five and nine in ten seconds" and of "recording a number of impulses between seven and eleven in ten seconds" are obviously compatible, that is *non exclusive*. Indeed, a number of eight impulses measured in ten seconds satisfy simultaneously both conditions. But the events consisting of "recording a number of impulses between five and eight in ten seconds" and of "recording a number of impulses between nine and eleven in ten seconds" are clearly *mutually exclusive*. As a natural conclusion, one may say that the ***simple events of sample space are always mutually exclusive.*** Also, it can be readily seen that any element of the sample space can be constructed from simple events through reunion and intersection operations. Therefore, the simple events constitute the essential part of a sample space.

Different experiments can sometimes be associated in more complex ones. As a consequence, their sample spaces should be combined in order to include the resulting complex events. But, since the sample spaces are usually very different, the most natural way to combine them is through their Cartesian product. Therefore, from two sample spaces, one can form a sample space consisting of the ordered couples of events belonging to the two experiments. For example, let an experiment consist in measuring the amount of fat food consumption in a certain population. Let another experiment consist in determining the incidence of heart diseases in the same population. A complex experiment can be built up from these two, showing the effects of the alimentary habits of the given population on the incidence of heart troubles. Thus, the couple consisting of the event of finding an individual that consumes more than 500 g of fat food a day and the event that the same human experience an episode of angina pectoris up to the age of fifty may be considered as an event of the aforementioned experiment. Such a procedure of designing complex experiments from simpler ones may be described in terms of the so-called ***associated events***. More formally, let E and F be the sample spaces associated with two ***different experiments***. The Cartesian product $E \times F$ can be considered as the sample space of a complex experiment made from the two simpler ones. Let *e* be an event of E and *f* an event of F. Then the ordered couple (e, f) is an event of $E \times F$ and we talk about e and f as of associated events through this procedure. In a similar way, several events belonging to ***different*** sample spaces can be associated in ordered multiples representing events of the associated sample space. When the sample spaces correspond to completely unrelated experiments and no functional relation can be established between the events belonging to their sample spaces then the experiments are termed as ***independent***, having ***independent sample spaces***. Accordingly, the events from different independent sample spaces are called ***independent events***.

A real non-negative number p, called ***probability***, can be assigned to each simple event e, of a sample space E. This number actually measures the relative frequency of the outcome of the event e in the given experiment. Defining the effective values for the probabilities of simple events depends on the amount of a priori knowledge on the results of the given experiment. Two different concepts of probability are currently used in science: ***the classical probability*** and ***the statistical probability*** [1].

Irrespective of the way of linking probabilities to simple events, the probability should be looked at as ***a real function defined on the sample space of a given experiment***, obeying to the following set of axioms:

P1) The values of any probability are confined between 0 and 1:

$$0 \le p \le 1. \tag{7.1}$$

P2) If a, b, c, … are any ***incompatible*** (***mutually exclusive***) ***events*** of a sample space then the probability of occurrence of their reunion is the sum of the probabilities of their separate occurrence:

$$p(a \cup b \cup c \cup \ldots) = p(a) + p(b) + p(c) + \ldots \tag{7.2}$$

P3) The probability of the impossible event is defined as 0 and the probability of the certain event is given the value 1 ($p(\varnothing) = 0, p(\sigma) = 1$).

As the simple events of the sample space E (denoted by e_j, j = 1, 2, …) are all mutually exclusive, ***any event of the sample space can be constructed from such points through reunion***. In particular, for the certain event one may obviously write $\sigma = \bigcup_{all\ j-s} e_j$. The reunion extends over all the simple events since, if one of them (e_1, for example) would be left aside, it might be an alternative to σ and therefore this one would no more represent the certain event. Hence, the last two axioms imply what is called ***the normalization condition for a probability***:

$$\sum_{all\ j-s} p(e_j) = 1 \tag{7.3}$$

7.1.2 The classical probability

When no detailed knowledge on the possible outcomes of an experiment is available, the most natural way of defining the probability is ***to assign equal probabilities to all its possible simple events***. If one finds W simple events in the sample space (or, upon the case, if W is the total measure of the certain event of this space) then the probability of each one of them is, by definition,

$$p = \frac{1}{W}. \tag{7.4}$$

The probabilities for compound events are then to be computed by using the previously stated general axioms P1)-P3) of the probability.

For example, when tossing a coin there are two possible outcomes, heads or tails. According to the classical rule the probability of getting heads in one throw is 0.5 for there are two possible outcomes ($W = 2 \Rightarrow p = 1/2$).

Assigning the same probability to all the possible simple outcomes is certainly a useful hypothesis in situations when there is no information about what would possibly happen. Nevertheless there are many cases when the errors brought in by this crude approach are definitely unacceptable. For example, the following question may be formulated in the science of weather: what is the number of rainy days in a given place on the Earth? There are certainly two main possibilities for a day: to be rainy or not. Thus we obviously get $W = 2$. The classical probability will give $p = 0.5$ and we are brought to the conclusion that each year we would have about 183 rainy days in that particular place. This conclusion would be obviously erroneous if one compares, for example, two distinct area places, namely London and Cairo. It is thus clear that more information would be needed in order to make more reasonable meteorological predictions.

7.1.3 The statistical probability

This is the second concept of probability by which one ***measures the relative frequency of an outcome of a certain experiment***. This is the so-called ***experimental method***, by which the values of the probabilities are inferred from the relative frequency of each outcome. Let's take again the example with the radioactivity measurement by means of the Geiger counter. Denote by N the total number of trials in a given experiment and let n_i be the number of outcomes of the event i, that is the number of times when one obtains the prescribed number i of impulses during a counting time of ten seconds. The ratio n_i/N will be called the ***relative frequency*** of the event i. Repeating the experiment for increasing trial numbers N and carefully preserving the experimental conditions (as allowed by our knowledge) it is found that the relative frequencies take some fluctuant values, which become closer and closer to some "limit" value. Each limit value will be called the ***statistical probability of the event i***: $p_i = "\lim_{N\to\infty}"\left(\frac{n_i}{N}\right)$.

More generally, the statistical probability attached to a certain event a is defined as ***the "limit" value of the sequence of the relative frequencies of occurrence at the indefinite repetition of the experiment in identical conditions***:

$$p(a) = "\lim_{N\to\infty}"\left(\frac{n_a}{N}\right), \tag{7.5}$$

where N is the number of repetitions of the experiment and n_a is the number of times when the event a occurred. The "*lim*" symbol in the preceding definition cannot have the same meaning as the limit of a sequence in ordinary Calculus: relative frequencies that differ considerably from the majority of the terms could be found above any value of N. Precise definitions for the statistical probability could be formulated in a more specialized framework [2]. Such approaches are too difficult to be included in an introductory textbook. Fortunately, the important fact here is that Eq. (7.5) can be safely used in Thermal Physics if the physical conditions are kept invariable and if the "fluctuations" of the values of the relative frequencies are reasonably small. As a matter of fact, in practice one always uses the relative frequency of occurrence of an event during a conveniently high number of trials as a very definition of its statistical probability.

7.1.4 The probability of statistically independent events

Both previous definitions of probability obviously allow the computation of the probabilities of associated events. Of particular practical importance is the case when the associated events are independent. Suppose that the probability is defined statistically. The number of repetitions of a complex experiment that attempts to correlate two simpler ones should be the product of the number of repetitions of each component. Moreover, if (e, f) is a pair of associated events belonging to this complex experiment, then its occurrence implies both occurrences of e and f. Since e and f are supposed as completely non-correlated, the number of times when they appear simultaneously should obviously equal the product of their separate occurrences. Therefore the relative frequency of occurrence of any pair (e, f) should be the product of the corresponding relative frequencies of occurrence of the separate events. One may then readily infer the same property for the corresponding probabilities: ***the probability of occurrence of any pair of independent events (e, f) is the product of the corresponding probability of occurrence of the separate events***:

$$p((e,f)) = p(e)\cdot p(f). \tag{7.6}$$

The same result may be also found when using the classical concept for the probability and the preceding result is therefore of a general applicability. Establishing the independence of two events is actually a not so straightforward procedure. It can usually be decided in practice on physical grounds. The reverse way of putting the problem is therefore more usual: to compute the probability of two (or more) associated events and to check if relations as Eq. (7.6) are satisfied. Then the corresponding events may be declared as statistically independent, or as ***having no correlation*** [1, 2].

***Notes*:**

a) It is important to stress again that ***independent events can only belong to distinct sample spaces***. For example it is easy to observe that two mutually exclusive events are not independent: their occurrences influence each other in the sense of exclusion and the probability of their simultaneous occurrence vanishes. Therefore two (simple or compound) events of the same sample space cannot be independent.

b) When applying the axiom P2) it is very important to make sure that the events are mutually exclusive. For example, when throwing a dice the probability of the apparition of any face is 1/6. The probability of obtaining an even number is obviously 1/2. The same value has the probability of obtaining a number less than 4. But the probability of obtaining a result that satisfies the first condition, or the second one, or both of them is obviously 5/6, which is different from the sum (1/2 + 1/2 = 1) of the probabilities of the two separate events.

7.1.5 Statistics and distributions

Suppose that we place a Geiger counter close to a certain amount of radioactive material and try to measure the number of impulses produced during a fixed time of ten seconds. The procedure

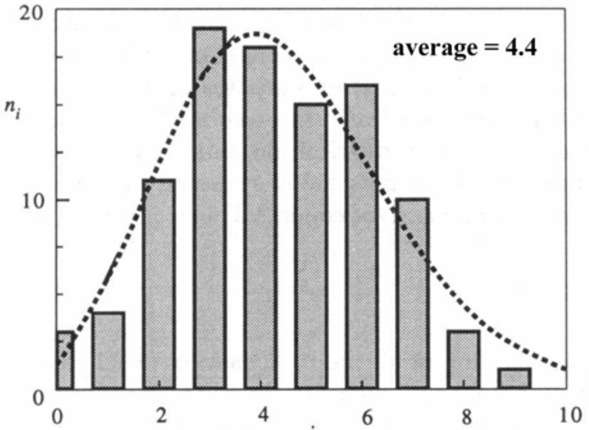


Figure 7.1: The histogram of the numbers of impulses obtained with a Geiger counter during 100 measurement procedures.

could be repeated for a high number (N) of times and a diagram could be constructed, like the one shown in Figure 7.1 (obtained for $N = 100$). This kind of diagram is called a ***histogram***. It is a set of columns, each one corresponding to a possible event. The height of the column attached to some event e_i is proportional to the occurrence number n_i of that event during the prescribed number N of trials in the given experiment. Thus, in the given example, e_i may be the event of recording a number of i impulses by the counter in a ten seconds trial. The corresponding column should be proportional to the number n_i of times (among all the N trials) when i impulses were recorded during a ten seconds measurement. Therefore, we'll have n_0 situations when no impulse was recorded during ten seconds, n_1 situations when only one impulse was detected in ten seconds, n_2 cases with two detected impulses in ten seconds, and so on. One can get a measure of the (statistical!) probabilities of occurrence of these events by considering them close to the relative frequencies $p_0 \approx n_0/N$, $p_1 \approx n_1/N$, $p_2 \approx n_2/N$, … For increasing N similar histograms are obtained, with some fluctuations in the height of each column. If N is large enough, the fluctuations become reasonably small and the tops of the columns seem to fit better and better a certain continuous curve (which is drawn in dot line in Figure 7.1). In Physics, all these operations are gathered under a brief expression by saying that one has made "***the statistics of the number of impulses in the given experiment***". We mean by this that the sequence of the relative frequencies $\{n_i/N\}$, $i = 0, 1, 2, \dots$ was obtained. This actually represents a function defined on the discrete set of the possible events (numbers of impulses) only. The dotted curve represents the extension of this function to the entire real (positive) axis.

The main purpose of this statistics is to compute the average number of impulses that one can get in a ten seconds recording. This average has ***a predictive value*** since it represents the number of impulses that we should expect to obtain in any further ten seconds record and is the best we can hope to get from such a low-information context. In order to compute the average number of impulses in a ten seconds catch, one should take in principle the arithmetic mean of all the results obtained during the N trials. When computing this mean one may readily observe that the event of zero impulses recording appears n_0 times, the record of only one impulse appears n_1 times, the number of two impulses appears in n_2 records, and so on. Thus, by associating the terms with the same numbers of impulses, the sum of the arithmetic mean restrains to the following form:

$$\langle i \rangle = \frac{1}{N}\sum_i n_i\, i = \sum_i \frac{n_i}{N} i \approx \sum_i p_i\, i\,. \tag{7.7}$$

Certainly there are deviations of the individual numbers of impulses with respect to the average value given by Eq. (7.7) and their study may become important for some features of the system under study. A useful measure of these deviations is the so-called ***standard deviation***, which may be defined by:

$$\Delta i = \sqrt{\sum_i p_i \left(i - \langle i \rangle\right)^2} = \sqrt{\left\langle \left(i - \langle i \rangle\right)^2 \right\rangle}. \tag{7.8}$$

Similar statistics can be constructed for any measurable physical quantity of our system. For example one can make the statistics of the energies of the emitted particles from the considered radioactive source. That is, by using suitable instruments, one can distinguish the emitted particles upon their energies. But, since the energy takes continuous values, a quite new problem is now to be faced. It is obviously senseless to try to define the relative frequency corresponding to one particular value of the energy. Rather, one may count the numbers of particles emerging with energies in some prescribed intervals. These will form thus a sort of "energy grid". One may therefore obtain the relative frequency corresponding to each interval of the grid. The energy grid used for this analysis can be refined as much as allowed by the measurement apparatus. A simple choice may be to take all the energetic grid intervals equal to some value δE. Denote by n_0, n_1, n_2, … the numbers of emitted particles with energies included in the intervals $(0, \delta E)$, $(\delta E, 2\delta E)$, $(2\delta E, 3\delta E)$, …, respectively. Such a construction for the energy grid is obviously the simplest but otherwise not the only one. Let N be the total number of measured particles. Then we'll obviously have $N = \sum_i n_i$ and the relative frequency corresponding to the energetic interval $(i\delta E, (i + 1)\delta E)$ equal to n_i/N. By approximately assigning to the probabilities ε_i (of getting a particle with the energy contained in the interval $(i\delta E, (i + 1)\delta E)$) the values of the frequencies n_i/N ($\varepsilon_i \approx n_i/N$), the average energy of an emerging particle can be computed as:

$$\langle E \rangle \cong \frac{1}{N}\sum_i n_i \left(i\,\delta E\right) = \sum_i \frac{n_i}{N} E_i \cong \sum_i \varepsilon_i\, E_i\,. \tag{7.9}$$

The energy standard deviation will be (if defined upon the pattern of Eq. (7.8)):

$$\Delta E = \sqrt{\sum_i \varepsilon_i \left(E_i - \langle E \rangle\right)^2} = \sqrt{\left\langle \left(E_i - \langle E \rangle\right)^2 \right\rangle}. \tag{7.10}$$

The energy E_i is the value that should be assigned to the interval $(i\delta E, (i + 1)\delta E)$. Since this interval is usually taken as very small with respect to the particle energies, we may approximately write $E_i \approx i\delta E$. It is straightforward to see that the maximum error induced in Eq. (7.9) by any possible choice of E_i in the interval $(i\delta E, (i + 1)\delta E)$ is of the order of δE.

The probabilities ε_i were intentionally denoted with a different letter than those linked to the statistics of the number of particles (p_i). This should remember to the beginning student that ***each***

microscopic measurable parameter of a thermodynamic system has a specific statistics (which has to be constructed experimentally or by applying certain theoretical models).

The previously applied schemes, for the counted numbers of impulses and for the emitted particle energies, can be generalized to any (discrete or continuous) microscopic parameter, x, of the microscopic units of a thermodynamic system. Let x_0, x_1, x_2, …, x_{max} be its representative values that constitute a grid for measuring x, as refined as needed. In Statistics such a parameter is usually called ***random variable*** (or ***parameter***). Let p_0, p_1, p_2, … be the probabilities that, by measuring x, one finds its value in one of the intervals (x_0, x_1), (x_1, x_2), (x_2, x_3), …, respectively. Finding a value of x in one of these intervals represents obviously ***mutually exclusive events***, that could be considered as ***simple events of a sample space*** defined by the analysis grid x_0, x_1, x_2, …, x_{max}. Each corresponding probability p_i is the "limit value" of the relative frequency of finding the value of x in the interval (x_i, x_{i+1}). Therefore the following relations will give the average value and the standard deviation of x:

$$\langle x \rangle = \sum_i p_i x_i \,, \tag{7.11}$$

$$\Delta x = \sqrt{\sum_i p_i \left(x_i - \langle x \rangle\right)^2} = \sqrt{\left\langle \left(x_i - \langle x \rangle\right)^2 \right\rangle} \,. \tag{7.12}$$

When the evaluation grid for x becomes infinitesimal, that is when $x_{i+1} - x_i = dx$, the probability of getting a value of x in such an interval becomes infinitesimal as well, $dp(x)$, of the same order of magnitude as the measure dx of the corresponding interval of x. This could be highlighted by letting this probability be proportional to dx, that is by writing $dp(x) = \pi(x)dx$. Therefore the sums in Eqs. (7.11) and (7.12) become integrals:

$$\langle x \rangle = \int_{x_0}^{x_{max}} x \, dp(x) = \int_{x_0}^{x_{max}} x \pi(x) dx \tag{7.13}$$

and

$$\varDelta x = \sqrt{\int_{x_0}^{x_{max}} \left(x - \langle x \rangle\right)^2 \pi(x) dx} = \sqrt{\left\langle \left(x - \langle x \rangle\right)^2 \right\rangle} \,. \tag{7.14}$$

The function $\pi(x)$ works as a "***probability density***" and is usually called in Thermal Physics ***distribution function*** of the parameter x. Since the probability $\pi(x)dx$ should be dimensionless, ***the units of $\pi(x)$ should be the inverse of the units of x***. As the general normalization relation (7.1) holds for any kind of probability, whether defined classically or statistically, it should be extended for the case of any random parameter x:

$$\sum_i p_i = 1 \text{, for discrete } x \text{ values, or } \int_{x_0}^{x_{max}} \pi(x)\,dx = 1 \text{, for continuous } x. \tag{7.15}$$

It is interesting to compute the probability $p([a, b])$ that a value of x may be found somewhere in the interval $[a, b]$, included into its range. Since finding a value of x in any of the infinitesimal intervals dx are mutually exclusive events, by directly applying the axiom P2, one obtains:

$$p([a,b]) = \int_a^b \pi(x)\,dx . \tag{7.16}$$

7.1.6 The normal distribution

Among the several usual distribution functions in Probability Theory, the one with the main importance in the statistical study of thermodynamic systems is by far the so-called ***Gauss's*** (or ***normal***) ***distribution***, which is defined by:

$$\pi(x) = \frac{1}{\sigma\sqrt{2\pi}} exp\left[-\frac{(x-x_m)^2}{2\sigma^2}\right],\ x \in (-\infty,\infty). \tag{7.17}$$

By applying the Poisson formula of Calculus:

$$\int_{-\infty}^{\infty} exp(-\alpha x^2)\,dx = \sqrt{\frac{\pi}{\alpha}},\quad \alpha \in R,\quad \alpha > 0, \tag{7.18}$$

one may easily verify that the Gauss's distribution is normalized.

The average value of x may be also computed by use of (7.18) and by properly handling some integrals:

$$\langle x \rangle = \int_{-\infty}^{\infty} x\,\pi(x)\,dx = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (u + x_m)\, exp\left(-\frac{u^2}{2\sigma^2}\right) du = x_m . \tag{7.19}$$

In order to compute the standard deviation of x, one should first obtain the relation:

$$\int_{-\infty}^{\infty} x^2\, exp(-\alpha x^2)\,dx = \frac{1}{2\alpha}\sqrt{\frac{\pi}{\alpha}},\quad \alpha \in R,\quad \alpha > 0, \tag{7.20}$$

which readily comes through the differentiation of the two sides of Eq. (7.18) with respect to α. We'll thus get:

$$(\Delta x)^2 = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} (x - \langle x \rangle)^2\, exp\left[-\frac{(x-x_m)^2}{2\sigma^2}\right] dx = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{\infty} u^2\, exp\left(-\frac{u^2}{2\sigma^2}\right) dx = \sigma^2 . \tag{7.21}$$

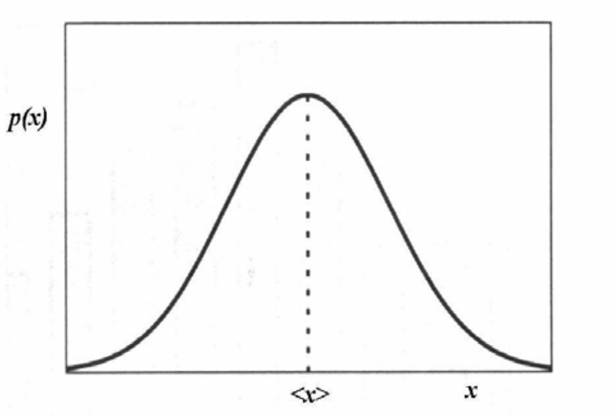


Figure 7.2: Gauss's (normal) distribution.

From Eqs. (7.19) and (7.21) it follows that the normal distribution (7.17) can be written in a more suggestive form:

$$\pi(x) = \frac{1}{\Delta x\sqrt{2\pi}} exp\left[-\frac{(x-\langle x\rangle)^2}{2(\Delta x)^2}\right], x \in (-\infty,\infty). \tag{7.22}$$

The function of (7.22) is represented graphically in Figure 7.2. One can see the specific bell-shape of the graph, whose maximum is placed at the average value of *x*. The bell wideness is controlled by the standard deviation *Δx*. Indeed, by applying the result (7.16) to this distribution, one may find through numerical integration that the probability for *x* to take a value in the interval [<*x*> - *Δx*, <*x*> + *Δx*] is 0.683. The corresponding probability for the interval [<*x*> - 2*Δx*, <*x*> + 2*Δx*] is 0.954 and the one for the interval [<*x*> - 3*Δx*, <*x*> + 3*Δx*] is 0.99994. It may be concluded that *Δx* represents a measure of the concentration of the outcomes of *x* around its average value.

7.1.7 Functions of random parameters

Very frequently one has to make the statistics not only for a random parameter *x*, but also for a certain function of *x*. For example, the absolute value of the translation velocity of a gas molecule, *υ*, can be regarded as a random parameter. However, in many situations, the statistics for the translation kinetic energy will be needed, that is for $m\upsilon^2/2$.

Thus, let us suppose that the statistics of a certain continuous function *h*(*x*), of the random variable *x*, is needed. Suppose that the distribution function of *x* is *π*(*x*). By definition the average value of *h*(*x*) will be:

$$\langle h(x)\rangle = \int_{x_0}^{x_{max}} h(x)\pi(x)dx. \tag{7.23}$$

If the random variable *x* takes discrete values, then the integral of Eq. (7.23) should be replaced by the corresponding sum.

From the general definition (7.23), several properties of the average value could be drawn. First, if $h(x)$ and $g(x)$ are two continuous functions of the random parameter x, then ***the average value of their sum is the sum of their averages***:

$$\begin{aligned}\langle h(x)+g(x)\rangle &= \int_{x_0}^{x_{max}}[h(x)+g(x)]\pi(x)dx = \\ &\int_{x_0}^{x_{max}} h(x)\pi(x)dx + \int_{x_0}^{x_{max}} g(x)\pi(x)dx = \langle h(x)\rangle + \langle g(x)\rangle\end{aligned}. \tag{7.24}$$

Then, one may readily see that, if c is a constant, then the average of the product between c and any continuous function h of x equals the product of c with the average value of $h(x)$:

$$\langle c\,h(x)\rangle = \int_{x_0}^{x_{max}} c\,h(x)\pi(x)dx = c\int_{x_0}^{x_{max}} h(x)\pi(x)dx = c\langle h(x)\rangle\,. \tag{7.25}$$

It follows that ***the average value of a constant is the constant itself***. Moreover, since the average value of any continuous function of x results in a constant, the average of the average of this function should equal its average:

$$\langle\langle h(x)\rangle\rangle = \int_{x_0}^{x_{max}}\langle h(x)\rangle\pi(x)dx = \langle h(x)\rangle\int_{x_0}^{x_{max}}\pi(x)dx = \langle h(x)\rangle\,, \tag{7.26}$$

where the normalization relation (7.15) was used.

The properties (7.24)-(7.26) allow a direct calculation of the standard deviation of a continuous function h of the random parameter x:

$$\begin{aligned}\Delta[h(x)] &= \sqrt{\left\langle[h(x)-\langle h(x)\rangle]^2\right\rangle} = \sqrt{\left\langle h(x)^2 - 2\langle h(x)\rangle h(x) + \langle h(x)\rangle^2\right\rangle} = \\ &\sqrt{\left\langle h(x)^2\right\rangle - 2\langle h(x)\rangle\langle h(x)\rangle + \left\langle\langle h(x)\rangle^2\right\rangle} = \sqrt{\left\langle h(x)^2\right\rangle - \langle h(x)\rangle^2}\end{aligned}. \tag{7.27}$$

The structure of the second term of (7.27) shows that the quantities under the radicals should be always positive. Thus one gets the following general inequality:

$$\left\langle h(x)^2\right\rangle \geq \langle h(x)\rangle^2\,. \tag{7.28}$$

7.1.8 Associated random parameters

In studying complex physical phenomena one has very often to deal with several random variables that have to be associated to the same effect. Sometimes, these variables are statistically independent and their corresponding sample spaces may be considered in products, in the way shown before. Nevertheless, there are plenty of cases when some underground correlation exists among such random parameters. This means that certain unknown relations work between these variables. If we knew these relations, some of the random variables could be treated as functions of the others. As in some given conjuncture one may ignore such relations, *all* the variables of the given problem should be treated as random. For example, a certain relation between the smoking habit and the lung cancer disease can obviously be suspected. Nevertheless, there is no strict relation between these two facts: not every smoker has got a lung cancer and not every lung cancer appears at smoking persons. Therefore, in making a statistics of the incidence of the lung cancer disease in a certain population, one should treat the random events of both finding a smoker in this group of people and finding a person who got a lung cancer as separate, but not independent. The whole study needs to ***associate*** these two events in order to get a meaningful conclusion.

Thus, even if each such associated random parameters can be separately determined in distinct experiments, their couple can be looked at as "multidimensional" random parameters to be determined in a complex experiment. To be more concrete, if x and y are two such associated one-dimensional random parameters, their couple (x, y) could be considered as an ***associated random parameter*** or a "***two-dimensional random variable***" that takes values in some two-dimensional range [1, 2]. Defining an analysis grid in this range is generally a more delicate problem, since ***several types of coordinate axes are possible in multidimensional spaces***. For simplicity, we shall further use only Cartesian coordinates in the corresponding space and we shall limit the discussion to the two-dimensional case only. Also, in view of further applications, we shall focus on the case of continuous random variables where the grid can be conveniently refined so that a grid unit becomes an ***infinitesimal "volume" element***.

Consider thus a two-dimensional random parameter, w, whose components, say x and y, are measured upon Cartesian axes $w = (x, y)$. Now it makes no more sense to talk about "values" of w, so we shall speak about the "points" of w in its two-dimensional range of variation, D. The grid unit (that is the "volume" element) will be $dx \cdot dy$ and the probability of the simple event of finding a point of w in a certain volume element $dx \cdot dy$ around (x, y) will be denoted by $\pi(x,y)dxdy$, where $\pi(x,y)$ is the corresponding ***two-dimensional associated distribution function***. The normalization relation will obviously take the form:

$$\iint_D \pi(x, y)\,dx\,dy = 1\,. \tag{7.29}$$

Nevertheless, it should always be remembered that x and y are separate random parameters and that distribution functions, $\xi(x)$ and $\chi(y)$, can be defined for each one of them. For convenience we shall refer to these variables as to the first and second, respectively. Thus, for a fixed value, x, of the first random parameter, the range of variation of the second one will be denoted by D_x. We need the probability of finding a value of the first parameter in a certain infinitesimal interval dx of it, around the value x, ***irrespective of the value of the second parameter into its corresponding range D_x***. This can be obtained by summing the probabilities of the incompatible events of finding the points of w in the "volume" elements $dx \cdot dy$, around (x, y), $y \in D_x$: $\left(\int_{D_x} \pi(x,y)dy \right) dx \equiv \xi(x)dx$. Therefore,

$$\xi(x) = \int_{D_x} \pi(x,y)dy . \tag{7.30}$$

In a similar manner by D_y one can denote the range of the first random parameter for a fixed value, y, of the second. One then readily obtains the probability density of finding a value of the second parameter in a certain infinitesimal interval dy of it, around the value y, ***irrespective of the value of the first parameter into its range D_y***:

$$\chi(y) = \int_{D_y} \pi(x,y)dx . \tag{7.30'}$$

***Notes*:**

a) A supplementary comment should be made about the integrals of the type appearing in Eq. (7.29). Certain mathematical difficulties may arise when the range D ***is not*** a subset of a metric space. Indeed, Riemann type integrals in multidimensional spaces can be defined only if these ones are provided with a suitable metric. Nevertheless, in Physics this is not always possible without loosing the real meaning of quantities (at least not in the usual Euclidean sense). Take for example the case when x is a position parameter and y is a momentum. They obviously have ***different units*** and a metric defined in D by the Euclidean way would be meaningless from the physical viewpoint, since quantities with different units cannot be added. Such situations are actually quite frequent in physical problems that deal with continuous random parameters. In order to avoid such a conflict one has two options: 1. To take integrals over non-metric ranges in a more general (e.g. Lebesgue) sense [3]. 2. To consider simply that only ***repeated integrals*** are involved in expressions like (7.29). Some regularity properties should be satisfied by the range D in this case (for example there must exist a finite coverage of D with multidimensional "parallelepipeds"), but no metric would be actually needed. Exceptions from such regularities for the ranges of the multidimensional random variables arise quite seldom in physical problems, so that no real restrictions appear in this way. The ***"volume" element*** would thus consist of an infinitesimal "parallelepiped" with sides parallel to the coordinate axes. By infinitesimal "parallelepiped" we mean here the one whose each edge is infinitesimally smaller than the unit dimension of the axe to which it is correspondingly parallel: dx << 1 unit of x; dy << 1 unit of y. This simpler way of understanding integration on multidimensional-multiunit spaces will be actually adopted throughout the present introductory textbook.

b) When passing from a given associated random variable (*x*, *y*) to another equivalent one (*x'*, *y'*), one should apply the usual rules of Calculus for the change of variables in the repeated integrals [3]. For example, let *f*(*x*,*y*) be a function of the associated random variable that should be averaged on the range *D* of (*x*, *y*). Let *g*(*x'*,*y'*) be the transformed function through the change of variables (*x*, *y*) → (*x'*, *y'*) and let *J*(*x'*,*y'*) the Jacobian of the matrix describing this change of variables. Then, for the statistical average value of *f* on the range *D*, one may write: $\langle f\rangle = \iint\limits_{D} f(x,y)\,\pi(x,y)\,dx\,dy = \iint\limits_{D'} g(x',y')\,\rho(x',y')\left|J(x',y')\right| dx'\,dy'$, where *D'* is the transformed average range and $\rho(x',y')$ is the corresponding transformed of the probability density $\pi(x,y)$. The product $\rho(x',y')\left|J(x',y')\right|$ plays the role of the new probability density. When restricting the last equality to a close neighborhood of a certain couple of values of the random variables, for $f(x,y) \equiv 1$, one gets: $\pi(x,y)\,dx\,dy = \rho(x',y')\left|J(x',y')\right| dx'\,dy'$, which represents the explicit form of the principle of the probability conservation through a change of the random parameters.

7.1.9 Associated independent random variables

A very important practical situation arises when the random parameters of a multidimensional random variable are statistically independent. In order to keep the discussion to a simple level we'll keep using the two-dimensional examples.

When random parameters behave independently, one should expect that the probability of the simple event of finding a result near a specified value of the associated variable to be the product of the corresponding probabilities of the component variables. More specifically, ***when ξ(x) and χ(y) are defined by Eqs. (7.30) and (7.30')***, one should have:

$$\pi(x,y)\,dx\,dy = \left(\xi(x)\,dx\right)\cdot\left(\chi(y)\,dy\right) \quad \Leftrightarrow \quad \pi(x,y) = \xi(x)\,\chi(y). \tag{7.32}$$

Eq. (7.32) represents the ***necessary and sufficient condition for the statistical independence*** of the two random variables *x* and *y*.

Note: By integrating both members of Eq. (7.32) with respect to *y* (for example) over D_x one gets:

$$\xi(x)\int\limits_{D_x} \chi(y)\,dy = \int\limits_{D_x} \pi(x,y)\,dy, \tag{7.33}$$

which is generally different from the definition (7.30) of *ξ*(*x*). As the range D_x of *y* still depends on the fixed value of *x*, the integral of the left side of (7.33) cannot equal unity for all values of *x*. In order to have an identity between (7.33) and (7.30) the ranges D_1 and D_2 of the two separate random parameters should be ***independent*** and *D* should equal their Cartesian product: $D = D_1 \times D_2$. In other words, ***we should have not only a local statistical independence*** (that is a simple splitting of the associated distribution in separate factors dependent each of only one variable)***, but also a "global" one, over the whole range of w = (x,y)***. In this case we would have $\int_{D_2} \chi(y)dy = 1$ in (7.33), by the normalization relation of $\chi(y)$, and Eq. (7.33) would coincide with (7.30).

In most practical cases the ranges D_1 and D_2 for each random parameter are real intervals: $D_1 = (a_x, b_x)$, $D_2 = (a_y, b_y)$. The average value of some function of w on such a "split"-range may therefore be written as:

$$\langle f \rangle = \int_{a_y}^{b_y}\int_{a_x}^{b_x} f(x,y)\pi(x,y)dx\,dy = \int_{a_y}^{b_y}\int_{a_x}^{b_x} f(x,y)\xi(x)\chi(y)dx\,dy\,. \tag{7.34}$$

If the function f consists of a product of two separate functions of x and y, $f(x,y) = u(x)\cdot\upsilon(y)$, then the repeated integrals in Eq. (7.34) split in separate factors and one may write:

$$\langle u(x)\upsilon(y)\rangle = \int_{a_y}^{b_y}\int_{a_x}^{b_x} u(x)\upsilon(y)\xi(x)\chi(y)dx\,dy = \int_{a_x}^{b_x} u(x)\xi(x)dx \int_{a_y}^{b_y} \upsilon(y)\chi(y)dy\,,$$

that is

$$\langle u(x)\upsilon(y)\rangle = \langle u(x)\rangle\langle \upsilon(y)\rangle\,. \tag{7.35}$$

In particular, for two statistically independent random variables one should have:

$$\langle x\,y\rangle = \langle x\rangle\langle y\rangle\,. \tag{7.36}$$

In summary, we can generalize the previous results to any number of associated random parameters by the following statement. ***Several random variables are statistically independent if and only if the distribution of their associate random variable equals the product of the corresponding separate distributions.***

It can also be proven that ***two random parameters are statistically independent if and only if the equality (7.35) is fulfilled for any couple of continuous functions u(x) and υ(y)***.

As an example, consider the experiment of randomly choosing a point in a circle of radius unity. If one takes as random variables the Cartesian coordinates of the point (with the origin at the center of the circumference) then ***they will not be statistical independent***. The probability to reach a point near some location (x, y) inside the circle will be $(1/\pi)\cdot dx\cdot dy$. The corresponding probability density is constant and equals $1/\pi$. Nevertheless, the probability of getting a point with the x coordinate close to 0.5, for example will obviously depend on the y value for the corresponding choice. More precisely, $\xi(x)=\frac{1}{\pi}\int_{-\sqrt{1-x^2}}^{\sqrt{1-x^2}}dy=\frac{2}{\pi}\sqrt{1-x^2}$, $\chi(y)=\frac{1}{\pi}\int_{-\sqrt{1-y^2}}^{\sqrt{1-y^2}}dy=\frac{2}{\pi}\sqrt{1-y^2}$ and $\frac{1}{\pi}\neq\xi(x)\chi(y)$. Moreover, when computing the statistical average of the product x^2y^2, one readily finds: $\left\langle x^2y^2\right\rangle=\frac{1}{\pi}\int_{-1}^{1}y^2\,dy\int_{-\sqrt{1-y^2}}^{\sqrt{1-y^2}}x^2\,dx=\frac{1}{24}$, while $\left\langle x^2\right\rangle=\left\langle y^2\right\rangle=\frac{1}{4}$. So, $\left\langle x^2y^2\right\rangle\neq\left\langle x^2\right\rangle\left\langle y^2\right\rangle$, which proves the ***statistical dependence*** of the two random variables. It is interesting to note that for this case $\langle x\,y\rangle=\langle x\rangle\langle y\rangle=0$, since all the averages involve integrals over symmetric ranges around the origin from odd integrands.

On the contrary, let's locate a point inside the unit disk by using the polar coordinates (r, φ). The range of the two-dimensional random variable (r,φ) can now be written as a Cartesian product, namely: $[0, 1]\times[0, 2\pi]$. The probability density of the associated random variable will be r/π, while the distributions for each separate variable are $\xi(r)=\frac{r}{\pi}\int_{0}^{2\pi}d\varphi=2r$ for r and $\chi(\varphi)=\frac{1}{\pi}\int_{0}^{1}r\,dr=\frac{1}{2\pi}$ for φ. We obviously have $\frac{r}{\pi}=\xi(r)\chi(\varphi)$, which shows the statistical independence of these two variables.

7.1.10 Covariance of associated random variables

In practice one very often faces the problem of establishing the statistical independence of various random variables. There is no formal procedure to follow in order to grant such independence ***before*** making any statistical experiments. One can only use speculative hypotheses on the statistical independence of random variables and try to check the models through experiments.

A measure of the statistical dependence of two random variables (x, y), is their so-called ***covariance***, which can be defined by the following expression:

$$cov(x,y)\equiv\left\langle(x-\langle x\rangle)(y-\langle y\rangle)\right\rangle=\langle x\,y\rangle-\langle x\rangle\langle y\rangle. \tag{7.37}$$

When the separate distributions of the two random variables are established through suitable experiments along with the distribution of the associate random variable (x, y), one can straightforwardly compute $cov(x,y)$. If a vanishing result is obtained then one has an indication of the possibility that the two variables behave as statistical independent ones. However, as illustrated in the last example of the preceding paragraph, the fact that $cov(x,y) = 0$ is not sufficient to ensure the statistical independence of x and y. Thus, when $cov(x,y) \neq 0$, its value can be used as ***a measure of the statistical dependence of the two random variables***.

7.1.11 Example: Maxwell's derivation of the distribution of gas molecules upon their translation velocities

The first realistic model for a perfect gas was formulated by James Clerk Maxwell in 1860 [4]. The gas molecules are considered as mass points with no reciprocal interactions, moving under the laws of Classical Mechanics in a force-free environment, with random translation velocities. Thus, if we denote by $\vec{\upsilon} = (\upsilon_x, \upsilon_y, \upsilon_z)$ the molecular velocity of translation, this will represent an associate random variable whose distribution (statistics) $f(\vec{\upsilon})$ is to be found. Maxwell's argument relies on two main hypotheses: 1) $f(\vec{\upsilon})$ actually ***depends on the absolute value of the translation velocity*** only (that is $f(\vec{\upsilon}) = \tilde{f}(\upsilon)$) and 2) the Cartesian components of the molecular translation velocity, $(\upsilon_x, \upsilon_y, \upsilon_z)$, are ***independent random parameters***. The first supposition is quite natural relies on the well-verified isotropy of a perfect gas away from the action of strong external fields. The second one is more artificial since the absence of collision among molecules allows kinetic energy conservation for a particular molecule and determines thus an analytical relation among the Cartesian components of the molecular translation velocity. One way out is to admit that very seldom collisions among gas molecules may take place and randomize their translation velocities along the Cartesian axes. Such events should be however so rare that the molecules behave as essentially independent from one another.

The isotropy of the gas state and the arbitrariness of the choice of the Cartesian axes should allow the Cartesian components of the molecular translation velocity (as separate random variables) to enjoy the same distribution function. We shall denote this (still unknown) function by f_1. Thus, for example, the probability that the x-component of the molecular translation velocity be found between υ_x and $\upsilon_x + d\upsilon_x$ may be written as: $f_1(\upsilon_x)d\upsilon_x$. Other two independent events are to find the y-component of the molecular translation velocity between υ_y and $\upsilon_y + d\upsilon_y$ and the its z-component between υ_z and $\upsilon_z + d\upsilon_z$. Therefore, the probability for the ***simultaneous occurrence of these three independent events is*** $f_1(\upsilon_x) f_1(\upsilon_y) f_1(\upsilon_z) d\upsilon_x d\upsilon_y d\upsilon_z$. An alternative expression for the simultaneous occurrence of the aforementioned independent events is to ask for the molecular translation velocity to be located in an infinitesimal neighborhood of $\vec{\upsilon} = (\upsilon_x, \upsilon_y, \upsilon_z)$. The probability of this event should be written in terms of the distribution $f(\vec{\upsilon})$, that is $\tilde{f}(\upsilon)\, d\upsilon_x d\upsilon_y d\upsilon_z$, according to the first model hypothesis.

Therefore one gets the following relation between the two distribution functions:

$$\tilde{f}(\upsilon) = f_1(\upsilon_x) f_1(\upsilon_y) f_1(\upsilon_z). \tag{7.38}$$

The derivative with respect to υ_x applied in both members of Eq. (7.38) gives:

$$\tilde{f}'(\upsilon)\frac{d\upsilon}{d\upsilon_x} = f_1'(\upsilon_x) f_1(\upsilon_y) f_1(\upsilon_z) = \tilde{f}(\upsilon)\frac{f_1'(\upsilon_x)}{f_1(\upsilon_x)}.$$

As $\upsilon = \sqrt{\upsilon_x^2 + \upsilon_y^2 + \upsilon_z^2}$, it follows that $\frac{d\upsilon}{d\upsilon_x} = \frac{\upsilon_x}{\upsilon}$ and Eq. (7.38) becomes:

$$\frac{1}{\upsilon}\frac{\tilde{f}'(\upsilon)}{\tilde{f}(\upsilon)} = \frac{1}{\upsilon_x}\frac{f_1'(\upsilon_x)}{f_1(\upsilon_x)}. \tag{7.39}$$

Applying the same procedure to Eq. (7.38) for υ_y and υ_z, one can analogously get:

$$\frac{1}{\upsilon}\frac{\tilde{f}'(\upsilon)}{\tilde{f}(\upsilon)} = \frac{1}{\upsilon_x}\frac{f_1'(\upsilon_x)}{f_1(\upsilon_x)} = \frac{1}{\upsilon_y}\frac{f_1'(\upsilon_y)}{f_1(\upsilon_y)} = \frac{1}{\upsilon_z}\frac{f_1'(\upsilon_z)}{f_1(\upsilon_z)}.$$

Therefore, since the last three terms of the previous chain of equalities each depend on a separate independent variable, one may conclude that the chain equals some constant value. We shall denote by -2γ this constant, for further convenience. It then follows that:

$$\frac{1}{\upsilon}\frac{\tilde{f}'(\upsilon)}{\tilde{f}(\upsilon)} = \frac{1}{\upsilon_x}\frac{f_1'(\upsilon_x)}{f_1(\upsilon_x)} = \frac{1}{\upsilon_y}\frac{f_1'(\upsilon_y)}{f_1(\upsilon_y)} = \frac{1}{\upsilon_z}\frac{f_1'(\upsilon_z)}{f_1(\upsilon_z)} = -2\gamma \tag{7.40}$$

By taking the last equality of Eq. (7.40), the following simple differential equation may be obtained:

$$\frac{f_1'(\upsilon_z)}{f_1(\upsilon_z)} = -2\gamma\,\upsilon_z,$$

that may be readily integrated to:

$$f_1(\upsilon_z) = a_1\, e^{-\gamma \upsilon_z^2}, \tag{7.41}$$

where a_1 is some integration constant. It can be determined by remembering that $f_1(\upsilon_z)d\upsilon_z$ represents the probability of finding *z*-component of the translation molecular velocity between υ_z and $\upsilon_z + d\upsilon_z$. As the molecule behaves as a classical (non-relativistic) object, the range of υ_z may be extended over the entire real axis. So, the corresponding normalization condition gives (see Eq. (7.15)):

$$\int_{-\infty}^{\infty} f_1(\upsilon_z)d\upsilon_z = 1 \quad \Rightarrow \quad a_1 = \left[\int_{-\infty}^{\infty} e^{-\gamma \upsilon_z^2}\, d\upsilon_z\right]^{-1}.$$

First, we should note that, in order to ensure the convergence of the previous integral (and so, the normalization of the distribution f_1), ***the constant γ should be strictly positive***. Then, by applying the result (7.18), one readily gets $a_1 = \sqrt{\frac{\gamma}{\pi}}$. Therefore Eq. (7.41) becomes:

$$f_1(\upsilon_z) = \sqrt{\frac{\gamma}{\pi}}\, e^{-\gamma \upsilon_z^2} . \tag{7.42}$$

By directly applying Eq. (7.38) and the first model hypothesis the needed distribution $f(\vec{\upsilon})$ can be written as:

$$f(\vec{\upsilon}) = \left(\frac{\gamma}{\pi}\right)^{3/2} e^{-\gamma \upsilon^2} \tag{7.43}$$

and the remaining problem is to identify the positive constant γ. No straightforward computation might provide a value for γ without going beyond the frame of the considered ideal gas model. The problem may be overcome by using a suitable comparison with some thermodynamic data. The state function that is in the closest connection with the translation speed of gas molecules is the pressure. The gas pressure on a wall of the vessel results from the very numerous and rapid collisions of the gas molecules with the wall, giving rise to a quasi-continuous momentum transfer from the gas to the wall.

We shall first attempt to compute the gas pressure in the Maxwell model of an ideal gas and then we shall compare the result with the expression of the gas pressure provided by the thermal equation of state of the perfect gas.

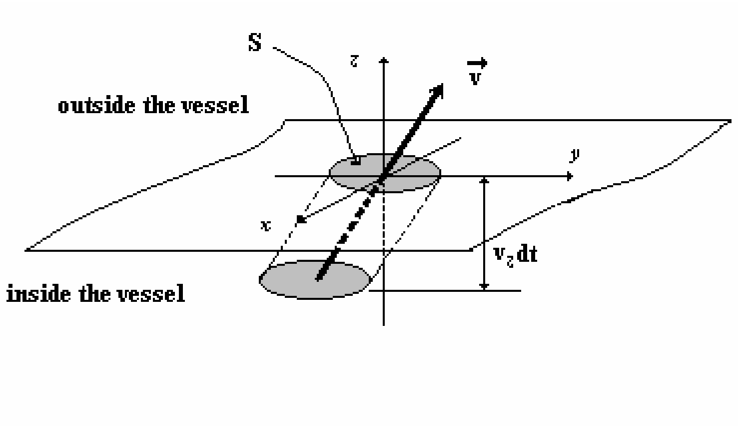


Figure 7.3

As a first step, consider the momentum transported towards a region of area S on the wall by the gas molecules moving with velocities close to some fixed vector $\vec{\upsilon}$. The molecules reaching the area S in a short time interval dt and moving with velocities close to $\vec{\upsilon}$ should obviously be contained in a oblique cylinder of height $\upsilon_z dt$, based on the area S and having the sides parallel to $\vec{\upsilon}$ (see Figure 7.3 for an illustration). Obviously only a fraction $f(\vec{\upsilon})\, d\upsilon_x d\upsilon_y d\upsilon_z$ of the gas molecules contained in this cylinder will have the velocity close to $\vec{\upsilon}$. Thus, if the particle density of the gas is *n*, then out of the $dN = n\,S\,\upsilon_z dt$ molecules included instantly in the cylinder, only $dN_{\vec{\upsilon}} = n\,S\,\upsilon_z\, f(\vec{\upsilon})\, d\upsilon_x d\upsilon_y d\upsilon_z\, dt$ will satisfy the required condition.

A gas molecule of mass m_0, when colliding ***elastically*** the recipient's wall with the velocity $\vec{\upsilon}$ will experience a momentum variation directed against the *z*-axis positive sense and weighing $-2m_0\,\upsilon_z$. Thus, if the collision takes place during the time interval *dt*, then the corresponding force exerted on the wall will equal $\frac{2m_0\,\upsilon_z}{dt}$. Summing the effect of all the $dN_{\vec{\upsilon}}$ molecular collisions that take place during the time interval *dt* and dividing the resultant force by the area *S* of the impact surface, one gets $dP_{\vec{\upsilon}} = 2n\,m_0\,\upsilon_z^2\, f(\vec{\upsilon})\, d\upsilon_x d\upsilon_y d\upsilon_z = \left(\frac{\gamma}{\pi}\right)^{3/2} 2n\,m_0\,\upsilon_z^2\, e^{-\gamma\upsilon^2}\, d\upsilon_x d\upsilon_y d\upsilon_z$ for the pressure exerted by the gas molecules that move towards the wall with the velocity $\vec{\upsilon}$. Thus, in order to obtain the total gas pressure on the wall, one should integrate upon all the velocity range, with the restriction of positive υ_z values only:

$$P = \left(\frac{\gamma}{\pi}\right)^{3/2} 2n\,m_0 \int_{-\infty}^{\infty} e^{-\gamma\upsilon_x^2}\, d\upsilon_x \int_{-\infty}^{\infty} e^{-\gamma\upsilon_y^2}\, d\upsilon_y \int_0^{\infty} \upsilon_z^2\, e^{-\gamma\upsilon_z^2}\, d\upsilon_z = \left(\frac{\gamma}{\pi}\right)^{3/2} 2n\,m_0 \sqrt{\frac{\pi}{\gamma}}\sqrt{\frac{\pi}{\gamma}} \int_0^{\infty} \upsilon_z^2\, e^{-\gamma\upsilon_z^2}\, d\upsilon_z .$$

Therefore

$$P = 2n\,m_0 \sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} \upsilon_z^2\, e^{-\gamma\upsilon_z^2}\, d\upsilon_z . \tag{7.44}$$

The last integral may be evaluated by means of the result (7.20). As the integration range of υ_z in Eq. (7.44) is half of the one in (7.20), one may finally write:

$$P = \frac{n\,m_0}{2\gamma} . \tag{7.45}$$

The last expression for the gas pressure is to be compared to the one obtained from the thermal equation of state of the perfect gas:

$$PV = \nu RT = N\frac{R}{N_A}T = NkT \quad \Rightarrow \quad P = nkT \quad \left(n = \frac{N}{V}\right). \tag{7.46}$$

It follows that $\gamma = \frac{m_0}{2kT}$ and this finally brings Eq. (7.43) to the form:

$$\boxed{f(\vec{\upsilon}) = \left(\frac{m_0}{2\pi kT}\right)^{3/2} e^{-\frac{m_0\upsilon^2}{2kT}}}, \tag{7.47}$$

which is the desired distribution. This formula laid the foundation of the statistical research of gases into the frame of the old ***kinetic-molecular theory***. While being essentially correct its derivation relies on hypothesis that are too tight to be used for other thermodynamic systems. The theory becomes useless even in the case of a gas where the reciprocal interactions between molecules become significant (the real gas model). Also, the derivation of the thermal equation of state requires the supplementary (very questionable!) hypothesis of elastic molecular collisions with the recipient's walls. This would obviously rise questions about the possibility of heat exchange between the gas and the thermostat. But, even if limited in use, Maxwell's kinetic-molecular theory allowed the more elaborated and general approach in Statistical Physics that begun with the work of Josiah Willard Gibbs [5]. An outline of the general principles of the Statistical Physics of systems in thermodynamic equilibrium is presented in the next section, for the use of the beginning student. Later on, in Chapter 12 of this lecture course, more statistical insight into the study of thermal phenomena (including rigorous derivations of various equations of state) is exposed.

7.2 The statistical viewpoint in Physics

As stressed at the beginning of this chapter, the microscopic information needed for a detailed description of a thermodynamic system is always totally overwhelming. The microscopic state of such a system can never be exactly specified. It can only be known with a certain probability. The sates of a thermodynamic system can thus be treated as (usually multidimensional) random variables. Finding the system in one or another of its thermodynamic states becomes a simple random event to which a probability may be assigned. The probabilities with which the given system can be found in one or another of its microscopic states (when some external conditions are imposed) represent the only detailed information we may hope to get about the system. ***The main target in Statistical Physics should then be to compute, by means of the known probabilities, the average values of various microscopic parameters of the system in the specified external conditions***.

7.2.1 The space of microscopic states of a system of particles

The first task in solving the previously stated problem should be ***the identification of all the available microscopic states of the system when some external conditions are imposed to it***. We shall use as a regular notation the symbol Γ for the set of all the available microscopic states of the system. The determination of Γ is not quite a problem for Thermal Physics. It is merely a dynamical problem and should be solved into the frame of Mechanics, whether quantum or classical. Consequently, we will not be concerned in what follows with the identification of the set of available microscopic states of a given system and we'll take this problem as already solved.

Nevertheless, it is useful for the convenience of the present discussion, to distinguish between the various types of states with which we should make statistics.

Speaking from a deterministic viewpoint, by a microscopic state of a given system one means a certain amount of data about that system at a certain moment, which allows the determination of a similar amount of data at any further moment. This operation should be performed through the use of some particular dynamical laws to which the microscopic units (particles) of the system are supposed to obey. Such a scheme of knowledge is called ***deterministic*** in the Philosophy of Science and is the main way of access to reality that is used in Physics.

Consider, for example, a ***system of N identical mass points*** whose motion is governed by the laws of Classical Dynamics. At a certain moment of time, the microscopic state of this system consists in a set of data containing the values of the position and momentum parameters of all the mass points at that given moment of time. For simplicity reasons, wherever no confusion is possible, a unique symbol, ζ, will be used in order to denote a microscopic state of a system. Thus, in Cartesian coordinates, a microscopic state of the considered set of N mass points may be written as:

$$\zeta \equiv \left(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, p_{x1}, p_{y1}, p_{z1}, \ldots, p_{xN}, p_{yN}, p_{zN}\right).$$

Obviously this is an element of a ***continuos Γ set*** of $6N$-dimensional vectors. In Mechanics this set plays a fundamental role and is called the ***phase space*** of the system. Thus, for the given system of identical N mass points, Γ can be organized as a $6N$-dimensional vector space. The corresponding ***"volume" element*** in Cartesian coordinates will be:

$$d\zeta = dx_1\, dy_1\, dz_1 \ldots dx_N\, dy_N\, dz_N\, dp_{x1}\, dp_{y1}\, dp_{z1} \ldots dp_{xN}\, dp_{yN}\, dp_{zN}\, .$$

In a similar way, from the mechanics of a ***classical biatomic gas***, the Γ (phase) space can be identified as a continuous $10N$-dimensional vector space. For a system with a microscopic quantum dynamics the states ζ may form an infinite dimensional Γ set, where the states may be indexed by some quantum numbers. While, from the statistical point of view, such cases often involve simpler mathematical procedures, for reasons of conceptual intuitiveness, only classical (i.e. non-quantum) systems will be statistically discussed in what follows.

7.2.2 The space of microscopic states of a classical (non-quantum) system

For classical (non-quantum) systems ***Γ is generally a finite dimensional vector space whose dimension should be proportional to the number of the microscopic units of the system***. We shall therefore use the generic notation $2 \cdot s \cdot N$ for the dimension of the Γ space of a classical system, where s is a parameter related to the specific dynamical structure of individual microscopic units, namely the ***number of dynamical degrees of freedom*** of each unit. More precisely, s is the number of parameters needed to uniquely specify the position of a microscopic unit. As is known from Mechanics, when specifying some state, to each position parameter it corresponds a momentum parameter. Therefore half of the number of parameters that specify a state of a classical system are position parameters and the other half are momentum parameters. We shall denote by q_i a generic position parameter and by p_i its corresponding (the term used in Mechanics is ***conjugate***) momentum parameter ($i = 1, 2, \ldots, s \cdot N$). The vector of all the position parameters will be denoted by q and the vector of all the momentum parameters will be written as p. Therefore q is an element of the space of position parameters (Γ_c, the so-called ***configuration space***) and p is an element of the space of momentum parameters, Γ_m. Thus, a microscopic state of the system will be an ordered couple of q and p and the Γ space may be written as a Cartesian product between Γ_c and Γ_m:

$$q \equiv (q_1, q_2, \ldots q_{sN}) \; ; \quad p \equiv (p_1, p_2, \ldots, p_{sN}) \; ; \quad \zeta \equiv (q, p) \; ; \quad \Gamma = \Gamma_c \times \Gamma_m . \tag{7.48}$$

Note: When generally speaking about the state of a system, one should also consider the case of an ***opened system***. For such cases, the ***particle number***, N, should also determine the microscopic state of the system, as a separate parameter. In order to emphasize this dependence, a microscopic state of the system should be denoted by the symbol (ζ, N), where ζ represents a vector of the state space of a N-particle system. However, for convenience reasons, we will keep denoting the state of a general system by ζ as long as this notation produces no confusion.

If the ***non-relativistic approach*** may be suitable for the considered system, then the range of each momentum parameter should obviously be the real axe, **R**. Consequently the space of the momentum parameters can be written as: $\Gamma_m = \underbrace{\mathbf{R} \times \mathbf{R} \times \ldots \times \mathbf{R}}_{sN\ times} \equiv \mathbf{R}^{sN}$.

The configuration space of a given classical system may also be split in a Cartesian product of configuration spaces corresponding to each microscopic unit. If the particles are identical then their individual configuration spaces will coincide. Let's denote by Γ_{c1} the configuration space of one particle in such a case (which will be actually the most frequent in what follows). One may therefore write: $\Gamma_c = \underbrace{\Gamma_{c1} \times \Gamma_{c1} \times \ldots \times \Gamma_{c1}}_{N\ times} \equiv \Gamma_{c1}^N$. Moreover, it is often very useful to distinguish among the position parameters of each microscopic unit the ***coordinates of its center of mass*** and the ***position parameters relative to the center of mass reference system***. It follows that the configuration space of a microscopic unit can be further written as a Cartesian product between the range of variation of the position of the unit's center of mass and the corresponding range of the relative coordinates: $\Gamma_{c1} = \Gamma_{c1}^{CM} \times \Gamma_{c1}^{rel}$.

In conclusion, ***the space of all the microscopic states of a classical non-relativistic system with N identical microscopic units can be written as***: $\Gamma = \left(\Gamma_{c1}^{CM}\right)^N \times \left(\Gamma_{c1}^{rel}\right)^N \times \mathbf{R}^{sN}$.

Another obvious (and very useful) decomposition of Γ may be obtained if one observes that the same microscopic state of the system may be unambiguously defined if the values of the position and momentum parameters are enumerated in a different order. Namely, one may specify the first particle through its position and momentum parameters, then write into the next locations the values of the position and momentum parameters for the second particle, and so on. For example, in the case of the previously considered set of N mass points, the same microscopic state may be written in Cartesian coordinates as:

$$\begin{aligned}\zeta &\equiv \left(x_1, y_1, z_1, \ldots, x_N, y_N, z_N, p_{x1}, p_{y1}, p_{z1}, \ldots, p_{xN}, p_{yN}, p_{zN}\right) \equiv \\ &\equiv \left(x_1, y_1, z_1, p_{x1}, p_{y1}, p_{z1}, \ldots, x_N, y_N, z_N, p_{xN}, p_{yN}, p_{zN}\right).\end{aligned}$$

Thus, by denoting the state space of each microscopic unit by Γ_1 ($\Gamma_1 = \Gamma_{c1} \times \mathbf{R}^s$), one obtains:

$$\Gamma = \Gamma_1^N = \left(\Gamma_{c1}^{CM} \times \Gamma_{c1}^{rel} \times \mathbf{R}^s\right)^N. \tag{7.48'}$$

The ***"volume" element of Γ***, $d\zeta$, should be interpreted as a measure of a subset of Γ consisting in a Cartesian product of $2 \cdot s \cdot N$ infinitesimal real intervals corresponding to each component of ζ. That is, $d\zeta$ is the "volume" of a $2 \cdot s \cdot N$ dimensional parallelepiped in Γ with infinitesimal edges. Therefore it may be expressed as the product of the "volume" element of the configuration space, dq, by the "volume" element, dp, of the space of momentum parameters: $\boldsymbol{d\zeta = dq \cdot dp}$. One may also think of $d\zeta$ as the product of the corresponding "volume" elements of each individual particle in its Γ_1 space: $\boldsymbol{d\zeta = d\zeta_1 \cdot d\zeta_2 \cdot \ldots \cdot d\zeta_N}$.

As was already pointed out, continuous Γ sets bring in some mathematical complications related mainly to the integration procedures: the Euclidean metric can make no sense in such Γ spaces, since it would imply sums of squared distance values with squared momentum values. A connected problem is the necessity for accounting for the (generally) inhomogeneous spread of the states ζ in the space Γ. Indeed, if one looks for ***the number dn(ζ) of microscopic states that can be found in an infinitesimal "volume" element dζ around the state ζ***, then it must be recognized that ***this number may depend on ζ***. Obviously, this number should be an infinitesimal quantity, of the same order of magnitude as $d\zeta$. Therefore we should write: $dn(\zeta) = g(\zeta) \cdot d\zeta$, where $g(\zeta)$ is a ***scalar nonnegative function*** called ***density of states*** in the Γ space. Consider, for example, some continuous function f defined on Γ, whose values should be summed over this space: $\sum_{\zeta \in \Gamma} f(\zeta)$.

Since the values of f must be very close in all the states of a given "volume" element $d\zeta$, for each such infinitesimal range, only one representative value of f may be approximately chosen and multiplied by the corresponding number of states in the given element. The number of terms dramatically decreases, since the sum can now be performed over the possible "volume" elements. Correspondingly, the summation symbol has to be changed to an integration one: $\int_{\Gamma}\ldots\int f(\zeta)dn(\zeta)=\int_{\Gamma}\ldots\int f(\zeta)g(\zeta)d\zeta$. The integral of f in such expressions has the meaning of a ***repeated integral***, as discussed in section 7.1. The use of multiple integration symbol is intended to suggest this. However, for reasons of writing simplicity, we'll use everywhere the symbol $\int_{\Gamma} f(\zeta)g(\zeta)d\zeta$ instead. Moreover, all summations over microscopic states should include a sum over the possible values of the particle number, N (this is for non-closed systems; for closed ones, the particle number is fixed and the sum over N reduces to only one term). Thus, strictly speaking, instead of $\int_{\Gamma} f(\zeta)g(\zeta)d\zeta$, one should have $\sum_{N}\int_{\Gamma(N)} f(\zeta,N)g(\zeta,N)d\zeta$, where $\Gamma(N)$ is the Γ space of a N-particle system and $g(\zeta,N)$ is the density of states in $\Gamma(N)$. Nevertheless, for convenience reasons, we'll make use of the complete notation only when some confusion may be generated.

Note: Since we will concentrate only on classical systems with continuous state spaces throughout these introductory lecture courses, the integration symbol will always be preferred. Nevertheless, when quantum systems come into discussion, it may happen that the space Γ be a discrete set. In such cases the symbol $\int_{\Gamma} f(\zeta)g(\zeta)d\zeta$ should be interpreted as a simple summation with $dn(\zeta) = g(\zeta)\cdot d\zeta = 1$.

7.2.3 The quantum corrections to the density of states in classical (non-quantum) systems

To this point it worth to make an important remark for the classical (non-quantum) systems: real world actually follows the laws of Quantum Physics and a "classical" system may be only a convenient approximation. Even if such approximations work with very good accuracy in many situations, by neglecting the fundamental laws of Quantum Physics the inherent errors accumulate and may lead to deeply erroneous results in some cases. In order to avoid such deviations, one should admit some fundamental quantum corrections in the classical approach.

Q1) One basic idea is that ***a position parameter and its conjugate momentum can be simultaneously determined only within a precision that is limited by the Planck's constant, h = 6.6261·10^{-34} J·s***. This is the so-called ***uncertainty principle***, which, if put into a more formal shape, reads: $dq_i dp_i \geq h$, $i = 1,2,\ldots,sN$. It follows that no conceivable experiment can reach states inside "volume" elements of the phase space that are smaller than h^{sN}. The phase space should be therefore divided into "cells" of "volume" h^{sN} and to each such "cell" one should attach ***at most one microscopic state***. The number of microscopic states that could be counted in a "volume" element, $d\zeta$, of a classical phase space Γ, around a certain given state ζ, would then be: $dn(\zeta) = d\zeta/h^{sN}$.

Q2) Another basic quantum idea is that ***non localized identical particles cannot be distinguished.*** This is the so-called ***identity principle***. Its practical consequence is that, when summing over the microscopic states of a system with N identical microscopic units, one same state is actually counted $N!$ times. Indeed, each interchange of two particles would produce a new microscopic state from the classical point of view, but should make no state change according to the identity principle. Therefore, in order to correctly account for the terms in phase space summations, one should divide the result by $N!$.

The previous quantum correction can be actually gathered in the following statement: ***the number of <u>distinct</u> microscopic states that could be counted in a "volume" element, $d\zeta$, of a classical phase space Γ, around a certain given state ζ, should be***: $dn(\zeta) = d\zeta/(N!\cdot h^{sN})$. Equivalently, one may say that ***the density of states in the phase space of a system of N identical classical particles is given by***:

$$g(\zeta, N) = \frac{1}{N!\,h^{sN}}. \tag{7.49}$$

Since Eq. (7.49) mixes both a classical state space defined by (7.48) and the previously stated quantum corrections, it is termed as the ***semi-classical approach*** for density of states of a non-quantum system.

7.2.4 The state space of weakly interacting systems

As was already pointed out, the problem of ***weakly interacting thermodynamic systems*** is of major interest in Thermal Physics. From the microscopic point of view, two systems are considered as weakly interacting if their individual state spaces are not significantly perturbed by the interaction. In other words, suppose that A and B are two systems (*irrespective of the type of their microscopic dynamics: classical or quantum*) and let Γ_A and Γ_B be their state spaces in the absence of any reciprocal interaction. By letting A and B interact one should actually deal with a compound system formed by their union, A∪B. ***If the state space of* A∪B *can be reasonably approximated by the Cartesian product of Γ_A and Γ_B ($\Gamma_{A\cup B} \cong \Gamma_A \times \Gamma_B$), then* A *and* B *are termed as weakly interacting systems***. For example, a mixture of two ideal gases of chemically and electrically neutral molecules, at room temperature and atmospheric pressure, could be treated with very good accuracy as a couple of weakly interacting systems. But, if one considers a gas of electrons and a gas of the same number of moles containing positive hydrogen ions in the same conditions of temperature and pressure, the situation turns out to be completely different. While being enclosed in separate containers the two systems have state spaces corresponding to mass points gases with Coulombian interactions. When mixed into the same container, a gas of neutral hydrogen atoms results (since the temperature is supposed to be sufficiently low to avoid further ionization) whose state space is clearly very much like the one of a classical ideal gas of ***neutral*** atoms.

Suppose that A and B are two weakly interacting systems. A state of the united system A∪B, (ζ,ξ), will be an ordered couple of a state ζ of A and a state ξ of B. Therefore, if the state spaces of A and B were continuous sets, then the same would be the case for $\Gamma_{A\cup B}$ and the "volume" element of $\Gamma_{A\cup B}$ would be the product of the corresponding "volume" elements of Γ_A and Γ_B: $d(\zeta,\xi) = d\zeta\cdot d\xi$. Moreover, the number, $dn(\zeta,\xi)$,of existing states of A∪B in a "volume" element $d(\zeta,\xi)$ around a certain state (ζ,ξ) should be the product of the corresponding number of states of A near ζ and of B near ξ: $dn(\zeta,\xi) = dn_A(\zeta)\cdot dn_B(\xi)$. It thus follows that the same relation could be written for the density of states: $g(\zeta,\xi) = g_A(\zeta)g_B(\xi)$.

7.2.5 The occupation probabilities

The second task in dealing with a Thermal Physics problem in statistical way is ***to associate suitable probabilities to every state*** $\boldsymbol{\zeta}$ ***from*** $\boldsymbol{\Gamma}$**:** $\boldsymbol{p(\zeta)}$. Thus, the set Γ becomes a ***sample space*** and $p(\zeta)$ plays the role of a distribution function of the random events of finding the system in one of its microscopic states ζ. Generally, these distribution function may vary in time due to various changes that may occur in the microscopic conditions of the system even if the structure of the set Γ remains unchanged. So, one should point out the time dependence in the arguments of the probabilities whenever this may be significant: $p(\zeta,t)$. For continuous Γ spaces one has to add a supplementary hypothesis: ***all the microscopic states available for the system in an infinitesimal "volume" element d***$\boldsymbol{\zeta}$ ***around the state*** $\boldsymbol{\zeta}$ **are** ***equally probable at any time***. Thus, ***the probability of finding the system in one of the dn***$\boldsymbol{(\zeta)}$ ***microscopic states around*** $\boldsymbol{\zeta}$ ***will be the sum of the probabilities of the incompatible events of finding the system in one of the microscopic states around*** $\boldsymbol{\zeta}$***, that is*** $\boldsymbol{p(\zeta,t)\cdot dn(\zeta) = p(\zeta,t)\cdot g(\zeta)\cdot d\zeta}$.

Whether Γ is a discrete or continuous sample space, the probabilities associated with every simple event of finding the system in a certain microscopic state ζ at a given moment t should satisfy the normalization condition:

$$\sum_{\zeta} p(\zeta,t) = 1, \text{ or } \int_{\Gamma} p(\zeta,t)\,dn(\zeta) = \int_{\Gamma} p(\zeta,t)\,g(\zeta)\,d\zeta = 1, \quad (\forall t), \tag{7.50}$$

for continuous Γ spaces.

Finding the distribution function $p(\zeta,t)$ is definitely the most important and the most difficult problem of Statistical Physics. Actually, from this point of view, Statistical Physics may be split into two major parts: one concerned with finding the probabilities $p(\zeta,t)$ and the other that starts from these probabilities in obtaining practical results to be used in Thermal Physics. The main purpose of the present introductory lecture courses is to provide the students with the essential tools for practical work in Thermal Physics. Therefore, the highly involved mathematical deduction of the probabilities $p(\zeta,t)$ from simpler principles will be skipped. Rather, by following the example some brilliant works of the literature [6], we'll take the expressions of these probabilities in specified conditions as ***fundamental laws*** and concentrate on the applications that could be solved therefrom.

The probabilities $p(\zeta,t)$ result most naturally as solutions of their equation of evolution, the so-called ***master equation*** [6, 7]. In constructing such an equation, one should ask for the rate of change of the probability that the system occupies one of its microscopic states ζ at a given instant t: $\frac{\partial}{\partial t} p(\zeta,t)$. This rate should be obviously the sum of two contributions: the ***positive contribution*** of all the possible transitions of the system ***from any other*** microscopic state ζ' towards the microscopic state ζ and the ***negative contribution*** of all the possible transitions from the microscopic state ζ ***towards any other*** microscopic state ζ'. In other words, the rate of change of the occupation probability for some microscopic state should be the difference between the rate of increasing the occupation probability and the rate of decreasing it.

The transition probability between two microscopic states of the system wears certain features when some external conditions are imposed to the system. For example, take ***a cold system that is put in thermal contact with a hotter thermostat***: while the system may jump at random from a microscopic state to another, ***the transitions towards microscopic states with higher energy will be preferred***. On the contrary, ***when the system is completely isolated, equal probabilities should be allowed for any transitions***. For convenience we'll denote by $W(\zeta' \rightarrow \zeta)$ ***the transition probability that the system may jump from the state*** ζ' ***towards the state*** ζ ***during one unit of time***. It will be necessarily a ***non-negative quantity***. The event that such a transition will ***effectively*** take place is however a compound event between the event of finding the system in the state ζ' and that of performing the transition during one unit of time. These events are supposed as ***independent***, so the probability of an effective transition from the state ζ' towards the state ζ during one unit of time may be written as: $W(\zeta' \rightarrow \zeta) \cdot p(\zeta',t) \cdot g(\zeta') \cdot d\zeta'$. Since the system may occupy only one microscopic state at a given moment of time, the transition from the various states ζ' towards the state ζ during one unit of time are obviously ***incompatible events***. Therefore, the ***total probability that a transition may occur <u>towards</u> the microscopic state*** ζ ***from any other microscopic state, during the unit of time*** should be written as: $\int_{\Gamma} W(\zeta' \to \zeta) p(\zeta',t) g(\zeta') d\zeta'$. In a similar way, one may write the ***total probability that a transition may occur <u>from</u> the microscopic state ζ towards any other microscopic state during the unit of time***: $\int_{\Gamma} W(\zeta \to \zeta') p(\zeta,t) g(\zeta') d\zeta' = p(\zeta,t) \int_{\Gamma} W(\zeta \to \zeta') g(\zeta') d\zeta'$. Therefore, the rate of change of the probability that, at a given instant t, the system occupies one of its microscopic states ζ, that is the ***master equation***, takes the following general form:

$$\frac{\partial}{\partial t} p(\zeta,t) = \int_{\Gamma} W(\zeta' \to \zeta) p(\zeta',t) g(\zeta') d\zeta' - p(\zeta,t) \int_{\Gamma} W(\zeta \to \zeta') g(\zeta') d\zeta' . \tag{7.51}$$

Apparently, this equation provides an easy way of finding the occupation probabilities $p(\zeta,t)$ when some initial conditions are specified. Unfortunately, this may be the case only in a very restraint number of situations. Even for very simple systems, the computation of the transition probabilities $W(\zeta' \to \zeta)$ is often an overwhelming task. Solving the master equation, even if simplified forms of these probabilities are used, is also a huge mathematical enterprise. Because of these enormous difficulties of solving the direct problem, some other ways were approached in order to go around it. For example, one may start with a solution corresponding to the thermodynamic equilibrium and then may try to construct other non-equilibrium states as perturbations of the equilibrium one [7]. Obviously, such an approach can work only for states that are not far from equilibrium.

Consequently, the master equation may not be of much use in finding the occupation probabilities $p(\zeta,t)$. ***Only general properties of the distribution function may be inferred from this equation***. For example, for some simple systems, it can be demonstrated that, in given homogeneous and isotropic external conditions, the long time evolution ($t \to \infty$) of a system leads to a unique ***macroscopic*** state, which is independent of its initial condition. This is essentially the ***Boltzmann H-theorem*** [6].

Also, by making use of Eq. (7.51) one can investigate the state of ***macroscopic (thermodynamic) equilibrium*** of a system. Let $A(\zeta)$ be a ***measurable*** parameter of the system in the microscopic state ζ. The macroscopic value of A will be a (generally time dependent) average of $A(\zeta)$:

$$A_{macroscopic}(t) \equiv \langle A(\zeta) \rangle (t) = \int_{\Gamma} A(\zeta) p(\zeta,t) g(\zeta) d\zeta . \tag{7.52}$$

The system is said to be in macroscopic equilibrium if the macroscopic value of <u>any</u> measurable parameter is independent of time (we should remember here that a hidden (that is non-measurable) parameter should have a zero-valued average at any time). Thus, in macroscopic equilibrium one should have:

$$\frac{d}{dt}A_{macroscopic}(t)=\int_{\Gamma}A(\zeta)\left[\frac{\partial}{\partial t}p(\zeta,t)\right]g(\zeta)d\zeta=0\,, \qquad (7.53)$$

for ***any measurable parameter*** *A* of the system. Eq. (7.53) can be satisfied for all the measurable parameters only if no explicit dependence of time appears in the distribution function, that is if and only if:

$$\boxed{\frac{\partial}{\partial t}p(\zeta,t)=0 \quad , \quad (\forall)\,\zeta\in\Gamma}, \qquad (7.54)$$

Eq. (7.54) represents the ***statistical condition for macroscopic equilibrium***. The situation described by Eq. (7.54) is also termed as ***complete equilibrium*** [8]. This is obviously a macroscopic situation, since an occupation probability for the microscopic states still exists and the system can thus evolve at the microscopic level. In other words, a (usually quite numerous) set of microscopic states are still available to the system in its complete equilibrium condition. There are strong experimental and theoretical reasons to believe that, ***if the external constraints of a system are fixed starting from a certain non-equilibrium state, after a sufficiently long time, the system reaches a unique complete equilibrium condition*** (that is a condition of macroscopic equilibrium with a unique distribution function; this conclusion can be termed as a ***generalized H-theorem*** [7]). Therefore, this unique complete equilibrium condition could be identified with the state of thermodynamic equilibrium under the corresponding external constraints.

In conclusion, ***the standard connection between Equilibrium Statistical Physics and Equilibrium Thermodynamics*** consists in the following**:** ***1. the identification of the complete equilibrium condition of a system with its thermodynamic equilibrium state***; *2.* ***the identification of the averages of the measurable microscopic parameters with corresponding thermodynamic quantities***. It should be stressed that this connection works only for the equilibrium case: the connection between Non-Equilibrium Statistical Physics and Non-Equilibrium Thermodynamics reduces simply to the identification of the averages of the measurable parameters with thermodynamic quantities.

By using the general form of the master equation (7.51), the complete equilibrium condition reduces to:

$$\int_{\Gamma}\left[W(\zeta'\to\zeta)p(\zeta')-W(\zeta\to\zeta')p(\zeta)\right]g(\zeta')d\zeta'=0\,. \qquad (7.55)$$

A sufficient requirement for which Eq. (7.55) may be accomplished is the so-called ***detailed balance condition***:

$$W(\zeta' \to \zeta)\, p(\zeta') = W(\zeta \to \zeta')\, p(\zeta). \tag{7.56}$$

This condition seems to be actually well satisfied by all the systems in thermodynamic equilibrium and may thus be used as a test for any theoretical model that provides the transition probabilities for a given system.

A particular case of the detailed balance condition arises when ***the system is completely isolated***, that is when ***there are no preferred transitions***: $W(\zeta' \to \zeta) = W(\zeta \to \zeta')$. For this case, Eq. (7.56) leads to:

$$p(\zeta') = p(\zeta), \tag{7.57}$$

which means that the occupation probability is ***uniformly distributed*** among all the possible microscopic states of the system. In Statistical Physics such a situation is termed as being described by a ***microcanonical distribution function***. In practice it is obviously impossible to have completely isolated systems, but the concept of microcanonical distribution function may be used as a theoretical device for obtaining the occupation probabilities for systems in various standard conditions. Such approaches may be found in any reference books of Statistical Mechanics [1, 7-11]. As was already stressed before, in the present introductory lecture courses we will content to take the occupation probabilities in standard thermodynamic equilibrium conditions as fundamental laws and use them in solving various applications.

The main connection between equilibrium statistical and thermodynamic results will be the following particular form of Eq. (7.52):

$$\boxed{A_{thermodynamic} \equiv \langle A(\zeta) \rangle = \int_{\Gamma} A(\zeta)\, p(\zeta)\, g(\zeta)\, d\zeta}. \tag{7.58}$$

7.2.6 The occupation probability of a union of weakly interacting systems

For a union of two ***weakly interacting systems***, A and B, the occupation probability should be computed as the distribution of associated ***independent*** random variables. Indeed, since the interaction between A and B is supposed to be weak, the event that A occupies the microscopic state ζ should be independent of the event that B occupies a microscopic state ξ. Therefore, the probability that the united system A∪B be found in the microscopic state (ζ,ξ) should be written as:

$$p((\zeta,\xi),t) = p_A(\zeta,t)\, p_B(\xi,t). \tag{7.59}$$

Before discussing any particular form of the distribution function, one may derive some general results related to the most important thermodynamic parameters, namely the energy and the entropy. To this purpose we shall consider the statistical counterparts of these parameters.

7.3 The statistical energy

The statistical energy is defined as the average of the energies of the available microscopic states of a given system:

$$\boxed{\langle E\rangle(t) = \int_{\Gamma} E(\zeta)\,p(\zeta,t)\,g(\zeta)\,d\zeta}. \tag{7.60}$$

As is well known, the energy of a microscopic state of a system ***is not a well defined*** quantity. It depends on a certain arbitrary scaling, that is on a reference value that should be taken as the origin of the energy. This inconvenience obviously propagates to the previously defined statistical average and therefore ***allows well defined values only for energy variations***. For a closed system no real problems may occur therefrom since, by arbitrarily defining an origin of the energy scale, any further value of the energy will be well defined. However, important difficulties may appear when mass exchange is allowed between two systems, A and B say: energy values of particles belonging to different systems, with different origins of the energy scale, should be compared. Obviously, ***a unique reference value for the energy*** should be used in dealing with such situations. Nevertheless, it very frequently turns out that, ***by defining the same origin of the energy scale for the two mass-exchange interacting systems, a certain shift appears between the minimum energy values of the particles in those systems*** (even if the microscopic units (particles) of the two systems are identical in their nature; see the illustration of Figure 7.4). This energy shift may originate, for example, in different interactions of the two systems with external fields. It works as a potential energy difference and allows particles of the ***same relative energy*** in the two systems to have ***different total actual energies***. That kind of potential energy will be termed as ***chemical energy*** in what follows and obviously ***should be determined only by the external constraints imposed to the system*** (***it should not depend of any particular microscopic state***). Therefore, when mass exchange is allowed between two systems, a preference will appear for the particles of the system with higher chemical energy to enter into the system where the chemical energy is lower. This effect manifests itself, for example, for the conduction electrons when two pieces of different metals are welded together: the electrons of one metal enter the other one in a diffusion process, until this tendency is compensated by the resulted electrical forces generated by the positive charges left uncompensated. The possibility of electron diffusion through the contacts between different solid crystals is far from being an academic issue. Actually, all the present electronic industry is based on this effect that leads to the formation of various electronic junctions. This may be a strong reason for the emphasis that we make on open systems in these (actually introductory) lectures.

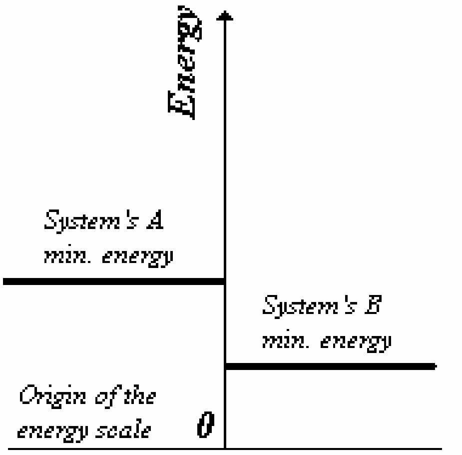


Figure 7.4

Suppose that a certain system is in thermodynamic equilibrium and that a particle is brought inside, at the lowest energy level in this system. This will obviously ***determine an increase of its the total energy***. If no other change occurs in this system, that is if all its other communication channels are closed, then the energy increase is produced by a certain chemical work that ***equals the value of the chemical potential per particle in this system, μ***. Thus, if the total number of particles in the system is N then its ***total chemical energy*** will be $\mu\cdot N$. Therefore, the ***non-chemical energy*** of a certain microscopic state, (ζ,N), of the system remains to be: $E(\zeta,N) - \mu\cdot N$ (the total energy of a microscopic state of the non-closed system will have a correspondingly explicit dependence on the particle number).

Note: In Statistical Physics it is usually preferred to express the ***chemical work*** through the ***chemical potential per particle***. Thus, instead of writing $dM = \mu\cdot dv$, one has $dM = \tilde{\mu}\cdot dN$, where dN is the variation of the particle number corresponding to a variation dv of the mole number. While μ and $\tilde{\mu}$ have different units, it is usual to make no notation distinction between these two quantities. ***We shall therefore denote both of them by the symbol μ***.

When ***weakly interacting systems*** come into discussion ***the total energy of a state of their union may be considered as the sum of the individual energies of the components***. Indeed, if A and B are two systems and if their interactions is weak, any state (ζ,ξ) of the union may be considered as an ordered couple of states ζ (of A in perfect isolation) and ξ (of B in perfect isolation). The ***interaction energy is therefore neglected***: $E_{A\cup B}(\zeta,\xi) = E_A(\zeta) + E_B(\xi)$. For the total average energy one may thus write:

$$\begin{aligned}\langle E\rangle_{A\cup B}(t) &= \int_{\Gamma_A\times\Gamma_B} E_{A\cup B}(\zeta,\xi)\, p((\zeta,\xi),t)\, dn(\zeta,\xi) = \\ &= \int_{\Gamma_A\times\Gamma_B} [E_A(\zeta)+E_B(\xi)]\, p_A(\zeta,t)\, p_B(\xi,t)\, dn_A(\zeta)\, dn_B(\xi) = \\ &= \int_{\Gamma_A\times\Gamma_B} E_A(\zeta)\, p_A(\zeta,t)\, p_B(\xi,t)\, dn_A(\zeta)\, dn_B(\xi) + \int_{\Gamma_A\times\Gamma_B} E_B(\xi)\, p_A(\zeta,t)\, p_B(\xi,t)\, dn_A(\zeta)\, dn_B(\xi) \\ &= \int_{\Gamma_A} E_A(\zeta)\, p_A(\zeta,t)\, dn_A(\zeta) \int_{\Gamma_B} p_B(\xi)\, g_B(\xi)\, d\xi + \int_{\Gamma_B} E_B(\xi)\, p_B(\xi,t)\, dn_B(\xi) \int_{\Gamma_A} p_A(\zeta)\, g_A(\zeta)\, d\zeta\end{aligned},$$

where use was made of Eq. (7.59) and of the corresponding relation between the density of states in the Γ spaces of the two systems. By separately applying the normalization relation (7.50) in both sample spaces Γ_A and Γ_B, one obtains:

$$\begin{aligned}\langle E\rangle_{A\cup B}(t) &= \int_{\Gamma_A} E_A(\zeta)\, p_A(\zeta,t)\, g_A(\zeta)\, d\zeta + \int_{\Gamma_B} E_B(\xi)\, p_B(\xi,t)\, g_B(\xi)\, d\xi = \\ &= \langle E\rangle_A(t) + \langle E\rangle_B(t)\end{aligned} . \tag{7.61}$$

Therefore ***the statistical energy behaves as an extensive quantity***. The previously stated correspondence between Equilibrium Statistical Physics and Equilibrium Thermodynamics may thus be applied. ***For fixed external conditions, the long-time limit of the statistical energy of a system (that is its energy in the complete equilibrium allowed by the given external conditions) can be identified with the corresponding internal energy of the system***:

$$\langle E\rangle(t\to\infty) \equiv U . \tag{7.62}$$

7.4 The statistical entropy

Entropy is a macroscopic parameter of a system that has no microscopic counterpart. This is the main reason for which a full understanding of its meaning is so difficult for the beginning students. The statistical definition of entropy was first given by Boltzmann and refined thereafter by many others [6]:

$$\boxed{S(t) = -k\int_{\Gamma} p(\zeta,t)\, ln[p(\zeta,t)]\, g(\zeta)\, d\zeta}, \tag{7.63}$$

where k is the universal ***Boltzmann constant*** (***k*** **= 1.3807·10^{-23} J/K**). The integration over Γ should also include the summation over the particle number if the system is not closed.

Several general properties can be demonstrated for this quantity.

a) We note first that ***S*(*t*) ≥ 0**. Indeed, as $p(\zeta,t)$ are numbers contained in the range [0, 1] (see axiom P1 of Section 7.1), $ln[p(\zeta,t)]$ should be all negative or zero and the same would be said about the integrand of (7.63) and of the integral itself.

b) ***The statistical entropy should be an extensive quantity***. Indeed, let A and B be two weakly interacting systems. The entropy of the united system A∪B becomes:

$$\begin{aligned} S_{A\cup B}(t) &= -k \int_{\Gamma_A\times\Gamma_B} p((\zeta,\xi),t)\, ln[p((\zeta,\xi),t)]\, dn(\zeta,\xi) = \\ &= -k \int_{\Gamma_A\times\Gamma_B} p_A(\zeta,t)\, p_B(\xi,t)\, ln[p_A(\zeta,t)\, p_B(\xi,t)]\, dn_A(\zeta)\, dn_B(\xi) = \\ &= -k \int_{\Gamma_A\times\Gamma_B} p_A(\zeta,t)\, p_B(\xi,t)[ln\, p_A(\zeta,t) + ln\, p_B(\xi,t)]\, dn_A(\zeta)\, dn_B(\xi) = \\ &= -k \int_{\Gamma_A} p_A(\zeta,t)\, ln\, p_A(\zeta,t)\, dn_A(\zeta) \int_{\Gamma_B} p_B(\xi,t)\, g_B(\xi)\, d\xi - \\ &\qquad - k \int_{\Gamma_B} p_B(\xi,t)\, ln\, p_B(\xi,t)\, dn_B(\xi) \int_{\Gamma_A} p_A(\zeta,t)\, g_A(\zeta)\, d\zeta . \end{aligned}$$

By separately applying the normalization relation (7.50) in both sample spaces Γ_A and Γ_B, one obtains:

$$\begin{aligned} S_{A\cup B}(t) &= -k \int_{\Gamma_A} p_A(\zeta,t)\, ln\, p_A(\zeta,t)\, g_A(\zeta)\, d\zeta - k \int_{\Gamma_B} p_B(\xi,t)\, ln\, p_B(\xi,t)\, g_B(\xi)\, d\zeta = \\ &= S_A(t) + S_B(t). \end{aligned} \tag{7.64}$$

c) ***The statistical entropy of an isolated system always increases in time and tends to a maximum value in the complete equilibrium condition of the system***. Indeed, one may write:

$$\begin{aligned} \frac{d}{dt} S(t) &= -k \int_{\Gamma} \left[\frac{\partial}{\partial t} p(\zeta,t)\right] ln[p(\zeta,t)]\, g(\zeta)\, d\zeta - k \int_{\Gamma} \frac{\partial}{\partial t} p(\zeta,t)\, g(\zeta)\, d\zeta = \\ &= -k \int_{\Gamma} \left[\frac{\partial}{\partial t} p(\zeta,t)\right] ln[p(\zeta,t)]\, g(\zeta)\, d\zeta \end{aligned} , \tag{7.65}$$

since the normalization relation implies $\int_{\Gamma} \frac{\partial}{\partial t} p(\zeta,t)\, g(\zeta)\, d\zeta = \frac{d}{dt} \int_{\Gamma} p(\zeta,t)\, g(\zeta)\, d\zeta = \frac{d}{dt} 1 = 0$. The time derivative of the distribution function can now be computed from the master equation:

$$\begin{aligned} \frac{d}{dt} S(t) &= -k \int_{\Gamma}\int_{\Gamma} W(\zeta' \to \zeta)\, p(\zeta',t)\, ln[p(\zeta,t)]\, g(\zeta')\, g(\zeta)\, d\zeta'\, d\zeta + \\ &\qquad + k \int_{\Gamma} p(\zeta,t)\, ln[p(\zeta,t)]\, g(\zeta)\, d\zeta \int_{\Gamma} W(\zeta \to \zeta')\, g(\zeta')\, d\zeta' = \\ &= -k \int_{\Gamma}\int_{\Gamma} W(\zeta' \to \zeta)\, p(\zeta',t)\, ln[p(\zeta,t)]\, g(\zeta')\, g(\zeta)\, d\zeta'\, d\zeta + \\ &\qquad + k \int_{\Gamma}\int_{\Gamma} W(\zeta \to \zeta')\, p(\zeta,t)\, ln[p(\zeta,t)]\, g(\zeta')\, g(\zeta)\, d\zeta'\, d\zeta . \end{aligned}$$

By suitably renaming the integration variables in the last term, we have:

$$\frac{d}{dt}S(t)=k\int_{\Gamma}\int_{\Gamma}W(\zeta'\to\zeta)p(\zeta',t)\{ln[p(\zeta',t)]-ln[p(\zeta,t)]\}g(\zeta')g(\zeta)d\zeta' d\zeta\,. \tag{7.66a}$$

A further interchange of the variables ζ and ζ' in the integrals of (7.66a) provides a new expression of the time derivative of the statistical entropy:

$$\frac{d}{dt}S(t)=-k\int_{\Gamma}\int_{\Gamma}W(\zeta\to\zeta')p(\zeta,t)\{ln[p(\zeta',t)]-ln[p(\zeta,t)]\}g(\zeta')g(\zeta)d\zeta' d\zeta\,. \tag{7.66b}$$

By adding Eqs. (7.66a) and (7.66b) one then gets:

$$\frac{d}{dt}S(t)=\frac{1}{2}k\int_{\Gamma}\int_{\Gamma}[W(\zeta'\to\zeta)p(\zeta',t)-W(\zeta\to\zeta')p(\zeta,t)]ln\left[\frac{p(\zeta',t)}{p(\zeta,t)}\right]g(\zeta')g(\zeta)d\zeta' d\zeta\,. \tag{7.67}$$

Eq. (7.67) takes place for any external conditions imposed to the system. However, when the system is completely isolated, no preferred transitions occur, so that:

$$W(\zeta'\to\zeta)=W(\zeta\to\zeta'). \tag{7.68}$$

From Eq. (7.67) it thus follows that:

$$\frac{d}{dt}S(t)=\frac{1}{2}k\int_{\Gamma}\int_{\Gamma}W(\zeta'\to\zeta)[p(\zeta',t)-p(\zeta,t)]ln\left[\frac{p(\zeta',t)}{p(\zeta,t)}\right]g(\zeta')g(\zeta)d\zeta' d\zeta\,. \tag{7.69}$$

In the last integral the quantities $W(\zeta'\to\zeta)$ are always non-negatives and any difference $p(\zeta',t) - p(\zeta,t)$ has always the same sign as the logarithm $ln\left[\frac{p(\zeta',t)}{p(\zeta,t)}\right]$. Therefore, the integrand is always non-negative and the same must be true for the integral. One may thus conclude that:

$$\boxed{\frac{d}{dt}S(t)\geq 0}. \tag{7.70}$$

and thus ***the statistical entropy of the isolated system is always increasing in time***. It tends to a maximum value when the integral of (7.69) vanishes. This can occur when the probability distribution becomes microcanonical that is when an equation of the type of (7.57) takes place at any time.

As emphasized by Eq. (7.63), the statistical entropy ***represents no average*** of some microscopic parameter of the system. So it cannot be put in correspondence with the thermodynamic entropy through the procedure indicated in Eq. (7.58). Nevertheless, the properties a)-c) are characteristic for the thermodynamic entropy and some connection between the statistical and thermodynamic concepts of entropy should exist. Actually it should be ***postulated*** that ***the entropy of Eq.*** **(7.63)**, ***for a system in complete equilibrium, is identical with the corresponding thermodynamic entropy***.

The definition (7.63) of the statistical entropy is by no means restricted to the case of many-particle systems. It can actually be applied to ***simple mechanical systems*** too. By a mechanical system we understand the one whose microscopic state ζ is specified with precision (due to the small number of state parameters of the system). Therefore, for this state we should have $p(\zeta) = 1$ and for any other state the occupation probability should vanish. The sum over states in (7.63) would then have only one term for which $ln[p(\zeta)] = 0$. Consequently, ***the entropy of a mechanical system is zero-valued***. A similar conclusion should be drawn for any system whose microscopic state is well defined, as is the case for a thermodynamic system at zero absolute temperature, where any microscopic unit is supposed to reach its ***unique fundamental state***. Therefore, ***the entropy of a thermodynamic system at zero absolute temperature must be zero-valued***. This essentially statistical conclusion represents the very statement of The Third Law of Thermodynamics.

When a system occupies with certitude some given microscopic state, we say that it is in a ***state of maximum order***. By relaxing this strong requirement (for example, by placing the system in thermal contact with a thermostat) all the other microscopic states will be allowed to be occupied with some probabilities and the state of order in the system (that is the degree of knowledge about its instantaneous microscopic state) will degrade. The probabilities $p(\zeta,t)$ will increase in time for all the states and, since $\frac{\partial}{\partial t} p(\zeta,t) > 0$, the time derivative of the entropy given by (7.65) will be non-negative. It follows that the decrease of order in the system induces an increase of the entropy. This conclusion allows us to ***consider the entropy as a measure of the disorder of the system or as the measure of our ignorance about its instantaneous microscopic state***.

More formal support for this idea can be gained if one looks at the integral of the expression (7.63) defining the statistical entropy as to a statistical average of the logarithm of the occupation probability. Thus we may write (in a purely formal sense, of course, since no dynamical variable corresponds to the logarithm of the occupation probability): $S(t) = -k\langle ln[p(\zeta,t)]\rangle$. By identifying the quantity $\langle\langle p(\zeta,t)\rangle\rangle \equiv exp\{\langle ln[p(\zeta,t)]\rangle\}$ to a kind of ***mean occupation probability*** or ***average amount of information about the microscopic state of the system, one readily obtains***: $\boxed{\langle\langle p(\zeta,t)\rangle\rangle = e^{-S(t)/k}}$. It can therefore be seen that ***the information about the microscopic state of the system steeply degrades by the entropy increase***.

7.5 The fundamental laws of the Equilibrium Statistical Physics

The first two laws already appeared in the previous discussions about the complete equilibrium condition. We shall restate them here in a more general form together with the third law, which actually introduces an explicit form for the probability distribution of a given thermodynamic system.

1) ***The correspondence principle for measurable microscopic parameters. For any system in given external conditions the complete equilibrium condition is equivalent to the thermodynamic equilibrium state in these specified external conditions. A unique thermodynamic (macroscopic) parameter, $A_{thermodynamic}$, corresponds to each measurable microscopic parameter, A, of the system in complete equilibrium condition so that***:

$$\boxed{A_{thermodynamic} \equiv \sum_N \int_{\Gamma(N)} A(\zeta,N)\,p(\zeta,N)\,g(\zeta,N)\,d\zeta}. \tag{7.71}$$

2) ***The entropy principle. The thermodynamic entropy of a system that attains the complete equilibrium in some given external conditions is identical to the corresponding statistical entropy***:

$$\boxed{S_{thermodynamic} \equiv -k \sum_N \int_{\Gamma(N)} p(\zeta,N)\,ln\left[p(\zeta,N)\right]g(\zeta,N)\,d\zeta}, \tag{7.72}$$

3) ***The probability principle. For a system in complete equilibrium under fixed external conditions (that include the thermal equilibrium with a thermostat of temperature T and the equilibrium with a particle reservoir of chemical potential μ), the probability to be in some microscopic state (ζ,N) is proportional to an exponential that depends on the non-chemical energy of that state***, namely:

$$\boxed{p(\zeta,N) = \frac{1}{Z} exp\left[-\frac{E(\zeta,N) - \mu N}{k T}\right]}, \tag{7.73}$$

where Z is a suitable constant that makes Eq. (7.73) satisfy the normalization condition:

$$\boxed{Z = \sum_N \int_{\Gamma(N)} exp\left[-\frac{E(\zeta,N) - \mu N}{k T}\right] g(\zeta,N)\,d\zeta}. \tag{7.74}$$

The normalization constant Z is called ***partition function*** and, as it will become clear in the next chapters, it is of major importance in any equilibrium statistical computations. The general form of the occupation probability defined by Eq. (7.73) is mainly useful when ***the system is in thermal equilibrium with a thermostat, but is not closed (it should be actually in "chemical" equilibrium with a particle reservoir)***. It is known as the ***grand canonical distribution function***.

One remarkable particular case arises when the system is closed. In this case N is fixed and the sum over the particle number reduces to only one term. Since μ is determined by the external conditions only (it is a thermodynamic parameter and thus it should be independent of any particular microscopic state), the factor $exp[\mu \cdot N/(k \cdot T)]$ do not depend on ζ and may be included in the normalization constant. Therefore, Eq. (7.73) reduces to:

$$\boxed{p(\zeta)=\frac{1}{Z}exp\left[-\frac{E(\zeta)}{kT}\right] \quad ; \quad Z=\int_{\Gamma} exp\left[-\frac{E(\zeta)}{kT}\right]g(\zeta)d\zeta}, \qquad (7.75)$$

which is known as the ***canonical distribution function***. This distribution works for ***closed systems that are in thermal equilibrium with a thermostat***.

Finally, ***when the system is isolated***, the energy of each microscopic state should be the same, so that the exponential factor in the probability of (7.75) becomes independent of ζ. It means that the occupation probability becomes a constant over the state space and we are brought to the ***microcanonical distribution function***. Nevertheless, from the practical point of view, only the distributions of Eqs. (7.73) and (7.75) are of use in applications.

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Exercises [11]

7.1 What is the probability of getting either a seven or a six when throwing two dice?

Answer: $p_6 = 5/36$; $p_7 = 6/36$.

7.2 What is the probability of first drawing the ace of spades and then drawing any of the three remaining aces from a 52 card pack?
Answer: (1/52)·(3/51) = 1/884.

7.3 What is the probability that out of five people, none have the same birthday? You may assume that there are 365 days in a year for simplicity.
Hint/Answer: The probability that two people do not have the same birthday is p_2 = 364/365. The probability that three people do not have the same birthday is p_3 = (364/365)·(363/365). … The probability that five people do not have the same birthday is p_5 = (364/365)·(363/365)·(362/365)·(361/365).

7.4 If eight coins are thrown at random show that the probability of obtaining at least six heads is 37/256.
Hint/Answer: The favorable cases are when there are eight heads, or seven heads and a tails, or six heads and a tails. The probability of obtaining either heads or tails when throwing a coin is 1/2. Therefore, eight heads of eight coins can be obtained with the probability $p_8 = 1/2^8$. To obtain seven heads out of eight coins, the one tails can occur at one of the coins in C_8^1 = 8!/(7!1!) equivalent ways, so that $p_7 = (1/2^7)\cdot(C_8^1\cdot 1/2) = 8/2^8$. Finally, to obtain six heads out of eight coins, the two tails can occur at two of the coins in C_8^2 = 8!/(6!2!) equivalent ways, so that $p_6 = (1/2^6)\cdot(C_8^2\cdot 1/2^2) = 28/2^8$. The needed probability will be $p = (1 + 8 + 28)/2^8 = 37/256$.

7.5 The quantity x can take on values of -20, -10, and 30 with respective probabilities of 3/10, 1/5, and 1/2. Determine the average value of x and the standard deviation Δx.
Hint/Answer: The average value of x is: $\langle x\rangle$ = -20·(3/10) - 10·(1/5) + 30·(1/2) = 7. Also Δx = 23.26.

7.6 A device uses five silicon chips. Suppose the five chips are chosen at random from a batch of a hundred chips out of which five are defective. What is the probability that the device contains no defective chip when it is made up from one batch?
Hint/Answer: The probability that the first chip is good = 95/100. The probability that the first and the second are both good = (95/100)·(94/99). … The probability that the first five are good = (95/100)·(94/99)· (93/98)·(92/97)· (91/96) = 0.7696.

8. Equations of state

As outlined in the previous chapters, the first two laws of Thermodynamics establish *only* the general working frame for dealing with thermal phenomena. They simply affirm the *existence* of some state functions for a thermodynamic system: the internal energy and the entropy. Moreover, The Third Law brings in a reference value for the entropy that is necessary for its complete definition. However, none of these fundamental laws allows the *effective construction* of the state functions. The specific values of the internal energy and of the entropy in a certain equilibrium state of a thermodynamic system remain characteristics of the considered system. For each particular macroscopic piece of matter some functional connections between the state parameters can always be established. Such relations are called ***equations of state*** in Thermodynamics.

Only general properties of these equations can be inferred from the fundamental Laws of Thermodynamics. A small part of the equations of state can be established from arguments of theoretical Statistical Physics. This can be done only for quite simple systems. The value of theoretically established equations of state resides mainly in modeling and discussing more complicated situations. Nevertheless, most of the equations of state to be used in Thermodynamics are **experimental results**.

8.1 Caloric and thermal equations of state

It is usual to distinguish two types of equations of state, upon the experimental procedure for establishing them. Thus any thermodynamic system should have one ***caloric equation of state***, that is a relation of the form:

$$U = U(T, V, \nu) \tag{8.1}$$

whose construction needs *caloric* determinations (i.e. internal energy measurements by means of a calorimeter). Also, there should be one or several ***thermal equations of state***, that is relations of the form:

$$P = P(T, V, \nu) \tag{8.2}$$

which may be obtained through mechanical and temperature measurements only. The equations of the type:

$$\mu = \mu(T, V, \nu) \tag{8.3}$$

are usually included in the last category.

Sometimes it may become useful to solve Eq. (8.2) for the volume (and for the other configuration parameters too) and to replace it in Eqs. (8.1) and (8.3)

$$U = U(T,P,v), \tag{8.1'}$$

$$V = V(T,P,v) \tag{8.2'}$$

$$\mu = \mu(T,P,v). \tag{8.3'}$$

Strictly speaking, these new relations *do not represent equations of state*. Nevertheless, they contain the same amount of information and will be treated on equal foot with the true equations of state thereafter.

The caloric and thermal equations of state of a thermodynamic system contain all the information connected to the considered thermodynamic system. Nevertheless, as will be further demonstrated, the Laws of Thermodynamics induce a certain amount of redundancy in this information, which means that the equations of state are not strictly independent.

8.2 Functional relations between the equations of state of a thermodynamic system [1]

Actually these (quite numerous) relations are consequences of the fundamental Laws of Thermodynamics. For example take Eq. (6.6) written for a simple one-component system:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dv. \tag{8.4}$$

If one replaces the internal energy, the pressure and the chemical potential by the corresponding equations of state, then, by The Second Law, the obtained differential form should be still integrable (in the new variables, *T*, *V* and *v*):

$$dS = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,v} dT + \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T,v} + P\right]dV + \frac{1}{T}\left[\left(\frac{\partial U}{\partial v}\right)_{V,T} - \mu\right]dv. \tag{8.5}$$

The integrability of the form in (8.5) readily implies the following identities:

$$\frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T,v} + P\right]\right\} = \frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,v}\right], \tag{8.6}$$

$$\frac{\partial}{\partial v}\left\{\frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_{T,v} + P\right]\right\} = \frac{\partial}{\partial V}\left\{\frac{1}{T}\left[\left(\frac{\partial U}{\partial v}\right)_{V,T} - \mu\right]\right\} \tag{8.7}$$

and

$$\frac{\partial}{\partial v}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_{V,v}\right] = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\left(\frac{\partial U}{\partial v}\right)_{V,T} - \mu\right]\right\}. \tag{8.8}$$

Since the caloric equation of state (8.1) is supposed to be represented by a doubly differentiable function, one may write:

$$\frac{\partial^2 U}{\partial T\,\partial V}=\frac{\partial^2 U}{\partial V\,\partial T}. \tag{8.9}$$

Thus, from Eq. (8.6), it follows that:

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{T,\nu}=T\left(\frac{\partial P}{\partial T}\right)_{V,\nu}-P}. \tag{8.10}$$

Two other identities may be similarly obtained through Eqs. (8.7) and (8.8), respectively:

$$\boxed{\left(\frac{\partial \mu}{\partial V}\right)_{\nu,T}=-\left(\frac{\partial P}{\partial \nu}\right)_{V,T}}, \tag{8.11}$$

$$\boxed{\left(\frac{\partial U}{\partial \nu}\right)_{V,T}=\mu-T\left(\frac{\partial \mu}{\partial T}\right)_{V,\nu}}. \tag{8.12}$$

The identities (8.10)-(8.12) demonstrate the functional connections between the equations of state (8.1)-(8.3) and the redundancy of the thermodynamic information contained therein. There is some practical importance of this kind of relations: they allow the theoretical construction of some hardly measurable functions (like $\left(\frac{\partial U}{\partial V}\right)_{T,\nu}$) through the determination of other quantities.

By using equations of the form (8.1')-(8.3') one may obtain other functional connections of the same type as (8.10)-(8.12). Passing to the new variables *T*, *P* and *ν*, the fundamental relation (8.4) reads:

$$\begin{aligned} dS=&\frac{1}{T}\left[\left(\frac{\partial U}{\partial T}\right)_{P,\nu}+P\left(\frac{\partial V}{\partial T}\right)_{P,\nu}\right]dT+\frac{1}{T}\left[\left(\frac{\partial U}{\partial P}\right)_{T,\nu}+P\left(\frac{\partial V}{\partial P}\right)_{T,\nu}\right]dP+\\ &+\frac{1}{T}\left[\left(\frac{\partial U}{\partial \nu}\right)_{P,T}+P\left(\frac{\partial V}{\partial \nu}\right)_{P,T}-\mu\right]d\nu \end{aligned}. \tag{8.13}$$

The integrability conditions of Eq. (8.13) applied to the coefficients of *dP* and *dT* give (through the same arguments which produced Eq. (8.10)):

$$\left(\frac{\partial U}{\partial P}\right)_{T,\nu}=-T\left(\frac{\partial V}{\partial T}\right)_{P,\nu}-P\left(\frac{\partial V}{\partial P}\right)_{T,\nu}. \tag{8.14}$$

Another from of Eq. (8.14) can be obtain through the use of the general relation (4.33). Thus, one may write:

$$\left(\frac{\partial U}{\partial P}\right)_{T,\nu} = \left(\frac{\partial U}{\partial V}\right)_{T,\nu} \left(\frac{\partial V}{\partial P}\right)_{T,\nu}, \tag{8.15}$$

which, by Eq. (8.10), gives:

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_{T,\nu} = \left[T\left(\frac{\partial P}{\partial T}\right)_{V,\nu} - P\right]\left(\frac{\partial V}{\partial P}\right)_{T,\nu}}. \tag{8.16}$$

We shall not go further in obtaining such relations among the equations of state. In practice, the most important are Eqs. (8.10)-(8.12) and (8.16). The other ones are quite numerous and we find more useful to retain only the general deduction method for them.

8.3 Examples of equations of state for thermodynamic systems

a) Ideal (perfect) classical gas

This is the thermodynamic system consisting in a collection of identical independent molecules. They are supposed to interact only with the walls of the recipient through instantaneous collisions. The total mass of the system is taken as constant. This is the simplest possible model and the corresponding equations of state are supposed to be known to the reader:

$$U = \nu C_V T, \tag{8.17}$$

$$P = \frac{\nu R T}{V} \quad ; \quad R = 8{,}314 \frac{J}{mole \cdot K}. \tag{8.18}$$

C_V, the molar heat capacity of the gas (see the next chapters), is a parameter depending on the structure of the gas molecules.

For an ideal mixture of several perfect gases (that is a mixture whose components do not chemically interact) the equations of state become:

$$U = (\nu_1 C_{V1} + \nu_2 C_{V2} + \nu_3 C_{V3} \ldots) T, \tag{8.19}$$

$$P = \frac{\nu R T}{V} \quad ; \quad \nu = \nu_1 + \nu_2 + \nu_3 + \ldots \tag{8.20}$$

These last relations are direct consequences of the fundamental idea of a perfect gas: the molecules behave in the recipient without any reciprocal interaction and the total internal energy of the mixture should be the sum of the internal energies of the components). By similar arguments, the same addition property may be transferred to the partial pressures of the gas components.

b) The virial expansion [1, 2]

A thermal equation of state for a fluid with interactions among the molecules is known under this name. It is essentially represented by a series expansion of the fluid pressure upon the powers of the fluid density, *v*/*V*. The thermal equation of state for a perfect gas may actually be taken as a particular case of the virial expansion. In order to make a suitable comparison with this limit case, the factor *vRT*/*V* is forced out in front of this expansion:

$$P = \frac{vRT}{V}\left[1 + \frac{v}{V}B(T) + \left(\frac{v}{V}\right)^2 C(T) + \ldots\right]. \tag{8.21}$$

where $B(T)$, $C(T)$, … are the second, the third, … virial coefficients, respectively. They are independent of the mass and of the volume of the fluid. The virial coefficients depend only on the fluid temperature and on its internal structure and may be computed through statistical mechanical considerations, starting from a suitable model of reciprocal interaction between molecules. By comparing such results with available experimental data, evaluations of the values of the intermolecular forces become possible. For a classical ideal gas (see Eq. (8.18)) we'll obviously have $B = 0$ and $C = 0$ and the density appears only to the first degree in the virial expansion (see Eq. (8.20)). For high-density gases one may retain the second term of the parenthesis of Eq. (8.21) and write:

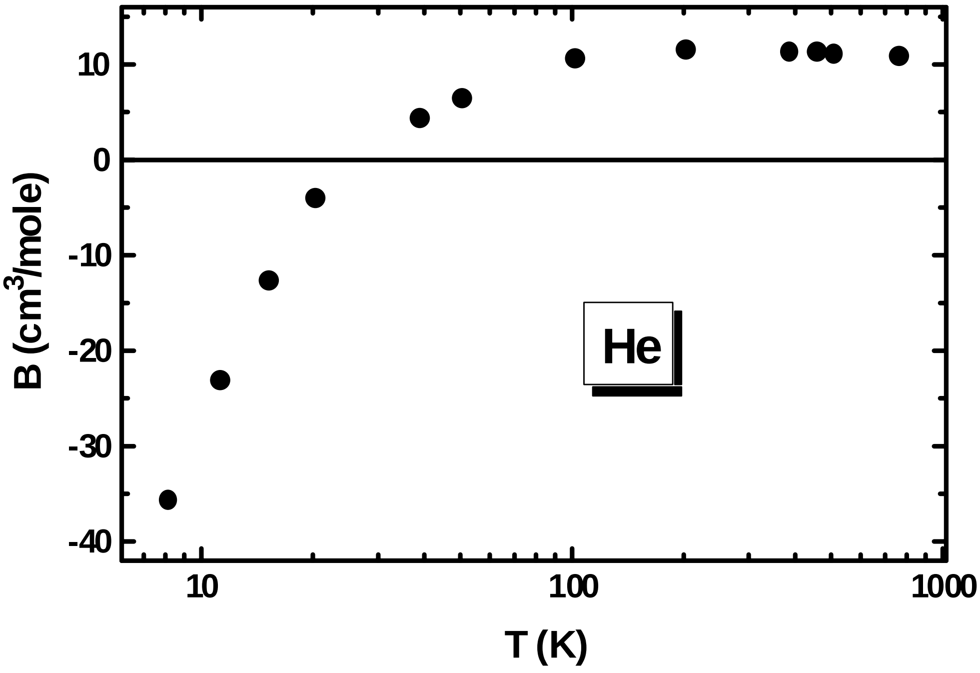

Figure 8.1

$$P = \frac{\nu R T}{V}\left[1 + \frac{\nu}{V} B(T)\right]. \tag{8.22}$$

At low temperatures the attractive (negative) potential energy between the molecules overcomes their (positive) kinetic energy. The total energy of a molecule will therefore be negative and its motion will be performed under the action of a global attraction towards the "interior" of the gas. Consequently, the gas pressure on the surrounding walls will decrease below the perfect gas case by a certain amount resulting from the dominant reciprocal attraction between the molecules. So, at low temperatures, $B(T)$ has to be negative.

On the contrary, by heating up the gas, the average kinetic energy should overcome the potential energy and each molecule becomes repealed from the "interior" of the gas. The pressure on the walls will therefore increase to values above the perfect gas case and $B(T)$ becomes positive. These qualitative previsions are actually experimentally confirmed, as can be seen in the example of Figure 8.1 [3] where the measured values of the second virial coefficient of gaseous He are plotted as a function of temperature.

c) *The thermal equation of state in the Van der Waals gas model*

The main form of this equation of state is the following:

$$\left(P + a\frac{\nu^2}{V^2}\right)(V - \nu b) = \nu R T . \tag{8.23}$$

The purpose of the model is to correct the ideal gas thermal equation for the errors that may arise both when neglecting the intermolecular forces and when considering the molecules as volume-less points, that is when neglecting their own volume. Indeed, at usual distances between the molecules of a (even dense) gas, the forces are mainly attractive. The gas pressure on the walls, P, should thus be lower than the pressure in the "interior" of the gas by a certain amount ΔP. On the other hand, the "inside" pressure is the one that should enter the perfect gas equation. One may conclude that the desired correction for the intermolecular forces should consist in replacing P in the thermal equation of a perfect gas by $P + \Delta P$. The correction ΔP should be proportional to the intensity of the intermolecular interactions, that is to the average number of possible interactions per unit volume of the gas. Given the total number of molecules of the gas, N, the number of distinct molecular couples that may be formed in a unit volume is essentially proportional to the squared molecular concentration N/V. We may thus write:

$$\Delta P = \tilde{a}\left(\frac{N}{V}\right)^2 = a\left(\frac{\nu}{V}\right)^2 , \tag{8.24}$$

where $\tilde{a}$ and a are positive constants depending on the nature of the gas molecules and of their reciprocal interactions.

The correction concerning the volume occupied by each molecule at rest, the so-called ***molecular volume***, should imply a decrease of the total volume (V) of the vessel. Thus, if the total molecular volume of the N molecules is ΔV, then the recipient volume available for free motion remains $V - \Delta V$. It is quite clear that the molecular volume ΔV should be proportional to the total number of molecules or, equivalently, to the number of moles of the gas: $\Delta V = b\nu$.

By performing these corrections in the perfect gas equation of state (8.20), one immediately gets the Van der Waals equation (8.23). This equation is in fact another particular case of the virial expansion. Indeed, by solving Eq. (8.23) with respect to the pressure, for low densities ($b\nu/V << 1$), one obtains:

$$P = \frac{\nu R T}{V}\left[\frac{1}{1-b\frac{\nu}{V}} - \frac{a}{RT}\frac{\nu}{V}\right] \cong \frac{\nu R T}{V}\left[1+\frac{\nu}{V}\left(b-\frac{a}{RT}\right)\right]. \tag{8.25}$$

Eq. (8.25) is identical to (8.22) if one takes:

$$B(T) = b - \frac{a}{RT},\ C(T) = 0, \dots\ . \tag{8.26}$$

One may also observe that B is negative for low temperatures ($T < \frac{a}{bR}$) and that it becomes positive when the temperature increases ($T > \frac{a}{bR}$). So, even if $B(T)$ of Eq. (8.26) shows no (slight) maximum value as is observed in the experimental curve of Figure 8.1, the Van der Waals equation of state may still be used as a good approximation for a gas at intermediate densities. This equation has also the very important advantage of analytical simplicity which allows the use the Van der Waals model as a test case for various statistical mechanical theories.

d) The thermal equation of state for a solid

The essential characteristic of a solid is its very weak compressibility and thermal expansivity. If one takes a reference volume V_1 for the considered piece of solid and if V is the volume resulting from a small temperature variation ($|T - T_1|/T_1 << 1$) and from a small pressure variation ($|P - P_1|/P_1 << 1$) then one may write the corresponding variation of the function $V(T,P)$ as a double power series expansion:

$$V - V_1 = \left(\frac{\partial V}{\partial T}\right)_P \bigg|_{(P_1,T_1)} \times (T - T_1) + \left(\frac{\partial V}{\partial P}\right)_T \bigg|_{(P_1,T_1)} \times (P - P_1) + \dots . \tag{8.27}$$

As it will be seen in the next chapters, there are specific notations for the volume derivatives with respect to the temperature and pressure:

$$\left(\frac{\partial V}{\partial T}\right)_P = V\alpha_P \quad ; \quad \left(\frac{\partial V}{\partial P}\right)_T = -V K_T , \tag{8.28}$$

where α_P and K_T are the ***isobaric dilatation*** and the ***isothermal compressibility*** of the system, respectively. By limiting the expansion (8.27) to the first degree terms only and by gathering the constant terms in a unique constant V_0:

$$V_0 = V_1 - \left(\frac{\partial V}{\partial T}\right)_P \bigg|_{(P_1,T_1)} \times T_1 - \left(\frac{\partial V}{\partial P}\right)_T \bigg|_{(P_1,T_1)} \times P_1 , \tag{8.29}$$

one obtains the desired equation:

$$V = V_0 \left(1 + \alpha_P T - K_T P\right). \tag{8.30}$$

In a good approximation, the parameters α_P and K_T may be treated as constants. In order to have an order of magnitude of the errors that may arise from the preceding approximations, the following data for silver may be of use:

$$Ag : \left| \begin{array}{l} K_T \cong 10^{-10} \dfrac{m^2}{N} = 10^{-5} \left(atm\right)^{-1} \\ \alpha_P \cong 10^{-4}\, K^{-1} \end{array} \right. .$$

Bibliography

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[2] W. Greiner, L. Neise, and H. Stöcker, *Thermodynamics and Statistical Mechanics*, Springer-Verlag, 1987.

[3] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, New York, 1954.

Exercises

8.1 A constant amount of gas satisfies the equation of state $PV = f(T)$ and also the relation $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Show that $f(T)$ is proportional to the absolute temperature. How would $f(T)$ be related to the absolute temperature if $\left(\frac{\partial U}{\partial V}\right)_T = b\,P$, where b is a constant?

Hint/Answer: Use Eq. (8.10): $T\left(\frac{\partial P}{\partial T}\right)_{V,\nu} - P = bP \Leftrightarrow \frac{T}{V} f'(T) = (b+1)\frac{f(T)}{V}$. It follows that $\frac{f'(T)}{f(T)} = (b+1)\frac{1}{T} \Leftrightarrow f(T) = constant \times T^{b+1}$. If $b = 0$ the function f reduces to the first power of the absolute temperature.

8.2 An ideal gas of constant mass satisfies the equation $\left(\frac{\partial U}{\partial V}\right)_T = 0$, corresponding to the postulate of the kinetic theory of gases that there are no forces between the molecules, and thus the internal energy of a gas does not vary with the intermolecular distance. Derive the most general equation of state of a material satisfying this condition.

Hint/Answer: Use Eq. (8.10): $T\left(\frac{\partial P}{\partial T}\right)_{V,\nu} - P = 0$. At constant volume, this is equivalent to $\frac{dP}{P} = \frac{dT}{T}$, which leads to the following general form of the equation of state: $P = T\,f(V)$ or $V = F\left(\frac{P}{T}\right)$, where f and F are arbitrary functions of their arguments. Besides the ideal gas, other materials that satisfy this kind of equation are magnetic substances obeying Curie's law.

8.3 Derive an expression for $\left(\frac{\partial U}{\partial P}\right)_T$ and show that it is negative for a van der Waals gas.

Hint/Answer: Use Eq. (8.16): $\left(\frac{\partial U}{\partial P}\right)_{T,\nu} = \left[T\left(\frac{\partial P}{\partial T}\right)_{V,\nu} - P\right] \Big/ \left(\frac{\partial P}{\partial V}\right)_{T,\nu}$ for the van der Waals equation of state $P = \frac{\nu RT}{V - \nu b} - a\frac{\nu^2}{V^2}$ (see Eq. (8.24)). One gets: $\left(\frac{\partial P}{\partial T}\right)_{V,\nu} = \frac{\nu R}{V - \nu b}$ and $\left(\frac{\partial P}{\partial V}\right)_{T,\nu} = -\frac{\nu RT}{(V-\nu b)^2} - 2a\frac{\nu^2}{V^3}$, so that $\left(\frac{\partial U}{\partial P}\right)_{T,\nu} = -\frac{\nu a}{RT}\frac{1}{2\frac{a\nu}{VRT} + \left(\frac{V}{V-\nu b}\right)^2} \cong -\frac{\nu a}{RT} < 0$.

9. Response functions of thermodynamic systems

9.1 Definitions [1]

The response functions of a thermodynamic system are the measures of the variations of the state quantities (such as internal energy, volume, pressure etc.) during the controlled variation of one or several parameters of the considered system. Depending on the particular conditions, the response may be through the mechanical, thermal or chemical channel.

In fact, the response functions are the only experimentally accessible quantities and thus represent the only way of constructing the state equations of a certain system from experiments. Specific designations exist for the response functions upon the specific channel to which they refer. Thus, we have mechanical response functions (like compressibilities) and thermal response functions (latent heats or heat capacities). As it will soon become clear, various functional relations allow the determination of the response functions through the chemical channel from other types of response functions. For this reason, the chemical response of a system do not wear any specific name.

a) The responses through the thermal channel

The corresponding response functions are the **heat capacities** (also termed sometimes as **thermal capacities**) and the **latent heats**.

The heat capacities of a thermodynamic system are the measures of the necessary energy exchanges through the thermal channel in order to reversibly modify the system's temperature by one unit in some specified external conditions:

$$\boxed{C_{conditions} \equiv (\delta Q)_{conditions} : dT}. \tag{9.1}$$

The heat capacity of one mole of substance is termed as the ***molar heat capacity*** and the heat capacity of the unit of mass is called ***specific heat***.

The latent heats measure the necessary amount of energy to be exchanged through the thermal channel of a thermodynamic system in order to reversibly modify one of its state parameters (except for the temperature) by one unit, when the temperature is fixed and possibly when some other external conditions are specified:

$$\boxed{\Lambda_X \equiv (\delta Q)_{T,other\ conditions} : dX}, \tag{9.2}$$

where X is the state parameter to be modified.

In a way similar with that for the heat capacities, one may define either the ***molar latent heats*** or the ***specific latent heats***, as the latent heats of one mole or one unit of mass of the given substance is considered, respectively.

Note: The response functions refer strictly to some ***reversible changes*** in the thermodynamic systems. In order to compute the response functions through the thermal channel, one should express the energy ***exchanged reversibly*** through this channel, δQ. This may be done either by The First Law, which gives the response functions as combinations of derivatives of the internal energy or by The Second Law for ***reversible infinitesimal processes*** ($\delta Q = TdS$), wherefrom the response functions become derivatives of the entropy.

b) The responses through the mechanical channel

The mechanical response functions measure ***the reversible relative variations of the system's volume through temperature or pressure variations, by placing the system in some specified conditions***. The responses to the pressure variations are called ***compressibilities*** ($K_{conditions}$) and the responses to the temperature variations are termed as ***thermal expansivities*** ($\alpha_{conditions}$). They are also known as ***coefficients***, for the compressibility and thermal expansion, respectively. Upon the conditions of measurement, one may distinguish isothermal, adiabatic, etc. compressibilities, or isobaric, adiabatic, etc. expansivities. The formal definitions are as follows:

$$\boxed{K_{conditions} \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{conditions}}, \tag{9.3}$$

$$\boxed{\alpha_{conditions} \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{conditions}}. \tag{9.4}$$

c) The response of the pressure to temperature variations

These kinds of responses are also considered of mechanical type, even if the volume may be sometimes kept constant:

$$\boxed{\beta_{conditions} \equiv \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_{conditions}}. \tag{9.5}$$

Note: It is tacitly supposed in the definitions (9.1) - (9.5) that, under the generic term "*conditions*", the ***mass invariability*** of the system is always included (even if almost never explicitly stated).

9.2 Expressing the thermal response functions through The First Law of Thermodynamics

Only the most common response functions will be treated in what follows. We will begin with the ***constant volume and constant pressure heat capacities*** for a simple thermodynamic system (more precisely for simple fluids):

$$C_V = (\delta Q)_V : dT = (dU + PdV)_V : dT = (dU)_V : dT \,,$$

since, at constant volume, $dV = 0$. We will thus have:

$$C_V = \left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV\right]_V : dT = \left[\left(\frac{\partial U}{\partial T}\right)_V dT\right]_V : dT \,,$$

that is:

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}. \tag{9.6}$$

In a similar way, one may write:

$$C_P = (\delta Q)_P : dT = \left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV\right]_P : dT \,.$$

At this point, the term $\left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)$ may be replaced with $T\left(\frac{\partial P}{\partial T}\right)_V$ by using Eq. (8.10). The volume variation dV can be expressed as a combination of pressure and temperature variations:

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \,.$$

Thus, one gets:

$$C_P = \left\{\left[\left(\frac{\partial U}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P\right] dT + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T dP\right\}_P : dT \,,$$

wherefrom:

$$\boxed{C_P = \left(\frac{\partial U}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}. \tag{9.7}$$

Eq. (9.6) was used in obtaining the preceding result.

Now, let us consider the ***latent heats for the volume and pressure variation***. By definition, we have:

$$\Lambda_V = (\delta Q)_T : dV = \left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right) dV\right]_T : dV = \left(\frac{\partial U}{\partial V}\right)_T + P .$$

By using again Eq. (810) one finally obtains:

$$\boxed{\Lambda_V = T\left(\frac{\partial P}{\partial T}\right)_V} . \tag{9.8}$$

Similarly we have:

$$\Lambda_P = (\delta Q)_T : dP = \left\{\left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT + \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP\right\}_T : dP ,$$

that is:

$$\boxed{\Lambda_P = \left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T} . \tag{9.9}$$

9.3 Expressing the thermal response functions through The Second Law of Thermodynamics (as entropy derivatives) [2]

Such expressions have a particular importance in studying phase equilibria and phase transitions. Starting again from the definitions and from the differential form of The Second Law, one readily gets:

$$C_V \equiv (\delta Q)_V : dT = (T\, dS)_V : dT = \left[T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV\right]_V : dT ,$$

which gives:

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V} . \tag{9.10}$$

Then we may also write:

$$C_P \equiv (\delta Q)_P : dT = (T\, dS)_P : dT = \left[T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP\right]_P : dT ,$$

which gives:

$$\boxed{C_P = T\left(\frac{\partial S}{\partial T}\right)_P} . \tag{9.11}$$

In a very similar way, one may obtain for the latent heats the following expressions:

$$\boxed{\Lambda_V = T\left(\frac{\partial S}{\partial V}\right)_T} \tag{9.12}$$

and

$$\boxed{\Lambda_P = T\left(\frac{\partial S}{\partial P}\right)_T}. \tag{9.13}$$

9.4 Relations between the response functions [1, 2]

- Let us first obtain an important relation between the mechanical response functions. To this purpose, remember the already proven identity (Eq. (4.30)):

$$\left(\frac{\partial x}{\partial y}\right)_{z,f}\left(\frac{\partial y}{\partial z}\right)_{x,f}\left(\frac{\partial z}{\partial x}\right)_{y,f} = -1,$$

for three parameters x, y and z implicitly dependent through $f(x,y,z) = 0$. Such a functional dependence may be a thermal equation of state in the form $f(P,V,T) = 0$. In such a case we obtain:

$$\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T = -1. \tag{9.14}$$

By further using the definitions (9.3) - (9.5), Eq. (9.14) may be readily transformed into:

$$\boxed{\alpha_P = P\,\beta_V\,K_T}. \tag{9.15}$$

Eq. (9.15) could be used further to recast Eq. (9.7) into the form:

$$\boxed{C_P - C_V = \frac{T\,V\,\alpha_P^2}{K_T}}, \tag{9.16}$$

which represents a kind of ***generalization of the Robert-Mayer relation*** from the perfect gas thermodynamics. As C_V is quite difficult to measure (one should keep a *constant volume* during the system's heating, which is much more difficult than maintaining a constant pressure, for example), Eq. (9.16) is particularly important in practice: It is generally easier to measure C_P, α_P and K_T and then compute C_V from Eq. (9.16).

- Another important consequence follows from the inequality $K_T \geq 0$, which is itself a consequence of the assumed stability of the equilibrium state of the considered thermodynamic system (see the related discussion in Chapter 13). Thus, Eq. (9.16) implies:

$$\boxed{C_P \geq C_V}. \tag{917}$$

The equality holds in (9.17) when $\alpha_P = 0$ or $K_T = \infty$. If $\alpha_P = 0$, then $\left(\frac{\partial V}{\partial T}\right)_P = 0$ and the function (of the temperature only) $V(T,P = constant)$ passes through a local extremum. This is, for example, the case of an amount of pure water at 4 ^{0}C and normal pressure, whose volume passes through a minimum. The other possibility, namely $\left(\frac{\partial P}{\partial V}\right)_T = 0$, may appear near the critical point of a fluid, where the isotherm has generally a zero-slope inflection point.

- One may also compute Λ_V by using some easy-measurable mechanical response functions. From Eqs. (9.8) and (9.5) the following form of Λ_V may be obtained:

$$\boxed{\Lambda_V = \frac{T\alpha_P}{K_T}}. \tag{9.18}$$

- For Λ_P one has to start from Eq. (9.9) to obtain:

$$\Lambda_P = \left(\frac{\partial U}{\partial P}\right)_T - P V K_T . \tag{9.19}$$

Further one needs the expression of $\left(\frac{\partial U}{\partial P}\right)_T$, which may be obtained from Eqs. (8.16) and (9.15) as:

$$\left(\frac{\partial U}{\partial P}\right)_{T,\nu} = \left[T\left(\frac{\partial P}{\partial T}\right)_{V,\nu} - P\right]\left(\frac{\partial V}{\partial P}\right)_{T,\nu} = P V K_T - T V \alpha_P . \tag{9.20}$$

Thus, Eq. (9.19) becomes:

$$\boxed{\Lambda_P = -T V \alpha_P = -V K_T \Lambda_V}. \tag{9.21}$$

- We terminate this section with another thermodynamic relation, which bears both theoretical and practical importance. This is essentially a relation between the isothermal (K_T) and adiabatic (K_S) compressibilities. We shall thus proceed by computing the adiabatic compressibility:

$$K_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S . \tag{9.22}$$

The adiabatic conditions imply that $\delta Q = 0$ during the compression processes (and constant mass, as stressed in a previous note):

$$(dU + P dV)_S = 0 . \tag{9.23}$$

By using a caloric state equation as a function of pressure and volume, $U(P,V)$, one obtains:

$$\left\{\left(\frac{\partial U}{\partial P}\right)_V dP+\left[\left(\frac{\partial U}{\partial V}\right)_P+P\right]dV\right\}_S=0\,. \tag{9.24}$$

The adiabatic conditions impose a supplementary condition that allows, for example, the volume to depend only on the pressure, upon eliminating the temperature from the thermal equation of state $V = V(P,T)$. Thus, in adiabatic conditions we have $V = V(P)$ only and Eq. (9.24) may be written as:

$$\left\{\left(\frac{\partial U}{\partial P}\right)_V+\left[\left(\frac{\partial U}{\partial V}\right)_P+P\right]\left(\frac{\partial V}{\partial P}\right)_S\right\}dP=\left\{\left(\frac{\partial U}{\partial P}\right)_V-\left[\left(\frac{\partial U}{\partial V}\right)_P+P\right]V\,K_S\right\}dP=0\,. \tag{9.25}$$

Therefore, one gets:

$$K_S=\frac{1}{V}\frac{\left(\frac{\partial U}{\partial P}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_P+P}\,. \tag{9.26}$$

In order to compute $\left(\frac{\partial U}{\partial V}\right)_P$ and $\left(\frac{\partial U}{\partial P}\right)_V$ one may write the differential of the caloric state equation as a function of P and V and then as a function of T and V:

$$dU=\left(\frac{\partial U}{\partial P}\right)_V dP+\left(\frac{\partial U}{\partial V}\right)_P dV=\left(\frac{\partial U}{\partial P}\right)_V\left(\frac{\partial P}{\partial T}\right)_V dT+\left[\left(\frac{\partial U}{\partial V}\right)_P+\left(\frac{\partial U}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\right]dV\,.$$

On the other hand, by using the variables T and V straight from the beginning, one may write:

$$dU=\left(\frac{\partial U}{\partial T}\right)_V dT+\left(\frac{\partial U}{\partial V}\right)_T dV\,.$$

So, by comparing the two forms of dU, one obtains:

$$\left(\frac{\partial U}{\partial T}\right)_V=\left(\frac{\partial U}{\partial P}\right)_V\left(\frac{\partial P}{\partial T}\right)_V \tag{9.27}$$

and

$$\left(\frac{\partial U}{\partial V}\right)_T=\left(\frac{\partial U}{\partial V}\right)_P+\left(\frac{\partial U}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T\,. \tag{9.28}$$

Eq. (9.27) may also be obtained as a direct consequence of the theorem on the implicit partial differentiation. The use of Eqs. (9.5), (9.6) and (9.15) allows Eq. (9.27) to be transformed as follows:

$$\left(\frac{\partial U}{\partial P}\right)_V = \frac{C_V}{P\beta_V} = \frac{K_T C_V}{\alpha_P}. \tag{9.29}$$

Similarly, by using Eqs. (8.10), (9.29) and (9.3) in Eq. (9.28), one obtains:

$$\left(\frac{\partial U}{\partial V}\right)_P = \frac{T\alpha_P}{K_T} + \frac{C_V}{V\alpha_P} - P. \tag{9.30}$$

By replacing Eqs. (9.29) and (9.30) in Eq. (9.26), one may then conclude that:

$$K_S = K_T \frac{\dfrac{K_T C_V}{V\alpha_P}}{T\alpha_P + \dfrac{K_T C_V}{V\alpha_P}}. \tag{9.31}$$

This last relation can be further transformed through the use of Eq. (9.16), which finally gives:

$$\boxed{\frac{K_S}{K_T} = \frac{C_V}{C_P}}. \tag{9.32}$$

By taking into account the inequality (9.17), Eq. (9.32) leads to the conclusion that the isothermal compressibility is always greater or equal to the adiabatic compressibility:

$$\boxed{K_T \geq K_S}. \tag{9.33}$$

In practice processes of adiabatic compression of fluids arise mostly in fast local density variations appearing, for example, during the propagation of sound waves through such media. The compression/depression processes are then so rapid that the energy exchange through the thermal channel has never enough time to proceed. Thus the inequality (9.33) actually expresses in a formal way a widely known experimental observation that the reaction of a fluid is more intense when the external pressure is applied faster. Moreover, Eq. (9.33) implies (if one takes into account the definition (9.3)) that:

$$\left|\left(\frac{\partial V}{\partial P}\right)_T\right| \geq \left|\left(\frac{\partial V}{\partial P}\right)_S\right| \Rightarrow \left|\left(\frac{\partial P}{\partial V}\right)_T\right| \leq \left|\left(\frac{\partial P}{\partial V}\right)_S\right|, \tag{9.34}$$

which means that, ***in a same (V, P) representation, the absolute value of the slope of an isotherm is always smaller than the absolute value of the slope of an adiabatic process that passes through the same state*** (point of the (*V*,*P*) plane). Needless to say that both processes must be reversible in order to have a plot of each one in the set of equilibrium states of the system.

9.5 The construction of state equations starting from the measured response functions

In order to keep the presentation as simple as possible, we shall still consider constant mass systems. To deal with more complicated (variable-mass) situations, one may use relations of the type (8.11) or (8.12).

We should always take into account that measurements of C_P, α_P and K_T can be usually achieved in simple convenient experimental setups. The differentials of the equations of state should therefore be normally expressed in terms of such easy-available response functions. Take, for example, the form $U(T,V)$ of the caloric equation of state. By using Eqs. (9.6) and (8.10) one gets:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = C_V dT + \left(T P \beta_V - P\right) dV .$$

Then, by help of Eqs. (9.14) and (9.16), one may finally write:

$$dU = \left(C_P - \frac{T V \alpha_P^2}{K_T}\right) dT + \left(\frac{T \alpha_P}{K_T} - P\right) dV . \tag{9.35}$$

The form $U(T,P)$ of the caloric equation of state can be treated in a similar way. To this purpose, note first that $\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_P V \alpha_P$ and take $\left(\frac{\partial U}{\partial V}\right)_P$ from Eq. (9.30). Then use Eq. (9.20) to express $\left(\frac{\partial U}{\partial P}\right)_T$. One readily obtains:

$$dU = \left(C_P - P V \alpha_P\right) dT + \left(P V K_T - T V \alpha_P\right) dP . \tag{9.36}$$

As for the thermal equations of state, one gets (through the use of Eqs. (9.3), (9.4) and (9.15)):

$$dP = \frac{\alpha_P}{K_T} dT - \frac{1}{V K_T} dV , \tag{9.37}$$

or

$$dV = V \alpha_P dT - V K_T dP . \tag{9.38}$$

The coefficients of the coupled equations (9.35), (9.37) and (9.36), (9.38) may be measured as functions of (T, V) and (T, P), respectively. The corresponding differentials may be then integrated, analytically or numerically, to obtain the desired equations of state: $U(T,V)$, $P(T,V)$, $U(T,P)$, $V(T,P)$.

For the beginner student, this procedure is possibly best exemplified by the simple case of the ideal classical gas model. Measurements on low-density gases show that, in a wide range of temperatures, the following equations hold:

$$C_P = constant \quad ; \quad \alpha_P = \frac{1}{T} \quad ; \quad K_T = \frac{1}{P}. \tag{9.39}$$

It thus follows that:

$$dU(T,V) = \left(C_P - \frac{PV}{T} \right) dT + (P - P)\, dV = \left(C_P - \frac{PV}{T} \right) dT, \tag{9.40}$$

$$dP(T,V) = P\frac{dT}{T} - P\frac{dV}{V} \tag{9.41}$$

and

$$C_P - C_V = \frac{PV}{T}. \tag{9.42}$$

Using Eq. (9.42) in (9.40), we obtain:

$$dU(T,V) = C_V\, dT \tag{9.43}$$

By integrating Eqs. (9.41) and (9.43), one readily gets:

$$\frac{PV}{T} = constant \equiv \nu R \tag{9.44}$$

and

$$U(T,V) = C_V\, T. \tag{9.45}$$

The integration constant of Eq. (9.44) has to be proportional to the mass of the system, a fact which follows from Eq. (9.42) by remembering that the "C" quantities are heat capacities and behave as extensive parameters. R is known as ***the ideal gas constant*** ($R = 8{,}3145\ J{\cdot}K^{-1}{\cdot}mol^{-1}$).

Finally, using the result of (9.44), Eq. (9.42) gives the well-known Robert-Mayer relation:

$$C_P - C_V = R. \tag{9.46}$$

Bibliography

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Exercises

9.1 A certain solid obeys the equation of state $V = V_0 - A{\cdot}P + B{\cdot}T$ and its internal energy is $U = C{\cdot}T - B{\cdot}P{\cdot}T + A{\cdot}P^2/2$, where A, B, C are constants. Find its heat capacities C_V and C_P.

Hint/Answer: Express the internal energy in terms of volume and temperature. Then: $C_V = \left(\frac{\partial U}{\partial T}\right)_V = C - B \cdot P + \left(A \cdot P - B \cdot T\right) \cdot \left(\frac{\partial P}{\partial T}\right)_V$. From the thermal equation of state one gets: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{B}{A}$, so that $C_V = C - \frac{B^2}{A} \cdot T$. For C_P, Eq. (916) gives: $C_P = C_V + \frac{T V \alpha_P^2}{K_T}$, where $\alpha_P = B/V$ and $K_T = A/V$, according to the definitions (9.3) and (9.4). Thus, $C_P = C$.

9.2 A monatomic ideal gas at *T*, *P*, *V* and constant mass is heated to temperature $T + dT$ under conditions such that the change of pressure, *dP* is related to the change of volume *dV* by $dP = a{\cdot}P{\cdot}dV/V$, where *a* is a constant, positive, zero, negative or infinite. Determine the molar heat capacity as a function of *a* for heating under these conditions.

Hint/Answer: As the mass is constant, $\delta Q = \nu C dT = dU + PdV$. One may thus write: $\nu C dT = 3\nu R dT/2 + PdV$. From the equation of state of the ideal gas $\nu dT = \frac{1}{R}\left(PdV + VdP\right) = \frac{a+1}{R} PdV \Rightarrow PdV = \frac{R}{a+1}\nu dT$. It then follows that $C = \left(\frac{3}{2} + \frac{1}{a+1}\right)R = \frac{3a+5}{2(a+1)}R$. *C* is infinite for $a = -1$ (isothermal process). $C = 3R/2$ for $a = \infty$ (constant volume). $C = 2$ for $a = 1$ (pressure proportional to volume). $C = 5R/2$ for $a = -1$ (constant pressure). $C = 0$ for $a = -5/3$ (adiabatic process).

9.3 The isobaric expansivity and the isothermal compressibility of a constant mass of a certain gas, within a limited range of pressures and temperatures, are $\alpha_P = \frac{nR}{PV}$; $K_T = \frac{1}{P} + \frac{a}{V}$, where *n*, *R* and *a* are constants. Find the equation of state valid within in these conditions.

Hint/Answer: From the data $\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$. Integrating $V = \frac{nRT}{P} + f(P)$, where *f*(*P*) is a function of pressure only. Also $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{V}{P} - a \Leftrightarrow f'(P) = -\frac{f(P)}{P} - a$ (at constant temperature) $\Leftrightarrow \left(P f(P)\right)' = -a P \Leftrightarrow f(P) = -\frac{1}{2} a P + \frac{constant}{P}$. It follows that $PV = nRT - \frac{1}{2} a P^2 + constant$. Since at very low pressures the gas should obey the ideal equation of state, the constant should be zero. Thus one may write: $PV = nRT - \frac{1}{2} a P^2$.

9.4 A constant mass of a hypothetical substance has the following isobaric expansivity and the isothermal compressibility: $\alpha_P = \frac{3aT^3}{V}$; $K_T = \frac{b}{V}$. Find the equation of state.

Hint/Answer: From $\left(\frac{\partial V}{\partial T}\right)_P = 3aT^3$ it readily follows that $V = \frac{3}{4}aT^4 + f(P)$, where $f(P)$ is a function of pressure only. From $\left(\frac{\partial V}{\partial P}\right)_T = -b$ one obtains $f'(P) = -b \quad \Leftrightarrow \quad f(P) = -bP + V_0$, where V_0 is a constant. Thus $V = \frac{3}{4}aT^4 - bP + V_0$.

9.5 Calculate the molar heat capacity C_V for mercury at 0^0C given that $C_P = 28.01$ J/(mole·deg), $\alpha_P = 1.81\times10^{-4}$ deg^{-1}, $K_T = 3.88\times10^{-11}$ m^2/N, $V = 14.72$ cm^3/mole.
Hint/Answer: Use Eq. (9.16). $C_V = 24.62$ J/(mole·deg).

9.6 Calculate C_P - C_V for a van der Waals gas.
Hint/Answer: Use Eqs. (8.23) and (9.7). For one mole of a van der Waals gas one readily obtains $C_P - C_V = R + \frac{2a}{VT}$.

9.7 Find a relation between the adiabatic and the isobaric expansion coefficients.
Hint/Answer: For constant mass, Eq. (9.23) holds. By using the temperature and the volume as independent variables, Eq. (9.23) can be transformed in the following relation $\left[\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\left(\frac{\partial U}{\partial V}\right)_T + P\right)dV\right]_S = 0$. Alternatively, by using Eqs. (9.6) and (8.10), one gets $C_V + TP\beta_V\left(\frac{\partial V}{\partial T}\right)_S = 0$. Thus $\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S = -C_V\frac{K_T}{TV\alpha_P} = -\alpha_P\frac{C_V}{C_P - C_V}$, where use was made of Eq. (9.16). Finally, by denoting $\frac{C_P}{C_V} \equiv \gamma$, one obtains $\boxed{\frac{\alpha_S}{\alpha_P} = -\frac{1}{\gamma - 1}}$.

9.8 A gas obeys the molar equation of state $P\cdot(V - b) = RT$ and its molar heat capacity C_V is $5R/2$. Find the ratio $\gamma = C_P/C_V$. It is proposed to generate sound waves in the gas at 300 K and a pressure of 100 atm. The pressure amplitude of the sound waves is to be 1 atm. Calculate the amplitudes of the dilation ($\Delta V/V$) and of the temperature variation in the sound wave, assuming that $b = 120$ cm^3/mole and $R = 8.3145$ J/(deg · mole).

Hint/Answer: $\frac{C_P}{C_V} = 1 + \frac{1}{C_V}\frac{T V \alpha_P^2}{K_T} = 1 - \frac{2}{5}\frac{T}{R}\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 = 1 + \frac{2}{5}\frac{T}{R}\frac{RT}{(V-b)^2}\left(\frac{R}{P}\right)^2 = \frac{7}{5}$. The local compressions and dilations in the sound wave are essentially adiabatic processes, so that $\frac{\Delta V}{\Delta P} \cong \left(\frac{\partial V}{\partial P}\right)_S = -V K_S = -\frac{V}{\gamma}K_T = \frac{1}{\gamma}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{\gamma}\frac{RT}{P^2}$. Also we have $V = \frac{RT + bP}{P}$, so that $\frac{\Delta V}{V} = -\frac{1}{\gamma}\frac{RT}{P(RT + bP)} = 0.00484$. Moreover, $\frac{\Delta T}{\Delta P} \cong \left(\frac{\partial T}{\partial P}\right)_S$ and $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial P}\right)_S$. Thus $\frac{\Delta T}{\Delta P} \cong -\frac{1}{\gamma}\frac{RT}{P^2}\frac{1}{V\alpha_S} = \frac{\gamma - 1}{\gamma}\frac{RT}{P^2}\frac{1}{V\alpha_P} = \frac{\gamma-1}{\gamma}\frac{RT}{P^2}\left(\frac{\partial T}{\partial V}\right)_P = \frac{\gamma-1}{\gamma}\frac{T}{P}$, if one takes into account the result of the preceding problem. Therefore $\Delta T = \frac{\gamma - 1}{\gamma}T\frac{\Delta P}{P} = 0.857$ K.

9.9 The pressure on 200 g of water is increased reversibly and isothermally from 0 to 3000 atm at 0^0C. (a) How much heat is transferred? (b) How much work is done? (c) What is the change in internal energy of the water? (Expansion coefficient of water at 0^0C, $\alpha_P = -67\times10^{-6}$ deg^{-1}; isothermal compressibility, $K_T = 43\times10^{-11}$ m^2/N).

Hint/Answer: Since the process is reversible and isothermal, from the definition of K_T, one gets $(dV)_T = -K_T V\, dP$, so that, for zero initial pressure, $V(P) = V_0 e^{-K_T P}$, where $V_0 = 2\times10^{-4}$ m^3 is the initial volume of the probe. (a) The heat exchanged isothermally in a small reversible compression may be given by (see Eqs. (9.2) and (9.21)) $(\delta Q)_T = \Lambda_P dP = -T\alpha_P V\, dP = -T\alpha_P V_0\, e^{-K_T P} dP$. It follows that the total heat exchange amounts $(Q)_T = -T\alpha_P V_0 \int\limits_0^{P_{max}} e^{-K_T P} dP = -\frac{T\alpha_P V_0}{K_T}\left(1 - e^{-K_T P_{max}}\right) =$ 1043 J. (b) The work done to infinitesimally compress the probe is given by $(\delta W)_T = -P(dV)_T = K_T P V(P) dP$. Therefore, the total compression work will be $(W)_T = K_T V_0 \int\limits_0^{P_{max}} e^{-K_T P} P\, dP = \frac{V_0}{K_T}\left[1 - \left(1 + K_T P_{max}\right)e^{-K_T P_{max}}\right] =$ 3642 J. (c) The variation of the internal energy of the probe during the process will then be $\Delta U = (Q)_T + (W)_T = 5085$ J.

10. Some general consequences of The Laws of Thermodynamics

10.1 The Euler relation

In the previous chapters it was repeatedly pointed out that the mass-dependence of thermodynamic quantities may behave in one of two ways: ***extensive*** or ***intensive***. It was stressed, for example, in the statements of The First and The Second Laws of Thermodynamics, that the internal energy and the entropy are typical extensive state parameters. On the contrary, the temperature always behaves as an intensive quantity. Up to now, this distinction made no particular importance. Nevertheless, it turns out that several important conclusions can be drawn therefrom.

First note that, in the following part of the presentation, the ***volume*** of a system will be always referred to as an ***extensive parameter***. Also, since an extensive parameter is proportional to the amount of substance existing in the system, it will be considered that ***any ratio of extensive quantities is an intensive parameter of the system***. This statement should be obviously extended to the derivatives of extensive parameters with respect to extensive variables. For example the density ($\rho = \frac{m}{V}$), the pressure ($P = -\left(\frac{\partial U}{\partial V}\right)_{S,\nu}$) and the chemical potential ($\mu = \left(\frac{\partial U}{\partial \nu}\right)_{S,V}$) are clearly intensive parameters.

Let us now concentrate on the consequences of the extensivity of the entropy. The form (6.6) of the fundamental equation of thermodynamics, when written for **a one-component system**, simplifies to:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}d\nu . \tag{10.1}$$

This can be looked at as a differential of the entropy when expressed as a function of the extensive parameters U, V and ν:

$$S = S(U,V,\nu). \tag{10.2}$$

The extensivity of the entropy means that, given two weakly interacting thermodynamic systems that are in thermal equilibrium, the entropy of their thermodynamic reunion is the sum of their individual entropies. More formally, by assigning the indexes 1 and 2 for the two systems, their entropies are:

$$S_1 = S(U_1,V_1,\nu_1), \tag{10.3}$$

and

$$S_2 = S(U_2,V_2,\nu_2) \tag{10.4}$$

and the entropy of their thermodynamic reunion can be written as:

$$S = S(U_1 + U_2, V_1 + V_2, v_1 + v_2) = S(U_1, V_1, v_1) + S(U_2, V_2, v_2). \tag{10.5}$$

If the two systems were identical, then we could write:

$$S(2U, 2V, 2v) = 2S(U, V, v).$$

Moreover, if *n* is a natural number and if one applies the previous argument for *n* identical copies of a given thermodynamic system, then we must have:

$$S(nU, nV, nv) = nS(U, V, v). \tag{10.6}$$

The change of notation $U_1 \to U$, $V_1 \to V$, $v_1 \to v$ allows Eq. (10.5) to be transformed in:

$$S(U - U_1, V - V_1, v - v_1) = S(U, V, v) - S(U_{1^{`}}, V_1, v_1). \tag{10.7}$$

When the size, the mass and the internal energy of a system simultaneously become smaller and smaller it is expected that the thermodynamic system behave more and more as a purely mechanical one. Its entropy should therefore tend to zero. Thus, by taking simultaneously the limits $U \to 0$, $V \to 0$ and $v \to 0$ in Eq. (10.7), one should obtain:

$$S(-U_1, -V_1, -v_1) = -S(U_{1^{`}}, V_1, v_1),$$

or, if we change again the notation $U_1 \to U$, $V_1 \to V$, $v_1 \to v$:

$$S(-U, -V, -v) = -S(U, V, v). \tag{10.8}$$

The results of Eqs. (10.6) and (10.8) may now be joined into the following:

$$S(zU, zV, zv) = zS(U, V, v), \tag{10.9}$$

where ***z* is any integer**. Then, for $z \neq 0$, the change of notation $zU \to U$, $zV \to V$, $zv \to v$ gives:

$$S\left(\frac{1}{z}U, \frac{1}{z}V, \frac{1}{z}v\right) = \frac{1}{z}S(U, V, v). \tag{10.10}$$

By further combining Eq. (10.9) with (10.10), one may write:

$$S(qU, qV, qv) = qS(U, V, v), \tag{10.11}$$

for **any rational number *q***.

Consider now a certain real number λ. It is known that λ can always be expressed as the limit of a sequence of rational numbers q_n: $\lim_{n \to \infty} q_n = \lambda$. Eq. (10.11) can be applied for any term of this sequence:

$$S(q_n U, q_n V, q_n v) = q_n S(U, V, v).$$

Since the entropy is a differentiable function of all its arguments (see the general statement of The Second Law), it follows that it is also continuous and that the previous relation holds also for the limit of the sequence q_n. Thus we may conclude that, **for any real number λ**, one may write:

$$\boxed{S(\lambda U, \lambda V, \lambda \nu) = \lambda S(U, V, \nu) \quad (\lambda \in \mathbf{R})}. \tag{10.12}$$

From the mathematical point of view, the property (10.12) is termed as ***first order homogeneity***. Stated generally, a function $f(x,y,z, \ldots)$ is termed as homogeneous of the n-th order if, for any real λ, one may write:

$$f(\lambda x . \lambda y, \lambda z, \ldots) = \lambda^n f(x, y . z, \ldots). \tag{10.13}$$

It is thus obvious that any intensive parameter of a thermodynamic system should be a ***homogeneous function of order zero***, when expressed in terms of ***extensive quantities*** of the system. Take for example a form of the caloric equation of state of the system: $T(U,V,\nu)$. For two weakly interacting systems in thermal equilibrium, one may write:

$$T(U_1 + U_2, V_1 + V_2, \nu_1 + \nu_2) = T(U_1, V_1, \nu_1) = T(U_2, V_2, \nu_2), \tag{10.14}$$

wherefrom an argument similar to the one that conducted to Eq. (10.12) gives:

$$\boxed{T(\lambda U, \lambda V, \lambda \nu) = \lambda^0 T(U, V, \nu) = T(U, V, \nu) \quad (\lambda \in \mathbf{R})}. \tag{10.15}$$

The differentiation of Eq. (10.13) with respect to λ leads to:

$$x \frac{\partial f}{\partial(\lambda x)} + y \frac{\partial f}{\partial(\lambda y)} + z \frac{\partial f}{\partial(\lambda z)} + \ldots = n \lambda^{n-1} f(x, y . z, \ldots),$$

for any real number λ. Then, for $\lambda = 1$ the preceding relation becomes:

$$x \frac{\partial f}{\partial x} + y \frac{\partial f}{\partial y} + z \frac{\partial f}{\partial z} + \ldots = n f(x, y . z, \ldots), \tag{10.14}$$

which in the theory of functions is known as ***Euler's identity*** for differentiable n-th order homogeneous functions [1, 2].

By applying this identity to the case of entropy (for which $n = 1$), one readily obtains:

$$U \left(\frac{\partial S}{\partial U} \right)_{V,\nu} + V \left(\frac{\partial S}{\partial V} \right)_{U,\nu} + \nu \left(\frac{\partial S}{\partial \nu} \right)_{U,V} = S .$$

This relation can be further transformed if Eq. (10.1) is taken into account to replace the partial derivatives:

$$\left(\frac{\partial S}{\partial U} \right)_{V,\nu} = \frac{1}{T} \quad ; \quad \left(\frac{\partial S}{\partial V} \right)_{U,\nu} = \frac{P}{T} \quad ; \quad \left(\frac{\partial S}{\partial \nu} \right)_{U,V} = -\frac{\mu}{T} .$$

Euler's identity takes then the following final thermodynamic form:

$$\boxed{T\,S = U + PV - \mu\,\nu}. \qquad (10.15)$$

10.2 The Gibbs – Duheim equation [1]

The fundamental relation (10.1) can be written as follows:

$$T\,dS = dU + P\,dV - \mu\,d\nu\,. \qquad (10.16)$$

On the other hand, by taking the differential of Euler's relation (10.15) one gets:

$$T\,dS + S\,dT = dU + P\,dV + V\,dP - \mu\,d\nu - \nu\,d\mu\,. \qquad (10.17)$$

From the combination of Eq. (10.16) and Eq. (10.17) the following equation results:

$$\boxed{\nu\,d\mu + S\,dT - V\,dP = 0}. \qquad (10.18)$$

This is the ***Gibbs – Duheim equation*** for simple one-component systems. Denoting by s and υ the molar entropy and molar volume, respectively ($s = S/\nu$, $\upsilon = V/\nu$), one may also write:

$$\boxed{d\mu = \upsilon\,dP - s\,dT}. \qquad (10.19)$$

As illustrated by the following examples, Eq. (10.19) is particularly useful in computing the chemical potential of simple thermodynamic one-component systems starting from the usual equations of state (8.1) and (8.2) or, more precisely, from (8.1') and (8.2'). The chemical potential results as a function of pressure and temperature through an integration procedure and obviously depends on some integration constant (for which a suitable choice has to be done). Thus, ***Eq. (10.19) essentially allows one to obtain, for a simple system, the thermal equation of state of the chemical potential, based on the caloric and other different thermal equations of state***. Nevertheless, for systems containing several chemical components, the Gibbs-Duheim equation is no more useful for computing individual chemical potentials. This is pretty obvious from the fact that the first term in Eq. (10.18) is replaced by $\sum_i \nu_i d\mu_i$ for a multi-component system.

We may also note in passing that Eq. (10.19) implicitly contains the ***typical intensive behavior of the chemical potential*** (since neither the molar volume nor the molar entropy depend on the amount of substance contained in the system).

10.3 The chemical potential of an ideal gas of photons

When an electromagnetic field is induced in a limited volume, the boundary conditions normally select a discrete set of modes that may indefinitely persist into the specified volume. In a similar way sound waves of discrete frequencies are selected by a resonant cavity, from a general oscillatory input: the specified frequencies are actually amplified and the other sound waves are dumped. A general mathematical trick allows the equivalence of the system of electromagnetic modes of the external field to an ideal gas of pseudo-particles called ***photons***. The term "**ideal**" for the photon gas means that one should completely neglect the interactions between individual particles. For example, such a situation appears typically in the case of the infrared radiation generated by the walls of a closed oven.

The equivalence of the electromagnetic field trapped in the cavity with the photon gas means that the macroscopic properties of the electromagnetic field are identical with those that can be deduced for the photon gas, taken as a thermodynamic system. Caloric and thermal equations of state can thus be deduced for the photon gas, which allows it to be treated in the frame of Thermodynamics. The caloric equation of state is known as the ***Stefan-Boltzmann law***:

$$U = \sigma V T^4 , \tag{10.20}$$

where σ is a universal constant. One of the thermal equations of state is represented by the temperature dependence of the light pressure:

$$P = \frac{1}{3}\sigma T^4 . \tag{10.21}$$

The problem is to build up the other equation of state, the one which connects the chemical potential of the system to the other state parameters. To solve it we shall use Eq. (10.19), but first let's express the entropy of the photon gas through Eqs. (10.15), (10.20) and (10.21):

$$s = \frac{U}{vT} + \frac{P}{T}\upsilon - \frac{\mu}{T} = \sigma \upsilon T^3 + \frac{1}{3}\sigma \upsilon T^3 - \frac{\mu}{T} = \frac{4}{3}\sigma \upsilon T^3 - \frac{\mu}{T} . \tag{10.22}$$

Then, by Eq. (10.21), we get:

$$\upsilon\, dP = \frac{4}{3}\sigma \upsilon T^3 dT$$

and Eq. (10.19) takes the form:

$$d\mu = \frac{\mu}{T} dT .$$

This equation is equivalent to the following:

$$\frac{1}{\mu} d\mu = \frac{1}{T} dT ,$$

which can be readily integrated to:

$$ln\frac{\mu}{\mu_0} = ln\frac{T}{T_0},$$

where μ_0 and T_0 are constants necessary to fix the units under the logarithms. It thus follows that:

$$\frac{\mu}{T} = \frac{\mu_0}{T_0} = constant. \tag{10.23}$$

At this point we should remember one of the consequences of The Third Law, namely Eq. (6.17):

$$\lim_{T \to 0} \frac{\mu}{T} = 0, \tag{10.24}$$

wherefrom the integration constant of Eq. (10.23) has to be zero. Thus, one should actually have $\frac{\mu}{T} = 0$ and it may be concluded that the chemical potential of an ideal gas of photons in thermodynamic equilibrium vanishes:

$$\mu = 0. \tag{10.25}$$

10.4 The chemical potential of a classical ideal gas [1]

The previous example obviously deals with a system whose intimate dynamics is strictly of quantum type. Let's solve now the same problem for another ideal gas, whose molecules behave upon the classical dynamical laws: the classical ideal gas. The same method can be used to obtain the corresponding chemical potential.

The following equations of state of the classical ideal gas are well known:

$$U = \nu C_V T \tag{10.26}$$

and

$$P = \frac{\nu R T}{V}. \tag{10.27}$$

Therefore, Euler's relation (10.15) reads:

$$S = \frac{1}{T}\left(U + PV - \mu \nu\right) \tag{10.28}$$

and the Gibbs-Duheim equation (10.18) takes the form:

$$\left(U + PV - \mu \nu\right)\frac{dT}{T} = V\,dP - \nu\,d\mu. \tag{10.29}$$

By replacing U from (10.26) and V from (10.27) we may write:

$$\left(C_V + R - \frac{\mu}{T}\right) dT = RT\frac{dP}{P} - d\mu . \tag{10.30}$$

If use is made of the Robert-Mayer relation (9.47) Eq. (10.30) can be re-ordered in the following form:

$$\frac{d\mu}{T} - \mu\frac{dT}{T^2} = -C_P\frac{dT}{T} + R\frac{dP}{P} . \tag{10.31}$$

In the right hand side of Eq. (10.31) it may be recognized the differential of μ/T, so that the integration of the both sides gives:

$$\boxed{\frac{\mu}{T} = -C_P \, ln\frac{T}{T_0} + R \, ln\frac{P}{P_0} - s_0 + C_P} . \tag{10.32}$$

The reason for denoting the integration constant by $C_P - s_0$ will become clear in the next section. T_0 and P_0 are constants necessary to fix the units under the logarithms.

10.5 The entropy of a classical ideal gas

Let's come back to the general relation of Eq. (10.28) for the entropy. We can use here Eqs. (10.26) and (10.27) to obtain for a classical ideal gas:

$$S = \nu\left(C_V + R - \frac{\mu}{T}\right) = -\nu\left(\frac{\mu}{T} - C_P\right) . \tag{10.33}$$

By further making use of Eq. (10.32) one readily gets:

$$\boxed{S(P,T) = \nu\left(C_P \, ln\frac{T}{T_0} - R \, ln\frac{P}{P_0} + s_0\right)} . \tag{10.34}$$

The significance of the integration constant s_0 in Eq. (10.32) becomes now clear: it represents the molar entropy of the gas in some reference state.

We also observe in passing that the perfect gas model is not always of practical use. Indeed, to the limit $T \to 0$, the Third Law gives $S \to 0$ for all thermodynamic systems. However, in an obvious contradiction, Eq. (10.34) gives $S \to -\infty$ when $T \to 0$. One may therefore expect that gases at low temperatures will not obey the ideal gas model represented by the equations of state (10.26) and (10.27). Nevertheless, this model may be safely used at relatively high temperatures only (around the room temperature of 300 K).

The molar entropy is frequently used in thermodynamic computations due to its mass independence:

$$\boxed{s(P,T) = C_P \ln\frac{T}{T_0} - R\ln\frac{P}{P_0} + s_0}. \tag{10.35}$$

Sometimes the entropy as a function of the temperature and of the (molar) volume may be needed. This can be readily obtained if the gas pressure is replaced from Eq. (10.27) into Eq. (10.35):

$$\boxed{s(\upsilon,T) = C_V \ln\frac{T}{T_0} + R\ln\frac{\upsilon}{\upsilon_0} + s_0}, \tag{10.36}$$

where

$$\upsilon_0 = \frac{R T_0}{P_0}. \tag{10.37}$$

Bibliography

[1] L. E. Reichl, *A Modern Course in Statistical Physics*, Edward Arnold (Publishers) Ltd., 1980.

[2] H. Callen, *Thermodynamics*, John Wiley & Sons, Inc., 1960.

Exercises

10.1 Find the chemical potential for the model of solid described by the equations of state given in Exercise 9.1.

Hint/Answer: The given equations of state are $V = V_0 - A\cdot P + B\cdot T$ and $U = C\cdot T - B\cdot P\cdot T + A\cdot P^2/2$. From the form (10.28) of the Euler's relation, the entropy readily follows: $S(T,P,\nu) = C + \frac{P V_0}{T} - \frac{A P^2}{2T} - \frac{\mu \nu}{T}$. Thus, with some simple algebra, Eq. (10.18) becomes $\nu\, d\left(\frac{\mu}{T}\right) = -C\frac{dT}{T} + d\left(\frac{P V_0}{T}\right) - d\left(\frac{A P^2}{2T}\right) + d(B P)$ and $\nu \mu = -C T \ln\frac{T}{T_0} + P V_0 - \frac{A P^2}{2} + B P T$.

11. Characteristic functions

11.1 The general extremum method of Equilibrium Thermodynamics

The main problem of Equilibrium Thermodynamics is finding the equations of state of a particular thermodynamic system (at least the most significant ones). As was already pointed out, the experimental method is most widely used to accomplish this task. Nevertheless, Statistical Physics brought in another method for obtaining equations of state: certain thermodynamic state quantities, termed as ***characteristic functions***, may first be computed through various statistical averaging procedures; the equations of state are then obtained as suitable derivatives of such functions.

The most important characteristic functions will be defined in this chapter and the fact that they contain the complete thermodynamic information on the particular system to which they belong will be demonstrated.

It is now an established fact that The Second Law of Thermodynamics states an essential connection between the entropy variation and the energy exchange (***through the thermal channel only!***) of a thermodynamic system (see Eq. (6.1)):

$$\Delta S = S_f - S_i \geq \int\limits_{(process)}^{i \to f} \frac{1}{T} \delta Q \,. \tag{11.1}$$

Besides this simple connection, Eq. (11.1) shows that ***the entropy of a thermodynamic system can be modified not only through the energy exchange between the system and its environment***. The energy exchange with the environment induces a partial variation of the entropy, $(\Delta S)^{ext} \equiv \int\limits_{(process)}^{i \to f} \frac{1}{T} \delta Q$, which is generally smaller than the total one ΔS. Thus, The Second Law implies that ***a non-negative internal entropy production always occurs in natural processes***: $\Delta S = (\Delta S)^{int} + (\Delta S)^{ext}\,;\quad (\Delta S)^{int} \geq 0$.

We must stress here ***that neither $(\Delta S)^{int}$, nor $(\Delta S)^{ext}$ represent variations of state parameters***: they generally depend on the process connecting the initial and final equilibrium states of the system. Also, while $(\Delta S)^{int}$ always takes non-negative values, ***$(\Delta S)^{ext}$ may be negative*** and may therefore compensate the internal entropy production. A system may thus experience irreversible processes during which its entropy decreases. ***A non-adiabatic enclosure of a certain system may also allow for isentropic processes ($\Delta S = 0$)***, if suitable amounts of heat is allowed to leak out in the environment.

The $(\Delta S)^{ext}$-generating (inward or outward) energy transfer through the thermal channel may be conceived only by instantaneous interactions of the system with various thermostats. Thus, in

$(\Delta S)^{ext} = \int\limits_{(process)}^{i\to f} \frac{1}{T}\delta Q$, ***T represents the temperature of the thermostats with which the system instantaneously interacts during the chosen process***. Strictly speaking, this temperature may be assigned to the system only if the corresponding process is designed as a chain of equilibrium states, that is if it is reversible. The quantity δQ is the heat exchanged by the system during its instantaneous interaction with the thermostat of temperature T, irrespective of the type of process involved. The local form (3.11) of The First Law applied to such an infinitesimal process gives:

$$\delta Q = dU - \delta W - \delta M , \tag{11.2}$$

so that Eq. (11.1), written for an infinitesimal segment of the process, takes the form:

$$\boxed{dS \geq \frac{1}{T}dU - \frac{1}{T}\delta W - \frac{1}{T}\delta M}, \tag{11.3}$$

When specific constraints are imposed to the system, the inequality (11.3) may lead to extremum conditions for some state functions [1], usually called ***characteristic functions***. The procedure is the following: an equilibrium state of the thermodynamic system may be looked at as a final state of an infinitesimal process that takes place under the given constraints and to which the general inequality (11.3) may be applied. Together with a set of specified external constraints, this inequality leads to the necessity that some characteristic function takes a (locally) extreme value in the given equilibrium state of the system. The characteristic function usually depends on both external and internal state parameters. As the external parameters are fixed by the constraints, the usual analytical extremum conditions should be applied to the internal parameter dependence of the characteristic function. The values of the internal parameters suitable for the given equilibrium state of the system may be found therefrom and thus the equilibrium state may be completely characterized. This is the so-called ***general extremum method of Equilibrium Thermodynamics***. The characteristic functions that take maximum values at some constrained equilibrium state of the system are usually called ***Massieu functions***. When a characteristic function takes a minimum value at thermodynamic equilibrium, it is termed as a ***thermodynamic potential***, in analogy with Mechanics, where an equilibrium configuration may be obtained through the ***minimum*** condition for the potential energy.

11.2 Examples of typical constraints for thermodynamic systems

(a) System in a rigid impermeable enclosure and in thermal equilibrium with a thermostat

Since the system's enclosure is assumed impermeable, the total chemical work is forced to vanish, even if the different parts of the system may reciprocally exchange particles. The same applies for the rigid-enclosure constraint: the total mechanical work should vanish, while the different parts of the system may experience deformations through the reciprocal mechanical interactions during the process. Under such conditions, for any natural infinitesimal process, the inequality (11.3) becomes:

$$dU - T\,dS \le 0\,. \tag{11.4}$$

Since the system is always supposed in thermal equilibrium with the thermostat of temperature *T*, one may write:

$$d(U - T\,S) \le 0\,. \tag{11.5}$$

By defining

$$\boxed{U - T\,S = F}, \tag{11.6}$$

which is obviously a state quantity, one may imagine that a certain equilibrium state of the system is the result of some natural infinitesimal process during which the variation of *F* should be negative (see 11.5):

$$dF \le 0\,. \tag{11.7}$$

As a function of the ***internal*** parameters of the system, ***<u>the state quantity F should therefore take a minimum value in the considered equilibrium state</u>***. Thus, under the described constraints, the function *F* is a thermodynamic potential. It is usually called ***<u>free energy</u>*** (or ***<u>Helmholtz potential</u>***).

The same conditions allow Eq. (11.4) to be written in a different form:

$$d\left(S - \frac{U}{T}\right) \ge 0\,, \tag{11.8}$$

which introduces another ***<u>state quantity that is to be maximized at thermodynamic equilibrium</u>***. It is therefore a Massieu function (under the aforementioned conditions imposed to the system) known as ***<u>Planck's function</u>*** [2, 3]:

$$\boxed{\Phi = S - \frac{U}{T}}. \tag{11.9}$$

(b) **System in an impermeable enclosure, at constant pressure and entropy**

Such conditions usually refer to systems of fluids behaving in a constant environmental pressure *P*. The total mechanical work on the system can therefore be written as $\delta W = -P \cdot dV$. The impermeable enclosure still keeps a vanishing total chemical work and the isentropical conditions implies $dS = 0$. The general inequality (11.3) for an infinitesimal process that brings the system in the considered equilibrium state under the aforementioned constraints takes the following form:

$$dU + P\,dV \le 0\,. \tag{11.10}$$

Since the overall pressure is constant, one may write:

$$dU + d(PV) = d(U + PV) \le 0\,, \tag{11.11}$$

which can be interpreted as the minimum condition for the following state quantity

$$\boxed{H = U + PV} \tag{11.12}$$

called ***enthalpy***. Obviously this should be a thermodynamic potential under the specified constraints imposed to the system.

It worth to stress again that the isentropic conditions are not at all equivalent to an adiabatic enclosure of the system: the internal entropy production in the system can be always compensated by suitably discarding some heat to the environment. Moreover, for an isobaric process driven in an impermeable enclosure, The First Law gives:

$$\Delta U = Q - P\Delta V = Q - \Delta(PV) \quad \Rightarrow \quad Q = \Delta(U + PV) = \Delta H\,, \tag{11.13}$$

which means that, in these circumstances, the enthalpy is a measure of the heat exchanged by the system. This is the reason for which the enthalpy is also called ***thermal function*** or ***thermal content*** of the system.

(c) System in an impermeable enclosure, at constant pressure and temperature

The system is still considered as consisting of several fluids in thermodynamic equilibrium. Since the total mass is also kept constant, the general inequality (11.3) for a corresponding infinitesimal natural process becomes:

$$dS \ge \frac{1}{T}dU + \frac{1}{T}P\,dV\,. \tag{11.14}$$

By taking into account that the overall pressure is fixed by the interaction with the environment and that the system is in thermal equilibrium with a thermostat, the relation (11.14) may be written as:

$$d(U - TS + PV) \le 0\,,$$

which implies that the state quantity

$$\boxed{G = U - TS + PV} \tag{11.15}$$

should take a minimum value in the considered equilibrium state of the system. G is therefore a thermodynamic potential (under the considered constraints). It is called ***free enthalpy*** (or ***Gibbs potential***).

For a one-component fluid the Euler's relation (10.15) combined with the definition (11.15) gives

$$G = \mu \nu \ . \tag{11.16}$$

Eq. (11.16) offers a direct interpretation of the chemical potential of a one-component system as being the corresponding molar free enthalpy.

(d) System in an impermeable rigid enclosure, at constant entropy

For a natural infinitesimal process developing in such conditions the general relation (11.3) reduces to:

$$dU \le 0 \, . \tag{11.17}$$

This also means that ***the internal energy*** should take a minimum value (and should therefore be considered as a thermodynamic potential) in a certain equilibrium state under the aforementioned constraints imposed to the system.

Note: From the practical point of view the constraints of type (a) appear most frequently. The conditions of type (b) are fulfilled in chemical reactions when no phase changes occur. Conditions of type (c) are well accomplished by systems containing several phases in equilibrium. The constraints of type (d) occur seldom in usual experimental setups. They are mainly useful to discuss low-temperature phenomena.

Sometimes it may become useful to address a still tighter constraint:

(e) Isolated system

Besides $\delta W = \delta M = 0$, for such a system one obviously has $dU = 0$. Therefore, the inequality (11.3) becomes simply:

$$dS \ge 0 \, . \tag{11.18}$$

So, an equilibrium state of an isolated system should be characterized by a maximum of its entropy. ***Entropy*** is thus a Massieu function of a thermodynamic system in complete isolation.

The free energy, the enthalpy, the free enthalpy and the energy are by far the most useful characteristic functions in Thermodynamics. They are all thermodynamic potentials and refer to the most usual experimental situations. Nevertheless, there may be defined another thermodynamic potential that proves of essential importance in establishing the connection between the statistical and the thermodynamic point of view in Thermal Physics. This is the so-called grand potential.

(f) Thermodynamic system at constant volume, in thermal equilibrium with a thermostat and at fixed chemical potential

Such external conditions refer mainly to open systems, that is to systems exchanging particles with their environment. Since the chemical work vanishes no more and is given by $\delta M = \mu \cdot dv$ (generalizations for several components are straightforward), the inequality (11.3) for simple fluids becomes:

$$dU - \mu\, dv - T\, dS \leq -P\, dV \,. \tag{11.19}$$

By accounting for the imposed constraints the right hand side of (11.19) vanishes and $\mu \cdot dv = d(\mu \cdot v)$, $T \cdot dS = d(T \cdot S)$. Therefore, in an infinitesimal natural process occurring in such conditions, the relation (11.19) turns out to:

$$d\left(U - T\,S - \mu\,v\right) \leq 0 \,. \tag{11.20}$$

Thus, the state quantity

$$\boxed{\Omega = U - T\,S - \mu\,v} \,. \tag{11.21}$$

works as a thermodynamic potential in the aforementioned conditions (since it should take a minimum value in a thermodynamic equilibrium state of a system constrained to comply to them). Ω is usually termed as the ***grand potential*** of the thermodynamic system [3].

11.3 Natural variables of the characteristic functions and the equations of state

An implicit conclusion of the preceding section is the fact that the obtained state quantities can take extremal values in the specified constraints only if they are expressed as functions of suitable external variables. As it will become clear soon characteristic functions embed all the thermodynamic information about a certain system only when determined as functions of such specific sets of external variables (and of the specific internal parameters too). That is to say, in these particular representations, ***the characteristic functions are equivalent to the equations of state*** of the thermodynamic system under study. For this reason, the variables that turn a certain state quantity into a characteristic function are termed as ***natural variables*** for the given characteristic function.

(a) Take first the case of the ***free energy***. Its differential can be obtained from the fundamental equation (6.4):

$$\boxed{dU = T\,dS - P\,dV + \mu\,dv}. \tag{11.22}$$

By adding –*d*(*TS*) in both members one readily gets:

$$\boxed{d(U - T\,S) = dF = -S\,dT - P\,dV + \mu\,dv}. \tag{11.23}$$

It thus follows that, ***if F is given as a function of T, V and v***, then:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,v}, \tag{11.24}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,v} \tag{11.25}$$

and

$$\mu = \left(\frac{\partial F}{\partial v}\right)_{T,V}. \tag{11.26}$$

When *F*(*T*,*V*,*v*) is known the last two equations clearly represent the thermal equations of state of the given system. As for Eq. (11.24), it is actually equivalent to the caloric equation of state of the system. Indeed, by replacing it together with Eqs. (11.25) and (11.26) into Euler's relation

$$U = T\,S - PV + \mu\,v, \tag{11.27}$$

one readily obtains *U*(*T*,*V*,*v*):

$$U = -T\left(\frac{\partial F}{\partial T}\right)_{V,v} + V\left(\frac{\partial F}{\partial V}\right)_{T,v} + v\left(\frac{\partial F}{\partial v}\right)_{T,V}. \tag{11.28}$$

Thus, the knowledge of *F*(*T*,*V*,*v*) suffices to get all the information about the given system.

On the reverse, when the equations of state *P*(*T*,*V*,*v*) and *μ*(*T*,*V*,*v*) are known they may be replaced in Euler's relation (11.27) to give $U - T\,S = -V\,P(T,V,v) + v\,\mu(T,V,v) = F(T,V,v)$.

Note in passing that, since the equations of state are related by the Gibbs-Duheim equation [4] (so they are not independent), the construction of *F*(*T*,*V*,*v*) is possible with only two (thermal) equations of state.

We may thus conclude that ***T, V and v are the natural variables of the free energy***. The function *F*(*T*,*V*,*v*) contains ***all the thermodynamic information*** on the given system. Any other representation of the free energy (as a function of other variables) can provide only partial information on the system [4].

The same conclusion may be easily drawn for the ***Planck's function***. Using Eq. (11.22) one may easily compute $d\Phi$:

$$\boxed{d\left(S-\frac{U}{T}\right)=d\Phi=\frac{U}{T^2}dT+\frac{P}{T}dV-\frac{\mu}{T}dv}, \tag{11.29}$$

so that the following equations of state may be obtained, once the Planck's function (of T, V and v) is known for a given system:

$$U(T,V,\mu)=T^2\left(\frac{\partial\Phi}{\partial T}\right)_{V,v}, \tag{11.30}$$

$$P(T,V,\mu)=T\left(\frac{\partial\Phi}{\partial V}\right)_{T,v} \tag{11.31}$$

and

$$\mu(T,V,\mu)=-T\left(\frac{\partial\Phi}{\partial v}\right)_{T,V}. \tag{11.32}$$

(b) The differential form of the ***enthalpy*** may be similarly obtained from Eq. (11.22) by adding $d(PV)$ in both members:

$$\boxed{d(U+PV)=dH=T\,dS+V\,dP+\mu\,dv}. \tag{11.33}$$

Therefore, if H is known as a function of S, P and v then one could straightforwardly write:

$$T=\left(\frac{\partial H}{\partial S}\right)_{P,v}, \tag{11.34}$$

$$V=\left(\frac{\partial H}{\partial P}\right)_{S,v} \tag{11.35}$$

and

$$\mu=\left(\frac{\partial H}{\partial v}\right)_{S,P}. \tag{11.36}$$

If the function $H(S,P,v)$ is given for some specific system, then Eq. (11.34) can be solved for the entropy, as a function of T, P and v: $S(T,P,v)$. If this is replaced in Eqs. (11.35) and (11.36) they become the thermal equations of state of that system: $V(T,P,v)$ and $\mu(T,P,v)$. By further replacing $S(T,P,v)$, $V(T,P,v)$ and $\mu(T,P,v)$ into Euler's relation (11.27), the caloric equation of state of the system is obtained: $U(T,P,v)$. The function $H(S,P,v)$ contains therefore all the thermodynamic information on the given system.

Reciprocally, the knowledge of the equations of state $U(T,P,v)$, $V(T,P,v)$ and $\mu(T,P,v)$ allows their replacement in Euler's relation (11.27) to give the following equation: $U(T,P,v) = T\,S - PV(T,P,v) + v\,\mu(T,P,v)$. This could be solved (in principle) for the temperature to give $T(S,P,v)$. Then, by replacing $T(S,P,v)$ in $\mu(T,P,v)$, the function $\mu(S,P,v)$ may be constructed. Finally, the use of $T(S,P,v)$ and $\mu(S,P,v)$ in Eq. (11.27) leads to: $U + PV = S\,T(S,P,v) + v\,\mu(S,P,v) = H(S,P,v)$.

Consequently, ***S, P and v are the natural variables of the enthalpy***. Given as a function of any other variables, the enthalpy provides only partial information on the system [4].

(c) A similar discussion can be carried out for the ***Gibbs potential*** (***the free enthalpy***). Its differential form may be obtained from the fundamental equation (11.22) by adding $d(PV - TS)$ in both members:

$$\boxed{d(U + PV - T\,S) = dG = -S\,dT + V\,dP + \mu\,dv}. \tag{11.37}$$

Thus, if G is known as a function of T, P and v then one could readily obtain:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,v}, \tag{11.38}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,v} \tag{11.39}$$

and

$$\mu = \left(\frac{\partial G}{\partial v}\right)_{T,P}. \tag{11.40}$$

Knowing the function $G(T,P,v)$ for some thermodynamic system, the last two equations represent the corresponding thermal equations of state $V(T,P,v)$ and $\mu(T,P,v)$. Eq. (11.38) gives the entropy as a function of T, P and v, which in turn can be used (along with Eqs. (11.39) and (11.40)) in Euler's relation (11.27) to obtain the caloric equation of state $U(T,P,v)$.

Conversely, when only the equation of state $\mu(T,P,v)$ is given, the free enthalpy can be recovered from Euler's relation: $U + PV - T\,S = v\,\mu(T,P,v) = G(T,P,v)$.

In conclusion ***T, P and v are the natural variables of the free enthalpy***. The function $G(T,P,v)$ contains ***all the thermodynamic information*** on some particular system. Given as a function of any other variables, the Gibbs potential provides only partial information on the system [4].

(d) The differential form of the ***internal energy*** follows directly from the fundamental equation (11.22). Thus, once the function $U(S,V,v)$ is known for a particular system, its partial derivatives are equivalent to the equations of state of the system. Indeed, Eq. (11.22) readily implies:

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,v}, \tag{11.41}$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,v} \tag{11.42}$$

and

$$\mu = \left(\frac{\partial U}{\partial v}\right)_{S,V}. \tag{11.43}$$

Eq. (11.41) can be solved for the entropy to get $S(T,V,v)$. This, in turn, if replaced in Eqs. (11.42) and (11.43) allows obtaining the functions $P(T,V,v)$ and $\mu(T,V,v)$, which are the thermal equations of state of the given system. Then, by replacing $S(T,V,v)$, $P(T,V,v)$ and $\mu(T,V,v)$ in Euler's relation (11.27), the caloric equation readily follows: $U(T,V,v) = T\,S(T,V,v) - V\,P(T,V,v) + v\,\mu(T,V,v)$.

Conversely, when the equations of state $U(T,V,v)$, $P(T,V,v)$ and $\mu(T,V,v)$ are given for a particular system, their replacement in Euler's relation (11.27) leads to the equation: $S = U(T,V,v) + V\,P(T,V,v) - v\,\mu(T,V,v)$. This could be solved (in principle) for the temperature to give $T(S,V,v)$. Then, by replacing $T(S,V,v)$ in $P(T,V,v)$ and in $\mu(T,V,v)$, the functions $P(S,V,v)$ and $\mu(S,V,v)$ may be constructed. Finally, the use of $T(S,V,v)$, $P(S,V,v)$ and $\mu(S,V,v)$ in Eq. (11.27) leads to: $U(S,V,v) = S\,T(S,V,v) - V\,P(S,V,v) + v\,\mu(S,V,v)$.

Consequently, ***S, V and v are the natural variables of the internal energy*** as a thermodynamic potential. Given in this form, the internal energy encloses all the thermodynamic information on a particular system. When taken as a function of any other variables, the internal energy provides only partial information on the system [4] (for example, the function $U(T,V,v)$ represents only the caloric equation of state of the system).

(e) ***The entropy*** as a Massieu function can be dealt with in a similar manner as was done for the previously considered characteristic functions. Its differential form follows directly from the fundamental equation (11.22):

$$\boxed{dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}d\nu}, \tag{11.44}$$

wherefrom the following relations (equivalent to a complete set of equations of state) can be written:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,\nu}, \tag{11.45}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,\nu} \tag{11.46}$$

and

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial \nu}\right)_{U,V}. \tag{11.47}$$

The equivalence between the function $S(U,V,\nu)$, given for a particular system, and the corresponding equations of state will be skipped since it can be proven in a similar way as for the other characteristic functions. We content only to conclude that ***U, V and ν are the natural variables of the entropy*** as a Massieu function. Given in this form, the entropy encloses all the thermodynamic information on a particular system.

(f) Finally, let us discuss ***the grand potential Ω***. Its differential form can be deduced from the general relation (11.22) by subtracting $d(TS + \mu\nu)$ from both members:

$$\boxed{d(U - TS - \mu\nu) = d\Omega = -S\,dT - P\,dV - \nu\,d\mu}. \tag{11.48}$$

Therefore, if Ω is known as a function of T, V and μ then one could straightforwardly write:

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \tag{11.49}$$

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \tag{11.50}$$

and

$$\nu = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}. \tag{11.51}$$

The last three relations represent essentially the equations of state of a given system for which the function $\Omega(T,V,\mu)$ has been constructed. Indeed, Eq. (11.51) can (in principle) be inverted to obtain the thermal equation of state $\mu(T,V,\nu)$. When this is replaced in Eq. (11.50) the other thermal equation of state is produced: $P(T,V,\nu)$. Then, by using $\mu(T,V,\nu)$ in Eq. (11.49), the function $S(T,V,\nu)$ results, which, together with $P(T,V,\nu)$ and $\mu(T,V,\nu)$ may be replaced in Euler's relation (11.27) to obtain the caloric equation of state $U(T,V,\nu)$.

Conversely, when the equations of state $P(T,V,\nu)$ and $\mu(T,V,\nu)$ are given for a thermodynamic system, ν can be eliminated from them to obtain $P(T,V,\mu)$. Then, if use is made of the Euler's relation (11.27), one gets: $U - T\,S - \mu\,\nu = -V\,P(T,V,\mu) = \Omega(T,V,\mu)$.

Consequently ***T, V and μ are the natural variables of the grand potential***. The function $\Omega(T,V,\mu)$ contains ***all the thermodynamic information*** on the given system.

11.4 Mnemonic diagram

As pointed out before the most frequent practical situations are those in which the energy, the enthalpy, the free energy and the free enthalpy take minimum values. These situations, when appearing in problems, claim a rapid display of the natural variables and of the corresponding differential forms. The beginning student may find a useful help in minding the simple diagram of Figure 11.1, inspired from how things are going on in Mother Nature [5]: from the **Sun** (S) the light falls down upon the **trees** (T), while the rivers flow from the **peaks** (P) to the **valleys** (V). Every such phenomenon follows the unique (**clockwise**) sense of time. Starting from the first quadrant with the (internal) energy E (that is U) one should proceed in alphabetic order with the free energy (F), the Gibbs potential (G) and the enthalpy (H). Besides the number of moles each thermodynamic potential has as natural variables the state parameters whose symbols are closest in the diagram. The corresponding differential form will thus be a linear combination of the differentials of these closest state parameters. As for the coefficients, they may be found following the arrows: with plus sign if the way coincides with the sense of the arrow and with minus sign if

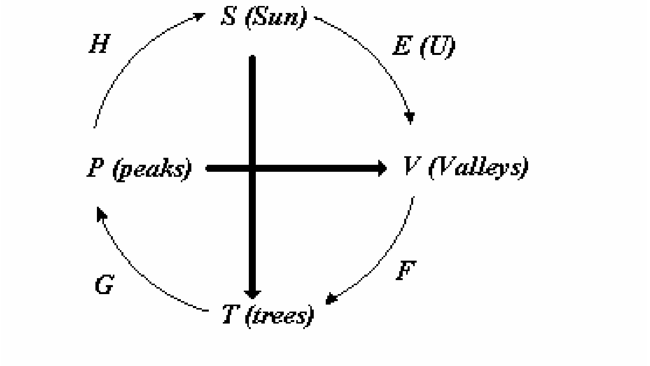

Figure 11.1

the coefficient is found in the opposite sense of the corresponding arrow.

Example: the differential form of the Gibbs potential should be a linear combination of dT and dP (the term μdv should be automatically added to the differential of any of the four characteristic functions). The coefficient of dP is found at the end of the arrow passing through P and it is $+V$ since one travels from P to V in the sense of the arrow. The coefficient of dT arise following the opposite sense of the arrow passing through T and it is therefore $-S$. Thus, the differential form of Eq. (11.37) may be readily recovered.

11.5 Simple applications of the extremum method: conditions for relative equilibrium

When the thermodynamic reunion of two weakly interacting systems gives a thermodynamic system in equilibrium one may also say that the two systems are in ***relative thermodynamic equilibrium***. A specific type of constraints may be defined for the reunion, which allow expressing the relative equilibrium state as the extremum of some characteristic function of the total system.

Consider, for example, the case of two amounts of fluid (for simplicity, *made of the same molecules*) that interact weakly through all the usual channels (thermal, mechanical and chemical), but whose thermodynamic reunion is a fixed-volume, fixed-temperature, system enclosed in an impermeable boundary. The free energy of the reunion should then show a local minimum in the considered equilibrium state. If U_1 and U_2 are the internal energies of the considered systems then the weak interaction ensures that the internal energy of the reunion equals the sum of the internal energies of the parts: $U = U_1 + U_2$. Moreover, the fixed temperature imposed to the system means that both its parts are in thermal equilibrium with a thermostat of some temperature T. So, the total entropy should be the sum of the entropies of the parts: $S = S_1 + S_2$. One may then write: $F = U_1 + U_2 - T\cdot(S_1 + S_2) = F_1 + F_2$, that is, ***for this case, the free energy is an additive quantity***. Since F (taken as a function of its natural variables and of the internal ones) is minimum in the considered thermodynamic state, the same should be true for the sum $F_1 + F_2$. Thus, the first variation (differential) of this sum around the considered state should vanish:

$$dF = dF_1 + dF_2 = -S\,dT - P_1 dV_1 - P_2 dV_2 + \mu_1 dv_1 + \mu_2 dv_2 = 0\,. \tag{11.52}$$

The parameters T, V_1, V_2, v_1 and v_2 are therefore ***internal variables*** of the reunion. Due to the imposed constraints they are not all independent. Thus, the fixed-volume condition reads: $V_1 + V_2 = V$ (fixed), while the impermeable closure ensures the constancy of the total mass: $v_1 + v_2 = v$ (fixed). These relations imply that $dV_2 = -dV_1$ and $dv_2 = -dv_1$. The fixed temperature implies $dT = 0$. Therefore Eq. (11.52) can be written in terms of the variations of the independent internal variables only:

$$dF = dF_1 + dF_2 = -(P_1 - P_2)dV_1 + (\mu_1 - \mu_2)d\nu_1 = 0 . \tag{11.53}$$

Consequently, the necessary minimum condition for the total free energy implies the vanishing of its partial derivatives with respect to the internal parameters:

$$\left(\frac{\partial F}{\partial V_1}\right)_{\nu_1} = -(P_1 - P_2) = 0 \quad ; \quad \left(\frac{\partial F}{\partial \nu_1}\right)_{V_1} = (\mu_1 - \mu_2) = 0 . \tag{11.54}$$

In other words, the relative equilibrium condition of the two fluids implies that both

$$\boxed{P_1 = P_2} \tag{11.55}$$

and

$$\boxed{\mu_1 = \mu_2} \tag{11.56}$$

In particular, since any fluid may be formally divided into parts, Eqs. (11.55-56) mean that, ***in a fluid brought at thermodynamic equilibrium, both the pressure and the chemical potential should be homogeneous state parameters***.

Note: The two simple fluids considered in this example are supposed to interact through both mechanical and chemical channels. When, for example, the mechanical interaction is blocked (that is when the two systems are separately enclosed in rigid envelopes) the condition of fixed total volume means that $dV_1 = dV_2 = 0$. This would no more necessarily mean that $P_1 = P_2$. Similarly, the equilibrium condition (11.56) may be taken as granted only if chemical interaction is allowed between the two fluids. Therefore, it may be concluded that Eqs. (11.55-56) are linked by no fundamental condition and that they may act separately.

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Exercises

11.1 The Helmholtz free energy of a constant-mass thermodynamic system in terms of the variables V, T is given by $F(T,V) = A - BT\,ln\frac{T}{T_0} - CT\,ln\frac{V}{V_0}$ (A, B, C, T_0 and V_0 are constants). Find the pressure, internal energy, enthalpy, entropy and Gibbs free energy in terms of T and V. Identify the system and explain the significance of the constants B and C.

Hint/Answer: First Eqs. (11.24) and (11.25) give $S(T,V) = B\,ln\dfrac{T}{T_0} + C\,ln\dfrac{V}{V_0} + B$ and $P(T,V) = \dfrac{C\,T}{V}$. Thus, $S(T,P) = (B+C)ln\dfrac{T}{T_0} - C\,ln\dfrac{P}{P_0} + B$, where $P_0 = CT_0/V_0$. Moreover, $U(T,V) = F(T,V) + T\,S(T,V) = A + BT$. Also, $H(T,V) = U(T,V) + V\,P(T,V) = A + (B+C)T$ and $G(T,V) = F(T,V) + V\,P(T,V) = A + C\,T - B\,T\,ln\dfrac{T}{T_0} - C\,T\,ln\dfrac{V}{V_0}$. The system is an ideal gas. The constant C is $v \cdot R$ (R = gas constant, v = number of moles), The constant B is the heat capacity at constant volume and $B + C$ is the heat capacity at constant pressure. Note that the thermal and caloric equations of state resulted from the expression of F as a function of T and V and thus $F(T,V)$ is a characteristic function of the system. On the contrary, the expressions of U, H and G as functions of T and V represent only different forms for the equations of state.

11.2 The molar Helmholtz free energy of a fluid depends of V and T as $F(T,V) = -B\,T\,ln\dfrac{T}{T_0} - R\,T\,ln\dfrac{V}{V_0}$, where B, T_0 and V_0 are constants. Derive an expression for the influx of heat during an infinitesimal reversible expansion of the fluid with $PV^f = constant$. Discuss in particular the cases $f = 1$ and $f = C_P/C_V$.

Hint/Answer: Eq. (11.24) gives $S(T,V) = B\,ln\dfrac{T}{T_0} + R\,ln\dfrac{V}{V_0} + B$ and, since the process is assumed reversible, $\delta Q = T\,dS = T\left(\dfrac{\partial S}{\partial T}\right)_V dT + T\left(\dfrac{\partial S}{\partial V}\right)_T dV = B\,dT + R\,T\dfrac{dV}{V}$. Also, $P = -\left(\dfrac{\partial F}{\partial V}\right)_T = \dfrac{R\,T}{V}$. Thus, from $PV^f = constant$, it follows $T\,V^{f-1} = constant$, which gives (through differentiation) $\dfrac{dT}{T} = -(f-1)\dfrac{dV}{V}$. Thus, the differential influx of heat becomes $\delta Q = -B(f-1)\dfrac{T\,dT}{V} + R\,T\dfrac{dV}{V} = P\,dV\left[1-(f-1)\dfrac{B}{R}\right]$. From the expression of $P(T,V)$ and from $U(T,V) = F(T,V) + T\,S(T,V) = B\,T$, one recognizes that the fluid is an ideal gas and that $B = C_V$. If $f = 1$, $\delta Q = PdV$, there is no change of internal energy, the influx of heat occurs isothermally. If $f = C_P/C_V$, $B(f-1) = C_P - C_V = R$ and $\delta Q = 0$, the process is adiabatic.

11.3 Determine the free energy of a constant amount of gas satisfying the van der Waals equations of state $P(T,V)=\frac{\nu RT}{V-\nu b}-a\frac{\nu^2}{V^2}$ and $U(T,V)=\nu C_V T-a\frac{\nu^2}{V}$.

Hint/Answer: Eq. (11.25) gives $\left(\frac{\partial F}{\partial V}\right)_T=-\frac{\nu RT}{V-\nu b}+a\frac{\nu^2}{V^2}$, so that the volume dependence of the free energy follows from a simple integration: $F(T,V)=-\nu RT\,ln\frac{V-\nu b}{V_0}-a\frac{\nu^2}{V}+f(T)$, where $f(T)$ is a function of temperature only. On the other hand, Eq. (11.24) implies for the entropy that $S(T,V)=-\left(\frac{\partial F}{\partial T}\right)_V=\nu R\,ln\frac{V-\nu b}{V_0}-f'(T)$. Therefore, by replacing this into $U(T,V)=F(T,V)+T\,S(T,V)$, the following differential equation for $f(T)$ results: $\left(\frac{f(T)}{T}\right)'=-\frac{\nu C_V}{T}$. Finally, one obtains $F(T,V)=-\nu C_V\,T\,ln\frac{T}{T_0}-\nu RT\,ln\frac{V-\nu b}{V_0}-a\frac{\nu^2}{V}$, where T_0 and V_0 are integration constants representing the temperature and the volume of the gas in a reference state.

12. The statistical approach in Equilibrium Thermodynamics

This chapter is devoted mainly to apply the laws of the Equilibrium Statistical Physics stated in Section 7.5 in order to (theoretically) get thermodynamic information on a certain system. The concept of characteristic function will get a crucial importance for the practical connection between Statistical Physics and Thermodynamics.

Following the (already used) convention of Statistical Physics, the amount of matter of a system will be measured by the number of particles N, instead of the number of moles ν. Even with different units, the chemical potential will be still denoted by the symbol μ. However, the student should constantly remember that the product $\mu \cdot \nu$ in Thermodynamics always equals the product $\mu \cdot N$ in Statistical Physics.

12.1 Recall of the probability principle

The probability principle stated in Section 7.5 reads: **for a system in complete equilibrium under fixed external conditions (that include the thermal equilibrium with a thermostat of temperature T and the equilibrium with a particle reservoir of chemical potential μ), the probability to be in some microscopic state (ζ,N) is proportional to an exponential that depends on the non-chemical energy of that state**, namely:

$$\boxed{p(\zeta,N) = \frac{1}{Z} exp\left[-\frac{E(\zeta,N) - \mu N}{kT} \right]}, \tag{12.1}$$

where Z is a suitable constant, called **<u>partition function</u>**, that makes the **<u>grand canonical distribution function</u>** (12.1) satisfy the normalization condition:

$$\boxed{Z = \sum_N \int_{\Gamma(N)} exp\left[-\frac{E(\zeta,N) - \mu N}{kT} \right] g(\zeta,N) d\zeta}. \tag{12.2}$$

At that time, the condition of fixed chemical potential imposed by the equilibrium with a particle reservoir of chemical potential μ was a quite vague statement. Presently, after the discussion of Section 11.5 about the relative equilibrium with reservoirs, it looks clear that, if it is desired to keep constant the chemical potential of an opened system, the only way is to set the system in chemical equilibrium with a suitable particle reservoir.

As was also discussed in Section 7.5, if the system's external constraints are even tighter, namely if its closure is impenetrable, then the particle number becomes a controllable parameter that may be kept constant and the distribution function simplifies to the **<u>canonical</u>** form:

$$\boxed{p(\zeta)=\frac{1}{Z}exp\left[-\frac{E(\zeta)}{kT}\right] \quad ; \quad Z=\int_{\Gamma} exp\left[-\frac{E(\zeta)}{kT}\right]g(\zeta)d\zeta}. \tag{12.3}$$

While apparently tight, the conditions for a system to obey to a grand canonical or canonical distribution are very frequently fulfilled in practice [1]. If, moreover, the system's volume is also kept constant, then the conditions for a grand canonical distribution match those for the grand canonic potential of the system to be a characteristic function. Similarly, at constant volume, the conditions for a canonical distribution to be attained by a certain system become identical with those for the free energy to be a characteristic function. The statistical approach to Equilibrium Thermodynamics should therefore focus on computing the grand canonic potential and the free energy for a given system of microscopic units with statistical behavior.

The subsequent discussions will always focus on classical (non-quantum) systems. Therefore the semi-classical density of states of Eq. (7.49) will be thoroughly used. Also, continuous phase spaces are considered everywhere. For an example of a discrete set of microscopic states, see Exercise 12.15.

12.2 Obtaining thermodynamic information from the distribution function of a given system

From the practical point of view, the conditions for a system to obey to a macrocanonical or canonical distribution differ only by the way of controlling the matter content of the system. There are two distinct procedures for this to be done. First, one may allow the chemical contact of the system with a particle reservoir of a given (controllable!) chemical potential. In this case the particle number in the system is floating freely and cannot be considered as an independent macroscopic parameter. The statistical distribution governing the microscopic evolution of the system will be of the ***grand canonical*** type, Eq. (12.1).

Second, one may enclose the system in some impermeable membrane and may add or remove controllable amounts of matter. The particle number becomes now a controllable parameter and determines (together with the temperature and the volume) the value of the chemical potential of the system, which cannot be considered as an independent macroscopic parameter. In this case the system will obey to a ***canonical*** statistical distribution (see Eq. (12.3)).

Let a given system be at fixed temperature and chemical potential. The statistical entropy of that system may be computed according to Eq. (7.72):

$$S=-k\sum_{N}\int_{\Gamma(N)} p(\zeta,N)ln[p(\zeta,N)]g(\zeta,N)d\zeta . \tag{12.4}$$

By taking into account Eq. (12.1), one may write:

$$ln[p(\zeta,N)] = -\frac{E(\zeta,N) - \mu N}{kT} - ln Z\,, \tag{12.5}$$

so that the expression (12.4) for the entropy becomes [2]:

$$\begin{aligned} S &= \frac{1}{T}\underbrace{\sum_N \int_{\Gamma(N)} E(\zeta,N)p(\zeta,N)g(\zeta,N)d\zeta}_{=\langle E(\zeta,N)\rangle} - \frac{\mu}{T}\underbrace{\sum_N \int_{\Gamma(N)} N\,p(\zeta,N)g(\zeta,N)d\zeta}_{=\langle N\rangle} + \\ &= k\,ln Z \underbrace{\sum_N \int_{\Gamma(N)} p(\zeta,N)g(\zeta,N)d\zeta}_{=1} \end{aligned}.$$

According to the statements of Section 7.5, the first term in the right-hand side is the mean energy of the system, the second term represents the mean particle number and the summation of the third term reduces to unity due to the normalization condition. Thus, one may readily write:

$$\langle E(\zeta,N)\rangle - T\,S - \mu\langle N\rangle = -kT\,ln Z\,. \tag{12.6}$$

By identifying the mean energy with the internal energy of the system and the product $\mu\langle N\rangle$ with its total chemical energy, the left-hand side of Eq. (12.6) can be easily recognized as being the formal definition of the ***grand potential*** defined in Section 11.2. Therefore, according to the correspondence principle of Section 7.5, the following very important relation is obtained [2]:

$$\boxed{\Omega = -kT\,ln Z}. \tag{12.7}$$

Now, if the partition function Z could be expressed as a function of the temperature, volume and chemical potential, Eq. (12.7) would represent the grand potential as a characteristic function of the given system and it would contain all the thermodynamic information about that system. That is to say, the equations of state of the system could follow from the derivatives of Ω (see also Eqs. (11.49)-(11.51) and their associated comments):

$$S(T,V,\mu) = k\,ln Z + \frac{kT}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,\mu}, \tag{12.8}$$

$$P(T,V,\mu) = \frac{kT}{Z}\left(\frac{\partial Z}{\partial V}\right)_{T,\mu}, \tag{12.9}$$

$$N(T,V,\mu) = -\frac{kT}{Z}\left(\frac{\partial Z}{\partial \mu}\right)_{T,V}. \tag{12.10}$$

The determination of the partition function's dependence on T, V and μ is therefore of crucial importance for the possibility to obtain thermodynamic information on a certain system from its microscopic statistical behavior.

Consider now the case of a system enclosed in an impermeable membrane, so that its particle number is fixed (that is controlled by some external means). In some sense, this may be looked as a restriction of the preceding discussion to a unique value of the particle number. The corresponding distribution function will now be of the canonical form (12.3) and the statistical entropy can be computed as:

$$S = -k \int_{\Gamma} p(\zeta) ln[p(\zeta)] g(\zeta) d\zeta . \tag{12.11}$$

Replacement of the probability from (12.3) gives:

$$ln[p(\zeta)] = -\frac{E(\zeta, N)}{kT} - ln\, Z , \tag{12.12}$$

so that the statistical entropy becomes:

$$S = \frac{1}{T} \int_{\Gamma} E(\zeta) p(\zeta) g(\zeta) d\zeta + k\, ln\, Z ,$$

that is:

$$\langle E(\zeta) \rangle - T\, S = -k\, T\, ln\, Z . \tag{12.13}$$

By identifying again the mean energy with the internal energy of the system, the left-hand side of Eq. (12.13) can be easily recognized as being the definition of the ***free energy*** of a closed (chemically isolated) system (see Section 11.2). Therefore, the correspondence principle of Section 7.5 allows the following relation to hold in this particular case [3-6]:

$$\boxed{F = -k\, T\, ln\, Z} . \tag{12.14}$$

If the partition function Z could be expressed as a function of the temperature, volume and particle number then Eq. (12.14) would represent the Helmholtz potential as a characteristic function of the given closed system and it would contain all the thermodynamic information about it. The equations of state of the system could follow from the derivatives of the free energy F:

$$S(T, V, N) = k\, ln\, Z + \frac{k\, T}{Z} \left(\frac{\partial Z}{\partial T} \right)_{V,N} , \tag{12.15}$$

$$P(T, V, N) = \frac{k\, T}{Z} \left(\frac{\partial Z}{\partial V} \right)_{T,N} , \tag{12.16}$$

$$\mu(T, V, N) = -\frac{k\, T}{Z} \left(\frac{\partial Z}{\partial N} \right)_{T,V} , \tag{12.17}$$

The determination of the partition function's dependence on T, V and N is therefore of main importance for the possibility to obtain thermodynamic information on a certain closed system from its microscopic statistical behavior.

It is interesting to compute the internal energy and the constant-volume heat capacity for such a closed system. By reminding that $U = T \cdot S + F$ and by using Eqs. (12.14) and (12.15), one may write:

$$U(T,V,N) = \frac{kT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N} . \tag{12.18}$$

Therefore, the constant-volume heat capacity reads:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 2\frac{kT}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N} - \frac{1}{k}\left[\frac{kT}{Z}\left(\frac{\partial Z}{\partial T}\right)_{V,N}\right]^2 + \frac{kT^2}{Z}\left(\frac{\partial^2 Z}{\partial T^2}\right)_{V,N} .$$

Making use of Eq. (12.18), the preceding relation becomes:

$$C_V = 2\frac{U}{T} - \frac{U^2}{kT^2} + \frac{kT^2}{Z}\left(\frac{\partial^2 Z}{\partial T^2}\right)_{V,N} . \tag{12.19}$$

The double derivative of Z can be made explicit in a similar way:

$$\left(\frac{\partial^2 Z}{\partial T^2}\right)_{V,N} = \left[\frac{\partial}{\partial T}\left(\frac{1}{kT^2}\int_{\Gamma} E(\zeta) exp\left[-\frac{E(\zeta)}{kT}\right] g(\zeta) d\zeta\right)\right]_{V,N} = -2\frac{ZU}{kT^3} + \frac{Z\left\langle E^2(\zeta)\right\rangle}{k^2 T^4} .$$

Therefore Eq. (12.19) takes the form:

$$C_V = \frac{\left\langle E^2(\zeta)\right\rangle - U^2}{kT^2}$$

and, by taking into account that $U = \left\langle E(\zeta)\right\rangle$, the following final expression for the constant-volume heat capacity is obtained [7]:

$$C_V = \frac{\{\Delta[E(\zeta)]\}^2}{kT^2}(\geq 0) , \tag{12.20}$$

which shows that, ***in complete equilibrium with a thermostat, a closed thermodynamic system must have nonnegative constant-volume heat capacity***. At the same time, if account is taken of (12.18), one may conclude that ***the internal energy of such a system should be always a non-decreasing function of temperature***:

$$\left(\frac{\partial U}{\partial T}\right)_V \geq 0 . \tag{12.21}$$

12.3 Particular case: system of non-interacting particles

If the reciprocal interaction between the microscopic units of a certain system is weak enough to be ignored when evaluating the total energy in a certain microscopic state of, the system it is said to consist of non-interacting particles. Very often, such an object is termed as an ***ideal gas***. The simplest case of identical particles will be dealt with.

The key point of this model is that the energy of a certain microscopic state (ζ,N) of the system may be written as the sum of the individual energies of the component particles:

$$E(\zeta,N)=\sum_{i=1}^{N} E^{(1)}(\zeta_i), \tag{12.22}$$

where $E^{(1)}(\zeta_i)$ is the individual energy of the particle i in the considered microscopic state (ζ,N) of the system.

As already mentioned, in the present lecture course we focus on non-quantum systems only. According to the discussion of Section 7.2 (see Eq. (7.48')), the state space of such a system can be decomposed as follows: $\Gamma(N)=\Gamma_1^N$, where Γ_1 represents the state space of each microscopic unit. Moreover, the appropriate form of the density of states is the semi-classical one, namely that given by Eq. (7.35): $g(\zeta,N)=\frac{1}{N!\,h^{sN}}$. Formally, for a non-closed system, the values of N may range between zero and infinity. Therefore, the ***grand canonical partition function*** of Eq. (12.2) becomes [8, 9]:

$$\begin{aligned} Z &= \sum_{N=0}^{\infty}\frac{1}{h^{sN}N!}exp\left(\frac{\mu N}{kT}\right)\int_{\Gamma_1^N} exp\left[-\frac{1}{kT}\sum_{i=1}^{N}E^{(1)}(\zeta_i)\right]d\zeta_1\,d\zeta_2\ldots d\zeta_N = \\ &= \sum_{N=0}^{\infty}\frac{1}{h^{sN}N!}exp\left(\frac{\mu N}{kT}\right)\prod_{i=1}^{N}\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_i)}{kT}\right]d\zeta_i \\ &= \sum_{N=0}^{\infty}\frac{1}{N!}\left\{\frac{1}{h^s}exp\left(\frac{\mu}{kT}\right)\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right]d\zeta_1\right\}^N \end{aligned} .$$

The last term may be easily recognized as being the series expansion of the exponential function and thus, the grand canonical partition function becomes:

$$\boxed{Z = exp\left\{\frac{1}{h^s}exp\left(\frac{\mu}{kT}\right)\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right]d\zeta_1\right\}}. \tag{12.23}$$

When the (non-quantum) system of non-interacting particles is closed in an impermeable membrane, similar arguments may be used to obtain the ***canonical partition function***:

$$\boxed{Z = \frac{1}{h^{sN} N!} \left\{ \int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1 \right\}^N}. \tag{12.24}$$

The main simplifying feature of the results (12.23) and (12.24) is that ***the partition function is no more dependent on the complexity of the microscopic states of the whole system. For non-interacting identical particles it may be computed by using only the dynamical states of one representative individual particle***.

In view of further applications it may also be interesting to consider the ***average values of microscopic parameters referring to one individual representative particle only (one particle parameter)***. Examples of this kind may be the absolute value of the translation velocity, the internal vibration energy, or the electric dipole moment of a gas molecule. We shall denote such a parameter by the generic symbol $A^{(1)}$. Its main characteristic is that it depends on the dynamical state of one particle only $A^{(1)}(\zeta_1)$. The average value should be computed through the general prescription of Section 7.5. Thus, for a system with a ***grand canonical distribution***, one gets:

$$\left\langle A^{(1)} \right\rangle = \frac{1}{Z} \sum_{N=0}^{\infty} \frac{exp\left(\frac{\mu N}{kT} \right)}{h^{sN} N!} \int_{\Gamma_1^N} A^{(1)}(\zeta_1) exp\left[-\frac{1}{kT} \sum_{i=1}^{N} E^{(1)}(\zeta_i) \right] d\zeta_1 \, d\zeta_2 \ldots d\zeta_N =$$

$$= \frac{1}{Z} \sum_{N=0}^{\infty} \frac{exp\left(\frac{\mu N}{kT} \right)}{h^{sN} N!} \int_{\Gamma_1} A^{(1)}(\zeta_1) exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1 \prod_{i=2}^{N} \int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_i)}{kT} \right] d\zeta_i$$

$$= \frac{\int_{\Gamma_1} A^{(1)}(\zeta_1) exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1}{\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1} \frac{1}{Z} \sum_{N=0}^{\infty} \frac{1}{N!} \left\{ \frac{exp\left(\frac{\mu}{kT} \right)}{h^s} \int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1 \right\}^N .$$

Therefore, the desired average takes the following simple form:

$$\left\langle A^{(1)} \right\rangle = \frac{1}{Z_1} \int_{\Gamma_1} A^{(1)}(\zeta_1) exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1 \quad ; \quad Z_1 = \int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT} \right] d\zeta_1 . \tag{12.25}$$

In a completely analogous way, the average of $A^{(1)}$ for a system with a ***canonical distribution*** one may write:

$$\left\langle A^{(1)}\right\rangle = \frac{1}{Z}\frac{1}{h^{sN}N!}\int_{\Gamma_1^N} A^{(1)}(\zeta_1)exp\left[-\frac{1}{kT}\sum_{i=1}^{N}E^{(1)}(\zeta_i)\right]d\zeta_1\,d\zeta_2\ldots d\zeta_N =$$

$$= \frac{\int_{\Gamma_1} A^{(1)}(\zeta_1)exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right]d\zeta_1}{\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right]d\zeta_1}\frac{1}{Z}\frac{1}{N!}\left\{\frac{1}{h^s}\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right]d\zeta_1\right\}^N ,$$

which, according to Eq. (12.24) leads again to the result (12.25). This outcome should not be unexpected since, in a system of independent particles, the microscopic properties of an individual should be (to some extent) independent on the number of particles in the system that is on whether the system is closed or open.

In a purely formal way, the average value of a one-particle parameter may therefore be computed as a statistical mean using the following ***one-particle distribution function***:

$$\boxed{p^{(1)}(\zeta_1) = \frac{1}{Z_1}exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right] \quad ; \quad \left\langle A^{(1)}\right\rangle = \int_{\Gamma_1} A^{(1)}(\zeta_1)\,p^{(1)}(\zeta_1)\,d\zeta_1}. \qquad (12.26)$$

12.4 Application: statistical derivation of the equations of state of a mass-points classical ideal gas

According to the discussion of Section 7.2, a dynamical state of a mass point is defined by a six-dimensional vector $\zeta_1 \equiv (x, y, z, p_x, p_y, p_z)$, so that $s = 3$. The corresponding state space may be decomposed as a Cartesian product between a three-dimensional configuration space and the set $\mathbf{R}^3$ of the non-relativistic translation momentum values: $\Gamma_1 = \Gamma_{c1} \times \mathbf{R}^3$. The energy of a state ζ of a particle is the sum of the kinetic with the potential energy of the particle. Usually, the potential energy depends on the position parameters only. This dependence normally introduces spatial inhomogeneities in the system, which may no more be considered as a simple one. We'll therefore take first the approximation that the potential energy of the particle is position independent, E_{p0}. This may arise if *the external field acts upon all the gas molecules in a homogeneous manner*. (As an example, take a gas of electric dipoles placed in a uniform electric field: each dipole has a definite potential energy depending on its orientation with respect to the external field axis, but not on its position in the container.) Therefore, in this simple approximation, the total energy of a mass point m_0 in a certain dynamical state ζ becomes:

$$E^{(1)}(\zeta_1) = \frac{p_x^2}{2m_0} + \frac{p_y^2}{2m_0} + \frac{p_z^2}{2m_0} + E_{p0}, \qquad (12.27)$$

where E_p is a constant. The integral of the grand canonical partition function (12.23) can be thus further simplified:

$$\begin{aligned}
&\int_{\Gamma_1} exp\left[-\frac{E^{(1)}(\zeta_1)}{kT}\right] d\zeta_1 = \\
&\quad = \left\{\int_{\Gamma_{c1}} exp\left(-\frac{E_{p0}}{kT}\right) dx\,dy\,dz\right\}\cdot\left\{\int_{\mathbf{R}^3} exp\left(-\frac{p_x^2+p_y^2+p_z^2}{2m_0 kT}\right) dp_x\,dp_y\,dp_z\right\} = \\
&\quad = V\,exp\left(-\frac{E_{p0}}{kT}\right)\left[\int_{-\infty}^{\infty} exp\left(-\frac{p_x^2}{2m_0 kT}\right) dp_x\right]^3 = \left(2\pi m_0 kT\right)^{3/2} V\,exp\left(-\frac{E_{p0}}{kT}\right),
\end{aligned} \tag{12.28}$$

where the last integral is of the Poisson type and can be computed through Eq. (7.18). Also, due to the homogeneous value of the potential energy, the integral over the configuration space gives the container volume times the constant exponential factor. The grand canonical partition function gets the following form:

$$Z = exp\left[V\left(\frac{2\pi m_0 kT}{h^2}\right)^{3/2} exp\left(\frac{\mu - E_{p0}}{kT}\right)\right]. \tag{12.29}$$

The corresponding grand canonic potential can then be written through Eq. (12.7) as:

$$\Omega(T,V,\mu) = -\left(\frac{2\pi m_0}{h^2}\right)^{3/2}(kT)^{5/2}\,V\,exp\left(\frac{\mu - E_{p0}}{kT}\right). \tag{12.30}$$

Now, differentiation with respect to the (natural) variables of the grand canonic potential lead to specialized forms of Eqs. (12.8)-(12.10):

$$S(T,V,\mu) = \left(\frac{2\pi m_0 kT}{h^2}\right)^{3/2} V\,exp\left(\frac{\mu - E_{p0}}{kT}\right) k\left(\frac{5}{2} - \frac{\mu - E_{p0}}{kT}\right), \tag{12.31}$$

$$P(T,V,\mu) = \left(\frac{2\pi m_0}{h^2}\right)^{3/2}(kT)^{5/2}\,exp\left(\frac{\mu - E_{p0}}{kT}\right) \tag{12.32}$$

and

$$\langle N\rangle(T,V,\mu) = \left(\frac{2\pi m_0 kT}{h^2}\right)^{3/2} V\,exp\left(\frac{\mu - E_{p0}}{kT}\right). \tag{12.33}$$

Elimination of μ between Eqs. (12.32) and (12.33) is immediate and gives:

$$P(T,V,\nu) = \frac{\langle N\rangle kT}{V} = \frac{\nu RT}{V}, \tag{12.34}$$

where v is the average number of moles of gas contained in the given volume. Moreover, elimination of μ between Eqs. (12.31) and (12.33) leads to the famous ***Sackur-Tetrode formula*** [8]:

$$S = \langle N \rangle k \left\{ ln\left[\frac{V}{\langle N \rangle} \left(\frac{2\pi m_0 kT}{h^2} \right)^{3/2} \right] + \frac{5}{2} \right\} = v R \left\{ ln\left[\upsilon \left(\frac{2\pi M RT}{h^2 N_A^{8/3}} \right)^{3/2} \right] + \frac{5}{2} \right\}, \tag{12.35}$$

where υ is again the molar volume of the gas and M is its molar mass. This formula was derived in 1913 through arguments implying only the old quantum theory of Planck. It was the first evidence of the need of quantum corrections even in the Classical Statistical Mechanics: neglecting the effects of the uncertainty principle would lead to infinity value of the integration constant of the thermodynamic entropy when computed by Eq. (10.35).

The chemical potential can be readily obtained by inverting Eq. (12.33):

$$\mu = E_{p0} - kT\, ln\left[\frac{V}{\langle N \rangle} \left(\frac{2\pi m_0 kT}{h^2} \right)^{3/2} \right], \tag{12.36}$$

so that, by using Eqs. (12.35), (12.34) and (12.36) in Euler's relation (10.15), one obtains:

$$U(T,V,v) = TS - PV + \mu v = \frac{3}{2}\langle N \rangle kT + \langle N \rangle E_{p0} = \frac{3}{2} v RT + v e_p, \tag{12.37}$$

where e_p is ***the average molar potential energy of the gas in the external field***.

Note: Eq. (12.34) is obtained here for mass-points gases only. However, it is a quite easy matter to prove it for gases with more complex molecules too [9]. This equation of state should therefore taken as granted for any gas with independent molecules.

12.5 Maxwell distribution of a gas molecules upon their translation velocities

The particular form of the one-particle energy defined by Eq. (12.27) leads also to a specific expression of the one-particle distribution function of Eq. (12.26). Thus, in computing the "partition function" Z_1 one has, according to Eq. (12.28):

$$Z_1 = (2\pi m_0 kT)^{3/2} V\, exp\left(-\frac{E_{p0}}{kT} \right). \tag{12.38}$$

Therefore, the one-particle distribution function becomes:

$$p^{(1)}(\vec{r}, \vec{p}) = \frac{1}{(2\pi m_0 kT)^{3/2} V} exp\left[-\frac{p_x^2 + p_y^2 + p_z^2}{kT} \right], \tag{12.39}$$

and $p^{(1)}(\vec{r},\vec{p})dV\,dp_x dp_y dp_x$ represents the probability that a particle is in a volume *dV* around the position $\vec{r}$ having the momentum in a neighborhood $dp_x{\cdot}dp_y{\cdot}dp_z$ of the value $\vec{p}$. Since the gas is supposed as homogeneous, the probability $f(\vec{\upsilon})d\upsilon_x d\upsilon_y d\upsilon_z$ that a particle have its velocity in a neighborhood $d\upsilon_x{\cdot}d\upsilon_y{\cdot}d\upsilon_z$ of a certain vector value $\vec{\upsilon}$ may then be easily computed through a simple integration over the position variables and through a suitable change of variable: $f(\vec{\upsilon})d\upsilon_x d\upsilon_y d\upsilon_z = \left[\int_{\Gamma_{c1}} p^{(1)}(\vec{r},\vec{p})dx\,dy\,dz\right] m_0^3 d\upsilon_x d\upsilon_y d\upsilon_z$. If this probability is assumed to equal the relative frequency $\frac{dN(\vec{\upsilon})}{N}$ for a molecule to have a velocity near the value $\vec{\upsilon}$, then one may write:

$$\begin{gathered} dN(\vec{\upsilon}) = N\left(\frac{m_0}{2\pi kT}\right)^{3/2} exp\left[-\frac{m_0\upsilon^2}{2kT}\right]d\upsilon_x d\upsilon_y d\upsilon_z\ ; \\ f(\vec{\upsilon}) = \left(\frac{m_0}{2\pi kT}\right)^{3/2} exp\left[-\frac{m_0\upsilon^2}{2kT}\right], \end{gathered} \tag{12.40}$$

which, in the old kinetic-molecular theory of gases, is called the ***Maxwell distribution of a gas molecules upon their translation velocities*** [8].

Notes:

a) Strictly speaking, the original formula deduced by Maxwell refers to the distribution of gas molecules upon the *moduli* of their translation velocities. This formula can be easily obtained from Eq. (12.40) by integration over all the possible velocity orientation. The integration can most easily be performed by introducing spherical velocity coordinates υ ($\in (0, \infty)$), θ ($\in (0, \pi)$) and φ ($\in (0, 2\pi)$) instead of the Cartesian ones υ_x, υ_y and υ_z: $\upsilon_x = \upsilon \sin\theta \cos\varphi$, $\upsilon_y = \upsilon \sin\theta \sin\varphi$, $\upsilon_z = \upsilon \cos\theta$, $d\upsilon_x d\upsilon_y d\upsilon_z = \upsilon^2 \sin\theta\, d\upsilon\, d\theta\, d\varphi$. The integration of Eq. (12.40) over θ and φ gives $4\pi\upsilon^2$, so ***that the Maxwell distribution of gas molecules upon the absolute values of their translation velocities*** reads:

$$
\begin{aligned}
dN(v) &= N\left(\frac{m_0}{2\pi kT}\right)^{3/2} exp\left[-\frac{m_0 v^2}{2kT}\right] 4\pi v^2\, dv \\
F(v) &= 4\pi\left(\frac{m_0}{2\pi kT}\right)^{3/2} v^2\, exp\left[-\frac{m_0 v^2}{2kT}\right].
\end{aligned}
\tag{12.41}
$$

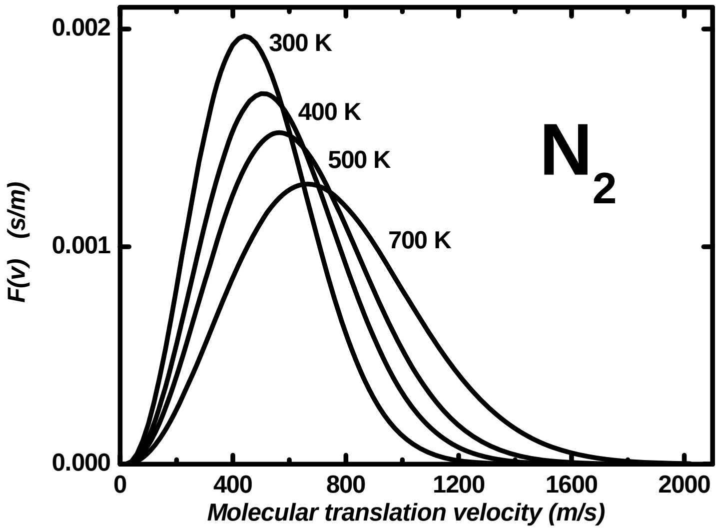

Figure 12.1: Equilibrium (Maxwell) distributions of gaseous nitrogen molecules upon their translation speeds at different temperatures.

The shape of this distribution is illustrated in Figure (12.1) for a nitrogen gas at different temperatures.

b) Maxwell distributions (12.40) and (12.41) involve only the translation velocity of a single molecule. Therefore, even if they are here obtained for mass-points gases only, the validity extends to gases with more complex (but independent) molecules [9] too.

The Maxwell distribution provide a practical way of computing averages of one-particle quantities involving the molecular translation velocity only. Two important examples, the averages of the absolute value and of the squared translation molecular velocity are considered in Appendix 12.1.

12.6 Classical ideal gas in a non-homogeneous external potential: the barometric formula

Equations (12.34), (12.36) and (12.37) contain all the thermodynamic information on the mass-points classical ideal gas placed in a homogeneous external potential. They are the equations of state of that system. As already stressed, ***if the gas molecules have a position-dependent potential energy in the external field, then the system stops being a simple one***. In these cases, all the previous theory presented before in these lectures should be applied to small, but macroscopic parts of the given system. These parts should be ***small enough in size*** to allow the potential energy to be approximated by a constant throughout the corresponding occupied volume. In the same time, the system parts should be ***macroscopic*** (that is containing a number of particles comparable to Avogadro's number) in order to allow statistical considerations to be valid in their dynamical analysis. Nevertheless, all the parts should be in relative thermal equilibrium that is they should show a ***unique temperature***. To each such homogeneous part of the system one may attach a ***macroscopic position*** (x,y,z), representing, for example, the position of its center of mass. A phase space may then be defined for the collection of particles contained in each homogeneous division, which must be dependent on the corresponding macroscopic position: $\Gamma(x,y,z)$. Also, the potential energy per particle can be approximated by $E_{p0}(x,y,z)$ in every point of the small volume assigned to the division (macroscopically) located at (x,y,z). The total one-particle energy of Eq. (12.27) will be therefore position dependent:

$$E^{(1)}(\zeta_1,x,y,z)=\frac{p_x^2}{2m_0}+\frac{p_y^2}{2m_0}+\frac{p_z^2}{2m_0}+E_{p0}(x,y,z), \qquad (12.42)$$

The gas pressure around the position (x,y,z) should then be given by the corresponding adaptation of Eq. (12.32):

$$P(T,\mu,x,y,z)=\left(\frac{2\pi m_0}{h^2}\right)^{3/2}(kT)^{5/2}\,exp\left(\frac{\mu-E_{p0}(x,y,z)}{kT}\right).$$

Denoting by P_0 the pressure around some reference position (x_0,y_0,z_0), one readily obtains:

$$P(T,\mu,x,y,z)=P_0(T,\mu)exp\left(-\frac{E_{p0}(x,y,z)-E_{p0}(x_0,y_0,z_0)}{kT}\right). \qquad (12.43)$$

This expression becomes even simpler if the reference position corresponds to the natural scaling of the potential energy, that is to the position where the potential energy is taken as zero-valued $E_{p0}(x_0,y_0,z_0)=0$:

$$\boxed{P(T,\mu,x,y,z)=P_0(T,\mu)exp\left(-\frac{E_{p0}(x,y,z)}{kT}\right)=P_0(T,\mu)exp\left(-\frac{e_p(x,y,z)}{RT}\right)}. \qquad (12.44)$$

Equation (12.44) actually represents the ***thermal equation of state*** for such an inhomogeneous gas. This is the general form of the so-called ***<u>barometric formula</u>***.

In a similar way, denoting by $n(x,y,z)$ the local average particle density of the gas (that is the average particle number in the unit volume around the position (x,y,z)), Eq. (12.33) gives:

$$\boxed{n(T,\mu,x,y,z) = n_0(T,\mu)exp\left(-\frac{E_{p0}(x,y,z)}{kT}\right) = n_0(T,\mu)exp\left(-\frac{e_p(x,y,z)}{RT}\right)}, \qquad (12.45)$$

where n_0 is the particle density around the reference position (x_0,y_0,z_0). This formula is known under the name of ***Boltzmann's Law*** for ideal gases [8].

Notes:

1) While the equations of state of a homogeneous classical ideal gas can be deduced through the canonical partition function - free energy correspondence, the barometric formula cannot be simply derived therefrom. Indeed, the various homogeneous parts into which the system has to be divided obey no more to a canonical distribution, since *they are not individual closed systems*. A more involved, mechanical equilibrium - based, argument should be used instead [9], so that the canonical distribution seems not quite naturally suited for dealing with continuously inhomogeneous systems.

2) Statistical computations performed for gases by means the Maxwell-Boltzmann distribution of the old kinetic-molecular theory give correct results when one particle dynamical parameters (or linear combinations of them) are to be averaged. Nevertheless, more involved statistical quantities, like the system's entropy, cannot be correctly obtained by neglecting the underground interactions (described by the quantum corrections to the density of states) that take place between the gas molecules, even if apparently the particles are considered as independent. Without such subtle interactions a set of molecules can never represent a system and have no statistical microscopic behavior.

3) Even if Eqs. (12.44) and (12.45) are here demonstrated for mass-points gases only, they may easily be proven (and should be therefore taken as granted) for gases with independent but more complex molecules too [9].

12.7 System with interacting particles. The Van der Waals equation of state.

Consider for simplicity a gas of N mass-points in an impermeable closure, outside of any external influence. Suppose that the molecules interact in pairs, that is, any two molecules, i and j say interact with a potential energy $\varphi(\vec{r}_i,\vec{r}_j)$ depending on their relative position only and independent of the presence of the other molecules. Thus, the total potential energy of this interaction for a given configuration of the system can be written as:

$$\Phi = \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} \varphi\left(\vec{r}_i,\vec{r}_j\right). \tag{12.46}$$

The preceding sum is constructed so that to avoid the interaction terms of one molecule with itself and the possibility of twice counting the interaction of a certain couple of molecules.

The state space of the system can be again decomposed as $\Gamma = \Gamma_1^N = \Gamma_{c1}^N \times \mathbf{R}^{3N}$ and the energy of a microscopic state of the system is:

$$E(\zeta) = \sum_{i=1}^{N} \frac{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}{2m_0} + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N} \varphi\left(\vec{r}_i,\vec{r}_j\right). \tag{12.47}$$

Therefore, the canonical partition function (12.3) takes the form [10-12]:

$$Z = (N!)^{-1}\left(\frac{2\pi m_0 kT}{h^2}\right)^{3N/2} \int_{\Gamma_{c1}^N} exp\left(-\frac{\Phi}{kT}\right) dx_1 \ldots dz_N \ . \tag{12.48}$$

The second factor comes from the repeated use of the Poisson formula (7.18) in the integration over $\mathbf{R}^{3N}$.

In order to go further from Eq. (12.48), one should provide an analytical expression for the intermolecular potential energy. This can be done by formulating a model of the interaction. While several models can be constructed for this, leading to important refinements of the theory [7, 10-12], we'll content only with the simplest one: ***the model of "hard spheres"***. There are ***two main approximations*** in this model. First, each molecule is conceived as plunged in a kind of homogeneous "mean field" produced by its neighbors. Therefore, the interaction energy of the *i*-th molecule with its environment, namely the sum $\sum_{\substack{j=1\\ j\neq i}}^{N} \varphi\left(\vec{r}_i,\vec{r}_j\right)$, should be proportional to the neighboring particle density:

$$\sum_{\substack{j=1\\ j\neq i}}^{N} \varphi\left(\vec{r}_i,\vec{r}_j\right) = -\frac{N}{V} 2\tilde{a} \quad (\tilde{a} > 0), \quad i = 1,2,\ldots,N \ . \tag{12.49}$$

The factor 2 in the preceding equation was chosen for convenience and the minus sign accounts for the fact that, at usual intermolecular distances in gases, the reciprocal interactions are essentially of attractive type. The second main point of our simple model is that each molecule is considered as a small hard sphere of volume b_0, so that the measure of the single-particle configuration space Γ_{c1} will be the "free volume" of the vessel where the gas is enclosed: $V - N \cdot b_0$ (that is the real volume V of the container minus the volume occupied by the N hard spheres, $N \cdot b_0$).

By using these two ideas in the general Equation (12.46), one may write (please remind that the sum over *i* has *N* terms):

$$\Phi = -\frac{N^2}{V}\tilde{a} . \tag{12.50}$$

The exponential factor in Eq. (12.48) becomes therefore a constant and the integration over each molecular position gives the "free volume" of the container:

$$Z = (N!)^{-1}\left(\frac{2\pi m_0 kT}{h^2}\right)^{3N/2}(V - N b_0)^N \, exp\left(\frac{N^2 \tilde{a}}{VkT}\right). \tag{12.51}$$

Since the partition function depends only on the temperature, volume and particle number, the free energy of the system computed through Eq. (12.14) will be a characteristic function and will allow obtaining the explicit form of the equations of state through Eqs. (12.15) - (12.17). Thus, Eq. (12.16) readily gives:

$$P = kT\left(\frac{\partial ln Z}{\partial V}\right)_{T,N} = \frac{NkT}{V - N b_0} - \left(\frac{N}{V}\right)^2 \tilde{a} = \frac{\nu RT}{V - \nu b} - \left(\frac{\nu}{V}\right)^2 a , \tag{12.52}$$
$$\left(a \equiv N_A^2 \tilde{a} \quad ; \quad b \equiv N_A b_0\right)$$

which can be immediately transformed into the form (8.24) of the Van der Waals equation of state:

$$\left(P + a\frac{\nu^2}{V^2}\right)(V - b\nu) = \nu RT . \tag{12.53}$$

The caloric equation of state for this model can also be obtained through Eq. (12.18):

$$\begin{aligned} U &= kT^2\left(\frac{\partial}{\partial T}(ln Z)\right)_{V,N} = kT^2\left(\frac{3N}{2}\frac{1}{T} - \frac{N^2}{V}\frac{\tilde{a}}{kT^2}\right) = \\ &= \frac{3}{2}\nu RT - \frac{\nu^2}{V}a = U_{ideal\ gas} + \Phi . \end{aligned} \tag{12.54}$$

As already stressed in Section 8.3*c* the Van der Waals model can be successfully used for high-density gases. The parameters *a* and *b* depend on the intimate properties of individual molecules and can be experimentally determined.

A bit more difficult is obtaining the equation of state for the chemical potential in the Van der Waals model. To this purpose one needs a suitable approximation for computing factorials of very large numbers. Thus, when *N* is a very large natural number (for example of the order of Avogadro's number N_A) the following relation holds (see the proof in the Appendix 12.2 of this chapter):

$$\boxed{ln(N!) \cong N\,ln(N) - N}, \tag{12.55}$$

which is known under the name of ***Stirling's formula***.

The free energy in the present model can be therefore approximated by:

$$F \cong N\,k\,T\,ln\,N - N\,k\,T - N\,k\,T\,ln\left[\left(\frac{2\pi\, m_0\, k\,T}{h^2}\right)^{3/2}\left(V - N\,b_0\right)\right] - \frac{N^2\,\tilde{a}}{V} \tag{12.56}$$

and the chemical potential can be computed through Eq. (12.17):

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -k\,T\,ln\left[\left(\frac{2\pi\, m_0\, k\,T}{h^2}\right)^{3/2}\left(\frac{V}{N} - b_0\right)\right] + \frac{N\,k\,T\,b_0}{V - N\,b_0} - 2\tilde{a}\frac{N}{V}.$$

By using the definitions of *a* and *b* given in Eq. (12.52) one may simplify the previous expression to:

$$\mu = -k\,T\,ln\left[\upsilon\left(\frac{2\pi\, m_0\, k\,T}{h^2 N_A^{2/3}}\right)^{3/2}\left(1 - \frac{b}{\upsilon}\right)\right] + k\,T\frac{b}{\upsilon}\frac{1}{1 - b/\upsilon} - \frac{2a}{N_A \upsilon}.$$

Moreover, if the fact that the ratio *b/υ* is usually very much less than unity is taken into account, the following approximate formula results:

$$\mu \cong -k\,T\,ln\left[\upsilon\left(\frac{2\pi\, m_0\, k\,T}{h^2 N_A^{2/3}}\right)^{3/2}\right] + k\,T\frac{2b}{\upsilon}\left(1 - \frac{a}{b\,R\,T}\right), \tag{12.57}$$

where the corrections due to the molecular interactions (see the chemical potential for the classical ideal gas Eq. (12.36) for comparison) were gathered in the second term.

12.8 More insight into the classical ideal gas: the molecular currents

When a small opening is pierced in a thin wall of a vessel containing a classical ideal gas a tiny outgoing current of molecules is obtained. This process, which is sometimes termed as ***effusion***, has surprisingly many practical applications ranging from preparation of high-performance semiconductor devices to micro-propulsion of satellites and preparation of enriched nuclear fuel. For all such applications it is therefore of main importance to know the connection between the thermodynamic parameters of the gaseous source of molecules and the structure and consistency of the outgoing molecular beam. In order to establish the properties of the currents of molecules in an as simple as possible exposure, we shall remain into the model of the mass-points gas. Since only the translation molecular motion comes into discussion, it is a straightforward matter to generalize the results for gases with more complicated molecules.

Consider the z-axis of a Cartesian referential to point outwardly in the middle of some small area dS of a thin wall of the vessel (Figure 12.2). The first problem is to construct a reasonable ***definition for the number of particles that have velocities close to some specified vector value*** $\vec{\upsilon} = (\upsilon_x, \upsilon_y, \upsilon_z)$ ***and hit the unit area of the wall in a unit time interval***. This is the so-called ***one-particle molecular current*** and will be denoted by $J^{(1)}(\vec{\upsilon})$. Definitions for the one-particle energy current and one particle momentum current will then be formulated. According to the illustration of Figure 12.2 the selected particles are in a skew cylinder based in dS and having the sides parallel to $\vec{\upsilon}$. The last molecule hitting the wall during the small time interval dt should be no farther than $\upsilon_z \cdot dt$ from the wall. The height of the considered cylinder should therefore be $\upsilon_z \cdot dt$. If the local particle density in the gas is n, then the total number of particles in this cylinder will be $n \cdot \upsilon_z \cdot dt \cdot dS$. By making the necessary specification that υ_z ***should be positive*** in order that the molecule hit the wall the ***one-particle molecular current*** will be defined as:

$$J^{(1)}(\vec{\upsilon}) = \begin{cases} n\upsilon_z & if \quad \upsilon_z > 0 \\ 0 & if \quad \upsilon_z \le 0 \end{cases}. \tag{12.58}$$

Multiplying the one-particle molecular current by the corresponding molecular translation kinetic energy $m_0\upsilon^2/2$ one readily gets the definition of the ***one-particle translation kinetic energy current***:

$$J_e^{(1)}(\vec{\upsilon}) = \frac{m_0\upsilon^2}{2} J^{(1)}(\vec{\upsilon}) = \begin{cases} \dfrac{n m_0}{2}\upsilon^2 \upsilon_z & if \quad \upsilon_z > 0 \\ 0 & if \quad \upsilon_z \le 0 \end{cases}. \tag{12.59}$$

Finally, if the one-particle molecular current is multiplied by the corresponding z-component

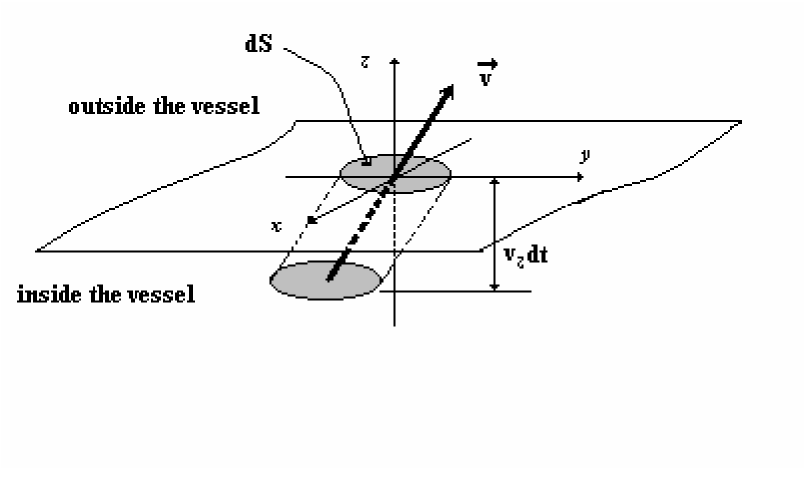

Figure 12.2

of the molecular translation momentum, $m_0 \upsilon_z$, the definition of the ***one-particle normal momentum current*** is obtained:

$$J_p^{(1)}(\vec{\upsilon}) = m_0 \upsilon_z J^{(1)}(\vec{\upsilon}) = \begin{cases} n\, m_0 \upsilon_z^2 & if \quad \upsilon_z > 0 \\ 0 & if \quad \upsilon_z \le 0 \end{cases} . \tag{12.60}$$

Now, the one-particle parameters defined by Eqs. (12.58) - (12.60) may be statistically averaged through the procedure indicated by Eq. (12.25) or, more directly, by the Maxwell distribution of Eq. (12.40). The corresponding averages will be denoted by J, J_e and J_p, respectively.

Thus, ***the total particle current*** J will be:

$$J = \left(\frac{m_0}{2\pi k T} \right)^{3/2} n \int_{-\infty}^{\infty} d\upsilon_x \int_{-\infty}^{\infty} d\upsilon_y \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon^2}{2kT} \right] \upsilon_z \, d\upsilon_z =$$
$$= \left(\frac{m_0}{2\pi k T} \right)^{3/2} n \int_{-\infty}^{\infty} exp\left[-\frac{m_0 \upsilon_x^2}{2kT} \right] d\upsilon_x \int_{-\infty}^{\infty} exp\left[-\frac{m_0 \upsilon_y^2}{2kT} \right] d\upsilon_y \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon_z^2}{2kT} \right] \upsilon_z \, d\upsilon_z =$$
$$= \left(\frac{m_0}{2\pi k T} \right)^{1/2} \frac{n}{2} \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon_z^2}{2kT} \right] d\left(\upsilon_z^2\right) = \frac{n}{2} \sqrt{\frac{2kT}{\pi m_0}} .$$

It is often more convenient to express the total particle current by the average of the absolute translation velocity of gas molecules deduced in Appendix 12.1, Eq. (12.A1):

$$\boxed{J = \frac{n \bar{\upsilon}}{4}} . \tag{12.61}$$

Next, the ***total translation kinetic energy current*** will take the form:

$$J_e = \left(\frac{m_0}{2\pi k T} \right)^{3/2} \frac{n\, m_0}{2} \int_{-\infty}^{\infty} d\upsilon_x \int_{-\infty}^{\infty} d\upsilon_y \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon^2}{2kT} \right] \upsilon^2 \upsilon_z \, d\upsilon_z .$$

The integrals may be most easily performed in spherical coordinates (defined in Section 12.5). Care must be taken of the range of the angle θ, which should be no larger than $\pi/2$ due to the restriction in the orientation of υ_z. We'll therefore get:

$$J_e = \left(\frac{m_0}{2\pi k T} \right)^{3/2} \frac{n\, m_0}{2} \int_{0}^{2\pi} d\varphi \int_{0}^{\pi/2} sin\,\theta \, cos\,\theta \, d\theta \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon^2}{2kT} \right] \upsilon^5 \, d\upsilon =$$
$$= \pi \frac{n\, m_0}{4} \left(\frac{m_0}{2\pi k T} \right)^{3/2} \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon^2}{2kT} \right] \upsilon^4 \, d\left(\upsilon^2\right) = \pi \frac{n\, m_0}{4} \left(\frac{m_0}{2\pi k T} \right)^{3/2} 2 \left(\frac{2kT}{m_0} \right)^3 .$$

By further arranging the factors and by using Eqs. (12.34) and (12.A1), one finally obtains:

$$\boxed{J_e = \frac{P \bar{\upsilon}}{2}} , \tag{12.62}$$

where P is the local value of the gas pressure.

As for the ***total normal momentum current***, the computation may follow a similar course:

$$J_p = n m_0 \left(\frac{m_0}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} d\upsilon_x \int_{-\infty}^{\infty} d\upsilon_y \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon^2}{2kT}\right] \upsilon_z^2 \, d\upsilon_z =$$

$$= n m_0 \left(\frac{m_0}{2\pi kT}\right)^{3/2} \int_{-\infty}^{\infty} exp\left[-\frac{m_0 \upsilon_x^2}{2kT}\right] d\upsilon_x \int_{-\infty}^{\infty} exp\left[-\frac{m_0 \upsilon_y^2}{2kT}\right] d\upsilon_y \int_{0}^{\infty} exp\left[-\frac{m_0 \upsilon_z^2}{2kT}\right] \upsilon_z^2 \, d\upsilon_z =$$

$$= n m_0 \sqrt{\frac{m_0}{2\pi kT}} \frac{\sqrt{\pi}}{4} \left(\frac{2kT}{m_0}\right)^{3/2} = \frac{nkT}{2} .$$

So, by using again Eq. (12.34), one gets:

$$\boxed{J_p = \frac{1}{2} P}, \tag{12.63}$$

An interesting physical application of the theory presented in this section is the possibility to ***estimate the condensation and evaporation rates for a given substance***.

Let's begin with the condensation rate q_c. The vapor phase may be well approximated by an ideal classical gas, so that the total mass condensing in the unit of time on the unit area of the interface will be given by:

$$q_{cond} \equiv m_0 J = \frac{n m_0 \bar{\upsilon}}{4} = P_{vap} \sqrt{\frac{m_0}{2\pi kT}} = P_{vap} \sqrt{\frac{M}{2\pi RT}} , \tag{12.64}$$

where use was again made of Eqs. (12.34) and (12.A1). P_{vap} represents the actual pressure of the vapors of the given substance in the surrounding atmosphere.

Under closure conditions the vapor phase may become saturated, that is its total mass remains constant under fixed temperature and fixed volume. The saturation status of the vapor phase is obviously equivalent to a balance between the condensation and evaporation rates. Therefore, at some given temperature, the evaporation rate should equal the condensation one at saturation:

$$q_{evap} = P_{sat}(T) \sqrt{\frac{m_0}{2\pi kT}} = P_{sat}(T) \sqrt{\frac{M}{2\pi RT}} , \tag{12.65}$$

where P_{sat} represents the pressure of the saturated vapors of the substance at the given temperature.

The net rate of variation of the mass of some given piece of substance through evaporation will thus be given by:

$$\frac{dm}{dt}(T) = \left(q_{cond} - q_{evap}\right) S = -\sqrt{\frac{M}{2\pi RT}} \left[P_{sat}(T) - P_{vap}\right] S . \tag{12.66}$$

When applying Eq. (12.66) attention must be paid to the fact that the vapor pressure P_{vap} strongly depends on the departure from the interface: the vapor concentration decreases steeply with the distance from the interface. Use of Eq. (12.66) with the value of the vapor pressure away from the interface would result in net evaporation rates that are much higher than the experimentally observed ones. However, under intense ventilation, one can assure a homogeneous concentration of the vapor and Eq. (12.66) may be applied. In such conditions the vanishing of the net evaporation rate allows the determination of the vapor pressure in the surrounding atmosphere:

$$\frac{dm}{dt} = 0 \quad \Rightarrow \quad P_{vap} = P_{sat}(T), \tag{12.67}$$

since the saturated vapor pressure is usually tabulated as a function of temperature. Thus, the vapor content (concentration) of the region outside the given piece of substance will be:

$$n_{vap} = \frac{P_{sat}(T)}{kT}. \tag{12.68}$$

Equation (12.68) is the basis of a convenient simple method of measuring the water vapor content (humidity) of the atmosphere. The vanishing of the net evaporation rate may be practically achieved through a proper reduction of the local temperature of the liquid phase. This cooling actually appears automatically in the evaporation process, so that one needs only to measure the final stationary value of the temperature when the cooling stops along with the net evaporation.

Appendix 12.1: Statistical averages of some important one-particle quantities

Consider first the average of the absolute value of the translation velocity of gas molecules, $\langle v \rangle$. This average is also frequently denoted by $\bar{v}$. That kind of averages, implying only the absolute value of the molecular translation velocity, may be obviously computed in the easiest way by using the Maxwell distribution (12.41). Thus, we have:

$$\bar{v} \equiv \langle v \rangle = \int_0^\infty v\, F(v)\, dv = 4\pi \left(\frac{m_0}{2\pi kT} \right)^{3/2} \int_0^\infty v^3\, exp\left[-\frac{m_0 v^2}{2kT} \right] dv =$$

$$= 2\pi \left(\frac{m_0}{2\pi kT} \right)^{3/2} \int_0^\infty v^2\, exp\left[-\frac{m_0 v^2}{2kT} \right] d\left(v^2\right) = 2\pi \left(\frac{m_0}{2\pi kT} \right)^{3/2} \left(\frac{2kT}{m_0} \right)^2 ,$$

so that

$$\boxed{\bar{v} \equiv \langle v \rangle = \sqrt{\frac{8kT}{\pi m_0}}}. \tag{12.A1}$$

Another interesting average is that of the squared absolute value of the molecular translation velocity, $<\upsilon^2>$ (also denoted by $\overline{\upsilon^2}$). Following the same preceding procedure one obtains:

$$\overline{\upsilon^2} \equiv \left\langle \upsilon^2 \right\rangle = \int_0^\infty \upsilon^2 F(\upsilon) d\upsilon = 4\pi \left(\frac{m_0}{2\pi k T} \right)^{3/2} \int_0^\infty \upsilon^4 \, exp\left[-\frac{m_0 \upsilon^2}{2kT} \right] d\upsilon =$$

$$= 4\pi \left(\frac{m_0}{2\pi k T} \right)^{3/2} \frac{3\sqrt{\pi}}{8} \left(\frac{2kT}{m_0} \right)^{5/2},$$

that is

$$\boxed{\overline{\upsilon^2} \equiv \left\langle \upsilon^2 \right\rangle = \frac{3kT}{m_0}}. \tag{12.A2}$$

In this connection, the so-called ***thermal velocity*** may be defined as:

$$\boxed{\upsilon_T \equiv \sqrt{\left\langle \upsilon^2 \right\rangle} = \sqrt{\frac{3kT}{m_0}}}. \tag{12.A3}$$

It may also be of interest to see that the maximum of the Maxwell distribution (12.41) provides a special value of the translation molecular velocity, ***namely the most probable velocity*** υ_p. This value corresponds to the maximum probability for a molecular speed to be measured in a perfect classical gas. The necessary condition for an extremum of $F(\upsilon)$ is that its first derivative vanishes at υ_p. It then readily follows that:

$$\boxed{\upsilon_p = \sqrt{\frac{2kT}{m_0}}}. \tag{12.A4}$$

Appendix 12.2: Stirling's approximation

For every natural N one may obviously write:

$$ln(N!) = \sum_{n=1}^{N} ln(n).$$

Moreover, for any natural n larger than unity one may also write:

$$\int_{-1/2}^{1/2} ln(n+x)dx = \int_{-1/2}^{1/2} \left[ln(n) + x\frac{1}{n} - x^2 \frac{1}{2n^2} + \ldots \right] dx = ln(n) - \frac{1}{12n^2} + \ldots,$$

which results from the term-by-term integration of the series expansion of the logarithm upon the powers of x. So, even if n is of the order of unity, the following approximation holds very well:

$$ln(n) \cong \int_{-1/2}^{1/2} ln(n+x)dx = \int_{n-1/2}^{n+1/2} ln(x)dx .$$

Therefore, the logarithm of the factorial becomes:

$$ln(N!) = \sum_{n=1}^{N} ln(n) \cong \sum_{n=1}^{N} \int_{n-1/2}^{n+1/2} ln(x)dx = \int_{1/2}^{N+1/2} ln(x)dx = \left(x\,ln(x) - x\right)\Big|_{1/2}^{N+1/2} \cong N\,ln(N) - N ,$$

which is actually the Stirling's formula (12.55).

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Exercises

12.1 A mixture of atomic and molecular hydrogen, of partial pressures P_a, P_m respectively, communicates with a manometer through a fine orifice. Calculate the pressure registered by the manometer if atoms recombine immediately after passing through the orifice, so that only molecules return to the mixture, and the temperature of the system is uniform throughout.

Hint/Answer: The total current of molecules returning from the manometer has two components: one consisting of the molecules that originally entered the manometer in a current J_m and the other containing molecules that were formed at the entrance through recombination from the current J_a of atoms coming from the vessel. Therefore, the total current of molecules returning to the vessel should be: $J_m + J_a/2$. On the other hand, this current can be expressed in terms of the molecular concentration in the manometer chamber, n, as $n\bar{v}_m/4$, where $\bar{v}_m$ is the average velocity of molecules at the corresponding temperature. The currents J_m and J_a, outgoing from the vessel can be expressed in terms of the corresponding (molecular and atomic) concentrations and of the average (molecular and atomic) velocities. Therefore: $\frac{n\bar{v}_m}{4} = \frac{n_m \bar{v}_m}{4} + \frac{1}{2}\frac{n_a \bar{v}_a}{4}$. In terms of pressures, this relation takes the form (remember that $\bar{v}_a/\bar{v}_m = \sqrt{2}$): $P = P_m + \frac{1}{\sqrt{2}} P_a$.

12.2 A vessel of surface area A and volume V contains a gas in equilibrium. Show that the ratio of the rate of collisions between molecules in the gas and the rate of collisions between the molecules and the vessel is given by $2V/(\lambda \cdot A)$ where λ is the mean free path of the molecules. Estimate this ratio at standard temperature and pressure for a spherical vessel of diameter 10 cm and for $\lambda = 6.6 \cdot 10^{-5}$ cm.

Hint/Answer: The mean free time of flight of a molecule may be estimated by $\lambda/\bar{v}$, so that a molecule experiences $\bar{v}/\lambda$ impacts per unit of time. Since there are $n \cdot V/2$ distinct pairs of molecules in the vessel, the total number of intermolecular impacts per unit of time will be $\frac{nV\bar{v}}{2\lambda}$.

On the other hand, the total number of collisions with the surface of the vessel in the unit of time should be: $\frac{nA\bar{v}}{4}$. Thus, the required ratio is: $\frac{2V}{\lambda A}$, which for the vessel in question gives $5.1 \cdot 10^4$.

12.3 Calculate the fractional change in resistance per unit of time, $\dot{R}/R$, due to evaporation from the surface, for a tungsten wire of mass 10^{-2} g and of surface area 10^{-1} cm^2 when heated to 2800 K. The saturated vapor pressure of tungsten at 2800 K is $7.5 \cdot 10^{-6}$ mm Hg, the atomic weight of tungsten is 184.

Hint/Answer: As is known from the general study of electric currents, the resistance of a wire is inversely proportional to the area of the cross section of the wire. Thus, denoting by a the diameter of the wire, one may write: $dR/R = -2\,da/a$. On the other hand, the mass of the wire is proportional to its volume and therefore to the cross sectional area: $dm/m = 2\,da/a$. Therefore $dR/R = -dm/m \quad \Rightarrow \quad \dot{R}/R = -\dot{m}/m$. Supposing that the evaporation takes place in vacuum, Eq. (12.66) may be further applied, with $P_{vap} = 0$: $\dot{R}/R = \frac{S}{m}\sqrt{\frac{M}{2\pi RT}}\, P_{sat}(T) = 10^{-6}$ s^{-1}.

12.4 Two vessels of equal volume containing an ideal gas have a common face consisting of a thin sheet pierced with a hole of diameter small compared to the mean free path of the gas molecules. At 0 ^{0}C the pressure in the system is 0.1 mm Hg. If one vessel is heated to 50 ^{0}C and the other to 100 ^{0}C, find the difference in pressure of the gas in the two vessels when the steady state is reached.

Hint/Answer: Let n_0 be the molecular density of the gas in the initial state and let n_1 and n_2 the molecular densities in the two vessels in the final state. Let P_0, P_1 and P_2 be the corresponding values of the gas pressure. Since the volumes are equal, the conservation of the total number of molecules leads to: $n_1 + n_2 = 2n_0$. When the equilibrium is established, the molecular currents from both sides of the hole should be equal: $n_1 \bar{v}_1 = n_2 \bar{v}_2 \Leftrightarrow \frac{n_1}{n_2} = \sqrt{\frac{T_2}{T_1}}$. In terms of pressures, these relations may be written as: $\frac{P_1}{T_1} + \frac{P_2}{T_2} = 2\frac{P_0}{T_0}$ and $\frac{P_1}{P_2} = \sqrt{\frac{T_1}{T_2}}$, so that $P_2 - P_1 = 2P_0 \frac{\sqrt{T_1 T_2}}{T_0} \frac{\sqrt{T_2} - \sqrt{T_1}}{\sqrt{T_2} + \sqrt{T_1}}$ = 0.0091 mm Hg.

12.5 A vessel contains two compartments with a common face consisting of a thin sheet. One compartment of volume *V* (the collector) is initially evacuated of any trace of gas. In the other compartment a gaseous mixture is pumped at a constant pressure, so that the ratio of the particle densities n_1/n_2 remains constant. The molecular weights of the two components are M_1 and M_2, respectively. A fine hole of diameter *d* small compared to the mean free path of the gas is suddenly pierced in the separating membrane. The overall temperature *T* is also kept constant. Find the time dependence of the ratio n'_1/n'_2 of the particle densities of the two gaseous components in the collector. Discuss the result for both long and short collecting time intervals. ***Note***: Such arrangements are currently used for preparation of enriched nuclear fuel. The two gaseous components are in this case uranium fluorides formed with two different isotopes of uranium.

Hint/Answer: Let *n'* be the instantaneous particle density of one of the gas components in the collector. The total number of molecules of this component in the collector is therefore *n'*·*V*. The variation in time of this number has two sources, one positive and the other negative. The positive term consists of the incoming molecules from the other compartment and the negative one is produced by the outgoing molecular flux that returns back to the source: $\dot{n}'(t)V = \frac{\pi d^2 \bar{v}}{16}\left(n - n'(t)\right)$. This is a first-order differential equation in *n'*(*t*) with the initial condition *n'*(0) = 0. With the notation $K = \frac{\pi d^2}{4}\sqrt{\frac{RT}{2\pi}}$, it is easy to integrate the equation to the solution $n'(t) = n\left(1 - e^{-\frac{Kt}{\sqrt{M}}}\right)$. By applying this result for the two components of the gaseous mixture in the collector, one obtains: $\frac{n_1'(t)}{n_2'(t)} = \frac{n_1}{n_2}\frac{1-e^{-\frac{Kt}{\sqrt{M_1}}}}{1-e^{-\frac{Kt}{\sqrt{M_2}}}}$. Thus, for long times ($t >> \frac{\sqrt{M_{1,2}}}{K}$), the exponentials both drop to zero and the ratio of the concentrations of the components in the collector recovers the its original value in the source. On the contrary, for times short enough ($t < \frac{\sqrt{M_{1,2}}}{K}$), one may approximate the exponentials with the first two terms of their power expansions: $e^{-\frac{Kt}{\sqrt{M_{1,2}}}} \cong 1 - \frac{Kt}{\sqrt{M_{1,2}}}$. It is therefore obtained: $\frac{n_1'(t)}{n_2'(t)} = \frac{n_1}{n_2}\sqrt{\frac{M_2}{M_1}}$. Thus, if $M_2 > M_1$ and if the collection time is properly adjusted, one may get in the collector an increased relative concentration of the first gaseous component.

12.6 A thermally insulated and completely evacuated vessel is closed with a thin membrane that is pierced with a hole of diameter small compared to the mean free path of the gas molecules. A molecular beam is directed from the outside of the vessel towards the orifice. The beam is perfectly collimated and consists of identical molecules of mass m_0 traveling with the same velocity υ_0. The particle density in the beam is n_0. After a certain long time an equilibrium pressure P and temperature T values are established in the vessel. Find P and T.

Hint/Answer: Since the vessel is thermally insulated, the equilibrium is attaint when both the net molecular current and the net kinetic energy current vanish: $J_0 - J = 0$, $J_{e0} - J_e = 0$. It follows that $\frac{P\bar{\upsilon}}{4kT} = n_0\upsilon_0$ and $P\bar{\upsilon} = m_0 n_0 \upsilon_0^3$, so that $T = \frac{m_0\upsilon_0^2}{4k}$. Next, one easily gets: $P = \sqrt{\frac{\pi}{2}}\, n_0 m_0 \upsilon_0^2$.

12.7 Making use of the Maxwell distribution function, find <1/υ>, the mean value of the reciprocal of the velocity of molecules in an ideal gas at a temperature T, if the mass of each molecule is equal to m_0. Compare the obtained value with the reciprocal of the mean velocity.

Hint/Answer: $\left\langle \frac{1}{\upsilon} \right\rangle = \int_0^\infty \frac{1}{\upsilon} F(\upsilon)d\upsilon = 4\pi\left(\frac{m_0}{2\pi kT}\right)^{3/2}\int_0^\infty exp\left(-\frac{m_0\upsilon^2}{2kT}\right)\upsilon\, d\upsilon = \sqrt{\frac{2m_0}{\pi kT}} = \frac{4}{\pi}\frac{1}{\langle \upsilon \rangle}$.

12.8 Find the fraction of the number of molecules of a perfect gas at the temperature T, have the translation kinetic energies higher than a certain value ε_0 ($\varepsilon_0 >> kT$). ***Hint***: for $\varepsilon_0 >> kT$ one may write $\int_{\varepsilon_0}^\infty \sqrt{\varepsilon}\, e^{-\varepsilon/kT}\, d\varepsilon \cong \sqrt{\varepsilon_0}\int_{\varepsilon_0}^\infty e^{-\varepsilon/kT}\, d\varepsilon$.

Hint/Answer: The distribution function of molecules upon their translation kinetic energy is obtainable through the condition of probability invariance: $\widetilde{F}(\varepsilon)d\varepsilon = F(\upsilon)d\upsilon$. Since $d\varepsilon = m_0 \upsilon\, d\upsilon$, it follows that $\widetilde{F}(\varepsilon) = \frac{2}{\sqrt{\pi}}(kT)^{-3/2}\sqrt{\varepsilon}\, exp\left(-\frac{\varepsilon}{kT}\right)$. The requested fraction will be therefore (using the approximation indicated in the text):

$$\frac{\Delta N}{N} = \int_{\varepsilon_0}^{\infty}\widetilde{F}(\varepsilon)d\varepsilon = \frac{2}{\sqrt{\pi}}(kT)^{-3/2}\int_{\varepsilon_0}^{\infty}\sqrt{\varepsilon}\, exp\left(-\frac{\varepsilon}{kT}\right)d\varepsilon \cong 2\sqrt{\frac{\varepsilon_0}{\pi}}(kT)^{-3/2}\int_{\varepsilon_0}^{\infty}exp\left(-\frac{\varepsilon}{kT}\right)d\varepsilon =$$

$$= 2\sqrt{\frac{\varepsilon_0}{\pi kT}}\, e^{-\frac{\varepsilon_0}{kT}}.$$

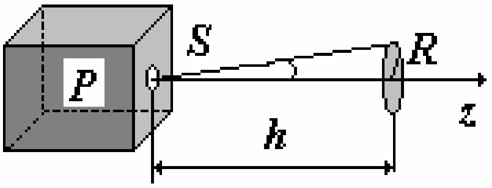
12.9 A closed tube containing carbon dioxide is rotated in a horizontal plane with the angular velocity ω around a vertical axis passing through one of its ends. The tube length is $l = 100$ cm and the overall temperature is $T = 300$ K. For which value of the angular velocity will the ratio of the gas densities at the tube ends equal the value $\eta = 2.0$?

Hint/Answer: The potential energy of a gas molecule in the centrifugal field is given by: $E_{p0}(x) = \frac{1}{2}m_0\omega^2 x^2$, where m_0 is the mass of the molecule and x is the distance from the rotation axis (the natural scaling of the potential energy is on the axis). Therefore, the Boltzmann distribution gives $\frac{n(l)}{n(0)} = exp\left(\frac{m_0\omega^2 l^2}{2kT}\right) = \eta$, wherefrom one readily obtains: $\omega = \sqrt{\frac{2RT}{Ml^2}ln\,\eta} = 280$ s^{-1}.

12.10 The potential energy of the molecules of a gas in a central field is of the form $U = a\cdot r^2$, $a > 0$. The gas temperature is T and the particle density in the center of the field is n_0. Calculate the following: (a) The number of gas molecules that can be found at distances between r and $r + dr$ from the center of the field. (b) The most probable distance that a molecule can have from the center of the field. (c) The fraction of the number of molecules that can be found at distances between r and $r + dr$ from the center of the field; (d) How many times will change the particle density in the center of the field if the temperature decreases η times. (e) The number of gas molecules whose potential energy ranges between U and $U + dU$. (f) The most probable value of the potential energy of a molecule. Compare this value with the potential energy of a molecule placed at the most probable distance from the center of the field.

Hint/Answer: (a) The Boltzmann distribution gives the local particle concentration in the external field: $n(\vec{r}) = n_0\, exp\left(-\frac{a\,r^2}{k\,T}\right)$. The requested number is therefore obtainable through integration over all orientations: $dN(r) = 4\pi\, n_0 r^2\, exp\left(-\frac{a\,r^2}{k\,T}\right)dr$. (b) The most probable distance, r_p, from the center of the field should maximize the previous distribution. Therefore, the vanishing of the first derivative of $r^2\, exp\left(-\frac{a\,r^2}{k\,T}\right)$ gives: $r_p = \sqrt{\frac{k\,T}{a}}$. The other root of the first derivative, namely $r = 0$, corresponds to a minimum of the probability. (c) The total particle number of the gas can be obtained by summing $dN(r)$ over all the space: $N = \int_0^\infty dN(r) = 4\pi\, n_0 \int_0^\infty r^2\, exp\left(-\frac{a\,r^2}{k\,T}\right)dr = n_0\left(\frac{\pi\, k\,T}{a}\right)^{3/2}$. Thus, assuming that this total number of particles is fixed, the density in the center of the field becomes temperature dependent: $n_0(T) = N\left(\frac{a}{\pi\, k\,T}\right)^{3/2}$. Then, the requested fraction becomes: $\frac{dN(r)}{N} = \left(\frac{a}{\pi\, k\,T}\right)^{3/2} 4\pi\, r^2\, exp\left(-\frac{a\,r^2}{k\,T}\right)dr$. (d) From the preceding results it readily follows that $\frac{n_0(T/\eta)}{n_0(T)} = \eta^{3/2}$. (e) The fraction computed at (c) represents the probability that a molecule can be found between r and $r + dr$. Thus, if we denote by $\varphi(U)\cdot dU$ the probability that a molecule can be found having the potential energy between U and $U + dU$, then probability invariance gives: $\frac{dN(r)}{N} = \varphi(U)dU$. Therefore, since $dU = 2\,a\,r\,dr$, one may write: $\varphi(U)2\,a\,r\,dr = \left(\frac{a}{\pi\, k\,T}\right)^{3/2} 4\pi\, r^2\, exp\left(-\frac{a\,r^2}{k\,T}\right)dr \Rightarrow \varphi(U) = \left(\frac{2}{k\,T}\right)^{3/2}\sqrt{\frac{U}{\pi}}\, exp\left(-\frac{U}{k\,T}\right)$. The number of gas molecules whose potential energy ranges between U and $U + dU$ will be then: $dN(U) = \varphi(U)dU = N\left(\frac{2}{k\,T}\right)^{3/2}\sqrt{\frac{U}{\pi}}\, exp\left(-\frac{U}{k\,T}\right)$. (f) The most probable value of the potential energy of a molecule, U_p, is obtainable through the maximum condition for the corresponding distribution $\varphi(U)$. One readily gets: $U_p = \frac{k\,T}{2}$. For comparison, $U(r_p) = k\,T = 2U_p$.

12.11 A small circular aperture of area S was pierced in the thin wall of a vessel containing a perfect gas (whose molecular translation velocities are distributed according the Maxwell distribution law). The pressure and temperature are kept constant inside the vessel at values of P and T, respectively. A circular disk of radius R faces co-axially the aperture in a parallel plane at a distance h apart. (a) Find the number of molecules (of individual mass m_0) that hit the disk in the unit of time. (b) Supposing that all the collisions to the disk are perfectly elastic, find the pressure exerted on it by the molecular beam leaving the vessel.



Hint/Answer: (a) The target disk "is seen" from the aperture at an angle θ_0, so that $tan\theta_0 = R/h$. The molecules that hit the disk are those who get out from the aperture at an angle less than θ_0. Therefore the desired collision rate of the disk can be found by suitably integrating the one-particle current: $\frac{dN}{dt} = S\int_0^{2\pi} d\varphi \int_0^{\infty} v^2 dv \int_0^{\theta_0} J^{(1)}(\vec{v}) f(\vec{v}) sin\theta\, d\theta$. If use is made of Eqs. (12.58) and (12.40) then this expression can be written explicitly: $\frac{dN}{dt} = 2\pi n S \left(\frac{m_0}{2\pi k T}\right)^{3/2} \int_0^{\infty} e^{-\frac{m_0 v^2}{2kT}} v^2 dv \int_0^{\theta_0} sin\theta\, cos\theta\, d\theta = n S \sqrt{\frac{kT}{2\pi m_0}} sin^2\theta_0$. In terms of pressure and of the geometrical configuration of the apparatus, one gets: $\frac{dN}{dt} = \frac{PS}{\sqrt{2\pi m_0 k T}} \frac{R^2}{R^2 + h^2}$. (b) Suppose that the aperture is covered. The force resulting from the elastic collisions of the molecules that hit the area S at angles less than θ_0 should equal twice the corresponding current of normal momentum: $F(\theta_0) = 2 J_p(\theta_0) S$, where $J_p(\theta_0)$ is the average current of molecular normal momentum brought by the molecules that hit the area S at angles less than θ_0 and the factor 2 appears from the momentum variation during an elastic collision of a molecule with the wall. The same force would be exerted on the disk when the aperture is opened. Therefore, the pressure on the disk will be $P_0 = \frac{F(\theta_0)}{\pi R^2}$.

The current $J_p(\theta_0)$ can be obtained by suitably averaging the one-particle current of transverse momentum from Eq. (12.60): $J_p(\theta_0) = n\,m_0\left(\frac{m_0}{2\pi kT}\right)^{3/2}\int_0^{2\pi} d\varphi \int_0^{\theta_0} \sin\theta \cos^2\theta \, d\theta \int_0^{\infty} \exp\left[-\frac{m_0 v^2}{2kT}\right] v^4 \, dv$.

That is, $J_p(\theta_0) = \frac{nkT}{2}\left(1-\cos^3\theta_0\right) = \frac{P}{2}\left[1-\frac{h^3}{\left(R^2+h^2\right)^{3/2}}\right]$. One then finally obtains:

$$P_0 = \frac{PS}{\pi R^2}\left[1-\frac{h^3}{\left(R^2+h^2\right)^{3/2}}\right].$$

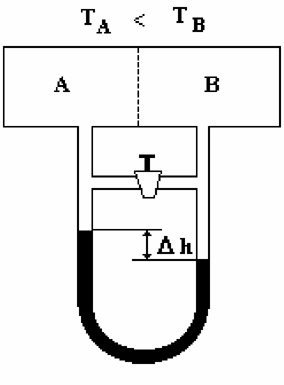
12.12 A cube of side *a* is moving with a speed *u*, parallel to one of its edges, in a rarefied atmosphere of density *ρ* (so small that the convective atmospheric movements can be completely neglected). Assume that the molecular collisions with the cube are perfectly elastic and that the mean velocity $\bar{v}$ of the molecules is known. Find the net resistance force against the cube motion in the following extreme cases: (a) The speed *u* is much smaller than the thermal velocity of the molecules in the neighboring atmosphere (resistance of the upper Earth atmosphere to the movement of satellites). (b) The speed *u* is much larger than the thermal velocity of the molecules in the neighboring atmosphere (resistance of the upper Earth atmosphere to the movement of incoming meteors).

Hint/Answer: Suppose that the *z* axis is directed along the cube velocity $\vec{u}$. The definitions of the one-particle currents (Eqs. (12.58)-(12.60)) should therefore contain the molecular speed relative to the wall moving with this velocity. Thus, the pressure exerted on such a wall by particles moving with the velocity $\vec{v}$ (elastic collisions) should be given by: $P^{(1)}(\vec{v},u) = \left|\begin{array}{ll} 2\,n\,m_0\left(v_z-u\right)^2, & for\ v_z > u \\ 0 & , for\ v_z < u \end{array}\right.$.

The total pressure on the back-face of the cube will be then: $P(u) = \int_{\mathbf{R}^3} P^{(1)}(\vec{v},u) f(\vec{v}) dv_x dv_y dv_z = 2\,n\,m_0\sqrt{\frac{m_0}{2\pi kT}}\int_u^{\infty}\left(v_z-u\right)^2 e^{-\frac{m_0 v_z^2}{2kT}} dv_z$. Similarly, the pressure on the front-face of the cube can be written as $P(-u) = 2\,n\,m_0\sqrt{\frac{m_0}{2\pi kT}}\int_u^{\infty}\left(v_z+u\right)^2 e^{-\frac{m_0 v_z^2}{2kT}} dv_z$ and the total pressure on the cube results from the corresponding difference: $P = P(-u) - P(u)$. Thus, since the integral $\int_{-u}^{u} e^{-\frac{m_0 v_z^2}{2kT}} v_z \, dv_z$ vanishes, one obtains: $P = 2\,n\,m_0\sqrt{\frac{m_0}{2\pi kT}}\left[4u\int_u^{\infty} e^{-\frac{m_0 v_z^2}{2kT}} v_z \, dv_z + \int_{-u}^{u}\left(v_z^2+u^2\right) e^{-\frac{m_0 v_z^2}{2kT}} dv_z\right]$, that is

$P = 2nm_0\left[u\bar{v}\,e^{-\frac{m_0u^2}{2kT}} + \sqrt{\frac{m_0}{2\pi kT}}\int\limits_{-u}^{u}\left(v_z^2+u^2\right)e^{-\frac{m_0v_z^2}{2kT}}\,dv_z\right]$. Now the two limiting cases can be considered: (a) $u \ll v_T = \sqrt{\frac{3kT}{m_0}} \Rightarrow \frac{m_0v_z^2}{2kT} < \frac{m_0u^2}{2kT} \ll 1$, so that $e^{-\frac{m_0v_z^2}{2kT}} \cong e^{-\frac{m_0u^2}{2kT}} \cong 1$. Therefore, $\int\limits_{-u}^{u}\left(v_z^2+u^2\right)e^{-\frac{m_0v_z^2}{2kT}}\,dv_z \cong \frac{8}{3}u^3$ and $P = 2nm_0\bar{v}u\left[1+\frac{8}{3}\sqrt{\frac{3}{2\pi}}\left(\frac{u}{v_T}\right)^2\right] \cong 2nm_0\bar{v}u$. The net resistance force against the cube motion will thus result through multiplication by the area of one of its faces: $F_{rez} = 2\rho a^2\bar{v}u$. Thus, at relatively low translation velocities of bodies in the upper Earth atmosphere, it is expected that the average resistance behave linearly with the displacement speed, like a force of Stokes type. (b) $u \gg v_T = \sqrt{\frac{3kT}{m_0}} \Rightarrow \frac{m_0u^2}{2kT} \gg 1$, so that $e^{-\frac{m_0u^2}{2kT}} \cong 0$ and both limits of the integral that enters the general expression of the total pressure can be safely extended to infinity: $\int\limits_{-u}^{u}\left(v_z^2+u^2\right)e^{-\frac{m_0v_z^2}{2kT}}\,dv_z \cong \int\limits_{-\infty}^{\infty}\left(v_z^2+u^2\right)e^{-\frac{m_0v_z^2}{2kT}}\,dv_z$. Therefore, $P \cong 2nm_0\sqrt{\frac{m_0}{2\pi kT}}\int\limits_{-\infty}^{\infty}\left(v_z^2+u^2\right)e^{-\frac{m_0v_z^2}{2kT}}\,dv_z = 2nm_0u^2\left(1+\frac{1}{3}\left(\frac{v_T}{u}\right)^2\right) \cong 2nm_0u^2$ and the net resistance force against the cube motion reads: $F_{rez} = 2\rho a^2u^2$. This is the kind of resistance expected for fast objects moving through the Earth's upper atmosphere (e.g. incoming meteors).

12.13 Consider the following experiment (Knudsen): a glass tube joins two compartments, A and B, of an evacuated vessel. A porous membrane separates the compartments of the vessel and the



two branches of the tube can be connected through a tap. A certain amount of mercury is present in the tube that can be used to measure the pressure difference in the two compartments of the vessel. These compartments are maintained at constant temperatures T_A, T_B, respectively ($T_A < T_B$). At a certain initial moment the tap is opened, so that the pressure equalizes in both parts of the apparatus. The tap is then closed again and, after some time, a level difference of mercury in the two branches, Δh, of the tube is observed to settle. Find the vapor pressure of mercury, P_A and P_B in the two compartments. The density ρ of the mercury is known and supposed approximately the same in the two branches of the tube.

Hint/Answer: The equilibrium condition between the mercury vapor in the two compartments is the equality of the molecular currents: $n_A \bar{v}_A = n_B \bar{v}_B \quad \Rightarrow \quad \frac{P_A}{\sqrt{T_A}} = \frac{P_B}{\sqrt{T_B}}$. Also, the mechanical equilibrium of the liquid reads: $P_A - P_B = \rho g \Delta h$. Therefore $P_A = \rho g \Delta h \frac{\sqrt{T_A}}{\sqrt{T_B} - \sqrt{T_A}}$ and $P_B = \rho g \Delta h \frac{\sqrt{T_B}}{\sqrt{T_B} - \sqrt{T_A}}$.

12.14 An effusion-based micro-propeller can be imagined to be used for driving space crafts in the gravitation-free inter-galactic vacuum. The device can be sketched as follows: a vessel of volume V is filled with an ideal gas of molar mass M at an initial pressure P_0. The mass of the empty vessel is m_1 and the external forces are negligible. Find the limit velocity of the vessel (initially at rest) after piercing one of its walls with a fine orifice of area S.

Hint/Answer: The evacuation of the vessel takes place due to the relative motion of the gas molecules. Hence it is not dependent on the overall speed of the device. If $n(t)$ and $P(t)$ are the instantaneous values of the particle density and gas pressure, respectively, then the rate of gas leakage from the vessel will be given by the outgoing molecular current times the area of the orifice: $V \dot{n}(t) = -\frac{1}{4} n(t) \bar{v} S$. Since the initial particle density is $P_0/(kT)$, the instantaneous value of n will be given by: $n(t) = \frac{P_0}{kT} e^{-\frac{S \bar{v}}{4V} t}$. The instantaneous mass of the container can be computed therefrom: $m(t) = m_1 + \frac{M P_0 V}{RT} e^{-\frac{S \bar{v}}{4V} t}$. Suppose that the instantaneous speed of the vessel is $u(t)$, which points towards the positive sense of the axis where the motion takes place. In a small time interval *dt*, a certain amount of gas |*dm*(*t*)| ($dm(t) = -\frac{M P_0 S \bar{v}}{4RT} e^{-\frac{S\bar{v}}{4V}t} dt$) is evacuated from the vessel. The mass |*dm*(*t*)| carries the ***relative*** momentum $-J_p S\,dt = -\frac{1}{2} n(t) S\,k\,T\,dt = -\frac{1}{2} P_0 S\,e^{-\frac{S\bar{v}}{4V}t} dt$. Therefore, its momentum in the absolute referential reads: $dp(t) = |dm(t)|u(t) - J_p S\,dt = \left(u(t) - \frac{2RT}{M\bar{v}}\right)\frac{M P_0 S\bar{v}}{4RT} e^{-\frac{S\bar{v}}{4V}t} dt$. Momentum conservation during this ejection event gives: $m(t)u(t) = [m(t) - |dm(t)|][u(t) + du] + dp(t)$, which, by neglecting infinitesimal terms of second order and by replacing *dm*(*t*) and *dp*(*t*) simplifies to $m(t)du = J_p S\,dt$, that is $du(t) = \frac{1}{2} P_0 S\left[m_1 + \frac{M P_0 V}{RT} e^{-\frac{S\bar{v}}{4V}t}\right]^{-1} e^{-\frac{S\bar{v}}{4V}t} dt$. A straightforward integration with the initial condition *u*(0)= 0 gives $u(t) = \frac{2RT}{M\bar{v}} ln\left(\frac{1 + \frac{m_1 RT}{M P_0 V}}{e^{-\frac{S\bar{v}}{4V}t} + \frac{m_1 RT}{M P_0 V}}\right)$, which in the long time limit turns out to: $u_{lim} = \sqrt{\frac{\pi R T}{2M}}\, ln\left(1 + \frac{M P_0 V}{m_1 R T}\right) = \sqrt{\frac{\pi}{3}}\, v_T\, ln\left(1 + \frac{M P_0 V}{m_1 R T}\right)$. It follows that the maximum attainable velocity is of the order of the thermal velocity of the molecules in the vessel.

12.15 ***Simplified model for the gas adsorbtion on a surface (Langmuir)*** [11]. Consider a surface with *M* adsorbtion sites where a variable number *N* of atoms are bound. We have necessarily $N \le M$. Each adsorbed particle is assumed to be bound to the surface with an energy *ε* (an inherently negative number) and to have no other degree of freedom. Each adsorbtion site can contain no more than one particle (this is actually like the adsorbed particles obey the Pauli exclusion principle of quantum mechanics). The two-dimensional "lattice gas" is supposed to be in relative equilibrium with a gas phase at pressure *P* and temperature *T*. Defining the average occupancy of available adsorbtion sites as *θ* = <*N*>/*M*, find the dependence of this parameter on the gas phase pressure, for a fixed temperature (the Langmuir isotherms).

Hint/Answer: The system (lattice gas) is controlled through the chemical and thermal contact with the gaseous phase and has a fixed "volume" (instead of volume one may take here the number of available sites *M* as properly quantifying the capacity of the space available to the system). It should therefore be described by a grand canonical distribution. Consider a microscopic state *ζ* of the system in which *N* particle are adsorbed. The system's total energy in this state will be therefore

$E(\zeta,N) = N\varepsilon$. The N particles can be arranged in the M locations in $\frac{M!}{(M-N)!}$ different ways, which apparently represent the number of different microscopic states that can be formed with the N particles. Let' take one of these states where the N atoms are arranged in N specified sites. According to the identity principle, the microscopic state is not changed if any permutation is performed among these atoms. Therefore, in order to account for this quantum correction, the number of states should be divided by the number of all the possible permutations of the N atoms, that is by $N!$. Thus, the real number of microscopic states that can be formed with the N particles will be $\frac{M!}{N!(M-N)!}$. To each such state it corresponds the energy $N\cdot\varepsilon$. The set of states $\Gamma(N)$ is a discrete one and the integral over ζ that appears in the expression (12.2) of the grand canonical partition function should be replaced by a summation. Since ζ has no continuous variation, no uncertainty correction will be needed: $Z = \sum_{N=0}^{M}\sum_{\zeta} exp\left(-\frac{E(\zeta,N)-\mu N}{kT}\right) = \sum_{N=0}^{M}\sum_{\zeta} exp\left(-\frac{\varepsilon N-\mu N}{kT}\right) = \sum_{N=0}^{M}\frac{M!}{N!(M-N)!}\left(e^{-\frac{\varepsilon-\mu}{kT}}\right)^{N}$. In the last sum one readily recognizes the expansion of the M-th power of a binomial: $Z = \left(1+e^{-\frac{\varepsilon-\mu}{kT}}\right)^{M}$.

Moreover, since $\Omega = -kT\,ln Z$ and $\langle N\rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,M}$, the average occupation number results in $\langle N\rangle = \frac{kT}{Z}\left(\frac{\partial Z}{\partial\mu}\right)_{T,M} = \frac{M e^{-\frac{\varepsilon-\mu}{kT}}}{1+e^{-\frac{\varepsilon-\mu}{kT}}} = \frac{M}{1+e^{\frac{\varepsilon-\mu}{kT}}}$, so that the average occupancy of available adsorbtion sites becomes $\theta = \frac{1}{1+e^{\frac{\varepsilon-\mu}{kT}}}$. Solving for the chemical potential, the preceding expression can be put under the following form: $\mu = \varepsilon + kT\,ln\frac{\theta}{1-\theta}$. On the other hand, one can use the expression (12.36) for the chemical potential of the gaseous phase, considered as an ideal classical gas in a region with vanishing external field: $\mu_{gas} = kT\,ln\left[n\left(\frac{h^2}{2\pi m_0 kT}\right)^{3/2}\right] = kT\,ln\left[\left(\frac{h^2}{2\pi m_0}\right)^{3/2}\frac{P}{(kT)^{5/2}}\right]$, where $n = \langle N_{gas}\rangle/V$ is the particle density of the gaseous phase. The relative equilibrium between the lattice gas and the gaseous phase implies that (see Eq. (11.63)) $\mu = \mu_{gas}$. Solving this equation for θ, one readily obtains:

$\theta(P,T)=\frac{P\,\chi(T)}{1+P\,\chi(T)}$, where $\chi(T)=\left(\frac{h^2}{2\pi\,m_0}\right)^{3/2}\frac{e^{-\frac{\varepsilon}{k\,T}}}{(k\,T)^{5/2}}$. For fixed temperature, the dependence of θ on the pressure in the gaseous phase is termed as a Langmuir isotherm and is seen to steadily increase from zero at low pressures towards a stationary value of one at high densities of the gaseous phase. On the other hand, the essential temperature dependence is seen to be steeply decreasing (since ε is a negative quantity). This explains the current experimental procedure of removing gas traces adsorbed on a surface by conveniently heating the corresponding material.

13. Fluctuations and stability of the equilibrium states of thermodynamic systems

An equilibrium state of a thermodynamic system can be obtained by imposing for a sufficient time some fixed external conditions. This can be done by using various macroscopically controllable constraints and weak interactions with various kinds of reservoirs. The thermodynamic equilibrium is reached when all the macroscopic parameters of the system begin to keep constant values in time. Nevertheless, from the microscopic point of view the macroscopic parameters represent statistical averages of some microscopic dynamical counterparts. It should therefore exist some microscopic level of experimental sensitivity for which a macroscopic parameter looks no more constant. Take for example the volume of a certain amount of gas. By a suitable external control (using a fixed-volume vessel), the system's volume cannot exceed a certain given value. But there is no guarantee that the actual gas volume remains all the time at that given value: due to disordered molecular motion the gas may always find itself in a real volume that is smaller than available. This fact becomes more visible when the gas density is significantly decreased and when such "fluctuations" in space occupation may even turn the concept of volume into a senseless parameter.

Therefore, ***even in a thermodynamic equilibrium state, the macroscopic parameters of a system are not strictly constant: their values are subject to fluctuations around some averages with various amplitudes, upon the specific condition of the system***. The fluctuations of the thermodynamic parameters have an intrinsic existence and they are due to the microscopic dynamics of the system's particles.

Usually the fluctuations do not have any influence on the average values of the macroscopic parameters. Such fluctuation phenomena ***are not natural processes*** because they do not lead to new thermodynamic equilibrium states, with new average values for the macroscopic parameters. ***A thermodynamic equilibrium state that may not be left spontaneously (that is through fluctuation processes) for another equilibrium state baring other values for the macroscopic parameters is termed as a stable thermodynamic equilibrium state*** [1]

Nevertheless, by suitably arranging the external conditions of a thermodynamic system, it may be brought in ***unstable equilibrium states***. The class of unstable equilibrium states is rather restraint and hardly available to experimental study since spontaneous fluctuations of sufficient amplitudes always exist and may switch the system to other average values of the macroscopic parameters, that is to other thermodynamic equilibrium states. Discussions on the stability of the thermodynamic equilibrium become particularly important, for example, in phase transition of substances where external conditions are brought to criticality so that any fluctuation may suddenly make dramatic structural changes [1, 2].

13.1 The stability of the equilibrium state of a thermodynamic system

We shall first discuss the consequences of the stability of the thermodynamic equilibrium. Starting from a state of stable equilibrium, the ***fluctuations will be considered as unnatural processes***. Also, the ***fluctuating variations of macroscopic parameters will be considered as very small (infinitesimal) with respect to their averages***.

Natural processes obey to The Second Law of Thermodynamics. In order to simplify the exposure, only simple one-component systems will be considered:

$$dS \geq \frac{1}{T}(dQ)_{rev} = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}d\nu \equiv (dS)^{ext} . \tag{13.1}$$

As fluctuations from stable equilibrium are unnatural processes, they are concluded with ***non-equilibrium states*** where at least some of the thermodynamic parameters become non-definable. Nevertheless, taking into account that the fluctuations are usually very small, the macroscopic parameters of the system may be considered as defined (at least in the statistical sense), even in such non-equilibrium states. An inequality opposite to (13.1) will therefore hold for unnatural fluctuating processes:

$$\boxed{dS - (dS)^{ext} = (dS)^{int} < 0}. \tag{13.2}$$

Moreover, if one supposes that the entropy is an analytic function in its variables, then its variation in a fluctuation process may be written as a series expansion over the powers of the corresponding variations for the arguments [3]:

$$\begin{aligned} dS = S(U+dU,V+dV,\nu+d\nu) - S(U,V,\nu) = \frac{\partial S}{\partial U}dU + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial \nu}d\nu + \\ + \frac{1}{2}\left[\frac{\partial^2 S}{\partial U^2}(dU)^2 + \frac{\partial^2 S}{\partial V^2}(dV)^2 + \frac{\partial^2 S}{\partial \nu^2}(d\nu)^2 + 2\frac{\partial^2 S}{\partial U\,\partial V}dU\,dV + \right. \\ \left. + 2\frac{\partial^2 S}{\partial U\,\partial \nu}dU\,d\nu + 2\frac{\partial^2 S}{\partial V\,\partial \nu}dV\,d\nu\right] + \frac{1}{3!}[Third\ order\ terms] + \ldots \end{aligned} \tag{13.3}$$

Since no confusion may arise, the specific indication of the variables that are kept constant during a differentiation was intentionally omitted for brevity. It should be stressed here that ***the analyticity hypothesis (that is the existence of the partial derivatives of any order) might work only for fluctuations around equilibrium states that are not close to critical points*** [4]. The range of our discussion will therefore be limited to such cases only. As a further simplification, one may consider neglecting the terms of order higher than second in the series expansion (13.3). The partial derivatives of the entropy with respect to U, V and v are taken in the stable equilibrium state. Therefore we have $\frac{\partial S}{\partial U}=\frac{1}{T}$, $\frac{\partial S}{\partial V}=\frac{P}{T}$ and $\frac{\partial S}{\partial v}=-\frac{\mu}{T}$. Thus, by suitably arranging the second order terms Eq. (13.3) becomes:

$$\begin{aligned} dS &\cong \frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv+\frac{1}{2}\frac{\partial}{\partial U}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dU+ \\ &+\frac{1}{2}\frac{\partial}{\partial V}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dV+\frac{1}{2}\frac{\partial}{\partial v}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dv= \\ &=(dS)^{ext}+\frac{1}{2}d\left((dS)^{ext}\right). \end{aligned} \tag{13.4}$$

So, by replacing this result in the fundamental inequality (13.2), one gets for unnatural fluctuating processes:

$$(dS)^{int}\cong\frac{1}{2}d\left((dS)^{ext}\right)<0 \quad\Rightarrow\quad d\left((dS)^{ext}\right)<0 \tag{13.5}$$

Using a new order of differentiation in the second order terms of Eq. (13.5) the expression of $d\left((dS)^{ext}\right)$ may be further detailed:

$$\begin{aligned} d\left((dS)^{ext}\right) &= \frac{\partial}{\partial U}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dU+\frac{\partial}{\partial V}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dV+ \\ &+\frac{\partial}{\partial v}\left[\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right]dv=\left[\frac{\partial}{\partial U}\left(\frac{1}{T}\right)dU+\frac{\partial}{\partial V}\left(\frac{1}{T}\right)dV+\frac{\partial}{\partial v}\left(\frac{1}{T}\right)dv\right]dU+ \\ &+\left[\frac{\partial}{\partial U}\left(\frac{P}{T}\right)dU+\frac{\partial}{\partial V}\left(\frac{P}{T}\right)dV+\frac{\partial}{\partial v}\left(\frac{P}{T}\right)dv\right]dV- \\ &-\left[\frac{\partial}{\partial U}\left(\frac{\mu}{T}\right)dU+\frac{\partial}{\partial V}\left(\frac{\mu}{T}\right)dV+\frac{\partial}{\partial v}\left(\frac{\mu}{T}\right)dv\right]dv=d\left(\frac{1}{T}\right)dU+d\left(\frac{P}{T}\right)dV-d\left(\frac{\mu}{T}\right)dv. \end{aligned} \tag{13.6}$$

However, the differentials of $1/T$, P/T and μ/T may be computed directly:

$$d\left(\frac{1}{T}\right)=-\frac{dT}{T^2};\quad d\left(\frac{P}{T}\right)=-\frac{P\,dT}{T^2}+\frac{dP}{T};\quad d\left(\frac{\mu}{T}\right)=-\frac{\mu\,dT}{T^2}+\frac{d\mu}{T}. \tag{13.7}$$

By replacing Eqs. (13.7) in (13.6) and by using the inequality (13.5) one further obtains (since T is a positive quantity):

$$-\left(\frac{1}{T}dU+\frac{P}{T}dV-\frac{\mu}{T}dv\right)dT+dP\,dV-d\mu\,dv=-(dS)^{ext}dT+dP\,dV-d\mu\,dv<0. \tag{13.8}$$

The differential form $(dS)^{ext}$ can be obtained from Eq. (13.4) as $dS - \frac{1}{2} d\left((dS)^{ext}\right)$ and, as the product $d\left((dS)^{ext}\right) dT$ is negligibly small (of the third order in infinitesimal variations), the preceding inequality may be written in the following final form [3]:

$$\boxed{dS\,dT - dP\,dV + d\mu\,d\nu > 0}. \tag{13.9}$$

Equation (13.9) is ***the necessary condition for an equilibrium state of a thermodynamic system consisting in a one-component fluid to be stable***. It can be easily extended, for example, to fluids with several components. When applying Eq. (13.9) no constraints are imposed to the fluid. Particular useful consequences of this equation arise when conditional equilibrium states are investigated. Some examples will be considered in what follows [3].

Suppose that the system's mass is fixed, $d\nu = 0$. If the volume fluctuations may be neglected ($dV = 0$), then Eq. (13.9) becomes:

$$(dS\,dT)_{V,\nu} > 0. \tag{13.10}$$

In fixed mass, fixed volume conditions S becomes a function of temperature only, so that Eq. (13.10) gives:

$$\left(\frac{\partial S}{\partial T}\right)_{V,\nu} > 0. \tag{13.11}$$

Now, recalling Eq. (9.10), Eq. (13.11) takes the following form:

$$T\,C_V > 0 \quad \Rightarrow \quad C_V > 0. \tag{13.12}$$

Thus, ***the thermodynamic equilibrium of a fluid at fixed mass would be unstable if its constant-volume heat capacity would be negative***. In other words, the positiveness of C_V for a fluid (already proved in Section (12.2) by statistical means) may also be looked at as a consequence of the stability of its thermodynamic equilibrium.

In a similar way, when the pressure fluctuations are negligible ($dP = 0$) in fixed-mass conditions ($d\nu = 0$), Eqs. (13.9) and (9.11) imply:

$$C_P > 0. \tag{13.13}$$

On the contrary, suppose that, besides the fixed value of the amount of substance, the temperature fluctuations of the fluid may be neglected ($dT = 0$). The volume becomes a function of pressure only and Eq. (13.9) reduces to:

$$(dP\,dV)_{T,\nu} < 0 \quad \Leftrightarrow \quad \left(\frac{\partial V}{\partial P}\right)_{T,\nu} (dV)^2 < 0 \quad \Rightarrow \quad K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\nu} > 0. \tag{13.14}$$

Also, when isentropic conditions are preserved ($dS = 0$) for a fixed-mass fluid Eq. (13.9) gives:

$$(dP\,dV)_{S,v} < 0 \quad \Leftrightarrow \quad \left(\frac{\partial V}{\partial P}\right)_{S,v} (dV)^2 < 0 \quad \Rightarrow \quad K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,v} > 0\,. \tag{13.15}$$

Therefore, ***the thermodynamic equilibrium of a fluid at fixed mass would be unstable if its isothermal or isentropic compressibilities would be negative***.

While more consequences of the stability of the thermodynamic equilibrium of a fluid (the so-called ***thermodynamic inequalities***) can be obtained, we content to conclude this section with an inequality resulting from neglecting the fluctuations of the fluid's temperature and volume. Only fluctuations in mass are allowed, which in a gas, for example, may arise from adsorbtion and desorbtion of molecules on the surface of the walls. Eq. (13.9) conduces to:

$$(d\mu\, dv)_{T,V} > 0 \quad \Leftrightarrow \quad \left(\frac{\partial \mu}{\partial v}\right)_{T,V} (dv)^2 > 0 \quad \Rightarrow \quad \left(\frac{\partial \mu}{\partial \rho}\right)_{T,V} > 0\,, \tag{13.16}$$

that is stability considerations imply that ***the chemical potential of a fluid should be an increasing function of its density ρ***.

13.2 The statistical theory of fluctuations in a thermodynamic system

Since the fluctuations of the values of the thermodynamic parameters in an equilibrium state of a system appear to be random events, one should obviously look for a statistical frame of their quantitative study. Among the most interesting related questions, the following may be cited as outstanding: 1) what is the "frequency" of apparition of a large-scale fluctuation that would endanger the structural stability of the system and how could be controlled this frequency by the external conditions; 2) how large may be the average amplitude of the fluctuations of a certain parameter of an apparatus in some given conditions and how these fluctuations may limit the precision of measurements made in these conditions (see Exercise 13.1 for an example).

General theories on fluctuations are available in the literature [1, 4, 5]. However, we shall content in these introductory lecture courses with the more intuitive derivation of Einstein [6], initially devised to explain the opalescence suddenly produced in a gas near the critical point (critical opalescence).

Consider a simple system enclosed in a rigid impermeable membrane, in thermal equilibrium with a thermostat. The system will be microscopically described by *a canonical distribution* and a stable equilibrium state will be characterized by a minimum of the free energy F. Let X be a macroscopic parameter of the system that is allowed to fluctuate around a certain average value. A macroscopic control is supposed to be exerted on X so that its value may be fixed or may range in a certain prescribed interval [4]. For example, if one takes for X the volume of the system then the rigid membrane allows V to be smaller than the prescribed volume of the enclosure. Let X_0 be ***the most probable value*** of X. Obviously, this value may differ from the average value of X, since the corresponding distribution is not necessarily symmetric. The most probable value of X should be also slightly different from the value corresponding to the stable state of equilibrium. For example, the most probable volume of a certain amount of gas should be slightly smaller than the maximum capacity of the container, since both positive and negative fluctuations of the gas volume are to be allowed.

To each imposed range of X it is supposed to correspond a collection of microscopic states $\Gamma(X)$. Since the probability that the system occupies a microscopic state ζ is $p(\zeta) = \frac{1}{Z} exp\left[-\frac{E(\zeta)}{kT}\right]$, the probability that the system takes for X the specified values becomes:

$$p(X) = \frac{1}{Z} \int_{\Gamma(X)} exp\left[-\frac{E(\zeta)}{kT}\right] g(\zeta) d\zeta . \tag{13.17}$$

Eq. (13.17) may be strictly valid (according to the probability principle) only if the system is in complete equilibrium. Obviously this is not the case if the parameter X is allowed to fluctuate, but the equilibrium probability formula is supposed to still hold (at least as long as the fluctuations remain small enough).

Denoting by

$$Z(X) = \int_{\Gamma(X)} exp\left[-\frac{E(\zeta)}{kT}\right] g(\zeta) d\zeta , \tag{13.18}$$

one may write:

$$p(X) = \frac{Z(X)}{Z} . \tag{13.19}$$

Also, by analogy with the fundamental formula $F = -kT \ln Z$, we may introduce the quantity:

$$F(X) = -kT \ln Z(X) . \tag{13.20}$$

So, the probability (13.19) becomes:

$$p(X) = \frac{1}{Z} exp\left[-\frac{F(X)}{kT}\right] . \tag{13.21}$$

The probability distribution of X, that is the probability that the macroscopic parameter X of the system to take values in some specified interval (X, $X + dX$), may be therefore obtained through differentiation:

$$dp(X) = -\frac{1}{Z}\frac{F'(X)}{kT} exp\left[-\frac{F(X)}{kT}\right] dX . \tag{13.22}$$

Since the probability must be positive with a maximum value at X_0, it follows that ***F(X) should be essentially decreasing function of X (-F(X)dX > 0), to a minimum F(X₀)***. Thus, $F(X)$ may be used to characterize the most probable behavior of the system's macroscopic state as a kind of free energy. The value of X_0 may be computed through the necessary extremum condition for the probability density of Eq. (13.22):

$$\left[\frac{F''(X_0)}{kT} - \left(\frac{F'(X_0)}{kT}\right)^2\right] exp\left[-\frac{F(X_0)}{kT}\right] = 0 \;\Rightarrow\; \frac{F'(X_0)}{kT} = -\sqrt{\frac{F''(X_0)}{kT}} . \tag{13.23}$$

For a state of macroscopic equilibrium it is usual [4] to ***approximate*** the second derivative of $F(X)$ in X_0 as the corresponding absolute value of the derivative of the free energy at thermodynamic equilibrium (the absolute value is needed since $F''(X_0)$ should be positive at the minimum of $F(X)$, while the derivative of the free energy may not be always positive):

$$F''(X_0) = \left| \frac{\partial^2 F}{\partial X^2}\bigg|_{thermodynamic\ equilibrium} \right| \equiv F_2 . \tag{13.24}$$

Moreover, Eq. (13.24) shows that, since the thermodynamic free energy is generally an extensive quantity (and therefore behaves proportionally with the particle number N), $F_2 = F''(X_0)$ should depend in a specific way on the number of particles in the system. Thus, if X is also an extensive parameter then F_2 should be proportional to $1/N$. Conversely, if X is an intensive quantity then F_2 should behave like F, that is proportionally to N:

$$F''(X_0) \sim \left| \begin{array}{l} \frac{1}{N}, \;\; if\ X\ is\ extensive \\ N, \;\; if\ X\ is\ intensive \end{array} \right. . \tag{13.25}$$

In any case, Eq. (13.25) implies that the dimensionless number $\frac{1}{X_0}\sqrt{\frac{kT}{F_2}}$ ***always behaves as*** $1/\sqrt{N}$ and be therefore much less than the unity for usually large systems.

By taking X_0 as a reference value of the parameter X one may write again (see Eq. (13.21)):

$$p_0 \equiv p(X_0) = \frac{1}{Z} exp\left[-\frac{F(X_0)}{kT}\right], \tag{13.26}$$

so that Eq. (13.21) may be put under the following form:

$$p(X) = p_1\, exp\left[-\frac{F(X)-F(X_0)}{kT}\right]. \tag{13.27}$$

Assuming that the system is not dominated by fluctuations, that is their amplitudes are relatively small, the difference $F(X)$ - $F(X_0)$ may generally be expanded in a Taylor series around X_0 (analyticity of the function $F(X)$ is also requested in order that this to be valid) and may be approximated by the first two terms of the expansion. If account is also taken of Eq. (13.23), one may write:

$$\begin{aligned}\frac{F(X)-F(X_0)}{kT} &\cong \frac{F'(X_0)}{kT}(X-X_0)+\frac{1}{2}\frac{F''(X_0)}{kT}(X-X_0)^2 = \\ &= \frac{1}{2}\frac{F_2}{kT}\left[(X-X_0)^2-2\sqrt{\frac{kT}{F_2}}(X-X_0)\right].\end{aligned} \tag{13.28}$$

This form of the exponent of Eq. (13.27) shows that the exponential should drop dramatically for departures of X from its most probable value. Therefore, if one restores the probability distribution of the values of X as was done in Eq. (13.22), the significant variation of this distribution will be in the exponential factor. The variation of the functional coefficient resulting from the differentiation of $F(X)$ being much smaller, it may be treated with a good approximation as a constant [4]:

$$dp(X) = p_2\, exp\left[-\frac{F(X)-F(X_0)}{kT}\right]dX. \tag{13.29}$$

Using the approximation of Eq. (13.28) and the symbol $X_1 = X_0\left[1+\frac{1}{X_0}\sqrt{\frac{kT}{F_2}}\right]$, Eq. (13.29) takes the form:

$$dp(X) = p_3\, exp\left[-\frac{1}{2}\frac{F_2}{kT}(X-X_1)^2\right]dX, \tag{13.30}$$

where p_2 is another convenient constant. This brings the probability distribution of the values of X to a normal (Gauss) form of the type (7.17). As demonstrated in Eq. (7.19), the average value of X is exactly X_1, which, as observed before, differs from X_0 by amounts proportional to $1/\sqrt{N}$. According to Eq. (7.21), the standard deviation of X from its average will be given by $\sqrt{\frac{kT}{F_2}}$ and therefore, the extent of ***the <u>relative</u> fluctuations of the system's parameter X in canonical conditions*** may be expressed as:

$$\boxed{\frac{\Delta X}{X_0} = \frac{1}{X_0}\sqrt{\frac{kT}{F_2}} \sim \frac{1}{\sqrt{N}}}, \tag{13.31}$$

where F_2 is given by Eq. (13.24) and for X_0 the value of the corresponding parameter at thermodynamic equilibrium may be taken. Eq. (13.30) shows that the probability of producing a fluctuation steeply increase with temperature. Also, Eq. (13.31) indicates that the amplitudes of the fluctuations increase with temperature, but should reduce to negligibly small relative values in very large systems.

As examples, we shall consider the ***fluctuations of volume and temperature*** in a simple thermodynamic system [7]. Thus, ***when X is the volume***, Eq. (13.24) gives:

$$F_2 = \left| \left(\frac{\partial^2 F}{\partial V^2} \right)_{T,\nu} \right| = -\left(\frac{\partial P}{\partial V} \right)_{T,\nu} = \frac{1}{V\, K_T},$$

so that

$$\frac{\Delta V}{V} = \sqrt{\frac{kT\, K_T}{V}} = \frac{1}{\sqrt{N}}\sqrt{n\,k\,T\, K_T}\ . \tag{13.32}$$

For a ***classical ideal gas*** ($K_T = 1/P$) this gives:

$$\frac{\Delta V}{V} = \sqrt{\frac{kT\, K_T}{V}} = \frac{1}{\sqrt{N}}. \tag{13.33}$$

When we take for X the system's temperature, Eq. (13.24) gives:

$$F_2 = \left| \left(\frac{\partial^2 F}{\partial T^2} \right)_{V,\nu} \right| = \left(\frac{\partial S}{\partial T} \right)_{V,\nu} = \frac{N\, C_V}{N_A\, T},$$

where C_V is the ***molar*** heat capacity at constant volume. Therefore we get:

$$\frac{\Delta T}{T} = \sqrt{\frac{k\, N_A}{N\, C_V}} = \frac{1}{\sqrt{N}}\sqrt{\frac{R}{C_V}}, \tag{13.34}$$

for any simple thermodynamic system.

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Exercises

13.1 A small body of mass m is suspended with a fine thread of length l in a gaseous atmosphere forming a gravitational pendulum. The overall temperature is T. As a result of molecular collisions with the body, the thread undergoes fluctuating deviations around the equilibrium position. Find the mean square deviation angle. Compute this deviation for $T = 300$ K $m = 1$ g and $l = 1$ m. Consider the same problem for a small mirror stuck on a quartz string that is stretched between two supports in a gaseous atmosphere: find the average twist angle of the mirror as a result of fluctuations. The elastic constant of torsion for the quartz string is $\gamma = 9.43 \cdot 10^{-16}$ Nm.

Hint/Answer: The gas and the pendulum may be considered as a thermodynamic reunion and the angular deviation of the thread from the vertical, θ, as an internal parameter (X) of the reunion. The pendulum is a zero-entropy component of the system and therefore the total free energy may be expressed as: $F = F_{gas} + m\,g\,l\left(1 - cos\,\theta\right) \cong F_{gas} + \frac{1}{2} m\,g\,l\,\theta^2$. Thus, Eq. (13.24) gives: $F_2 = m\,g\,l$. Then, the general formula (13.31) reads: $\Delta\theta = \sqrt{\frac{k\,T}{m\,g\,l}}$. For the given numerical data it follows that $\Delta\theta = 6.46 \cdot 10^{-10}$ radians, which allows the body to oscillate with a linear amplitude of 6.46 Å. This is obviously a completely unperceptive displacement from the macroscopic point of view. For the case of the quartz string the approach is similar: $F = F_{gas} + \frac{1}{2}\gamma\theta^2$, $F_2 = \gamma$ and $\Delta\theta = \sqrt{\frac{k\,T}{\gamma}}$. For the given numerical data $\Delta\theta = 2 \cdot 10^{-3}$ radians. The deviations of the mirror can be visualized by the angular deflection of a reflected light ray collected on a scale properly positioned away from the mirror [7]. The reflection takes place at angles that are twice the twist angle of the mirror, so that on a scale placed 1 m away one can clearly see 4 mm amplitude linear fluctuating oscillations of the light spot.

14. Equilibrium between phases

As was discussed in Chapter 13, the state of equilibrium of a thermodynamic system can be stable only when inequalities like (13.12)-(13.16) are satisfied. If the equations of state of a substance indicates that these inequalities break down at certain values of the thermodynamic parameters then the corresponding state fails to be stable and the system has to break up into separate phases (liquid and vapor, for example), to which other values correspond for the state parameters. From the microscopic point of view, the separation in phases leads to different structural organization of molecules over macroscopic regions of the occupied space. Thus, the system becomes a reunion of thermodynamic subsystems that are in full thermodynamic interaction. ***The macroscopic homogeneous parts containing molecules in a definite structural organization are termed as phases***. Each phase is supposed to occupy a definite volume and the total volume of the system is obtained by summing the volumes of its phases.

Usually, at constant pressure, one can pass through different phases of a substance by heating the material. This idea may lead to a convention for denoting the parameters corresponding to different phases. Thus, to each phase a numerical index is designated. ***If a phase j is obtainable from a phase i through absorption of energy (heating), then j > i***. For example, if we attach the index 0 to the solid phase of a material, then we should denote the liquid phase by the index 1 and the vapor phase by index 2.

14.1 The equilibrium between two phases of a substance. The Clausius-Clapeyron equation.

We shall focus first only on ***phases of pure substances***. When the system contains more than one component, reciprocal influences appear between the components, which we are not yet prepared to deal with.

Thus, consider two phases, *i* and *j*, of a given substance. The relative thermodynamic equilibrium between these phases implies the equality of the corresponding chemical potentials (see Section (11.5)) [1, 2]:

$$\mu_i = \mu_j . \tag{14.1}$$

Since each phase is supposed as chemically pure, the corresponding chemical potentials equal the molar Gibbs potential for each phase:

$$\frac{G_i}{\nu_i} = \frac{G_j}{\nu_j} \quad \Leftrightarrow \quad g_i = g_j . \tag{14.2}$$

As is already known, for a pure substance, $G = U + PV - TS = \nu\mu$, so that $g = \frac{G}{\nu} = u + P\upsilon - Ts = \mu$ is an intensive quantity that is independent of the number of moles of the given piece of material. Therefore *g* is a function of temperature and pressure only (remember that the natural variables of *G* are *T*, *P* and *ν*) and Eq. (14.2) may be written as:

$$g_i(T,P) = g_j(T,P). \tag{14.3}$$

Eq. (14.3) is essentially a relation that should be satisfied by the pressure and the temperature in the system in order to maintain the equilibrium between the two phases. Such a relation is usually called ***phase diagram***.

A more detailed analysis of a phase diagram may be performed if two neighbor states are considered to satisfy this condition [3]:

$$\begin{gathered} g_i(T+dT,P+dP) = g_j(T+dT,P+dP) \\ g_i(T,P) = g_j(T,P). \end{gathered} \tag{14.4}$$

Subtracting these equalities gives:

$$g_i(T+dT,P+dP) - g_i(T,P) = g_j(T+dT,P+dP) - g_j(T,P). \tag{14.5}$$

Expanding then both members in series of powers of the pressure and temperature variations and retaining only the linear terms, one obtains:

$$\left(\frac{\partial g_i}{\partial T}\right)_P dT + \left(\frac{\partial g_i}{\partial P}\right)_T dP = \left(\frac{\partial g_j}{\partial T}\right)_P dT + \left(\frac{\partial g_j}{\partial P}\right)_T dP. \tag{14.6}$$

But, as $dG = -S\,dT + V\,dP + \mu\,d\nu$, for the ***fixed*** value of ν = 1 mole, one should have $dg = -s\,dT + \upsilon\,dP$. Therefore, Eq. (14.6) becomes:

$$-s_i\,dT + \upsilon_i\,dP = -s_j\,dT + \upsilon_j\,dP,$$

or, in another form,

$$(\upsilon_j - \upsilon_i)dP = (s_j - s_i)dT. \tag{14.7}$$

Since, according to Eq. (14.3), on a phase diagram the pressure depends only on temperature, we may write Eq. (14.7) as:

$$\frac{dP}{dT} = \frac{s_j - s_i}{\upsilon_j - \upsilon_i}. \tag{14.8}$$

The variation of the molar entropy when passing from the phase *i* to the phase *j* takes place at some specified values of *T* and *P*. If multiplied by the corresponding equilibrium temperature this entropy variation gives the heat exchange that is necessary to cross the line of the phase diagram, from one phase to the other. This "amount of heat" is fixed for each kind of transition at some given values of *P* and *T* and should be a molar latent heat. It will be denoted by $\lambda_{i\to j}$:

$$s_j - s_i \equiv \frac{\lambda_{i\to j}}{T}. \tag{14.9}$$

For the reverse transition we'll have obviously $\lambda_{j\to i} = -\lambda_{i\to j}$. Therefore, Eq. (14.8) reads:

$$\boxed{\frac{dP}{dT} = \frac{\lambda_{i\to j}}{T\left(\upsilon_j - \upsilon_i\right)}}, \tag{14.10}$$

which is the most general form of the so-called Clausius-Clapeyron relation. This is essentially a differential equation for the corresponding phase diagram.

As a useful application we shall discuss the equilibrium of the vapor phase (*j*) with a condensate phase (*i*, liquid or solid) of a substance. The most important simplification arising in this case is the fact that the molar volume of the condensate, υ_i, becomes negligibly small with respect to the molar volume of the vapor phase υ_j. Moreover, the vapor molar volume can be estimated from the equation of state of the perfect gas, so that $\upsilon_j = \frac{RT}{P}$. Also, since the vapor phase is obtained from the condensate through heating, one may write $\lambda_{i\to j} \equiv \lambda_{vap} > 0$. Therefore, Eq. (14.10) becomes:

$$\frac{dP}{dT} = \frac{\lambda_{vap}}{T}\frac{P}{RT} \quad \Leftrightarrow \quad \frac{dP}{P} = -\lambda_{vap}\, d\left(\frac{1}{T}\right). \tag{14.11}$$

As the molar latent heat is a constant for not very wide temperature ranges, Eq. (14.11) readily integrates to:

$$\boxed{P(T) = P_0 e^{-\frac{\lambda_{vap}}{RT}}}, \tag{14.12}$$

where P_0 is the pressure in the system in some reference state.

Note: The vapor phase of a substance that is in equilibrium with a condensate phase of the same substance is termed as ***saturated vapor***. A useful numerical data that should be remembered in problems is for pure water: at normal pressure of the saturated vapor, P_0 = 1 atmosphere = $1.013\cdot10^5$ N/m^2, the corresponding equilibrium temperature should be 100 ^{0}C. Eq. (14.12) shows that the pressure of the saturated vapor steeply increases with temperature. If the overall pressure on the system at a certain temperature exceeds the pressure of the saturated vapor at that temperature then the vapor phase cannot appear. On the contrary, when the overall pressure is smaller than the corresponding vapor pressure, then the vapor phase is likely to appear. In the case of liquids, the apparition of the vapor phase may happen in all the points of the liquid if the overall pressure drops under the threshold of the vapor pressure at the given temperature. The current temperature of the liquid is then termed as the ***boiling point*** of the liquid at the given overall pressure. Vapor bubbles appear all over the occupied volume and the phenomenon is termed as liquid ***boiling***.

14.2 Number of phases of a mixture of several components: the Gibbs phase rule

Without entering into the details of the thermodynamic properties of mixtures, a simple algebraic argument can be used in order to obtain a relation referring to the possible number of different phases that can be simultaneously in equilibrium for such a mixture. Only ***ideal mixtures*** will be considered here (that is where the components do not chemically react).

The number of components will be denoted by K and the number of phases they can simultaneously form in equilibrium by F. It will be admitted that ***all the components are present in each phase***. Otherwise osmotic forces may appear at the interfaces between the phases and the mechanical equilibrium should be imposed with outside constraints (fixed walls between phases). Besides the temperature T and the overall pressure P the thermodynamic state of the system should be determined by the molar concentrations of the components. Let c_{fk} be the molar concentration of the substance k in the phase f (that is the ratio of the number of moles of k in the phase f to the total number of moles of the phase f). For each phase f one may therefore write [1, 3]:

$$\sum_{k=1}^{K} c_{fk} = 1 , \quad f = 1,2,\ldots,F . \tag{14.13}$$

The first index will always be reserved for indicating the phase (and will be denoted by f) and the second index will be linked to a component and will be usually denoted by k.

As the number of the molar concentrations is $K \cdot F$, the total number of parameters of the given system will be $K \cdot F + 2$.

All phases can communicate through each chemical channel corresponding to a component. The relative equilibrium between phases will therefore imply the equality of the chemical potential of a given component in every phase:

$$\mu_{1k} = \mu_{2k} = \ldots = \mu_{Fk} , \quad k = 1,2,\ldots,K . \tag{14.14}$$

For each k, the equalities (14.14) represent F - 1 relations between the state parameters of the system. One may therefore obtain $K \cdot (F - 1)$ relations of this type. Together with Eqs. (14.13) one gets therefore a system of $F + K\cdot(F - 1)$ relations between the $K\cdot F + 2$ parameters of the system. In order to ensure the compatibility the ***number of equations should not exceed the number of variables***:

$$F + K\left(F - 1\right) \leq K\,F + 2\,. \tag{14.15}$$

The inequality (14.15) readily simplifies to:

$$\boxed{F \leq K + 2}, \tag{14.16}$$

which represents the so-called ***Gibbs phase rule***. This inequality settles a limit to the number of different phases that can simultaneously be in equilibrium for an ideal mixture of K components. In particular, for a pure substance ($K = 1$), one obtains $F \leq 3$. In other words, for three phases of one component, three equations may be constructed, which provide a definite fixed value for each of the three state parameters of the system. This gives one and only one state: ***there exists only one definite thermodynamic state where three phases of a pure substance can be simultaneously in equilibrium***. This state is termed as the ***triple point*** of the given substance.

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Exercises

14.1 For the Knudsen apparatus described in the Exercise 12.13 find the molar latent heat of mercury as a function of the temperatures of the two compartments T_A, T_B.

Hint/Answer: Use Eq. (14.12) in the equilibrium equation $\frac{P_A}{\sqrt{T_A}} = \frac{P_B}{\sqrt{T_B}}$. It follows that

$$e^{\frac{\lambda_{vap}}{R}\left(\frac{1}{T_B}-\frac{1}{T_A}\right)} = \sqrt{\frac{T_A}{T_B}}\text{, and } \lambda_{vap} = R\frac{T_A T_B}{T_B - T_A}\, ln\sqrt{\frac{T_B}{T_A}}\,.$$

14.2 Given a box of air with wall temperature T_1. There is a small amount of water lying on the floor of the box, at equilibrium. The volume is V_1 and the pressure is P_1. The volume of the box is now slowly increased, keeping the temperature T_1 constant. When the volume has doubled $V_2 = 2\cdot V_1$ the water on the floor has essentially disappeared. (a) If $P_1 = 3$ atmospheres and $P_2 = 2$ atmospheres, what is the wall temperature T_1? (b) If the volume is doubled once more to $V_3 = 2\cdot V_2$, what will be the pressure P_3? (c) If V_2 = 44.8 liters, what is the mass of the water (liquid or vapor) in the box? What is the mass of air?

Hint/Answer: (a) The water vapor is saturated from the state 1 to the state 2. As the system's temperature remains constant, the same should be true for the vapor pressure: $P_{\upsilon 1} = P_{\upsilon 2}$. On the other hand, assigning the index *a* for the air component of the gas in the box, one may write the Boyle-Mariotte equation: $P_{a1}V_1 = P_{a2}V_2 \;\Rightarrow\; P_{a2} = \frac{1}{2}P_{a1}$. Therefore, for the states 1 and 2, one may write: $P_{\upsilon 1} + P_{a1} = P_1$ and $P_{\upsilon 1} + \frac{1}{2}P_{a1} = P_2$, wherefrom the following values result: $P_{a1} = 2\left(P_1 - P_2\right)$ = 2 atmospheres and $P_{\upsilon 1} = 2P_2 - P_1$ = 1 atmosphere. Since the water vapor is saturated in the state 1, we may conclude that the corresponding temperature should be 100 ^{0}C, that is T_1 = 373 K. (b) The process from the state 2 to the state 3 is governed by the Boyle-Mariotte equation for both gases in the system: $P_3V_3 = P_2V_2$. Therefore $P_3 = \frac{1}{2}P_2$ = 1 atmosphere. (c) By using the results of question (a) in the thermal equation of state for each gaseous component in the state 1, where the volume is $V_1 = V_2/2$ = 22.4 liters, one readily obtains that $v_{water} = v_{air}$ = 1.46 moles. Therefore m_{water} = 26.28 g and m_{air} = 42.34 g.

14.3 Find the boiling point of water on top of a mountain where the atmospheric pressure has a value equal to 0.9 that at sea level. (Molar latent heat of water is 40.698 J/mole.)

Hint/Answer: Eq. (14.12) can be used for both levels. By dividing both members of the obtained equations, one gets: $\frac{P_{mountain}}{P_{sea}} = 0.9 = e^{\frac{\lambda_{vap}}{R}\left(\frac{1}{T_{sea}} - \frac{1}{T_{mountain}}\right)}$. Assuming that the atmospheric pressure at the sea level is at the normal value then the corresponding boiling point T_{sea} = 373 K. Therefore, the boiling point on top of the mountain gives: $T_{mountain}$ = 370.2 K (97.0 ^{0}C).