Graduate courses in Physics

Thermodynamics & Statistical Physics

applied to Gases and Solids

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Preface

The script was developed for the course *Physical Chemistry and Thermodynamics o Solids* (SFI5769) offered by the Institute of Physics of São Carlos (IFSC) of the University of São Paulo (USP).

The course is intended for masters and PhD students in physics. The script is a preliminary version continually being subject to corrections and modifications. Error notifications and suggestions for improvement are always welcome. The script incorporates exercises the solutions of which can be obtained from the author.

Information and announcements regarding the course will be published on the website:
http://www.ifsc.usp.br/ strontium/ $->$ Teaching $->$ Semester

The student's assessment will be based on written tests and a seminar on a special topic chosen by the student. In the seminar the student will present the chosen topic in 15 minutes. He will also deliver a 4-page scientific paper in digital form. Possible topics are:
- The Legendre transform,
- The Bose-Einstein condensation.

The following literature is recommended for preparation and further reading:

Ph.W. Courteille, script on *Thermodynamics applied to gases and solids* (2024)

R.T. DeHoff, *Thermodynamics in Material Science*, Boca Raton: CRC/Taylor Francis (1985)

H.B. Callen, *Thermodynamics*, New York: Wiley (2006)

C. Kittel, *Introduction to Solid State Physics*, ed. Hoboken, New York: Wiley (2005)

A.R. West, *Basic Solid State Chemistry*, Chichester: Wiley (2006)

D. Mc Quarry, *Statistical Thermodynamics*, New York: Harper & Row (1973)

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Chapter 1

Foundations and mathematical formalism

Thermodynamics is a central branch of modern science, and its general laws govern the physical and chemical processes which occur in our world. An important early application of thermodynamics dealt with steam (or heat) engines, in which heat is converted to mechanical energy. Phenomenological thermodynamics was developed in the nineteenth and in the beginning of the twentieth century by Watt, Carnot, Clausius, Joule, von Helmholtz, Lord Kelvin, Nernst, Boltzmann, and Gibbs, culminating in the discovery of the Laws of Thermodynamics. These laws set general limits for the conversion of one form of energy, for example heat or chemical energy, to another one, for example mechanical work.

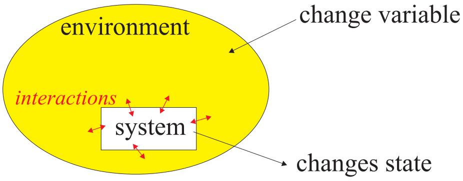

Figure 1.1: Reaction of a system to a sudden change in its environment.

The generic question addressed by thermodynamics is, how a given system responds to environmental changes. Indeed, the sudden modification of an environment will force the system to seek a new state of equilibrium, as illustrated in Fig. 1.1. On the other hand, thermodynamics is limited to describing equilibrium. It does not tell us step by step, *how* the new equilibrium is reached, only *what* the final state will be. Nevertheless, this is sufficient to establish complete *phase diagrams*, which are maps of equilibrium states. Fig. 1.2 shows as an example the phase diagram of water.

1.1 Phenomenological thermodynamics at equilibrium

To begin with, we consider each system as structureless glop endowed with properties to be identified and defined, such as temperature, pressure, composition, heat capacity, expansion coefficient, compressibility, entropy, and various measures of the system's energy. The minimum set of properties on which information is necessary to compute the state of the system depends on its complexity. For example, a unary system, i.e. an ensemble of identical particles belonging to the same species, is completely characterized by its heat capacity, expansion coefficient, and compressibility, while additional information is required for systems exhibiting several phases or made up of several chemical components, or even subject to chemical reactions [13].

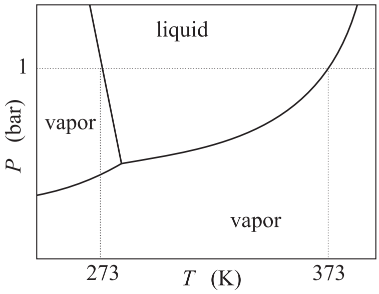

Figure 1.2: Phase diagram of water.

Fundamental concepts of thermodynamics, such as temperature, pressure, or heat have been unraveled before the discovery, that any type of matter consist of smallest components, atoms and molecules. The fact that heat flows from hot to cold bodies brought into contact is an everyday experience. *Joseph Michel and Jacques Etienne Montgolfier* demonstrated that hot air is lighter than cold air. And *James Watt* invented the steam engine before *Amedeo Avogadro* and *John Dalton* reintroduced the notion of the atom, which had initially been postulated by Democritus 500 A.C.. With the knowledge of the composition of any matter we could in principle give up the phenomenologically derived laws that represent the framework of thermodynamics. To characterize a system with N particles, we just need to specify the position and velocity of each particle as well as the forces acting between them or exerted by external fields. However, in the case of a macroscopic system, the number of particles is extremely large and this task becomes very difficult.

An alternative approach to the problem is to work with averaged values, which represent the behavior of a system as a whole. Let's embark on this approach by defining some macroscopic quantities that determine the state of the system. Let us consider a gas made up of N molecules in a container of volume V. Microscopically, the movement of each particle is rectilinear and uniform, until it collides with another molecule or with the walls of the container. This type of movement is called *Brownian motion*. The average distance that the particle travels between two successive collisions is called the *mean free path*.

The collisions of the particles with the walls of the container result in momentum transfers and, consequently, in an average force exerted onto the walls. Integrated over a surface, this force generates a pressure that the gas exerts on the walls, and despite its microscopic origin, the pressure represents a macroscopic quantity that describes an average property of the global system. Apart from pressure, other macroscopic quantities that are important for the description of a system are its volume, internal energy and temperature, the two latter ones being associated with the translational, vibrational and rotational movement of the particles. All these macroscopic quantities can be measured experimentally, and the objective of thermodynamics is to establish relationships between them, in order to predict the behavior of some quantities when other quantities are changed.

When the macroscopic properties of a system do not change over time, we say it is in *thermodynamic equilibrium*. In this case, the system of interest must be kept in contact with a second system, called a *reservoir* or *heat bath*, which determines the parameters of the equilibrium. The set of macroscopic quantities associated with a system in equilibrium is called a *macroscopic state*. It should be noted that the *microscopic state* of the system determines the macroscopic state, but the inverse does not hold, because from average values it is impossible to find $\mathbf{r}$ and $\mathbf{p}$ for all particles in the system.

Macroscopic quantities are somehow interconnected. To see this, we may consider a piston containing a gas, as schematized in Fig. 1.3(a), and heat it. As a consequence, the system temperature will increase. If we keep the position of the piston fixed, the pressure will increase, as well. If, on the other hand, we leave the piston moveable with friction, the volume will increase. Thus, both the increase in pressure and volume are consequences of an increasing temperature, from which we conclude that these quantities are, in some way, related.

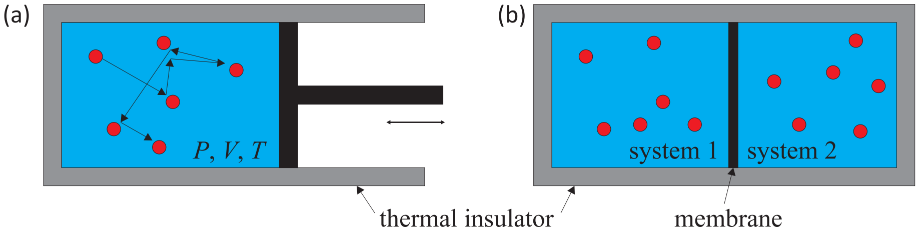

Figure 1.3: (a) Cylinder with a piston containing a gas. (b) Interaction between two systems through a wall.

If we have two systems in thermal contact, it is important to know in which way they interact. An interaction is often made through walls, as shown in Fig. 1.3(b). If the wall is at a fixed position and the temperature of one of the systems is varied, either (i) the temperature of the other system does not change, which is the case of a perfectly *insulating wall* (also called adiabatic wall) or (ii) the temperature of the other system follows the changes of the first and, which is the case of a *diathermal wall*. In case (ii), the temperatures of the two systems evolve, until they reach a common value. When the temperatures of the two systems are equal, the systems are considered to be at thermal equilibrium.

1.1.1 Temperature

Temperature is, in general, measured by observing some quantity which is sensitive to its variation. Defining a temperature scale on this quantity in a particular system, we construct a *thermometer*. An example is the *mercury thermometer*, where a certain volume of liquid mercury is placed in a capillary glass tube and the thermal expansion of mercury is observed as a function of temperature. The length L of the mercury column (usually calibrated in degrees Celsius) varies approximately linearly with temperature T, that is, $T = aL + b$, where a and b are two constants that depend on chosen reference temperatures. Conventionally, the melting temperatures of ice (triple point) at 0 °C and the boiling temperature of water at 100 °C are used, so that,

$$a = \frac{100}{L_v - L_g} \quad \text{and} \quad b = \frac{100L_g}{L_v - L_g} \ . \tag{1.1}$$

The *gas thermometer* illustrated in Fig. 1.4 is another possible realization, in which the volume of a gas is used as thermometric quantity.

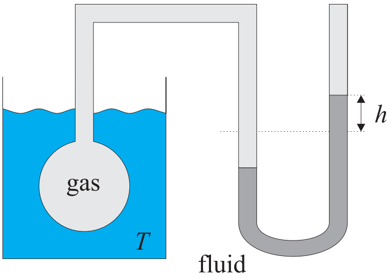

Figure 1.4: (a) Gas thermometer.

The aforementioned *Celsius* temperature scale is widely used in everyday life. In scientific applications, the *Kelvin* (or absolute) scale is mostly employed. We will see later, that it is based on microscopic properties of matter. The zero on this scale corresponds to the temperature at which all energy (except zero point fluctuations) is removed from the system. The scale is related to the Celsius scale through the expression: $T_K = \frac{1\,\mathrm{K}}{1\,^\circ\mathrm{C}} T_C + 273.15\,\mathrm{K}$. Another scale only used the USA is the *Fahrenheit* scale, which is related to the Celsius scale through the expression: $T_F = \frac{9\,^\circ\mathrm{F}}{5\,^\circ\mathrm{C}} T_C + 32\,^\circ\mathrm{F}$.

1.1.1.1 Ideal and real gases

The *equation of state* of a system is a mathematical relationship between the various macroscopic quantities that define the state of the system. In general, knowing the state equation allows to compute all thermodynamic properties of the system.

For gases with very low pressures, interactions between molecules in the system can be neglected. In this case, the gas is called *ideal* and the relationship between the macroscopic quantities that define its thermodynamic state is given by,

$$\boxed{PV = Nk_BT} \ . \tag{1.2}$$

where T is the absolute temperature (in K), N is the number of molecules contained in the volume V, and k_B is the Boltzmann constant. This is the most famous equation of state, and it is based on experimental observations of *Boyle*, *Mariotte*, and *Gay-Lussac*. Eq. (1.3) can also be written in terms of the number of moles, which is a quantity defined by $n = N/N_A$, where N_A is Avogadro's number. In this case,

$$PV = nR_gT \ , \tag{1.3}$$

where $R_g = N_A k_B = 8.314\,\mathrm{J/mol\ K} = 0.082\,\mathrm{atm}\cdot\mathrm{l/mol\ K}$ is called *universal gas constant*.

The gas thermometer and the barometric formula are examples of the numerous applications of the ideal gas law. In Excs. 1.1.4.1 and 1.1.4.2 we will study gas thermometers and in Excs. 1.1.4.3 to 1.1.4.6 applications of the barometric formula. Real gas models will be studied in Sec. 1.2.7.

1.1.2 Kinetic theory and microscopic interpretation of temperature

We will now develop a microscopic theory of temperature following a line of thought proposed by Maxwell. Let us consider a cubic box with volume V and surface A, and let us suppose that

(i) the gas is made up of a large number N of particles that collide elastically with each other and with the walls of the container;

(ii) there are no attractive forces between the particles (ideal gas approximation);

(iii) the movement is completely random, with no direction or position privileged.

We also disregard external forces. Since the movement is completely random, the average velocities are the same in the x, y, and z directions, $\bar{v}_x = \bar{v}_y = \bar{v}_z$, so that we may restrict our considerations to the x-direction.

Looking at a small portion of the gas in the vicinity of the wall (see Fig. 1.5), we can imagine that a large number of particles will collide with this wall. We divide the particles into i classes of velocities v_{xi}, each one filled with N_i particles. Because collisions with the wall are elastic, the momentum transferred when a single particle encounters the wall of the box is,

$$\Delta p_{xi} = 2mv_{xi} \ . \tag{1.4}$$

Since half of the particles move to the left, the number of collisions in the time interval Δt is given by,

$$\# = \frac{1}{2}\frac{N_i}{V}\,Av_{xi}\Delta t \ . \tag{1.5}$$

The total change of momentum is,

$$\Delta I = \Delta p_{xi}\# = \frac{N_i m v_{xi}^2 A\Delta t}{V} \ , \tag{1.6}$$

and the pressure is,

$$P_i = \frac{\Delta I}{A\Delta t} = \frac{N_i m v_{xi}^2}{V} \ . \tag{1.7}$$

Hence, as the movement is isotropic,

$$P = \sum_i P_i = \frac{m}{V}\sum_i N_i v_{xi}^2 \equiv \frac{m}{V}\overline{v_x^2} = \frac{N}{3V}m\overline{v^2} = \frac{2}{3}N\bar{E}_{kin} \ . \tag{1.8}$$

See Excs. 1.1.4.7 to 1.1.4.8.

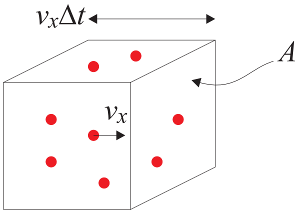

Figure 1.5: Box with N molecules colliding with the wall of a container.

Using the ideal gas state equation (1.3), Eq. (1.8) yields,

$$\boxed{\frac{3}{2}k_BT = \frac{mv^2}{2}} \ , \tag{1.9}$$

from which we conclude that temperature is associated with translational energy of ideal gas molecules. This expression is also known as the theorem of energy *equipartition theorem*. Generally speaking, we assign to each degree of freedom of a system the term $\frac{1}{2}k_BT$. In the example above, we have 3 degrees of freedom, which correspond to translations in the x, y and z directions. If energy can be stored in vibrations or rotations of a molecule, we also have to assign a term $\frac{1}{2}k_BT$ to each of these degrees of freedom.

> **Example 1 (*Johnson noise*):** As an example demonstrating the usefulness of the energy equipartition theorem, let us consider a resistor R subject to a certain temperature T. If we associate $\frac{1}{2}k_BT$ with the average power $\bar{P}_J$ dissipated by the resistor within a time Δt we have,
>
> $$\bar{P}_J\Delta t = \frac{\bar{U}_J^2}{R}\Delta t = \frac{1}{2}k_BT \Longrightarrow \bar{U}_J = \sqrt{\frac{k_BTR}{2\Delta t}} \ , \tag{1.10}$$
>
> that is, a small voltage $\bar{U}_J$ appears at the resistor terminals, which is known as *Johnson noise*. For a $1\,\Omega$ resistor at ambient temperature we find $\bar{U}_J \approx 4.0\,\text{nV}$ averaged over 1 second. This voltage is small, but must be taken into account in high precision measurements.

1.1.2.1 Thermal expansion

When we heat a solid, it generally changes size. This is due to the fact that the potential energy between its constituents, atoms or molecules idealized as being connected by springs, has non-harmonic terms, as shown in Fig. 1.6(a). As we increase temperature, we give more energy to the system and the atoms of the solid vibrate with great amplitude, producing on average a greater separation between the constituents of the system.

The variation in the length of a solid along a direction $i = x, y, z$ follows the law,

$$\Delta L_i = \alpha L_i \Delta T \ , \tag{1.11}$$

where α is called the linear expansion coefficient and characteristic for each material, as shown in Tab. 1.1, although it generally also depends on temperature. Consequently,

$$L_i = L_{i0}(1 + \alpha\Delta T) \ . \tag{1.12}$$

The surface expansion of a body is then, with $A = L_1L_2 = L_{10}L_{20} + 2\alpha L_{10}L_{20}\Delta T + L_{10}L_{20}\alpha^2\Delta T^2$ and assuming α to be very small,

$$\Delta A \simeq A_0 2\alpha\Delta T \ . \tag{1.13}$$

Similarly, volumetric expansion is described by,

$$\Delta V \simeq V_0 3\alpha\Delta T \ . \tag{1.14}$$

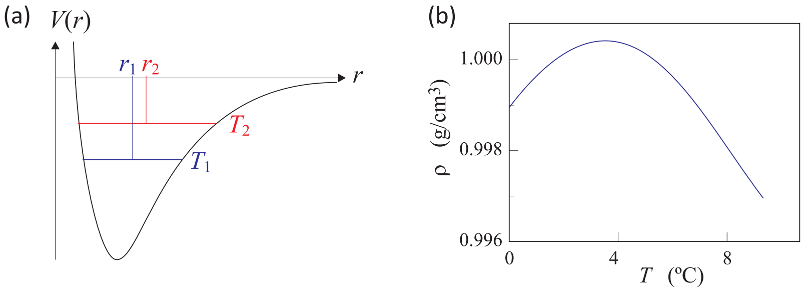

Figure 1.6: (a) Interaction energy between two atoms. (b) temperature-dependence of the density of water.

Table 1.1: Expansion coefficient, compressibility, and heat capacity coefficients ($C_P(T) = a + bT + c/T^2$) for selected materials at 298 K.

material	$\alpha \times 10^6$	$\kappa \times 10^7$	a	$b \times 10^3$	$c \times 10^{-5}$
	(K^{-1})	(bar^{-1})	(J/K)	(J/K^2)	(J K)
aluminum	23.5	12	20.7	12.3	-
silver	-	-	21.3	8.5	1.5
graphite	-	340	-	-	-
diamond	-	-	9.12	13.2	-
steel	11	-	-	-	-
invar	0.7	-	-	-	-
silica glas	22.2	42	15.6	11.4	-
tungsten	-	2.9	24.0	3.2	-
pyrex	32	-	-	-	-

Liquids and gases also undergo volume variations with temperature. In this case, it is quite common to work with the fluid density instead of volume:

$$\rho = \frac{m}{V} \quad \Longrightarrow \quad \Delta\rho = -\frac{m}{V^2}\Delta V = -\frac{m}{V^2}\gamma V\Delta T \ , \tag{1.15}$$

where γ is the volumetric expansion coefficient. Therefore, $\Delta\rho = -\gamma\rho_0\Delta$. In general, γ is positive and the density of the fluid decreases with temperature. An exception to this rule is the case of water, as shown in Fig. 1.6(b), which below 4 °C it has $\gamma < 0$ and thus, between 4 °C and 0 °C the density increases with the temperature. This explains why during winter lakes freeze starting from the surface. Do the Excs. 1.1.4.9 to 1.1.4.12.

1.1.3 Heat and work

When we place two bodies with different temperatures in thermal contact, there is a transfer of energy from one body to the other so that the two temperatures evolve towards a common value. The energy transferred is called *heat*. We cannot say that a body at a given temperature contains a certain amount of heat. Heat is the *change in energy* between one state and another. In this sense, heat is very similar to mechanical work, and we will denote this fact by assigning to both the symbol δ, that is δQ for heat changes and δW for work executed.

Analogously to mechanical inertia, a body has a certain heat inertia called *heat capacity*, which is the capacity of a body to retain thermal energy. The formal definition of heat capacity is,

$$\boxed{C \equiv \frac{\delta Q}{dT}} \ . \tag{1.16}$$

The unit of heat is the Joule J, but it is also very common to use the calorie, which is the amount of heat required to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C. The mechanical equivalent of a calorie is 1 cal = 4.184 J. The unit of heat capacity is therefore J/°C. Do the Exc. 1.1.4.13 to 1.1.4.14.

Instead of heat capacity, it is common to use the *specific heat* defined as,

$$c \equiv \frac{C}{m} \ , \tag{1.17}$$

where m is the mass of the system. Hence,

$$\delta Q = mc\, dT \ , \tag{1.18}$$

meaning that when a certain amount of heat is given to the system, this one increases its temperature. This expression, however, is not always valid. For example, upon phase transitions from solid to liquid or from liquid to gas, the temperature does not change when heat is supplied to the system. For a certain mass m of material, the heat supplied for the phase transition to occur is,

$$\delta Q = mL \ , \tag{1.19}$$

where L is called the *latent heat* of fusion or evaporation.

When several bodies are placed in thermal contact, heat flows between them in such a way that,

$$\sum_{i=1}^{N} \delta Q_i = 0 \ . \tag{1.20}$$

This is due to energy conservation, and this property is important for the determination of the specific heat of any of the bodies. When heat stops flowing, the bodies are all in thermal equilibrium and, in this case, the 0th law of thermodynamics applies: *If a body A is in thermal equilibrium simultaneously with bodies B and C, then B is in equilibrium with C.*

1.1.3.1 Heat transport

Heat can be transported in three different ways: through conduction, radiation or convection. In the case of *conduction*, although a material medium conducting the heat is needed, no mass is transported. In a solid, molecules in the hot part of the solid vibrate with large amplitudes and transmit this vibration via collision to neighboring molecules. In metals, conduction electrons also participate in the heat transport mechanism.

In the case of *convection*, heat is transported via displacement of masses. When part of a fluid is heated, density and/or pressure variations cause matter to move and carry heat from one volume to another. One already mentioned example is a freezing lake, where cold and therefore less dense water moves to the surface. When the fluid is forced to move due to the action of some external agent, for example a fan, we speak of forced convection.

The third way of transporting heat is through *radiation*. In this case, the presence of a material medium is not required to transmit energy. This transport is caused by (mostly infrared) electromagnetic radiation, which is emitted from any hot body.

In this following we will concentrate on heat transport through conduction. Let us consider a bar of cross section A and length L, whose ends are in thermal contact with two bodies of temperatures T_1 and $T_2 < T_1$, as shown in Fig. 1.7. For given position x along the bar, the amount of heat per unit of time (thermal current) crossing the surface A at that position depends on the following factors:

(i) Type of bar material. – There are materials that conduct heat better than others, e.g. copper conducts heat better than steel. A measure is provided by the thermal conductivity K.

(ii) The cross section A. – The larger it is, the greater the thermal current, as more atoms are participating in the conduction process.

(iii) The temperature gradient. – The thermal current depends on the difference in temperature between adjacent layers of atoms (left and right of the plane at position x).

Based on the above considerations, we can write the following expression for the thermal current H:

$$H = \frac{\delta Q}{dt} = -KA\frac{dT}{dx} \ . \tag{1.21}$$

If the bar is thermally insulated, as is the case in Fig. 1.7, the current is conserved, that is, all the heat entering one end of the bar will come out at the other, as there are no losses. In this situation, H is independent of x and, consequently, $\frac{dT}{dx}$ is constant. Hence,

$$\frac{dT}{dx} = \frac{T_2 - T_1}{L} \ , \tag{1.22}$$

and consequently,

$$H = KA\frac{T_2 - T_1}{L} \ . \tag{1.23}$$

In this case, the temperature distribution is a straight line, as shown in Fig. 1.7(b). On the other hand, if the side surface of the bar is not insulated, there will be heat losses by convection and the thermal current decreases as x increases. In this case, $\frac{dT}{dx}$ also decreases and, as a consequence, we have a temperature distribution like the one illustrated by the dotted line in Fig. 1.7(b).

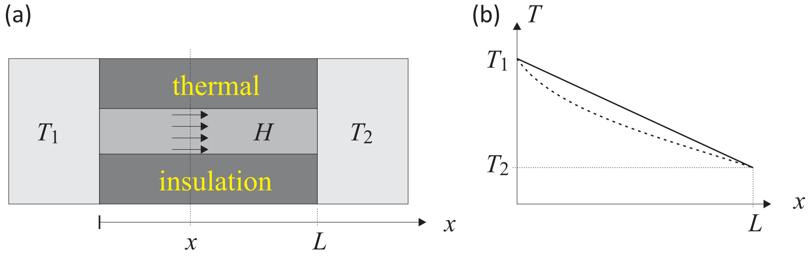

Figure 1.7: (a) Heat conduction through a laterally insulated bar. (b) Temperature distribution along an insulated bar (a) and not isolated (b) laterally.

We will now analyze two examples where the equation of conductivity (1.23) applies.

Example 2 (*Thermal conduction along rods*): In the first example, we will consider two bars having the same cross-section, but made of different materials and thus having different conductivities, as shown in Fig. 1.8(a). The bars are thermally insulated on their sides. We want to determine the temperature at the junction between the two bars. As the bars are insulated, the thermal current is constant and, therefore:

$$H = K_1 A \frac{T_1 - T}{L_1} = K_2 A \frac{T - T_2}{L_2} \ , \tag{1.24}$$

yielding,

$$T = \frac{K_2 L_1 T_2 + K_1 L_2 T_1}{K_2 L_1 + K_1 L_2} \ . \tag{1.25}$$

Substituting this in the expression for H we get,

$$H = \frac{K_1 K_2 A}{K_2 L_1 + K_1 L_2} (T_1 - T_2) \ . \tag{1.26}$$

In the particular case in which $K_1 = K_2$ we recover the result (1.23) derived for a single isolated bar. The temperature distribution along the bars depends on the ratio between K_1 and K_2. If $K_1 > K_2$, we have the temperature distribution shown in Fig. 1.8(b).

Example 3 (*Thermal conduction in a hollow cylinder*): As a second example, let us consider a hollow cylinder with outer radius b and inner radius a. The inner part of the cylinder is kept at a temperature T_1, while the external temperature is maintained at T_2 ($T_2 < T_1$). The length of the cylinder is L and the conductivity is K. The orientation of the thermal current is obviously radial. The area is given by $A = 2\pi r L$ and, therefore:

$$H = -KA \frac{dT}{dr} = -K 2\pi r L \frac{dT}{dr} \ . \tag{1.27}$$

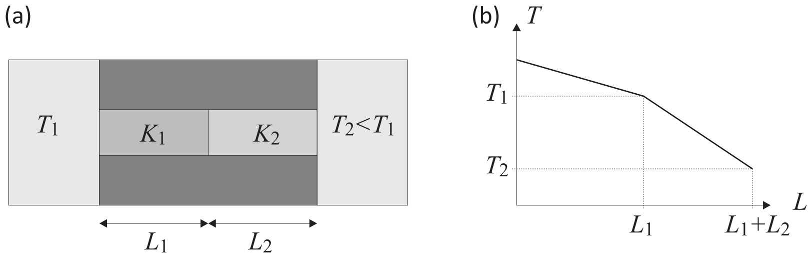

Figure 1.8: (a) Bars of different materials placed in series. (b) Temperature distribution along two bars of different materials placed in series.

> As H is constant, since there are no losses, we can integrate this equality between $a \leq r \leq b$ assuming $T_1 \geq T \geq T_2$. We find the result,
>
> $$H = \frac{2\pi LK}{\ln(b/a)}(T_1 - T_2) \ . \tag{1.28}$$

Let us now briefly cover the other two types of heat transmission mentioned in the beginning. In the case of convection, we are typically interested in the following type of problem: given a body at a temperature T surrounded by atmospheric air colder by an amount ΔT, how much heat does it lose per unit of time? The thermal current from the body to the air is described by a similar formula as thermal conduction,

$$H = hA\Delta T \ , \tag{1.29}$$

where A is the area through which heat is being lost and h is a number that depends on ΔT (in general $h \propto \Delta T^{1/4}$), the geometry of the body and its orientation in space (since convection is due to the fact that hot air rises). Therefore, a lying plate has a different h as compared to a standing plate.

Heat transport by radiation is proportional to T^4, where T is the absolute temperature (in Kelvin):

$$R = e\sigma T^4 \ . \tag{1.30}$$

Here, R is the thermal current emitted per unit area, e is the emissivity of the body ($0 \leq e \leq 1$), and σ is the Stefan-Boltzmann constant. Do the Exc. 1.1.4.15 to 1.1.4.18.

1.1.3.2 Work

Heat can be injected into a system in various ways, e.g. via thermal contact with a reservoir, via electrical dissipation or discharge, or by carrying out mechanical work. The amount of energy (translational, rotational and vibrational) contained in a system is called *internal energy*. The law of energy conservation demands that the heat δQ supplied to a system is used to change its internal energy E and/or to perform mechanical work δW. This principle is known as the 1st law of thermodynamics and can be expressed mathematically as:

$$\boxed{dE = \delta Q + \delta W} \ . \tag{1.31}$$

Let us consider an ideal gas contained in a cylinder with a piston, as shown in Fig. 1.3(a). By moving the piston, it is possible to compress or expand the gas, and in this process there will be pressure and/or temperature variation, since these variables are linked by the ideal gas equation (1.3).

Now, we imagine that the pressure P of the gas is greater than the atmospheric pressure. In this situation, the gas will try to push the piston out of the cylinder. If the piston slowly moves by a distance dx, the work done by the gas will be,

$$dW = Fdx = PAdx = PdV \ , \tag{1.32}$$

where A is the cross area of the piston and $dV = Adx$ is the variation of volume during expansion. Thus, if the gas expands from a volume V_1 to a volume V_2, the total work done is,

$$\delta W = \int_{V_1}^{V_2} PdV \ . \tag{1.33}$$

If we follow the evolution of pressure with volume on a PV diagram, as in Fig. 1.9(a), the work done by the gas will be the area under the curve. This area obviously depends on how the gas is taken from point 1 to point 2: the area under the path (i) is different from that under the path (ii). This means that work can be done along a closed path, as shown in Fig. 1.9(b): The system initially undergoes an isochoric transformation (constant volume), followed by a isobaric one (constant pressure), then again an isochoric, and finally an isobaric transformation. The area under the curve (i) corresponds to the work $P_1(V_2 - V_1)$, and the area under the curve (ii) to the work $P_2(V_1 - V_2)$. Although the processes are different, they produce the same variation in the internal energy of the gas $\Delta E = E_2 - E_1$, as this only depends on the initial and final states of the system. For a closed loop the total change in internal energy is zero, $\Delta E = 0$, and therefore, by the 1st law of thermodynamics, the transferred heat must compensate the executed work,

$$\delta W = -\delta Q \ . \tag{1.34}$$

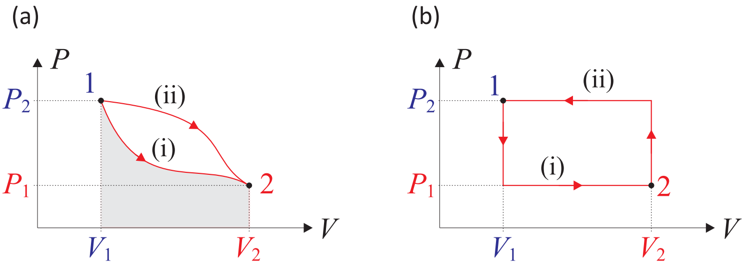

Figure 1.9: (a) PV diagram of a gas showing work carried out in two different processes leading from an initial state (1) to a final state (2). (b) Work performed in a complete gas cycle.

The internal energy of an ideal gas, as we discussed previously, essentially comes from the kinetic energy of its constituents,

$$\boxed{E = \tfrac{3}{2}Nk_BT} \ , \tag{1.35}$$

that is, for processes maintaining the temperature constant, $\Delta E = 0$. This relationship was experimentally verified by *Joule*, who found that when a gas adiabatically expands (without heat exchange nor work executed) its temperature stays constant.

After the warm up provided by the previous sections, let us now start setting up the framework of phenomenological thermodynamics in the following sections.

1.1.4 Exercises

1.1.4.1 Ex: Gas thermometer

A gas thermometer filled with an ideal gas and working at a constant volume is calibrated on the one hand in dry ice (carbon dioxide in its solid state at a temperature of $-80.0\,°\mathrm{C}$) and on the other hand in boiling alcohol ($78.0\,°\mathrm{C}$). At these respective temperatures, the pressure in the gas thermometer is $0.900\,\mathrm{bar}$ or $1.635\,\mathrm{bar}$. At absolute zero, the gas in the thermometer is still gaseous, but the pressure has dropped to $0.000\,\mathrm{bar}$.
a. At what °C is the absolute zero?
b. What is the pressure at the freezing point of water and what is it at the boiling point?

1.1.4.2 Ex: Gas thermometer

A gas thermometer 'a is connected to a second gas thermometer 'b, which is kept in a water bath at a constant temperature. The connecting capillary has a cross-sectional area A and is filled with mercury ($\rho = 13.5\,\mathrm{g/cm^3}$). At the same temperature T_0 in the two thermometers, the mercury level in both capillaries is the same. Now the gas in thermometer 'a' is heated by ΔT. This increases the pressure P_a and thus the volume $V_a \rightarrow V_a + \Delta V$. The mercury column is displaced accordingly.
a. What is the relationship between the volume increase ΔV and the temperature increase ΔT in this setup?
b. To simplify, assume that the volumes $V_a = V_b = V_0$ and thus the particle numbers $N_a = N_b = N_0$ are the same. How much has the temperature of the gas in thermometer 'a' increased if the following conditions exist in the coupled thermometer: $N_0 = 10^{22}$, $h = 5\,\mathrm{mm}$, $T_0 = 300\,\mathrm{K}$, $V_0 = 1000\,\mathrm{cm^3}$, $A = 1\,\mathrm{cm^2}$?

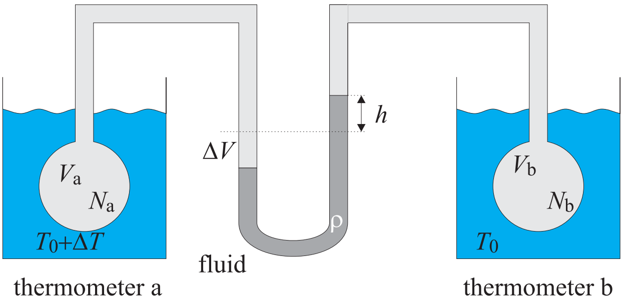

Figure 1.10: Gas thermometer.

1.1.4.3 Ex: Barometric formula

The air pressure P at a height h is equal to the weight mg of the air column, which at this height rests on an (imaginary) horizontal base divided by the base area A of the column ($m = m(h)$: mass of the air column, neglect the curvature of the Earth and the height dependence of the temperature). Therefore, we have for the change dP of the pressure upon a small change of height dh, with the local density $\rho = \rho(h)$:

$$dP = \frac{g\,dm}{A} = \frac{g\rho\,dV}{A} = -g\rho\,dh \ . \tag{1.36}$$

Here $dV = -A\ dh$ is the change in volume of the air column (located above the base). The air should be treated approximately as a substance with a uniform molar mass $\tilde{M}$.

a. Show with the help of the ideal gas equation that Eq. (1.36) can be cast into the form $dP = -kP\ dh$ under the given conditions with the constant k. Which is the expression for k?

b. What is the integral relationship $P = P(h)$? At what height h is the air pressure at $T = 273\,\mathrm{K}$ and $\tilde{M} = 29\,\mathrm{g/mol}$ only half the size of $P(0)$?

c. What is the air pressure on the Mont Blanc (4794 m) and the Mount Everest (8848 m) at $T = 273\,\mathrm{K}$ as compared to $P(0)$ at sea level? How big is the pressure difference ΔP compared to normal zero on the Tübingen market place ($h = 341\,\mathrm{m}$)?

1.1.4.4 Ex: Barometric formula

The barometric height formula is usually derived assuming constant temperature. Now suppose that the temperature depends on the height h above the surface of the Earth according to the relationship $T = T_0/(1 + \alpha h)$.

a. Show that the pressure p then must satisfy the following differential equation,

$$\frac{dP}{dh} = -\frac{mg}{k_B T_0}(1 + \alpha h)P \ .$$

b. Find the solution to this differential equation. What is the sign of the constant α? Is the pressure at a fixed height larger or smaller than the value resulting from the height formula at a fixed temperature?

1.1.4.5 Ex: Depth gauge

You want to build a depth gauge for diving operations and take advantage of the compressibility of air. To do this, you take a glass cylinder with a movable flask (volume $V = Ax$, footprint A) and a millimeter scale located in the flask. To what water depth h can the device deliver the targeted measuring accuracy of ±1 m, if the piston position x can be read with an accuracy of ±1 mm and $x(P_0) = 0.2\,\mathrm{m}$ at the water surface?

1.1.4.6 Ex: Scuba diving

A diver is at a water depth of h_0 and breathes air from a compressed air bottle. When exhaling, he creates (spherical) air bubbles with the volume V_0. Assume that

the surface water temperature is T_1 and decreases evenly to a depth of h_0 by an amount of temperature α per meter.
a. Assume a constant water density ρ and calculate the pressure P depending on the water depth at an atmospheric pressure P_1.

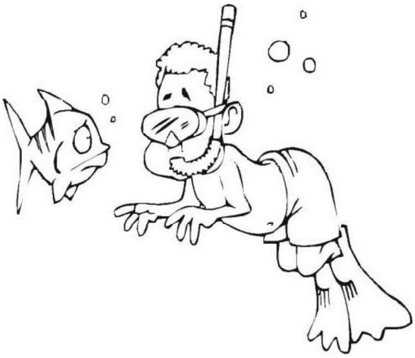

Figure 1.11: Jacques Mayol

b. Calculate the volume of the bubbles as a function of water depth. How big is the volume just below the water surface? Why is it important for the diver to exhale continuously as he ascends?
Numerical values: Water depth $h_0 = 40\,\mathrm{m}$, $V_0 = 1\,\mathrm{cm}^3$, $T_1 = 20\,°\mathrm{C}$, $\alpha = 0.2\,°\mathrm{C/m}$, $\rho = 1\,\mathrm{kg/l}$, and $P_1 = 1013\,\mathrm{hPa}$.

1.1.4.7 Ex: Particle collisions with a container

How many particle collisions Z does a wall surface $A = 1\,\mathrm{dm}^2$ experience in $\Delta t = 1\,\mathrm{s}$ at $T = 298\,\mathrm{K}$ and $P = 1\,\mathrm{bar}$ through the particles of an ideal gas, if $\langle |v_x| \rangle$, the mean value of the particle velocity in the x direction, has the value $330\,\mathrm{m/s}$?
Hint: Imagine a cuboid box in an xyz coordinate system and assume the wall surface of interest as one of the cuboid surfaces perpendicular to the x-axis. The width of the box is Δx, so its volume is $V = A \cdot \Delta x$. There is a simple relationship for the mean number $\langle \nu_x \rangle$ of impacts that a single particle does exert on the wall within a time Δt depending on Δx, Δt and $\langle |v_x| \rangle$. To get Z you have to consider that the gas contains N particles.

1.1.4.8 Ex: Kinetic pressure

A closed box with end face A and side length L is divided into two equal halves by a movable plate (see figure). Both halves contain one mole of helium under a pressure of P_0. The movable plate is now shifted to the right by the distance x. The shift takes place at constant temperature $T = 20\,°\mathrm{C}$.
a. Give the volume of the right or left sub-box as a function of x. Give the pressure in the right or left sub-box as a function of x.
b. Calculate the work W that needs to be done to move the plate from $x = 0$ to $x = L/4$. Specify W in Joules.

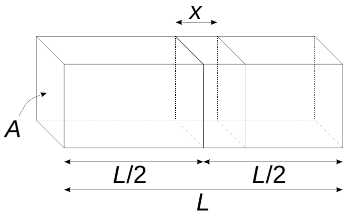

Figure 1.12: Ideal gas in a box.

1.1.4.9 Ex: Bi-metal

Two bars of different materials, with lengths, Young's modules and thermal expansion coefficients given respectively by L_1, L_2, Y_1, Y_2, α_1, and α_2, are pinched between two walls, as shown in the figure. Calculate the distance traveled by the junction point of the bars when the system is heated by an amount ΔT. What is the tension on the bars?

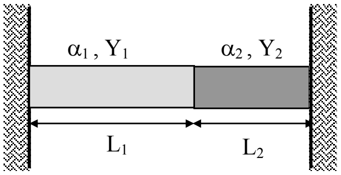

Figure 1.13:

1.1.4.10 Ex: Bi-metal

In the sketched construction two thin metal strips with different linear expansion coefficients (aluminum and copper) $\alpha_{Al} = 24 \cdot 10^{-6}\,\text{K}^{-1}$ and $\alpha_{Cu} = 17 \cdot 10^{-6}\ \text{K}^{-1}$ are connected to each other by $L = 10\,\text{cm}$ bars so that they have a fixed distance $d = 1\,\text{mm}$. When the temperature increases, the two strips expand so that they form circular segments with different radii, as shown in the figure. An angle of the circle segment of $\phi = 1°$ is measured. How big is the temperature increase?

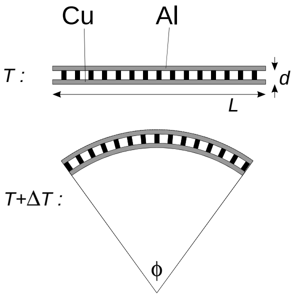

Figure 1.14: Bimetal.

1.1.4.11 Ex: Linear expansion

The length of a 10 cm long spacer made of quartz glass with linear expansion coefficient $\alpha_1 = -1\,\text{cm/m/}^\circ\text{C}$ is to be kept constant by using a spacer made of Invar steel with a linear expansion coefficient $\alpha_1 = 10\,\text{cm/m/}^\circ\text{C}$. How long must the spacer be?

1.1.4.12 Ex: Thermal expansion

Consider a solid body with momentum of inertia I. Show that due to a small temperature variation ΔT, this momentum varies by $\Delta I = 2\alpha\Delta T$, where α is the linear expansion coefficient. With this result, calculate how much the period of a physical pendulum varies when subject to a temperature variation ΔT.

1.1.4.13 Ex: Heat capacity and energy of air

a. How many air molecules are in one kilogram of air, knowing that air has the relative molecular mass $m_{air} \approx 29u$.
b. Supposing air is essential composed of oxygen and nitrogen, what is are the relative abundances of both elements.
c. Estimate the molar and specific heat capacities of air.
d. Calculate the kinetic energy as well as the average molecular velocity in 1 kg of air at $T = 300\,\text{K}$.

1.1.4.14 Ex: Calorimetry

a. A calorimeter initially contains a volume of $V_1 = 100\,\text{ml}$ of water in thermal equilibrium with the calorimeter at temperature $T_1 = 15\,^\circ\text{C}$. Now we add a volume $V_2 = 100\,\text{ml}$ of water at temperature $T_2 = 40\,^\circ\text{C}$. After reaching thermal equilibrium again, the temperature becomes $T_f = 25\,^\circ\text{C}$. What is the thermal capacity of the calorimeter?
b. Starting from the final condition of the previous item, we add to the calorimeter a metallic body with mass $m_3 = 80\,\text{kg}$ and temperature $T_3 = 90\,^\circ\text{C}$. After reaching thermal equilibrium again, the temperature becomes $T_{ff} = 35\,^\circ\text{C}$. What is the specific heat of the body?

1.1.4.15 Ex: Thermal conduction

Show that the thermal current in a substance of conductivity K located between the surfaces of two concentric spheres is given by:

$$\frac{dQ}{dt} = H = (T_1 - T_2)\frac{4\pi k r_1 r_2}{r_2 - r_1} \ ,$$

where r_1 and r_2 are respectively the radii of the inner and outer surfaces and $T_1 > T_2$.

1.1.4.16 Ex: Thermal conduction

A bar with thermal expansion coefficient α and Young's modulus Y $\left(\frac{F}{A} = Y\frac{\Delta L}{L}\right)$ is stuck between two walls, as shown in the figure. Calculate the stress in the bar when the temperature is increased by ΔT.

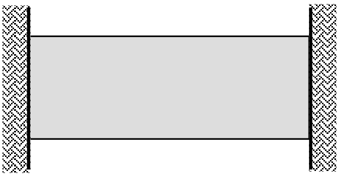

Figure 1.15:

1.1.4.17 Ex: Thermal conduction

Find the temperature gradient and thermal current in a bar of conductivity K, length L and irregular cross section, as shown in the figure.

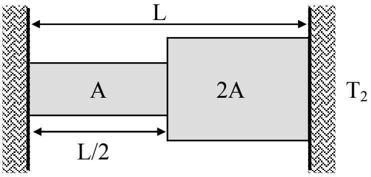

Figure 1.16:

1.1.4.18 Ex: Tramway

A tram with mass $m_B = 12500\,\mathrm{kg}$ brakes from a speed $v = 57.6\,\mathrm{km/h}$ to standstill. What is the temperature of the eight cast iron brake blocks when the mass of each block is $9.0\,\mathrm{kg}$ and 60% of the kinetic energy flows into the heating of the blocks?

1.2 Canonical formulation of thermodynamics

Thermodynamics is different from other physical theories, such as classical mechanics, electrodynamics or quantum mechanics, in the sense that it describes phenomena emerging from the presence of large numbers of identical (microscopic) subsystems, which are absent in the individual subsystems, in particular the tendency of large (macroscopic) systems to evolve towards certain equilibrium states. This claim makes thermodynamics pervasive and applicable to all kind of systems that can appear to be completely different. Its task is to provide a way of organizing information on systems' behavior, generating phase diagrams and data bases on their physical and chemical properties.

Following textbook didactics we approach the area of thermodynamics in two main steps. The first step, outlined in the present chapter 1, is known as *phenomenological thermodynamics*. It ignores the microscopic composition as far as possible. We will, however, see that certain features of the microscopic subsystems can have crucial impact on the macroscopic behavior. This step attempts to structure the macroscopic observations by identifying characteristic physical quantities and formulating laws governing their dynamics.

In the second step, exposed in the subsequent chapter 2, is called *statistical thermodynamics*. It aims at explaining the laws found in phenomenological thermodynamics by deriving them from features of the microscopic subsystems. In particular, some subsystems are small (or cold) enough to behave according to the rules of quantum mechanics, and this can have an important impact on the macroscopic behavior. This is studied in the field of quantum statistics exposed in Sec. 2.2.

The methods introduced in the first two chapters will be illustrated with simple examples (mainly ideal gases and solids). In Chp. 3 we apply them to complex real systems, e.g. multi-component, heterogeneous, or chemically interacting systems.

1.2.1 Tackling thermodynamic systems

The subject of thermodynamics are many-body *systems* the properties of which are characterized by physical quantities, called *thermodynamic variables*, and their *relationships*. We will now attempt to structure the fundamental concepts of the field following the textbook of DeHoff [13].

1.2.1.1 Classification of thermodynamic systems

Before starting to tackle a new unknown system, trying to characterize all of its properties, it is always a good idea to classify them in order to identify those properties which are essential for the information we want to extract from the system. This prevents a waste of efforts into gathering irrelevant data and provides a guideline for the system's characterization. In general a system can be

1. *unary* or *multicomponent* (e.g. a gas of pure argon or atmospheric air),
2. *homogeneous* or *heterogeneous* (e.g. a single phase or two coexisting phases like water and vapor),
3. *closed* or *open* (e.g. isolated from environment or exchanging energy or particles),
4. *non-reacting* or *reacting* (e.g. the molecules of a two-component system may react to form a third component),
5. otherwise *simple* or *complex*.

At first we will exemplify the introduced concepts mostly restricting to unary, homogeneous, non-reacting, otherwise simple systems. In later sections, we will turn our attention to complex systems.

1.2.1.2 State functions and process variables

Thermodynamic variables fall into two distinct classes, *process variables* and *state functions*.

The state of stationary thermodynamic systems may be expressed by *state functions* (or state variables), whose values only depend upon the current state of the system. The most common ones are temperature, pressure, entropy, volume, particle number, chemical potential, and internal energy,

$$T, S, P, V, N, \mu \ . \tag{1.37}$$

The pressure and volume may be replaced by other mechanical variables. Their equilibrium dynamics is confined to trajectories obeying so-called *state equations*, that is, functional relationships such as,

$$f(T, S, P, ...) = 0 \ , \tag{1.38}$$

or their illustration in phase diagrams, such as the one shown in Fig. 1.2. Such state equations are obviously extremely useful, as they allow to abstract from the physical process which led to a particular state of a system, and which might be very complicated. In fact, their discovery represents one of the major achievements of thermodynamics.

In contrast to state functions, the values of *process variables* depend upon the path followed by the process. Consequently, they only have a meaning for changing systems, i.e. for systems traversing a sequence of different states. The process variables fall into two category, *mechanical work* and *exchanged heat*,

$$\delta Q, \delta W \ . \tag{1.39}$$

The concept of *work* is developed in classical mechanics as the path integral over a force acting on a body along a given path, $W = \int_{\mathcal{S}} \mathbf{F}(\mathbf{s}) \cdot d\mathbf{s}$, and it can be brought into the context of thermodynamics considering, e.g. a piston working against the pressure of a confined gas, as illustrated in Fig. 1.3. Work depends on changes $d\mathbf{s}$ and thus cannot be associated with stationary systems. Any of the forces known in physics, inertial forces in accelerated or rotating systems, electromagnetic forces, or molecular forces, can work.

Work is associated with a displacement of macroscopic matter, e.g. the movement of a piston. Systems may, however, *exchange energy without net displacement of masses via the exchange of heat.* By itself the notion of a 'quantity of heat' in a system is meaningless. Only the amount of heat exchanged with another system in a given process can be quantified.

1.2.1.3 Extensive and intensive properties

State functions can further be classified into extensive and intensive variables of the system. To understand the difference, we imagine the system under consideration subdivided into smaller, identical and not interconnected subsystems. Now, an *intensive variable* describes a *global property*, i.e. a property that does not depend on the system size or the amount of material in the system, for example, temperature or the hardness of an object. No matter how small a diamond is cut, it maintains its intrinsic hardness. Intensive variables are those which can be represented as a *field*, such as the local temperature variation $T(\mathbf{r})$ across the system or the pressure variation in the barometric formula. Nevertheless, intensive properties can also be derived from extensive ones via the concept of *densities*, e.g. the local particle density $n(\mathbf{r}) \equiv dN/dV$. In general, the ratio of two extensive properties is scale-invariant and hence an intensive property.

Examples of intensive parameters are: the chemical potential, concentration, density (or specific gravity), ductility, elasticity, electrical resistivity, hardness, magnetic field, magnetization, malleability, melting point and boiling point, molar absorptivity, pressure, specific energy.

By contrast, an *extensive variable* adds up when independent, non-interacting subsystems are combined. The property is proportional to the amount of material in the system. For example, both the mass and the volume of a diamond are directly proportional to the amount that is left after cutting it from the raw mineral. Mass and volume are extensive properties. An extensive variable characterizes the system as a whole, e.g. the volume of a recipient, the number of enclosed particles, the internal energy or the entropy.

In uniform systems the value of intensive variables does not change, so that the system is characterized by a unique value. This is useful for the description of systems in equilibrium. However, it does not mean that intensive quantities turn into extensive ones. Intensive properties cannot exclusively depend on extensive ones. For example, in the ideal gas equation extensive and intensive quantities are interrelated in such a way that the two intensive quantities $P = P(\mathbf{r})$ and $T = T(\mathbf{r})$ are proportional to each other. Extensive properties can be expressed as integrals of intensive ones over the extend of the system, e.g. $N = \int_V n(\mathbf{r}) d^3r$.

Examples of extensive parameters are: energy, entropy, Gibbs energy, length, mass, particle number, momentum, number of moles, volume, magnetic moment, electrical charge, weight.

1.2.1.4 Classification of thermodynamic relationships

The thermodynamic variables characterizing a system, the state function as well as the process variables, are interrelated by mathematical expressions, and the apparatus of thermodynamics allows to generate connections between new sets of variables, thus leading to an unmanageable number of expressions. It is thus helpful to introduce a classification of thermodynamic relationships into

1. *thermodynamic laws* forming the physical basis for all other relations;
2. *definitions* of new quantities expressed in terms of previously formulated variables with the motivation of simplifying the description of specific classes of systems;
3. *coefficient relations* between differential forms emerging from the description of changes in state function;
4. *Maxwell relations* relating second derivatives to one another and reflecting the fact that the order of differential operators can be switched; and finally
5. *equilibrium conditions*, which are sets of equations describing the relationships between state functions to be satisfied in a system at equilibrium and used for establishing maps and phase diagrams.

The concept of equilibrium is central to thermodynamics. It describes a situation in which a system coupled to an environment *does not change its state autonomously.* The situation is expressed by a set of equations called equilibrium conditions, relating internal properties of the system.

Example 4 (*Thermodynamic relationships*): Examples for definitions are,

$$H \equiv E - PV \qquad \text{or} \qquad C_P \equiv \left(\frac{\partial E}{\partial T}\right)_{N,P} .$$

An example for a coefficient relation emanating from the real gas equation $T = T(P,V) = \frac{1}{Nk_B}(P+P^*)(V-V^*)$ is,

$$dT = AdP + BdV = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV = \frac{V-V^*}{Nk_B}dP + \frac{P+P^*}{Nk_B}dV .$$

An example for a Maxwell relation using the above example is,

$$\left(\frac{\partial A}{\partial V}\right)_P = \left(\frac{\partial}{\partial V}\left(\frac{\partial T}{\partial P}\right)_V\right)_P = \left(\frac{\partial}{\partial P}\left(\frac{\partial T}{\partial V}\right)_P\right)_V = \left(\frac{\partial B}{\partial P}\right)_V .$$

Finally, an example for an equilibrium condition considering a mixture of two gases A and B, is the request that their temperatures be equal, $T_\text{A} = T_\text{B}$.

1.2.2 The laws of thermodynamics

The laws of thermodynamics are highly condensed expressions forming the basis of empirical thermodynamics. Although not deduced from fundamental principles, they are universal, general, and pervasive. Before discussing them in detail, let us enunciate them altogether:

0. The zeroth law affirms that two systems each one in thermal equilibrium with a third are in equilibrium themselves,

$$\boxed{T_1 = T_2 \;\wedge\; T_2 = T_3 \quad\Longrightarrow\quad T_1 = T_3} . \tag{1.40}$$

1. The first law states that the total energy is always conserved,

$$\boxed{dE = \delta Q + \delta W} . \tag{1.41}$$

2. The second law states that the entropy of any closed system goes always increasing,

$$\boxed{dS \geq 0} . \tag{1.42}$$

3. The third law states that for $T \to 0$, the entropy difference between systems connected by a reversible process vanishes,

$$\boxed{\lim_{T\to 0} S = 0} . \tag{1.43}$$

This last law has its origins in quantum mechanics.

1.2.2.1 The 0th law of thermodynamics

The zeroth law is a necessary assumption for the existence of a temperature scale for all substances in nature and provides an absolute measure of their tendencies to exchange heat, as already discussed in Sec. 1.1.3.

1.2.2.2 The 1st law of thermodynamics

According to the first law of thermodynamics, there is a property of the universe, called energy, which cannot change no matter what process occurs. The energy can, however, change its appearance (e.g. between kinetic, potential of internal energy), or be exchanged between subsystems or between a system and its environment across the system's boundaries. Hence, defining a thermodynamic state function called *internal energy* E of the system, the first laws states that this quantity can only increase by working on the system or by transferring heat to it. Put in this way, the statement also fixed the sign convention, see Fig. 1.17.

It its mathematical formulation the differential d represents a change in a state function, while the prefix δ just denotes an infinitesimal quantity of work or heat, but cannot be considered a differential: There is no mathematical state function W or Q of which dW or dQ could be a differential.

Despite its fundamental importance, in its form (1.41) the first law is not ready for use in practical applications, because it does not tell us how to evaluate δW or δQ.

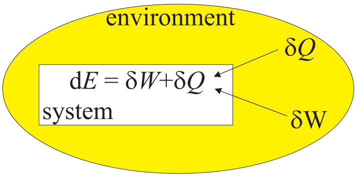

Figure 1.17: Any change of a system's internal energy is due to either work done on it or heat transferred through its borders.

1.2.2.3 The 2nd law of thermodynamics

Many processes in nature are irreversible. Although no fundamental law of physics prevents heat to flow from cold to hot places or mixed gases to spontaneously separate into the components, this is never observed. Time seems to flow in one direction. The second law of thermodynamics distills this aspect of experience and states it succinctly and quantitatively, albeit abstractly, introducing a state function called *entropy*. When summed up for a system and its surroundings, the entropy always increases [1].

While the second law postulates that any closed system always produces (or maintains) entropy dS_{prod}, this does not preclude entropy reduction for this system, provided the entropy can be removed from the system via transfer dS_{trans} through its boundaries faster than being produced. The net entropy balance of the system is then,

$$dS_{syst} = dS_{prod} + dS_{trans} \leq 0 \ . \tag{1.44}$$

Indeed, many practical applications are based on entropy reduction in subsystems, e.g. lasers. Since entropy transfer between a system and its environment does not change the overall entropy balances, the total entropy production of the universe, consisting of the system plus its environment, must remain positive [2].

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[1] Note that the sign of entropy increase is fixed by convention.

The concept of irreversibility is intrinsically connected to the notion of spontaneous breaking of time reversal symmetry, which plays a fundamental role e.g. in quantum optics of open systems. Let us consider an atomic two-level system interacting with a light mode. While coherent processes, such as absorption and stimulated emission of a photon, maintain irreversibility, spontaneous emission into the reservoir of electromagnetic vacuum modes cannot be undone. The size of the phase space potentially occupied by the spontaneously emitted photon is simply to large to yield any reasonable probability for spontaneous reabsorption.

Processes linking systems with a relatively small number of degrees of freedom to much larger systems are called *dissipative*, and the rate of entropy production is a quantitative measure for this dissipation. It not only depends on the strength of the dissipation, but also on how far away the system is from equilibrium: the closer to equilibrium, the smaller dissipation. A quantitative treatment of the correlation between dissipation and distance from equilibrium is, however, very complicated.

For processes sufficiently slow never to move away very far from equilibrium the entropy production is correspondingly small. It completely vanishes, when the system is infinitesimally close to equilibrium, for example, exerting work in incremental steps or adding heat in incremental portions always allowing the system to equilibrate before applying the next change. Systems undergoing such processes can change their entropy only via exchange with other systems, and as no entropy is produced they are reversible. Obviously, the concept of reversibility represents an idealization, since any real process is afflicted with dissipation.

In contrast, systems undergoing quick drastic changes instantaneously deviate from equilibrium and transiently occupy states, in which entropy is produced, before they return to equilibrium. Such processes are irreversible.

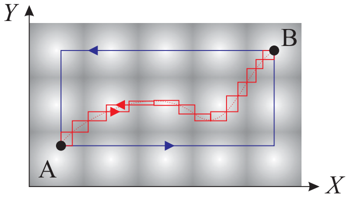

Figure 1.18: Illustration of (blue) an irreversible process forced through an inhomogeneous parameter landscape and (red) a reversible sequence of infinitesimal irreversible processes following a given path. As long as the infinitesimal processes do not recede much from equilibrium (dashed red line), entropy production can be neglected.

For reversible processes the *process variables* are readily calculated, since each intermediate state (red dashed line in Fig. 1.18) is described by just a few state functions, e.g. temperature or pressure. In contrast, this is very complicated for irreversible processes carrying the system to a state whose state functions depend on the trajectory on which the state was reached.

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[2] We may formulate a continuity-type equation for entropy density and entropy flow.

On the other hand, *changes of state functions* are easy to calculate also for irreversible processes, since these only depend on the initial and final states. Thus, changes in state functions for a given complex irreversible process may be calculated by substituting the process by a reversible one. E.g. in Fig. 1.18 instead of following solid red lines, we substitute them by dashed red lines connecting the same initial and final states. This procedure illustrates the fundamental role of state functions and reversible processes in thermodynamics.

Let us now analyze entropy transfer for reversible processes. Let δQ_{rev} be the heat absorbed in an infinitesimal step and T the temperature of the system. Now, although δQ_{rev} is a process variable, $\delta Q_{rev}/T$ is the differential of a state function, that is, the state function for an infinitesimal process. To prove this, it is sufficient to show that for a general cyclic process, such as the Carnot cycle, the path integral

$$\oint \frac{\delta Q_{rev}}{T} = 0 \tag{1.45}$$

vanishes. The state function $\delta Q_{rev}/T$ is defined to be the *entropy*,

$$\boxed{\delta Q_{rev} = TdS} \ . \tag{1.46}$$

The expression allows us to evaluate the heat absorbed during a reversible process by integrating a combination of two state functions, $Q_{rev} = \oint TdS$. Note, that Q_{rev} still depends on the path and thus remains a process variable.

Since entropy is a state function, the entropy change for a process can not depend on whether the process is reversible or not. That is,

$$\Delta S_{rev} = \oint \frac{\delta Q_{rev}}{T} = \Delta S_{irr} \ . \tag{1.47}$$

However, an irreversible process will also *produce* entropy,

$$\Delta S_{rev} = \Delta S_{irr,trans} + \Delta S_{irr,prod} \ , \tag{1.48}$$

with $\Delta S_{irr,prod} > 0$. Associating the irreversible entropy change not due to entropy production with irreversible heat transfer, we find,

$$\Delta S_{irr,trans} = \oint \frac{\delta Q_{irr}}{T} < \oint \frac{\delta Q_{rev}}{T} = \Delta S_{rev} \ , \tag{1.49}$$

which means that the maximum heat transport is observed for reversible processes. Or in other words, irreversible heat transfer is subject to losses resulting in entropy production.

An analogous treatment can also be done for work. We express reversible work by a combination of state functions,

$$\boxed{\delta W_{rev} = -PdV} \ . \tag{1.50}$$

Combining the first and second law of thermodynamics Eqs. (1.41), (1.46), and (1.50), we find for reversible processes,

$$\boxed{dE = TdS - PdV} \ . \tag{1.51}$$

1.2.2.4 The 3rd law of thermodynamics

Experiments have shown that temperature, as defined in Sec. 1.1.1, does not go below a certain value, consequently identified as *absolute zero temperature*. Experiments have also shown that all substances in any thermodynamic state have the same entropy at $T = 0$. This finding motivates the choice of setting the entropy at absolute zero temperature to zero,

$$\boxed{S(T \to 0) \to 0} \ . \tag{1.52}$$

Example 5 (*Entropy change in chemical reactions*): Experimentally, the process of heating from $T = 0$ a mixture of two atomic species to a temperature where they react to form molecules and then cooling the molecules down back to $T = 0$ is found not to produce entropy, although the initial substances are different from the final ones. This fact can be exploited for the determination of the entropy balance in chemical reactions. For example, given that the absolute entropy at 298 K for the substances Al, O_2, and Al_2O_3 are, respectively,

$$S_{\text{Al}} = 28.3\,\text{J/mol K} \quad , \quad S_{\text{O}_2} = 205.03\,\text{J/mol K} \quad , \quad S_{\text{Al}_2\text{O}_3} = 51.1\,\text{J/mol K} \ ,$$

together with the stoichiometrically balanced reaction, $2\text{Al} + \frac{3}{2}\text{O}_2 = \text{Al}_2\text{O}_3$, yields the entropy change,

$$\Delta S = S_{\text{Al}_2\text{O}_3} - (2S_{\text{Al}} + \tfrac{3}{2}S_{\text{O}_2}) = -313.19\,\text{J/mol K} \ .$$

1.2.3 Thermodynamic potentials

With the statements outlined in Secs. 1.2.1 and 1.2.2 we have laid the foundations of a conceptual world of thermodynamics. Now, we need to show how to use it in practice.

So far we defined the *process variables*

$$Q, W \tag{1.53}$$

and the *state functions*

$$P, V, T, S, E \tag{1.54}$$

appearing in the laws of thermodynamics. In very simple systems, being in equilibrium with themselves and with the environment, the state is completely fixed by *two* state variables. This means that, if two of the five enumerated state functions are known, all others can be expresses as their functions, for example, $V = V(T, P)$ or $E = E(S, V)$ for an ideal gas consisting of exactly N particles.

Furthermore, we already got in contact with *material variables*, such as thermal expansion, compressibility, heat capacity at constant pressure or at constant volume,

$$\alpha, \kappa, C_P, C_V \ . \tag{1.55}$$

These material properties may also depend on temperature or pressure. For a given substance the state equations can be computed from those properties.

The general procedure to tackle a problem is the following:

1. Identify the properties of the system about which information is available. These are the independent variables, for example, T and P.
2. Identify the properties of the system about which information is requested. This property is a dependent variable, which means that it is a function of the independent variables, for example $V = V(T, P)$.
3. Such functions will necessarily contain material properties, which will have to be looked up from data bases.

The crucial step in this procedure is evidently the second one, which consists in finding the appropriate state function.

Another class of thermodynamic relationships, falling under the category of definitions, is the introduction of state functions with the dimension of energy known as *thermodynamic potentials*. Apart from internal energy, the potentials used in canonical ensembles are the enthalpy, the Helmholtz free energy, and the Gibbs free energy,

$$E, H, F, G \ . \tag{1.56}$$

Which one of the defined potentials is used as a state function in a particular problem is, in principle, arbitrary. However, some processes are easier to describe in terms of particular potentials. Before we define them below, let us present a useful mathematical framework facilitating the conversion between state functions called *Legendre transform*.

1.2.3.1 Legendre transform in thermodynamics

Assume that for a system characterized by three state variables (X, Y, Z) we know the state function $W = W(X, Y, Z)$, so that for given system parameters (A, B, C), we know how the system will evolve upon a set of variations (dX, dY, dZ),

$$\boxed{\begin{aligned} dW &= \left(\frac{\partial W}{\partial X}\right)_{Y,Z} dX + \left(\frac{\partial W}{\partial Y}\right)_{X,Z} dY + \left(\frac{\partial W}{\partial Z}\right)_{X,Y} dZ \\ &\equiv A dX + B dY + C dZ \end{aligned}} \ . \tag{1.57}$$

The partial derivatives A, B, C are evaluated assuming that the derived quantities do not depend on other variables. Since the order of the derivatives can be inverted, we know,

$$\begin{aligned} \left(\frac{\partial A}{\partial Y}\right)_{X,Z} &= \left(\frac{\partial}{\partial Y}\left(\frac{\partial W}{\partial X}\right)_{Y,Z}\right)_{X,Z} = \left(\frac{\partial}{\partial X}\left(\frac{\partial W}{\partial Y}\right)_{X,Z}\right)_{Y,Z} = \left(\frac{\partial B}{\partial X}\right)_{Y,Z} \\ \left(\frac{\partial A}{\partial Z}\right)_{X,Y} &= \left(\frac{\partial}{\partial Z}\left(\frac{\partial W}{\partial X}\right)_{Y,Z}\right)_{X,Y} = \left(\frac{\partial}{\partial X}\left(\frac{\partial W}{\partial Z}\right)_{X,Y}\right)_{Y,Z} = \left(\frac{\partial C}{\partial X}\right)_{Y,Z} \ , \end{aligned} \tag{1.58}$$

and analogously for all other second derivatives. Applied to thermodynamic systems these expression are called *Maxwell relations*.

Now, we want to predict how the system will evolve when a different set of variations is applied, for instance (dA, dY, dZ). To solve the problem we first define a new state function $V = V(A, Y, Z)$ via,

$$\boxed{V \equiv W - AX} \ . \tag{1.59}$$

This substitution is called *Legendre transform*. The new differential is,

$$\begin{aligned} dV &= dW - AdX - XdA = -XdA + BdY + CdZ \\ &= -\left(\frac{\partial V}{\partial A}\right)_{Y,Z} dA + \left(\frac{\partial V}{\partial Y}\right)_{A,Z} dY + \left(\frac{\partial V}{\partial Z}\right)_{A,Y} dZ \ , \end{aligned} \tag{1.60}$$

and each of these three expressions has a physical meaning. The thermodynamic potentials introduced in the next section will exemplify the procedure. Do the Exc. 1.2.8.1.

Useful mathematical identities when working with partial derivatives are,

$$\left(\frac{\partial X}{\partial Z}\right)_Y \left(\frac{\partial Z}{\partial X}\right)_Y = 1 \quad , \quad \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X = -1 \ . \tag{1.61}$$

1.2.3.2 Enthalpy

The energy function called *enthalpy* is defined as,

$$\boxed{H \equiv E + PV} \ . \tag{1.62}$$

With the expression (1.51) the differential enthalpy becomes,

$$dH = dE + PdV + VdP = TdS + VdP \ . \tag{1.63}$$

It has the same level of generality as the combined first and second laws.

Historically, the enthalpy was introduced to simplify the description of heat engines taken through cycles at atmospheric pressure, $dP = 0$. For isobaric processes in simple systems, $dH_P = TdS_P = \delta Q_{rev,P}$, the enthalpy provides a direct measure of the reversible heat exchange of the engine with the environment.

1.2.3.3 Helmholtz free energy

The energy function called *Helmholtz free energy* is defined as,

$$\boxed{F \equiv E - TS} \ . \tag{1.64}$$

With the expression (1.51) the differential enthalpy becomes,

$$dF = dE - TdS - SdT = -SdT - PdV \ . \tag{1.65}$$

It has the same level of generality as the combined first and second laws.

This function was devised to simplify the description of processes occurring at a fixed (if necessary stabilized) temperature, $dT = 0$. For isothermal processes in simple systems, $dF_T = -PdV_T = \delta W_{rev,T}$, the Helmholtz free energy reports the total reversible work done on the system.

1.2.3.4 Gibbs free energy

The energy function called *Gibbs free energy* is defined as,

$$\boxed{G \equiv E + PV - TS} \ . \tag{1.66}$$

With the expression (1.51) the differential enthalpy becomes,

$$dG = dE + PdV + VdP - TdS - SdT = -SdT + VdP \ . \tag{1.67}$$

It has the same level of generality as the combined first and second laws.

This function was introduced to simplify the description of processes occurring at both temperature, $dT = 0$, and constant pressure, $dP = 0$. For isobaric and isothermal processes in simple systems, $dG_{T,P} = 0$. But in systems undergoing phase transformations or chemical reactions, the Gibbs free energy yields the total work *other than mechanical work*, $dG_{T,P} = \delta W'_{T,P}$.

1.2.3.5 Summary of thermodynamic potentials for canonical ensembles

The following list summarizes the *thermodynamic potentials* for *canonical ensembles*, which are the total energy E, the free enthalpy H, the Helmholtz free energy F, and the Gibbs free energy G,

$$\boxed{\begin{array}{lcl} & & \delta Q_{rev} = TdS \\ & & \delta W_{rev} = -PdV \\ E = Q_{rev} + W_{rev} & \Longrightarrow & dE = TdS - PdV \\ H = E + PV & \Longrightarrow & dH = TdS + VdP \\ F = E - TS & \Longrightarrow & dF = -SdT - PdV \\ G = E + PV - TS & \Longrightarrow & dG = -SdT + VdP \end{array}} \tag{1.68}$$

1.2.3.6 Material properties

Database variables are defined as conditional derivatives of the state functions or thermodynamic potentials. Mechanical properties such as the *compressibility* κ, the *thermal expansion coefficient* α, and the *stress coefficient* β are prominent examples. In the case of a single substance system, they are defined by,

$$\boxed{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad , \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad , \quad \beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V} \ . \tag{1.69}$$

Table 1.1 lists the coefficient for several materials.

Example 6 (*Link between thermal expansion coefficient and compressibility*): Maxwell's relations applied to the thermal expansion coefficient and the compressibility defined in (1.69) immediately tell us,

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \left(\frac{\partial \kappa}{\partial T}\right)_P \ ,$$

for any system.

Thermal properties are grasped by the concept of *heat capacity*. This quantity is measured via the temperature rise of a substance due to reversible absorption of a defined quantity of heat. Since heat is a process variable, the heat capacity measurement will depend on the circumstances, i.e. whether the pressure is kept constant during the measurement or the volume. The heat capacity will be for the respective cases,

$$\boxed{C_P \equiv \left(\frac{\delta Q_{rev}}{dT}\right)_P \qquad \text{or} \qquad C_V \equiv \left(\frac{\delta Q_{rev}}{dT}\right)_V} \; . \tag{1.70}$$

Using the relationships listed in (1.68), we find immediately,

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{or} \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \; . \tag{1.71}$$

For a system held at constant pressure, absorption of heat will lead to both, an increase in temperature but also an expansion of volume, which corresponds to work. For a system held at constant volume, absorption of heat will only increase temperature, hence, $C_P > C_V$.

Empirically, the heat capacities are found to depend on temperature. A frequently used interpolation expression giving good results at temperatures above room temperature is,

$$C_P(T) = a + bT + c/T^2 + dT^2 \; , \tag{1.72}$$

where the coefficients are listed in Tab. 1.1 for several materials.

1.2.3.7 Coefficient and Maxwell relations

The differential forms listed in (1.68) immediately allow to express state functions via partial derivatives of thermodynamic potentials in the following coefficient relations,

$$\begin{aligned} T &= \left(\frac{\partial E}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \quad , \quad & -S &= \left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P \\ -P &= \left(\frac{\partial E}{\partial V}\right)_S = \left(\frac{\partial F}{\partial V}\right)_T \quad , \quad & V &= \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T \; . \end{aligned} \tag{1.73}$$

Furthermore, taking the second derivatives of the expressions for the temperature and the pressure, we find,

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S \; , \tag{1.74}$$

and similarly for the other potentials.

1.2.4 Strategy for deriving thermodynamic relations

The conceptual framework of terms and definitions erected in the previous sections allows us to derive a totally general equation expressing any state variable as a function of two (for simple systems) other state variables. For complex systems, more free state variables may be necessary. Below we will provide a recipe for a rigorous general procedure.

As a preparation for the employment of the procedure we will express all state variables as functions of temperature T and pressure P, which are the most commonly used free variables. Once equations for volume $V = V(T,P)$ and entropy $S = S(T,P)$ are found, expressions for the four energy variables as functions of (T,P) readily follow. At the end, we will show how to convert functions of (T,P) into functions of any other pair of variables.

1.2.4.1 State variables as functions of T and P

The differential form of the function $V = V(T,P)$ is,

$$dV = AdT + BdP = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP = \alpha V dT - \kappa V dP \ , \tag{1.75}$$

where we used the definitions of the material coefficients (1.69). Analogously, the differential form of the function $S = S(T,P)$ is,

$$dS = A'dT + B'dP = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_P}{T} dT - \alpha V dP \ . \tag{1.76}$$

For the first coefficient we used the definitions of the heat capacities (1.71). The second coefficient follows from the Maxwell relation applied to the Gibbs free energy differential, $dG = -SdT + PdV$, yielding,

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \ . \tag{1.77}$$

Inserting the expressions (1.75) and (1.76) into the differential forms (1.68) and separating the coefficients of the differential dT ad dP, we immediately get,

$$\boxed{\begin{array}{rcl} V = V(T,P) & \Longrightarrow & dV = \alpha V dT - \kappa V dP \\ S = S(T,P) & \Longrightarrow & dS = \frac{C_P}{T} dT - \alpha V dP \\ E = E(T,P) & \Longrightarrow & dE = (C_P - \alpha P V)dT + (\kappa P - \alpha T)V dP \\ H = H(T,P) & \Longrightarrow & dH = C_P dT + (1 - \alpha T)V dP \\ F = F(T,P) & \Longrightarrow & dF = -(S + \alpha P V)dT + \kappa P V dP \\ G = G(T,P) & \Longrightarrow & dG = -SdT + V dP \end{array}} \tag{1.78}$$

1.2.4.2 Recipe for change of variables

With the results (1.78) we may now devise the following recipe for changing the independent variables,

1. Identify the new free and dependent state variables: $W = W(X,Y)$.
2. Write the differential form: $dW = AdX + BdY$.

3. Use the Eqs. (1.78) to express dX and dY in terms of the variables dT and dP:

$$dX = \left(\frac{\partial X}{\partial T}\right)_P dT + \left(\frac{\partial X}{\partial P}\right)_T dP \quad , \quad dY = \left(\frac{\partial Y}{\partial T}\right)_P dT + \left(\frac{\partial Y}{\partial P}\right)_T dP \; , \tag{1.79}$$

   where the derivatives are the coefficients of dT and dP in the expressions for dX and dY in (1.78).

4. Insert the expressions for dX and dY into the differential form dW and collect terms:

$$dW = \left[A\left(\frac{\partial X}{\partial T}\right)_P + B\left(\frac{\partial Y}{\partial T}\right)_P\right] dT + \left[A\left(\frac{\partial X}{\partial P}\right)_T + B\left(\frac{\partial Y}{\partial P}\right)_T\right] dP \; . \tag{1.80}$$

5. Obtain $W = W(T,P)$ from (1.78),

$$dW = \left(\frac{\partial W}{\partial T}\right)_P dT + \left(\frac{\partial W}{\partial P}\right)_T dP \; . \tag{1.81}$$

6. By comparison of the coefficients of the equations (1.80) and (1.81),

$$\left(\frac{\partial W}{\partial T}\right)_P = A\left(\frac{\partial X}{\partial T}\right)_P + B\left(\frac{\partial Y}{\partial T}\right)_P \quad , \quad \left(\frac{\partial W}{\partial P}\right)_T = A\left(\frac{\partial X}{\partial P}\right)_T + B\left(\frac{\partial Y}{\partial P}\right)_T \; . \tag{1.82}$$

7. Solve the set of equations (1.82) by A and B,

$$A = \frac{\left(\frac{\partial W}{\partial P}\right)_T \left(\frac{\partial Y}{\partial T}\right)_P - \left(\frac{\partial W}{\partial T}\right)_P \left(\frac{\partial Y}{\partial P}\right)_T}{\left(\frac{\partial X}{\partial P}\right)_T \left(\frac{\partial Y}{\partial T}\right)_P - \left(\frac{\partial X}{\partial T}\right)_P \left(\frac{\partial Y}{\partial P}\right)_T} \quad , \quad B = \frac{\left(\frac{\partial W}{\partial T}\right)_P \left(\frac{\partial X}{\partial P}\right)_T - \left(\frac{\partial W}{\partial P}\right)_T \left(\frac{\partial X}{\partial T}\right)_P}{\left(\frac{\partial X}{\partial P}\right)_T \left(\frac{\partial Y}{\partial T}\right)_P - \left(\frac{\partial X}{\partial T}\right)_P \left(\frac{\partial Y}{\partial P}\right)_T} \; . \tag{1.83}$$

Example 7 (*Relating entropy to temperature and volume*): As an example of the procedure developed in the previous sections, we will now express entropy as a function of temperature and volume.

1. The wanted expression is: $S = S(T,V)$.
2. Its differential form is: $dS = AdT + BdV$.
3. Substituting dV from (1.78)(i): $dS = AdT + B(\alpha V dT - \kappa V)dP$.
4. Collecting terms: $dS = (A + B\alpha V)dT - B\kappa V dP$.
5. Obtain $S = S(T,P)$ from (1.78)(i): $dS = (C_P/T)dT - \alpha V dP$.
6. Compare coefficients: $A + B\alpha V = C_P/T$ and $-B\kappa V = -\alpha V$.
7. Solve by A and B: $A = (C_P/T) - (\alpha^2 V/\kappa)$ and $B = \frac{\alpha}{\kappa}$.

The expression is thus,

$$dS = \left(\frac{C_P}{T} - \frac{\alpha^2 V}{\kappa}\right) dT + \frac{\alpha}{\kappa} dV \; . \tag{1.84}$$

Example 8 (*Relating entropy to pressure and volume*): As second example of the procedure developed in the previous sections, we will now express entropy as a function of pressure and volume.

1. The wanted expression is: $S = S(P, V)$.
2. Its differential form is: $dS = AdP + BdV$.
3. Substituting dV from (1.78)(i): $dS = AdP + B(\alpha V dT - \kappa V)dP$.
4. Collecting terms: $dS = B\alpha V dT + (A - B\kappa V)dP$.
5. Obtain $S = S(T, P)$ from (1.78)(i): $dS = (C_P/T)dT - \alpha V dP$.
6. Compare coefficients: $B\alpha V = C_P/T$ and $A - B\kappa V = -\alpha V$.
7. Solve by A and B: $A = \frac{\kappa C_P}{\alpha T} - \alpha V$ and $B = \frac{C_P}{\alpha V T}$.

The expression is thus,

$$dS = \left(\frac{\kappa C_P}{\alpha T} - \alpha V\right) dP + \frac{C_P}{\alpha T V} dV \ . \tag{1.85}$$

1.2.5 Ideal gases

One of the most common systems to apply thermodynamic concepts are ideal gases, for which we know that they obey the state equation,

$$\boxed{PV = Nk_B T} \ , \tag{1.86}$$

where we consider for now a fixed number of particles $N = const$. The thermal expansion coefficient and the compressibility are readily calculated from their definitions (1.69),

$$\begin{aligned} \alpha_{id} &= \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial N k_B T/P}{\partial T}\right)_P = \frac{1}{T} \\ \kappa_{id} &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial N k_B T/P}{\partial P}\right)_T = \frac{1}{P} \ . \end{aligned} \tag{1.87}$$

The relationship between the heat capacities at constant volume and pressure is directly obtained from (1.84),

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = C_P - \frac{\alpha_{id}^2 T V}{\kappa_{id}} = C_P - N k_B \ . \tag{1.88}$$

Hence, for an ideal gas, the heat capacities do not depend on T not P, but only on the number of atoms N and their configuration in each gas molecule,

$$\boxed{C_V = \tfrac{3}{2} N k_B} \ . \tag{1.89}$$

We will see later, that for a molecular gas with f degrees of freedom (accessible at the temperature), the results must be generalized to,

$$C_V = \tfrac{f}{2} N k_B \ . \tag{1.90}$$

The differential form for the internal energy $E = E(T, P)$ is,

$$dE = (C_P - \alpha_{id}PV)dT + (\kappa_{id}P - \alpha_{id}T)VdP = (C_P - Nk_B)dT = C_V dT \ . \quad (1.91)$$

Thus, E only depends on T, and since E is a state function, this holds for any process, whether reversible or irreversible. For the other thermodynamic potentials we get, exploiting the relationships (1.68),

$$\boxed{\begin{array}{rclcrcl} E &=& C_V T &,& F &=& (C_V - S)T \\ H &=& C_P T &,& G &=& (C_P - S)T \end{array}} \quad (1.92)$$

Do the Excs. 1.2.8.2 to 1.2.8.12.

1.2.5.1 Adiabatic reversible processes

In thermodynamics *adiabatic processes* are called those in which no heat is exchanged between the system and its environment,

$$\delta Q_{adiab} = 0 \ . \quad (1.93)$$

If additionally a process is reversible,

$$\delta Q_{adiab,rev} = TdS = 0 \ , \quad (1.94)$$

it is *isentropic process*, that is, entropy is neither produced nor transferred.

Let us compute the change in temperature of a reversibly and adiabatically compressed ideal gas. As usual, we start identifying the relevant state variables, $T = T(S, V)$. From (1.68)(iii), using the definition of the heat cavity at constant volume C_V, we find,

$$dT = \frac{TdS - PdV}{C_V} \ , \quad (1.95)$$

and since $dS = 0$,

$$dT_S = -\frac{P}{C_V}dV_S = -\frac{Nk_BT}{C_VV}dV_S \ . \quad (1.96)$$

Integrating this equation,

$$\int_{T_1}^{T_2}\frac{dT}{T} = \ln\frac{T_2}{T_1} = -\frac{Nk_B}{C_V}\ln\frac{V_2}{V_1} = -\frac{Nk_B}{C_V}\int_{V_1}^{V_2}\frac{dV}{V} \ , \quad (1.97)$$

we finally find,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{Nk_B/C_V} = \left(\frac{P_2}{P_1}\right)^{Nk_B/C_P} \quad \text{or} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V} \ . \quad (1.98)$$

The ratio

$$\gamma \equiv \frac{C_P}{C_V} \ , \quad (1.99)$$

is called the *adiabaticity coefficient*. For the ideal gas studied in the previous section we have, $\gamma = \frac{5}{3}$, and for a molecular gas with f degrees of freedom $\gamma = 1 + \frac{2}{f}$.

With the adiabaticity coefficient the state functions for adiabatic reversible processes can be written,

$$\boxed{PV^\gamma = const \qquad \text{and} \qquad TV^{\gamma-1} = const} \ , \tag{1.100}$$

where the second relation follows from the ideal gas equations (1.86). Such a process is shown in the PV-diagram of Fig. 1.21.

Since the specific heat can be obtained from the heat capacity simply by dividing by the mass, $c \equiv C/m$, the ratio of the specific heat at constant pressure and to the specific heat at constant volume is also equal to the constant γ, that is, $\gamma = c_P/c_V$. Do the Excs. 1.2.8.13 to 1.2.8.22.

1.2.5.2 Isothermal, isobaric, and isochoric processes

We consider an ideal gas confined in a rigid, thermally insulated box, so that all processes occurring with the box are adiabatic, since no heat is exchanged with the surroundings, $\delta Q = 0$. Now, we divide the box into two volumes separated by a rigid wall but connected by a valve, which may be opened or closed, as shown in Fig. 1.19. Initially, the entire gas is in volume V_1, and when the valve is opened it expands into the volume V_2. Since, the walls of the box do not move, no work is done on the surroundings, $\delta W = 0$.

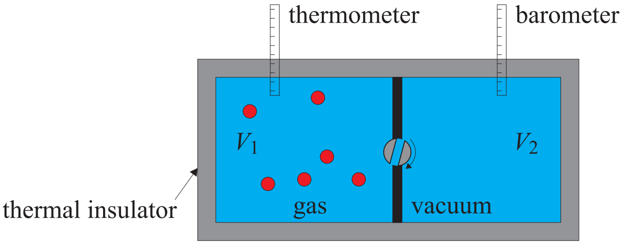

Figure 1.19: Free expansion of a gas.

Since no entropy can flow out of the system, any change in entropy must come from local production arising from irreversible processes. The expansion of the gas is a complicated process occurring far from equilibrium. Nevertheless, since entropy is a state function, the gain in entropy is same as for a fictive reversible process leading to the same final state. Since the initial state of the gas is known (V_1, T_i) as well as the final volume, $V_f = V_1 + V_2$, the final temperature T_f is determined. Now, since the internal energy does not change during expansion, $dE = \delta Q + \delta W = 0$, and since for an ideal gas the internal energy is proportional to temperature, the temperature doesn't change,

$$\boxed{PV = Nk_BT = const} \ . \tag{1.101}$$

Such a process is called *isothermal* and is shown in the PV-diagram of Fig. 1.21.

On an isotherm of an ideal gas, we have $PdV + VdP = Nk_BT = 0$ and therefore $\delta W = PdV = -VdP$. Nonetheless,

$$P = \frac{Nk_BT}{V} \quad \Rightarrow \quad dP = -\frac{Nk_BT}{V^2}dV \quad \Rightarrow \quad \delta W = Nk_BT\frac{dV}{V} \ , \tag{1.102}$$

and so, the work done when the gas goes from V_1 to V_2 is,

$$\Delta W_{1-2} = \int_{V_1}^{V_2} N k_B T \frac{dV}{V} = N k_B T \ln \frac{V_2}{V_1} \ . \tag{1.103}$$

Similar considerations can be made for *isobaric* and *isochoric processes*. The results are summarized in Tab. 1.2.

1.2.5.3 Entropy of ideal gases

As an example, let us consider entropy changes in PV space. Via Legendre transform we derive from the relationships (1.78) obtained for $S = S(T, P)$,

$$S = S(P, V) \qquad \text{with} \qquad dS = \left(\frac{\kappa C_P}{\alpha T} - \alpha V\right) dP + \frac{C_P}{\alpha T V} dV \tag{1.104}$$
$$\longrightarrow C_V \frac{dP}{P} + C_P \frac{dV}{V} \ ,$$

where the last step holds for ideal gases. We can integrate this expression either holding pressure or volume constant,

$$\Delta S_P = \int_{V_i}^{V_f} C_P \frac{dV}{V} = C_P \ln \frac{V_f}{V_i} \qquad \text{or} \qquad \Delta S_V = \int_{P_i}^{P_f} C_V \frac{dP}{P} = C_V \ln \frac{P_f}{P_i} \ . \tag{1.105}$$

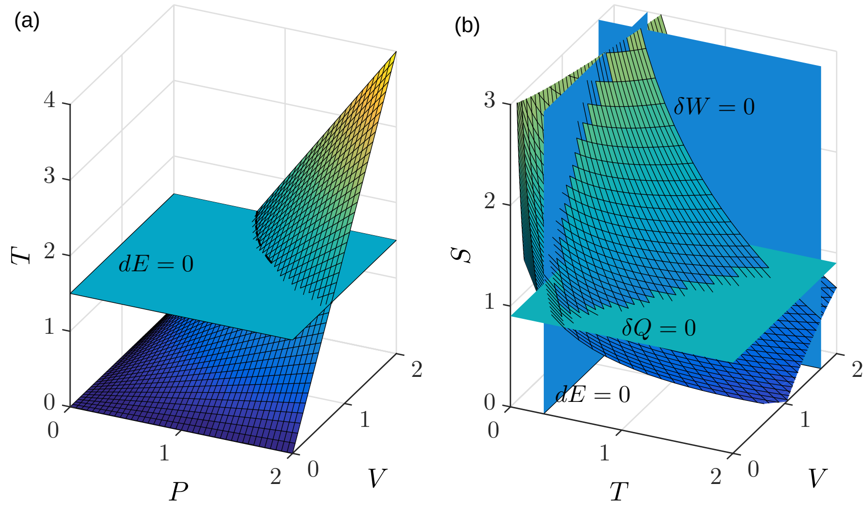

Figure 1.20: (code) (a) Qualitative behavior of the ideal gas law in TPV space. (b) Qualitative behavior of the Sackur-Tetrode formula in TSV space with planes corresponding to $\delta Q = 0$, $\delta W = 0$, and $\delta Q + \delta W$.

Since, entropy is a state function, it is possible to calculate the entropy at any point $S_2 = S(P_2, V_2)$ from the entropy change along an arbitrary path starting from any other point $S_1 = S(P_1, V_1)$, e.g.,

$$\begin{aligned} S(P_2, V_2) &= S(P_2, V_1) + C_P \ln \frac{V_2}{V_1} \qquad (1.106) \\ &= S(P_1, V_1) + C_P \ln \frac{V_2}{V_1} + C_V \ln \frac{P_2}{P_1} = S(P_1, V_2) + C_V \ln \frac{P_2}{P_1} \ . \end{aligned}$$

We conclude,

$$\boxed{\Delta S_{1\to 2} = C_P \ln \frac{V_2}{V_1} + C_V \ln \frac{P_2}{P_1} = C_V \ln \frac{P_2 V_2^\gamma}{P_1 V_1^\gamma} = C_V \ln \frac{T_2 V_2^{\gamma-1}}{T_1 V_1^{\gamma-1}}} \ . \qquad (1.107)$$

Assuming a mono-atomic gas, for which $\gamma = \frac{5}{3}$. We obtain,

$$\Delta S_{1\to 2} = N k_B \ln \frac{V_2 T_2^{3/2}}{V_1 T_1^{3/2}} \ , \qquad (1.108)$$

which is known as the *Sackur-Tetrode formula* plotted in Fig. 1.20(b).

1.2.5.4 Entropy, heat and work balance during reversible processes

The heat absorbed and work done during reversible processes can be computed via integration of TdS or $-PdV$ along the path of the process. The integration is simplified if one of the state functions is kept constant during the process. We will now study particularly simple cases, where one of the three variables T, S, P, V is held constant. 12 combinations are possible: (i) isothermal process entropy change, (ii) isothermal pressure change, (iii) isothermal volume change, (iv) isentropic process temperature change, (v) isentropic pressure change, (vi) isentropic volume change, (vii) isobaric process temperature change, (viii) isobaric entropy change, (ix) isobaric volume change, (x) isochoric process temperature change, (xi) isochoric entropy change, and (xii) isochoric pressure change. If one of the six variables $T, S, P, V \mu, N$ is held constant, there are 30 possible combinations.

Table 1.2 summarize the entropy, heat, and work balances for all 12 processes, which will be derived in Exc. 1.2.8.23. Marked in red are those processes not requiring Legendre transforms for calculating entropy, heat, and work changes.

Table 1.2: Summary of entropy, heat, and work balances upon various state changes.

process	$\Delta S_{1\to2} = \int_{S_1}^{S_2} dS =$	$\Delta Q_{1\to2} = \int_{S_1}^{S_2} TdS =$	$\Delta W_{1\to2} = -\int_{V_1}^{V_2} PdV =$
isotherm	$\int dS_T \to \quad S_2 - S_1$	$\int TdS_T \to \quad T(S_2 - S_1)$	$-\int \frac{\kappa}{\alpha} PdS_T \to \quad -\Delta Q_{1\to2}$
	$-\int \alpha V dP_T \to \quad -Nk_B \ln \frac{P_2}{P_1}$	$-\int \alpha V dP_T \to \quad -Nk_B T \ln \frac{P_2}{P_1}$	$\int \kappa PV dP_T \to \quad -\Delta Q_{1\to2}$
	$\int \frac{\alpha}{\kappa} dV_T \to \quad Nk_B \ln \frac{V_2}{V_1}$	$\int \frac{\alpha}{\kappa} dV_T \to \quad Nk_B T \ln \frac{V_2}{V_1}$	$-\int PdV_T \to \quad -\Delta Q_{1\to2}$
isentropic	0	0	$\int (\frac{\kappa C_P}{\alpha T} - \alpha V) PdT_S \to \quad C_V(T_2 - T_1)$
	0	0	$\int (\frac{\alpha^2 TV}{C_P} - \kappa) PV dP_S \to \quad \frac{P_2V_2 - P_1V_1}{\gamma - 1}$
	0	0	$-\int PdV_S \to \quad \frac{P_2V_2 - P_1V_1}{\gamma - 1}$
isobar	$\int \frac{C_P}{T} dT_P \to \quad C_P \ln \frac{T_2}{T_1}$	$\int C_P dT_P \to \quad C_P(T_2 - T_1)$	$-\int \alpha PV dT_P \to \quad -Nk_B(T_2 - T_1)$
	$\int dS_P \to \quad S_2 - S_1$	$\int TdS_P \to \quad C_P T_1(e^{\Delta S_P/C_P} - 1)$	$-\int \frac{\alpha TV}{C_P} dS_P \to \quad -\frac{Nk_B}{C_P} \int TdS_P$
	$\int \frac{C_P}{\alpha TV} dV_P \to \quad C_P \ln \frac{V_2}{V_1}$	$\int \frac{C_P}{\alpha TV} dV_P \to \quad \frac{C_P P}{Nk_B}(V_2 - V_1)$	$-\int PdV_P \to \quad -P(V_2 - V_1)$
isochor	$\int \left(\frac{C_P}{T} - \frac{\alpha^2 V}{\kappa}\right) dT_V \to \quad C_V \ln \frac{T_2}{T_1}$	$\int (\frac{C_P}{T} - \frac{\alpha^2 V}{\kappa}) dT_V \to \quad C_V(T_2 - T_1)$	0
	$\int dS_V \to \quad S_2 - S_1$	$\int TdS_V \to \quad C_V T_1(e^{\Delta S_V/C_V} - 1)$	0
	$\int dP_V \to \quad C_V \ln \frac{P_2}{P_1}$	$\int (\frac{\kappa C_P}{\alpha T} - \alpha V) dP_V \to \quad \frac{C_V V}{Nk_B}(P_2 - P_1)$	0

1.2.6 Cyclic processes

Thermal machines are based on cyclic processes. Examples are the Clément-Desormes cycle studied in the next section, the Carnot cycle in Exc. 1.2.8.24, the *Otto cycle* studied in Exc. 1.2.8.25, or the *Diesel cycle* studied in Exc. 1.2.8.26, and others studied in Excs. 1.2.8.27 to 1.2.8.33.

From the first law of thermodynamics $dE = \delta Q + \delta W$ we expect that for cyclic processes going through a sequences of processes j the heat and work balances are compensated,

$$0 = \oint TdS - \oint PdV = \sum_j \Delta Q^{>0}_{j\rightarrow j+1} + \sum_j \Delta W_{j\rightarrow j+1} \ . \tag{1.109}$$

We define the efficiency of a cyclic process as the ratio between net work performed and heat absorbed (not delivered),

$$\boxed{\eta \equiv \frac{-\sum_j \Delta W_{j\rightarrow j+1}}{\sum_j \Delta Q^{>0}_{j\rightarrow j+1}}} \ . \tag{1.110}$$

1.2.6.1 The Cléments-Desormes method for determining γ

The specific heat of solids and liquids is usually measured with samples under atmospheric conditions and without control of the volume of the material, i.e. we generally measure c_P. In contrast, gases are easier to study when they are contained in a rigid recipient, such as a glass bulb with little thermal expansion within the temperature range of the experiment. Then, the specific heat is measured at constant volume c_V. The value c_P of a gas is larger than c_V because in the experiment, at constant pressure, the heat delivered to the gas also causes its expansion, which means that part of that energy is been converted into work and not into an increase the thermal energy of the gas molecules. The ratio between the specific heats at constant pressure and volume, $\gamma = c_P/c_V$, is a value that often appears in the description of thermodynamic processes in gases. This ratio can be measured by isobaric and isochoric processes, respectively measuring c_P and c_V. The first experiment to measure the factor γ in gases was performed in 1819 by *Desormes* and *Clément*. The method consists in applying to a gas (assume to be ideal), a sequence of three processes illustrated in Fig. 1.21: an isothermal expansion from state (1) to (2), followed by an isochoric cooling from (2) to (3), and finally an adiabatic compression from (3) back to (1). During the adiabatic process from (3) to (1) the relation between pressure and volume is described by $PV^\gamma = const$. Monitoring both during the process thus allows us to measure the adiabaticity coefficient γ.

The heat and work balance of the Clément-Desormes cycle is summarized in the following table. The heats and works exchanged with the reservoir can be looked up in Tab. 1.2,

process		$\Delta Q_{j\rightarrow j+1} =$	$\Delta W_{j\rightarrow j+1} =$
$1\rightarrow 2$	isotherm	$T_1(S_2 - S_1) = Nk_BT_1 \ln\frac{V_2}{V_1} > 0$	$-\Delta Q_{1\rightarrow 2}$
$2\rightarrow 3$	isochor	$C_V(T_3 - T_2) < 0$	0
$3\rightarrow 1$	isentropic	0	$C_V(T_1 - T_3)$

(1.111)

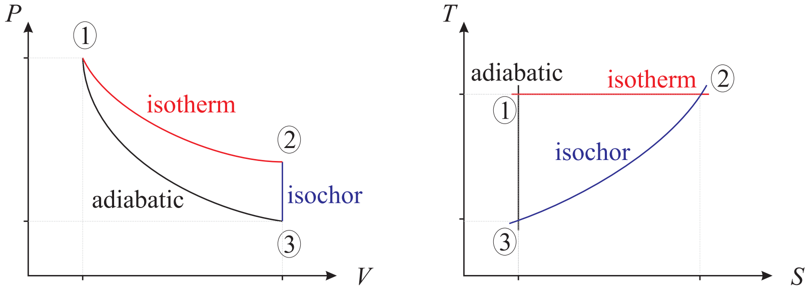

Figure 1.21: PV-diagram (left) and TS-diagram (right) for the Clément-Desormes cyclic process.

with $T_1 = T_2 > T_3$. The efficiency is defined as,

$$\eta = \frac{-\sum \Delta W_{j\rightarrow j+1}}{\sum \Delta Q^{>0}_{i\rightarrow j}} = \frac{-T_1(S_2 - S_1) + C_V(T_1 - T_3) + 0}{T_1(S_2 - S_1)} \qquad (1.112)$$
$$= 1 - \frac{C_V(T_1 - T_3)}{Nk_BT_1 \ln \frac{V_2}{V_1}} \; .$$

Example 9 (*Rüchardt's method for determining* γ): *Rüchardt's method* shown in Fig. 1.22 allows the measurement of ratio $\gamma = C_P/C_V$ of a gas. Let us consider a gas confined in a large container with volume V. Connected to this container is a tube with cross section A, inside which a metal ball of mass m (which fits perfectly in the tube) can slide up and down thus acting like a piston. Due to the compression and decompression of the gas, this mass oscillates in around its equilibrium position ($y = 0$). The presence of the metallic sphere increases the internal pressure to $P = P_a + mg/A$ in equilibrium position, where P_a is the external (atmospheric) pressure. We will call τ the period of oscillation. See also Exc. 1.2.8.13. Given a displacement y on the sphere, the change in the volume of the gas is $\Delta V = yA$, so that there is a pressure variation ΔP accompanying ΔV. This increase in pressure produces a restoring force $F = \Delta PA$. Assuming that the process is nearly static and adiabatic, we have,

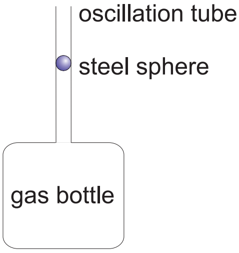

Figure 1.22: Rüchardt's method for determining γ.

$$PV^\gamma = const \quad \Rightarrow \quad \gamma PV^{\gamma-1}\Delta V + V^\gamma \Delta P = 0 \; . \qquad (1.113)$$

Using $\Delta P = F/A$ and $\Delta V = yA$, we obtain,

$$\gamma PV^{\gamma-1}yA + V^\gamma F/A = 0 \quad \Rightarrow \quad F = -\frac{\gamma PA^2}{V}y \; , \qquad (1.114)$$

which leads us to the following equation of motion for the sphere,

$$m\frac{d^2y}{dt^2} + \frac{\gamma PA^2}{V}y = 0 \ , \tag{1.115}$$

which is the differential equation of a simple harmonic motion of frequency:

$$\omega_0^2 = \frac{\gamma PA^2}{mV} \ . \tag{1.116}$$

In this way, knowing P, V, m and A, we can measure τ and obtain γ as,

$$\tau = 2\pi\sqrt{\frac{mV}{\gamma PA^2}} \ . \tag{1.117}$$

1.2.6.2 Carnot cycle

A *Carnot cycle* is an ideal thermodynamic cycle providing, by Carnot's theorem, an upper limit on the efficiency of any classical thermodynamic engine during the conversion of heat into work, or conversely, the efficiency of a refrigeration system in creating a temperature difference through the application of work to the system.

In a Carnot cycle, an engine transfers energy in the form of heat between two thermal reservoirs at temperatures T_{hot} and T_{cold}, and a part of this transferred energy is converted to the work done by the system. The cycle is reversible and hence isentropic. In other words, entropy is conserved; it is only transferred between the thermal reservoirs. When work is applied to the system, heat moves from the cold to hot reservoir, which is exploited in *heat pumps* and *refrigerators*, depending on whether the heat increase of the hot reservoir is exploited or the heat decrease of the cold reservoir. When heat moves from the hot to the cold reservoir, the system applies work to the environment, which can be exploited in *heat engines*.

The work W done by the system or engine to the environment per Carnot cycle depends on the temperatures of the thermal reservoirs and the entropy transferred from the hot reservoir to the system ΔS per cycle such as,

$$\Delta W = (T_{hot} - T_{cold})\Delta S = (T_{hot} - T_{cold})\frac{\Delta Q_{hot}}{T_{hot}} \ , \tag{1.118}$$

where Q_{hot} is heat transferred from the hot reservoir to the system per cycle.

The heat and work balance of the Carnot cycle is summarized in the following table (see Fig. 1.23):

process		$\Delta Q_{j\rightarrow j+1} =$	$\Delta W_{j\rightarrow j+1} =$
$1 \rightarrow 2$	isotherm	$T_1(S_2 - S_1) = Nk_BT_1 \ln\frac{V_2}{V_1} < 0$	$-\Delta Q_{1\rightarrow 2} > 0$
$2 \rightarrow 3$	isentropic	0	$C_V(T_3 - T_2) > 0$
$3 \rightarrow 4$	isotherm	$T_3(S_4 - S_3) = Nk_BT_3 \ln\frac{V_4}{V_3} > 0$	$-\Delta Q_{3\rightarrow 4} < 0$
$4 \rightarrow 1$	isentropic	0	$C_V(T_1 - T_4) < 0$

, (1.119)

with $T_3 = T_4 > T_1 = T_2$ and $S_2 = S_3 > S_1 = S_4$. Because E is a state function a cyclic process must necessarily satisfy, $\Delta E = \sum \Delta W_{j\rightarrow j+1} + \sum \Delta Q_{j\rightarrow j+1} = 0$. The

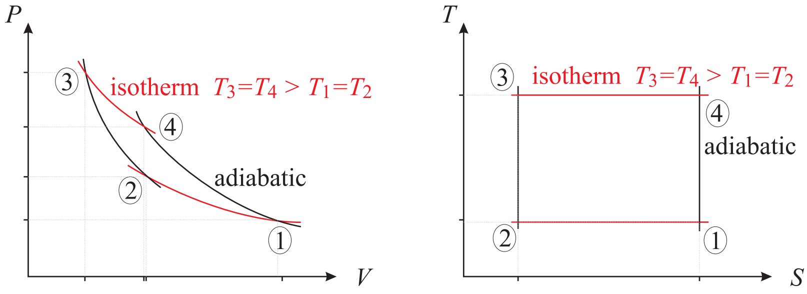
P
V
③
④
②
①
isotherm T_3=T_4 > T_1=T_2
adiabatic
T
S
③
④
②
①
isotherm T_3=T_4 > T_1=T_2
adiabatic

Figure 1.23: PV-diagram (left) and TS-diagram (right) for the Carnot cycle.

efficiency is defined as,

$$\begin{aligned}\eta &\equiv \frac{-\sum \Delta W_{j\to j+1}}{\sum \Delta Q^{>0}_{j\to j+1}} \qquad (1.120)\\ &= -\frac{-T_1(S_2-S_1)+C_V(T_3-T_2)-T_3(S_4-S_3)+C_V(T_1-T_4)}{T_3(S_4-S_3)} = 1-\frac{T_1}{T_3}\ .\end{aligned}$$

Example 10 (*Efficiency of the Carnot cycle*): According to Eq. (1.109) the total work and heat balances of a cyclic process correspond to the enclosed areas in the PV, respectively, TS-diagrams, and both areas are equal. As illustrated in Fig. 1.24, for given temperatures of the hot and cold reservoir, the largest area $\Delta W = \Delta Q = \oint TdS$ is occupied by a rectangle corresponding to the Carnot cycle.

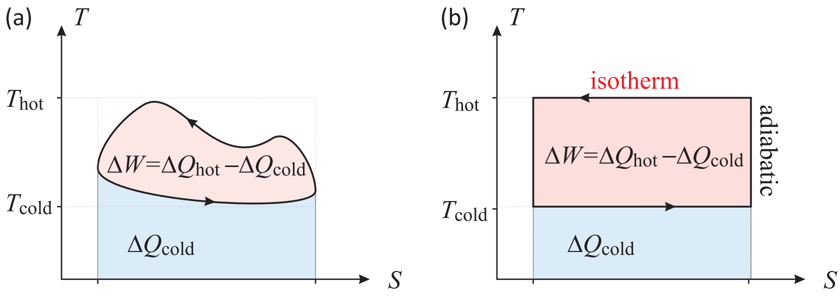
(a)
T
T_{hot}
T_{cold}
ΔW=ΔQ_{hot} −ΔQ_{cold}
ΔQ_{cold}
S
(b)
T
T_{hot}
T_{cold}
isotherm
adiabatic
ΔW=ΔQ_{hot} −ΔQ_{cold}
ΔQ_{cold}
S

Figure 1.24: TS-diagram for an arbitrary cyclic process (left) and for the Carnot cycle (right).

1.2.7 Real gases, liquids and solids

As long as real gases, liquids, and solids qualify as unary, homogeneous, closed, non-reacting, and otherwise simple systems, the laws and procedures outlined in Secs. 1.2.1 to Sec. 1.2.3 apply to them in the same way as for ideal gases. Additionally, in solids and liquids the material constants α, κ, C_P are generally to a good approximation constant.

The ideal gas law (1.3) is only valid for non-interacting particles. In reality, interparticle interactions increase the effective pressure and the finite size of the molecules reduces the effective volume. Indeed, even at $T = 0$ the volume V of a real gas cannot be zero, because the molecules have their own volume V^*. And as molecules interact attract each other, the pressure is zero even before $T = 0$. In the van der Waals model the ideal gas equation is generalized to,

$$(P+P^*)(V-V^*) = Nk_BT \quad \text{with} \quad P^* = \frac{a}{V^2}\left(\frac{N}{N_A}\right)^2 \quad \text{and} \quad V^* = b\left(\frac{N}{N_A}\right) \tag{1.121}$$

where a and b are empirical constants specifically depending on the gas. Real gases are studied in Excs. 1.2.8.34 to 1.2.8.36. Using molar functions denoted by a tilde $(\tilde{.})$, $N \to N_A$, $N_Ak_B \to R_g$, $V\frac{N}{N_A} \to \tilde{V}$, etc.,

$$\boxed{\left(P + \frac{a}{\tilde{V}^2}\right)(\tilde{V} - b) = R_gT} \; . \tag{1.122}$$

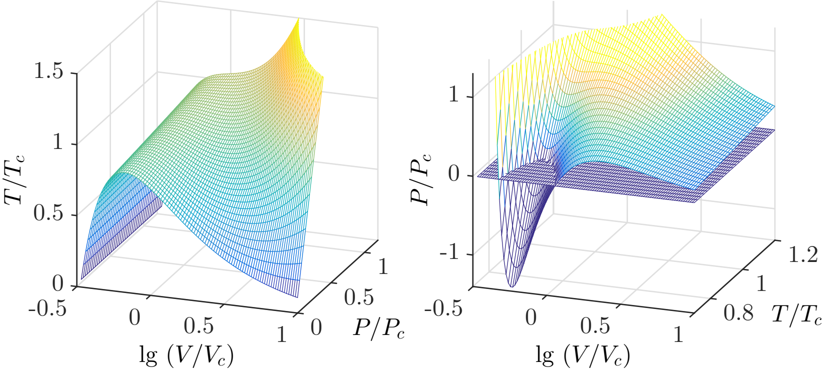

Figure 1.25: (code) Phase diagrams of a real gas.

1.2.7.1 Joule-Thomson effect

The *Joule-Thomson effect* describes the temperature change of a real gas or liquid (as differentiated from an ideal gas), when it is forced through a valve or porous plug while keeping it insulated so that no heat is exchanged with the environment (see Exc. 1.2.8.37).

The relationships (1.78)(ii) and (iii) express energy and entropy as a function of temperature and pressure, $\tilde{E} = \tilde{E}(T,P)$ and $\tilde{S} = \tilde{S}(T,P)$. Using the procedure outlined in Sec. 1.2.4 to express energy and entropy as a function of temperature and volume, $\tilde{E} = \tilde{E}(T, \tilde{V})$ and $\tilde{S} = \tilde{S}(T, \tilde{V})$, we find,

$$\begin{aligned} d\tilde{E} &= \left(\tilde{C}_P + P - \alpha P\tilde{V} - \frac{\alpha^2 T\tilde{V}}{\kappa}\right) dT + \left(\frac{\alpha T}{\kappa} - P\right) d\tilde{V} \\ d\tilde{S} &= \left(\frac{\tilde{C}_P}{T} - \frac{\alpha^2\tilde{V}}{\kappa}\right) dT + \frac{\alpha}{\kappa} d\tilde{V} \ . \end{aligned} \tag{1.123}$$

Hence,

$$\left(\frac{\partial\tilde{E}}{\partial\tilde{V}}\right)_T = T\left(\frac{\partial\tilde{S}}{\partial\tilde{V}}\right)_T - P \ . \tag{1.124}$$

From the Maxwell relation derived from, $d\tilde{F} = -\tilde{S}dT - Pd\tilde{V}$, we find,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\left(\frac{\partial\tilde{F}}{\partial\tilde{V}}\right)_T\right)_V = -\left(\frac{\partial}{\partial V}\left(\frac{\partial\tilde{F}}{\partial T}\right)_V\right)_T = \left(\frac{\partial\tilde{S}}{\partial\tilde{V}}\right)_T \ . \tag{1.125}$$

Hence,

$$\left(\frac{\partial\tilde{E}}{\partial\tilde{V}}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \ . \tag{1.126}$$

Now, we consider a dense real van der Waals gas according to Eq. (1.122) but neglecting the volume parameter, $b = 0$. The pressure P then behaves as a function of temperature T and molar volume $\tilde{V}$ according to the following state equation,

$$P = \frac{R_g T}{\tilde{V}} - \frac{a}{\tilde{V}^2} \ , \tag{1.127}$$

where a is a positive constant and R_g is the universal gas constant. From the equation of state we obtain,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R_g}{\tilde{V}} \ , \tag{1.128}$$

which, replaced in the expression (1.126), gives,

$$\left(\frac{\partial\tilde{E}}{\partial\tilde{V}}\right)_T = T\frac{R_g}{\tilde{V}} - P = \frac{a}{\tilde{V}^2} \ . \tag{1.129}$$

Integrating this equation yields,

$$\tilde{E} = -\frac{a}{\tilde{V}} + K(T) \tag{1.130}$$

where $K(T)$ depends only on T. We now have the molar energy $\tilde{E}$ expressed as a function of molar volume $\tilde{V}$.

We now assume that the heat capacity $\tilde{C}_V$ be constant. Differentiating the expression (1.130) by temperature gives,

$$\tilde{C}_V = \left(\frac{\partial\tilde{E}}{\partial T}\right)_V = K'(T) \ . \tag{1.131}$$

Inserting the integral of (1.131), $K(T) = \tilde{C}_V T + K_0$, into (1.130), we end up with,

$$\boxed{\tilde{E} = -\frac{a}{\tilde{V}} + \tilde{C}_V T + K_0} \ . \tag{1.132}$$

In a process of free expansion, $\tilde{E}$ remains invariant and $\tilde{V}$ grows. Thus, resolving (1.132) by temperature and deriving by volume,

$$\left(\frac{\partial T}{\partial \tilde{V}}\right)_E = \left(\frac{\partial}{\partial V}\frac{\tilde{E} + a/\tilde{V} - K_0}{C_V}\right)_E = \frac{-a}{C_V \tilde{V}^2} \ . \tag{1.133}$$

For an ideal gas, $a = 0$, we expect no temperature change. For a gas with positive (negative) a the variation (1.133) will be negative (positive).

Example 11 (*Microscopic interpretation of Joule-Thomson cooling*): In the discussion of the the process illustrated in Fig. 1.19 we stated that an ideal gas does not changes its temperature when it expands flowing through a nozzle from one volume into another. This is in contrast to the behavior of a real gas. Indeed, in a compressed gas the molecules are closer to each other and thus feel attractive (or repulsive) van der Waals forces. When the gas expands, the molecules must overcome these forces at the cost (gain) of kinetic energy.

1.2.8 Exercises

1.2.8.1 Ex: Material parameters

The compressibility κ, the thermal expansion coefficient α, and the stress coefficient β are important material parameters. In the case of a unary system (single substance), they are defined by,

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{\nu,T} \quad , \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{\nu,P} \quad , \quad \beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_{\nu,V} \ .$$

Here ν is the number of moles.
a. Show that these relationships can be rewritten, using the molar volume $\tilde{V}$, to,

$$\kappa = -\frac{1}{\tilde{V}}\left(\frac{\partial \tilde{V}}{\partial P}\right)_{T} \quad , \quad \alpha = \frac{1}{\tilde{V}}\left(\frac{\partial \tilde{V}}{\partial T}\right)_{P} \quad , \quad \beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_{\tilde{V}} \ .$$

b. Use the total differential of $V = V(T, P, \nu)$ to show that, in general,

$$\beta = \frac{\alpha}{\kappa P} \ .$$

c. Calculate κ, α and β for an ideal gas as functions of P and T. Show that the relationship from (b) is also fulfilled.

1.2.8.2 Ex: 1. law of thermodynamics

In a thermally insulated container there is one mole of air at the temperature $T = 400\,\text{K}$. Now, it is reversibly compressed, doing the work $W = 1.987\,\text{cal}$. Calculate the ratio V_f/V_i between the final and initial volume. Assume that the air behaves like an ideal gas and that the container itself does not absorb heat from the air.

1.2.8.3 Ex: Specific heat

The specific heat for an isobaric transformation is defined as $C_P = R_g + C_V$. A mass of $m_{N_2} = 10\,\mathrm{g}$ of nitrogen is heated at constant pressure $P = 2\,\mathrm{atm}$ and an initial temperature of $T_i = 20\,°\mathrm{C}$ until its volume increases by 20%. Calculate the initial volume V, the final temperature T_f, and the heat supplied Q.

1.2.8.4 Ex: Volumetric thermal expansion of an ideal gas

a. Calculate the volumetric thermal expansion coefficient of an ideal gas at constant pressure.
b. Calculate the volumetric thermal expansion coefficient of an ideal gas during an adiabatic expansion.

1.2.8.5 Ex: Specific heat at constant volume/pressure

a. Explain why the specific heat at constant volume is less than the specific heat at constant pressure.
b. Show that for a diatomic gas $\gamma = \frac{C_P}{C_V} = \frac{7}{5}$.

1.2.8.6 Ex: Heat capacities

a. Two gas containers are brought into thermal contact. They contain gases with the temperatures T_1 and T_2, as well as the heat capacities C_1 and C_2. The thermal capacity of the containers is negligible. What is the temperature of the gases after an equilibrium has been reached?
b. Now consider the temperature equilibrium of three containers, each with 100 g of the gas H_2 at the temperature $T_{H_2} = 10\,°\mathrm{C}$, 50 g of the gas He at the temperature $T_{He} = 15\,°\mathrm{C}$, and 200 g of the gas N_2 at temperature $T_{N_2} = 20\,°\mathrm{C}$. What is the final temperature?

1.2.8.7 Ex: Gas compression

Calculate the temperature change resulting from *adiabatic* compression of an ideal gas of volume $V(T_1)$ to $V(T_2) = V(T_1)/10$.
Compare this with the temperature change through an analog *isobaric* compression of an equally ideal gas. **Note:** $\gamma = c_P/c_V = 1.4$ (for air), $T_1 = 293\,\mathrm{K}$.

1.2.8.8 Ex: Gas compression

An oxygen bottle with the volume $V_2 = 40\,\mathrm{l}$ contains a filling ex works that would have the volume $V_1 = 6\,\mathrm{m}^3$ at atmospheric pressure $P_1 = 101\,\mathrm{kPa}$. The bottle, which has been emptied to atmospheric pressure, is refilled at a constant temperature of $T_1 = 18\,°\mathrm{C}$. What mechanical work W must be added to the gas to compress it isothermally from P_1 to the filling pressure?

1.2.8.9 Ex: Gas expansion

1 kmol of nitrogen under normal conditions ($P_0 = 1.01 \times 10^5\,\mathrm{Pa}$, $T = 0\,^\circ\mathrm{C}$) adiabatically expands from V_1 to $V_2 = 5V_1$. Calculate the change in the internal energy of the gas and the amount of work the gas does as it expands.

1.2.8.10 Ex: Adiabatic expansion

a. During the adiabatic expansion of a gas the pressure P and the volume V of the gas satisfy the relationship $PV^\gamma = \alpha$, where α is a constant, and γ is the factor of the gas that gives the ratio between the specific heats at constant pressure and volume, i.e. $\gamma = c_P/c_V$. A gas was placed in a cylinder with a movable (frictionless) plunger completely insulated from the external environment. The assembly makes it possible to measure the volume and pressure of the gas during its expansion and the experimental values obtained are given in the table below.
a. From the values in the table below, and using the least squares method, determine the gas factor and the constant α. (**Hint:** To obtain a linear relationship, take $x = \lg V$ and $y = \lg P$.).
b. Determine, through the method of least squares, the uncertainties in the values obtained for γ and α.
c. Using a log×log paper, prepare a graph $P \times V$ and determine the values of γ and α. Compare with the results obtained by the least squares method.
Notes: When displaying the values of γ and α, be sure to indicate the units in which they are expressed.
Display the values of S_x, S_y, S_{x2} and S_{xy} used in the least squares method calculations.

V (l)	P (atm)
40	1.20
41	1.16
43	1.10
44	1.05
46	0.98
47	0.96
49	0.90
50	0.87

1.2.8.11 Ex: 1. law of thermodynamics

In a thermally insulated container B there are n mol of an ideal gas and a body K with the heat capacity C. Specify the relationship between pressure P and volume V, whereby the change in V is carried out so slowly that the following always applies to body and gas: $T_\mathrm{K} = T_\mathrm{G}$.
Note: Body and gas exchange heat. Assume that the container itself does not take heat from the gas or the body.

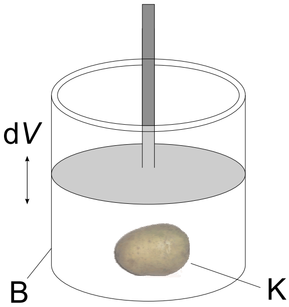

Figure 1.26: Potato.

1.2.8.12 Ex: 1. law of thermodynamics

A container with 1 mol helium and a container of the same size with 1 mol nitrogen are both heated with the same heating power $P_Q = 10\,\mathrm{W}$.
a. Calculate how long it takes to warm up the containers from $T_1 = 20\,^\circ\mathrm{C}$ to $T_2 = 100\,^\circ\mathrm{C}$, if the thermal capacity of the container is $C_{rec} = 10\,\mathrm{J/K}$.
b. How long does it take to warm up to 1000 °C assuming that the vibrational degrees freedom of N_2 molecules can be excited above 500 °C? Neglect heat loss.

1.2.8.13 Ex: Rüchardt's calorimetric method

A mono-atomic ideal gas with the adiabatic coefficient $\gamma = 1.4$ is in a thermally insulated bottle with a long neck. The total volume of the bottle and the neck is $V_0 = 10\,\mathrm{l}$. At the beginning there is atmospheric pressure. A thermally insulating ball with mass $m = 20\,\mathrm{g}$ is now inserted into the neck (precision tube with a diameter of $d = 16\,\mathrm{mm}$), which hermetically seals the bottle to the outside. The ball can move smoothly.
a. Determine the equilibrium position of the ball. What is the pressure and volume in the part of the bottle sealed by the ball?
b. The ball is now pushed down slightly from the equilibrium position and then released. With what period τ does the ball vibrate.
Help: Relate the instantaneous pressure p in the bottle to small volume changes ΔV and linearize the expression using a Taylor expansion.

1.2.8.14 Ex: Calorimeter for mixtures

The specific heat capacity of platinum c_{Pt} is to be measured with a mixing calorimeter. For this purpose, a platinum body is heated to 100 °C and then thrown into water of 20 °C. To simplify the evaluation, the mass of the water is chosen to be that of the platinum body. The heat absorption of the calorimeter body should be neglected. The specific heat capacity of water is $c_{\mathrm{H_2O}} = 4.19\,\mathrm{J/(g\,K)}$, the relative atomic mass of platinum is $m_{\mathrm{Pt}} = 195\,\mathrm{u}$, the linear expansion coefficient $\alpha = 9.0 \cdot 10^{-6}\,\mathrm{K^{-1}}$.
a. The mixing temperature is 22.41 °C. What value follows for c_{Pt}?
b. What is the value for c_{Pt} when applying the Dulong-Petit rule?
c. The platinum body and the water have the same mass. What is the ratio of the

number of platinum atoms to the number of water molecules?
d. How many degrees does the platinum body have to be heated to increase its volume by 1 %?

1.2.8.15 Ex: Calorimeter for mixtures

The equation of state of an ideal gas $PV = Nk_BT$ applies and the energy is given as $E = C_VT$.
a. Show that for the entropy change of an ideal gas from state A with temperature T_A and volume V_A to state B with temperature T_B and volume V_B holds: $\Delta S = C_V \ln(T_B/T_A) + Nk_B \ln(V_B/V_A)$.
b. Two insulated containers with the same volume $V = 10\,\mathrm{cm}^3$, the same pressure $P = 1\,\mathrm{bar}$ and the same temperature $T = 100\,^\circ\mathrm{C}$ are filled with nitrogen and oxygen, respectively. Determine the change in entropy when connecting the containers so that the gases can mix.

1.2.8.16 Ex: 2. law of thermodynamics

A thermally insulated container with a total volume of $10\,\mathrm{l}$ is separated into two equal parts by a disc. In each part there are $10\,\mathrm{mol}$ of an ideal atomic gas. In one part the gas has the temperature $T_1 = 300\,\mathrm{K}$, in the other the temperature $T_2 = 400\,\mathrm{K}$. Calculate the change in the total entropy of the system ΔS in the event that:
a. the disc does not insulate heat;
b. a small hole opens in the disc through which the gases can mix slowly and which at the end closes again;
c. the disc is suddenly removed and then put back in after some time without any work being done.
In all three cases there we wait for equilibrium to establish.

1.2.8.17 Ex: 2. law of thermodynamics

A heat engine works between two heat sources with temperatures $T_2 > T_1$. If we take away the heat δQ from the second heat source, what is the maximum and minimum work δW_{max} and δW_{min} that the heating machine can do? What could the corresponding processes look like?

1.2.8.18 Ex: Specific heat

Calculate the specific heat per mol of an ideal gas for a reversible process according to the law $PV^\gamma = const$ with $\gamma \in \mathbb{R}$. Can such specific heat be negative? Justify the result.

1.2.8.19 Ex: Expansion of a gas

One mole of a simple ideal gas, defined by $E = cR_gT$, $PV = R_gT$, is contained in a container of initial volume V_0 and pressure P_0. The gas expands from that initial state to the state corresponding to a final volume $2V_0$, through several different processes. Determine the work W done by the gas and the heat Q received by the gas for each of these processes. Final answers should be given only in terms of (V_0, P_0) and the

constant c.
a. Free expansion: also determine the temperature variation ΔT.
b. Isentropic expansion: also obtain the final pressure P_f, using the fact that in this process for an ideal gas $PV^\gamma = constant$, where $\gamma = (c+1)/c$.
c. Isobaric quasi-static expansion.
d. Isothermal quasi-static expansion.

1.2.8.20 Ex: Adiabatic expansion

A diatomic gas is initially maintained at a pressure of $P_i = 4000\,\text{hPa}$ in a piston of volume $V_i = 1\,\text{l}$ at temperature $T_i = 100\,°\text{C}$. Now the gas pressure forces the piston to move until it reaches half the pressure. Considering the expansion as an adiabatic process,
a. calculate the number of moles η inside the piston;
b. calculate the thermal capacities at constant volume C_V of the gas, as well as at constant pressure C_P, and determine the adiabatic coefficient γ;
c. calculate the final volume of the piston;
d. calculate the final temperature of the gas;
e. calculate the work done by the gas on the piston.
f. Now, the gas cools down gradually while the piston is held fix. Calculate the pressure P_r when the temperature reached $T_r = 20\,°\text{C}$.

1.2.8.21 Ex: Entropy changes

a. What entropy increase results when 200 g of (liquid) water at 0 °C and 200 g water at 90 °C are mixed at constant pressure in a heat-insulated recipient? The molar heat c_p of the water should be 75.5 J/(mol K) regardless of the temperature.
b. $1\,\text{dm}^3$ helium at $P_0 = 1\,\text{bar}$ and $T_0 = 0\,°\text{C}$ are heated to the temperature $T = 500\,\text{K}$. How big is the change in entropy upon isochoric and isobaric heating?

1.2.8.22 Ex: Heat capacity

When drilling a brass block of mass $m = 500\,\text{g}$ ($c = 0.1\,\text{cal/(g K)}$), a power of 300 W is provided for 2 minutes. What is the temperature rise of the block, if 75% of the heat generated warms it up? What happens to the remaining 25%?

1.2.8.23 Ex: Heat and work upon thermodynamic processes in an ideal gas

Calculate for an ideal the heat generated and the work executed for all equilibrium thermodynamic processes involving the active change of one of the state variables T, S, P, V, while maintaining one other variable fixed. Check with the expressions listed in Tab. 1.2.

1.2.8.24 Ex: Heat power engine and heat pump based on Carnot cycle

Consider a heat power engine and a heat pump based on the Carnot cycle. Calculate the efficiency and the generated, respectively, consumed power as a function of the temperature difference between the hot and the cold bath.

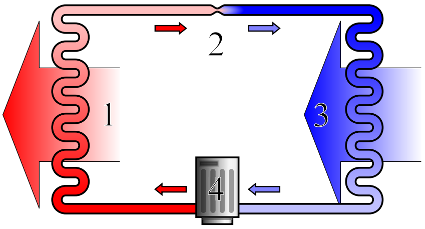

Figure 1.27: Principle of a heat pump.

1.2.8.25 Ex: The Otto cycle

Calculate the yield $\eta = \Delta W/\Delta Q$ of the *Otto cycle*, where ΔQ is the heat received by the system and ΔW the work executed, (see Fig. 1.28).

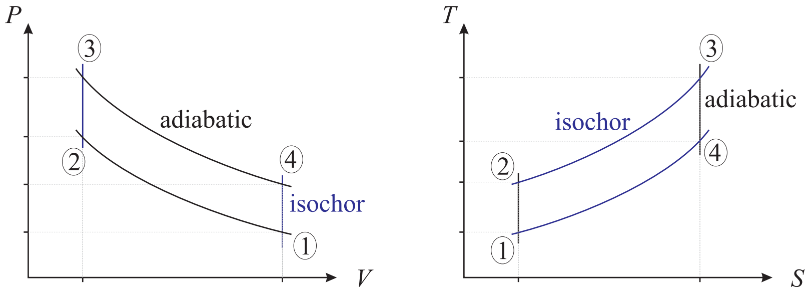
P
③
adiabatic
②
④
isochor
①
V
T
③
adiabatic
isochor
②
④
①
S

Figure 1.28: Otto cyclic process. The black branches are adiabatic processes.

1.2.8.26 Ex: The Diesel cycle

Calculate the yield $\eta = \Delta W/\Delta Q$ of the *Diesel cycle*, where ΔQ is the heat received by the system and ΔW the work executed, (see Fig. 1.29).

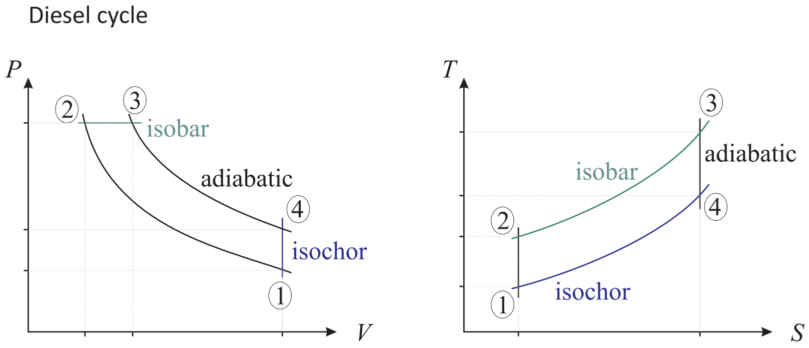
Diesel cycle
P
②
③
isobar
adiabatic
④
isochor
①
V
T
③
adiabatic
isobar
②
④
isochor
①
S

Figure 1.29: PV-diagram (left) and TS-diagram (right) for the Diesel cycle. The black branches are adiabatic processes.

1.2.8.27 Ex: Brayton cycle modeling a gas turbine

Calculate the efficiency of the Brayton cycle modeling a gas turbine, as shown in Fig. 1.30.

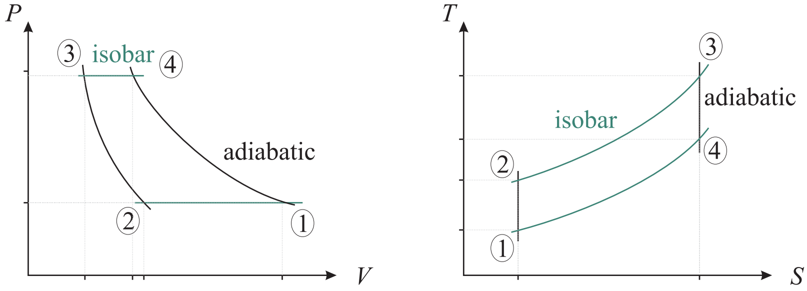

Figure 1.30: PV-diagram (left) and TS-diagram (right) for the Brayton cycle.

1.2.8.28 Ex: Cyclic process

An ideal gas with N atoms and the heat capacities $C_V = \frac{3}{2}Nk_B$ and $C_P = \frac{5}{2}Nk_B$ goes through the cycle shown in Fig. 1.31. For the starting point (1) its pressure P_1, volume V_1, and thus also the temperature T_1 are known.
a. Calculate P_2, T_2, P_3 and T_3, if $V_2 = V_3 = 3V_1$.
b. Calculate the work done and the heat input for all three steps of the cyclic process, as well as the efficiency.

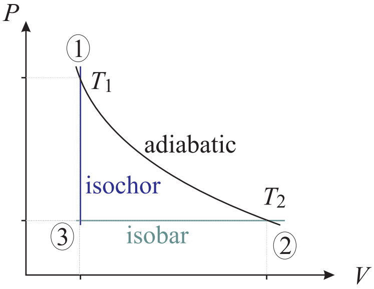

Figure 1.31: Cyclic process.

1.2.8.29 Ex: Heat engine cycle with two isochoric phases

In a heat power machine (illustrated in Fig. 1.32), the working gas (helium) is sealed off in a cylinder by a movable piston. The gas is alternately heated and cooled from the outside. The piston moves back and forth periodically and drives a shaft. The initial state is: $P = 0.2 \cdot 10^6$ Pa, $V = 150\,\mathrm{cm}^3$, $T = 300\,\mathrm{K}$.
a. Calculate the mass of the enclosed helium and the adiabaticity coefficient.
b. During a complete work cycle, the gas undergoes the following changes in its state:
$1 \to 2$ isochoric heating to twice the temperature,

2 → 3 isothermal expansion to twice the volume,
3 → 4 isochoric cooling to the initial temperature,
4 → 1 isothermal compression to initial volume.
Calculate the work done and the heat input for all three steps of the cyclic process.

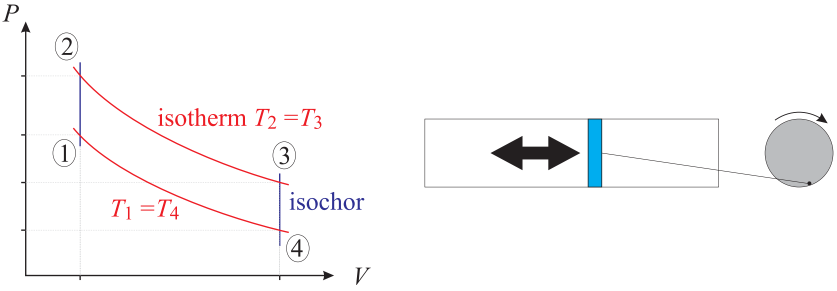

Figure 1.32: Cyclic process and scheme of a heat power engine

1.2.8.30 Ex: Heat engine cycle with two isochoric phases

An engine, whose four work steps consist of two isothermal and two isochoric processes, runs at a speed of $N = 500\,\text{min}^{-1}$. There is $\nu = 0.5\,\text{mol}$ of an ideal, monoatomic gas in the volume of the engine. The parameters for the individually labeled working steps are $T_1 = 50\,°\text{C}$, $P_1 = 2\,\text{bar}$, and $P_2 = 5\,\text{bar}$.
a. Determine the volumes $V_1 = V_2$ and $V_3 = V_4$, the pressure P_4, and the temperature T_2.
b. What efficiency η does the cycle have?
c. How high is the net power P of the engine?

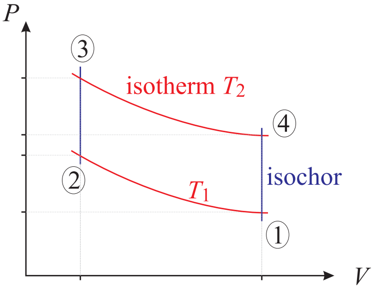

Figure 1.33: Cyclic process.

1.2.8.31 Ex: Cyclic process

A thermodynamic system is brought from an initial state (1) to another state (2), then to (3), and finally back to (1), as illustrated in the diagram in Fig. 1.34. Calculate the work and heat balance for the entire cycle.

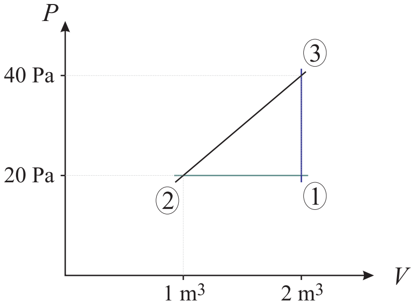

Figure 1.34: Cyclic process

1.2.8.32 Ex: Cyclic process

An ideal gas with N atoms and the heat capacities $C_V = \frac{3}{2}Nk_B$ and $C_P = \frac{5}{2}Nk_B$ goes through the cycle shown in Fig. 1.35: First an isotherm from (1) to (2), then an isobar from (2) to (3) and finally an isochor from (3) to (1). For the starting point (1), the temperature T_1 and the volume V_1 are known, for (2) V_2 is given.
a. Calculate the work done and the heat input for all three steps of the cyclic process, as well as the efficiency as a function of V_1 and V_2 and alternatively of T_1 and T_3.
b. Calculate the total changes of internal energy and entropy. Show explicitly that $\Delta Q/T$ remains the same, regardless of whether we go from (1) to (2) via a reversible isothermal process or first with a reversible isobaric process and then with a reversible isochoric process.

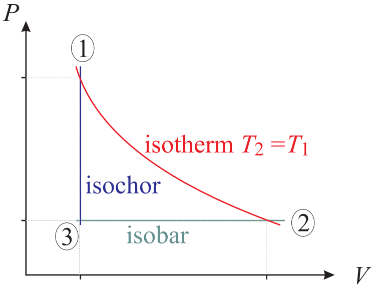

Figure 1.35: Cyclic process.

1.2.8.33 Ex: Cyclic process

Calculate the yield $\eta = \Delta W/\Delta Q$ of the process depicted in Fig. 1.36).

1.2.8.34 Ex: Real gas

Here we study a *real gas* whose state equation be given by the van der Waals formula (1.122).
a. Why is the critical point for the liquid-gas phase transition defined by to the

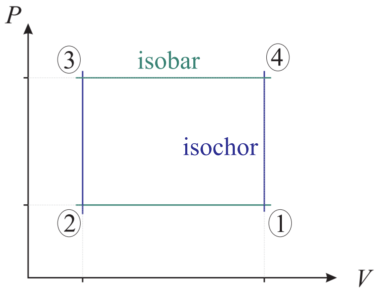

Figure 1.36: Cyclic process.

conditions,

$$\frac{dP}{d\tilde{V}} = \frac{d^2P}{d\tilde{V}^2} = 0 \ ?$$

b. Show that the temperature of the critical point T_c and the volume of the system at the critical point $\tilde{V}_c$ are linked to the material constants a and b by the relationships:

$$T_c = \frac{8a}{27R_g b} \qquad \text{and} \qquad \tilde{V}_c = 3b \ .$$

c. Calculate the pressure at the critical point P_c as a function of a and b.
d. Express the van der Waals formula in terms of rescaled parameters, $\tilde{V}_r \equiv \tilde{V}/\tilde{V}_c$, $T_r \equiv T/T_c$, $P_r \equiv P/P_c$, e. For CO_2 the values $a = 3.6 \cdot 10^{-6}\,\text{bar m}^6\,\text{mol}^{-2}$ and $b = 4.3 \cdot 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$ are suitable parameters of the van der Waals equation. Consider a mole of CO_2 and calculate the values for the critical point $\tilde{V}_c$, T_c and P_c.

1.2.8.35 Ex: Dieterici model for a real gas

Assume that one mole of a real gas satisfies the *Dieterici* equation of state (an alternative to the van der Waals equation),

$$Pe^{\alpha/(R_g T\tilde{V})}(\tilde{V} - \beta) = R_g T \ ,$$

where α and β are parameters.
a. In what units α and β have to be specified? What sign do you expect for each parameter?
b. Express the parameters of the critical point T_c and V_c by α and β.

1.2.8.36 Ex: Isothermal expansion

Calculate the work done during isothermal expansion from V_1 to V_2 of a real gas.

1.2.8.37 Ex: Joule-Thomson process

Here we study the *Joule-Thomson effect*. A gas is forced under constant pressure P_1 from a container B1 through a porous partition into a container B2 with constant pressure $P_2 < P_1$. The constancy of the pressures in the containers is ensured by

increasing or decreasing their volumes. Finally, it is assumed that the gas is adiabatically isolated from the environment and therefore only exchanges with it energy in the form of work.
a. Show that the enthalpy H remains constant in both recipients during this process.
b. Show that,

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] ,$$

and calculate $(\partial T/\partial P)_H$ explicitly for an ideal gas.
c. For a real gas, the so-called inversion curve $P(T)$ defined by $(\partial T/\partial P)_H$ is obtained in the PT-plane. Physically interpret the areas above and below this curve. Calculate the inversion curve for the van der Waals gas using the thermal equation of state for real gases.
d. Discuss the behavior of entropy in this process.

1.3 Thermodynamic equilibrium

Until now, we always assumed a system to be in thermal equilibrium, but we did not say how to determine what this state is. In the following, we will lay out general criteria for equilibrium and devise strategies for the calculation of equilibrium maps and phase diagrams.

Upfront let as note that *in an isolated system, the entropy is maximum at equilibrium.* We will translate this principle into a mathematical language consisting in a set of equations, called equilibrium conditions, which determine the relationships that the internal properties of the system must satisfy to find itself in equilibrium.

To discuss equilibrium conditions for a system, we need to allow it to be out of equilibrium. This obviously is not possible with the simple systems studied so far. The mere fact that they can be fully described by a single state function is due to the assumption that they are in equilibrium already, e.g. with the environment. We will thus illustrate the equilibrium conditions at a unary, two-phase system.

The notion of equilibrium is introduced in classical mechanics as a balance of forces. In thermodynamics the factors that influence the evolution of a systems are more general: whatever is doing work, transferring heat, or providing matter can drive a system out of equilibrium. To be at equilibrium a system must (i) be at rest and (ii) be balanced. The first condition means that, if not perturbed by external factors, the system does not change its state during time. The second condition means, that after a transient perturbation driving the system out of equilibrium the system finds back to its original state.

A system can be at steady-state while being driven by external influences, as illustrated in Fig. 1.37. We will, however, consider a system to be at equilibrium only, when it is stationary while being isolated from the environment. In that case, no entropy is exchanged with the environment, $dS_{trans} = 0$, so that all changes in entropy must result from internal production, $dS_{prod} > 0$. And since in equilibrium the entropy production comes to a halt, the *state of equilibrium is necessarily the one with the highest entropy.* This principle will be used as a criterion to help us in the quest for the equilibrium state of an isolated system [3].

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[3] Note that it doesn't matter how the equilibrium state was reached, e.g. whether it had interacted

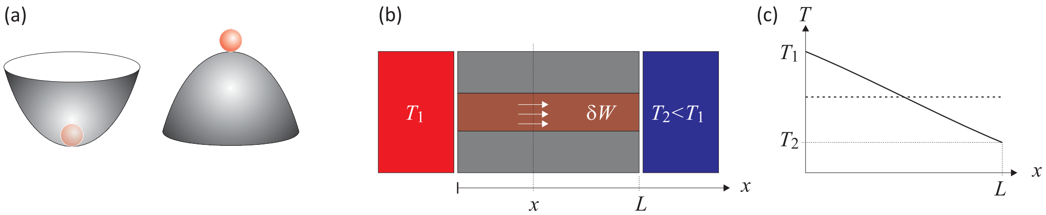

Figure 1.37: (a) Stable and unstable equilibrium positions in a mechanical system. (b) A thermally insulated copper rod conducting heat from a hot source to a cold sink develops a stationary temperature profile across its length (solid line in c). However, when disconnected from its surroundings (source and sink) it changes a temperature profile (dashed line in c).

1.3.1 Conditions for equilibrium

Mathematically the condition for equilibrium is spelled out by requesting the state to sit at an extremum of the state function. For instance, the state function $W = W(X,Y)$, whose differential is,

$$dW = \left(\frac{\partial W}{\partial X}\right)_Y dX + \left(\frac{\partial W}{\partial Y}\right)_X dY \ , \tag{1.134}$$

will have minima at those points (X_0, Y_0) satisfying the conditions,

$$\left(\frac{\partial W}{\partial X}\right)_{Y=Y_0} = 0 = \left(\frac{\partial W}{\partial Y}\right)_{X=X_0} \ . \tag{1.135}$$

The nature of the extrema, whether maximum, minimum, or saddle point, depends on the second derivatives of W at those points. The procedure can easily be extended to state functions of more variables. This procedure holds for independent variables, which generally is not the case. For instance, if the variables depend on each other, $Y = Y(X)$, we got a constraint.

A general procedure to handle this is the following:

1. Consider the state function, $W = W(X_1, X_2, ...)$, with the constraints $X_k = X_k(X_1, X_2, ...)$.

2. Write the differential forms for all equations, for the state equation:

$$dW = A_1 dX_1 + A_2 dX_2 + ... \qquad \text{with} \qquad A_j \equiv \left(\frac{\partial W}{\partial X_j}\right)_{\{X_{i|i\neq j}\}} \ , \tag{1.136}$$

   and for the constraints:

$$dX_k = B_{1k} dX_1 + B_{2k} dX_2 + ... \qquad \text{with} \qquad B_{1k} \equiv \left(\frac{\partial X_k}{\partial X_j}\right)_{\{X_{i|i\neq j}\}} \ . \tag{1.137}$$

3. Substitute dX_k in Eq. (1.136) and collect the coefficients C_l of the remaining terms $dX_{l|l\neq k}$,

$$dW = C_1 dX_{l_1} + C_2 dX_{l_2} + ... \ . \tag{1.138}$$

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transiently with some pump or sink. If it stays stationary once the pump or sink is removed, it should be considered at equilibrium.

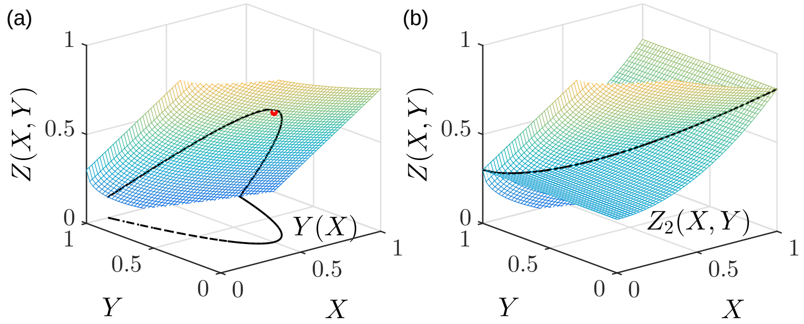


Figure 1.38: (code) Illustration of state function and constraints. The surface in (a) visualizes a state function depending on two variables; the black curve illustrates a possible constraint $Y = Y(x)$ between the variables. Fig. (b) shows the same surface as in (a), now constrained by and additional surface $Z_2 = Z_2(X, Y)$.

4. Set the coefficients to zero, $C_l = 0$. The solution of the system of equations yields the extremum under the constraint.

Example 12 (*Equilibrium condition with four variables*): To illustrate the procedure, let us consider the state function $W = W(U, V, X, Y)$ with two constraints, $U = U(X, Y)$ and $V = V(X, Y)$. The differential form are,

$$dW = AdU + BdV + CdX + DdY \quad , \quad dU = EdX + FdY \quad , \quad dV = GdX + HdY \ , \tag{1.139}$$

where the coefficients A to H are the partial derivatives taken with all other variables being help constant. Substituting dU and dV and collecting terms, we get,

$$\begin{aligned} dW &= A(EdX + FdY) + B(GdX + HdY) + CdX + DdY \\ &= (AE + BG + C)dX + (AF + BH + D)dY \ . \end{aligned} \tag{1.140}$$

Now, setting terms in the brackets to zero,

$$AE + BG + C = 0 = AF + BH + D \ , \tag{1.141}$$

we obtain the desired conditions for the extremum.

1.3.2 Entropy maximization in two-phase systems, chemical potential

Let us consider a unary, two-phase, non-reacting, and otherwise simple system. Both phases are characterized by their own set of extensive and intensive parameters. Now, the values of the extensive properties of both systems sum up,

$$S_1 + S_2 = S_{tot} \ , \tag{1.142}$$

and analogously for the other state functions V_j, E_j, H_j, F_j, G_j with $j = 1, 2$, but also for the number of particles N_j in each phase. If we now allow particles to move between the phases, as the state functions depend on the particle number, we need to consider this dependency,

$$E_j = E_j(S_j, V_j, N_j) \ , \tag{1.143}$$

and so on for the other state functions. This leads to a generalization of the differential form (1.68),

$$dE_j = T_j dS_j - P_j dV_j + \mu_j dN_j \ , \tag{1.144}$$

where we introduced the coefficient,

$$\boxed{\mu_j \equiv \left(\frac{\partial E_j}{\partial N_j}\right)_{S_j,V_j}} \ , \tag{1.145}$$

called *chemical potential* of the component j.

Resolving Eq. (1.144) by dS_j, we may now calculate the total entropy change,

$$dS_{tot} = dS_1 + dS_2 = \frac{1}{T_1}dE_1 + \frac{1}{T_2}dE_2 + \frac{P_1}{T_1}dV_1 + \frac{P_2}{T_2}dV_2 - \frac{\mu_1}{T_1}dN_1 - \frac{\mu_2}{T_2}dN_2 \ . \tag{1.146}$$

The fact that the system is closed implies, $dE_1 + dE_2 = 0$, $dV_1 + dV_2 = 0$, and $dN_1 + dN_2 = 0$. Using these constraints in (1.146) we get,

$$dS_{tot} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 \ . \tag{1.147}$$

Hence, the systems comes to equilibrium once the following conditions are fulfilled,

$$\boxed{\begin{array}{lcll} T_1 & = & T_2 & \text{thermal equilibrium} \\ P_1 & = & P_2 & \text{mechanical equilibrium} \\ \mu_1 & = & \mu_2 & \text{chemical equilibrium} \end{array}} \ . \tag{1.148}$$

Alternative formulations of the equilibrium criteria may be derive in terms of other thermodynamic state functions. A quick look at the expressions (1.68) informs us, that for systems constraint to

- $S = const$ and $V = const$, E is minimum at equilibrium;
- $S = const$ and $P = const$, H is minimum at equilibrium;
- $T = const$ and $V = const$, F is minimum at equilibrium;
- $T = const$ and $P = const$, G is minimum at equilibrium.

Application of any of these criteria leads to the same set of conditions for equilibrium.

1.3.3 Exercises

1.3.3.1 Ex: Gibbs free energy

Prove the relationship,

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V .$$

1.4 Thermodynamic ensembles

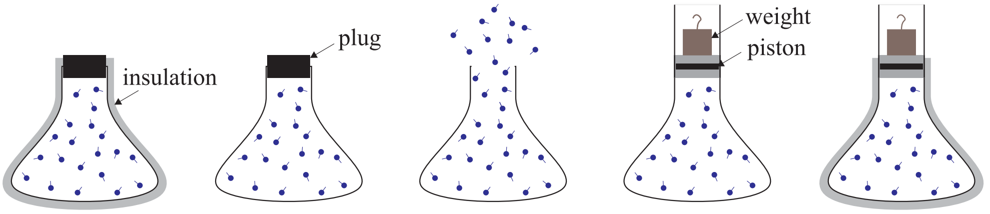
When we introduced the main thermodynamic potentials for canonical ensembles (1.68) we implicitly supposed that the particle number N is fixed. If we want to consider N as an equilibrium parameter, it must be treated as an independent state variable, as shown in Sec. 1.3.2, and consequently the thermodynamic potentials must be generalized.

The following eqs. (1.149) introduce several new energy state variables. The defined potential $\Omega(T,V,\mu)$ is the called the *Landau grand-canonical potential*. The potentials $\Psi(S,V,\mu)$ and $\Phi(S,P,\mu)$ are not used in practice. The potential $O(T,P,\mu)$ only depends on intensive variables and therefore cannot be a state energy, i.e. it must be zero, $O=0$. This is known as the *Gibbs-Duhem equation*, which will be treated in Sec. 3.2. The potentials will be discussed briefly in Sec. 1.4.1 and in detail in Chps. 2 and 3.

$$\boxed{\begin{aligned}
& & \delta Q_{rev} &= TdS \\
& & \delta W_{rev} &= -PdV \\
E &= \int(TdS - PdV + \mu dN) &\Longrightarrow\quad dE &= TdS - PdV + \mu dN \\
\Psi &= E - \mu N &\Longrightarrow\quad d\Psi &= TdS - PdV - Nd\mu \\
H &= E + PV &\Longrightarrow\quad dH &= TdS + VdP + \mu dN \\
\Phi &= H - \mu N &\Longrightarrow\quad d\Phi &= TdS + VdP - Nd\mu \\
F &= E - TS &\Longrightarrow\quad dF &= -SdT - PdV + \mu dN \\
\Omega &= F - \mu N &\Longrightarrow\quad d\Omega &= -SdT - PdV - Nd\mu \\
G &= H - TS &\Longrightarrow\quad dG &= -SdT + VdP + \mu dN \\
O &= G - \mu N = 0 &\Longrightarrow\quad dO &= -SdT + VdP - Nd\mu
\end{aligned}} \tag{1.149}$$

1.4.1 Coupling of thermodynamic ensembles to reservoirs

Application of the thermodynamic apparatus on physical systems requests certain idealizations. In the preceding sections, for instance, we studied the case of systems in equilibrium with themselves, but insulated from the environment. Often, we also tacitly assumed that the number of particles be fixed and termed this condition as *canonical ensemble*. There are, however, numerous real world situations deviating from the above conditions, for example, when a system is held at a given temperature



microcanonical (constant NVS) · canonical (constant NVT) · grand canonical (constant μVT) · isotherm-isobar (constant NPT) · isenthalpic-isobar (constant NPS)

Figure 1.39: Insulated or heat conducting, closed or open, rigid or working systems.

via thermal contact with a 'reservoir', or when chemical equilibrium is maintained via particle exchange with a 'reservoir'.

A *reservoir* is here regarded as a system with infinite resources of heat, work, and particles. Thermal, mechanical, or chemical contact with a reservoir will thus force any finite system to equilibrate to the conditions imposed by the reservoir. In practice, the details of the coupling between system and reservoir may however vary, as illustrated in Fig. 1.39. With respect to coupling to a reservoir a system may be insulated ($dS = 0$) or heat conducting ($T \to T_{eq}$), rigid ($dV = 0$) or compressible ($P \to P_{eq}$), closed ($dN = 0$) or open to particle exchange ($\mu \to \mu_{eq}$). From the intensive parameters (T, P, μ) only those parameters whose extensive counterpart are NOT held constant may act as equilibrium parameters. For example, holding S fixed the variable T cannot be an equilibrium parameter, and the system will be unable to exchange heat with the reservoir; holding V fixed the variable P cannot be an equilibrium parameter, and the system will be unable to work; holding N fixed the variable μ cannot be an equilibrium parameter, and the system will be unable to assimilate particles. This is summarized in Tab. 1.3.

Table 1.3: Various types of couplings to a reservoir.

type of coupling		equilibrium parameter
insulated	$dS = 0$	-
heat conducting	$dS \neq 0$	T
rigid	$dV = 0$	-
compressible	$dV \neq 0$	P
closed	$dN = 0$	-
open	$dN \neq 0$	μ

1.4.2 Thermodynamic potentials associated to specific ensembles

The choice of which parameters are held fixed and which are treated as equilibrium parameters depends on the properties of the system under consideration. Idealized theoretical models have been developed in the past by Helmholtz, Gibbs, and Landau, among others, for several paradigmatic physical situations. These models are called *thermodynamic ensembles*. They are named after the variables considered as invariant within this model. For example, assuming that holding the entropy, the volume, and the particle number is a good description of a particular physical system, we will model it by a NVS-ensemble. This frequently used model is also called *microcanonical ensemble*. From Eqs. (1.149) we see that if $dS = dV = dN = 0$, then the internal energy as well cannot change, $dE = 0$. That is, E is the characteristic energy associated to the microcanonical ensemble [4]. Do the Exc. 1.4.6.1.

Analogous statements hold for other ensembles, as summarized in Tab. 1.4. The most common ones are the microcanonical, the canonical, and the grand (or macro-) canonical ensembles. We will briefly introduce them in the following and postpone an in-depth discussion to Chp. 2. It is important, however, to keep in mind that all those ensembles only are approximative models for particular physical situations. The predictions obtained from these ensembles will only be as good as the assumptions they are based on represent a realistic image of the physical reality.

Table 1.4: Various thermodynamic ensembles.

ensemble name	const.param.	extensive parameter	assoc.pot.	equil.param.
microcanonical	NVS	$dS = dV = dN = 0$	$dE = 0$	-
	μVS	$dS = dV = 0$	$d\Psi = 0$	μ
isenthalpic-isobar	NPS	$dS = dN = 0$	$dH = 0$	P
	μPS	$dS = 0$	$d\Phi = 0$	P, μ
canonical	NVT	$dV = dN = 0$	$dF = 0$	T
grand canonical	μVT	$dV = 0$	$d\Omega = 0$	T, μ
isotherm-isobar	NPT	$dN = 0$	$dG = 0$	T, P
	μPT		$dO = 0$	T, P, μ

In the following we will qualitatively discuss the most common ones, which are the microcanonical, the canonical, and the grand-canonical ensembles.

1.4.3 Microcanonical ensemble

The *microcanonical ensemble* is used to represents the possible microstates of a mechanical system whose total energy E is exactly specified. The system is assumed to be isolated in the sense that it cannot exchange energy or particles with its environment, so that the energy of the system does not change with time. The primary macroscopic variables of the microcanonical ensemble are the total number of particles N in the system, the system's volume V, as well as the total energy E in the system.

In the microcanonical ensemble an equal probability $\mathfrak{P}(E)$ is assigned to every microstate whose energy falls within a range centered at E. All other microstates are given a probability of zero. Since the probabilities must add up to 1, the probability is the inverse of the number of microstates W within the range of energy,

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[4] For this reason, the microcanonical ensemble is also called NVE-ensemble.

$$\boxed{\mathfrak{P} = W^{-1}}\ . \tag{1.150}$$

The range of energy ΔE is then reduced in width until it is infinitesimally narrow, still centered at E. The microcanonical ensemble is obtained in the limit of this process. For a given mechanical system (fixed N, V) and a given range of energy, the uniform distribution of probability $\mathfrak{P}$ over microstates maximizes the ensemble average $-\langle \ln \mathfrak{P} \rangle$.

The quantum mechanics the density operator and partition function are given by,

$$\boxed{\begin{array}{rcl} \hat{\rho} & = & \frac{1}{\Xi} \sum_k |\psi_k\rangle f(\frac{E-\varepsilon_k}{\Delta E}) \langle \psi_k| \\ \Xi & = & \sum_k f(\frac{E-\varepsilon_k}{\Delta E}) \qquad \text{with} \qquad f(x) = \theta(\frac{1}{2} - |x|) \end{array}}\ . \tag{1.151}$$

1.4.3.1 Applicability

Because of its connection with the elementary assumptions of equilibrium statistical mechanics (particularly the postulate of a priori equal probabilities), the microcanonical ensemble is an important conceptual building block in the theory and is sometimes considered to be the fundamental distribution of equilibrium statistical mechanics. It is also useful in some numerical applications, such as molecular dynamics. On the other hand, most nontrivial systems are mathematically cumbersome to describe in the microcanonical ensemble, and there are also ambiguities regarding the definitions of entropy and temperature. For these reasons, other ensembles are often preferred for theoretical calculations.

The applicability of the microcanonical ensemble to real-world systems depends on the importance of energy fluctuations, which may result from interactions between the system and its environment as well as uncontrolled factors in preparing the system. Generally, fluctuations are negligible if a system is macroscopically large, or if it is manufactured with precisely known energy and thereafter maintained in near isolation from its environment. In such cases the microcanonical ensemble is applicable. Otherwise, different ensembles are more appropriate, such as the canonical ensemble (fluctuating energy) or the grand canonical ensemble (fluctuating energy and particle number).

1.4.3.2 Thermodynamic quantities

The fundamental thermodynamic potential of the microcanonical ensemble is entropy. Various definitions of entropy are possible, each given in terms of the phase volume function $v(E)$, which counts the total number of states with energy less than E.

- The Boltzmann entropy is,

$$S_B = k_B \ln W = k_B \ln \left(\Delta E \frac{dv}{dE} \right)\ , \tag{1.152}$$

- the 'volume entropy' is,

$$S_{vol} = k_B \ln v\ , \tag{1.153}$$

- and the 'surface entropy' is,

$$S_{sur} = k_B \ln \frac{dv}{dE} = S_B - k_B \ln \Delta E \ . \tag{1.154}$$

In the microcanonical ensemble, the temperature is a derived quantity rather than an external control parameter. It is defined as the derivative of the chosen entropy with respect to energy. For example, one can define the 'temperatures' T_{vol} and T_{sur} as follows:

$$\frac{1}{T_{vol}} = \frac{\partial S_{vol}}{\partial E} \quad , \quad \frac{1}{T_{sur}} = \frac{\partial S_{sur}}{\partial E} = \frac{\partial S_B}{\partial E} \ . \tag{1.155}$$

Like entropy, there are multiple ways to understand temperature in the microcanonical ensemble. Particularly for finite systems, the correspondence between these ensemble-based definitions and their thermodynamic counterparts is not perfect.

The microcanonical pressure and chemical potential are given by:

$$\frac{P}{T} = \frac{\partial S}{\partial V} \quad , \quad \frac{\mu}{T} = -\frac{\partial S}{\partial N} \ . \tag{1.156}$$

1.4.3.3 Phase transitions and thermodynamic analogies

Under their strict definition, phase transitions correspond to non-analytic behavior in the thermodynamic potential or its derivatives. Using this definition, phase transitions in the microcanonical ensemble can occur in systems of any size. This contrasts with the canonical and grand canonical ensembles, for which phase transitions can occur only in the thermodynamic limit– i.e. in systems with infinitely many degrees of freedom. Roughly speaking, the reservoirs defining the canonical or grand canonical ensembles introduce fluctuations that 'smooth out' any non-analytic behavior in the free energy of finite systems. This smoothing effect is usually negligible in macroscopic systems, which are sufficiently large that the free energy can approximate non-analytic behavior exceedingly well. However, the technical difference in ensembles may be important in the theoretical analysis of small systems.

The volume entropy S_{vol} and associated temperature T_{vol} form a close analogy to thermodynamic entropy and temperature. It is possible to show exactly that,

$$dE = T_{vol} dS_{vol} - \langle P \rangle dV \ , \tag{1.157}$$

where $\langle P \rangle$ is the ensemble average pressure, as expected for the first law of thermodynamics. A similar equation can be found for the surface entropy and its associated temperature T_{sur}, however the 'pressure' in this equation is a complicated quantity unrelated to the average pressure.

The microcanonical T_{vol} and T_{sur} are not entirely satisfactory in their analogy to temperature. Outside of the thermodynamic limit, a number of artefacts occur.

- Nontrivial result of combining two systems: Two systems, each described by an independent microcanonical ensemble, can be brought into thermal contact and be allowed to equilibriate into a combined system also described by a microcanonical ensemble. Unfortunately, the energy flow between the two systems cannot be predicted based on the initial T's. Even when the initial T's are equal, there may be energy transferred. Moreover, the T of the combination is different from the initial values. This contradicts the intuition that temperature should be an intensive quantity, and that two equal-temperature systems should be unaffected by being brought into thermal contact.

- Strange behavior for few-particle systems: Many results, such as the microcanonical equipartition theorem acquire a one- or two-degree of freedom offset when written in terms of T_{sur}. For a small systems this offset is significant, and so if we make S_{sur} the analogue of entropy, several exceptions need to be made for systems with only one or two degrees of freedom.

- Spurious negative temperatures: A negative T_{sur} occurs whenever the density of states decreases with energy. In some systems the density of states is not monotonic in energy, and so T_{sur} can change sign multiple times as the energy is increased. The preferred solution to these problems is to avoid using the microcanonical ensemble. In many realistic cases a system is thermostatted to a heat bath so that the energy is not precisely known. Then, a more accurate description is the canonical ensemble or grand canonical ensemble, both of which have complete correspondence to thermodynamics.

Example 13 (*Ideal gas*): The fundamental quantity in the microcanonical ensemble is $W(E,V,N)$, which is equal to the phase space volume compatible with given (E,V,N). From W, all thermodynamic quantities can be calculated. For an ideal gas, the energy is independent of the particle positions, which therefore contribute a factor of V^N to W. The momenta, by contrast, are constrained to a $3N$-dimensional (hyper-)spherical shell of radius $\sqrt{2mE}$; their contribution is equal to the surface volume of this shell. The resulting expression for W is,

$$W = \frac{V^n}{N!}\frac{2\pi^{3N/2}}{\Gamma(3N/2)}(2mE)^{(3N-1)/2} \ .$$

where $\Gamma(.)$ is the gamma function, and the factor $N!$ has been included to account for the indistinguishability of particles (see Gibbs paradox). In the large N limit, the Boltzmann entropy $S = k_B \ln W$ is,

$$S = k_B N \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3}\frac{E}{N}\right)^{3/2}\right] + \frac{5}{2}k_B N + O(\ln N) \ .$$

This is also known as the Sackur-Tetrode equation.
The temperature is given by,

$$\frac{1}{T} \equiv \frac{\partial S}{\partial E} = \frac{3}{2}\frac{Nk_B}{E} \ .$$

which agrees with analogous result from the kinetic theory of gases. Calculating the pressure gives the ideal gas law,

$$\frac{P}{T} \equiv \frac{\partial S}{\partial V} = \frac{Nk_B}{V} \ .$$

Finally, the chemical potential μ is,

$$\mu \equiv -T\frac{\partial S}{\partial N} = k_B T \ln\left[\frac{V}{N}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] \ .$$

Example 14 (*Ideal gas in a uniform gravitational field*): The microcanonical phase volume can also be calculated explicitly for an ideal gas in a uniform gravitational field.
The results are stated below for a 3-dimensional ideal gas of N particles, each with mass m, confined in a thermally isolated container that is infinitely long in the z-direction and has constant cross-sectional area A. The gravitational field is assumed to act in the minus z direction with strength g. The phase volume $W(E,N)$ is,

$$W(E,N) = \frac{(2\pi)^{3N/2} A^n m^{N/2}}{g^n \Gamma(5N/2)} E^{\frac{5N}{2}-1} \,.$$

where E is the total energy, kinetic plus gravitational.
The gas density $\rho(z)$ as a function of height z can be obtained by integrating over the phase volume coordinates. The result is,

$$\rho(z) = \left(\frac{5N}{2} - 1\right) \frac{mg}{E} \left(1 - \frac{mgz}{E}\right)^{\frac{5N}{2}-2} \,.$$

Similarly, the distribution of the velocity magnitude $|\mathbf{v}|$ (averaged over all heights) is,

$$f(|\mathbf{v}|) = \frac{\Gamma(5N/2)}{\Gamma(3/2)\Gamma(5N/2 - 3/2)} \times \frac{m^{3/2}|\mathbf{v}|^2}{2^{1/2}E^{3/2}} \times \left(1 - \frac{m|\mathbf{v}|^2}{2E}\right)^{\frac{5(N-1)}{2}} \,.$$

The analogues of these equations in the canonical ensemble are the barometric formula and the Maxwell-Boltzmann distribution, respectively. In the limit $N \to \infty$, the microcanonical and canonical expressions coincide; however, they differ for finite N. In particular, in the microcanonical ensemble, the positions and velocities are not statistically independent. As a result, the kinetic temperature, defined as the average kinetic energy in a given volume Adz, is nonuniform throughout the container,

$$T_{\text{kinetic}} = \frac{3E}{5N-2} \left(1 - \frac{mgz}{E}\right) \,.$$

By contrast, in the canonical ensemble the temperature is uniform, for any N.

1.4.4 Canonical ensemble

The *canonical ensemble* is used to represent the possible microstates of a mechanical system in thermal equilibrium with a heat bath at a fixed temperature. The system can exchange energy with the heat bath, so that the states of the system will differ in total energy. The principal thermodynamic variable of the canonical ensemble, determining the probability distribution of states, is the absolute temperature T. The ensemble typically also depends on mechanical variables, such as the number of particles N in the system and the system's volume V, each of which influence the nature of the system's internal states.

The canonical ensemble assigns a probability $\mathfrak{P}(E)$ to each distinct microstate given by the following exponential,

$$\boxed{\mathfrak{P} = e^{\beta(F-E)} = \tfrac{1}{\Xi} e^{-E/(kT)} \qquad \text{with} \qquad \Xi = e^{-F/(kT)}} \,, \tag{1.158}$$

where E is the total energy of the microstate and Ξ the canonical partition function.

In quantum mechanics the density operator and partition function are,

$$\boxed{\begin{array}{lcl} \hat{\rho} & = & e^{\beta(F-\hat{H})} = \frac{e^{-\beta\hat{H}}}{\Xi} = \frac{1}{\Xi}\sum_k |\psi_k\rangle e^{\beta(F-E_k)}\langle\psi_k| \\ \Xi & = & \mathrm{Tr}\; e^{-\beta\hat{H}} = e^{-\beta F} = \sum_k e^{-\beta E_k} \end{array}} \; . \qquad (1.159)$$

The Helmholtz free energy F is constant for the ensemble. However, the probabilities and F will vary if different N, V, T are selected. The free energy F serves two roles: first, it provides a normalization factor for the probability distribution (the probabilities, over the complete set of microstates, must add up to one); second, many important ensemble averages can be directly calculated from the function $F(N, V, T)$.

1.4.4.1 Applicability

The canonical ensemble is the ensemble that describes the possible states of a system that is in thermal equilibrium with a heat bath. It applies to systems of any size; while it is necessary to assume that the heat bath is very large (i.e. take a macroscopic limit), the system itself may be small or large.

The condition that the system is mechanically isolated is necessary in order to ensure it does not exchange energy with any external object besides the heat bath. In general, it is desirable to apply the canonical ensemble to systems that are in direct contact with the heat bath, since it is that contact that ensures the equilibrium. In practical situations, the use of the canonical ensemble is usually justified either (1) by assuming that the contact is mechanically weak, or (2) by incorporating a suitable part of the heat bath connection into the system under analysis, so that the connection's mechanical influence on the system is modeled within the system.

When the total energy is fixed but the internal state of the system is otherwise unknown, the appropriate description is not the canonical ensemble but the microcanonical ensemble. For systems where the particle number is variable (due to contact with a particle reservoir), the correct description is the grand canonical ensemble.

Example 15 (*Boltzmann distribution for a separable system*): A system of non-interacting particles can be separated into independent parts. If such a system is described by a canonical ensemble, then each part can be seen as a system unto itself and described by a canonical ensemble having the same temperature as the whole. In this way, the canonical ensemble provides exactly the Maxwell-Boltzmann statistics for systems of any number of particles. In comparison, the justification of the Boltzmann distribution from the microcanonical ensemble only applies for systems with a large number of particles, that is, in the thermodynamic limit. The Boltzmann distribution itself is one of the most important tools in applying statistical mechanics to real systems, as it dramatically simplifies the study of systems that can be separated into independent parts (e.g. particles in a gas, electromagnetic modes in a cavity, etc.).

1.4.4.2 Thermodynamic quantities

The partial derivatives of the function $F(N, V, T)$ yield important canonical ensemble average quantities: the average pressure is,

$$\langle P \rangle = -\frac{\partial F}{\partial V} \ , \tag{1.160}$$

the entropy is,

$$\langle S \rangle = -k_B \langle \ln \mathfrak{P} \rangle = -\frac{\partial F}{\partial T} \ , \tag{1.161}$$

the partial derivative $\partial F/\partial N$ is approximately related to chemical potential, although the concept of chemical equilibrium does not exactly apply to canonical ensembles of small systems, and the average energy is,

$$\langle E \rangle = F + T\langle S \rangle \ . \tag{1.162}$$

From the above expressions, it can be seen that, for a given N, the function $F(V, T)$ has the exact differential,

$$dF = -\langle S \rangle dT - \langle P \rangle dV \ . \tag{1.163}$$

Substituting the above relationship for $\langle E \rangle$ into the exact differential of F, an equation similar to the first law of thermodynamics is found,

$$d\langle E \rangle = TdS - \langle P \rangle dV \ . \tag{1.164}$$

The energy in the system is uncertain and fluctuates in the canonical ensemble. The variance of the energy is,

$$\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} \ . \tag{1.165}$$

Example 16 (*Ising model of strongly interacting systems*): In a system of strongly interacting particles, it is usually not possible to find a way to separate the system into independent subsystems as done in the Boltzmann distribution. In these systems it is necessary to resort to using the full expression of the canonical ensemble in order to describe the thermodynamics of the system when it is thermostatted to a heat bath. The Ising model, which is a widely discussed toy model for the phenomena of ferromagnetism, is one of the simplest models showing a phase transition.

1.4.5 Grand-canonical ensemble

The *grand-canonical ensemble* is used to represent the possible microstates of a system of particles that are in thermal and chemical equilibrium with a reservoir. The system is said to be open in the sense that the system can exchange energy and particles with a reservoir, so that various possible states of the system can differ in both their total energy and total number of particles. The system's volume, shape, and other external coordinates are kept the same in all possible states of the system.

The thermodynamic variables of the grand canonical ensemble are chemical potential μ and absolute temperature T. The ensemble is also dependent on mechanical variables such as volume V which influence the nature of the system's internal states. As each of these is assumed to be constant in the grand-canonical ensemble, it is sometimes called the μVT ensemble.

The grand-canonical ensemble assigns a probability $\mathfrak{P}(E)$ to each distinct microstate given by the following exponential [5],

$$\boxed{\mathfrak{P} = e^{\beta(\Omega+\mu N-E)} = \tfrac{1}{\Xi} e^{\beta(\mu N-E)} \qquad \text{with} \qquad \Xi = e^{-\beta\Omega}}\,, \tag{1.166}$$

where N is the number of particles in the microstate and E is the total energy of the microstate.

The quantum mechanics the density operator and partition function are,

$$\boxed{\begin{array}{rcl} \hat{\rho} & = & e^{\beta(\Omega+\mu\hat{N}-\hat{H})} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi} = \frac{1}{\Xi}\sum_k |\psi_k\rangle e^{\beta(\Omega+\mu n_k-E_k)}\langle\psi_k| \\ \Xi & = & \mathrm{Tr}\; e^{-\beta(\hat{H}-\mu\hat{N})} = e^{-\beta\Omega} = \sum_k e^{\beta(\mu n_k-E_k)} \end{array}}\,. \tag{1.167}$$

The grand potential Ω is constant for the ensemble. However, the probabilities and Ω will vary if different μ, V, T are selected. The grand potential Ω serves two roles: to provide a normalization factor for the probability distribution (the probabilities, over the complete set of microstates, must add up to one); second, many important ensemble averages can be directly calculated from the function $\Omega(\mu, V, T)$.

1.4.5.1 Applicability

The grand canonical ensemble is the ensemble that describes the possible states of an isolated system that is in thermal and chemical equilibrium with a reservoir. The grand canonical ensemble applies to systems of any size, small or large; it is only necessary to assume that the reservoir with which it is in contact is much larger (i.e. to take the macroscopic limit).

The condition that the system is isolated is necessary in order to ensure it has well-defined thermodynamic quantities and evolution. In practice, however, it is desirable to apply the grand canonical ensemble to describe systems that are in direct contact with the reservoir, since it is that contact that ensures the equilibrium. The use of the grand canonical ensemble in these cases is usually justified either (1) by assuming that the contact is weak, or (2) by incorporating a part of the reservoir connection into the system under analysis, so that the connection's influence on the region of interest is correctly modeled. Alternatively, theoretical approaches can be used to model the influence of the connection, yielding an open statistical ensemble.

Another case in which the grand canonical ensemble appears is when considering a system that is large and thermodynamic (a system that is 'in equilibrium with itself'). Even if the exact conditions of the system do not actually allow for variations in energy or particle number, the grand canonical ensemble can be used to simplify calculations of some thermodynamic properties. The reason for this is that various thermodynamic ensembles (microcanonical, canonical) become equivalent in some aspects to the grand canonical ensemble, once the system is very large. Of course, for small systems, the different ensembles are no longer equivalent even in the mean. As a result, the grand canonical ensemble can be highly inaccurate when applied to small systems of fixed particle number, such as atomic nuclei [6].

---

[5] In the case where more than one kind of particle is allowed to vary in number, the probability expression generalizes to $\mathfrak{P} = e^{\beta(\Omega+\mu_1 N_1+\mu_2 N_2+\ldots-E)}$, where μ_j is the chemical potential for the j-th kind of particles, N_j the number of that kind of particle in the microstate.

Grand ensembles are apt for use when describing systems such as electrons in a conductor or photons in a cavity, where the shape is fixed but the energy and number of particles can easily fluctuate due to contact with a reservoir (e.g. an electrical ground or a dark surface, in these cases). The grand canonical ensemble provides a natural setting for an exact derivation of the Fermi-Dirac statistics or Bose-Einstein statistics for a system of non-interacting quantum particles.

1.4.6 Exercises

1.4.6.1 Ex: Thermodynamic potential

What is the most suitable thermodynamic potential to describe a compressible system with fixed particle number held at constant temperature via thermal contact with a large reservoir. How is the corresponding ensemble called?

1.5 Further reading

H.M. Nussenzveig, Edgar Blucher (2014), *Curso de Fisica Basica: Fluidos, Vibrações e Ondas, Calor - vol 2* [ISBN]

R. DeHoff, *Thermodynamics in Material Science* [ISBN]

H.B. Callen, *Thermodynamics* [ISBN]

C. Kittel, *Introduction to Solid State Physics* [ISBN]

A.R. West, *Basic Solid State Chemistry* [ISBN]

D. Mc Quarry, *Statistical Thermodynamics* [ISBN]

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[6] Note that even in the thermodynamic limit, in the presence of long range interactions, the ensembles may not be equivalent.

Chapter 2

Statistical thermodynamics

All thermodynamic quantities studied so far (extensive or intensive) were quasi-continuous, i.e. macroscopic. The laws of thermodynamics found to rule the behavior of large systems were discovered empirically via experimental observations. The nature of the laws is thus phenomenological, i.e. not derived from first principles. Until now we totally neglected the fact that matter (gases, fluid, or solids) is composed of microscopic elementary particles (atoms or molecules). Nevertheless, it already became clear that the behavior of a system is somehow related to the properties of the particles that compose it. E.g. the degrees of freedom of a molecule that can be excited have an influence on the heat capacity of a gas composed of these molecules; the Joule-Thomson effect is due to intermolecular forces; and what we experience as heat, is actually an outward manifestation of molecular and atomic motion, as we already pointed out in Sec. 1.1.2. Tracing back macroscopic properties and phenomena to microscopic models bears a formidable potential of deepening our level of understanding thermodynamic systems. It may even provide insight into the physical meaning of mysterious or elusive phenomenological concepts such as entropy production.

An atomistic description acknowledges the fact that matter is quantized into small portions called molecules [1]. Each molecule is understood as a (not necessarily rigid) body characterized by its center-of-mass coordinates, but also its rotations or internal vibrations. With typically 10^{23} atoms in just one liter of air the task of describing the *microstate* by all its coordinates is hopeless. The mathematical discipline that provides the tools capable of handling such big numbers is *statistics*, and the primary tool supplied for the purpose is the concept of the *distribution function*. The idea is to lump atoms having similar properties together to classes, e.g. energy levels. The distribution function then simply reports the number of particles in each class, which dramatically reduces the amount of information. The task of *statistical thermodynamics* is now the description of a thermodynamic state in terms of a distribution function called *macrostate*. The formulation of statistical thermodynamics by *Boltzmann* and *Gibbs* provided a solid microscopic foundation of phenomenological thermodynamics.

We will begin this chapter with a calculation of the *Boltzmann distribution* of microstates over the macrostates in Sec. 2.1 and introduce the concept of *partition function*, from which all macroscopic state functions may be computed. As applications of this algorithm we will revisit the ideal gas and the Einstein model of a crystalline solid.

---

[1] The 'quantization' of matter is not to be understood in the quantum mechanical sense. Nevertheless, the particles themselves are generally microscopic and, under certain circumstances, may behave following rules dictated by quantum mechanics. This can lead to macroscopically observable phenomena studied in the area of quantum statistics, as we will learn in Chp. 2.2.

2.1 Microstates, macrostates, and entropy

2.1.1 Probabilities of microstates and the partition function

We consider a unary thermodynamic system composed of a very large number N of identical (albeit distinguishable) particles, each one sufficiently specified by a set of numbers (coordinates and internal quantum numbers). The list combining the sets of all particles completely describes the microstate of the system. It changes if a single number of just one particle is changed. The microstate also changes when we just exchange two particles, although the physics of the system cannot change if the particles are identical. Clearly, the macrostate of a system is invariant upon particle exchange.

On the other hand, the number of macrostates we attribute to a system depends on the information we want to gather. For example, we could split the volume occupied by a gas into two parts, V_1 and V_2, and call macrostate the situation when a specific number N_1 of particles is in volume V_1, no matter which particles. Or we could classify the particles by their velocities and prepare a histogram. Any distribution of the particles over the possible velocity classes leading to the exact same histogram would then belong to the same macrostate.

In general, the microstates outnumber the macrostates by many orders of magnitude such that, when a system evolves through a thermodynamic process, it moves through a large number of microstates. And since, a priori, all microstates have the same probability, the likeliness of a macrostate is just the number of microstates it encompasses. Let $1, 2, .., j, .., r$ denote the possible single-particle states that the system has to offer, n_j the number of particles being in the single-particle state j, and $\{n_1, n_2, .., n_j, .., n_r\}$ the actual macrostate. The number of microstates contributing to the same macrostate is easily found by combinatorial analysis,

$$\boxed{W_{\{n_j\}} = \frac{N!}{n_1!n_2!...n_r!}} , \tag{2.1}$$

with the total number of particles $N = n_1 + n_2 + ... + n_r$. The total number of possible microstates is obviously r^N. Hence, the probability to encounter the system in a particular macrostate is,

$$\mathfrak{P}_{\{n_j\}} = \frac{N!}{n_1!n_2!...n_r!}\frac{1}{r^N} = \frac{N!}{n_1!r^{n_1}\, n_2!r^{n_2}...n_r!r^{n_r}} . \tag{2.2}$$

Of all possible macrostates, there will be one containing the largest number of microstates, and the probability to encounter the system in this macrostate is highest. Examination of $\mathfrak{P}_{\{n_j\}}$ for a variety of macrostates $\{n_j\}$ reveals that the probability distribution is sharply peaked, and that macrostates deviating only slightly are already very unlikely. The most probable state is now interpreted as the *state of equilibrium*, and this hypothesis forms the basis for connecting phenomenological thermodynamics to an atomistic statistical description.

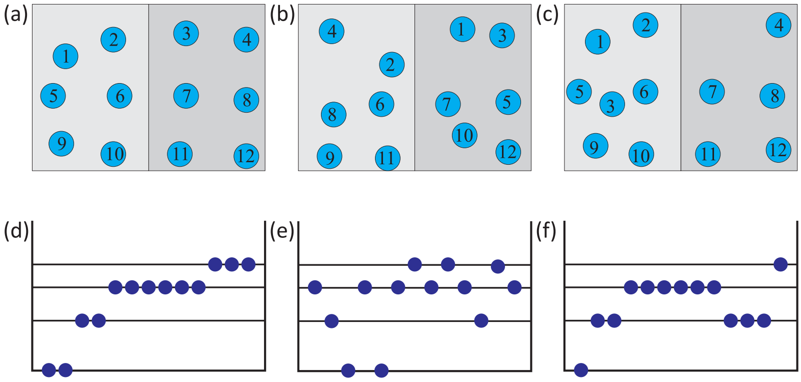

Figure 2.1: Illustration of micro- and macrostates with identical indistinguishable: (a-c) Distribution of 12 particles over 2 boxes. (d-f) Distribution of 13 particles over 4 energy levels. All schemes show different microstates, but only the schemes (a) and (b), respectively, (d) and (e) correspond to same macrostates.

The equilibrium condition for highest probability in the statistical description is similar to the request for highest entropy in phenomenological thermodynamics, which suggests that both concepts are connected. But while the entropy is additive (the entropies of subsystems sum up to a global entropy), the number of macrostates is multiplicative. This led Boltzmann to his famous hypothesis,

$$\boxed{S = k_B \ln W} \ . \tag{2.3}$$

Do the Excs. 2.1.7.1 to 2.1.7.7.

2.1.2 Equilibrium in statistical thermodynamics

Evaluating Eq. (2.3) involves computation of large factorials, which is a challenging numerical task. Fortunately, large factorials can be very well approximated by *Stirling's formula*,

$$\ln n! \simeq n \ln n - n \ . \tag{2.4}$$

With this formula we can simplify Eq. (2.3),

$$\begin{aligned} S = k_B \ln \frac{N!}{\prod_{j=1}^r n_j!} &\simeq k_B(N \ln N - N) - k_B \sum_{j=1}^r (n_j \ln n_j - n_j) \\ &= k_B N \ln N - k_B \sum_{j=1}^r n_j \ln n_j = -k_B \sum_{j=1}^r n_j \ln \frac{n_j}{N} \ . \end{aligned} \tag{2.5}$$

This expression allows to compute the entropy of any macrostate of the system.

To find the equilibrium macrostate $\{n_1, n_2, .., n_j, .., n_r\}_{eq}$ in the atomistic description, we have to maximize the entropy (2.5). That is, we have to evaluate the total differential of entropy in the direction of changes $\{dn_1, dn_2, .., dn_j, .., dn_r\}$ of the macrostate under the constraint $N = \sum_{j=1}^{r} n_j$,

$$dS = \sum_{j=1}^{r} \left(\frac{\partial S}{\partial n_j}\right) dn_j + \left(\frac{\partial S}{\partial N}\right) dN = -k_B \sum_{j=1}^{r} \left(1 + \ln \frac{n_j}{N}\right) dn_j + k_B \sum_{j=1}^{r} \frac{n_j}{N} dN \ , \tag{2.6}$$

yielding,

$$\boxed{dS = -k_B \sum_{j=1}^{r} \ln \frac{n_j}{N}\ dn_j} \ . \tag{2.7}$$

Application of the equilibrium criterion requires isolation from the environment, which sets constraints to the entropy evaluation in terms of particle and energy exchange,

$$N = \sum_{j=1}^{r} n_j \qquad \text{and} \qquad E = \sum_{j=1}^{r} \varepsilon_j n_j \ , \tag{2.8}$$

or equivalently [2],

$$dN = \sum_{j=1}^{r} dn_j = 0 \qquad \text{and} \qquad dE = \sum_{j=1}^{r} \varepsilon_j dn_j = 0 \ . \tag{2.9}$$

The maximum of the entropy function (2.5) under the constraints (2.9) can be found using the technique of Lagrange multipliers, which consists in solving the equation

$$0 = dS - \alpha k_B\, dN - \beta k_B\, dE = k_B \sum_{j=1}^{r} \left(-\ln \frac{n_j}{N} - \alpha - \beta \varepsilon_j\right) dn_j \tag{2.10}$$

for arbitrary factors α and β. This implies,

$$\frac{n_j}{N} = e^{-\alpha} e^{-\beta \varepsilon_j} \ , \tag{2.11}$$

for $j = 1, 2, ..., r$. The Lagrange multiplier α can readily be eliminated using the normalization constraint (2.8)(i),

$$1 = \sum_{j=1}^{r} \frac{n_j}{N} = e^{-\alpha} \sum_{j=1}^{r} e^{-\beta \varepsilon_j} \ , \tag{2.12}$$

leaving us with,

$$\frac{n_j}{N} = \frac{e^{-\beta \varepsilon_j}}{\sum_{j=1}^{r} e^{-\beta \varepsilon_j}} \ , \tag{2.13}$$

where we used the so-called *partition function*,

$$\Xi \equiv \sum_{j=1}^{r} e^{-\beta \varepsilon_j} = e^{\alpha} \ . \tag{2.14}$$

---

[2] Note that $d\varepsilon_j = 0$, if the energy levels do not vary along a thermodynamic process, only their population with particles.

To determine the Lagrange multiplier β, we compare the expressions obtained for the entropy variations in statistical and phenomenological thermodynamics. Solving (2.10) by dS and substituting α taken from (2.14) we get,

$$dS = -k_B \sum_{j=1}^{r} \ln \frac{e^{-\beta\varepsilon_j}}{\Xi}\, dn_j = k_B \sum_{j=1}^{r} (\beta\varepsilon_j + \ln\Xi)\, dn_j = k_B\beta\; dE + k_B \ln\Xi\; dN \; . \tag{2.15}$$

And from (1.146) we get,

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \; , \tag{2.16}$$

where μ is the chemical potential per atom and $dV = 0$, since we assumed in this derivation, that every atom has access to the whole volume of the system. A comparison of the expressions (2.15) and (2.16) then yields,

$$\beta = \frac{1}{k_BT} \qquad \text{and} \qquad \mu = k_BT\ln\Xi \; . \tag{2.17}$$

Substitution into (2.13) and (2.14) finally yields,

$$\boxed{\frac{n_j}{N} = \frac{1}{\Xi}e^{-\varepsilon_j/k_BT} \qquad \text{with} \qquad \Xi = \sum_{j=1}^{r} e^{-\varepsilon_j/k_BT}} \; . \tag{2.18}$$

This expression is known as *Boltzmann distribution*.

2.1.3 Thermodynamic potentials in canonical ensembles

We wish now to express all state functions of the system in terms of the partition function (2.14). To this end we begin calculating the Helmholtz free energy using the expressions for the total energy (2.8)(ii) and the entropy (2.5),

$$F = E - TS = \sum_{j=1}^{r} n_j\varepsilon_j + k_BT \sum_{j=1}^{r} n_j \ln \frac{e^{-\beta\varepsilon_j}}{\Xi} = -k_BTN\ln\Xi \; . \tag{2.19}$$

Hence, $\Xi = e^{-\beta F}$ and,

$$\frac{n_j}{N} = e^{\beta(F-\varepsilon_j)} \tag{2.20}$$

confirming the role of the free energy (1.159) for normalization of the canonical probability distribution.

The entropy function can now be expressed by the coefficient relation (1.73)(ii),

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk_B\ln\Xi + Nk_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_V \; , \tag{2.21}$$

the internal energy becomes,

$$E = F + TS = Nk_BT^2\left(\frac{\partial\ln\Xi}{\partial T}\right)_V \; , \tag{2.22}$$

and the heat capacity (1.71)(ii),

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 2Nk_BT\left(\frac{\partial \ln \Xi}{\partial T}\right)_V + Nk_BT^2\left(\frac{\partial^2 \ln \Xi}{\partial T^2}\right)_V \quad . \tag{2.23}$$

To compute the remaining thermodynamic potentials, V, H, G, and C_P, we need to generalize the partition function to include pressure dependence. This will be done later in Sec. 2.5.2.

In summary, the state of thermodynamic equilibrium is characterized by the fact the particles are distributed over the available energy levels according to the exponential function (2.11). Once the energy levels are known for a system, the partition function and all the thermodynamic potentials can be calculated. We will now study the algorithm at several examples.

2.1.4 Two-level systems

Let us consider a system consisting of only two allowed energy levels $\varepsilon_j = 0, \varepsilon$, that is, we set the energy of the ground state to zero. This system is relevant for atomic system in equilibrium with radiation fields driving electronic transitions between excitation levels. The Boltzmann partition function and the population (2.18) then become,

$$\Xi = \sum_{j=1}^{r} e^{-\beta\varepsilon_j} = 1 + e^{-\beta\varepsilon} \qquad , \tag{2.24}$$

$$\frac{n_1}{N} = \frac{1}{\Xi} = \frac{1}{1+e^{-\beta\varepsilon}} \qquad , \qquad \frac{n_2}{N} = \frac{e^{-\beta\varepsilon}}{\Xi} = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} \ . \tag{2.25}$$

In particular, the ratio between populations of consecutive levels is, $n_1/n_2 = e^{-\beta\varepsilon}$. At low temperature, $k_BT \ll \varepsilon$, the excited state population is negligibly small, while at high temperature, $k_BT \gg \varepsilon$, both energy levels have almost the same population. Do the Exc. 2.1.7.8.

With the partition function it is easy to evaluate the potentials,

$$\begin{aligned}
F &= -Nk_BT\ln\Xi = -Nk_BT\ln(1+e^{-\beta\varepsilon}) \qquad (2.26)\\
S &= Nk_B\ln\Xi + Nk_BT\left(\frac{\partial \ln \Xi}{\partial T}\right)_V = Nk_B\ln(1+e^{-\beta\varepsilon}) + \frac{N\varepsilon}{T}\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\\
E &= Nk_BT^2\left(\frac{\partial \ln \Xi}{\partial T}\right)_V = N\varepsilon\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\\
C_V &= 2Nk_BT\left(\frac{\partial \ln \Xi}{\partial T}\right)_V + Nk_BT^2\left(\frac{\partial^2 \ln \Xi}{\partial T^2}\right)_V = \frac{N\varepsilon^2}{k_BT^2}\frac{e^{-\beta\varepsilon}}{(1+e^{-\beta\varepsilon})^2} \ .
\end{aligned}$$

2.1.5 Einstein-Debye model of solids

According to the equipartition theorem, every atom has three degrees of freedom due to its translational motion. Describing a solid simply as a conjunction of N atoms bound by a common potential, we expect the total energy and the specific heat following the *Dulong-Petit law*,

$$E = 3Nk_BT \qquad \text{resp.} \qquad C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B \ , \tag{2.27}$$

for all solids regardless of temperature.

It was observed, however, that the specific heat of solids decreases like $C_V \propto T^3$ as T approaches zero. Einstein proposed an alternative model treating the N atoms as three-dimensional harmonic oscillators vibrating in a lattice. Indeed, many solids are crystalline, which means that they arrange in a periodic structure, in the simplest case a cubic lattice, where each atom has six neighbors arranged along Cartesian coordinates, as illustrated in Fig. 2.2. The interatomic bonds are described by springs storing energies like a quantized 3D harmonic oscillator,

$$\varepsilon_j = (j + \tfrac{3}{2})\hbar\omega \ . \tag{2.28}$$

The normal-mode frequency ω is related to the spring constant of the atomic bond and the atomic mass. The spectrum (2.27) completely defines the model.

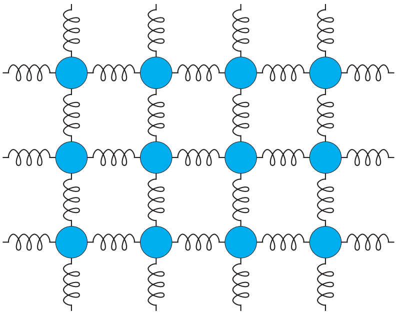

Figure 2.2: Einstein's model of a solid.

The partition function is,

$$\Xi = \sum_{j=1}^{r} e^{-\beta\varepsilon_j} = e^{-3\beta\hbar\omega/2}\sum_{j=1}^{r} e^{-\beta\hbar\omega j} \simeq e^{-3\beta\hbar\omega/2}\sum_{j=0}^{\infty} e^{-\beta\hbar\omega j} = \frac{e^{-3\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}} \ . \tag{2.29}$$

The discrete energies $n\hbar\omega$ are identified with quasi-particles called *phonons*. The quantum nature of atoms does not matter, they just provide the medium supporting the phonons.

With the partition function it is easy to evaluate the potentials,

$$\begin{aligned} F &= -Nk_BT\ln\Xi = \frac{3N\hbar\omega}{2} + 3Nk_BT\ln\left(1-e^{-\beta\hbar\omega}\right) \qquad (2.30) \\ S &= Nk_B\ln\Xi + Nk_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_V = -3Nk_B\ln\left(1-e^{-\beta\hbar\omega}\right) + \frac{3N\hbar\omega}{T}\frac{1}{e^{\beta\hbar\omega}-1} \\ E &= Nk_BT^2\left(\frac{\partial\ln\Xi}{\partial T}\right)_V = \frac{3N\hbar\omega}{2}\frac{e^{\beta\hbar\omega}+1}{e^{\beta\hbar\omega}-1} \\ C_V &= 2Nk_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_V + Nk_BT^2\left(\frac{\partial^2\ln\Xi}{\partial T^2}\right)_V = -3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} \ . \end{aligned}$$

2.1.5.1 Debye model

In his model Einstein applied Planck's law on the distribution of energy in electromagnetic radiation, which treats radiation as a gas of *photons*, to the energy distribution of atomic vibrations in a solid, treating them as a gas of *phonons* in a box (the box being the solid). Most of the steps of the calculation are identical, as both are examples of a massless bosonic gas with linear dispersion relation.

Following the Bose-Einstein statistics, we must replace in (2.27),

$$k_BT \longrightarrow \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1} , \tag{2.31}$$

yielding,

$$E = \frac{3N\hbar\omega}{e^{\beta\hbar\omega}-1} \qquad \text{resp.} \qquad C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{(e^{\hbar\omega/k_BT}-1)^2} , \tag{2.32}$$

in accordance with (2.30).

Still, the disappearance of the specific heat at low temperatures,

$$C_V \simeq \frac{3N(\hbar\omega)^2}{k_BT^2}e^{-\hbar\omega/(k_BT)} , \tag{2.33}$$

which is related to the finite localization energy of harmonic oscillators, does not describe experimental observations very well, and the model had to be refined by Debye, later on.

While Einstein assumed monochromatic lattice vibrations, *Debye's* approach was to allow a *spectrum* of vibrational frequencies. With the density of states,

$$\rho(\nu)d\nu = (4\pi Vv^3)\nu^2 d\nu , \tag{2.34}$$

where v is the velocity of sound propagation, the formula is totally equivalent to the density-of-states for photons in a cavity. Assuming that there is an upper bound ν_m for the vibrational frequencies, we normalize as $3N_0 = \int_0^{\nu_m} \rho(\nu)d\nu$. The energy now is [3],

$$E = \int_0^{\nu_m} \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}\frac{4\pi V}{v^3}\nu d\nu = 9Nk_B\frac{T^4}{\theta^3}\int_0^{\theta/T}\frac{x^3dx}{e^x-1} . \tag{2.35}$$

The *Debye temperature* $\theta = h\nu_m/k_B$ is characteristic for the metal. The derivative is then,

$$C_V = 9Nk_B\left[4\left(\frac{T}{\theta}\right)^3\int_0^{\theta/T}\frac{x^3dx}{e^x-1} - \frac{\theta}{T}\frac{1}{e^{\theta/T}-1}\right] . \tag{2.36}$$

At low temperatures this formula reproduces the *Debye law*,

$$C_V = \frac{12\pi^4}{5}Nk_B\left(T/\theta\right)^3 . \tag{2.37}$$

2.1.6 Maxwell-Boltzmann distribution of ideal gases

Here we consider a gas composed of identical monoatomic particles enclosed in a box of volume $V = \int_V d^3r$. The energy of every atom is just its kinetic energy associated with its flight through space,

$$\varepsilon = \frac{m}{2}v^2 = \frac{m}{2}v_x^2 + \frac{m}{2}v_y^2 + \frac{m}{2}v_z^2 . \tag{2.38}$$

---

[3] The fact that the electron gas also has a heat capacity is neglected.

The partition function,

$$\Xi = \sum_{x,y,z\in V} \sum_{v_x,v_y,v_z=-\infty}^{\infty} e^{-\beta\varepsilon_j} = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} e^{-\beta\varepsilon} d^3r d^3v \tag{2.39}$$

$$= V\int_0^\infty 4\pi v^2 e^{-\beta mv^2/2} dv = V\left(\frac{2\pi k_BT}{m}\right)^{3/2} .$$

We will see later how to generalize the procedure in the presence of an inhomogeneous trapping potential $U(\mathbf{r})$. Insertion of the kinetic energy (2.38) generates the well-known *Maxwell-Boltzmann distribution*,

$$\boxed{\frac{n(\varepsilon)}{N} = \frac{1}{\Xi}e^{-\beta mv^2/2}} , \tag{2.40}$$

which will be studied in Excs. 2.1.7.9 to 2.1.7.16.

The potentials are easily calculated,

$$F = -Nk_BT\ln\Xi = -Nk_BT\left(\ln V + \frac{3}{2}\ln\frac{2\pi k_BT}{m}\right) \tag{2.41}$$

$$S = Nk_B\ln\Xi + Nk_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_V = Nk_B\left(\ln V + \frac{3}{2} + \frac{3}{2}\ln\frac{2\pi k_BT}{m}\right)$$

$$E = Nk_BT^2\left(\frac{\partial\ln\Xi}{\partial T}\right)_V = \frac{3}{2}Nk_BT$$

$$C_V = 2Nk_BT\left(\frac{\partial\ln\Xi}{\partial T}\right)_V + Nk_BT^2\left(\frac{\partial^2\ln\Xi}{\partial T^2}\right)_V = \frac{3}{2}Nk_B .$$

Furthermore,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} . \tag{2.42}$$

2.1.6.1 Inclusion of vibrational and rotational degrees of freedom

See [13], p.155.

2.1.7 Exercises

2.1.7.1 Ex: Probabilities

In a game, 5 ideal dice are rolled.
a. What is the probability that exactly two of these dice show the number one?
b. What is the probability that at least one die shows the number one?

2.1.7.2 Ex: Probabilities

With what probability have out of
a. 1000 random numbers between 1 and 100 exactly five the value 50;
b. 100 two people on birthday January 1st.

2.1.7.3 Ex: Probabilities

What is the probability that you inhale at least one molecule that Julius Caesar exhaled during his last breath (Tu quoque, Brute, fili mi!)? Assume a breathing volume of 3 liters and an atmosphere height of approximately $h = 10\,\text{km}$. Assume the density of the atmosphere is approximately homogeneous.

2.1.7.4 Ex: Idiots roulette

A Bavarian, a Swabian and an East Frisian play Russian roulette together, each according to their own rules. The Bavarian inserts two cartridges into the drum of a six-shot revolver, sets the drum in a rapid rotation, aims at his own head and pulls the trigger once. The Swabian puts a cartridge in the revolver and pulls the trigger twice, the East Frisian puts a cartridge in the revolver, pulls the trigger once, turns the drum a second time and pulls the trigger again. What is the chance of survival of the three crazy people?

2.1.7.5 Ex: Students roulette

A student writes a multiple choice test in physics. It consists of 18 tasks. For each task, only one of the four proposed solutions is correct. Since he does not understand much about the topic, he trusts his luck and checks the possible solutions by chance. What is the probability that the student meets the minimum requirement of 8 correct answers?

2.1.7.6 Ex: Slot machine

A slot machine consists of three concentric rings. Each ring is evenly divided into 10 sections and the sections in each ring are labeled with letters from ’a’ to ’j’. By pressing the start button, the three rings start to rotate independently. If the lock button is pressed, the rings brake independently of one another and three letters appear side by side in the viewing window. With three ’a’ you win, with two ’a’ there is a free spin.
a. Calculate the probability for one free spin per game.
b. What is the probability of getting exactly 3 free spins in 10 games?
c. What is the probability of winning at least once in 10 games?

2.1.7.7 Ex: Binomial distribution

Two drunks stagger on the x-axis. Starting from the origin, they take a step to the right or to the left with the same probability. The steps take place synchronously, and the steps of both people are the same and constant. Determine the probability that they will meet again after N steps.

2.1.7.8 Ex: Simple model for a solid

Consider a system of N atomic particles at a temperature T. The individual atoms can only be in one of two states. Either in state ’0’ at the energy $\varepsilon_0 = 0$ or in state ’1’ at energy $\varepsilon_1 = \varepsilon$. Apart from this energy ε_i, the atoms have no kinetic or other

energies.
a. Choosing the Boltzmann distribution, determine the probability w_i that a certain atom is in state i. How should the normalization be chosen?
b. Determine the statistical mean $\bar{\varepsilon}$ for the energy of one atom. What is the expression for the total energy E of N atoms? Which values result for $k_BT = \varepsilon$?
c. Calculate the population probability w_j to find a certain atom at the energy ε if for temperatures satisfy: $k_BT_j = 0.1 \times j\varepsilon$ for $j = 1, 2, 3, 4$. Also calculate the energy E_j of the entire system at these temperatures.
d. Find an expression for the heat capacity c of this N atom system. Note: For this system, the total energy is identical to the thermal energy.
e. Calculate the heat capacities c_j especially for the temperatures T_j from subtask (a). What does this result have to do with 'freezing degrees of freedom'?

2.1.7.9 Ex: Velocity distribution

The Maxwellian velocity distribution or Boltzmann distribution of a one-dimensional ideal gas of identical particles of mass m at temperature T is,

$$f(v)dv = \sqrt{\frac{m}{2\pi k_BT}} e^{-mv^2/2k_BT} dv \ .$$

This gives the average kinetic energy for each molecule of $\langle E_{kin} \rangle = \frac{1}{2}k_BT$. According to the equipartition theorem, Maxwell's velocity distribution of a three-dimensional gas is given by $f(v_x)dv_x \ f(v_y)dv_y \ f(v_z)dv_z$.
a. Write down the velocity distribution explicitly and determine the average kinetic energy of a molecule in the three-dimensional gas at temperature T.
Determine the average absolute velocity $\langle v \rangle = \langle |\mathbf{v}| \rangle$ and compare $\langle v \rangle^2$ with $\langle v^2 \rangle$ for the three-dimensional case.
c. What is the number of particles $F(v)dv$ with an absolute velocity $v = |\mathbf{v}|$ in the range v and $v + dv$.
d. Consider a gas made of rubidium atoms ($m = 87 \cdot 1.67 \cdot 10^{-27}$ kg) and sketch $F(v)$ for temperatures between 100 K and 300 K.
e. Consider the rubidium gas at room temperature ($T = 300$ K). What is the proportion of molecules whose average velocity $\langle v \rangle$ is greater than 1000 m/s?

2.1.7.10 Ex: Maxwell-Boltzmann distribution

Calculate the number of particles in an ideal homogeneous gas having velocities slower than $2v_{rms}$.

2.1.7.11 Ex: Maxwell-Boltzmann distribution

Using the Maxwell-Boltzmann distribution $f(v)$ and the following formulas, calculate the velocities $\bar{v} \equiv \int_0^\infty vf(v)v^2dv$ and $v_{rms} \equiv \sqrt{\overline{v^2}}$:

$$\int_0^\infty x^n e^{-x^2} dx = \tfrac{1}{2}\Gamma(\tfrac{n+1}{2}) = \begin{cases} \frac{(2k-1)!!\sqrt{\pi}}{2^{k+1}} & \text{for} \quad n = 2k \\ \frac{k!}{2} \quad \text{for} & n = 2k+1 \end{cases} \ .$$

2.1.7.12 Ex: Mean velocity in a gas

The average velocity of the molecule in an ideal gas is 500 m/s. If the gas maintains the same temperature and the molecular masses are doubled, what will be the new average velocity?

2.1.7.13 Ex: Evaporation

a. A three-dimensional homogeneous gas consisting of $N = 10^8$ rubidium atoms (mass $m = 87 \cdot u$) has the temperature $T = 100\,\mu\text{K}$. How many atoms are faster on average than $v_1 = 10\,\text{cm/s}$?
b. Now suppose that all atoms with a velocity $v > v_1$ were suddenly removed. After some time, a new thermal equilibrium is established due to collisions. What is the temperature of the gas now?

Help: Formula for partial integration: $\int y^n e^{-y^2} dy = -\frac{y^{n-1}}{2} e^{-y^2} + \frac{n-1}{2} \int y^{n-2} e^{-y^2} dy$
You can take the value of the error function given by $\text{erf}\,(y_1) \equiv \frac{1}{\sqrt{\pi}} \int_{y_1}^{\infty} e^{-y^2} dy$ from the sketched curve.

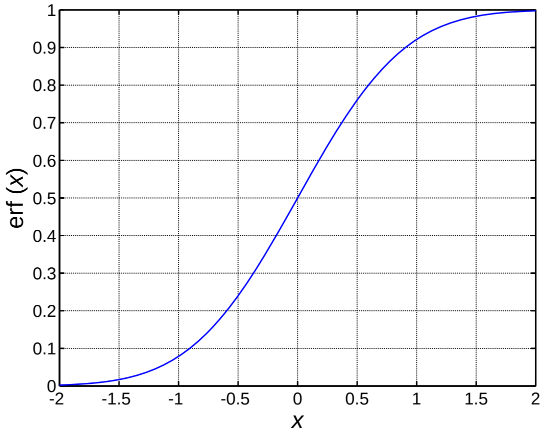

Figure 2.3:

2.1.7.14 Ex: Trapped gases

The density distribution of a rubidium gas in a three-dimensional harmonic potential can be expressed by,

$$n(\mathbf{r}) d^3r = n_0 e^{-U(\mathbf{r})/k_BT} d^3r \ ,$$

where $U(\mathbf{r}) = \frac{m}{2} \omega^2 r^2$. Numerical values: $m = 87 \cdot 1.67 \cdot 10^{-27}$ kg and $\omega = 2\pi \cdot 50$ Hz.
a. Determine the expansion of the gas ($1/e$ width of the distribution) at a given temperature $T = 100\,\mu\text{K}$.
b. Determine the maximum density n_0 of the gas when $N = \int n(\mathbf{r}) d^3r = 10^8$ is the total number of atoms.

c. The effective volume is defined by $V_{eff} = N/n_0$. How many atoms are in the effective volume?

2.1.7.15 Ex: Trapped gases

Calculate the internal energy and heat capacity of an ideal gas stored in a harmonic trap and compare the result with a free gas.

2.1.7.16 Ex: Trapped gases

An ultracold gas made of 10^8 rubidium atoms (mass number 87) is trapped in a three-dimensional potential of the form $U(r) = \frac{m}{2}\omega^2 r^2$ with the oscillation frequencies $\omega/2\pi = 100\,\text{Hz}$.
a. Assume the spatial distribution function for the atoms to be $n(\mathbf{r}) = n_0 e^{-U(r)/k_BT}$. What is its width at $1/\sqrt{e}$ of the maximum height? How does the width of the distribution function change when the number of atoms is doubled?
b. The trap potential is suddenly switched off. The atoms are robbed of their potential energy, while their kinetic energy leads to the ballistic expansion of the cloud. $20\,\text{ms}$ after switching off the trapping potential, a $1/\sqrt{e}$ width of $\bar{r}_a = 0.2\,\text{mm}$ is experimentally measured for the distribution of the expanded atomic cloud. What was the temperature of the atomic cloud in the trap?
Help: Assume that the final size of the atomic cloud is much larger than the size of the trap. Neglect collisions between the atoms.

2.2 Quantum statistics

Considering a closed isolated system in a fixed volume (NVE-ensemble where $E, N, V = const$) we have derived in Sec. 2.1.1 the partition function for *microcanonical ensembles*, from which we obtained in Sec. 2.1.2 the *Boltzmann distribution* function.

The combinatorial derivation of the number of microstates contributing to the same macrostate (2.1) was based on the observation, that all particles constituting the system were identical, but distinguishable. The expression (2.1) is just the multinomial coefficient, i.e. the number of ways of arranging N items into r boxes, the j-th box holding n_j items, ignoring the permutation of items in each box. The problem, however, is that quantum mechanics postulates that identical particles are indistinguishable, and this has an impact on the numbers of states available upon permutation. Consequently, the partition function (2.1) needs to be corrected.

The problems ultimately results from the fact that *phase space* is quantized. It this weren't the case, the cells' size could be chosen so small that they admit at most one particle. Then quantum statistics would not apply, the system would be classical.

2.2.1 Wavefunction symmetrization and detailed balance

Quantum statistical (anti-)symmetrization of the wavefunction of a cold system leads to Bose-enhancement (Pauli blocking). Take a state $\Psi = \psi_\alpha(1)\psi_\beta(2)$ and symmetrize it to

$$\Psi_{s,a} = \tfrac{1}{\sqrt{2}}[\psi_\alpha(1)\psi_\beta(2) \pm \psi_\alpha(2)\psi_\beta(1)] \ . \tag{2.43}$$

Now assume that the single particle wavefunctions do overlap,

$$\alpha = \beta \qquad \Longrightarrow \qquad |\Psi|^2 = (s+1)\ |\psi_\alpha(1)|^2 |\psi_\beta(2)|^2 \ , \tag{2.44}$$

where $s = 0$ for Boltzmann particles (called *boltzons* here for simplicity), $s = 1$ for bosons, and $s = -1$ for fermions. Generalized to arbitrary numbers of particles we state: *If n bosons (fermions) are in state Ψ, the probability for another bosons (fermions) to joint this state is $1+sn$ times the probability without quantum statistics.*

An intuitive derivation of the quantum statistical distribution function is based on the postulate of *detailed balance*. Let us consider the most fundamental process in physics, which is the collision between two particles initially in states 1 and 4 ending up in two other states 2 and 3 [see Fig. 2.4(a)]. All four states j are initially occupied with populations n_j. The detailed balance postulate claims that *equality of the rates $R_{14\rightarrow 23}$ for two particles to change their states and the rate for the inverse process $R_{23\rightarrow 14}$ is a sufficient condition for thermal equilibrium*,

$$\begin{aligned} R_{14\rightarrow 23} &= |M_{14,23}|^2 n_1 n_4 (1+sn_2)(1+sn_3) \\ R_{23\rightarrow 14} &= |M_{14,23}|^2 n_2 n_3 (1+sn_1)(1+sn_4) \ . \end{aligned} \tag{2.45}$$

Hence,

$$\frac{n_1}{1+sn_1}\frac{n_4}{1+sn_4} = \frac{n_2}{1+sn_2}\frac{n_3}{1+sn_3} \ . \tag{2.46}$$

Energy conservation requires

$$\varepsilon_1 + \varepsilon_4 = \varepsilon_2 + \varepsilon_3 \ . \tag{2.47}$$

For a grand-canonical ensemble in thermal equilibrium

$$f(\varepsilon_i) = n_i \ . \tag{2.48}$$

To satisfy Eqs. (2.46) and (2.47) f must have the functional form,

$$f(\varepsilon_i) = \frac{1}{e^{\beta(\varepsilon_i-\mu)} - s} \ . \tag{2.49}$$

This can be verified easily by plugging the formula (2.49) into the Eq. (2.46).

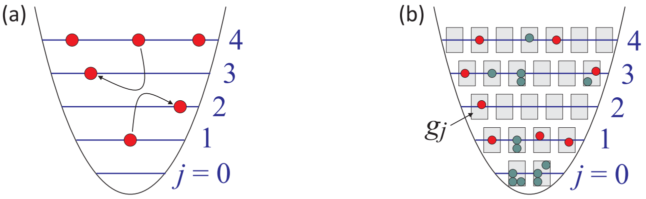

Figure 2.4: (a) Detailed balance entails thermal equilibrium. (b) Subdivision of energy levels j in subboxes g_j. Red circles are fermions and green particles bosons.

2.2.2 Microcanonical ensembles of indistinguishable particles

2.2.2.1 Boltzons

In order to hold for indistinguishable particles, the partition function (2.1) must be generalized allowing for the possibility that there is more than one way to put n_j particles into the box j. If the j-th box has a 'degeneracy', that is, it has g_j 'sub-boxes' with the same energy ε_j, such that any way of filling the j-th box where the number in the sub-boxes is changed is a distinct way of filling the box, then in order to get the right number of macrostates, the number of ways of filling the j-th box must be increased by the number of ways of distributing the n_j objects in the g_j sub-boxes. The number of ways of placing n_j distinguishable objects in g_j sub-boxes is $g_j^{n_j}$, since any particle can go into any of the g_j boxes. Thus the number of ways $W_{\{n_j\}}$ that a total of N particles can be classified into energy levels according to their energies, while each level j having g_j distinct states such that the j-th level accommodates n_j particles is:

$$\boxed{W_{\{n_j\}} = N!\prod_{j=1}^{r}\frac{g_j^{n_j}}{n_j!}} \ . \tag{2.50}$$

In analogy to the procedure outlined in Sec. 2.1.2 we derive the Boltzmann distribution by first taking the logarithm from (2.50) and then simplifying it using Stirling's formula (4.1),

$$\ln W = \ln N! + \sum_j[n_j\ln g_j - \ln n_j!] \simeq \ln N! + \sum_j[n_j\ln\frac{g_j}{n_j} + n_j] \ , \tag{2.51}$$

then calculating the differential,

$$d\ln W = \sum_j\left(\frac{\partial\ln W}{\partial n_j}\right)dn_j = \sum_j\ln\frac{g_j}{n_j}dn_j \ . \tag{2.52}$$

introducing Lagrange multipliers α and β and minimizing the functional,

$$f(\{n_j\}) \equiv \ln W + \alpha(N - \sum_j n_j) + \beta(U - \sum_j\varepsilon_j n_j) \ , \tag{2.53}$$

Relating the condition,

$$0 = df(n_j) = d\ln W - \alpha\sum_j dn_j - \beta\sum_j\varepsilon_j dn_j = \sum_j\left(\ln\frac{g_j}{n_j} - \alpha - \beta\varepsilon_j\right)dn_j \tag{2.54}$$

via the Boltzmann hypothesis (2.16) to entropy,

$$dS = \tfrac{1}{T}dE + \tfrac{P}{T}dV - \tfrac{\mu}{T}dN = k_B\beta dE + k_B\alpha dN = k_B d\ln W \ , \tag{2.55}$$

we identify the Lagrange multipliers,

$$\beta = \frac{1}{k_BT} \qquad \text{and} \qquad \alpha = -\frac{\mu}{k_BT} \ , \tag{2.56}$$

and finally obtain the Boltzmann distribution from (2.54),

$$\boxed{n_j = \frac{g_j}{e^{\beta(\varepsilon_j-\mu)}}} \ . \tag{2.57}$$

2.2.2.2 Bosons

Boltzmann's fundamental equation (2.3) relates the thermodynamic entropy S to the logarithm of the number of microstates $W_{\{n_j\}}$. It was pointed out by Gibbs however, that the above expression (2.50) does not yield an extensive entropy, and is therefore faulty. This problem is known as the *Gibbs paradox*. The problem is that the particles considered by the above equation are *not indistinguishable*. In other words, for two particles (i and j) in two energy sublevels the population represented by $[i, j]$ is considered distinct from the population $[j, i]$, while for indistinguishable particles, they are not. Indeed, bosons have anti-symmetric wavefunctions, Fermions have symmetric ones. Boltzons have all wavefunctions as eigenfunctions. In the limit of high temperatures all particles behave like boltzons. Discretize the one-particle energies in small cells labeled j of constant energy ε_j. Let n_j be their number and g_j their degeneracy [see Fig. 2.4(b)].

For bosons, each level g_j can hold arbitrarily many of the n_j particles. If we carry out the argument for indistinguishable particles, we are led to the expression for the partition function for bosons [4],

$$\boxed{W_{\{n_j\}} = \prod_{j=1}^{r} \binom{n_j + g_j - 1}{n_j}} \,. \tag{2.58}$$

Analogously to (2.51) we calculate the logarithm using Stirling's formula,

$$\begin{aligned} \ln W &= \sum_j \left[\ln(n_j + g_j - 1)! - \ln n_j! - \ln(g_j - 1)!\right] \qquad (2.59)\\ &\simeq \sum_j \left[n_j \ln \frac{g_j - 1 + n_j}{n_j} + (g_j - 1) \ln \frac{g_j - 1 + n_j}{g_j - 1}\right] \,, \end{aligned}$$

the differential,

$$d \ln W = \sum_j \left(\frac{\partial \ln W}{\partial n_j}\right) dn_j = \sum_j \ln \frac{n_j + g_j - 1}{n_j} dn_j \,, \tag{2.60}$$

and obtain the condition,

$$\begin{aligned} 0 = df(n_j) &= d \ln W - \alpha \sum_j dn_j - \beta \sum_j \varepsilon_j dn_j \qquad (2.61)\\ &= \sum_j \left(\ln \frac{n_j + g_j - 1}{n_j} - \alpha \sum_j - \beta \sum_j \varepsilon_j\right) dn_j \end{aligned}$$

with the same Lagrange multipliers. This yields the Bose-Einstein distribution,

$$\boxed{n_j = \frac{g_j - 1}{e^{\beta(\varepsilon_j - \mu)} - 1}} \,. \tag{2.62}$$

---

[4] Note that this partition function converges toward the one for boltzons for $g_j \gg n_j \gg 1$, which can be seen by simplifying it using the Stirling formula.

The Maxwell-Boltzmann distribution follows from this Bose-Einstein distribution for temperatures well above absolute zero, implying that $g_j \gg 1$. The Maxwell-Boltzmann distribution also requires low density, implying that $g_j \gg n_j$. Under these conditions, we may use Stirling's approximation (4.1) for the factorial: $N! \approx N^N e^{-N}$.

2.2.2.3 Fermions

For fermions, each level g_j can hold at most one of the n_j particles, which implies that necessarily $g_j > n_j$ [see Fig. 2.4(b)]. Let us consider a single energy level j. The first of the n_j particles has the choice between g_j boxes. Since no box can be filled with more than one particle, the second particle has only $g_j - 1$ boxes at its disposal, and so on until all particles have been assigned. This corresponds to $g_j!/n_j!$ possible choices. However, we still need to respect the indistinguishability requirement. The overcounting can be removed by dividing by $(g_j - n_j)!$. The procedure is now repeated with all energy levels j, which leads to the partition function for fermions,

$$\boxed{W_{\{n_j\}} = \prod_{j=1}^{r} \binom{g_j}{n_j}} \;. \tag{2.63}$$

Again we calculate the logarithm using Stirling's formula,

$$\begin{aligned} \ln W &= \sum_j \left[\ln g_j! - \ln n_j! - \ln(g_j - n_j)!\right] \\ &\simeq \sum_j \left[n_j \ln \frac{g_j - n_j}{n_j} - g_j \ln \frac{g_j - n_j}{g_j}\right] \;, \end{aligned} \tag{2.64}$$

the differential,

$$d\ln W = \sum_j \left(\frac{\partial \ln W}{\partial n_j}\right) dn_j = \sum_j \ln \frac{g_j - n_j}{n_j} dn_j \;. \tag{2.65}$$

and obtain the condition,

$$\begin{aligned} 0 = df(n_j) &= d\ln W - \alpha \sum_j dn_j - \beta \sum_j \varepsilon_j dn_j \\ &= \sum_{j=1}^{r} \left(\ln \frac{g_j - n_j}{n_j} - \alpha - \beta\varepsilon_j\right) dn_j \;, \end{aligned} \tag{2.66}$$

with the same Lagrange multipliers. This yields the Fermi-Dirac distribution for $g_j \gg 1$,

$$\boxed{n_j = \frac{g_j}{e^{\beta(\varepsilon_j - \mu)} + 1}} \;. \tag{2.67}$$

Do the Exc. 2.2.6.1.

2.2.2.4 Thermodynamic potentials for bosons and fermions

Using the abbreviation $s = +1$ for bosons, $s = -1$ for fermions, and $s = 0$ for boltzons the distribution function can be expressed as,

$$\boxed{n_j = \frac{g_j}{e^{\beta(\varepsilon_j - \mu)} - s}} \ . \tag{2.68}$$

The chemical potential μ is fixed by the boundary conditions,

$$N = \sum_{j=1}^{r} n_j \qquad \text{and} \qquad E = \sum_{j=1}^{r} \varepsilon_j n_j \ , \tag{2.69}$$

With this, knowing the energy spectrum ε_i and the distribution of states g_j of the system, we are able to calculate all thermodynamic potentials. E.g. the entropy reads,

$$\begin{aligned} S = k_B \ln W_{\{n_j\}} &= k_B \sum_j \left[n_j \ln\left(s + \frac{g_j}{n_j}\right) + s g_j \ln\left(1 + s\frac{n_j}{g_j}\right)\right] \\ &= k_B \sum_j \left[\frac{s g_j \beta(\varepsilon_j - \mu)}{1 - s e^{-\beta(\varepsilon_j - \mu)}} + s g_j \ln\left(e^{\beta(\varepsilon_j - \mu)} - s\right)\right] \ . \end{aligned} \tag{2.70}$$

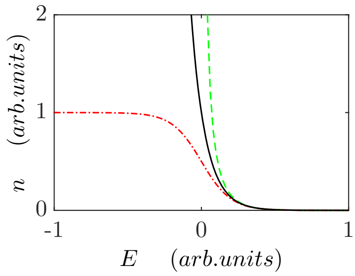

Figure 2.5: Quantum statistic weight for fermions (dash-dotted line), bosons (solid line) and boltzons (dotted line).

The Bose-Einstein and the Fermi-Dirac distribution both have many applications in quantum mechanics, e.g. for the explanation of the blackbody radiation, the heat capacity of metals, the laser, the Bose-Einstein condensation, and much more. In fact, these distributions must be used whenever quantum statistical effects are important. Prominent examples of systems where a quantum statistical treatment is crucial are electrons in metals and ultracold quantum gases. We will discuss the latter in Secs. 2.3 and 2.4.

2.2.3 Density-of-states in a trapping potential

An important boundary condition for the discussion of the quantum statistics of gases is that the atoms are often confined in trapping potentials. Suspended in free space far from massive walls, they escape the perturbative influence of the environment.

This however implies, that the system becomes inhomogeneous, which means that the number of states available to the atoms varies in space. In order to prepare subsequent evaluations of thermodynamic potentials, let us first characterize this spatial dependence by the introduction of the concept of the density-of-states.

In three dimensions the Hamiltonian of a trapped atoms is,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \ . \tag{2.71}$$

As the wavefunction is localized, the spectrum of possible energies organizes into discrete levels, and the atoms are allocated in populations of these levels. Such multidimensional systems are often degenerate, which means that the same total energy can be realized with different sets of quantum numbers [5]. The way an atomic cloud accommodates itself inside a trapping potential is governed by the density of available states. We now introduce the *density of states* $\eta(\epsilon)$ for an arbitrary potential via,

$$\boxed{\int \eta(\varepsilon)d\varepsilon \equiv \frac{1}{(2\pi)^3}\int d^3r d^3k = \frac{(2m)^{3/2}}{(2\pi)^2\hbar^3}\int d^3r \int d\varepsilon\sqrt{\varepsilon - U(\mathbf{r})}} \ , \tag{2.72}$$

with the substitution $k = \sqrt{\frac{2m}{\hbar^2}[\varepsilon - U(\mathbf{r})]}$.

As an example, let us consider a box potential of volume V. In this case, the expression (2.72) simply yields,

$$\boxed{\eta(\varepsilon) = \frac{(2m)^{3/2}}{(2\pi)^2\hbar^3}\int_V d^3r\sqrt{\varepsilon} = \frac{(2m)^{3/2}}{(2\pi)^2\hbar^3}V\sqrt{\varepsilon}} \qquad (\text{box potential}) \ . \tag{2.73}$$

In the following we derive the density-of-states for the case of an harmonic oscillator potential. More general potentials are discussed in the Exc. 2.3.4.1.

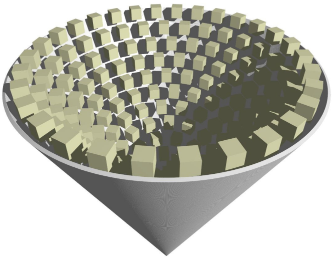

Figure 2.6: Artists's view of phase space cells in a trapping potential.

Example 17 (*Density-of-states for a cylindrical harmonic oscillator potential*): Let us consider a cylindrical harmonic oscillator,

$$U(\mathbf{r}) = \frac{m}{2}\omega_r^2 r^2 + \frac{m}{2}\omega_z^2 z^2 \qquad \text{where} \qquad r^2 = x^2 + y^2 \ , \tag{2.74}$$

---

[5] This can be checked easily with separable potentials, such as the rectangular 3D box potential or the 3D harmonic oscillator, where the same energy $E = E_x + E_y + E_z$ can be reached with different combinations of E_x, E_y, and E_z.

which can also be given in the form,

$$U(\mathbf{r})=\frac{m}{2}\omega_r^2\rho^2 \quad \text{where} \quad \rho^2=x^2+y^2+\lambda^2z^2 \quad \text{with} \quad \lambda=\frac{\omega_z}{\omega_r}\ . \tag{2.75}$$

We also define the mean oscillation frequency,

$$\bar{\omega}=(\omega_r^2\omega_z)^{1/3}=\lambda^{1/3}\omega_r\ . \tag{2.76}$$

The single-particle levels of this Hamiltonian are,

$$\varepsilon_{n_xn_yn_z}=\hbar\omega_xn_x+\hbar\omega_yn_y+\hbar\omega_zn_z\ , \tag{2.77}$$

where the coefficients n_j with $j=x,y,z$ are integer numbers. For the cylindrical harmonic trap defined in (2.73), we find with a little help from Dr. Bronstein [6],

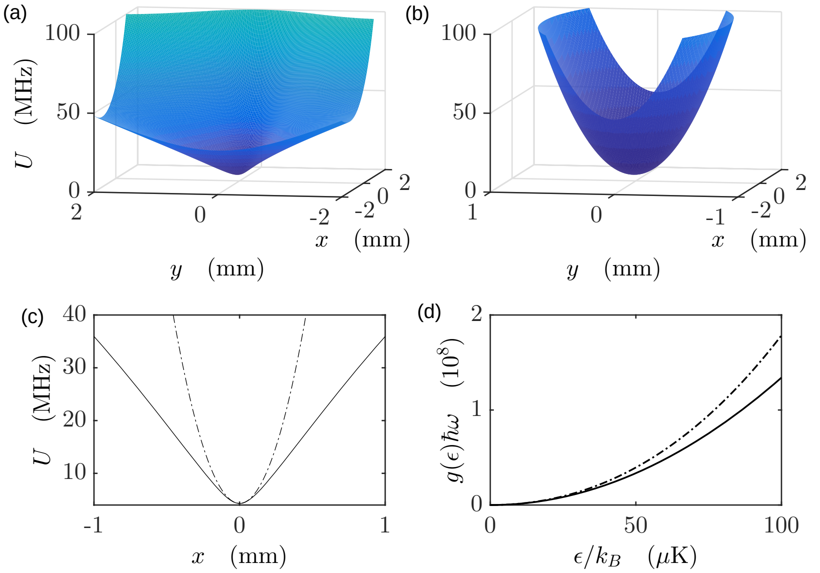

Figure 2.7: (code) (a) The figure shows two dimensions of a Ioffe-Pritchard type magnetic trapping potential (characterized by being approximately linear at large distances from the center and harmonic near the center). (b) Harmonic approximation (most experimentally feasible potentials are approximately harmonic near the center). (c) One-dimensional cut through the potential of (a,b). (d) Density of states for a harmonic (dotted line) and a Ioffe-Pritchard type potential (solid line).

$$\begin{aligned}\eta(\varepsilon)&=\frac{(2m)^{3/2}}{(2\pi)^2\hbar^3}\int d^3r\sqrt{\varepsilon-\frac{m}{2}\omega_r^2\rho^2} &(2.78)\\ &=\frac{1}{(2\pi)^2}\frac{8\varepsilon^2}{(\hbar\bar{\omega})^3}\int_{-1}^{1}d\tilde{x}\int_{-\sqrt{1-\tilde{x}^2}}^{\sqrt{1-\tilde{x}^2}}d\tilde{y}\int_{-\sqrt{1-\tilde{x}^2-\tilde{y}^2}}^{\sqrt{1-\tilde{x}^2-\tilde{y}^2}}d\tilde{z}\sqrt{1-\tilde{x}^2-\tilde{y}^2-\tilde{z}^2}\ .\end{aligned}$$

The resolution of the integral gives,

$$\boxed{\eta(\varepsilon)=\frac{\varepsilon^2}{2(\hbar\bar{\omega})^3}} \qquad (\text{harmonic potential})\ . \tag{2.79}$$

2.2.3.1 Application to the microcanonical partition function

Let us now come back to the distribution functions for ideal quantum gases introduced in Sec. 2.2.2. In the *thermodynamic limit*, $N \to \infty$, the distribution of states is assumed so dense, that it can be expressed by a continuous density,

$$\begin{array}{ccccl}
 & & \varepsilon_i & \longrightarrow & \varepsilon = \varepsilon_{\mathbf{r},\mathbf{p}} \\
 & & g_i & \longrightarrow & \eta(\varepsilon) \\
n_i & = & \frac{g_i}{e^{\beta(\varepsilon_i-\mu)}-s} & \longrightarrow & \frac{\eta(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-s} = \eta(\varepsilon)w_{T,\mu}(\varepsilon) \\
 & & \sum_i g_i & \longrightarrow & \int \eta(\varepsilon)d\varepsilon = \int d^3r d^3k \\
N & = & \sum_i n_i & \longrightarrow & \int \frac{\eta(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}-s} = \int \eta(\varepsilon)w_{T,\mu}(\varepsilon)d\varepsilon \\
E & = & \sum_i \varepsilon_i n_i & \longrightarrow & \int \frac{\varepsilon\eta(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}-s}
\end{array} \tag{2.80}$$

where $s = 0$ stands for the 'Boltzmann', $s = -1$ for the 'Bose-Einstein', and $s = +1$ for the 'Fermi-Dirac' distributions derived in (2.57), (2.62), and (2.67). We also introduced the symbol $w_{T,\mu}$ to denote the statistical distribution function. In the following sections we will calculate all system variables based on the expressions (2.80) in the thermodynamic limit.

2.2.4 Grand-canonical ensembles of ideal quantum gases

The grand-canonical ensemble is particularly useful for developing the thermodynamics of large ideal trapped quantum gases, as we will show in the following. Because the particles are supposed *not to interact*, it is possible to compute a series of single-particle stationary states, each of which represents a separable part that can be included into the total quantum state of the system. Let us call these single-particle stationary states 'orbitals' in order to avoid confusion with the total many-body state. Every orbital has a distinct set of quantum numbers and may be occupied by several particles or be empty. In this sense, each orbital forms a separate grand canonical ensemble by itself, one so simple that its statistics can be immediately derived. Focusing on just one orbital labeled i, the total energy for a microstate of N particles in this orbital will be $N\varepsilon_i$, where ε_i is the characteristic energy level of that orbital. The grand potential for the orbital is given by [6],

$$\Omega = -k_B T \ln \sum_{\text{microstates}} e^{\beta(\mu N - E)} . \tag{2.81}$$

which is required for the microstates' probabilities to add up to 1.

In quantum mechanics the orbitals are understood as the eigenstates $|\psi_i\rangle$ of a single-particle Hamiltonian,

$$\hat{h}_i = \frac{\hat{\mathbf{p}}_i^2}{2m} + V_{tr}(\hat{\mathbf{r}}_i) , \tag{2.82}$$

---

[6] In case of multi-species ensembles, the potentials add up like $\mu_1 N_1 + \mu_2 N_2 + \ldots$.

with $i = 1, \dots, N$ whose spectrum is $\varepsilon_i = \langle\psi_i|\hat{h}_i|\psi_i\rangle$. That is, every single particle is completely characterized by the quantum number ε_i. A microstate $|\Psi_k\rangle$ is now identified as an eigenstate of the total many-particle Hamiltonian,

$$\hat{H} = \sum_{i=1}^{N} \hat{h}_i \qquad \text{with} \qquad |\Psi_k\rangle = \prod_{i=1}^{N} |\psi_i\rangle_k \ . \tag{2.83}$$

The request that the particles do not interact makes the system separable. The density operator and the grand-canonical partition function are [10],

$$\boxed{\hat{\rho} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi} \qquad \text{and} \qquad \Xi = e^{-\beta\Omega} = \text{Tr}\ e^{-\beta(\hat{H}-\mu\hat{N})}} \ , \tag{2.84}$$

obviously satisfying Tr $\hat{\rho} = 1$. For the grand canonical ensemble the basis states of the total Hamiltonian $\hat{H}$ are all microstates composed of many particles, and the operators $\hat{N}$ and $\hat{\rho}$ can be expressed in the same basis.

We now change from the single-particle product state basis $\{|\Psi_k\rangle\}$ to a Fock state basis assigning a given number of particles n_m to every possible energy level ε_m, where $m = 1, \dots, \infty$, as illustrated in Fig. 2.8,

$$|\Psi_k\rangle \longrightarrow |n_1, n_2, \dots, n_m, \dots\rangle \ . \tag{2.85}$$

I.e. we replace the distribution of microstates by a distribution of populations $\{n_m\}$ among the energy levels. Since the energy and particle numbers are separately conserved, the corresponding operators commute, $[\hat{H}, \hat{N}] = 0$, and therefore it is possible to find a complete basis of simultaneous eigenstates,

$$\hat{H}|\dots n_m \dots\rangle = E|\dots n_m \dots\rangle \quad \text{with} \quad \hat{N}|\dots n_m \dots\rangle = N|\dots n_m \dots\rangle \tag{2.86}$$

with,

$$E = \sum_{m=0}^{\infty} \varepsilon_m n_m \qquad \text{and} \qquad N = \sum_{m=0}^{\infty} n_m \ . \tag{2.87}$$

In other words, we can rewrite the Hamiltonian and the number operator of any non-interacting system like,

$$\hat{H} = \sum_{\{n_m\}} \varepsilon_m \hat{a}_m^\dagger \hat{a}_m \qquad \text{and} \qquad \hat{N} = \sum_{\{n_m\}} \hat{a}_m^\dagger \hat{a}_m \ , \tag{2.88}$$

where $\hat{a}_m^\dagger$ and $\hat{a}_m$ are the particle creation and annihilation operators introduced in second quantization.

We can now evaluate the partition function (2.84),

$$\begin{aligned} \Xi &= \sum_{k\in\{\text{microstates}\}} \langle\Psi_k|e^{-\beta(\hat{H}-\mu\hat{N})}|\Psi_k\rangle \\ &= \sum_{\{n_m\}} \langle\dots n_m \dots|e^{-\beta(\hat{H}-\mu\hat{N})}|\dots n_m \dots\rangle = \sum_{\{n_m\}} e^{-\beta(E-\mu N)} \ . \end{aligned} \tag{2.89}$$

The density operator in this new basis is,

$$\hat{\rho} = \sum_{\{n_m\}} \frac{|\dots n_m \dots\rangle e^{-\beta(E-\mu N)} \langle \dots n_m \dots |}{\sum_{\{n_m\}} e^{-\beta(E-\mu N)}} \ . \tag{2.90}$$

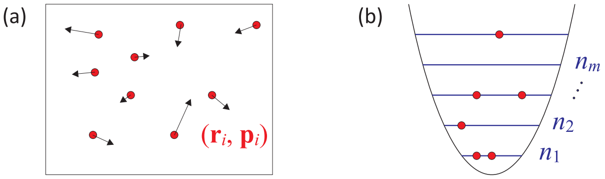

Figure 2.8: (a) Ensemble of N particles with different positions and velocities. (b) Distribution of the particles over the spectrum of allowed energies.

Using the conditions (2.87), the partition function becomes,

$$\begin{aligned} \Xi &= \sum_{n_1,n_2,\dots} \langle \dots n_m \dots | e^{-\beta(\hat{H}-\mu\hat{N})} | \dots n_m \dots \rangle \\ &= \sum_{n_1} \langle n_1 | e^{-\beta(n_1\hat{h}_1 - n_1\mu)} | n_1 \rangle \sum_{n_2} \langle n_2 | e^{-\beta(n_2\hat{h}_2 - n_2\mu)} | n_2 \rangle \times \dots \equiv \prod_{m=1}^{\infty} \Xi_m \ , \end{aligned} \tag{2.91}$$

where in the last step we defined a partial partition sum,

$$\Xi_m \equiv \sum_{n_m} e^{-\beta(\varepsilon_m n_m - \mu n_m)} \ , \tag{2.92}$$

accounting for all possible populations of a particular energy level ε_m. Analogously, the density operator becomes,

$$\begin{aligned} \hat{\rho} &= \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi} = \frac{1}{\Xi} e^{-\beta\left(\sum_{\{n_m\}}(\varepsilon_m - \mu)\hat{n}_m\right)} \\ &= \frac{1}{\Xi} e^{-\beta(\varepsilon_1-\mu)\hat{n}_1} e^{-\beta(\varepsilon_2-\mu)\hat{n}_2} \times \dots = \prod_{m=1}^{\infty} \hat{\rho}_m \ . \end{aligned} \tag{2.93}$$

since $[\hat{n}_k, \hat{n}_m] = 0$, and where we defined in the last step,

$$\hat{\rho}_m \equiv \frac{e^{-\beta(\varepsilon_m-\mu)\hat{n}_m}}{\Xi_m} = |n_m\rangle \frac{e^{-\beta(\varepsilon_m-\mu)}}{\Xi_m} \langle n_m| \ . \tag{2.94}$$

The problem with this expression is, that the global wavefunction $|\Psi\rangle$ has not yet been (anti-)symmetrized according the particles' bosonic or fermionic nature. For bosons, N may be any non-negative integer and each value of N counts as one microstate due to the indistinguishability of particles. For fermions, the Pauli exclusion principle allows only two microstates for the orbital (occupation of 0 or 1), giving a two-term series,

$$\Xi_m = \begin{cases} \sum_{n_m=0}^{\infty} e^{-\beta(n_m\varepsilon_m - n_m\mu)} = \frac{1}{1-e^{-\beta(\varepsilon_m-\mu)}} & \text{for bosons} \\ \sum_{n_m=0}^{1} e^{-\beta(n_m\varepsilon_m - n_m\mu)} = 1 + e^{-\beta(\varepsilon_m-\mu)} & \text{for fermions} \end{cases} \tag{2.95}$$

Hence,

$$\boxed{\Xi = \prod_{m=1}^{\infty} (1 - se^{-\beta(\varepsilon_m - \mu)})^{-s}} \; , \tag{2.96}$$

where the upper signs hold for bosons and the lower for fermions.

The grand-canonical potential per microstate becomes,

$$\Omega_m = -k_B T \ln \Xi_m = sk_B T \ln(1 - se^{-\beta(\varepsilon_m - \mu)}) \; . \tag{2.97}$$

Considering again the entire system, the total Landau grand potential is found by adding up the Ω_m for all orbitals,

$$\Omega = \sum_{m=1}^{\infty} \Omega_m \; . \tag{2.98}$$

In any case the value

$$\boxed{n_m = -\frac{\partial \Omega_m}{\partial \mu} = \frac{1}{e^{\beta(\varepsilon_m - \mu)} - s} \equiv w_{T\mu}} \tag{2.99}$$

gives the thermodynamic average number of particles on the orbital: the *Fermi-Dirac distribution* for fermions, and the *Bose-Einstein distribution* for bosons.

The problem is completely analogous to Planck's treatment of blackbody radiation, where the Bose-Einstein distribution function followed as a corollary from the Boltzmann statistics in thermal equilibrium and Planck's quantization hypothesis, $E = N\varepsilon_i$.

2.2.4.1 Grand potential, ensemble averages, and fluctuations

Evaluating partial derivatives of the function $\Omega(\mu, V, T)$, we find for the averages of numbers of particles, the Gibbs entropy, the average pressure, and the average energy,

$$\begin{array}{rll} 1 & = \text{Tr}\ \hat{\rho} & \\ \langle N \rangle & = \text{Tr}\ \hat{N}\hat{\rho} & = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \\ S & = \text{Tr}\ \hat{\rho} \ln \hat{\rho} & = -\left(\frac{\partial \Omega}{\partial T}\right)_{\mu,V} \\ \langle P \rangle & & = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu} \\ \langle E \rangle & = \text{Tr}\ \hat{H}\hat{\rho} & = TS + \mu N + \Omega \end{array} \; . \tag{2.100}$$

Example 18 (*Calculation of ensemble averages*): Thermodynamic fluctuations can be calculated via the variances in energy and particle numbers. Starting from,

$$-\beta\Omega = \ln \Xi = \ln \text{Tr}\ e^{-\beta(\hat{H} - \mu\hat{N})} \tag{2.101}$$

it is easy to show, that,

$$\begin{aligned}\frac{\partial\Xi}{\partial\mu} &= \beta\mathrm{Tr}\ \hat{N}e^{-\beta(\hat{H}-\mu\hat{N})} = \beta\Xi\langle\hat{N}\rangle \\ -\beta\frac{\partial\Omega}{\partial\mu} &= \frac{\mathrm{Tr}\ \hat{N}e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi} = \beta\langle\hat{N}\rangle \\ -\beta\frac{\partial^2\Omega}{\partial\mu^2} &= \frac{\Xi\frac{\partial}{\partial\mu}\mathrm{Tr}\ \hat{N}e^{-\beta(\hat{H}-\mu\hat{N})} - \mathrm{Tr}\ \hat{N}e^{-\beta(\hat{H}-\mu\hat{N})}\frac{\partial}{\partial\mu}\Xi}{\Xi^2} = \beta(\langle\hat{N}^2\rangle - \langle\hat{N}\rangle^2)\ .\end{aligned} \tag{2.102}$$

Also [7],

$$\begin{aligned}\langle E^2\rangle - \langle E\rangle^2 &= k_BT^2\frac{\partial\langle E\rangle}{\partial T} + k_BT\mu\frac{\partial\langle E\rangle}{\partial\mu} \\ \langle N^2\rangle - \langle N\rangle^2 &= k_BT\frac{\partial\langle N\rangle}{\partial\mu}\ .\end{aligned} \tag{2.103}$$

If different species are present it is interesting to calculate correlations in fluctuations. The covariances of particle numbers and energy are then,

$$\begin{aligned}\langle N_1N_2\rangle - \langle N_1\rangle\langle N_2\rangle &= k_BT\frac{\partial\langle N_2\rangle}{\partial\mu_1} = k_BT\frac{\partial\langle N_1\rangle}{\partial\mu_2} \\ \langle N_1E\rangle - \langle N_1\rangle\langle E\rangle &= k_BT\frac{\partial\langle E\rangle}{\partial\mu_1}\ .\end{aligned} \tag{2.104}$$

2.2.4.2 Exact differentials

From the above expressions, it can be seen that the function Ω has the exact differential,

$$d\Omega = -SdT - \langle N\rangle d\mu - \langle P\rangle dV\ . \tag{2.105}$$

Substituting the above relationship for $\langle E\rangle$ into the exact differential of Ω, an equation similar to the *first law of thermodynamics* is found, except with average signs on some of the quantities,

$$d\langle E\rangle = TdS + \mu d\langle N\rangle - \langle P\rangle dV\ . \tag{2.106}$$

2.2.4.3 Meaning of chemical potential, generalized particle number

The key behind second quantization is to remove the restriction that the number of particles is fixed. Instead, the theory is built around the idea of Fock space, where the number of particles is not fixed. This is highly advantageous when dealing with many-body systems. This same idea, when extended to finite temperatures, is what we call the grand-canonical ensemble. What we want is to consider some finite temperature density matrix $\hat{\rho} \sim e^{-\beta\hat{H}}$, where the number of particles is not fixed, but can fluctuate.

However, we cannot let it fluctuate arbitrarily since that would make no physical sense. Instead, the basic idea of the grand-canonical ensemble is to impose that the number of particles is only fixed on average. That is, we impose that,

$$\langle\hat{N}\rangle = N\ , \tag{2.107}$$

---

[7] See Landi script.

where $\hat{N}$ is the number operator and N is the number of particles in the system. In some systems, the number of particles does indeed fluctuate. This happens, for instance, in chemical solutions: if we look at a certain region of a liquid, the number of molecules there is constantly fluctuating due to molecules moving around from other parts. Of course, in many other systems on the other hand, the number of particles is fixed. However, it turns out that even in these cases, pretending it can may still give good answers, provided N is large (the thermodynamic limit). The reason is because, as we will show below, the variance of $\hat{N}$ scales as $\Delta^2\hat{N} \sim N$ so that,

$$\frac{\sqrt{\Delta^2\hat{N}}}{\langle\hat{N}\rangle} \sim \frac{1}{\sqrt{N}} \;, \tag{2.108}$$

which is thus small when N is large. Hence, when N is large, the grand-canonical ensemble will give accurate answers, even if the number of particles is not actually allowed to fluctuate. This is the idea behind ensemble equivalence: we are allowed to use an ensemble where the number of particles fluctuate, even though it actually doesn't, because in the thermodynamic limit the fluctuations are small. Our focus here will be on a system described within the language of second quantization, with a Hamiltonian $\hat{H}$ and a number operator $\hat{N}$. We assume that,

$$[\hat{H}, \hat{N}] = 0 \;, \tag{2.109}$$

meaning that the number of particles is a conserved quantity. This means that $\hat{H}$ and $\hat{N}$ can be simultaneously diagonalized. The eigenvalues of $\hat{N}$ are all possible numbers of particles N. Thus, $\hat{H}$ is divided in sectors with well defined N; in other words, $\hat{H}$ is block diagonal, so there are no terms connecting sectors with different N. The eigenvalues E are thus labeled by two indices $E(N;j)$, where j labels the quantum states within each sector.

Suppose now that the system is in thermal equilibrium with exactly N particles. The corresponding canonical partition function will be,

$$\wp(N) = \sum_j e^{-\beta E(N,j)} \;. \tag{2.110}$$

This is a constrained sum since we are only summing over that sector that has exactly N particles. This constraint makes it notoriously difficult to compute the sum in practice.

Instead, in the grand-canonical ensemble we allow the number of particles to fluctuate but only fix them on average (2.107). To summarize what we will learn below, to accomplish this we must introduce a new parameter μ, called the chemical potential, so that the grand-canonical equilibrium state is transformed to,

$$\rho_{eq} = \frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\Xi} \qquad , \qquad \Xi = \mathrm{Tr}\; e^{-\beta(\hat{H}-\mu\hat{N})} \;. \tag{2.111}$$

As can be seen, the chemical potential enters by shifting the Hamiltonian from,

$$\hat{H} \to \hat{H} - \mu\hat{N} \;. \tag{2.112}$$

The logic behind μ is twofold. When the number of particles is allowed to fluctuate, the value of μ is fixed externally (like the temperature). As a consequence the number of particles $\langle\hat{N}\rangle = N(\mu;T)$ is interpreted as a function of μ and T. Conversely, if the number of particles N is fixed, then $\mu = \mu(N;T)$ is to be interpreted as a function of N and T, which is to be determined as the solution of the implicit equation,

$$\langle\hat{N}\rangle = \frac{\text{Tr } \hat{N}e^{-\beta(\hat{H}-\mu\hat{N})}}{\text{Tr } e^{-\beta(\hat{H}-\mu\hat{N})}} = N \ . \tag{2.113}$$

We will explore both scenarios in a second. But before that, we still have to convince ourselves that Eq. (2.111) makes sense.

In order for a particle number to have an associated chemical potential, it must be conserved during the internal dynamics of the system, and only able to change when the system exchanges particles with an external reservoir. If the particles can be created out of energy during the dynamics of the system, then an associated μN term must not appear in the probability expression for the grand canonical ensemble, i.e. we require $\mu = 0$ for that kind of particle. Such is the case for photons in a black cavity, which can be annihilated or created due to absorption and emission on the cavity walls [8], see Exc. 2.2.6.2.

In some cases the number of particles is not conserved and the N represents a more abstract conserved quantity:

- Chemical reactions can convert one type of molecule to another; if reactions occur then the N_i must be defined such that they do not change during the chemical reaction.

- In high energy particle physics, ordinary particles can be spawned out of pure energy, if a corresponding antiparticle is created. Then, neither the number of particles nor antiparticles are conserved, only their difference.

- In a system composed of multiple compartments that share energy but do not share particles it is possible to set the chemical potentials separately for each compartment, for example, when a capacitor composed of two isolated conductors is charged by applying a difference in electron chemical potential.

- In some slow quasi-equilibrium situations it is possible to have distinct populations of the same kind of particle in the same location, which are each equilibrated internally but not with each other.

2.2.5 Thermodynamic limit and Riemann's zeta function

The partition functions (2.58) resp. (2.63) for microcanonical and (2.96) for grand canonical ensembles are evaluated over discrete distributions of microstates. Also, in Sec. 2.2.3 we argued that, in view of the huge number of microstates, it is desirable to introduce continuous distribution functions,

$$\sum_{\mathbf{r},\mathbf{p}} \ldots \longrightarrow h^{-3}\int d^3r d^3p \ldots \longrightarrow h^{-3}\int d\varepsilon\eta(\varepsilon) \ldots \ , \tag{2.114}$$

---

[8] Note that photons in a highly reflective cavity can be conserved and caused to have a non-zero chemical potential μ.

which, for confined ensembles, can even be simplified using the concept of density-of-states $\eta(\varepsilon)$. As long as we are deep in the thermodynamic limit, $N \longrightarrow \infty$, we expect to obtain reliable results. Let us now do this exercise for an ideal quantum gas confined in a box potential of volume V, whose density-of-states is given by (2.73).

We begin with the request that the chemical potential satisfies the normalization condition,

$$N = \iint w_{T,\mu}(\mathbf{r},\mathbf{k})d^3rd^3k = \int w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon = \frac{V\sqrt{2m}}{(2\pi)^2\hbar^3}\int_0^\infty \frac{\sqrt{\varepsilon}d\varepsilon}{e^{\beta(\varepsilon-\mu)}\mp 1} \ . \tag{2.115}$$

Introducing the *thermal de Broglie wavelength*,

$$\boxed{\lambda_{th} \equiv \sqrt{\frac{2\pi\hbar^2}{mk_BT}}} \ , \tag{2.116}$$

and defining the *fugacity*,

$$\boxed{Z \equiv e^{\beta\mu}} \ , \tag{2.117}$$

and we may also write,

$$N = \frac{V}{\lambda_{th}^3}\int_0^\infty \frac{\sqrt{x}dx}{Z^{-1}e^x \mp 1} \ . \tag{2.118}$$

At this point, to simplify the notation, we introduce the *Bose function* and its integral representation,

$$g_\xi^+(Z) = \sum_{t=1}^\infty \frac{Z^t}{t^\xi} = \frac{1}{\Gamma(\xi)}\int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x - 1} \ . \tag{2.119}$$

where $\Gamma(\eta)$ denotes the Gamma function. Analogically, we can define the *Fermi function* via,

$$g_\xi^-(Z) = \sum_{t=1}^\infty -\frac{(-Z)^t}{t^\xi} = \frac{1}{\Gamma(\xi)}\int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x + 1} \ . \tag{2.120}$$

For classical particles,

$$g_\xi^0(Z) = \frac{1}{\Gamma(\xi)}\int_0^\infty \frac{x^{\xi-1}dx}{Z^{-1}e^x + 0} = Z \ . \tag{2.121}$$

A particular value is the *Riemann zeta-function*,

$$g_\xi^+(1) = \zeta(\xi) \ . \tag{2.122}$$

With all these definitions we can now rewrite the expression (2.118),

$$\boxed{N = \frac{V}{\lambda_{th}^3}g_{3/2}^{(s)}(Z)} \ , \tag{2.123}$$

where $s = +$ for bosons, $s = -$ for fermions, and $s = 0$ for boltzons. In a similar way we could now derive analytic expressions for all other thermodynamic potentials. We will, however, see in the next Sec. 2.3, that for ideal bosonic gases the result (2.123) must be corrected.

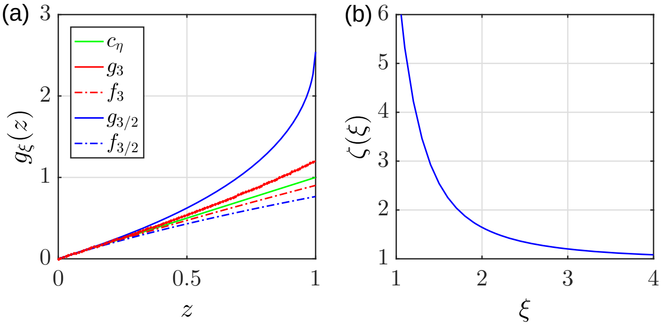

Figure 2.9: (code) (a) Bose and Fermi functions for box potentials ($g_{3/2}$ and $f_{3/2}$) and for harmonic potentials (g_3 and f_3). Also shown is the Boltzmann limit (2.121). (b) Riemann function.

2.2.6 Exercises

2.2.6.1 Ex: Quantum statistics

n particles are distributed over $g > n$ different cells with the same probability. Calculate the probabilities
a. that there is exactly one particle in each one of the first n cells;
b. that there is no cell with more than one particle.
Use the three different assumptions that:
i. the particles are boltzon, i.e. they are identifiable and arbitrarily many particles can be assigned to each cell;
ii. the particles are bosons, i.e. they are NOT identifiable and arbitrarily many particles can be assigned to each cell;
iii. the particles are fermions, i.e. they are NOT identifiable and only a single particle may be assigned to each cell.

2.2.6.2 Ex: Black-body radiation

Derive the thermodynamics of the phenomenon of *black-body radiation*.
a. Which is the appropriate thermodynamic ensemble, and why?
b. For a single mode of a cavity, calculate the partition function, the density operator, the total energy, and the Helmholtz free energy.
c. Generalize the results for an arbitrary black-body.
d. Introducing the density-of-states, calculate the energy density in the cavity as a function of temperature.

2.2.6.3 Ex: Electron gas model

A simple model for the behavior of electrons in a metal is the *Fermi gas model*. In this model the electrons move in a square well potential, a mean-field approach accounts globally for the periodic lattice of ions and the influence of all other electrons. The density of states and the electron density are the same as for blackbody radiation,

$$\rho(\varepsilon)d\varepsilon = \frac{V(2m^3)^{1/2}}{\pi^2\hbar^3}\sqrt{\varepsilon}d\varepsilon \ ,$$
$$n(\varepsilon)\rho(\varepsilon)d\varepsilon = \frac{1}{e^{(\varepsilon-\varepsilon_F)/k_BT}+1}\rho(\varepsilon)d\varepsilon \ .$$

Calculate the maximum energy at $T = 0$.

2.3 Bose-Einstein condensation of an ideal Bose gas

The clearest manifestation of quantum statistical effects is probably the phenomenon of Bose-Einstein condensation (BEC) predicted by Bose and Einstein in 1926 [4]. With the achievement of BEC in a dilute gas of atomic rubidium in 1995, Cornell *et al.* [8] confirmed the theory. Quantum degeneracy in Fermi gases was also observed a bit later [14, 32]. In this and the subsequent section, we will present a quantum statistical theory of *ideal* quantum gases for the cases of bosons, respectively, fermions. Clearly, the theory is unable to grasp many phenomena observed in BECs and linked to interatomic interactions, such as superfluidity. These will be discussed elsewhere [9].

2.3.1 Condensation of a gas confined in a box potential

One of the keys to understanding BEC is the behavior of the chemical potential μ at very low temperatures. The chemical potential is responsible for the concentration of a large number of atoms in the ground state N_0. A system with a large number of non-interacting bosons condenses to the ground state when the temperature approaches zero, $N_0 \to N$. The Bose-Einstein distribution function (2.62) gives the population of the ground state, $\varepsilon = 0$, in the zero temperature limit, $N = \lim_{T\to 0}(e^{-\beta\mu}-1)^{-1} = -1/\beta\mu$, or in terms of the *fugacity* defined by the expression (2.117), we may write, $Z \simeq 1 - 1/N$. It should be noted that the chemical potential in a bosonic system must always be less than the ground state energy in order to guarantee non-negative occupation $w_{T,\mu}(\varepsilon)$ of any state. $Z \simeq 1$ denotes macroscopic occupation of the ground state. We define the critical temperature for Bose-Einstein condensation via the occupation of the ground state. Above this temperature the occupancy of ground state is not macroscopic, below it is.

For a free gas with energy spectrum, $\varepsilon = p^2/2m$, we derived the density-of-states $\eta(\varepsilon)$ in (2.73) [10]. Using the occupation number $w(\varepsilon)$ for the Bose-Einstein distribution (2.117) in the thermodynamic limit, let us calculate the total number of particles,

$$N = N_0 + \int_0^\infty w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon = N_0 + \frac{V}{\lambda_{th}^3}g_{3/2}(Z) \ , \tag{2.124}$$

where the ground state population N_0 is maintained explicitly. In the process of converting the sum to an integral (2.114) the density of states disappears when we approach the ground state. This error is corrected by adding a contribution of an explicit term N_0 to the integral.

---

[9] See script on *Quantum mechanics* (2023).

[10] We must, however, keep in mind that the state density approach is an approximation not valid for experiments with a limited number of atoms.

2.3.1.1 Critical temperature and condensed fraction

We can use Eq. (2.124) to calculate the critical temperature[11] $T_c^{(3/2)}$ defined for $N_0 \nearrow 0$ and $\mu \to 0$. Above the phase transition, $T > T_c^{(3/2)}$, the population is distributed over all states, each individual state being weakly populated. Below $T_c^{(3/2)}$ the chemical potential is fixed by $\mu = 0$ and the number of the particles occupying the excited states is,

$$N_{th} = \frac{V}{\lambda_{th}^3(T)} g_{3/2}(1) = N \left(\frac{T}{T_c^{(3/2)}} \right)^{3/2} \quad , \tag{2.125}$$

with $g_{3/2}(1) = 2.612$. Since $N_0 + N_{th} = N$, the number of particles in the ground state is given by,

$$\boxed{\frac{N_0}{N} = 1 - \left(\frac{\min(T, T_c^{(3/2)})}{T_c^{(3/2)}} \right)^{3/2} \qquad \text{with} \qquad k_B T_c^{(3/2)} = \frac{2\pi\hbar^2}{m} \left(\frac{N}{V g_{3/2}(1)} \right)^{2/3}} \; , \tag{2.126}$$

N_0/N is the fraction of the atomic cloud which is condensed in the ground state. The abrupt occurrence of a finite occupation in a single quantum state at temperature below $T_c^{(3/2)}$ indicates a spontaneous change in the system and a thermodynamic phase transition. Solve Exc. 2.3.4.2.

2.3.1.2 Thermodynamic potentials in a grand canonical ensemble

In order to calculate the density of states, state equation, mean values in the grand canonical ensemble, we start from the definitions of the partition sum Ξ (2.96) (upper signs for bosons and lower signs for fermions), the grand canonical potential Ω, the fugacity Z, the density operator $\hat{\rho}$, and the trace,

$$\Xi \equiv \prod\nolimits_{m=1}^{\infty} (1 \mp Z e^{-\beta\varepsilon_m})^{\mp 1} \qquad \text{and} \qquad \Omega \equiv -k_B T \ln \Xi \qquad \text{and} \qquad Z \equiv e^{\beta\mu} \tag{2.127}$$

$$\hat{\rho} \equiv \frac{e^{-\beta(\hat{H}_N - \mu\hat{N})}}{\Xi} \qquad \text{and} \qquad \text{Tr} \; \ldots \equiv \sum_k \langle\psi_k| \ldots |\psi_k\rangle \; .$$

The parameters μ, V, T are held fixed. As we have seen, for large systems in the thermodynamic limit, the sum can be replaced by an integral, which, in turn, may be expressed by the Riemann zeta-function (see Secs. 2.2.5 and 4.1.2). The thermodynamic potentials and their expressions are summarized in the following table [12],

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[11] The superscript (3/2) denotes the box potential shape of the trapping potential. See 2.3.4.3 for an explanation of the notation.

		$\mathrm{Tr}\ \hat\rho$	$\ln\Xi$	$\sum_{m=1}^{\infty}$	$\lim_{N\to\infty}$
Ω			$-\frac{1}{\beta}\ln\Xi$	$\sum\frac{\ln(1\mp Ze^{-\beta\varepsilon_m})}{\pm\beta}$	
μ			$\frac{1}{\beta}\ln Z$		
1		$\mathrm{Tr}\ \hat\rho$			
n_m	$-\left(\frac{\partial\Omega_m}{\partial\mu}\right)_{T,V}$	$w_{T,\mu}$	$-\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_m}\ln\Xi$	$\frac{1}{e^{\beta\varepsilon_m}/Z\mp1}$	
N	$-\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}$	$\mathrm{Tr}\ \hat N\hat\rho$	$Z\frac{\partial}{\partial Z}\ln\Xi$	$\sum n_m$	$\frac{V}{\lambda_{th}^3}g_{3/2}^{\pm}+\left\{\frac{N}{1-Z}\right\}$
S/k_B	$-\left(\frac{\partial\Omega}{k_B\partial T}\right)_{\mu,V}$	$\mathrm{Tr}\ \hat\rho\ln\hat\rho$	$\ln\Xi$	$\pm\sum\ln\frac{n_m e^{\beta\varepsilon_m}}{Z}$	$\frac{5V}{2\lambda_{th}^3}g_{5/2}^{\pm}-\{\ln Z\}$
P	$-\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}$		$\frac{1}{\beta V}\ln\Xi$		$\frac{V}{\lambda_{th}^3}g_{5/2}^{\pm}-\{N\ln(1-Z)\}$
E	$TS+\mu N+\Omega$	$\mathrm{Tr}\ \hat H\hat\rho$	$-\frac{\partial}{\partial\beta}\ln\Xi$	$\sum n_m\varepsilon_m$	$\frac{3k_BTV}{2\lambda_{th}^3}g_{5/2}^{\pm}\simeq\frac{3PV}{2}$
C_V	$\left(\frac{\partial E}{\partial T}\right)_{N,V}$				$\frac{15V}{4\lambda_{th}^3}g_{5/2}^{\pm}-\left\{\frac{9Ng_{3/2}^{\pm}}{4g_{1/2}^{\pm}}\right\}$

(2.128)

With the particle number N we calibrate the chemical potential μ. The internal energy with fixed volume is proportional to the pressure. Note that $\lim_{N\to\infty}S=0$ and $\lim_{N\to\infty}C_V=0$.

The Bose-Einstein phase transition occurs at some critical temperature T_c. At high temperature $T>T_c$ the ground state population vanishes. At low temperature $T<T_c$, we have to substitute in the above equations Z by 1. Since $g_{3/2}$ is limited for $Z=0,..,1$ the population balance must be equilibrated by an additional term describing the ground state population:

$$\frac{N}{V}=\begin{cases}\frac{g_{3/2}^{+}(1)}{\lambda_{th}^3}+\frac{N_0}{V} & \text{for} \quad T\leq T_c\\ \frac{g_{3/2}^{+}(Z)}{\lambda_{th}^3} & \text{for} \quad T\geq T_c\end{cases}$$

$$\frac{P}{k_BT}=\begin{cases}\frac{g_{5/2}^{+}(1)}{\lambda_{th}^3} & \text{for} \quad T\leq T_c\\ \frac{g_{5/2}^{+}(Z)}{\lambda_{th}^3} & \text{for} \quad T\geq T_c\end{cases} \tag{2.129}$$

In the thermal Bose-gas phase, $T\geq T_c$, we get from (2.129) the state equation,

$$\boxed{\frac{PV}{Nk_BT}=\frac{g_{5/2}^{+}(Z)}{g_{3/2}^{+}(Z)}\overset{T\to\infty}{\longrightarrow}1}\,. \tag{2.130}$$

In the classical limit, obtained by noticing $g_\xi^0(Z)=Z$, follows the well-known classical ideal gas equation. In the Bose-condensate phase, $T\leq T_c$, using the definition of the critical temperature, we recover from (2.129) the state equation (2.126).

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[12] The red terms in {} brackets only hold for bosons, because the integral diverges otherwise.

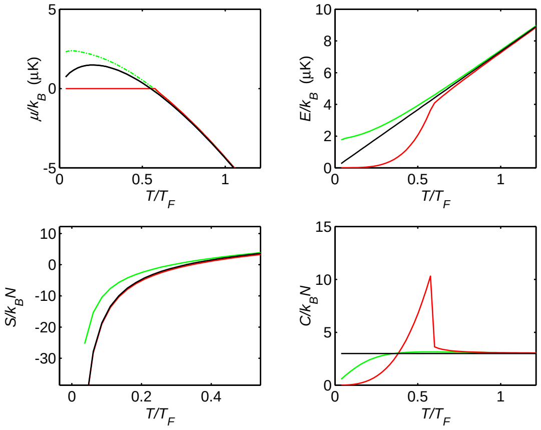

Figure 2.10: (code) Thermodynamic potentials for fermion (green), bosons (red), and boltzons (black).

Example 19 (*Fluctuations*): It is also interesting to look at fluctuations, variances, and covariances,

$$\begin{aligned}\Delta^2 N &\equiv \langle\hat{N}^2\rangle - \langle\hat{N}\rangle^2 = k_B T\left(\frac{\partial N}{\partial\mu}\right)_{T,V} \qquad (2.131)\\ \Delta^2 E &\equiv \langle\hat{H}^2\rangle - \langle\hat{H}\rangle^2 = k_B T^2\left(\frac{\partial E}{\partial T}\right)_{\mu,V} + \mu k_B T\left(\frac{\partial E}{\partial\mu}\right)_{T,V}\\ \Delta^2(EN) &\equiv \langle\hat{H}\hat{N}\rangle - \langle\hat{H}\rangle\langle\hat{N}\rangle = k_B T\left(\frac{\partial E}{\partial\mu}\right)_{T,V} .\end{aligned}$$

The derivation is left to the interested reader.

2.3.1.3 Micro- and macrocanonical Bose-condensates

The question which *canonical ensemble* is the correct assumption depends on the experimental situation. The question is particularly interesting in the context of Bose-Einstein condensation: Here it is related to the question which state better describes a BEC: A Fock or a Glauber state.

The condensates experimentally produced in alkali gases consisted of relatively small atom numbers between 1000 to 10^7, so that the validity of the thermodynamic approximation and the use of the density of states approach has been questioned [20]. Also, the decision whether to use the grand canonical, the canonical or the microcanonical ensemble for calculating the thermodynamic quantities noticeably influences the results. Herzog and Olshanii [22] have shown that for small atom numbers on the order of 100 the canonical and grand canonical statistics lead to predictions on the condensed fraction that differ by up to 10%. On the other hand, they give the same results if the particle numbers are large. Which canonical statistics is more appropriate is not a trivial question and depends on the experimental setup and in particular on the time scale of the measurements. If we look at the sample for short times, the number of condensed atoms will be fixed, and we can assume a canonical ensemble. For longer times, however, the atom number may be an equilibrium parameter depending on the contact of the sample with a reservoir, and the grand canonical statistics is better suited.

2.3.2 Condensation of a harmonically confined gas

The critical temperature T_c^0 can be significantly altered, when the atoms are confined to a spatially inhomogeneous potential. The critical temperature depends on the general shape and the tightness of the potential. Let us consider N particles of an ideal Bose gas distributed over several quantum states of an arbitrary potential. The occupation number $w_{T,\mu}(\varepsilon)$ of particles at an energy level ε is still given by (2.117), the ground state energy is defined as zero. In the thermodynamic limit, the relation between the chemical potential and the total number of particles is still given by Eq. (2.124), with an adequate density of states $\eta(\varepsilon)$. The state density for an arbitrary confinement potential $U(\mathbf{r})$ can be found by generalizing the calculation to the free gas. The phase space volume between the energy surfaces ε and $\varepsilon + d\varepsilon$ is proportional to the number of states in this energy range. However, the external potential limits the space available for the gas. For a harmonic potential (2.75) with the mean secular frequency $\bar{\omega}$ the density-of-states $\eta(\varepsilon)$ has already been calculated in Eq. (2.79). With this, we can analogically to (2.124) and (2.123), calculate,

$$\begin{aligned} N &= N_0 + \int_0^\infty w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon \\ &= N_0 + \frac{1}{2(\hbar\bar{\omega})^3}\int_0^\infty \frac{\varepsilon^2 d\varepsilon}{e^{\beta(\varepsilon-\mu)}-1} = N_0 + \left(\frac{k_B T}{\hbar\bar{\omega}}\right)^3 g_3(Z) \ . \end{aligned} \tag{2.132}$$

In the same way as for a potential well we find for a harmonic potential,

$$N_{th} = \left(\frac{k_B T}{\hbar\bar{\omega}}\right)^3 g_3(1) = N\left(\frac{T}{T_c^{(3)}}\right)^3 \ , \tag{2.133}$$

with $g_3(1) = 1.202$. Since $N_0 + N_{th} = N$, the number of particles in the ground state is,

$$\boxed{\frac{N_0}{N} = 1 - \left(\frac{\min(T, T_c^{(3)})}{T_c^{(3)}}\right)^3 \qquad \text{with} \qquad k_B T_c^{(3)} = \hbar\bar{\omega}\left(\frac{N}{g_3(1)}\right)^{1/3}} \ . \tag{2.134}$$

The superscript (3) indicates the harmonic shape of the trap.

Fig. 2.11(left) traces the condensed fraction N_c/N measured as a function of the reduced temperature $T/T_c^{(3)}$. Experiments [21, 16] confirm Bose's ideal gas theory in the thermodynamic limit.

We note that smaller trapping volumes (or tighter potentials) increase the critical temperature T_c, thus allowing for quantum degeneracy at higher temperatures, which can be advantageous in experimentation. Also, at a given temperature, a strongly confining potential reduces the total minimum number of atoms required to reach condensation.

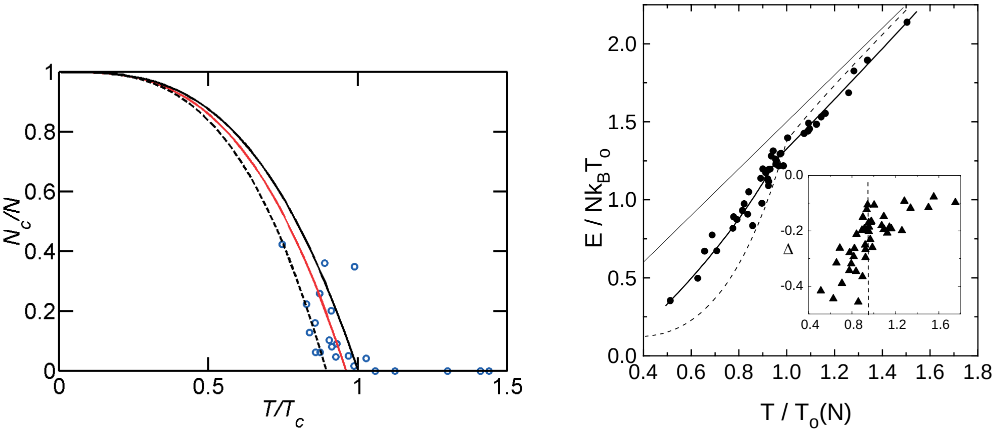

Figure 2.11: Left: Condensed fraction N_c/N as a function of reduced temperature $T/T_c^{(3)}$. The circles represent measured values. The upper solid line shows the theory for an ideal gas, the intermediate solid line shows a curve fitted to the measurements, and the lower part is a theoretical curve taking into account finite size effects and interatomic interactions. Right: Measurement of the release energy [16].

2.3.2.1 Energy and heat capacity

When the number of atoms is limited, $N < \infty$, we expect a slightly reduced critical temperature [20]. In addition, the interatomic interaction reduces the critical temperature [1]. The technical resolution of most experiments today is not sufficient to permit the study of these effects. However, measurements of other thermodynamic quantities such as energy and heat capacity [14, 16] showed significant deviations from the ideal gas behavior due to interaction effects. Therefore, although temperature being the most basic variable of the thermodynamic state, the system needs to be characterized by other quantities.

Heat is not a state variable because the amount of heat needed to raise the temperature of the system depends on how the heat is transferred. The *heat capacity* quantifies the system's ability to secure its energy. In conventional systems, the heat capacity is typically given either specified at constant volume or at constant pressure. Together with this specification, heat capacities are extensive state variables. When crossing a phase transition, the temperature-dependent heat capacity measures the degree of change in the system above and below the critical temperature and provides valuable information about the general type of phase transition.

The total energy $E/N \equiv N^{-1} \int \varepsilon w_{T,\mu} d^3x d^3k$ per particle is given by,

$$\frac{E}{N} = \frac{\int \varepsilon w_{T,\mu}(\mathbf{x},\mathbf{k}) d^3x d^3k}{\int w_{T,\mu}(\mathbf{x},\mathbf{k}) d^3x d^3k} = \frac{\int \varepsilon \eta(\epsilon)(e^{\beta(\varepsilon-\mu)}-1)^{-1} d\varepsilon}{\int \eta(\varepsilon)(e^{\beta(\varepsilon-\mu)}-1)^{-1} d\varepsilon} = 3k_B T \frac{g_4(Z)}{g_3(Z)} . \tag{2.135}$$

For a confined gas, volume and temperature are interdependent, and the concept of pressure is somewhat vague. In this case, we can not refer to the heat capacity at constant volume or pressure. However, one can define the heat capacity for a fixed

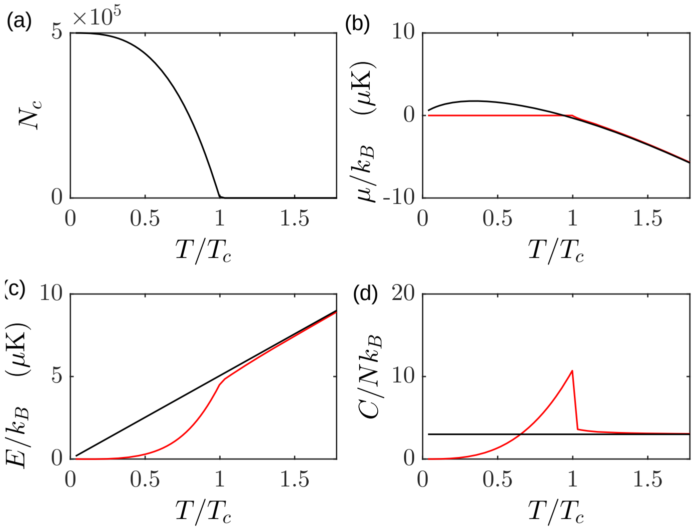

Figure 2.12: (code) Numerical calculation of thermodynamic potentials for a Bose gas as a function of temperature for a given trapping potential. (a) Chemical potential, (b) energy, (c) heat capacity per particle, and (d) total heat capacity.

number of particles,

$$C(T) = \frac{\partial E(T)}{\partial T} \ . \tag{2.136}$$

Recalling the implicit dependencies of the thermodynamic variables on temperature, we can evaluate (2.134):

$$C(T) = \beta \int_0^\infty \varepsilon f(\varepsilon)^2 \rho(\varepsilon) \left[\mu'(T) + \frac{\varepsilon - \mu}{T}\right] e^{\beta(\varepsilon-\mu)} d\varepsilon \ , \tag{2.137}$$

where the derivative of the chemical potential approaching the phase transition from above, $T \searrow T_c^0$, is

$$\mu'(T_c^+) = -\frac{1}{T} \frac{\int_0^\infty \varepsilon f(\varepsilon)^2 \rho(\varepsilon) e^{\beta\varepsilon} d\varepsilon}{\int_0^\infty f(\varepsilon)^2 \rho(\varepsilon) e^{\beta\varepsilon} d\varepsilon} \ . \tag{2.138}$$

Calculating the second moments of the distributions obtained for the same density by time-of-flight of absorption images, we obtain the kinetic energy,

$$E = \int \frac{p^2}{2m} n(\mathbf{p}) d^3\mathbf{p} \ . \tag{2.139}$$

For confined ideal gases, the virial theorem ensures $E_{kin} + E_{pot} = 2E_{kin}$. For real gases, the repulsive energy of the mean field adds to this energy, $E = E_{kin} + E_{pot} + E_{self}$. The sudden extinction of the trapping potential before time-of-flight takes away the potential energy E_{pot} non-adiabatically. The kinetic energy and the self-energy of the condensate are fully converted into kinetic energy during ballistic expansion. It is this energy, $p^2/2m = E_{kin} + E_{self}$, which is sometimes called *release energy*, which is measured after ballistic expansion [13]. Fig. 2.11(right) shows a measurement of the release energy. Solve the Exc. 2.3.4.3.

2.3.3 Density and momentum distribution for a Bose gas

Bose-Einstein condensates consist of atoms sharing a single quantum state. In inhomogeneous potentials, the condensate and the thermal fraction form spatially separated clouds, concentrated around the center of the potential and therefore very dense. For this reason, interatomic interaction effects generally dominate the density and momentum distribution of the condensed fraction. However, the non-condensed (or normal, or thermal) fraction is also subject to modifications due to the bosonic nature of the atoms. Since the density of the normal fraction is generally much smaller, these modifications are weak. In this section, we will only discuss these effects briefly, but we note that the calculations are analogous to the calculations for fermionic gases presented in Sec. 2.4.4.

For an ideal Bose gas the density and momentum distributions are expressed by Bose functions $g_{3/2}(Z)$ [9]. For example, as will be derived in Exc. 2.3.4.4(a), the density and momentum distributions are,

$$\boxed{\begin{aligned} n(\mathbf{x}) &= \frac{1}{\lambda_{th}^3}\, g_{3/2}(e^{-\beta[U(\mathbf{x})-\mu]}) \\ n(\mathbf{k}) &= \frac{a_{trap}^6}{\lambda_{th}^3}\, g_{3/2}(e^{\beta(\mu-\mathbf{p}^2/2m)}) \end{aligned}} \quad \text{(bosonic distribution functions)}\ . \tag{2.140}$$

In the classical limit, we can calibrate the chemical potential by Eq. (2.124) for a box potential or by (2.132) for a harmonic potential,

$$g_{3/2}(e^{\beta\mu}) \to c_{3/2}(e^{\beta\mu}) = e^{\beta\mu} = \begin{cases} \frac{N}{V}\lambda_{th}^3 & \text{(for a box potential)} \\ c_3(e^{\beta\mu}) = N\left(\frac{\hbar\bar{\omega}}{k_BT}\right)^3 & \text{(for a harmonic potential)} \end{cases} . \tag{2.141}$$

Hence, we obtain for the classical density distribution,

$$\begin{aligned} n(\mathbf{x}) &= \frac{1}{\lambda_{th}^3} c_{3/2}(e^{-\beta[U(\mathbf{x})-\mu]}) = \frac{e^{\beta\mu}}{\lambda_{th}^3} e^{-\beta U(\mathbf{x})} \\ &= \begin{cases} \frac{N}{V} e^{-\beta U(\mathbf{x})} & \text{(for a box potential)} \\ N\sqrt{\frac{m\bar{\omega}^2}{2\pi k_BT}}^3 e^{-\beta m\bar{\omega}^2 x^2/2} & \text{(for a harmonic potential)} \end{cases} . \end{aligned} \tag{2.142}$$

---

[13] It is interesting to measure the heat capacity of a partially condensed cloud near the critical point and analyze the discontinuity, because it contains important information about interatomic interactions and finite-size effects ([9], Sec. 3.4). In addition, the classification of Bose-Einstein condensation as a phase transition depends very much on the behavior of the thermodynamic potential near the critical point [27, 24].

Similarly, the momentum density distribution is given by,

$$n(\mathbf{k}) = \frac{a_{trp}^6}{\lambda_{th}^3} c_{3/2}(e^{\beta(\mu - p^2/2m)}) = \frac{a_{trp}^6 e^{\beta\mu}}{\lambda_{th}^3} e^{-\beta p^2/2m} \tag{2.143}$$
$$= \begin{cases} \frac{N}{V} a_{trp}^6 e^{-\beta U(\mathbf{x})} & \text{(for a box potential)} \\ N\hbar^3 \sqrt{\frac{1}{2\pi m k_B T}}^3 e^{-\beta p^2/2m} & \text{(for a harmonic potential)} \end{cases} .$$

We see that we recover the Maxwell-Boltzmann velocity distribution, as seen in Fig. 2.13,

$$n(\mathbf{v}) = n(\mathbf{k}) \frac{m^3}{\hbar^3} = N \sqrt{\frac{m}{2\pi k_B T}}^3 e^{-\beta m v^2/2} . \tag{2.144}$$

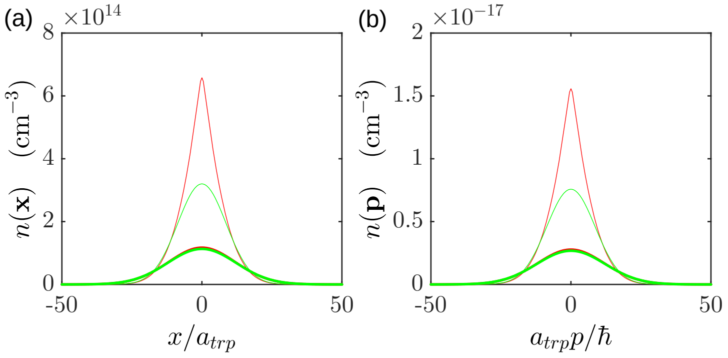

Figure 2.13: (code) (a) Density and (b) momentum distribution of a Bose gas (red) and a Boltzmann gas (green) at $T = 1.1T_c$ (solid line) and at $T = 2T_c$ (dotted line).

2.3.3.1 Ballistic expansion

To describe the density distribution of an ultracold Bose-gas after a time-of-flight we replace in the second Eq. (2.140): $\mathbf{k} = m\mathbf{r}/\hbar t_{tof}$. We obtain the density distribution,

$$n_{tof}(\mathbf{r}, t_{tof}) = \left(\frac{m}{\hbar t_{tof}}\right)^3 n(\mathbf{k} = m\mathbf{r}/\hbar t_{tof}) = \left(\frac{m}{\hbar t_{tof}}\right)^3 \frac{a_{trp}^6}{\lambda_{th}^3} g_{3/2}(e^{(\mu - mr^2/2t_{tof}^2)/k_B T})$$
$$\xrightarrow{T\to\infty} \left(\frac{m}{\hbar t_{tof}}\right)^3 N\hbar^3 \sqrt{\frac{1}{2\pi m k_B T}}^3 e^{-mr^2/2t_{tof}^2 k_B T} = \frac{N}{(2\pi)^{3/2} r_{rms}^3} e^{-r^2/2r_{rms}^2} , \tag{2.145}$$

where we defined,

$$r_{rms} \equiv \sqrt{\frac{k_B T}{m}} t_{tof} . \tag{2.146}$$

This distribution does not directly depend on the potential $U(\mathbf{r})$, that is, the expansion is isotropic. However, the chemical potential does depend on the potential. For very long flight times (usually several 10 ms) the density resembles a Gaussian distribution [9]. In Exc. 2.3.4.4(b) we determine the time-of-flight density distribution of an ultracold Bose gas.

In a time-of-flight experiment, any deviation observed between the results (2.145) and (2.146) points towards an impact of quantum statistics. However, absorption images only record projections of the time-of-flight distribution on a plane.

Example 20 (*Heat capacity measurement*): For an ideal Bose gas trapped in a harmonic potential the temperature dependence of the heat capacity at the threshold to condensation can easily be obtained as follows. The condensed fraction determines the chemical potential through,

$$N = N_0 + \left(\frac{k_BT}{\hbar\omega}\right)^3 g_3(Z) \; , \tag{2.147}$$

where $Z(T) = e^{\mu/k_BT}$ for a grand canonical ensemble and g_n denotes the Riemann zeta function. The condensed fraction vanishes above the critical temperature, the chemical potential vanishes below the critical temperature. $(k_BT/\hbar\omega)^3 = 2\pi(a_{trap}/\lambda_{th})^3$ denotes the normalized volume of a phase space cell. Knowing $Z(T)$ from equation (2.147), we can calculate the total energy, the heat capacity and all the other thermodynamic potentials:

$$C_N = 12k_B\left(\frac{k_BT}{\hbar\omega}\right)^3 g_4(Z) - 9k_BN\frac{g_3(Z)}{g_2(Z)} \; . \tag{2.148}$$

For an interacting Bose-gas we expect that the Eqs. (2.147) and (2.148)) are not scrupulously obeyed. Indeed, the abrupt discontinuous change in the heat capacity at the phase transition to BEC, expected for ideal gases, is smeared out by atomic collisions [1].

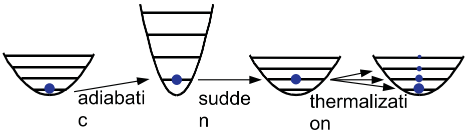

Figure 2.14: Population variation during a slow adiabatic compression followed by a sudden non-adiabatic decompression.

2.3.3.2 Adiabatic compression

Adiabaticity of a process means reversibility, while tha atom number is unchanged $N = const$ and, hence, constant entropy $S - const$. This implies an unchanged population distribution $n_j = const$ and $\beta\varepsilon_j/T = const$ also we get $\beta\mu, \beta E = const$. Furthermore, the phase space density keeps unchanged $\rho = const$. The process of adiabatically compressing a harmonic trap therefore changes the temperature like $T' = T\omega'/\omega$. This is valid above and below the transition point. The measure is repeated twice: With and without adiabatic-sudden variation. The heat capacity then follows from equation...

2.3.4 Exercises

2.3.4.1 Ex: Density of states for non-harmonic potentials

Calculate the density of states for non-harmonic potentials, $\hat{H} = \frac{\hbar^2 k^2}{2m} + \left|\frac{x}{2\bar{x}}\right|^p + \left|\frac{y}{2\bar{y}}\right|^l + \left|\frac{z}{2\bar{z}}\right|^q$ using Ref. [1]. Apply the result to a quadrupolar potential.

2.3.4.2 Ex: Monoatomic gas as a canonical ensemble

Consider a classical monoatomic gas made up of N non-interacting atoms of mass m confined in a container of volume V, at temperature T. The Hamiltonian corresponding to an atom is given by $\hat{H} = (\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2)/2m$.
a. Show that the atomic canonical partition function is $\xi = V/\lambda_{th}^3$, where λ_{th} is the thermal de Broglie wavelength defined in Eq. (2.116).
b. Using ξ of the previous item, obtain the system's partition function Ξ and the Helmholtz free energy F. Also obtain the free energy per atom $f = F/N$ in the thermodynamic limit $N \longrightarrow \infty$, $V \longrightarrow \infty$, such that $v = N/V$ fixed.
c. Obtain internal energy E and the gas pressure p.
d. Calculate the chemical potential and entropy per atom in the thermodynamic limit, thus deriving the so-called *Sackur-Tetrode formula*.

2.3.4.3 Ex: Generalization for arbitrary potentials in reduced dimensions

The calculation of the thermodynamic potentials can be generalized to arbitrary trapping potentials and dimensions [4, 15, 12, 2, 35, 17, 3, 20, 22, 26, 25, 30, 27, 29, 16]. To do so, we consider a generic power law potential confining an ideal Bose gas in α dimensions,

$$U(\mathbf{r}) = \sum\nolimits_{i=1}^{\alpha} \left|\frac{x_i}{a_i}\right|^{t_i} ,$$

and define a parameter describing the confinement power of the potential,

$$\xi = \frac{\alpha}{2} + \sum\nolimits_{i=1}^{\alpha} \frac{1}{t_i} .$$

For example, for a three-dimensional potential, $\alpha = 3$. Now, for a 3D harmonic potential, $\xi = 3$, and for 3D box potential, $\xi = 3/2$.
a. Calculate the density of states η using the equation (2.72) employing Bose functions (2.119).

b. Prove the following expressions:

(bosonic potentials)

$$\boxed{\begin{array}{rcl} \frac{N_0}{N} &=& 1-\left(\frac{\min(T,T_c)}{T_c}\right)^{\xi} \\ \frac{E}{Nk_BT} &=& \xi\frac{g_{\xi+1}(Z)}{g_\xi(Z)}\left(\frac{\min(T,T_c)}{T_c}\right)^{\xi} \\ \frac{S}{Nk_B} &=& 4\frac{g_{\xi+1}(Z)}{g_\xi(Z)}-\frac{2\mu}{k_BT} \\ \frac{C}{Nk_B} &=& \xi(\xi+1)\frac{g_{\xi+1}(Z)}{g_\xi(Z)}\left(\frac{\min(T,T_c)}{T_c}\right)^{\xi}-\xi^2\frac{g_\xi(Z)}{g_{\eta-1}(Z)}\frac{\max(T-T_c,0)}{T-T_c} \\ \frac{C_{T>T_c}}{Nk_B} &=& \xi(\xi+1)\frac{g_{\xi+1}(Z)}{g_\xi(Z)}-\xi^2\frac{g_\xi(Z)}{g_{\xi-1}(Z)} \quad , \quad \frac{C_{T<T_c}}{Nk_B}=\xi(\eta+1)\frac{g_{\xi+1}(1)}{g_\xi(1)} \\ \frac{\Delta C_{T_c}}{Nk_B} &=& \frac{C_{T_c^-}-C_{T_c^+}}{Nk_B}=\xi^2\frac{g_\xi(1)}{g_{\xi-1}(1)} \end{array}} .$$

2.3.4.4 Ex: Time-of-flight distribution of a Bose-gas

a. Derive the formulae (2.140) describing the density and momentum distribution of an ultracold Bose-gas.
b. Calculate the time-of-flight distribution of a Bose-gas as a function of temperature (i) analytically for a harmonic potential and (ii) numerically for an arbitrary potential.

2.4 Quantum degeneracy of an ideal Fermi gas

Atoms are fermions or bosons, or depending on their spin is integer or semi-integer. For example, ^{87}Rb atoms with their total integer spin of F are bosons, while ^{40}K atoms having a half-integer spin are fermions. At high phase space densities, atoms have to figure out how they will organize their coexistence. Bosons encourage each other to occupy the same phase space cell, in contrast to the reluctant fermions, which prefer to follow Pauli's exclusion principle. The different behavior is described by different quantum statistics that determine how the phase space (i.e., the available energy levels) has to be filled by the atoms. The Bose-Einstein distribution is valid for bosons, the distribution of Fermi-Dirac for fermions and both asymptotically approach the Boltzmann distribution at high temperatures. We have seen that bosons undergo a phase transition and condense in the ground state when the temperature is reduced below a critical threshold. On the other hand, the fermions organize their phase space, so that their energy levels are arranged like a ladder. The impact of fermionic quantum statistics on a cold cloud of atoms were observed experimentally by DeMarco and Jin [14, 32]. They cooled a two-components Fermi gas of 7×10^5 potassium atoms down to 300 nK, which corresponded to 60% of the atoms populating energy levels below the Fermi energy. The measured density distribution was found to deviate from the one expected for an ideal Boltzmann gas [14].

2.4.1 Chemical potential and Fermi radius for a harmonic trap

The phase space density for a *degenerate Fermi gas* has already been given in (2.117). In the same way as for a Bose gas, the chemical potential must satisfy the normalization condition,

$$N=\int w_{T,\mu}(\varepsilon)\eta(\varepsilon)d\varepsilon=\frac{1}{2(\hbar\bar{\omega})^3}\int_0^\infty\frac{\varepsilon^2d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1}=\left(\frac{k_BT}{\hbar\bar{\omega}}\right)^3f_3(Z)\ . \tag{2.149}$$

In the last line, we inserted the density of the states into a harmonic potential (2.80) and used the definition of the Fermi functions (2.120).

For low temperatures, $x\equiv\mu\gg1$, we can use the Sommerfeld expansion which in first order gives $f_\eta(e^x)\simeq x^\eta/\Gamma(\eta+1)$. From this we immediately obtain the energy, the Fermi radius and the momentum of free particles,

$$E_F=\mu(T=0)=\hbar\bar{\omega}(6N)^{1/3} \tag{2.150}$$

$$r_F=\sqrt{\frac{2E_F}{m\omega_r^2}}\quad\text{and}\quad z_F=\sqrt{\frac{2E_F}{m\omega_z^2}}$$

$$K_F=\sqrt{\frac{2mE_F}{\hbar^2}}\ .$$

Using the second order of the Sommerfeld expansion, $f_\xi(e^x)\simeq\frac{x^\xi}{\Gamma(\xi+1)}\left(1+\frac{\pi^2\xi(\xi-1)}{6x^2}+...\right)$, we obtain for the chemical potential the equation, $0=\mu^3+(\pi k_BT)^2\mu-E_F^3$. The approximate solution of this equation, neglecting terms such as $4\pi^6k_B^6T^6\ll27E_F^6$, is

$$\mu=E_F\left[1-\frac{\pi^2}{3}\left(\frac{k_BT}{E_F}\right)^2\right]\ . \tag{2.151}$$

In the limit of high temperatures, $f_\eta(Z)\xrightarrow{Z\rightarrow1}Z$

$$N=\left(\frac{k_BT}{\hbar\bar{\omega}}\right)^3e^{\beta\mu}=\left(\frac{k_BT}{\hbar\bar{\omega}}\right)^3(1+\beta\mu+...)\ , \tag{2.152}$$

$$\mu\approx k_BT\ln N\left(\frac{\hbar\bar{\omega}}{k_BT}\right)^3=k_BT\ln\frac{1}{6}\left(\frac{E_F}{k_BT}\right)^3\ .$$

This means that we recover the *Boltzmann gas*, which satisfies an ideal gas equation similar to that of particles in a box potential,

$$N=\left(\frac{k_BT}{\hbar\bar{\omega}}\right)^3\qquad\text{(Boltzmann)}\ . \tag{2.153}$$

---

[14] We note that meanwhile ultracold two-components Fermi gas have been demonstrated to form bosonic Cooper-pairs, similarly to the phenomena known as superconductivity in some metals and as superfluidity of the fermionic ^{3}He.

For comparison, for bosons we have,

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^3 \frac{g_3(Z)}{g_3(1)} \qquad \text{(Bose)} \ . \tag{2.154}$$

The chemical potentials are calculated in Fig. 2.15(a).

2.4.2 Energy

The total energy $E_1 \equiv E/N \equiv N^{-1} \int \epsilon w d^3\mathbf{x} d^3k$ per particle is given by,

$$\begin{aligned} E_1 &= \frac{\int \epsilon w_{T,\mu}(\mathbf{x},\mathbf{k}) d^3\mathbf{x} d^3k}{\int w_{T,\mu}(\mathbf{x},\mathbf{k}) d^3\mathbf{x} d^3k} \\ &= \frac{\int \epsilon \eta(\epsilon) \left(e^{\beta(\epsilon-\mu)} + 1\right)^{-1} d\varepsilon}{\int \eta(\epsilon) \left(e^{\beta(\epsilon-\mu)} + 1\right)^{-1} d\varepsilon} = 3k_BT \frac{f_4(Z)}{f_3(Z)} \ . \end{aligned} \tag{2.155}$$

Again using the Sommerfeld approximation, we see that for $T \to 0$ the energy is limited by

$$\begin{aligned} E_1 &= \frac{3}{N\beta(\beta\hbar\bar{\omega})^3} f_4(e^{\beta\mu}) \\ &= \frac{3\mu^4}{4E_F^3}\left(1 + \frac{2\pi^2}{(\beta\mu)^2} + ...\right) \xrightarrow{T\to 0} \frac{3}{4}E_F \qquad \text{(Fermi)} \ . \end{aligned} \tag{2.156}$$

because the atoms are forced to adopt a state of larger dynamics in the outermost regions of the trap. This implies, $E_1/E_F \xrightarrow{T\to 0} 3/4$.

In the limit of high temperatures, $T \to \infty$, a classical gas has the energy per particle,

$$E_1 = \frac{3}{N\beta(\beta\hbar\bar{\omega})^3} f_4\left(f_3^{-1}\left(\frac{(\beta E_F)^3}{6}\right)\right) \approx 3k_BT \qquad \text{(Boltzmann)} \ , \tag{2.157}$$

which is seen by taking the high temperature limit $f_\eta(Z) \xrightarrow{Z\to 0} Z$ and extrapolating to all Z. This implies, $E_1/E_F \xrightarrow{T\to\infty} 3k_BT/E_F$.

Comparing with bosons,

$$E_1 = 3k_BT\frac{g_4(1)}{g_3(1)} \approx 2.7 \qquad \text{(Bose)} \ . \tag{2.158}$$

2.4.3 Entropy and heat capacity

The entropy $S = -k_B \int g(\epsilon) \left[w \ln w + (1-w)\ln(1-w)\right] d\epsilon$ per particle is,

$$S_1 = 4k_B\frac{f_4(Z)}{f_3(Z)} - \frac{\mu}{T} = \frac{4E_1}{3T} - \frac{\mu}{T} \ . \tag{2.159}$$

The heat capacity per particle $C_1 = \frac{\partial E_1}{\partial T}\big|_N$ is easily calculated using $Zf_\eta'(Z) = f_{\eta-1}(Z)$,

$$C_1 = 3k_B\frac{f_4(Z)}{f_3(Z)} - \frac{3\mu}{T}\left(1 - \frac{f_4(Z)f_2(Z)}{f_3(Z)^2}\right) = \frac{E_1}{T} - \frac{3\mu}{T}\left(1 - \frac{f_4(Z)f_2(Z)}{f_3(Z)^2}\right) \ . \tag{2.160}$$

For fermions well below the Fermi temperature, $T \to 0$, using the Sommerfeld approximation, we calculate,

$$C_1 \xrightarrow{T\to 0} \frac{3\pi^2}{2}\frac{k_BT}{T_F} \qquad \text{(Fermi)}\ . \tag{2.161}$$

For high temperature T

$$C_1 \approx 3k_B \qquad \text{(Boltzmann)}\ . \tag{2.162}$$

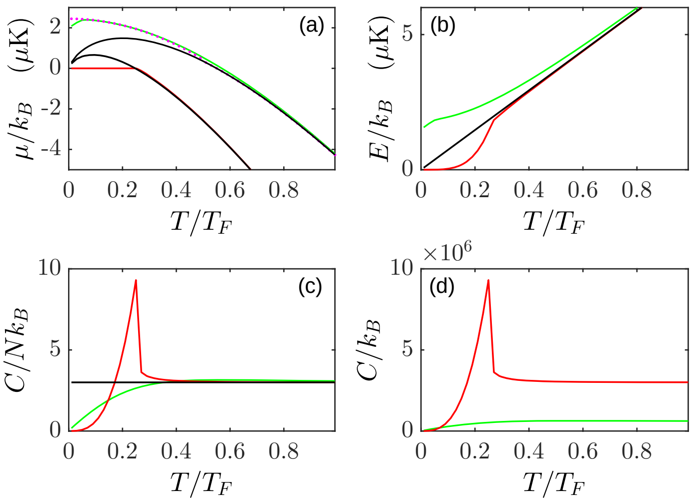

Figure 2.15: (code) Numerical calculation of thermodynamic potentials for Bose (red) and Fermi (green) gases as a function of temperature for a given harmonic trapping potential. (a) Chemical potential, (b) energy, (c) heat capacity per particle, and (d) total heat capacity. The dotted magenta line in (a) shows the chemical potential calculated from the Sommerfeld approximation.

2.4.4 Density and momentum distribution for a Fermi gas

2.4.4.1 Spatial distribution

The density distribution is,

$$\begin{aligned} n(\mathbf{x}) &= \int w_{T,\mu}(\mathbf{x},\mathbf{k})d^3\mathbf{k} = \frac{1}{(2\pi)^2}\int \frac{2k^2dk}{e^{\beta[\hbar^2k^2/2m+U(\mathbf{x})-\mu]}+1} \\ &= \frac{1}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int\frac{\sqrt{\varepsilon}d\varepsilon}{e^{\beta[\varepsilon+U(\mathbf{x})-\mu]}+1} = \frac{1}{(2\pi)^2}\left(\frac{2m}{\beta\hbar^2}\right)^{3/2}\Gamma(3/2)f_{3/2}(e^{-\beta[U(\mathbf{x})-\mu]})\ , \end{aligned} \tag{2.163}$$

such that,

$$\boxed{n(\mathbf{x}) = \lambda_{th}^{-3}f_{3/2}(e^{-\beta[U(\mathbf{x})-\mu]})} \qquad \text{(Fermi)}\ . \tag{2.164}$$

At low temperatures, $T \to 0$, we can apply the Sommerfeld expansion [7], which to first order gives $\mu \to E_F$,

$$\begin{aligned} n(\mathbf{x}) &\approx \frac{1}{(2\pi)^2}\frac{\Gamma(3/2)}{\Gamma(5/2)}\left(\frac{2m}{\hbar^2}\left[\mu - U(\mathbf{x})\right]\right)^{3/2} \\ &= \frac{1}{(2\pi)^2}\frac{2}{3}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left(E_F - \frac{m}{2}\omega_r^2\rho^2\right)^{3/2} = \frac{8\lambda}{\pi^2}\frac{N}{R_F^3}\left(1 - \frac{\rho^2}{R_F^2}\right)^{3/2} . \end{aligned} \tag{2.165}$$

At high temperatures, $T \to \infty$, we should recover the Boltzmann gas situation,

$$\begin{aligned} n(\mathbf{x}) &= \lambda_{th}^{-3} f_{3/2}(e^{-\beta[U(\mathbf{x})-\mu]}) \\ &\approx \lambda_{th}^{-3} N \left(\beta\hbar\bar{\omega}\right)^3 e^{-\beta U(\mathbf{x})} = \left(\frac{m\beta\bar{\omega}^2}{2\pi}\right)^{3/2} N e^{-\beta m(\omega_x^2x^2+\omega_y^2y^2+\omega_z^2z^2)/2} . \end{aligned} \tag{2.166}$$

It's easy to check, $\int n(\mathbf{x}) d^3\mathbf{x} = N$. Introducing the peak density n_0, we obtain,

$$\boxed{n(\mathbf{x}) = n_0 e^{-m\omega^2\rho^2/2k_BT}} \qquad \text{(Boltzmann)} . \tag{2.167}$$

The *rms*-radius of the distribution is $\sigma_j = \sqrt{k_BT/m\omega_j^2}$, which seems contrary to the above results, $\frac{m}{2}\omega_j^2 \left\langle x_j^2 \right\rangle = k_BT$. In comparison,

$$\boxed{n(\mathbf{x}) = \lambda_{th}^{-3} g_{3/2}\left[e^{\beta(\mu-U(\mathbf{x}))}\right]} \qquad \text{(Bose gas above } T_c\text{)} . \tag{2.168}$$

where $\lambda_{th} = \sqrt{2\pi\hbar^2/mk_BT}$ e $a_{tr} = \sqrt{\hbar/m\bar{\omega}}$.

2.4.4.2 Momentum distribution

The momentum distribution is,

$$\begin{aligned} \tilde{n}(\mathbf{k}) &= \int w_{T,\mu}(\mathbf{x},\mathbf{k}) d^3\mathbf{x} = \frac{1}{(2\pi)^2}\int \frac{r dr dz}{e^{\beta[\varepsilon(k)+m\omega_r^2\rho^2/2-\mu]}+1} \\ &= \frac{1}{(2\pi)^3}\int \frac{4\pi\rho^2 d\rho}{e^{\beta[\varepsilon+m\omega_r^2\rho^2/2-\mu]}+1} \\ &= \frac{1}{(2\pi)^2}\left(\frac{2}{\beta m\omega_r^2}\right)^{3/2}\int \frac{\sqrt{t}dt}{e^{\beta[\varepsilon+t-\mu]}+1} = \frac{1}{(2\pi)^2}\left(\frac{2}{\beta m\omega_r^2}\right)^{3/2}\Gamma(3/2) f_{3/2}(e^{\beta(\mu-\varepsilon)}) , \end{aligned} \tag{2.169}$$

such that,

$$\boxed{\tilde{n}(\mathbf{k}) = \lambda_{th}^{-3} a_{tr}^6 f_{3/2}(e^{\beta(\mu-\varepsilon)})} \qquad \text{(Fermi)} . \tag{2.170}$$

At low temperatures, $T \to 0$,

$$\begin{aligned} \tilde{n}(\mathbf{k}) &\approx \frac{1}{(2\pi)^2}\left(\frac{2}{\beta m\omega_r^2}\right)^{3/2}\frac{\Gamma(3/2)}{\Gamma(5/2)}\left(\beta\left[\mu-\varepsilon\right]\right)^{3/2} \\ &\approx \frac{1}{(2\pi)^2}\left(\frac{2}{m\omega_r^2}\right)^{3/2}\frac{2}{3}\left(E_F - \frac{\hbar^2k^2}{2m}\right)^{3/2} = \frac{8}{\pi^2}\frac{N}{K_F^3}\left(1 - \frac{k^2}{K_F^2}\right)^{3/2} . \end{aligned} \tag{2.171}$$

This can easily be integrated by dimensions,

$$\tilde{n}_{T\rightarrow 0}(k_z)=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\tilde{n}_{cl}(\mathbf{k})dk_xdk_y=\frac{8}{\pi^2}\frac{N}{K_F^3}\int\int_{|k|\leq K_F}\left(1-\frac{k^2}{K_F^2}\right)^{3/2}dk_xdk_y \tag{2.172}$$

$$=\frac{8}{\pi^2}\frac{N}{K_F^3}\int_0^{2\pi}\int_0^{\sqrt{K_F^2-k_z^2}}\left(1-\frac{k_z^2}{K_F^2}-\frac{k_\rho^2}{K_F^2}\right)^{3/2}k_\rho dk_\rho d\phi=\frac{16}{5\pi}\frac{N}{K_F}\left(1-\frac{k_z^2}{K_F^2}\right)^{5/2} .$$

It is easy to check $\int_{-\infty}^{\infty}\tilde{n}_{T\rightarrow 0}dk_z=N$, with Maple.

At high temperatures, $T\rightarrow\infty$, we should recover the Boltzmann gas situation,

$$\boxed{\tilde{n}(\mathbf{k})\approx\left(\frac{\hbar^2\bar{\omega}^2}{2\pi m\omega_r^2}\right)^{3/2}Ne^{-\beta\varepsilon}}\qquad\text{(Boltzmann)}\ . \tag{2.173}$$

Since ε is the kinetic energy, the *rms*-radius $\sqrt{k^2}$ of this distribution is $\beta\hbar^2\langle k^2\rangle=m$. In comparison,

$$\boxed{\tilde{n}_B(\mathbf{k})=\lambda_{th}^{-3}a_{tr}^6\ g_{3/2}\left[e^{\beta(\mu-\mathbf{p}^2/2m)}\right]}\qquad\text{(Bose gas above }T_c)\ . \tag{2.174}$$

Example 21 (*Integrated momentum distribution of a Fermi gas*): To integrate the momentum distribution of finite temperature Fermi gas by dimensions,

$$\tilde{n}(k_z)=\frac{1}{(2\pi)^3}\left(\frac{2}{\beta m\tilde{\omega}_{tr}^2}\right)^{3/2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_0^{\infty}\frac{4\pi\tilde{r}^2d\tilde{r}}{e^{\beta\varepsilon-\beta\mu+\tilde{r}^2}+1}dk_ydk_x \tag{2.175}$$

$$=\frac{1}{(2\pi)^3}\left(\frac{2}{\beta m\tilde{\omega}_{tr}^2}\right)^{3/2}2\pi\int_0^{\infty}\int_0^{\infty}\frac{4\pi\tilde{r}^2d\tilde{r}}{e^{\beta\hbar^2k_z^2/2m+\beta\hbar^2k_\rho^2/2m-\beta\mu+\tilde{r}^2}+1}k_\rho dk_\rho$$

$$=\frac{1}{\pi}\left(\frac{2}{\beta m\tilde{\omega}_{tr}^2}\right)^{3/2}\frac{2m}{\beta\hbar^2}\int_0^{\infty}\int_0^{\infty}\frac{\tilde{k}_\rho d\tilde{k}_\rho}{e^{\beta\hbar^2k_z^2/2m-\beta\mu+\tilde{r}^2+\tilde{k}_\rho^2}+1}\tilde{r}^2d\tilde{r}$$

$$=\frac{1}{\pi}\left(\frac{2}{\beta m\tilde{\omega}_{tr}^2}\right)^{3/2}\frac{2m}{\beta\hbar^2}\frac{1}{2}\int_0^{\infty}\tilde{r}^2\ \ln\frac{1}{1+e^{-\beta\hbar^2k_z^2/2m+\beta\mu-\tilde{r}^2-k_\rho^2}}\Bigg|_0^{\infty}d\tilde{r}$$

$$=\frac{2}{\pi\left(\beta\hbar\tilde{\omega}_{tr}\right)^2}\left(\frac{2}{\beta m\tilde{\omega}_{tr}^2}\right)^{1/2}\int_0^{\infty}\tilde{r}^2\ln\left(1+e^{\beta\mu-\beta\hbar^2k_z^2/2m-\tilde{r}^2}\right)d\tilde{r}\ .$$

2.4.4.3 Time-of-flight distribution

To describe time-of-flight images we substitute $\mathbf{k}=m\mathbf{r}/\hbar t$. We obtain the density distribution from a convolution,

$$n_{ToF}(\mathbf{x},t)=\frac{1}{(2\pi)^3}\int d^3\mathbf{x}_0d^3\mathbf{k}\frac{\delta^3(\mathbf{x}-\mathbf{x}_0-\mathbf{p}t/m)}{e^{\beta(H(\mathbf{x}_0,\mathbf{p})-\mu)}+1} \tag{2.176}$$

$$=\frac{1}{(2\pi)^3}\int\frac{d^3\mathbf{k}}{e^{\beta(H(\mathbf{x}+\mathbf{p}t/m,\mathbf{p})-\mu)}+1}$$

$$=\frac{1}{(2\pi)^3}\int\frac{dk_xdk_ydk_z}{e^{\beta\Sigma_j\left[\hbar^2k_j^2/2m+\frac{1}{2}m\omega_j^2(x_j+\hbar k_jt/m)^2\right]}/Z+1}\ .$$

We rewrite the exponent,

$$\hbar^2k_j^2/2m+\tfrac{1}{2}m\omega_j^2\left(x_j+\hbar k_jt/m\right)^2=\hbar^2k_j^2/2m(1+\omega_j^2t^2)+\omega_j^2tx_j\hbar k_j+\tfrac{1}{2}m\omega_j^2x_j^2 \tag{2.177}$$

$$=\left(\sqrt{\frac{\hbar^2k_j^2}{2m}(1+\omega_j^2t^2)}+\frac{\omega_j^2tx_j\sqrt{2m}}{2\sqrt{1+\omega_j^2t^2}}\right)^2+\frac{m\omega_j^2x_j^2}{2(1+\omega_j^2t^2)}$$

$$=\xi_j+\frac{m}{2}\breve{\omega}_j^2x_j^2\ .$$

where we define $\breve{\omega}_i\equiv\omega_i\left(1+\omega_i^2t^2\right)^{-1/2}$. With the substitution $d\xi_j=dk_j\sqrt{\frac{2\hbar^2}{m}\xi_j\left(1+\omega_j^2t^2\right)}$ we obtain

$$n_{ToF}(\mathbf{x},t)=\frac{1}{(2\pi)^3}\left(\frac{mk_BT}{2\hbar^2}\right)^{3/2}\frac{1}{\prod_i\left(1+\omega_i^2t^2\right)}\int\frac{\beta^{3/2}\left(\xi_x\xi_y\xi_z\right)^{-1/2}d\xi_xd\xi_yd\xi_z}{e^{\beta\Sigma_j\left[\xi_j+\frac{m}{2}\breve{\omega}_j^2x_j^2\right]}/Z+1} \tag{2.178}$$

$$=\frac{1}{2^3\pi^{3/2}}\frac{1}{\lambda_{th}^3}\frac{\tilde{\omega}^3}{\bar{\omega}^3}\int\frac{\beta^{3/2}\xi^{-3/2}4\pi\xi^2d\xi}{e^{\beta\Sigma_j\left[\xi+\frac{m}{2}\breve{\omega}_j^2x_j^2\right]}/Z+1}\ ,$$

where $\bar{\omega}\equiv(\omega_x\omega_y\omega_z)^{1/3}$ and $\breve{\omega}\equiv(\breve{\omega}_x\breve{\omega}_y\breve{\omega}_z)^{1/3}$.

$$\boxed{n_{ToF}(\mathbf{x},t)=\frac{1}{\lambda_{th}^3}\frac{\breve{\omega}^3}{\bar{\omega}^3}f_{3/2}\left(e^{\beta\mu-\frac{1}{2}\beta m\Sigma_j\breve{\omega}_j^2x_j^2}\right)}\ . \tag{2.179}$$

For long times-of-flight $t\gg\omega^{-1}$,

$$n_{ToF}(\mathbf{x},t)=\frac{1}{\lambda_{th}^3}\frac{1}{\bar{\omega}^2t^2}f_{3/2}\left(e^{\beta\left(\mu-m\mathbf{x}^2/2t^2\right)}\right)=\left(\frac{m}{\hbar t}\right)^3\tilde{n}(m\mathbf{x}/t)\ . \tag{2.180}$$

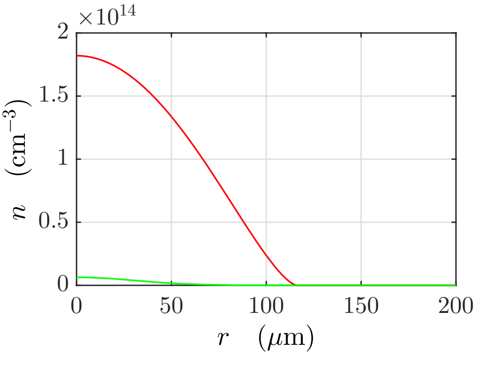

Figure 2.16: (code) Time-of-flight velocity distribution of (red) a Li Fermi gas at $T=0$ with vanishing initial spatial distribution [7] and (green) a thermal gas at $T=T_F$.

At low temperatures,

$$n_{ToF}(\mathbf{x},t) = \left(\frac{m}{\hbar t}\right)^3 \frac{N}{K_F^3}\frac{8}{\pi^2}\left(1-\frac{(m\mathbf{x}/\hbar t)^2}{K_F^2}\right)^{3/2} \tag{2.181}$$
$$= \left(\frac{m}{\hbar t}\right)^3 \frac{R_F^3}{6\pi^2\lambda}\left[1-\left(\frac{R_F m\mathbf{x}/\hbar t}{(48N\lambda)^{1/3}}\right)^2\right]^{3/2}$$

At high temperatures,

$$n_{ToF}(\mathbf{x},t) = \frac{1}{\lambda_{th}^3}\frac{1}{\bar{\omega}^2 t^2} f_{3/2}(e^{\beta(\mu-m\mathbf{x}^2/2t^2)}) \tag{2.182}$$
$$\approx \frac{1}{\lambda_{th}^3}\frac{1}{\bar{\omega}^2 t^2} e^{\beta(\mu-m\mathbf{x}^2/2t^2)}$$
$$\approx \left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}\frac{1}{\bar{\omega}^2t^2}N\left(\frac{\hbar\bar{\omega}}{k_BT}\right)^3 e^{-\beta m\mathbf{x}^2/2t^2} \approx N\frac{\bar{\omega}}{t^2}\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\beta m\mathbf{x}^2/2t^2} .$$

A *rms*-width is,

$$\langle r_{ToF}^2\rangle = \int r^2 n_{ToF}(\mathbf{x},t)d^3\mathbf{x} \tag{2.183}$$
$$= \frac{1}{\lambda_{th}^3}\frac{\breve{\omega}^3}{\bar{\omega}^3}\int r^2 f_{3/2}\left(e^{\beta\mu-\frac{1}{2}\beta m\Sigma_j\breve{\omega}_j^2x_j^2}\right)d^3\mathbf{x}$$
$$= \frac{2}{m\breve{\omega}_r^2N}\int\frac{\varepsilon g(\varepsilon)d\varepsilon}{e^{\beta(\varepsilon-\mu)}+1} = \frac{k_BT}{m\breve{\omega}_r^2}\frac{g_4(Z)}{g_3(Z)} .$$

This shows that the width of the flight-of-time distribution can simply be obtained from the spatial distribution by substituting $\omega \to \omega/\sqrt{1+\omega^2t^2}$. Of course this does not hold for condensed gases Bose.

Example 22 (*Equipartition theorem*): We find for harmonic traps,

$$E_{pot,1} = \frac{\int U(\mathbf{x})w_{T,\mu}(\mathbf{x},\mathbf{k})d^3\mathbf{x}d^3\mathbf{k}}{\int w_{T,\mu}(\mathbf{x},\mathbf{k})d^3\mathbf{x}d^3\mathbf{k}} = \frac{1}{(2\pi)^3N2}\int\frac{m\omega^2r^2d^3\mathbf{x}d^3\mathbf{k}}{e^{\beta\left[\hbar^2k^2/2m+m\omega^2r^2/2-\mu\right]}+1}$$
$$= \frac{16}{\pi N\beta^4(\hbar\omega)^3}\int\frac{u^4v^2dudv}{e^{u^2+v^2}/Z+1} \tag{2.184}$$
$$= \frac{1}{(2\pi)^3N2m}\int\frac{\hbar^2k^2d^3\mathbf{x}d^3\mathbf{k}}{e^{\beta\left[\hbar^2k^2/2m+m\omega^2r^2/2-\mu\right]}+1} = \frac{\int\hbar^2k^2w_{T,\mu}(\mathbf{x},\mathbf{k})d^3\mathbf{x}d^3\mathbf{k}}{2m\int w_{T,\mu}(\mathbf{x},\mathbf{k})d^3\mathbf{x}d^3\mathbf{k}} = E_{kin,1} .$$

This confirms the *equipartition theorem* for confined particles, which postulates,

$$E = E_{kin} + E_{pot} = 2E_{kin} . \tag{2.185}$$

In flight time, however, E_{pot} suddenly vanishes.

2.4.4.4 Calibrating the number of atoms

Experimentally, to calibrate N, we can use either the measured value of $\langle k^2\rangle$ at $T=0$, which gives $\mu = E_F = 4E/3$ and consequently,

$$N = \frac{32}{3}\left(\frac{\hbar^2\langle k^2\rangle}{6m\hbar\bar{\omega}}\right)^3 . \tag{2.186}$$

Or we determine the temperature T_g where the Boltzmann gas turns into a Fermi gas $3\mu/4 = 3k_BT_g$,

$$N = \frac{32}{3}\left(\frac{k_BT_g}{\hbar\bar{\omega}}\right)^3 \ . \tag{2.187}$$

2.4.5 Density and momentum distribution for anharmonic potentials

2.4.5.1 Width of momentum distribution for anharmonic potentials

If the potential is non-harmonic, the widths of Fermi distributions must in general be calculated numerically. I.e. first $g(\epsilon)$ is determined by integrating for every value of ϵ the root $\sqrt{\epsilon - U(\mathbf{x})}$ over the entire volume, where $U(\mathbf{x}) < \epsilon$, i.e. in the case of cylindrical symmetry,

$$g(\epsilon) = \frac{(2m)^{3/2}}{2\pi\hbar^3}\int\sqrt{\epsilon - U(r,z)}rdrdz \ . \tag{2.188}$$

Second the chemical potential must also be calculated numerically from $N = \int g(\epsilon)\left(e^{\beta(\epsilon-\mu)}+1\right)^{-1}d\epsilon$ by minimizing the function,

$$o(Z) = \left|\beta N - \int\frac{g(x/\beta)dx}{e^x/Z+1}\right| \ . \tag{2.189}$$

Finally, the *rms*-momentum width of a degenerate Fermi-gas is calculated from,

$$\frac{\langle k^2\rangle}{k_F^2} = \frac{E_1}{E_F} = \frac{1}{NE_F}\int\frac{\epsilon g(\epsilon)d\epsilon}{e^{\beta(\epsilon-\mu)}+1} \ . \tag{2.190}$$

It is important to note that the temperature cannot be obtained from $\hbar^2\left\langle k^2\right\rangle/2m = 3Nk_BT$ any more. Rather for a given $\langle k^2\rangle$ the parameter β in the integral (2.188) must be fitted to satisfy the equation.

Alternatively, we may assume a polynomial potential for which the density of states can be described by $g(\epsilon) \propto \epsilon^n$. Then,

$$\frac{\langle k^2\rangle}{k_F^2} = \frac{1}{E_F}\frac{\int\epsilon g(\epsilon)\left(e^{\beta(\epsilon-\mu)}+1\right)^{-1}d\epsilon}{\int g(\epsilon)\left(e^{\beta(\epsilon-\mu)}+1\right)^{-1}d\epsilon} = \frac{T}{T_F}\frac{(n+1)f_{n+2}(Z)}{f_{n+1}(Z)} \ , \tag{2.191}$$

For a harmonic potential we recover the energy formula,

$$\frac{\langle k^2\rangle}{k_F^2} = \frac{3T}{T_F}\frac{f_4(Z)}{f_3(Z)} \ , \tag{2.192}$$

and for hot clouds the classical limit holds,

$$\frac{\langle k^2\rangle}{k_F^2} = \frac{n+1}{\beta E_F} \ . \tag{2.193}$$

Must for a single dimension the value be divided by three? $\hbar^2\langle k_j^2\rangle = 2mk_BTf_4(Z)/f_3(Z)$ setting $\epsilon = \hbar^2k^2/m$.

For a harmonic potential $g(\epsilon) \propto \epsilon^2$ and for a linear potential $g(\epsilon) \propto \epsilon^{7/2}$. Intermediate values are possible for non isotropic traps, which are linear in some directions and harmonic in others, e.g. for a radially quadrupolar and axially harmonic trap, we expect $g(\epsilon) \propto \epsilon^3$ and thus $E = 4Nk_BT$. In general, we may have more complicated situations, where the trap becomes non-harmonic beyond a certain distance from the origin. In those cases, the density of states may be approximated by series,

$$g(\epsilon) \propto \epsilon^2 + \eta\epsilon^3 \ , \tag{2.194}$$

where η is a small parameter, so that,

$$\frac{\langle k^2 \rangle}{k_F^2} = \frac{1}{E_F} \frac{\int (\epsilon^3 + \eta\epsilon^4)(e^{\beta(\epsilon-\mu)} + 1)^{-1} d\epsilon}{\int (\epsilon^2 + \eta\epsilon^3)(e^{\beta(\epsilon-\mu)} + 1)^{-1} d\epsilon} = \frac{T}{T_F} \frac{3f_4(Z) + 12\eta f_5(Z)}{f_3(Z) + 3\eta f_4(Z)} \ , \tag{2.195}$$

which in the classical limit gives rise to energies $E = 3..4Nk_BT$ depending on the value of η.

Such effects must be considered when the time-of-flight method is used for temperatures measurements. For example, if we underestimate $g(\varepsilon)$ by assuming a harmonic potential at all ε, although the potential is quadrupolar at large $\varepsilon \gg k_BT$, we get a wrong estimate for the temperature $T_{wrng} = E/3Nk_B$ instead of $T_{corr} = E/4Nk_B$.

2.4.5.2 Width of the density distribution for anharmonic potentials

The result also permits to calculate the *rms* spatial width,

$$\sum\nolimits_{j=1}^{3} \frac{m}{2}\omega_j^2 \langle x_j^2 \rangle = 3k_BT \frac{f_4(Z)}{f_3(Z)} \ . \tag{2.196}$$

Let us for simplicity assume $\omega_i = \omega_j$. So in the classical limit,

$$\frac{\langle x_j^2 \rangle}{R_F^2} = \frac{\langle \mathbf{x}^2 \rangle}{3R_F^2} = \frac{E_1}{3E_F} = \frac{1..1.3T}{T_F} \ . \tag{2.197}$$

If the potential is non-harmonic, the widths of Fermi distributions must in general be calculated numerically. We may use the same results for the density of states and the chemical potential as for the momentum width calculations. Then,

$$\frac{\langle x_j^2 \rangle}{R_F^2} = \frac{E_1}{3E_F} = \frac{1}{3E_F} \frac{\int \epsilon g(\epsilon) \left(e^{\beta(\epsilon-\mu)} + 1\right)^{-1} d\epsilon}{\int g(\epsilon) \left(e^{\beta(\epsilon-\mu)} + 1\right)^{-1} d\epsilon} \ . \tag{2.198}$$

2.4.6 Classical gas limit

For a harmonic potential [11] the fraction of particles with energy smaller than ηk_BT is,

$$N(\eta) = \frac{1}{2N(\hbar\bar{\omega})^3} \int_0^{\eta k_BT} \frac{d\epsilon}{e^{\beta\epsilon}/Z - 0} \approx 1 - \frac{2 + 2\eta + \eta^2}{2e^\eta} \tag{2.199}$$

$$E(\eta) = \frac{1}{2N(\hbar\bar{\omega})^3} \int_0^{\eta k_BT} \frac{\epsilon^2 d\epsilon}{e^{\beta\epsilon}/Z - 0} \approx 3 - \frac{6 + 6\eta + 3\eta^2 + \eta^3}{6e^\eta} \ ,$$

while for a quadrupole potential,

$$\begin{aligned} N(\eta) &\approx -2\sqrt{Z}\frac{105+70\eta+28\eta^2+8\eta^3}{\sqrt{\pi}105e^\eta}+\operatorname{erf}(\sqrt{\eta}) \\ E(\eta) &\approx -\frac{2}{9}\sqrt{Z}\frac{945+630\eta+252\eta^2+72\eta^3+16\eta^4}{\sqrt{\pi}105e^\eta}+\frac{9}{2}\operatorname{erf}(\sqrt{\eta})\ . \end{aligned} \tag{2.200}$$

2.4.6.1 Momentum distribution for a classical gas

For high temperatures, $T \to \infty$, we should recover the ideal Boltzmann gas situation, $f_{3/2} \to id$,

$$\begin{aligned} \tilde{n}_{T\to\infty}(\mathbf{k}) &= \frac{1}{(2\pi)^3}\int\frac{4\pi\rho^2 d\rho}{e^{\beta[\varepsilon+m\omega_{tr}^2\rho^2/2-\mu]}} = \frac{1}{2\pi^2}e^{-\beta(\varepsilon-\mu)}\int e^{-\beta m\omega_{tr}^2\rho^2/2}\rho^2 d\rho \\ &= \left(\frac{1}{2\pi\beta m\omega_{tr}^2}\right)^{3/2} e^{-\beta(\varepsilon-\mu)} = \lambda_{th}^{-3}a_{tr}^6\ e^{\beta(\mu-\varepsilon)}\ . \end{aligned} \tag{2.201}$$

Since the chemical potential satisfies the normalization, $\int \tilde{n}_{T\to\infty}(\mathbf{k})d^3\mathbf{k} = 1$,

$$\tilde{n}_{T\to\infty}(\mathbf{k}) = \left(\frac{1}{2\pi\beta m\omega_{tr}^2}\right)^{3/2} N\left(\frac{\hbar\omega_{tr}}{k_BT}\right)^3 e^{-\beta\varepsilon} = N\sqrt{\frac{\hbar^2}{2\pi mk_BT}}^{\,3} e^{-\hbar^2k^2/2mk_BT}\ . \tag{2.202}$$

This is easy to integrate by dimensions, so that,

$$\tilde{n}_{T\to\infty}(k_z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\tilde{n}_{T\to\infty}(\mathbf{k})dk_xdk_y = N\sqrt{\frac{\hbar^2}{2\pi mk_BT}}e^{-\hbar^2k_z^2/2mk_BT}\ . \tag{2.203}$$

The rms-width of this distribution is,

$$\Delta k_z = \frac{\sqrt{mk_BT}}{\hbar}\ . \tag{2.204}$$

2.4.6.2 Correlating fluctuations in the number of atoms

Experimentally the atom number will fluctuate. To minimize this problem we can renormalize it to a norm number N_{norm} by multiplying the measured time-of-flight variance $\langle x_{tof}^2\rangle$ with,

$$\begin{aligned} C_T(N) &= \frac{\langle\tilde{x}_{tof}^2\rangle}{\langle x_{tof}^2\rangle} = \frac{N}{N_{norm}}\frac{f_4(\tilde{Z})}{f_4(Z)} \\ &= \frac{N}{N_{norm}}\frac{f_4\left[f_3^{-1}(N_{norm}(\beta\hbar\bar{\omega})^3)\right]}{f_4\left[f_3^{-1}(N(\beta\hbar\bar{\omega})^3)\right]}\ . \end{aligned} \tag{2.205}$$

2.4.7 Signatures for quantum degeneracy of a Fermi gas

Whether an atom is a *fermion* or a *boson* uniquely depends on its total spin. Halfinteger spin particles are fermions, integer spin particles are bosons. E.g. Rb atoms have in the ground state $J = 1/2, I = 7/2$, integer F, and are therefore bosons. Ca$^+$ ions have $J = 1/2$ and no hyperfine structure so that F is halfinteger, and are therefore fermions. ^{6}Li has half-integer F and is a boson.

For a *composite particle* the quantum statistical nature may depend on the interaction strength of the partners. For weak interaction, e.g. Feshbach the total spins of the partners will couple to a total total spin, which determines the nature of the composite particle. A fermion pairing with a fermion or a boson pairing with a boson will be bosons. A fermion pairing with a boson will be a fermion. Composite trimers may be either bosonic or fermionic depending on the coupling scheme. Can the quantum nature change with the tightness of the binding? What is the total spin of a deeply bound molecule? [34, 5, 18], [19, 23, 33]

2.4.7.1 Optical density of a Fermi gas

With the local density of a Fermi gas,

$$n_{loc} = \frac{k_F^3}{3\pi^2} \tag{2.206}$$

the *optical density* is at $T = 0$,

$$\begin{aligned}\int \sigma n dy &= \frac{8\sigma}{\pi^2}\frac{N}{R_F^3}\int_{-R_F}^{R_F}\left(1-\frac{x^2+y^2}{R_F^2}-\frac{z^2}{Z_F^2}\right)^{3/2}dy \qquad (2.207)\\ &= \frac{8\sigma}{\pi^2}\frac{N}{R_F^3}\left(1-\frac{x^2}{R_F^2}-\frac{z^2}{Z_F^2}\right)^{3/2}\int_{-R_F}^{R_F}\left(1-\frac{y^2}{R_F^2-x^2-R_F^2z^2/Z_F^2}\right)^{3/2}dy\ .\end{aligned}$$

Writing $a = R_F/\sqrt{R_F^2 - x^2 - R_F^2 z^2/Z_F^2}$,

$$\begin{aligned}\int \sigma n dy &= \frac{8\sigma}{\pi^2}\frac{N}{R_F^2 a^4}\int_{-a}^{a}(1-\tilde{y}^2)^{3/2}d\tilde{y} \qquad (2.208)\\ &= \frac{2\sigma}{\pi^2}\frac{N}{R_F^2 a^4}\left(9a\sqrt{1-a^2}-2a^3\sqrt{1-a^2}+3\arcsin a\right)\ .\end{aligned}$$

In the center, $a = 1$,

$$\int \sigma n dy = \frac{3N\sigma}{\pi R_F^2} = \frac{9m\omega_r^2 N}{k_L^2 E_F}\ , \tag{2.209}$$

such that for $E_F \simeq 1\mu$K we expect $n_{loc} \simeq 4 \times 10^{12}$ cm^{-3}.

2.4.7.2 Superfluid suppression of sympathetic cooling

The fermions inside the bosonic cloud can be regarded as impurities. If they travel too slow, $v < c$, and if the condensed fraction is too large, the motion will be frictionless and thermalization stops. If they travel fast, quasiparticles are excited, which can be removed by evaporation. With the typical velocity of sound in the BEC $c = \hbar\sqrt{16\pi n a}/2m_B \approx 2$ mm/s, or $\frac{m}{2}c^2 \approx k_B \times 20$ nK, we see that this is no real danger.

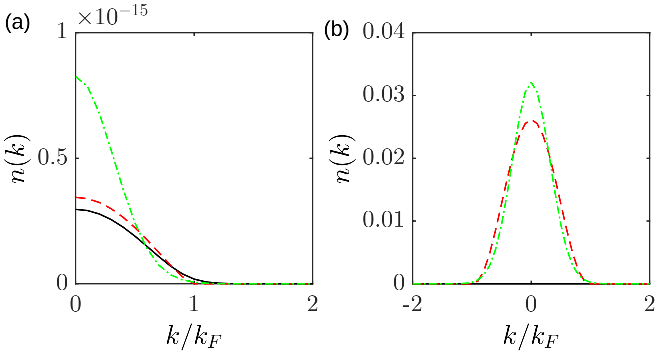

Figure 2.17: (code) (a) Radial momentum distribution and (b) distribution of momentum classes in the direction of k_z for a Fermi gas at $T/T_F = 0.2$ μK (solid), a classical gas (dash-dotted), and a Fermi gas at $T = 0$ (dashed).

2.4.7.3 Component separation

If the interspecies interaction h is stronger than the inter-bosonic interaction, the components may separate [31]. Otherwise a small fermionic cloud stays inside the BEC.

2.4.7.4 Excess energy modifies 2nd moment

Independent on any model, just look deviation from Gaussian (interaction energy plays no role for the fermions). Also calculate the 2nd moment $E = \int E_{kin}(k)n(k)dk$, where $n(k)$ is measured in time-of-flight and $E_{kin} = \hbar^2k^2/2m$.

2.4.7.5 Modification of light scattering

The unavailability of final momentum states inhibits scattering in a similar way as the Lamb-Dicke effect. Forward scattering is suppressed, because all small momentum states are occupied. Furthermore, spontaneous emission is suppressed like in photonic band gaps. However, here it is rather an atomic momentum band gap. Could it be that because scattering is suppressed, in-situ images of fermions are hampered?

A condition for this effect to play a role is $k_{rec} \ll k_F$. For Li the temperature must be $k_BT_F = \hbar^2k_F^2/2m = \hbar\bar{\omega}(6N)^{1/3} \gg \hbar^2k_L^2/2m \approx k_B \times 3\,\mu\text{K}$. I.e. we need quite large Fermi gases.

2.4.7.6 Hole heating

Loss processes that remove particles from an atom trap leave holes behind in the single particle distribution if the trapped gas is a degenerate fermion system. The appearance of holes increases the temperature, because of an increase in the energy share per particle if cold particles are removed. Heating is significant if the initial temperature is well below the Fermi temperature. Heating increases the temperature to $T > T_F/4$ after half of the systems lifetime, regardless of the initial temperature.

The *hole heating* has important consequences for the prospect of observing Cooper pairing in atom traps.

2.4.8 Fermi gas in reduced dimensions

In n dimensions with the energy $\varepsilon = ap^s + br^t$ [28] we have to generalize the results of the last chapter,

$$N = g\frac{\Gamma\left(\frac{n}{s}+1\right)\Gamma\left(\frac{n}{t}+1\right)}{(2\hbar)^n a^{n/s} b^{n/t}\Gamma\left(\frac{n}{2}+1\right)^2}(k_BT)^{n/s+n/t} f_{n/s+n/t}(z) \ . \tag{2.210}$$

This gives for a harmonic trap where $\varepsilon = \frac{1}{2m}p^2 + \frac{m}{2}\omega^2 r^2$ and with the spin degeneracy factor $g = 1$,

$$N = \left(\frac{k_BT}{\hbar\omega}\right)^n f_n(z) \ . \tag{2.211}$$

The Fermi energy again follows from Sommerfeld's expansion,

$$E_F = (n!N)^{1/n}\hbar\omega \ . \tag{2.212}$$

We now assume a $1D$ potential $V = \frac{m}{2}\omega_z^2 r^2$ embedded in a $3D$ trap. A true $1D$ situation arises when the atoms occupy all low-lying axial levels with the lowest radial vibrational quantum number, i.e. $E_F \ll \hbar\omega_r$ which gives,

$$N \ll \frac{\omega_r}{\omega_z} \ . \tag{2.213}$$

Such quantum degenerate $1D$ fermion gases realize the so-called *Luttinger liquid*. One of the hallmarks of Luttinger liquids is *spin-charge separation*.

Example 23 (*Estimations for 1D*): Let us consider a Fermi gas in a very elongated microtrap: $\omega_r = \sqrt{\frac{87}{7}}2\pi \times 1.4$ kHz and $\omega_z = \sqrt{\frac{87}{7}}2\pi \times 15$ Hz for Rb. With $N_{Li} = 10^5$ the Fermi temperature is as high as $T_F \simeq 5\ \mu$K. However we need $N \ll 100$ to see $1D$ features.
Assume $\varepsilon = \frac{1}{2m}p^2 + \frac{m^2}{4}b^4 r^4$,

$$N = \frac{1}{(\hbar b)^n}\frac{\Gamma\left(\frac{n}{4}+1\right)}{\Gamma\left(\frac{n}{2}+1\right)}(k_BT)^{3n/4} f_{3n/4}(z)$$
$$E_F \approx (\hbar b)^{4/3}\left(N\frac{\Gamma\left(\frac{n}{2}+1\right)\Gamma(\frac{3n}{4}+1)}{\Gamma\left(\frac{n}{4}+1\right)}\right)^{4/3n} \ .$$

In $1D$,

$$N = \frac{1.02}{\hbar b}(k_BT)^{3/4} f_{3/4}(z)$$
$$E_F \approx 0.87(N\hbar b)^{4/3} \ .$$

2.4.8.1 Fermi degeneracy

A completely analogous treatment to the Bose-gas yield for the case of fermion

$$E = \frac{3}{2}k_BTN\left(1 + 2^{-5/2}n\lambda_{th}^3\right) + \dots \ . \tag{2.214}$$

Bosonic ^{4}He has a very different behavior than fermionic ^{3}He. It stays gaseous at very low temperatures and becomes a Fermi gas before becoming fluid. Fermi gases have a higher pressure then classically predicted.

Electrons in a solid are characterized by a high density and a low mass. Hence, $n\lambda_{th}^3 \approx 10^3$. The interelectronic repulsion is canceled by atomic attraction, so that they may be considered an ideal gas. For the density of states we get the same formula as for bosons in a box multiplied with the factor 2 to account for the spin degree of freedom. Thus, from

$$N = \int_0^{E_F} \rho f_{FD} d\varepsilon \ , \tag{2.215}$$

we derive the Fermi energy $E_F = \frac{h^2}{8m}(3N/\pi V)^(2/3)$. The free electron gas is deep in the Fermi regime, the classical statistics may only be used at temperatures above $T > 10^5\,$K. Hence the energy is temperature-independent and the heat capacity vanishes, *i.e.* the electron gas does not contribute to the heat capacity of a metal. It is only at very low temperatures of a few K, when the heat capacity of the atomic lattice drops due to the underlying bosonic statistics, that the electrons contribute.

Now, make the metallic box potential having a finite depth. An electron can then leave the metal, if it surmounts the *exit work* $W = -V_{min} - E_F \simeq 10$ eV, which is the difference between the potential depth and the Fermi energy. At high temperatures, the tail of the Fermi-Dirac distribution can leak into the unbound regime, which gives rise to *thermoionic emission*. This feature explains the existence of *contact potentials*: Metals with different W and E_F brought into contact exchange charges until their Fermi level is at same height.

2.4.9 Exercises

2.4.9.1 Ex: Li Fermi gas

Programs on Li Fermi gases.

2.5 Further reading

2.5.1 on quantum statistics

R. DeHoff, *Thermodynamics in Material Science* [ISBN]

H.B. Callen, *Thermodynamics* [ISBN]

C. Kittel, *Introduction to Solid State Physics* [ISBN]

A.R. West, *Basic Solid State Chemistry* [ISBN]

D. Mc Quarry, *Statistical Thermodynamics* [ISBN]

2.5.2 on ideal quantum gases

V.S. Bagnato et al., *Bose-Einstein Condensation in an External Potential* [DOI]

D.A. Butts et al., *Trapped Fermi gases* [DOI]

Chapter 3

Thermodynamics applied to fluids and solids

In the present chapter we will apply the notion in thermodynamics acquired in Chp. 1 to various physical systems including multi-component, heterogeneous, chemically reacting gases and solids.

3.1 Unary heterogeneous systems

Let us first focus on unary systems, i.e. samples composed by a single species of molecules, e.g. H_2O, which nevertheless may be encountered in different states of aggregation: solid, liquid, gaseous, also called *phases*. We call *homogeneous* a system consisting of a single such phase and *heterogeneous*, when two or three phases coexist. Note that the list of phases is not exhaustive, as solids can exist in various allotropic phases depending on how the atoms arrange into a crystalline structure. For example, solid carbon may be exist as graphite or diamond.

3.1.1 Unary phase diagrams in PT-space

Allotropic phases are typically represented in phase diagrams, such as the one shown in Fig. 1.2. They are characterized by lines dividing PT-space into domains:

- Every area corresponds to a *stability domain of each single phase.*
- Every line corresponds to a *stability domain for two phases coexisting in equilibrium.*
- Every point corresponds to a *stability domain for three phases coexisting in equilibrium.*
- There are no regions where more than three phases coexist at equilibrium.

Heterogeneous systems may evolve between different phases when thermodynamic variables are changed in a process called *phase transition*. If such a system is taken through a reversible process represented by a path in the PT-diagram, when that path intersects a phase boundary, the change on pressure and temperature will be arrested while the phase transformation occurs. When the allotropic change is complete, the path may resume.

Let us define intensive variables as extensive ones per particle (or per mole),

$$\boxed{\tilde{X} \equiv \left(\frac{\partial X}{\partial N}\right)_{T,P}} \;, \tag{3.1}$$

from now on we designate intensive properties which have been converted from extensive ones by a tilde ($\tilde{.}$). With the Gibbs free energy $G = E + PV - TS$ defined in (1.66) we find the differential form (1.149),

$$dG = -SdT + VdP + \mu dN \;, \tag{3.2}$$

from which we get the Gibbs free energy *per particles*,

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} = \tilde{G} \;, \tag{3.3}$$

with its differential form,

$$\begin{aligned} d\tilde{G} &= \left(\frac{\partial \tilde{G}}{\partial G}\right)_{T,P} dG + \left(\frac{\partial \tilde{G}}{\partial N}\right)_{T,P} dN = \frac{1}{N}dG - \frac{G}{N^2}dN \\ &= -\frac{S}{N}dT + \frac{V}{N}dP + \mu\frac{1}{N}dN - \frac{\tilde{G}}{N}dN = -\tilde{S}dT + \tilde{V}dP \;, \end{aligned} \tag{3.4}$$

or

$$\boxed{d\mu = -\tilde{S}dT + \tilde{V}dP} \;. \tag{3.5}$$

For heterogeneous systems,

$$\mu^\alpha = \mu^\alpha(T^\alpha, P^\alpha) \qquad \text{and} \qquad \mu^\beta = \mu^\beta(T^\beta, P^\beta) \;. \tag{3.6}$$

describe surfaces in $TP\mu$-space. Where those surfaces intersect, as illustrated in Fig. 1.38, the phases can coexist. That is, if,

$$\boxed{T^\alpha = T^\beta \quad \wedge \quad P^\alpha = P^\beta \qquad \Longrightarrow \qquad \mu^\alpha(T^\alpha, P^\alpha) = \mu^\beta(T^\beta, P^\beta)} \;, \tag{3.7}$$

or simply $\mu^\alpha(T, P) = \mu^\beta(T, P)$, then the two phases α and β coexist.

Analogously, the coexistence of three phases, α, β, γ, is described by the intersection of three surfaces in $PT\mu$-space.

3.1.1.1 Calculation of the chemical potential surface for a single phase

Because the chemical potential is a state function, if it is known at a reference point $\mu(T_0, P_0)$, its value at any other point $\mu(T, P)$ is determined, and we may parametrize an arbitrary path to go from one point to the other. For example, we may first hold T constant and integrate $d\mu$ given by Eq. (3.5) until reaching an intermediate point $\mu(T_0, P)$. In a second step, we hold P constant and continue integrating $d\mu$ until teaching the end point $\mu(T, P)$. Repeating this procedure for all T and P, we generate a chemical potential surface.

Example 24 (*Chemical potential surface for constant heat capacity*): For example, let us consider an ideal gas, whose heat capacity does not depend on T nor P. Then, the two-step path integral can be solved analytically. The functional dependence of the volume on (T, P) is given by the ideal gas equation,

$$\tilde{V}^{\alpha}(T,P) = \frac{R_g T}{P} \ . \tag{3.8}$$

The functional dependence of the entropy on (T, P) can be integrated from Eq. (1.71)(i),

$$\tilde{S}^{\alpha}(T) = \tilde{S}^{\alpha}(T_0) + \int_{T_0}^{T} \frac{C_P^{\alpha}(T)}{T} dT = \tilde{S}^{\alpha}(T_0) + C_P^{\alpha} \ln \frac{T}{T_0} \ . \tag{3.9}$$

Now, we first hold the temperature fixed. $dT = 0$, and integrated the chemical potential over pressure thus generating an isobaric section,

$$\mu^{\alpha}(T_0, P) = \mu^{\alpha}(T_0, P_0) + \int_{P_0}^{P} \tilde{V}^{\alpha} dP' = \mu^{\alpha}(T_0, P_0) + R_g T \ln \frac{P}{P_0} \ . \tag{3.10}$$

Then we hold the pressure fixed, $dP = 0$, and integrate the chemical potential over temperature thus generating an isothermal section,

$$\begin{aligned} \mu^{\alpha}(T, P) &= \mu^{\alpha}(T_0, P) - \int_{T_0}^{T} \tilde{S}^{\alpha}(T) dT \qquad (3.11) \\ &= \mu^{\alpha}(T_0, P) - \tilde{S}^{\alpha}(T_0, P_0)(T - T_0) + C_P^{\alpha}(\tfrac{1}{2}T^2 - T_0 T + \tfrac{1}{2}T_0^2) \ . \end{aligned}$$

All we need to do, is choose a reference temperature T_0 and pressure P_0, where we can look up in data bases the molar entropy $\tilde{S}^{\alpha}(T_0, P_0)$ and the molar heat capacity C_P. Note, that in general the heat capacity may be temperature-dependent. See Excs. 3.1.3.1 to 3.1.3.2.

3.1.1.2 Chemical potential change upon crossing a phase transition

The integration demonstrated in the example 24 may be repeated for all phases, taking care that the reference state specified by T_0 is the same for all phases. The intersection of the curves then marks the phase transitions.

If the temperature-dependent heat capacities of both phases, C_P^{α} and C_P^{β}, are known, as well as the entropy change, $\Delta S^{\alpha\to\beta}(T_m) \equiv S^{\beta}(T_m) - S^{\alpha}(T_m)$, upon phase transition at a specific temperature T_m, then the entropy difference between two states in different phases and at different temperatures is simply,

$$\tilde{S}^{\beta}(T) = \tilde{S}^{\alpha}(T_0) + \int_{T_0}^{T_m} \frac{C_P^{\alpha}(T')}{T'} dT' + \Delta\tilde{S}^{\alpha\to\beta}(T_m) + \int_{T_m}^{T} \frac{C_P^{\beta}(T')}{T'} dT' \ . \tag{3.12}$$

Such a path is illustrated in Fig. 3.1.

In order to determine the change in chemical potentials between states localized at different phases and at different temperatures T_0 and T, we need to integrate $\mu^{\alpha}(T, P_0)$ from T_0 to the phase boundary at T_m and continue integrating $\mu^{\beta}(T, P_0)$ from T_m to the end point T_m, remembering that within a single phase $\gamma = \alpha, \beta$,

$$\tilde{S}^{\gamma}(T) = \tilde{S}^{\gamma}(T_0) + \int_{C_P^{\gamma}(T_0)}^{C_P^{\gamma}(T)} \frac{dC_P^{\gamma}}{T} = \tilde{S}^{\gamma}(T_0) + \int_{T_0}^{T} \frac{C_P^{\gamma}(T')}{T'} dT' \ , \tag{3.13}$$

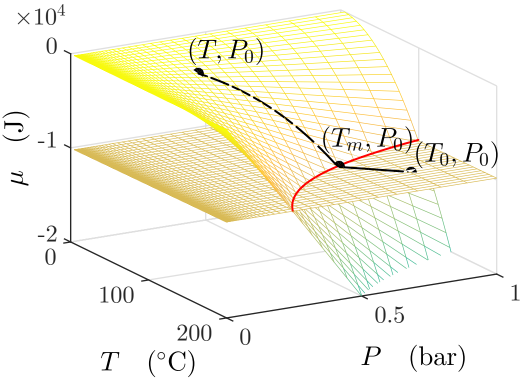

Figure 3.1: (code) Intersecting chemical potential surfaces. The points $(T_0, P_{})$ can be related to each other (see text).

and

$$\mu^\gamma(T) = \mu^\gamma(T_0) + \int_{\mu^\gamma(T_0)}^{\mu^\gamma(T)} d\mu^\gamma = \mu^\gamma(T_0) - \int_{T_0}^{T} \left(\tilde{S}^\gamma(T_0) + \int_{T_0}^{T''} \frac{C_P^\gamma(T')}{T'} dT' \right) dT'' \ . \tag{3.14}$$

We calculate,

$$\begin{aligned}
\mu^\beta(T) &= \mu^\alpha(T_0) + \int_{\mu^\alpha(T_0)}^{\mu^\alpha(T_m)} d\mu^\alpha + \int_{\mu^\beta(T_m)}^{\mu^\beta(T)} d\mu^\beta \\
&= \mu^\alpha(T_0) - \int_{T_0}^{T_m} \left(\tilde{S}^\alpha(T_0) + \int_{T_0}^{T''} \frac{C_P^\alpha(T')}{T'} dT' \right) dT'' - \int_{T_m}^{T} \left(\tilde{S}^\beta(T_0) + \int_{T_m}^{T''} \frac{C_P^\beta(T')}{T'} dT' \right) dT'' \\
&= \mu^\alpha(T_0) - \tilde{S}^\alpha(T_0)(T_m - T_0) - \tilde{S}^\alpha(T_m)(T - T_m) - \Delta\tilde{S}^{\alpha\to\beta}(T_m)(T - T_m) \\
&\qquad - \int_{T_0}^{T_m} \int_{T_0}^{T''} \frac{C_P^\alpha(T')}{T'} dT' dT'' - \int_{T_m}^{T} \int_{T_m}^{T''} \frac{C_P^\beta(T')}{T'} dT' dT'' \\
&= \mu^\alpha(T_0) - \tilde{S}^\alpha(T_0)(T - T_0) - \left(\Delta\tilde{S}^{\alpha\to\beta}(T_m) + \int_{T_0}^{T_m} \frac{C_P^\alpha(T'')}{T''} dT'' \right)(T - T_m) \\
&\qquad - \int_{T_0}^{T_m} \int_{T_0}^{T''} \frac{C_P^\alpha(T')}{T'} dT' dT'' - \int_{T_m}^{T} \int_{T_m}^{T''} \frac{C_P^\beta(T')}{T'} dT' dT'' \ .
\end{aligned} \tag{3.15}$$

Hence, knowing entropy $\tilde{S}^\alpha(T_0)$ at a specific temperature in one of the phases, the entropy change between the phases at a specific temperature, $\Delta\tilde{S}^{\alpha\to\beta}(T_m)$, and the temperature-dependent heat capacities on both phases, $C_P^\alpha(T)$ and $C_P^\beta(T)$, we can relate the chemical potentials at any temperature of both phases.

3.1.2 The Clausius-Clapeyron equation, latent heat

Let us have another look at the three equations (3.7) ruling two-phase coexistence,

$$\begin{aligned} T^\alpha = T^\beta \quad &\Longrightarrow \quad dT^\alpha = dT^\beta \equiv dT \\ P^\alpha = P^\beta \quad &\Longrightarrow \quad dP^\alpha = dP^\beta \equiv dP \\ \mu^\alpha = \mu^\beta \quad &\Longrightarrow \quad d\mu^\alpha = d\mu^\beta \equiv d\mu \ . \end{aligned} \tag{3.16}$$

From (3.5) we conclude,

$$-\tilde{S}^\alpha dT + \tilde{V}^\alpha dP = d\mu = -\tilde{S}^\beta dT + \tilde{V}^\beta dP \ , \tag{3.17}$$

This expression can be rewritten as,

$$\boxed{\frac{dP}{dT} = \frac{\Delta\tilde{S}^{\alpha\to\beta}}{\Delta\tilde{V}^{\alpha\to\beta}}} \ , \tag{3.18}$$

which is one form of the *Clausius-Clapeyron equation*. It states that state changes along a phase coexistence curve (red line in Fig. 3.1) are ruled by the ratio between the molar entropy change and the molar volume change. Knowing this ratio, we can integrate the $P(T)$ dependence.

In practice, $\Delta\tilde{S}^{\alpha\to\beta}$ is not measured in experiments, but rather the heat produced or absorbed under the transformation (e.g. condensation of evaporation). Since, transformation occurs isobarically under reversible conditions,

$$\delta Q^{\alpha\to\beta} = \Delta H^{\alpha\to\beta} \ . \tag{3.19}$$

Recalling that $G = H - TS$ and $G^\alpha = G^\beta$, we have,

$$\Delta\tilde{H}^{\alpha\to\beta} = T\Delta\tilde{S}^{\alpha\to\beta} \ , \tag{3.20}$$

so that

$$\boxed{\frac{dP}{dT} = \frac{\Delta\tilde{H}^{\alpha\to\beta}}{T\Delta\tilde{V}^{\alpha\to\beta}}} \ , \tag{3.21}$$

which is the most frequently used form of the Clausius-Clapeyron equation.

3.1.2.1 Integration of the Clausius-Clapeyron equation

Integrating Eq. (3.21) requires knowledge of,

$$\Delta H^{\alpha\to\beta} = \Delta H^{\alpha\to\beta}(T,P) \ . \tag{3.22}$$

From (1.78) we know,

$$d\tilde{H} = C_P dT + (1 - \alpha_{th}T)\tilde{V} dP \ . \tag{3.23}$$

Hence,

$$\begin{aligned} d\Delta\tilde{H}^{\alpha\to\beta} &= d\tilde{H}^\beta - d\tilde{H}^\alpha \\ &= C_P^\beta dT - C_P^\alpha dT + [(1 - \alpha_{th}^\beta T)V^\beta]dP - (1 - \alpha_{th}^\alpha T)\tilde{V}^\alpha dP \\ &= \Delta C_P^\beta dT + [(1 - \alpha_{th}^\beta T)\tilde{V}^\beta - (1 - \alpha_{th}^\alpha T)\tilde{V}^\alpha]dP \ . \end{aligned} \tag{3.24}$$

In practice, it turns out that the prefactor of the pressure differential is zero for pressure changes below 100000 bar, so that the enthalpy change is very well approximated by,

$$d\Delta\tilde{H}^{\alpha\rightarrow\beta}(T,P) = \Delta C_P^\beta\, dT \ . \tag{3.25}$$

Using the empirical equation, $C_p = a + b\,T + c\,T^{-2} + d\,T^2$, we find,

$$\begin{aligned}\Delta\tilde{H}^{\alpha\rightarrow\beta}(T,P) &= \int_{T_0}^{T} (\Delta a + \Delta b\,T + \Delta c\,T^{-2} + \Delta d\,T^2)dT \\ &= \Delta a\,T + \Delta b\,T^2 - \Delta c\,T^{-1} + \tfrac{1}{3}\Delta d\,T^{-3} + \Delta\tilde{H}^{(0)} \ .\end{aligned} \tag{3.26}$$

To evaluate the volume change,

$$\Delta\tilde{V}^{\alpha\rightarrow\beta} = \Delta\tilde{V}^{\alpha\rightarrow\beta}(T,P) \ , \tag{3.27}$$

let us consider a fluid-gas phase transition. Then, to a good approximation, we may neglect the volume change of the fluid phase, $\tilde{V}^\beta \gg \tilde{V}^\alpha$,

$$\Delta\tilde{V}^{\alpha\rightarrow\beta} = \tilde{V}^\beta = \frac{R_g T}{P} \ . \tag{3.28}$$

In this case,

$$\frac{dP}{P} = \frac{\Delta\tilde{H}^{\alpha\rightarrow\beta}}{\Delta\tilde{V}^{\alpha\rightarrow\beta}}\frac{dT}{PT} = \frac{1}{R_g}\left[\frac{\Delta a}{T} + \frac{\Delta b}{2} - \frac{\Delta c}{T^3} + \frac{\Delta d}{3}T + \frac{\Delta H^{(0)}}{T^2}\right]dT \tag{3.29}$$

with the solution,

$$\begin{aligned}&\ln\frac{P}{P_0} \\ &= \frac{1}{R_g}\left[\Delta a\ln\frac{T}{T_0} + \frac{\Delta b}{2}(T-T_0) + \frac{\Delta c}{2}\left(\frac{1}{T^2}-\frac{1}{T_0^2}\right) + \frac{\Delta d}{6}(T^2-T_0^2) - \Delta H^{(0)}\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \ .\end{aligned} \tag{3.30}$$

Good as long a empirical approximation formula holds and gas remains ideal, this formula describes well the gas-fluid coexistence curves.

Often the enthalpy change can even be considered as almost temperature-independent. Then,

$$\frac{dP}{P} = \frac{\Delta\tilde{H}^{\alpha\rightarrow\beta}}{\Delta\tilde{V}^{\alpha\rightarrow\beta}}\frac{dT}{PT} = \frac{\Delta\tilde{H}^{\alpha\rightarrow\beta}}{R_g}\frac{dT}{T^2} \ , \tag{3.31}$$

with the solution,

$$\boxed{\ln\frac{P}{P_0} = -\frac{\Delta\tilde{H}^{\alpha\rightarrow\beta}}{R_g}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \ . \tag{3.32}$$

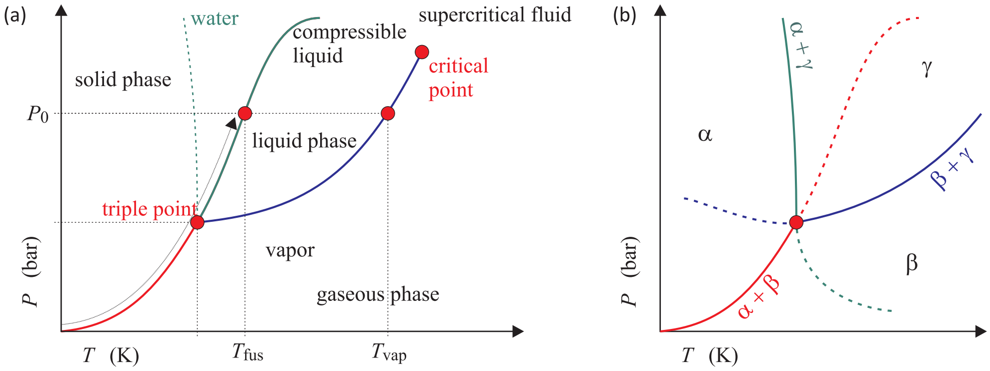
(a)
water
compressible liquid
supercritical fluid
critical point
solid phase
P_0
liquid phase
triple point
vapor
gaseous phase
P (bar)
T (K)
T_{fus}
T_{vap}
(b)
$\alpha+\gamma$
γ
α
$\beta+\gamma$
β
$\alpha+\beta$
P (bar)
T (K)

Figure 3.2: (a) PT-phase diagram. (b) Stable and metastable equilibrium lines near a triple point.

3.1.2.2 Triple points

Three chemical potential surfaces intersect in a point called *triple point*. The point (P_t, T_t) is also the intersection of three equilibrium lines, as illustrated in Fig. 3.2, and thus simultaneously satisfies three Clausius-Clapeyron equations.

It is an important characteristic of a triple point, that property changes across phase boundaries sum up, when several boundaries are crossed. It is ultimately, a corollary of the fact that properties are state functions. For example,

$$\Delta\tilde{V}^{\alpha\to\gamma} = \tilde{V}^{\gamma} - \tilde{V}^{\alpha} = \tilde{V}^{\beta} - \tilde{V}^{\alpha} + \tilde{V}^{\gamma} - \tilde{V}^{\beta} = \Delta\tilde{V}^{\alpha\to\beta} + \Delta\tilde{V}^{\beta\to\gamma} , \tag{3.33}$$

and the same holds for $\tilde{S}$ and $\tilde{H}$, e.g.,

$$\Delta\tilde{H}^{sub} = \Delta\tilde{H}^{fus} + \Delta\tilde{H}^{vap} . \tag{3.34}$$

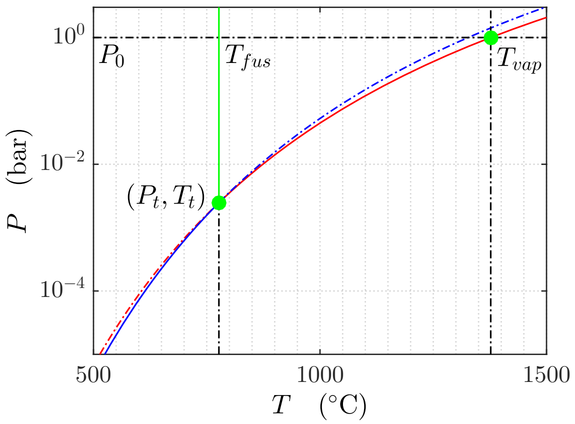

Figure 3.3: (code) (a) Vapor pressure of strontium obtained with $\Delta\tilde{H}^{fus} = 144\,\text{kJ/mol}$.

The sublimation curve and the vaporization curve both share a boundary to the gaseous phase, to that we may use the Clausius-Clapeyron relation for both,

$$\begin{aligned} P_{vap}(T) &= P_0 e^{(\Delta\tilde{H}^{vap}/R_g)(1/T_{vap}-1/T)} \\ P_{sub}(T) &= P_t e^{(\Delta\tilde{H}^{sub}/R_g)(1/T_t-1/T)} \ . \end{aligned} \tag{3.35}$$

Obviously, with $P_0 = 1\,\text{bar}$, the vapor curve $P_{vap} = P_{vap}(T)$ is fully determined, but not the sublimation curve $P_{sub} = P_{sub}(T)$, as long as the triple point is unknown. However, using,

$$T_t = T_{fus} \qquad \text{and} \qquad \Delta\tilde{H}^{sub} = \Delta\tilde{H}^{fus} + \Delta\tilde{H}^{vap} \ , \tag{3.36}$$

we are a good step further. We just need to find the triple pressure using the information, that both curves share the triple point,

$$P_{vap}(T_t) = P_t = P_{sub}(T_t) = P_{sub}(T_{fus}) \ . \tag{3.37}$$

With this we find,

$$P_t = P_0 e^{(\Delta\tilde{H}^{vap}/R_g)(1/T_{vap}-1/T_t)} \ , \tag{3.38}$$

and finally,

$$\boxed{\begin{aligned} P_{sub}(T) &= P_t e^{(\Delta\tilde{H}^{sub}/R_g)(1/T_t-1/T)} \\ &= P_0 e^{(\Delta\tilde{H}^{vap}/R_g)(1/T_{vap}-1/T)+(\Delta\tilde{H}^{fus}/R_g)(1/T_{fus}-1/T)} \end{aligned}} \tag{3.39}$$

The triple point and the vaporization point are marked with green circles in Fig. 3.3.

Example 25 (*Vapor pressure of strontium*): Eq. (3.39) can be used to obtain the vapor pressure of substances, for example, the partial pressure of metals contained in a cell under vacuum at a fixed volume. All one need to know is the set of data $\Delta\tilde{H}^{fus}$, $\Delta\tilde{H}^{vap}$, T_{fus}, and T_{vap}, which is specific for the metal. As an example, the curve in Fig. 3.4(a) shows the vapor pressure of strontium as a function of temperature.

3.1.2.3 The vacuum

Vacuum pumps and pressure measurement, partial pressures

3.1.3 Exercises

3.1.3.1 Ex: Chemical potential surface

a. Compute and plot the chemical potential surface: (T, P) for a monatomic ideal gas in the range $5\,\text{K} < T < 1000\,\text{K}$ and $10^{-5}\,\text{bar} < P < 10\,\text{bar}$. Suppose the gas is helium with $S_{298} = 126.04\,\text{J/(mol K)}$ and $C_P = 5193.2\,\text{J/(kg K)}$.
b. On the same graph sketch plausible surfaces for the chemical potential of the liquid and solid phases as functions of temperature and pressure.
c. Use these sketches to illustrate the construction of the phase diagram for a system that exhibits these three phases.

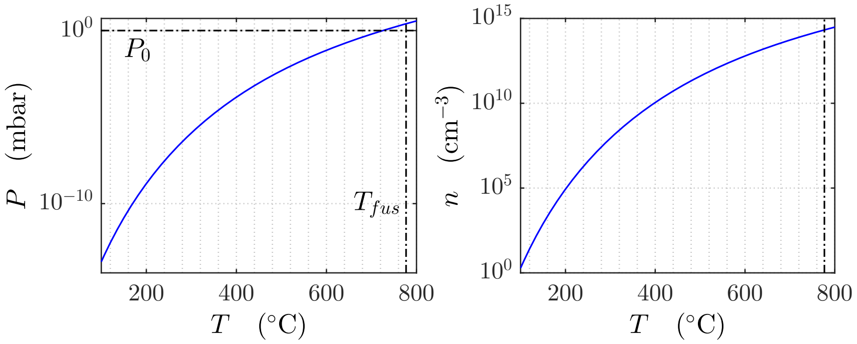

Figure 3.4: (code) (a) Vapor pressure of strontium obtained with $\Delta\tilde{H}^{fus} = 144\,\text{kJ/mol}$, $\Delta\tilde{H}^{vap} = 8.3\,\text{kJ/mol}$, $T_{fus} = 1050\,\text{K}$, and $T_{vap} = 1650\,\text{K}$. (b) Density of the strontium vapor corresponding to the partial pressure according to the ideal gas law: $n = P/k_BT$.

3.1.3.2 Ex: Clausius-Clapeyron relationship

Show that the *Clausius-Clapeyron equation*,

$$\frac{dP}{dT} = \frac{L}{T(V_{gas} - V_{fl})}$$

can also be derived via a cycle analogous to Carnot's cycle. The working fluid is an evaporating liquid, and the efficiency of this fictitious machine is dT/T, because the temperature difference between the two isotherms is dT. From the heat Q used in the evaporation and the work done $\oint PdV$, which are related on one hand to the latent heat L and on the other to the volume difference of V_{fl} and V_{gas}, results the rise in vapor pressure dP/dt.

3.1.3.3 Ex: Measurement of latent heat upon water condensation

A calorimeter with thermal capacity $C = 209\,\text{J/K}$ initially contains $m_1 = 250\,\text{ml}$ of water in thermal equilibrium at a temperature of $T_1 = 20\,°\text{C}$. Now, an amount of $m_2 = 40\,\text{ml}$ of water vapor is added. After reaching thermal equilibrium again, the temperature is $T_f = 92\,°\text{C}$. Calculate the latent heat of water condensation.

3.1.3.4 Ex: Latent heat in a sauna

A Finnish sauna of $10\,\text{m}^3$ volume is heated to 95 °C. To increase the thermal conductivity of the air, 100 ml of water at a temperature of 20 °C is added to the oven container, where the water is evaporated. How does the temperature of the sauna evolve if, for simplicity, the impact of the oven on the temperature is disregarded.

3.1.3.5 Ex: Latent heat

How much heat is needed to transform 1 g of ice at $-10\,°\text{C}$ ($c_{ice} = 0.55\,\text{cal/g/K}$, $L_{fus} = 80\,\text{cal/g}$) in a vapor at 100 °C ($c_{aq} = 1\,\text{cal/g/K}$, $L_{vap} = 540\,\text{cal/g}$)?

3.1.3.6 Ex: Latent heat

A metal bar with specific heat capacity $c_{mt} = 0.2\,\mathrm{cal/g/K}$ at $100\,^\circ\mathrm{C}$ is placed on a large block of ice at $0\,^\circ\mathrm{C}$. What is the mass of the bar if, when the system reaches thermal equilibrium, $m_{aq} = 500\,\mathrm{g}$ of ice have melted?

3.1.3.7 Ex: Latent heat

An ice block with the mass $m_{ice} = 500\,\mathrm{g}$ and the temperature $-20\,^\circ\mathrm{C}$ is put in an airtight container together with $m_{vap} = 200\,\mathrm{g}$ of water vapor at $100\,^\circ\mathrm{C}$. What will be the final temperature of the system?

3.1.3.8 Ex: A lake in winter

How long does it take at an air temperature of $-6\,^\circ\mathrm{C}$ to form a $d = 4\,\mathrm{cm}$ thick layer of ice on the surface of a lake (thermal conductivity of ice: $\kappa = 1.7 \times 10^{-2}\,\mathrm{J}\,/(\mathrm{s\ cm\ K})$; density of ice: $\rho = 0.92\,\mathrm{g/cm^3}$; amount of heat that must be dissipated to form 1 g of ice: 335 J)
Note: First consider a layer of ice of thickness z, and then think about how much heat has to be dissipated from the lake in order to to form additional layer of thickness dz.

3.2 Multi-component, homogeneous, non-reacting systems

In this section we will analyze systems made of more than one independent chemical component, in particular, mixtures or solutions. The chemical content of such a system is described by specifying the number of particles N_j (or moles n_j) of each component j, which is an extensive property. In order to handle the multi-component system, we introduce independent chemical potentials μ_j for every component, which are intensive variables.

The composition of a system N_j can vary due (i) to exchange with reservoir or (ii) to conversion via chemical reactions. In this section concentrate on case (i).

3.2.1 The Gibbs-Duhem equation

In Sec. 1.4.5 below Eq. (1.149) we already argued that the potential defined as,

$$O = G - \sum_j \mu_j N_j \quad \Longrightarrow \quad dO = -SdT + VdP - \sum_j N_j d\mu_j \tag{3.40}$$

cannot be a state potential, because it would only depend on intensive variables. Hence, $G = 0 = dG$, or,

$$\boxed{G = \sum_j \mu_j N_j \quad \Longrightarrow \quad -SdT + VdP = \sum_j N_j d\mu_j}\ . \tag{3.41}$$

This important result is termed the *Gibbs-Duhem equation*. This equation shows that intensive properties are not independent but related. When pressure and temperature are variable, for a system with J components only $J-1$ components have independent values of chemical potential [1].

Example 26 (*Derivation of the Gibbs-Duhem equation*): Another way to derive the Gibbs-Duhem equation is by noticing that, as an extensive state function, the Gibbs potential should satisfy $\lambda G(X) = G(\lambda X)$ for any extensive variable X, that is, it should be linear in the particle numbers, so that,

$$G = \sum_j N_j \frac{\partial G}{\partial n_j} = \sum_j \mu_j N_j \qquad \text{or} \qquad dG = \sum_j \mu_j dN_j + \sum_j N_j d\mu_j \ .$$

Comparing this to the definition of the Gibbs potential,

$$dG = -SdT + VdP + \sum_j \mu_j dN_j$$

we must conclude,

$$-SdT + VdP = \sum_j N_j d\mu_j \ .$$

3.2.2 Partial molal properties

We already mentioned that the number of particles N_j (or moles n_j) of each component j are extensive properties. Corresponding intensive properties that can be defined are the *fractions of particles* N_j/N_{tot} with $N_{tot} = \sum_j N_j$ (or the molar fractions n_j/n_{tot}). Now, for any extensive property $X = X(T, P, N_1, N_2, ...)$ of the system, which can be any of the state functions $X = E, S, V, H, F, G$, we may define a corresponding *partial molal property* of only the component j,

$$\boxed{\bar{X}_j \equiv \left(\frac{\partial X}{\partial N_j}\right)_{P,T,N_{k\neq j}}} \ , \tag{3.42}$$

by holding pressure, temperature, and the number of moles of all other components fixed. Nota that, in contrast to the previous decoration $(\tilde{.})$, which referred to quantities per *total number of particles*, the new decoration $(\bar{.})$ refers to quantities per *number of particles of that species*. Then, the total differential form is,

$$dX = \left(\frac{\partial X}{\partial T}\right)_{P,\{N_j\}} dT + \left(\frac{\partial X}{\partial P}\right)_{T,\{N_j\}} dP + \sum_j \bar{X}_j dN_j \ . \tag{3.43}$$

Example 27 (*Partial molal volume*): Considering, for example, volume $V = V(T, P, N_1, N_2, ...)$. Then,

$$\begin{aligned} dV &= \left(\frac{\partial V}{\partial T}\right)_{P,\{N_j\}} dT + \left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} dP + \sum_j \left(\frac{\partial V}{\partial N_j}\right)_{P,T,N_k\neq N_j} dN_j \qquad (3.44) \\ &= \alpha V \ dT - V\kappa \ dP + \sum_j \bar{V}_j \ dN_j \ . \end{aligned}$$

---

[1] The Gibbs-Duhem equation cannot be used for small thermodynamic systems due to the influence of surface effects and other microscopic phenomena.

with the definitions (1.69) of the thermal expansion coefficient and the compressibility,

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\{N_j\}} \quad , \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\{N_j\}} \quad . \tag{3.45}$$

The quantity $\bar{V}_j$ is called *partial molal volume*, and analogous procedure can be followed for $\bar{E}_j, \bar{S}_j, \bar{V}_j, \bar{H}_j, \bar{F}_j, \bar{G}_j$.

For the particular extensive property $X \to G$ and $\bar{X}_j \to \mu_j$ we derived the Gibbs-Duhem equation (3.41), but the result holds for any extensive property satisfying (3.42). E.g. holding temperature and pressure constant,

$$dX_{T,P} = \sum_j \bar{X}_j dN_j \ . \tag{3.46}$$

That is, changes of the partial molal properties of the components *add up* to a total change of the system. The value of the extensive state function $X_{T,P}$ is obtained by integrating (3.46). Fortunately, as an intensive property, $\bar{X}_j$ can only depend on other intensive properties. Furthermore, changes of state functions are path-independent. Hence, the total state $X_{T,P}$ reached by adding all the components is,

$$X_{T,P} = \sum_j \int_0^{N_j} \bar{X}_j dN_j = \sum_j \bar{X}_j \int_0^{N_j} dN_j = \sum_j \bar{X}_j N_j \ . \tag{3.47}$$

When we differentiate (3.47),

$$dX_{T,P} = \sum_j \bar{X}_j dN_j + \sum_j N_j d\bar{X}_j = 0 \ , \tag{3.48}$$

which only coincides with Eq. (3.46), if the second term vanishes. Hence,

$$\boxed{\sum_j N_j d\bar{X}_j = 0} \ . \tag{3.49}$$

Substituting $\bar{X}_j \to \mu_j$, we recover the Gibbs-Duhem equation (3.41) for the case $T, P = cnst$.

The important message of the Gibbs-Duhem equation is, that the partial molal properties are not all independent. Its integration provides a recipe, how to calculate values of partial molal properties of one component from those of the other components, as we will see later.

3.2.2.1 The mixing process

Temperature, pressure, volume and, according to the third law of thermodynamics, entropy, all have absolute non-zero values. In contrast, the energy functions E, H, F, G are only defined *with respect to some reference state*, i.e. only their *changes* are really of interest.

We will now study the mixing process resulting from putting together several components at constant pressure and temperature, and waiting for them to form a

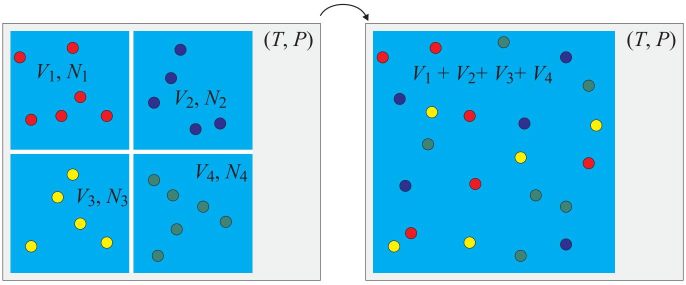

Figure 3.5: Initial 'reference state' and final mixture.

homogeneous *solution*. In order to guarantee that only the mixing process by itself is studied, we start from a 'reference state' in which all components are spatially separated by held at the same temperature and pressure, as illustrated in Fig. 3.5,

$$X^0 = \sum_j \bar{X}_j^0 N_k \ . \tag{3.50}$$

Mixing changes the value of state functions,

$$X^0 \curvearrowright X^{sol} = X^0 + \Delta X^{mix} \ . \tag{3.51}$$

Now,

$$\Delta X^{mix} = \sum_j \left(\bar{X}_j^{sol} - \bar{X}_j^0\right) N_j = \sum_j \Delta \bar{X}_j^{mix} N_j \ . \tag{3.52}$$

$\Delta \bar{X}_j^{mix}$ measures the change per particle of type j that the state function suffers from being put into the surrounding composed by all other particle types, and ΔX^{mix} is the weighted sum of all these changes. Differentiating Eq. (3.52),

$$\begin{aligned} d\Delta X^{mix} &= \sum_j \Delta \bar{X}_j^{mix} dN_j + \sum_j N_j d\Delta \bar{X}_j^{mix} \\ &= \sum_j \Delta \bar{X}_j^{mix} dN_j + \sum_j N_j d\bar{X}_j^{sol} = \sum_j \Delta \bar{X}_j^{mix} dN_j + 0 \ , \end{aligned} \tag{3.53}$$

from which we deduce,

$$\boxed{\sum_j N_j d\Delta \bar{X}_j^{mix} = 0} \ , \tag{3.54}$$

which is Gibbs-Duhem equation applied to the mixing process.

3.2.2.2 Partial molal properties from total properties

Obviously, all relationships derived in this section can be normalized to the total number of particles (or moles) N_{tot}. We just need to replace all extensive state functions E, S, V, H, F, G by molar quantities, $X \rightarrow \tilde{X}$, and particle numbers (or partial moles) by fractions $N_j \rightarrow \eta_j \equiv N_j / N_{tot}$, with $\sum_j \eta_j = 1$.

Let us consider a binary system and rewrite Eq. (3.52) for normalized quantities,

$$\Delta\tilde{X}^{mix} = \eta_1 \Delta\bar{X}_1^{mix} + \eta_2 \Delta\bar{X}_2^{mix} \ . \tag{3.55}$$

Also from (3.53),

$$d\Delta\tilde{X}^{mix} = \Delta\bar{X}_1^{mix} d\eta_1 + \Delta\bar{X}_2^{mix} d\eta_2 \qquad \text{with} \qquad d\eta_1 = -d\eta_2 \ , \tag{3.56}$$

which gives,

$$\frac{d\Delta\tilde{X}^{mix}}{d\eta_2} = \Delta\bar{X}_1^{mix} - \Delta\bar{X}_2^{mix} \ . \tag{3.57}$$

Isolating the terms $\bar{X}_1^{mix}$ and $\bar{X}_2^{mix}$ from the system of equations (3.55) and (3.57),

$$\boxed{\Delta\bar{X}_j^{mix} = \Delta\tilde{X}^{mix} + (1-\eta_j)\frac{d\Delta\tilde{X}^{mix}}{d\eta_j}} \qquad \text{with} \qquad j = 1, 2 \ . \tag{3.58}$$

Example 28 (*Partial molal enthalpies upon mixing a binary solution*): In this example we calculate the partial molal enthalpies upon mixing a binary solution for a model enthalpy given by $\Delta H^{mix} = a\eta_1\eta_2$ and satisfying $\lim_{\eta_1 \to 0} \Delta H^{mix} = 0$. Using $\eta_1 + \eta_2 = 1$ the enthalpy can be rewritten,

$$\Delta H^{mix} = a(\eta_1 - \eta_1^2) = a(\eta_2 - \eta_2^2) \ .$$

Evaluating,

$$\frac{d\Delta\bar{H}^{mix}}{d\eta_j} = a(1 - 2\eta_j) \ ,$$

we get,

$$\Delta\bar{H}_1^{mix} = \Delta H^{mix} + (1-\eta_1)\frac{d\Delta\bar{H}^{mix}}{d\eta_1} = a\eta_2^2 \ ,$$

and finally,

$$\Delta\bar{H}_j^{mix} = a\eta_{i\neq j}^2 \ .$$

A consistency check yields,

$$\Delta H^{mix} = \Delta\bar{H}_1^{mix}\eta_1 + \Delta\bar{H}_2^{mix}\eta_2 \ .$$

3.2.2.3 Partial molal properties of one component from those of the others

The partial molal version of the Gibbs-Duhem relation is,

$$\sum_j \eta_j d\Delta\bar{X}_j^{mix} = 0 \ , \tag{3.59}$$

or restricting to two species,

$$d\Delta\bar{X}_1^{mix} = -\frac{\eta_2}{\eta_1} d\Delta\bar{X}_2^{mix} \ . \tag{3.60}$$

Now, $\lim_{\eta_2 \to 0} \bar{X}_2^{sol} = \bar{X}_2^0$, since there is nothing to mix. Hence, $\lim_{\eta_2 \to 0} \Delta \bar{X}_2^{mix} = 0$. Now, integrating the last expression,

$$\Delta \bar{X}_1^{mix} = -\int_0^{\Delta \bar{X}_2^{mix}} \frac{\eta_2}{\eta_1} d\Delta \bar{X}_2^{mix} = -\int_0^{\eta_2} \frac{\eta_2}{\eta_1} \frac{d\Delta \bar{X}_2^{mix}}{d\eta_2} d\eta_2 \ . \tag{3.61}$$

Do the Exc. 3.2.5.2.

Example 29 (*Partial molal enthalpies upon mixing a binary solution*): Assume that we have a partial molal enthalpy of component 2 depending on the square of the abundance of the other component 1,

$$\Delta H_2^{mix} = a\eta_1^2 \ .$$

Then, the above recipe yields,

$$\Delta \bar{H}_2^{mix} = -\int_0^{\eta_2} \frac{\eta_2}{\eta_1} \frac{d\Delta \bar{H}_2^{mix}}{d\eta_2} d\eta_2 = -\int_0^{\eta_2} \frac{\eta_2}{\eta_1} \frac{da(1-\eta_2)^2}{d\eta_2} d\eta_2 = a\eta_2^2 \ .$$

3.2.2.4 Relationships among partial molal properties

As seen in Sec. 3.2.2, application of the operator,

$$\left(\frac{\partial}{\partial N_j} \right)_{T,P,N_{k\neq j}} \tag{3.62}$$

to any total property X yields the corresponding molal property. Applying this operator to the definitions, laws, coefficient relations, and Maxwell equations, we obtain the corresponding molal expressions. For example, the counterpart of the relation $H = E + PV$ is,

$$\bar{H}_j \equiv \left(\frac{\partial H}{\partial N_j} \right)_{T,P,N_{k\neq j}} = \left(\frac{\partial E}{\partial N_j} \right)_{T,P,N_{k\neq j}} + P \left(\frac{\partial V}{\partial N_j} \right)_{T,P,N_{k\neq j}} \equiv \bar{E}_j + P\bar{V}_j \ , \tag{3.63}$$

and analogously for all other equations. For a solution with various components, we can simply substitute any extensive variable X for each component j,

$$X \longrightarrow \bar{X}_j \ . \tag{3.64}$$

3.2.3 Chemical potential in solutions

Initially introduce for unary systems in Sec. 1.3.2, the concept of chemical potential can be extended to multicomponent systems. We will show below that, if the chemical potential is known as a function of temperature, pressure and composition, then *all of the partial molal properties of the system may be computed.* The thermodynamic state of a system with J components depends on $J + 2$ variables,

$$E = E(T, P, N_1, ..., N_J) \quad \Longrightarrow \quad dE = TdS - PdV + \sum_{j=1}^{J} \mu_j dN_j \tag{3.65}$$

with

$$\mu_j \equiv \left(\frac{\partial E}{\partial N_j}\right)_{S,V,N_{j\neq l}} \quad . \tag{3.66}$$

Comparing this expression with the first law, we identify,

$$\boxed{\delta A_{rev} = \sum_{j=1}^{J} \mu_j dN_j} \tag{3.67}$$

as an additional non-mechanical work. We simply need to substitute,

$$\mu dN \longrightarrow \sum_{j=1}^{J} \mu_j dN_j \tag{3.68}$$

in (1.149) to obtain the corresponding expression for multicomponent systems.

Although the chemical potential can be expressed as partial derivatives of various state energies,

$$\mu_j = \left(\frac{\partial E}{\partial N_j}\right)_{S,V,N_{k\neq j}} = \left(\frac{\partial H}{\partial N_j}\right)_{S,P,N_{k\neq j}} = \left(\frac{\partial F}{\partial N_j}\right)_{T,V,N_{k\neq j}} = \left(\frac{\partial G}{\partial N_j}\right)_{T,P,N_{k\neq j}} = \bar{G}_j \ , \tag{3.69}$$

only the last one is a partial molal property, distinguished by the fact that temperature and pressure are held constant, e.g. $\mu_j \neq \bar{U}_j$. If energies other than the Gibbs free energy are to be expressed as partial molal properties, they need to be related to the Gibbs energy using the expressions (1.149),

$$\begin{aligned}
\bar{G}_j &= \mu_j \\
\bar{S}_j &= -\left(\tfrac{\partial \bar{G}_j}{\partial T}\right)_{P,N_k} &&= -\left(\tfrac{\partial \mu_j}{\partial T}\right)_{P,N_k} \\
\bar{V}_j &= \left(\tfrac{\partial \bar{G}_j}{\partial P}\right)_{T,N_k} &&= \left(\tfrac{\partial \mu_j}{\partial P}\right)_{T,N_k} \\
\bar{H}_j &= \bar{G}_j + T\bar{S}_j &&= \mu_j - T\left(\tfrac{\partial \mu_j}{\partial T}\right)_{P,N_k} \\
\bar{F}_j &= \bar{G}_j - P\bar{V}_j &&= \mu_j - P\left(\tfrac{\partial \mu_j}{\partial T}\right)_{T,N_k} \\
\bar{E}_j &= \bar{G}_j + T\bar{S}_j - P\bar{V}_j &&= \mu_j - T\left(\tfrac{\partial \mu_j}{\partial T}\right)_{P,N_k} - P\left(\tfrac{\partial \mu_j}{\partial T}\right)_{T,N_k}
\end{aligned} \quad . \tag{3.70}$$

The linearity of the expressions allows us to extend them to changes of states, $\Delta\mu_j = \mu_j - \mu_j^0$. For example, for a binary system, the Gibbs-Duhem formula (3.60) applied to Gibbs free energy, $X \equiv G$, reads,

$$\eta_1 d\Delta\bar{G}_1 + \eta_1 d\Delta\bar{G}_2 = \eta_1 d\Delta\mu_1 + \eta_1 d\Delta\mu_2 = 0 \ , \tag{3.71}$$

and the integrated version,

$$\Delta\mu_1 = -\int_0^{\eta_2} \frac{\eta_2}{\eta_1}\frac{d\Delta\mu_2}{d\eta_2} d\eta_2 \ . \tag{3.72}$$

Thus, if $\Delta\mu_2$ is known as a function of composition at any temperature and pressure, we can also calculate $\Delta\mu_1$ and all other partial molar state functions according to (3.70), as well as the total properties according to (3.55).

3.2.3.1 Activity in ideal solutions

In experiments, instead of the chemical potential, the *activity of a component* a_j or the activity coefficient γ_j are frequently measured,

$$a_j \equiv e^{\Delta\mu_j/k_BT} \equiv \eta_j\gamma_j \ . \tag{3.73}$$

When a mixture is produced by combining ideal gases initially stored in different volumes at the same temperature and pressure, as illustrated in Fig. 3.5, every species by itself generates a smaller *partial pressure* in the total volume, corresponding to its abundance. Summed up, however, they reproduce the initial pressure. This is called *Dalton's law*,

$$\boxed{P_j \equiv \eta_j P \qquad \text{such that} \qquad P = \sum_j P_j} \ . \tag{3.74}$$

Now, we focus on the change experienced by an individual component j during the mixing process, which corresponds to an isothermal expansion of the component, $(T_0, P_0) \longrightarrow (T_0, P_j = \eta_j P_0)$. The corresponding change in chemical potential is,

$$d\mu_j = d\bar{G}_j = -\bar{S}_j dT + \bar{V}_j dP \quad \overset{dT=0}{\longrightarrow} \quad \bar{V}_j dP \ , \tag{3.75}$$

since temperature does not change. The partial molal volume can be evaluated from,

$$\begin{aligned} \bar{V}_j &= \left(\frac{\partial V}{\partial N_j}\right)_{T,P,N_{k\neq j}} \qquad (3.76) \\ &\overset{ideal}{\longrightarrow} \quad \left(\frac{\partial \frac{Nk_BT}{P}}{\partial N_j}\right)_{T,P,N_{k\neq j}} = \left(\frac{\partial \sum_k \frac{N_k k_BT}{P}}{\partial N_j}\right)_{T,P,N_{k\neq j}} = \frac{k_BT}{P} \ , \end{aligned}$$

assuming ideal gases. With this we can now proceed to integrate the chemical potential,

$$\begin{aligned} \Delta\bar{G}_j = \Delta\mu_j = \mu_j - \mu_j^0 &= \int_{P_0}^{P_j} \bar{V}_j dP_T \qquad (3.77) \\ &= k_BT \ln\frac{P_j}{P_0} = k_BT\ln\eta_j = k_BT\ln a_j \ . \end{aligned}$$

We see that, for ideal gases the abundance and the activity are identical. Based on the expressions (3.70), we can also calculate the dependence of other partial molal property on the abundance,

$$\begin{array}{llll|ll}
 & \text{partial molal property} & & & \text{total property} & \\
\hline
\Delta\bar{G}_j & & = k_BT\ln\eta_j & & \Delta G_j^{mix} & = k_BT\sum\eta_j\ln\eta_j \\
\Delta\bar{S}_j & = -\left(\frac{\partial\Delta\bar{G}_j}{\partial T}\right)_{P,N_k} & = -k_B\ln\eta_j & & \Delta S_j^{mix} & = -k_B\sum\eta_j\ln\eta_j \\
\Delta\bar{V}_j & = \left(\frac{\partial\Delta\bar{G}_j}{\partial P}\right)_{T,N_k} & = 0 & & \Delta V_j^{mix} & = 0 \\
\Delta\bar{H}_j & = \Delta\bar{G}_j + T\Delta\bar{S}_j & = 0 & & \Delta H_j^{mix} & = 0 \\
\Delta\bar{F}_j & = \Delta\bar{G}_j - P\Delta\bar{V}_j & = k_BT\ln\eta_j & & \Delta F_j^{mix} & = k_BT\sum\eta_j\ln\eta_j \\
\Delta\bar{E}_j & = \Delta\bar{G}_j + T\Delta\bar{S}_j - P\Delta\bar{V}_j & = 0 & & \Delta E_j^{mix} & = 0
\end{array} \tag{3.78}$$

The dependencies are plotted in Fig. 3.6, where we notice that (i) the curves are symmetric with respect to $\eta_j \leftrightarrow 1-\eta_j$; (ii) their slopes are vertical for $\eta_j \longrightarrow 0,1$; (iii) ΔS_j^{mix} is temperature-independent.

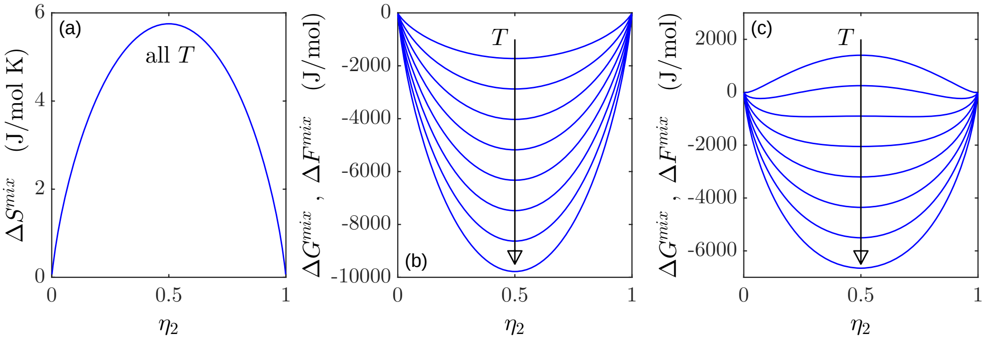

Figure 3.6: (code) Dependence of state functions of composition. (a) Entropy for an ideal and a real gas. (b) Gibbs free and Helmholtz free energy for an ideal gas and (c) for a real gas.

This *ideal solution* is extremely useful to benchmark deviations from it observed in real solutions.

3.2.3.2 Fugacity in real solutions

For *real solutions* for which the ideal gas equation does not hold, the partial molal volume cannot be determined from Eq. (3.76), but must be experimentally determined. It is often interesting to define a 'deviation volume',

$$\mathfrak{V}_j \equiv \bar{V}_j - \frac{k_BT}{P} \ . \tag{3.79}$$

The chemical potential change can then be written,

$$\begin{aligned}\Delta\mu_j &= \int_{P_0}^{P_j} \bar{V}_j dP = \int_{P_0}^{P_j} \left(\frac{k_B T}{P} + \mathfrak{V}_j\right) dP \\ &= k_B T \ln \frac{P_j}{P_0} + \int_{P_0}^{P_j} \alpha_j dP \equiv k_B T \ln \frac{f_j}{P_0} \ .\end{aligned} \tag{3.80}$$

The *fugacity* of a component of a mixture, defined in the last expression of (3.80), now reads,

$$f_j = P_j \exp\left(\frac{1}{k_B T}\int_{P_0}^{P_j} \mathfrak{V}_j dP\right) \ . \tag{3.81}$$

As the deviation from ideal gas behavior, measured by $\mathfrak{V}_j$ diminishes, the fugacity of component j approaches its partial pressure. Measurement of the fugacity of one component over a range of temperature, pressure, and composition is sufficient to describe the behavior of real gas mixtures completely in that range.

3.2.3.3 Activity in real solutions

Remembering that the chemical potential can also be expressed in terms of activity via Eq. (3.77), we see that activity and fugacity are intrinsically related,

$$f_j = P_0 a_j \ . \tag{3.82}$$

From (3.77),

$$\begin{aligned}&\Delta\bar{G}_j = k_B T \ln a_j = k_B T \ln \eta_j\gamma_j = \Delta\bar{G}^{id} + \Delta\bar{G}^{xs} \\ &\text{with} \qquad \Delta\bar{G}^{id} \equiv k_B T \ln \eta_j \qquad \text{and} \qquad \Delta\bar{G}^{xs} \equiv k_B T \ln \gamma_j \ .\end{aligned} \tag{3.83}$$

The activity coefficient $\gamma_j = \gamma_j(T, P, \eta_j)$ quantifies the deviation from ideal solution behavior; if $\gamma_j > 1$ then the component j 'acts' as if its abundance were more than expected from a supposed ideal gas behavior.

Using the expressions for the thermodynamic potentials of the first column of Tab. (3.78), we can also express the other partial molal thermodynamic potentials in terms of activity or activity coefficient,

PMP	as a function of activity	activity coefficient
$\Delta\bar{G}_j/k_B T$	$= \ln a_j$	$= \ln(\gamma_j\eta_j)$
$\Delta\bar{S}_j/k_B$	$= -\ln a_j - T\left(\frac{\partial \ln a_j}{\partial T}\right)_{P,N_k}$	$= -\ln(\gamma_j\eta_j) - T\left(\frac{\partial \ln \gamma_j}{\partial T}\right)_{P,N_k}$
$\Delta\bar{V}_j/k_B T$	$= \left(\frac{\partial \ln a_j}{\partial P}\right)_{T,N_k}$	$= \left(\frac{\partial \ln \gamma_j}{\partial P}\right)_{T,N_k}$
$\Delta\bar{H}_j/k_B T$	$= -T\left(\frac{\partial \ln a_j}{\partial T}\right)_{P,N_k}$	$= -T\left(\frac{\partial \ln \gamma_j}{\partial T}\right)_{P,N_k}$
$\Delta\bar{F}_j/k_B T$	$= \ln a_j - P\left(\frac{\partial \ln a_j}{\partial P}\right)_{T,N_k}$	$= \ln(\gamma_j\eta_j) - P\left(\frac{\partial \ln \gamma_j}{\partial P}\right)_{T,N_k}$
$\Delta\bar{E}_j/k_B T$	$= -T\left(\frac{\partial \ln a_j}{\partial T}\right)_{P,N_k} - P\left(\frac{\partial \ln a_j}{\partial P}\right)_{T,N_k}$	$= -T\left(\frac{\partial \ln \gamma_j}{\partial T}\right)_{P,N_k} - P\left(\frac{\partial \ln \gamma_j}{\partial P}\right)_{T,N_k}$

(3.84)

3.2.4 Models of real solutions

The ideal solution assumption disregards any features emanating from properties of the microscopic constituents. Hence, at same temperature and composition all ideal solutions are equal. More sophisticated models are required to remove this degeneracy.

3.2.4.1 Regular solutions

One real solution model is the *regular solutions* model. It is based on two assumptions:

1. The mixing entropy is that of an ideal solution:

$$\Delta\tilde{S}^{mix,rl} = \Delta\tilde{S}^{mix,id} = -R_g \sum_j \eta_j \ln \eta_j \ . \tag{3.85}$$

2. The solution enthalpy is a function of composition, and not zero as in ideal solutions,

$$\Delta\tilde{H}^{mix,rl} = \Delta\tilde{H}^{mix,xs}(\eta_j) \ . \tag{3.86}$$

Because, the excess mixing entropy vanishes $\Delta\tilde{S}^{mix,xs} \equiv \Delta\tilde{S}^{mix,rl} - \Delta\tilde{S}^{mix,id} = 0$, the excess Gibbs free energy $\tilde{G} = \tilde{H} - T\tilde{S}$ becomes equal to the excess mixing enthalpy,

$$\begin{aligned}\Delta\tilde{G}^{mix,xs} &= (\Delta\tilde{H}^{mix,rl} - T\Delta\tilde{S}^{mix,rl}) - (\Delta\tilde{H}^{mix,id} - T\Delta\tilde{S}^{mix,id}) \\ &= \Delta\tilde{H}^{mix,xs} \ .\end{aligned} \tag{3.87}$$

Since $\tilde{S} = (\partial\tilde{G}/\partial T)_{P,N_j}$, we conclude that $\Delta\tilde{G}^{mix,xs} = \Delta\tilde{H}^{mix,xs}$ are temperature-independent. For the components, we have from Eq. (3.77),

$$\Delta\bar{G}^{mix,xs} = k_B T \ln \gamma_j \qquad \Longrightarrow \qquad \gamma_j = e^{\Delta\bar{H}_j^{mix,xs}/k_B T} \ . \tag{3.88}$$

Since, all properties of a solution can be calculated from a known activity coefficient, the regular solution model with focuses upon the heat of mixing as a function of composition.

> **Example 30 (*Real solution model with a single adjustable parameter*):** Let us suppose the heat of mixing for a binary solution can be described by the simple formula,
>
> $$\Delta\bar{H}_j^{mix} = \Delta\bar{G}_j^{mix,xs} = a_0\eta_1\eta_2 \ .$$
>
> Then,
>
> $$\begin{aligned}\Delta\bar{G}^{mix} &= \sum_j \eta_j(\Delta\bar{G}^{mix,id} + \Delta\bar{G}^{mix,xs}) \\ &= k_B T(\eta_1 \ln \eta_1 + \eta_2 \ln \eta_2) + a_0\eta_1\eta_2 \ .\end{aligned}$$
>
> The behavior is shown in Fig. 3.6(c).

3.2.4.2 Non-regular solutions

Non-regular solutions model,

$$\Delta\bar{H}_j^{mix} = \eta_1\eta_2[(a_1(T)\eta_1 + a_2(T)\eta_1] \ . \tag{3.89}$$

3.2.4.3 Atomistic model for solutions of real gases

3.2.5 Exercises

3.2.5.1 Ex: Partial pressures

A closed cylindrical reservoir with the base area $S = 10\,\text{cm}^2$ is kept at a constant temperature $T = 27\,°\text{C}$. It is divided in two volumes by an airtight mobile disk with the mass $m = 10\,\text{kg}$. The upper volume V_{O_2} contains $\eta_{O_2} = 1\,\text{mol}$ of oxygen, the lower volume V_{N_2} contains the same amount of nitrogen. Due to its weight the disc finds an equilibrium position when the lower volume is $V_{N_2} = 10\,\text{l}$.
a. What are the masses m_{O_2} and m_{N_2} of the gases?
b. What are the pressures P_{O_2} and P_{N_2}?
c. What is the upper volume V_{O_2}?
d. What are the densities n_{O_2} and n_{N_2}?
e. Now the disc has a hole, so that the gases can mix and the disc falls to the bottom of the reservoir. What is the final pressure of the mixture?

3.2.5.2 Ex: Gibbs-Duhem integration

For an ideal solution, it is known that for component 2,

$$\Delta\bar{G}_2 = R_g T \ln \eta_2 \ .$$

Use the Gibbs-Duhem integration (3.61) to derive the corresponding relation for component 1.

3.2.5.3 Ex: Oxygen concentration in a metal

Titanium metal is capable of dissolving up to 30 atomic percent oxygen. Consider a solid solution in the system Ti-O containing an atom fraction, $\eta_\text{O} = 0.12$. The molar volume of this alloy is $\tilde{V}_{\text{Ti+O}} = 10.68\,\text{cm}^3/\text{mol}$. Calculate:
a. The weight percent of O in the solution.
b. The molar concentration (mol/cm^3) of O in the solution.
c. The mass concentration (g/cm^3) of O in the solution.
Use these calculations to deduce general expressions for weight percent, molar and mass concentrations of a component in a binary solution in terms of the atom fraction, η_2, the molar volume $\tilde{V}_{1+2}$, and the molecular weights of the elements involved.

3.2.5.4 Ex: Gibbs-Duhem rule

Given that the volume change on mixing of a solution obeys the relation $\tilde{V}^{mix} = a\eta_1\eta_2^2$,
a. Derive expressions for the partial molal volumes of each of the components as functions of composition.
b. Demonstrate that your result is correct by using it to compute)Vmix, demonstrating that the equation above is recovered.

3.2.5.5 Ex: Hydrogen concentration in a metal

The concentration of hydrogen c_H, which is dissolved in a metal in the form of H atoms, depends on the pressure P of the H_2 gas around the metal. Determine the relationship between concentration and pressure!
Hint: In equilibrium the chemical reaction $H_2 = 2H$ is determined by $\mu_{H_2} = 2\mu_H$, where $\mu_{H_2} = k_B T \ln P + \chi_{H_2}(T)$. Consult the textbooks to find a suitable ansatz for the chemical potential of a substance (and thus also for atomic hydrogen) in dilute solution.

3.3 Multi-component, heterogeneous, non-reacting systems

3.3.1 Equilibrium conditions

Expressions for multi-component require addition of terms describing particle exchange, $\sum_j \mu_j dN_j$. For example, the combined first and second law for homogeneous multi-component reads,

$$dE = TdS - PdV + \sum_{j=1}^{J} \mu_j dN_j \ . \tag{3.90}$$

Now, we assume that each component exists in Γ different phases. Each phase viewed as a system exchanges heat, work, and matter with the other phases and with the reservoir,

$$dE^\gamma = T^\gamma dS^\gamma - P^\gamma dV^\gamma + \sum_{j=1}^{J} \mu_j^\gamma dN_j^\gamma \ , \tag{3.91}$$

for all phases $\gamma = \alpha, \beta, ...$ For the extensive properties V, S, E, H, F, G the value for the property of the system is the sum of the parts,

$$X^{syst} = \sum_{\gamma=1}^{\Gamma} X^\gamma \ . \tag{3.92}$$

When the system is taken through an arbitrary change in state, then the change in X^{syst} is simply the sum of the changes that each phase experiences,

$$dX^{syst} = d\left(\sum_{\gamma=1}^{\Gamma} X^\gamma\right) = \sum_{\gamma=1}^{\Gamma} dX^\gamma \ . \tag{3.93}$$

As an example, let us regard a change in internal energy,

$$dE^{syst} = \sum_{\gamma=1}^{\Gamma} \left(T^\gamma dS^\gamma - P^\gamma dV^\gamma + \sum_{j=1}^{J} \mu_j^\gamma dN_j^\gamma \right) \ . \tag{3.94}$$

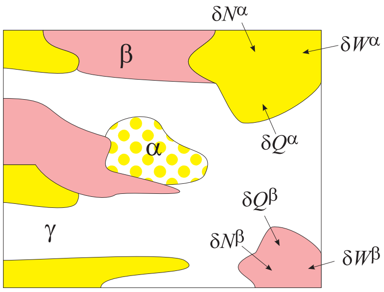

Figure 3.7: Heat work, and particle exchange in a micro structure with 3 components and two phases.

To find the equilibrium conditions, we need to express the entropy. We solve the Eq. (3.91) for dS^γ and sum up the entropies for all phases,

$$dS^{syst} = \sum_{\gamma=1}^{\Gamma} dS^\gamma = \sum_{\gamma=1}^{\Gamma} \left(\frac{1}{T^\gamma} dE^\gamma + \frac{P^\gamma}{T^\gamma} dV^\gamma - \frac{1}{T^\gamma} \sum_{j=1}^{J} \mu_j^\gamma dN_j^\gamma \right) . \tag{3.95}$$

The condition for equilibrium is $S^{syst} = maximal$. Eq. (3.95) contains $\Gamma \times (2+J)$ variables, but their number is reduced if the system is isolated from the reservoir, $dE^{syst} = dV^{syst} = dN^{syst} = 0$. Let us suppose there are only two phases $\gamma = \alpha, \beta$. Then the isolation assumption reads,

$$dE^\alpha = -dE^\beta \quad , \quad dV^\alpha = -dV^\beta \quad , \quad dN^\alpha = -dN^\beta \ , \tag{3.96}$$

and the expression (3.95) becomes,

$$dS^{syst,iso} = \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) dE^\alpha + \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) dV^\alpha - \sum_{j=1}^{J} \left(\frac{1}{T^\alpha} \mu_j^\alpha - \frac{1}{T^\beta} \mu_j^\beta \right) dN_j^\alpha$$
$$\overset{!}{=} 0 \ . \tag{3.97}$$

From this follows,

$$\begin{aligned} T^\alpha &= T^\beta && \text{thermal equilibrium} \\ P^\alpha &= P^\beta && \text{mechanical equilibrium} \\ \mu_j^\alpha &= \mu_j^\beta \quad , \quad \forall j \leq J && \text{chemical equilibrium} \end{aligned} \tag{3.98}$$

This rule can be easily generalized to more than two phases by pairwise comparison of the phases. We immediately see that,

$$\boxed{\begin{aligned} T^\alpha &= T^\beta &&= \ldots = T^\Gamma && && \text{thermal equilibrium} \\ P^\alpha &= P^\beta &&= \ldots = T^\Gamma && && \text{mechanical equilibrium} \\ \mu_j^\alpha &= \mu_j^\beta &&= \ldots = T^\Gamma && , \quad \forall j \leq J && \text{chemical equilibrium} \end{aligned}} \tag{3.99}$$

These equations form the basis for the construction and calculation of multi-component multi-phase phase diagrams.

3.3.1.1 The Gibbs phase rule

An interesting question is, how many independent variables are needed to completely describe a composite system. This number f is called the number of macroscopic thermodynamic degrees of freedom.

The system (3.99) consists of $(\Gamma - 1) \times (2 + J)$ equations and contains $\Gamma \times (2 + J)$ variables. However, the Gibbs-Duhem equation imposes additional constraints relating the chemical potentials between the components for all Γ allotropic phases. Hence,

$$f = \Gamma \times (2 + J) \quad - \quad (\Gamma - 1) \times (2 + J) \quad - \quad \Gamma \,, \tag{3.100}$$

that is,

$$\boxed{f = J + 2 - \Gamma} \,. \tag{3.101}$$

The rule assumes the components do not react with each other. The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without determining one another.

3.3.2 Structure of phase diagrams

Phase diagrams are graphical representations of the domains of stability of ??? mostly in (T, P, η_j)-space.

3.3.3 Exercises

3.4 Continuous, non-uniform systems exposed to external forces

When we discussed thermodynamic equilibrium in Secs. 1.3 and 3.1, we tacitly assumed that the intensive properties within a phase are uniform, i.e. a single temperature, pressure, or composition can be assigned to a particular phase α, and the same holds for the chemical potential and all partial molal properties. Nevertheless, those properties can vary from phase to phase.

In the presence of external force fields the situation is different. Equilibrated systems may then exhibit temperature, pressure, or composition profiles. One example is the atmosphere on Earth, whose vertical temperature and pressure profile is described by the barometric formula studied in Excs. 1.1.4.3 and 1.1.4.3; an atomic gas confined in a harmonic trapping potential develops a radial density profile studied in Excs. 2.1.7.14 to 2.1.7.16; mixtures submitted to centrifuges may experience a separation of their components; and an electrostatic field will separate components with different charges.

To handle thermodynamic properties in such locally homogeneous but globally non-uniform systems, we need to introduce the concept of *densities* of extensive thermodynamic quantities, e.g. the energy density, which are scalar fields, i.e. local intensive properties associated with each point of the system in space.

3.4.1 Thermodynamic densities

For each extensive property of a system, $X \in \{S, V, E, F, H, G, N_j\}$, we may define a corresponding local density,

$$\boxed{x(\mathbf{r}) \equiv \frac{dX}{dV}} \ , \tag{3.102}$$

where the V is a volume element near the point located at the coordinates $\mathbf{r}$. Then, $x(\mathbf{r})dV$ is the total value of the extensive property X in the volume element and,

$$X = \int_V x(\mathbf{r})dV \tag{3.103}$$

in the whole system. Changes of this property along a thermodynamic process are expressed as usual,

$$dX_V = \int_V dx(\mathbf{r})dV \ , \tag{3.104}$$

where we assume that these changes do not modify the volume.

Let us now calculate the differential of the energy density (3.102) for a thermodynamic process. Since the process does not change the volume element, we can write,

$$\begin{aligned} de(\mathbf{r}) = \frac{dE_V}{dV} &= \frac{d}{dV}\left(TdS_V - PdV_V + \sum_j \mu_j dN_{jV}\right) \\ &= T\frac{dS_V}{dV} + \sum_j \mu_j \frac{dN_{jV}}{dV} = Tds(\mathbf{r}) + \sum_j \mu_j dn_j(\mathbf{r}) \ , \end{aligned} \tag{3.105}$$

where s is the entropy density and n_j the molar density of the component j. That is, we can derive local versions for all thermodynamic relationships.

3.4.2 Equilibrium conditions

3.4.2.1 Without external force field

Integrating Eq. (3.105) we get, resolved by entropy

$$dS = \int_V \left(\frac{1}{T}de - \frac{1}{T}\sum_j \mu_j dn_j\right) dV \ . \tag{3.106}$$

If during the thermodynamic process the system isolated against energy and particle exchange,

$$0 = dE = \int_V de(\mathbf{r})dV \qquad \text{and} \qquad 0 = dN_j = \int_V dn_j(\mathbf{r})dV \ . \tag{3.107}$$

Equilibrium is reached when the entropy is maximum, and a necessary condition for that is,

$$dS + \alpha dE + \sum_j \beta_j dN_j = 0 \ . \tag{3.108}$$

Hence, for any value of the Lagrange multipliers α_j and β,

$$0 = dS - k_B\beta dE - \sum_j k_B\alpha_j dN_j \tag{3.109}$$

$$= \int_V \left(\frac{1}{T}de(\mathbf{r}) - \frac{1}{T}\sum_j \mu_j dn_j(\mathbf{r})\right) dV - k_B\beta \int_V de(\mathbf{r})dV - \sum_j k_B\alpha_j \int_V dn_j(\mathbf{r})dV \ ,$$

which implies,

$$0 = \left(\frac{1}{T} - k_B\beta\right) de(\mathbf{r}) - \sum_j \left(\frac{\mu_j}{T} + k_B\alpha_j\right) dn_j(\mathbf{r}) \ . \tag{3.110}$$

We conclude,

$$\beta = \frac{1}{k_BT} \quad , \quad \alpha_j = \frac{\mu_j}{k_BT} \ . \tag{3.111}$$

Since α_j and β are constants, this means that temperature and chemical potential cannot depend on position,

$$\boxed{\nabla T = 0 = \nabla\mu_j} \ . \tag{3.112}$$

To derive the condition for mechanical equilibrium, we apply the operator (3.42) on (3.41),

$$\left(\frac{\partial}{\partial N_j}\right)_{P,T,N_{k\neq j}} \qquad \text{applied to} \qquad N_j d\mu_j = -SdT + VdP - \sum_{k\neq j} N_k d\mu_k \ , \tag{3.113}$$

and obtain the partial molal equation,

$$d\mu_j = -\bar{S}_j dT + \bar{V}_j dP - \sum_{k\neq j} N_k \left(\frac{\partial d\mu_k}{\partial N_j}\right)_{P,T,N_{k\neq j}} \ . \tag{3.114}$$

We interpret the differential forms as gradients, $d \to d_{\mathbf{r}} \to \nabla$,

$$\nabla\mu_j = -\bar{S}_j \nabla T + \bar{V}_j \nabla P - \sum_{k\neq j} N_k \left(\frac{\partial \nabla\mu_k}{\partial N_j}\right)_{P,T,N_{k\neq j}} \ . \tag{3.115}$$

As we already found the equilibrium conditions $\nabla T = 0 = \nabla\mu_j$, we get,

$$\bar{V}_j \nabla P = \sum_{k\neq j} N_k \left(\frac{\partial \nabla\mu_k}{\partial N_j}\right)_{P,T,N_{k\neq j}} \ . \tag{3.116}$$

Multiplying both sides with η_j and summing over all components, and exploiting the fact that summation over all partial molar volumes produces the total molar volume, $\sum_j \eta_j \bar{V}_j = V$,

$$V\nabla P = \sum_j \eta_j \sum_{k\neq j} N_k \left(\frac{\partial \nabla\mu_k}{\partial N_j}\right)_{P,T,N_{k\neq j}} \ . \tag{3.117}$$

The right-hand side can be shown to vanish using the Gibbs-Duhem equation. Hence,

$$\boxed{\nabla P = 0 \ .} \tag{3.118}$$

The results (3.112) and (3.116) were expected and only tell us that there is nothing wrong with the density formalism.

3.4.2.2 With external force field

Let us now study the impact of time invariant external forces. The time invariance is obviously necessary to allow the system to reach a steady state. If the force is conservative, it can be derived from a potential,

$$\mathbf{F}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) \ . \tag{3.119}$$

The work executed by this force, $\delta W_{ext} = dW_{ext} = \mathbf{F}\cdot d\mathbf{r}$, then does not depend on the path taken between start and end point,

$$W_{ext} = \int_{\mathbf{r}_1}^{\mathbf{r}_2} \mathbf{F}\cdot d\mathbf{r} = -\int_{\mathbf{r}_1}^{\mathbf{r}_2} \nabla\Phi(\mathbf{r})\cdot d\mathbf{r} = -\int_{\Phi(\mathbf{r}_1)}^{\Phi(\mathbf{r}_2)} d\Phi(\mathbf{r}) = \Phi(\mathbf{r}_1) - \Phi(\mathbf{r}_2) \ . \tag{3.120}$$

Forces act on masses, or charges carried by massive particles. The mass contained in a volume element dV is,

$$dm = \sum_j M_j n_j dV \ . \tag{3.121}$$

The total potential energy is the sum of the potential energies to which the mass elements dm are subject,

$$E_{pot} = \int_V \frac{d\Phi(\mathbf{r})}{dV} dV = \int_V \frac{d\Phi(\mathbf{r})}{dm} dm(\mathbf{r}) = \int_V \frac{d\Phi(\mathbf{r})}{dm} \sum_j M_j n_j dV \ . \tag{3.122}$$

Including the internal energy the total energy differential is then,

$$dE_{tot} = dE + dE_{pot} = \int_V de(\mathbf{r})dV + \int_V \frac{d\Phi(\mathbf{r})}{dm} \sum_j M_j dn_j dV \ . \tag{3.123}$$

Repeating the entropy maximization procedure, we now get,

$$\begin{aligned} 0 &= dS - k_B\beta dE - \sum_j k_B\alpha_j dN_j \qquad (3.124)\\ &= \int_V \left(\frac{1}{T} de(\mathbf{r}) - \frac{1}{T}\sum_j \mu_j dn_j(\mathbf{r}) \right) dV \\ &\quad - k_B\beta \left(\int_V de(\mathbf{r}) + \int_V \frac{d\Phi(\mathbf{r})}{dm} \sum_j M_j dn_j(\mathbf{r}) \right) dV - \sum_j k_B\alpha_j \int_V dn_j(\mathbf{r})dV \ , \end{aligned}$$

which implies,

$$0 = \left(\frac{1}{T} - k_B\beta\right) de(\mathbf{r}) - \sum_j \left(\frac{\mu_j}{T} + k_B\beta \frac{d\Phi(\mathbf{r})}{dm} M_j + k_B\alpha_j \right) dn_j(\mathbf{r}) \ . \tag{3.125}$$

We conclude,

$$T = \frac{1}{k_B\beta} \qquad , \qquad \frac{\mu_j}{T} + k_B\beta \frac{d\Phi(\mathbf{r})}{dm} M_j + k_B\alpha_j = 0 \ . \tag{3.126}$$

Since α_j and β are constants,

$$\boxed{\nabla T = 0 = \nabla\left(\mu_j + M_j\frac{d\Phi(\mathbf{r})}{dm}\right)} . \tag{3.127}$$

To derive the condition for mechanical equilibrium, we use again the expression (3.115), but now inserting the equilibrium conditions (3.127), we obtain an equation generalizing (3.116),

$$\bar{V}_j\nabla P = -\nabla\left(M_j\frac{d\Phi(\mathbf{r})}{dm}\right) - \sum_{k\neq j}N_k\left(\frac{\partial\nabla\mu_k}{\partial N_j}\right)_{P,T,N_{k\neq j}} . \tag{3.128}$$

Again, multiplying both sides with η_j and summing over all components,

$$V\nabla P = -\nabla\left(\sum_j\eta_jM_j\frac{d\Phi(\mathbf{r})}{dm}\right) , \tag{3.129}$$

or,

$$\boxed{\nabla P = -\frac{M}{V}\frac{d\nabla\Phi(\mathbf{r})}{dm}} . \tag{3.130}$$

In particular, for an ideal gas,

$$\nabla P \overset{ideal}{\longrightarrow} -\frac{MP}{Nk_BT}\frac{d\nabla\Phi(r)}{dm} = -\frac{\tilde{M}P}{R_gT}\frac{d\nabla\Phi(\mathbf{r})}{dm} , \tag{3.131}$$

with the solution,

$$P = P_0\exp\left(-\frac{\tilde{M}}{R_gT}\frac{d\Phi(\mathbf{r})}{dm}\right) . \tag{3.132}$$

Solve the Excs. 3.4.3.1 to 3.4.3.3.

Example 31 (*Earth gravitation*): Here, we consider a system in the Earth's gravitational field, whose force is described by,

$$\mathbf{F}(\mathbf{r}) = -\nabla(mgz) = -mg\hat{\mathbf{e}}_z . \tag{3.133}$$

The force can be derived from a potential,

$$\Phi(\mathbf{r}) = mgz \qquad \text{or} \qquad \frac{d\Phi(\mathbf{r})}{dm} = gz . \tag{3.134}$$

The conditions for equilibrium are,

$$\nabla T = 0 \qquad \text{and} \qquad \nabla\mu_j = -\nabla\left(M_j\frac{d\Phi(\mathbf{r})}{dm}\right) = -M_jg\hat{\mathbf{e}}_z , \tag{3.135}$$

and,

$$\nabla P = -\frac{M}{V}\frac{d\nabla\Phi(\mathbf{r})}{dm} = -\frac{M}{V}g\hat{\mathbf{e}}_z . \tag{3.136}$$

Hence, for an ideal gas,

$$dP = -\frac{M}{V}gdz \overset{ideal}{\longrightarrow} -\frac{\tilde{M}g}{R_gT}Pdz \ , \tag{3.137}$$

with the solution,

$$P = P_0 e^{-\tilde{M}gz/R_gT} \ , \tag{3.138}$$

where $\tilde{M}$ is the molar mass.

Example 32 (*Centrifugal field*): Here, we consider system rotating at constant angular velocity ω about the z-axis and thus subject to radial acceleration,

$$\mathbf{a} = \omega^2\rho \ . \tag{3.139}$$

The centrifugal force can be derived from a potential,

$$\Phi(\mathbf{r}) = -\frac{m}{2}\omega^2(x^2+y^2) \ . \tag{3.140}$$

The conditions for equilibrium are $\nabla T = 0$ and,

$$\nabla\mu_j = -\nabla\left(M_j\frac{d\Phi(\mathbf{r})}{dm}\right) = M_j\omega^2\rho\hat{\mathbf{e}}_\rho \ , \tag{3.141}$$

and,

$$\nabla P = -\frac{M}{V}\frac{d\Phi(\mathbf{r})}{dm} = -\frac{M}{V}\omega^2\hat{\mathbf{e}}_\rho \ . \tag{3.142}$$

Hence, for an ideal gas,

$$dP = \frac{M}{V}\omega^2\rho dz \overset{ideal}{\longrightarrow} \frac{\tilde{M}\omega^2\rho}{R_gT}Pdz \ , \tag{3.143}$$

with the solution,

$$P = P_0 e^{\tilde{M}\omega^2\rho z/R_gT} \ . \tag{3.144}$$

3.4.2.3 With electrostatic field

In electrostatics the Lorentz force is,

$$\mathbf{F}(\mathbf{r}) = q\mathbf{E}(\mathbf{r}) \qquad \text{with} \qquad \mathbf{E}(\mathbf{r}) = -\nabla\Phi_{el}(\mathbf{r}) \ , \tag{3.145}$$

where Φ_{el} is the electrostatic potential. In thermodynamics,

$$\mathbf{F}(\mathbf{r}) = -\nabla\Phi(\mathbf{r}) = -q\nabla\Phi_{el}(\mathbf{r}) \quad \Longrightarrow \quad \Phi_{el}(\mathbf{r}) = \frac{d\Phi(\mathbf{r})}{dq} \ . \tag{3.146}$$

The mass and the charge elements are, respectively,

$$dm_j = M_jn_jdV \qquad \text{and} \qquad dQ_j = en_jdV \ . \tag{3.147}$$

Conditions for equilibrium are,

$$\nabla T = 0 \qquad \text{and} \qquad \nabla\mu_j = -\nabla\left(\frac{M_j}{V}\frac{d\Phi(\mathbf{r})}{dm}\right) = -\frac{M_j}{V}\nabla\frac{d}{dm}\int\Phi_{el}(\mathbf{r})dq \ . \tag{3.148}$$

The quantity

$$\mu_j + \frac{M_j}{V}\frac{d}{dm}\int \Phi_{el}(\mathbf{r})dq \tag{3.149}$$

is also called electrochemical potential, and in thermodynamic equilibrium it should be homogeneous, i.e. its gradient should vanish. For mechanical equilibrium we request,

$$\nabla P = -\frac{M}{V}\frac{d\nabla\Phi(\mathbf{r})}{dm} = -\frac{M}{V}\nabla\frac{d}{dm}\int \Phi_{el}(\mathbf{r})dq \ . \tag{3.150}$$

Example 33 (*Electrostatic field*): Here we,

$$. \tag{3.151}$$

3.4.3 Exercises

3.4.3.1 Ex: Pressure in a harmonically trapped ideal gas

Calculate the local pressure in a harmonically trapped ideal gas in thermodynamic equilibrium.

3.4.3.2 Ex: Atmosphere of a planet

Assume the atmosphere of planet X to be composed of a binary mixture of hydrogen and nitrogen. Derive an expression for the variation of composition with altitude treating the elements as ideal gases. Assuming that the planet has a gravitational acceleration of $g = 10\,\mathrm{m/s^2}$, a temperature of $T = 800\,\mathrm{K}$, and a $\mathrm{H_2}$ abundance on the planetary surface of $\eta_{\mathrm{H_2}} = 0.35$, calculate the atmosphere composition at 100 km above the surface.

3.4.3.3 Ex: Centrifuges

Consider a dilute solution of $^{85}\mathrm{Rb}$ and $^{87}\mathrm{Rb}$ whose natural abundances are $72.17 : 27.83$. Placed in a centrifuge, how fast should it rotate in order to reach ratio of $10 : 90$ near the outside radius $\rho = 1\,\mathrm{m}$.

3.5 Reacting systems

Matter consists of molecules and molecules are composed of atoms chosen out of a small number of species. Being the elementary building blocks, the atoms cannot mutate into atoms of another species. However, they may associate to a large variety of molecules in a multitude of geometric and energetic configurations in a process called *chemical reaction*. The molecules are represented by chemical formulas describing succinctly the numbers of atoms, e.g. $\mathrm{CO_2}$ for carbon dioxide, and a chemical reaction is represented by an equation comparing the number of atoms before and after an association or dissociation, e.g.,

$$2\,\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O} \ . \tag{3.152}$$

As already formulated by *Lavoisier* the number of atoms in a closed system is always conserved.

A system that consists of K elements and J chemical components, some of which are molecules, has

$$R = J - K \tag{3.153}$$

independent reactions. For example, for a system containing H_2, O_2, and H_2O we have $J = 3$ and $K = 2$, so that $R = 1$. Such systems are called *univariant reacting systems*. Now assume that we have also H_2O_2 in the system. Then we expect two independent chemical reactions,

$$\begin{aligned} 2\,H_2 + O_2 &\longrightarrow 2\,H_2O \\ H_2 + O_2 &\longrightarrow H_2O_2 \ . \end{aligned} \tag{3.154}$$

Other reactions that may be formulated, e.g.,

$$2\,H_2O + O_2 \longrightarrow H_2O_2 \tag{3.155}$$

are linear combinations of (3.154). Systems with $R > 1$ are called bivariant, respectively, multivariant.

In the next section we will first focus on the gas phase, where the components unambiguously exist as molecules. In solids, which are characterized by the existence of multiple bonds between molecules, this is more complicated. Also, we will first treat univariant systems before progressively generalizing to multivariant systems.

3.5.1 Univariant chemical reactions in the gas phase

Let us study again the univariant system composed of H_2, O_2, and H_2O. The objective is to derive conditions for thermodynamic equilibrium. From the combined first and second law of thermodynamics we derive the entropy for the multi-component system,

$$\begin{aligned} dS &= \frac{1}{T}dE + \frac{P}{T}dV - \frac{1}{T}\sum_j \mu_j dN_j \\ &= \frac{1}{T}dE + \frac{P}{T}dV - \frac{1}{T}\left[\mu_{H_2}dN_{H_2} + \mu_{O_2}dN_{O_2} + \mu_{H_2O}dN_{H_2O}\right] \ . \end{aligned} \tag{3.156}$$

As usual, for a closed isolated system, we ask for the entropy to be at maximum, under the constraint that the internal energy and the volume cannot change, $dE = 0 = dV$. On the other hand, the third isolation constraint $dN_j = 0$ does not hold any more, since the components may transform into one another. The total number of atoms of one species, however, does not change. Hence, from the chemical reaction (3.152), we obtain the constraint,

$$2dN_{H_2} = dN_{O_2} = -2dN_{H_2O} \ . \tag{3.157}$$

Inserting all the constraints into Eq. (3.156) we get,

$$dS^{iso} = -\frac{1}{T}\left[-\mu_{H_2} - \tfrac{1}{2}\mu_{O_2} + \mu_{H_2O}\right] dN_{H_2O} \equiv -\frac{A}{T}dN_{H_2O} \ . \tag{3.158}$$

The linear combination of chemical components in brackets is called *affinity* for the reaction (3.152). If temperature, pressure, and composition of the gas mixture are known, then the chemical potential of the components and hence the affinity can be computed.

The affinity can be positive or negative, depending on the chemical potentials of the reactants and products. The third law of thermodynamics, however, requests that for any process $dS^{iso} > 0$, so that in Eq. (3.158) the affinity and dN_{H_2O} must have opposite signs. In other words, the affinity decides in which direction a chemical reaction will take place. A state of equilibrium is reached, when $dS^{iso} > 0$, which implies $A = 0$. The chemical reaction comes to a halt, when the sum of the chemical potentials of the reactants and products are equal, and this condition may require an excess of reactants or products, as illustrated in Fig. 3.8.

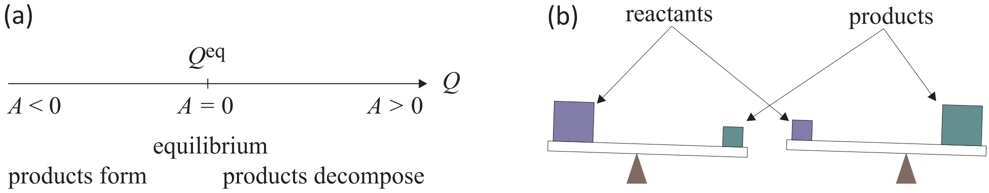

Figure 3.8: (a) Direction of a chemical reaction as a function of affinity. (b) The equilibrium of a chemical reaction may be on the left or right side.

As stated earlier, what is usually reported in experimental studies of solutions are the activities of the components. In order to express the affinity in terms of activities of the components, we stress Eq. (3.77) saying,

$$\mu_j = \mu_j^0 + R_g T \ln a_j = \tilde{G}_j^0 + R_g T \ln a_j \ , \tag{3.159}$$

where $\tilde{G}_j^0$ is the molar Gibbs free energy of component j, when it is in its reference state. Let us now consider an arbitrary chemical reaction,

$$p\,\mathrm{P} + q\,\mathrm{Q} \longrightarrow x\,\mathrm{X} + y\,\mathrm{Y} \ , \tag{3.160}$$

for which,

$$\begin{aligned} A &= \mu_{\text{product}} - \mu_{\text{reactants}} = x\mu_{\mathrm{X}} + y\mu_{\mathrm{Y}} - p\mu_{\mathrm{P}} - q\mu_{\mathrm{Q}} \\ &= x\tilde{G}_{\mathrm{X}}^0 + y\tilde{G}_{\mathrm{Y}}^0 + p\tilde{G}_{\mathrm{P}}^0 + q\tilde{G}_{\mathrm{Q}}^0 + R_g T \left[x \ln a_{\mathrm{X}} + y \ln a_{\mathrm{Y}} - p \ln a_{\mathrm{P}} - q \ln a_{\mathrm{Q}}\right] \\ &\equiv \Delta G^0 + R_g T \ln \frac{a_{\mathrm{X}} a_{\mathrm{Y}}}{a_{\mathrm{P}} a_{\mathrm{Q}}} \ , \end{aligned} \tag{3.161}$$

where the abbreviation ΔG^0 comprises the four Gibbs free energy terms and describes the change in Gibbs free energy upon complete conversion of p moles of P and q moles of Q in their standard states into x moles of X and y moles of Y in their standard states. The quotient in the logarithm is called the ratio of activities for the reaction,

$$Q \equiv \frac{a_{\mathrm{X}} a_{\mathrm{Y}}}{a_{\mathrm{P}} a_{\mathrm{Q}}} \ . \tag{3.162}$$

As already mentioned, a reaction will go on until the system reaches equilibrium,

$$A = 0 = \Delta G^0 + R_g T \ln Q^{\text{eq}} \ . \tag{3.163}$$

Example 34 (*Synthesis of water*): Let us consider a gas mixture composed of $\nu_{\mathrm{H}_2} = 0.01\,\mathrm{mol}$, $\nu_{\mathrm{O}_2} = 0.03\,\mathrm{mol}$, and $\nu_{\mathrm{H}_2\mathrm{O}} = 0.96\,\mathrm{mol}$ at atmospheric pressure. At $700\,^\circ\mathrm{C}$ the reaction (3.152) liberates the Gibbs free energy $\Delta G^0 = -440\,\mathrm{kJ}$. The equilibrium constant can be calculated from (3.163),

$$Q^{\mathrm{eq}} = e^{-\Delta G^0/R_g T} \approx 4.2 \times 10^{23} \ .$$

A gas mixture may be considered an ideal solution, so that the activities of their components are given by their molar fractions,

$$Q = \frac{a^2_{\mathrm{H}_2\mathrm{O}}}{a^2_{2\mathrm{H}_2} a_{\mathrm{O}_2}} = \frac{\eta^2_{\mathrm{H}_2\mathrm{O}}}{\eta^2_{2\mathrm{H}_2} \eta_{\mathrm{O}_2}} \approx 3.1 \times 10^5 \ .$$

Thus, $Q/Q_{\mathrm{eq}} \approx 7.2 \times 10^{-19}$, which means that the equilibrium is far on the $\mathrm{H}_2\,\mathrm{O}$ side. In the reaction process, the 0.01 mol of hydrogen will be completely used up. However, there is an excess of oxygen in the system, as only 0.005 mol are used. Hence, the final composition will be $\nu_{\mathrm{H}_2} \approx 0$, $\nu_{\mathrm{O}_2} = 0.0025\,\mathrm{mol}$, and $\nu_{\mathrm{H}_2\mathrm{O}} = 0.97\,\mathrm{mol}$. Note also that the total number of moles is reduced to $\nu_{\mathrm{H}_2} + \nu_{\mathrm{O}_2} + \nu_{\mathrm{H}_2\mathrm{O}} = 0.995\,\mathrm{mol}$.

3.5.2 Multi-variant chemical reactions in the gas phase

The general strategy for determining the equilibrium composition in a multi-variant reacting system makes use of the independent conditions for chemical equilibrium and conservation laws for the number of atoms of every involved element. For a single-phase system with J components and K different atomic elements, $\mathfrak{A}_{kj}$ denotes the number of atoms of a given species k bound in a molecule representing the j-th component of the mixture.

The strategy can be summarized in the following sequence of calculations:

1. Identify the types j of molecules involved and their numbers N_j^{in} (or moles or molar fractions) before a chemical reaction is initiated.

2. Determine the chemical structure of each type of molecules j in terms of numbers of atoms $\mathfrak{A}_{kj}$ of each element k.

3. Calculate the total number of atoms of each atomic element in the system from,

$$\mathcal{A}_k = \sum_{j=1}^{J} \mathfrak{A}_{kj} N_j^{in} \qquad \forall\, k = 1, ..., K \ . \tag{3.164}$$

4. The numbers of atoms per species $\mathfrak{A}_{kj}$ and the chemical composition of the mixture N_j change when the atoms reorganize into different molecules through chemical reactions (labeled $r = 1, ..., R$). Thus, in parallel, we need to identify all R possible chemical reactions transforming a group of molecules $\{j_r\}$ into a group $\{j'_r\}$, and vice versa, with $j_r, j'_r = 1, ..., J$ labeling the types of molecules.

5. The numbers of molecules are controlled by equilibrium conditions associated to every possible chemical reaction. As stated in Eq. (3.153), there are $R = J - K$

independent reactions in this system, and each reaction has its equilibrium condition,

$$\begin{aligned} \Delta G_r^0 &= -R_g T \ln Q_r^{eq} = -N_A k_B T \ln \frac{\prod_{j'_r} a_{j'_r}^{eq}}{\prod_{j_r} a_{j_r}^{eq}} \\ &\xrightarrow{ideal} -N_A k_B T \ln \frac{\prod_{j'_r} \eta_{j'_r}^{eq}}{\prod_{j_r} \eta_{j_r}^{eq}} = -N_A k_B T \ln \frac{\prod_{j'_r} N_{j'_r}^{eq}}{\prod_{j_r} N_{j_r}^{eq}} \qquad \forall\, r = 1, ..., R \ , \end{aligned} \tag{3.165}$$

for an ideal solution. Thus, each of the equilibrium constants Q_r^{eq} ruling a chemical reaction r is related to the composition of the system through a non-linear equation.

6. The number of atoms $\mathcal{A}_k$ of a given atomic element is conserved and does not change with time during the reaction process. Hence, the K equations (3.164) also hold after chemical equilibrium is reached. Together with R equations (3.165) we obtain a sufficient set of equations,

$$\boxed{\begin{array}{rcl} \sum_{j=1}^{J} \mathfrak{A}_{kj} N_j^{eq} & = \mathcal{A}_k & \forall\, k = 1, ..., K \\ \sum_{j'_r} \ln N_{j'_r}^{eq} - \sum_{j_r} \ln N_{j_r}^{eq} & = -\frac{\Delta G_r^0}{R_g T} & \forall\, r = 1, ..., R \end{array}} \tag{3.166}$$

While the first equations are linear in the J unknown values N_j^{eq}, the second equations are non-linear.

Note, that the equilibrium composition of the mixture depends on the initial composition that the system had while it was still isolated, but only via the *numbers of atoms of all involved atomic elements*, no matter how these were distributed among the molecular components before these were mixed. The task is to express the final composition N_j^{eq} as a function of the $\mathcal{A}_k$ and the Q_r^{eq}.

Example 35 (*Chemical equilibrium of a gas mixture*): A gas mixture has the following initial composition,

molecular component	H_2	O_2	H_2O	CO	CO_2	CH_4
initial molar fraction η_j^{in}	0.05	0.05	0.15	0.25	0.40	0.10

(3.167)

and the goal is to find the equilibrium composition at 600 °C.
We start setting up the equations (3.164),

$$\begin{pmatrix} \mathcal{A}_{\mathrm{C}} \\ \mathcal{A}_{\mathrm{O}} \\ \mathcal{A}_{\mathrm{H}} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 1 & 2 & 0 \\ 2 & 0 & 2 & 0 & 0 & 4 \end{pmatrix} \begin{pmatrix} N_{\mathrm{H_2}} \\ N_{\mathrm{O_2}} \\ N_{\mathrm{H_2O}} \\ N_{\mathrm{CO}} \\ N_{\mathrm{CO_2}} \\ N_{\mathrm{CH_4}} \end{pmatrix} , \tag{3.168}$$

which hold at any time before and after the reactions. Therefore, before the reaction, we have,

$$\begin{aligned} \mathcal{A}_{\mathrm{C}} &= (1\eta_{\mathrm{CO}}^{in} + 1\eta_{\mathrm{CO_2}}^{in} + 1\eta_{\mathrm{CH_4}}^{in}) N_{tot}^{in} &&= 0.75 N_{tot}^{in} \\ \mathcal{A}_{\mathrm{O}} &= (2\eta_{\mathrm{O_2}}^{in} + 1\eta_{\mathrm{H_2O}}^{in} + 2\eta_{\mathrm{CO}}^{in} + 2\eta_{\mathrm{CO_2}}^{in}) N_{tot}^{in} &&= 1.30 N_{tot}^{in} \\ \mathcal{A}_{\mathrm{H}} &= (2\eta_{\mathrm{H_2}}^{in} + 2\eta_{\mathrm{H_2O}}^{in} + 4\eta_{\mathrm{CH_4}}^{in}) N_{tot}^{in} &&= 0.80 N_{tot}^{in} \end{aligned} \tag{3.169}$$

with $N_j^{eq} = \eta_j^{eq} N_{tot}^{eq}$ and the total number of molecules $N_{tot}^{eq} = N_{\mathrm{CO}}^{eq} + N_{\mathrm{CO_2}}^{eq} + N_{\mathrm{O_2}}^{eq}$. After the reaction, we have,

$$\begin{aligned}
\mathcal{A}_{\mathrm{C}} &= (1\eta_{\mathrm{CO}}^{eq} + 1\eta_{\mathrm{CO_2}}^{eq} + 1\eta_{\mathrm{CH_4}}^{eq})N_{tot}^{eq} && = 0.75 N_{tot}^{eq} \\
\mathcal{A}_{\mathrm{O}} &= (2\eta_{\mathrm{O_2}}^{eq} + 1\eta_{\mathrm{H_2O}}^{eq} + 2\eta_{\mathrm{CO}}^{eq} + 2\eta_{\mathrm{CO_2}}^{eq})N_{tot}^{eq} && = 1.30 N_{tot}^{eq} \\
\mathcal{A}_{\mathrm{H}} &= (2\eta_{\mathrm{H_2}}^{eq} + 2\eta_{\mathrm{H_2O}}^{eq} + 4\eta_{\mathrm{CH_4}}^{eq})N_{tot}^{eq} && = 0.80 N_{tot}^{eq}
\end{aligned} \tag{3.170}$$

with $N_j^{eq} = \eta_j^{eq} N_{tot}^{eq}$ and a different total number of molecules $N_{tot}^{eq} = N_{\mathrm{CO}}^{eq} + N_{\mathrm{CO_2}}^{eq} + N_{\mathrm{O_2}}^{eq}$. The equations now read,

$$\begin{aligned}
\eta_{\mathrm{H_2}}^{eq} + \eta_{\mathrm{O_2}}^{eq} + \eta_{\mathrm{H_2O}}^{eq} + \eta_{\mathrm{CO}}^{eq} + \eta_{\mathrm{CO_2}}^{eq} + \eta_{\mathrm{CH_4}}^{eq} &= 1 \\
\eta_{\mathrm{CO}}^{eq} + \eta_{\mathrm{CO_2}}^{eq} + \eta_{\mathrm{CH_4}}^{eq} &= 0.75 \frac{N_{tot}^{in}}{N_{tot}^{eq}} \\
2\eta_{\mathrm{O_2}}^{eq} + \eta_{\mathrm{H_2O}}^{eq} + 2\eta_{\mathrm{CO}}^{eq} + 2\eta_{\mathrm{CO_2}}^{eq} &= 1.30 \frac{N_{tot}^{in}}{N_{tot}^{eq}} \\
2\eta_{\mathrm{H_2}}^{eq} + 2\eta_{\mathrm{H_2O}}^{eq} + 4\eta_{\mathrm{CH_4}}^{eq} &= 0.80 \frac{N_{tot}^{in}}{N_{tot}^{eq}} \ .
\end{aligned} \tag{3.171}$$

Now, with $J = 6$ and $K = 3$ we have $R = 3$ independent reactions,

$$\begin{aligned}
2\,\mathrm{H_2} + \mathrm{O_2} &\longleftrightarrow 2\,\mathrm{H_2O} && \text{(i)} \\
2\,\mathrm{CO} + \mathrm{O_2} &\longleftrightarrow 2\,\mathrm{CO_2} && \text{(ii)} \quad . \\
\mathrm{CH_4} + 2\,\mathrm{O_2} &\longleftrightarrow 2\,\mathrm{H_2O} + \mathrm{CO_2} && \text{(iii)}
\end{aligned} \tag{3.172}$$

The standard free energy for these reactions at the specified temperature are,

$$\Delta G_{\mathrm{i}}^0 = -404.2\,\mathrm{kJ} \quad , \quad \Delta G_{\mathrm{ii}}^0 = -414.5\,\mathrm{kJ} \quad , \quad \Delta G_{\mathrm{iii}}^0 = -797.9\,\mathrm{kJ} \ . \tag{3.173}$$

The corresponding equilibrium constants, assuming an ideal gas mixture so that the activities are equal to the molar fractions, are,

$$\frac{(\eta_{\mathrm{H_2O}}^{eq})^2}{(\eta_{\mathrm{H_2}}^{eq})^2 \eta_{\mathrm{O_2}}^{eq}} = Q_{\mathrm{i}}^{eq} \quad , \quad \frac{(\eta_{\mathrm{CO_2}}^{eq})^2}{(\eta_{\mathrm{CO}}^{eq})^2 \eta_{\mathrm{O_2}}^{eq}} = Q_{\mathrm{ii}}^{eq} \quad , \quad \frac{(\eta_{\mathrm{H_2O}}^{eq})^2 \eta_{\mathrm{CO_2}}^{eq}}{\eta_{\mathrm{CH_4}}^{eq} (\eta_{\mathrm{O_2}}^{eq})^2} = Q_{\mathrm{iii}}^{eq} \ . \tag{3.174}$$

With (3.171) and (3.174) there are thus seven equations for the six unknown equilibrium molar fractions and the ratio of total numbers of molecules before and after the reactions $N_{tot}^{in}/N_{tot}^{eq}$, that can be solved numerically. A MATLAB code which is available here, yields,

molecular component	H_2	O_2	H_2O	CO	CO_2	CH_4
final molar fraction η_j^{eq}	0.136	0.144	0.231	0.445	0.052	1.6×10^{-24}

(3.175)

3.5.3 Exercises

3.5.3.1 Ex: Final composition of an ideal gas mixture

An ideal gas at 1000 K has the following composition,

molecular component	CO	CO_2	O_2
initial molar fraction η_j^{in}	0.50	0.38	0.12

a. Compute the affinity for the reaction,

$$CO + \tfrac{1}{2}\,O_2 \longleftrightarrow CO_2 \ .$$

b. Calculate the molecular composition after the reaction.

3.6 Classification of thermodynamic phase transitions

The old *Ehrenfest classification* [24] calls a phase transition of nth order if the derivative $\partial^n\mu/\partial T^n$ is discontinuous. Thus BEC of a trapped ideal gas is a first-order phase transition, because the chemical potential suddenly changes its slope at T_c.

The modern *Landau classification* distinguishes two types of phase transitions in homogeneous systems: First-order phase transitions exhibit a discontinuity in the order parameter, while for continuous phase transitions the order parameter does not make jumps.

First order phase transitions are characterized by 1. equilibrium between phases (liquid-gas, liquid-solid), 2. discontinuous entropy, therefore latent heat, 3. at least one derivative of a thermodynamic potential is discontinuous. **The two phases coexist at the transition point.** E.g. at $T = 0\,^\circ$C in a closed system water and ice coexist.

Continuous phase transitions are characterized by 1. no equilibrium, 2. no latent heat, but often discontinuous heat capacity, 3. first order derivatives are all continuous, but second order is discontinuous. **There is no phase coexistence at the critical point**. E.g. at $T = T_c$ there no condensate; only below T_c.

3.6.1 Solid-liquid-vapor

In the case of the *liquid-vapor transition* the two phases are only quantitatively distinct, but have the same symmetry. Therefore, a discontinuity of the thermodynamic potentials is required to reveal the phase transition.

In the case of the *solid-liquid transition* the two phases are qualitatively distinct due to different symmetries. We do not need a discontinuity to distinguish the phases. Landau's theory holds for this class of transitions. It establishes a relationship between symmetry considerations and physical characteristics by introducing the notion of the *order parameter* and *free energy.*

3.6.2 Bose-Einstein condensation

Is the observed Bose-Einstein condensation in trapped gases really a phase transition? A homogeneous gas has strong fluctuations near T_c that can heavily be influenced by interactions, which could result in phase domains. In contrast, a trapped gas is quite robust near T_c due to the modification of the density of states for small energies by the trapping potential, which make the interaction less important (see stabilization of attractive gases). However, T_c is not precisely defined and far from T_c interactions become very important (Thomas-Fermi limit).

The dynamics of phase transition is rules by a competition between internal energy which tries to minimize itself and entropy which tries to maximize itself.

3.7 Materials

3.7.1 Electrons in solids

3.7.1.1 Types of solids

In contrast to a gas, which in most cases consists of isolated particles, the interparticle interaction plays a dominant role in crystals. Solids, or more specifically crystals, are classified according to the predominant type of binding. 1. Molecular binding is responsible for the solidification of binary gases like O_2. Here, fluctuating dipole moments inducing dipole moments in neighboring molecules lead to van der Waals attractive forces on the order of $E_{bind} \simeq 10^{-2}\,\mathrm{eV}$ going like r^{-7}. 2. Ionic binding gives rise to periodic structures alternating positive and negative charges, as in NaCl. 3. Covalent binding is directional. This directionality determines the crystalline structure, such as in graphite and diamonds. In those three binding types there are no free electrons and hence no conductance. However, covalently bound crystals can sometimes be semiconductors or transparent. 4. Metallic binding is a limit of covalent binding, in which the valence electrons, which shared by all atoms, overrule the repulsion between the ions. The ionic lattice is immersed in a gas of free electrons. The ions have filled shells and are spherically symmetric. The electrons can easily absorb light, which makes the crystal opaque. The type of binding is studied via X-ray diffraction, via the dielectric properties, etc..

3.7.1.2 Band model

The number of orbitals in the isolated atoms forming the crystal gives the number of states available to the free electron gas. The exchange interaction of the fermionic electrons lifts the degenerescence (generalization of the H_2 molecule) and gives rise to a band structure. The electronic localization determines the width of the band: very delocalized electrons move in large bands. The interatomic distance also influences the band width. The closer the atoms the stronger the interaction, the larger the bands.

Bands connecting to different orbital may finally overlap. Note that the m_l degeneracy is lifted because spherical symmetry is broken by the crystal $[E(3s) \neq E(3p)]$.

3.7.1.3 Electrical conductance

Electrons can only move in presence of a sufficient number of unpopulated states, even under the influence of an external force. If no states are available the crystals becomes isolating. Overlapping filled and empty bands reserve many states and allow for good conductance.

If the Fermi energy E_F lies between a completely filled conducting band and an empty valence band. The crystal is isolating. However, at $T > 0$, if the forbidden band is narrow as in the case of semiconductors (for Si $\Delta E \simeq 1\,\mathrm{eV}$), the gap may be bridged by thermal excitations.

The electrons collide with crystal impurities, defects and phonons. While the velocity of the electrons is about $\bar{v} \simeq 10^7\,\mathrm{cm/s}$, the short mean free path λ limits the drift velocity to $v_d \simeq 10^{-2}\,\mathrm{cm/s}$. The Lorentz force eE/m accelerates the electrons between successive collisions occurring at a rate $\bar{v}/\lambda$, such that

$$\frac{j}{ne} = v_d = \frac{eE}{m} \times \frac{\lambda}{\bar{v}} \ , \tag{3.176}$$

where j is the current density and ne the charge density. The fact that $\bar{v}$ and λ do not depends on the electric field is known as Ohm's law. The mobility $\mu \equiv v_d/E$ allows to write the electrical conductance as

$$\rho^{-1} = n_- e_- \mu_- + n_+ e_+ \mu_+ \ . \tag{3.177}$$

The value and sign of the Hall coefficient $1/ne$ can be measured by the Hall effect. It is positive if the conductance occurs primarily through holes and negative if it occurs through electrons.

3.7.1.4 Semiconductors

There is an intrinsic temperature-dependent conductivity (for Si $\rho(600\,\mathrm{K})/\rho(300\,\mathrm{K}) \approx 10^9$). Extrinsic conductivity can be induced by photoexcitation or doping. E.g. Ar/Ga in a Ge crystal has one weakly bound electron more/less than required to fit into the lattice. This generates discrete energy levels slightly below the conducting/above the valence band, $min(E_c) - E_n, E_p - max(E_v) \simeq 0.01\,\mathrm{eV}$.

The Fermi energy E_F is the energy, where half of the electrons are below that. In an isolator is between $max(E_v)$ and $min(E_c)$. In the presence of doping E_F is shifted by the additional amount of electrons/holes toward E_n, E_p. If n and p-doped materials are combined, electrons drift from the n to the p region, such as to minimize energy and obtain a uniform E_F across the hole crystal.

Thermally excited electrons may drift and recombine with holes. The junction is maintained by a steady flux in a dynamic equilibrium. An external voltage can higher/lower the barrier, because the potential drops mostly near the junction, where the resistance is highest. In this case the thermal current is not equilibrated, the diode either blocks or opens. The electrons move to try to rectify E_F.

A transistor is a series of junctions in *npn* of *pnp* configuration. The base-emitter current can be used to switch a collector-emitter current by injecting electrons. A tunnel diode acts like a normal diode except that when the bands come closer together within the junction (at low voltages in conduction polarization), electrons may pass by tunneling from the conducting into the valence band. This flow gradually stops when E_F is leveled (for zero voltage). Tunneling currents react much faster than thermal drift currents.

3.7.2 Plasmas

3.7.2.1 Debye length

Consider a mixture of charges + and −, that is, a *plasma*. Energy seeks to be minimized by local compensation of charge imbalance. However, thermal motion spoils perfect homogeneity. That is, if on the one hand, looking at large scales, the environment seems neutral and homogeneous, at small scales there may be charge imbalances producing potential sites with exponentially decreasing ranges,

$$\frac{1}{\lambda_D} = \frac{1}{\lambda_{D-}} + \frac{1}{\lambda_{D+}} = \frac{ne^2}{\varepsilon_0}\left(\frac{1}{k_B T_+} + \frac{1}{k_B T_-}\right) . \tag{3.178}$$

The *Debye length* naturally enters the thermodynamic description of large systems of mobile charges. We consider a system of 2 different species of charges $q_\pm$ and $n_\pm(\mathbf{r})$ at locations $\mathbf{r}$. According to the so-called *primitive model*, these charges are distributed in a continuous medium characterized only by its relative static permittivity, ε_r. This distribution of charges through the medium generates an electric potential $\Phi(\mathbf{r})$ that satisfies the *Poisson equation*:

$$\varepsilon\nabla^2\Phi(\mathbf{r}) = -q_+n_+(\mathbf{r}) - q_-n_-(\mathbf{r}) - \rho_E(\mathbf{r}) , \tag{3.179}$$

where $\varepsilon \equiv \varepsilon_r\varepsilon_0$, ε_0 is the dielectric constant, and ρ_E is the charge density outside the medium (logically, not spatially).

The mobile charges do not only generate $\Phi(\mathbf{r})$, but also are moved according to the associated Coulomb force, $-q_\pm\nabla\Phi(\mathbf{r})$. Assuming the system to be in thermodynamic equilibrium with a heat reservoir at an absolute temperature T, the concentrations of discrete charges, $n_\pm(\mathbf{r})$, can be considered as thermodynamic averages (ensemble average) and the associated electrical potential as a thermodynamic mean field. With these assumptions, the concentration of species j is described by the Boltzmann distribution,

$$n_\pm(\mathbf{r}) = n_\pm^0 e^{-q_\pm\Phi(\mathbf{r})/k_BT} , \tag{3.180}$$

where n_j^0 is the mean field concentration of the charge species j.

Identifying the instantaneous concentrations and the potentials in the Poisson equation with their mean-field counterparts in the Boltzmann distribution, we obtain the Poisson-Boltzmann equation:

$$\varepsilon\nabla^2\Phi(\mathbf{r}) = -q_+n_+^0e^{-q_+\Phi(\mathbf{r})/k_BT} - q_-n_-^0e^{-q_-\Phi(\mathbf{r})/k_BT} - \rho_E(\mathbf{r}) . \tag{3.181}$$

Solutions of this nonlinear equation are known for simple systems. Solutions for more general systems can be obtained in the high-temperature (or low-coupling) limit, $q_j\Phi(\mathbf{r}) \ll k_BT$, by Taylor expansion of the exponential,

$$e^{-q_\pm\Phi(\mathbf{r})/k_BT} \approx 1 - \frac{q_\pm\Phi(\mathbf{r})}{k_BT} . \tag{3.182}$$

This approximation gives the linearized Poisson-Boltzmann equation,

$$\varepsilon\nabla^2\Phi(\mathbf{r}) = \left(\frac{n_+^0q_+^2}{k_BT} + \frac{n_-^0q_-^2}{k_BT}\right)\Phi(\mathbf{r}) - n_+^0q_+ - n_-^0q_- - \rho_e(\mathbf{r}) \tag{3.183}$$

also known as *Debye-Hückel equation*. The second term on the right side disappears for electrically neutral systems. The term in parentheses divided by ε, has the unit $1/\text{m}^2$. By a dimensional analysis, it leads to a definition of a characteristic length scale,

$$\lambda_D = \left(\frac{\varepsilon k_BT}{n_+^0q_+^2 + n_-^0q_-^2}\right)^{1/2} \tag{3.184}$$

usually called *Debye-Hückel length*. Being the only characteristic length scale of the Debye-Hückel equation, λ_D defines the scale of variations in the potential and the concentrations of the charged species. All charged species contribute to the Debye-Hückel length in the same manner regardless of the charge signal. For an electrically neutral system, the Poisson equation is,

$$\nabla^2 \Phi(\mathbf{r}) = \lambda_D^{-2} \Phi(\mathbf{r}) - \frac{\rho_e(\mathbf{r})}{\varepsilon} \ . \tag{3.185}$$

To illustrate the Debye shielding, the potential produced by an external point-like charge $\rho_e = Q\delta(\mathbf{r})$ is,

$$\Phi(\mathbf{r}) = \frac{Q}{4\pi\varepsilon r} e^{-r/\lambda_D} \ . \tag{3.186}$$

The bare Coulomb potential is exponentially shielded by the medium over a distance corresponding to the Debye length.

The length of Debye-Hückel can be expressed in terms of the length of Bjerrum λ_B as,

$$\lambda_D = \left(4\pi\lambda_B \sum_{j=1}^{N} n_j^0 \, z_j^2 \right)^{-1/2} , \tag{3.187}$$

where $z_j = q_j/e$.

3.7.2.2 Typical values

In plasmas in space, where the electron density is small, the Debye's length can reach macroscopic values.

system	density n_e (m^{-3})	electronic temp. T(K)	magn.field B(T)	Debye length λ_D(m)
solar core	10^{32}	10^7	-	10^{-11}
Tokamak	10^{20}	10^8	10	10^{-4}
gas discharge	10^{16}	10^4	-	10^{-4}
ionosphere	10^{12}	10^3	10^{-5}	10^{-3}
magnetosphere	10^7	10^7	10^{-8}	10^2
solar wind	10^6	10^5	10^{-9}	10
interstellar medium	10^5	10^4	10^{-10}	10
intergalactic medium	1	10^6	-	10^5

3.7.2.3 Length of Debye in a plasma

In a plasma, the background medium may be treated as the vacuum ($\varepsilon_r = 1$), and the length of Debye is,

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B / q_e^2}{n_e/T_e + \sum_j z_j^2 n_j / T_j}} , \tag{3.188}$$

where $T_\pm$ are the temperatures of the electrons and ions, n_- is the density of the electrons and n_+ that of the atomic species j, with positive ionic charge $z_+ q_e$. The ion term is often neglected, giving,

$$\lambda_D = \sqrt{\frac{\varepsilon_0 k_B T_e}{n_e q_e^2}} \ , \tag{3.189}$$

although this is valid only, when the mobility of ions is negligible on the time scale of the process.

3.7.3 Exercises

3.8 Further reading

H.M. Nussenzveig, Edgar Blucher (2014), *Curso de Fisica Basica: Fluidos, Vibrações e Ondas, Calor - vol 2* [ISBN]

Chapter 4

Appendices to 'Thermodynamics'

4.1 Quantities and formulas in thermodynamics

4.1.1 Statistical formulas

Stirling's formula is,

$$\ln n! = n\ln n - n + O(\ln n) \qquad \text{or} \qquad N! \simeq n^n e^{-n} \ . \tag{4.1}$$

4.1.2 Polylogarithm

The polylogarithm (or Joncquière's function) is a function defined as,

$$Li_\eta(z) \equiv \sum_{t=1}^{\infty} \frac{z^t}{t^\eta} = \frac{1}{\Gamma(\eta)} \int_0^\infty \frac{x^{\eta-1}dx}{z^{-1}e^x - 1} \ . \tag{4.2}$$

It serves to express the Bose and Fermi functions used in quantum statistics,

$$g_\eta^{(\pm)}(z) = \pm Li_\eta(\pm z) \ . \tag{4.3}$$

The upper sign holds for bosons, the lower for fermions.

4.1.2.1 Riemann zeta-function

The definition of the *Riemann zeta-function* is,

$$g_\eta(1) = \zeta(\eta) \ . \tag{4.4}$$

The *Sommerfeld expansion*,

$$\begin{aligned}\int_0^\infty \frac{g(x)dx}{e^{x-y}+1} &= \int_0^y g(x)dx + \int_0^\infty \frac{g(y+x)^{\eta-1}dx}{e^x+1} - \int_0^x \frac{g(y-x)^{\eta-1}dx}{e^x+1} \\ &\approx \int_0^y g(x)dx + \frac{\pi^2}{6}g'(x) + \ldots\end{aligned} \tag{4.5}$$

holds for $z \gg 1$ and yields,

$$f_\eta(e^y) \approx \frac{x^\eta}{\Gamma(\eta+1)}\left(1+\frac{\pi^2\eta(\eta-1)}{6x^2}+\frac{7\pi^4\eta(\eta-1)(\eta-2)(\eta-3)}{360x^4}+...\right) \ . \tag{4.6}$$

For small z both functions converge towards,

$$c_\eta(z) = \frac{1}{\Gamma(\eta)}\int_0^\infty \frac{x^{\eta-1}dx}{z^{-1}e^x} = c_{\eta-1}(z) = z \ . \tag{4.7}$$

The derivative is,

$$\frac{\partial f_\eta(Z)}{\partial Z} = \frac{\partial}{\partial Z}\sum_{t=1}^\infty -\frac{(-Z)^t}{t^\eta} = \sum_{t=1}^\infty \frac{(-Z)^{t-1}}{t^{\eta-1}} = \frac{1}{Z}\sum_{t=1}^\infty -\frac{(-Z)^t}{t^{\eta-1}} = \frac{f_{\eta-1}(Z)}{Z} \ , \tag{4.8}$$

or,

$$\begin{aligned}\frac{\partial f_\eta(Z)}{\partial Z} &= \frac{1}{\Gamma(\eta)}\frac{\partial}{\partial Z}\int_0^\infty \frac{x^{\eta-1}dx}{Z^{-1}e^x+1} = \frac{1}{\Gamma(\eta)}\int_0^\infty \frac{x^{\eta-1}Z^{-2}e^x dx}{(Z^{-1}e^x+1)^2} \\ &= \frac{1}{Z\Gamma(\eta)}\int_0^\infty x^{\eta-1}\frac{d}{dx}\frac{-1}{Z^{-1}e^x+1}dx = \frac{\eta-1}{Z\Gamma(\eta)}\int_0^\infty \frac{x^{\eta-2}}{Z^{-1}e^x+1}dx = \frac{f_{\eta-1}(Z)}{Z} \ .\end{aligned} \tag{4.9}$$

4.2 Data tables

4.2.1 Material data

The following table shows the specific latent heats and change of phase temperatures (at standard pressure) of some common fluids and gases:

Substance	SLH of fusion (kJ/kg)	melting point (°C)	SLH of vaporization (kJ/kg)	boiling point (°C)
ethyl alcohol	108	−114	855	78.3
ammonia	332.17	−77.74	1369	−33.34
carbon dioxide	184	−78	574	−78.46
helium			21	−268.93
hydrogen	58	−259	455	−253
lead	23.0	327.5	871	1750
strontium	0.72	777	12.6	1377
methane	59	−182.6	511	−161.6
oxygen	13.9	−219	213	−183
silicon	1790	1414	12800	3265
water	334	0	2264.705	100

The specific latent heat of condensation of water in the temperature range from −25 °C to 40 °C is approximated by the following empirical cubic function. For sublimation and deposition from and into ice, the specific latent heat is almost constant in the temperature range from −40 °C to 0 °C and can be approximated by the following empirical quadratic function:

$$\begin{aligned}L_{water}(T) &\simeq \left[2500.8 - 2.36\tfrac{T}{°\mathrm{C}} + 0.0016\left(\tfrac{T}{°\mathrm{C}}\right)^2 - 0.00006\left(\tfrac{T}{°\mathrm{C}}\right)^3\right] \mathrm{J/g} \\ L_{ice}(T) &\simeq \left[2834.1 - 0.29\tfrac{T}{°\mathrm{C}} - 0.004\left(\tfrac{T}{°\mathrm{C}}\right)^2\right] \mathrm{J/g} \ .\end{aligned} \tag{4.10}$$

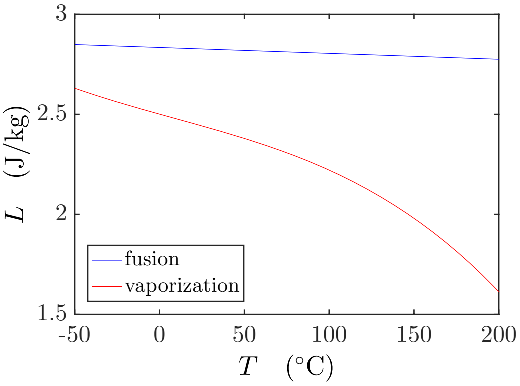

Figure 4.1: (code) Specific latent heat of fusions and condensation of water.

4.3 Further reading

R. DeHoff, *Thermodynamics in Material Science* [ISBN]

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