

Chapter 2

Energy of macroscopic systems

2.1 Introduction

From now on we will focus on macroscopic systems. These are systems containing many, say $N = 10^{20}$, particles. To fully specify such a system would require the specification of equally many particle positions and momenta (for classical particles) or quantum numbers (for small particles). Fortunately, this is not necessary. Experimentally it is found that isolated systems evolve spontaneously to simple terminal states, called *equilibrium states*. Macroscopically, these equilibrium states can be characterised by a surprisingly small number of variables, such as the number of particles, the volume and the energy.

2.2 Energy levels and degeneracy

2.2.1 The energy ladder

Let us first consider the energy U of a macroscopic system. The energy of this system not only depends on a set of quantum numbers $\{n_1, n_2, \dots\}$ specifying the state, but also on the number of particles N and external parameters such as the system volume V , or external fields like an electric field \mathbf{E} or magnetic field \mathbf{B} . For simplicity we restrict ourselves to N and V .

If we order each possible energy state according to its energy value along the vertical axis, we get a so-called energy ladder, see Fig. 2.1. We may now ask: where is the current system located on this energy ladder? Instead of specifying a huge list of quantum numbers, we will give a single number $\Phi(N, V, U)$ defined as¹

$$\Phi(N, V, U) = \text{“ Number of states with } (E(n_1, n_2, \dots; N, V) \leq U) \text{”}. \quad (2.1)$$

¹Do not confuse this Φ with the potential energy.

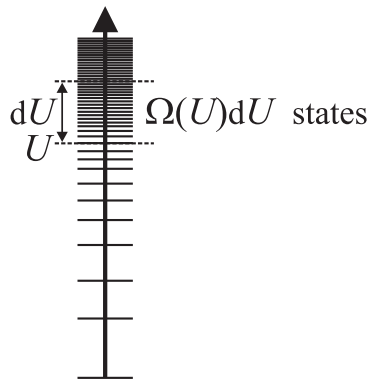


Figure 2.1: The energy ladder of a macroscopic system. Usually the energy levels are very close together. In that case the number of states with energy $E_{n,m} \in [U, U + dU]$ is equal to $\Omega(U)dU$, where $\Omega(U)$ is the density of states.

In other words, Φ is the ordinal number of the state of the system, if we order all states according to their energies.

There is one complication. From quantum mechanics we know that not all states have different energies. With N and V fixed, the *same* energy may be accomplished by a number of different combinations of quantum numbers $\{n_1, n_2, \dots\}$. It is therefore useful to alter our notation and use two quantum numbers n and m to specify a certain state: n to numerate the energy *level*, and m to specify the state within that level. Thus we denote the wave function of an energy eigenstate as

$$\psi_{n,m} \quad (m = 1, \dots, \Omega_n), \quad (2.2)$$

where Ω_n is the *degeneracy* of level n . If a system is prepared in a certain energy eigenstate $\psi_{n,m}$, after which it is perfectly isolated, it will remain in this state forever. However, perfect isolation is never possible, and small perturbations cause the system to continuously jump between different states $\{\psi_{n,m} : m = 1, \dots, \Omega_n\}$. All this time, the energy level remains the same, and the energy of the system is therefore given by

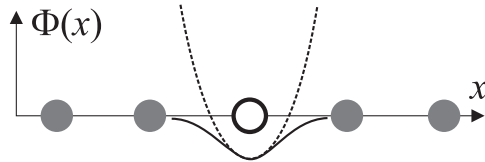
$$U = E_{n,m}(N, V) = E_n(N, V). \quad (2.3)$$

If we now ask the question where the current system is located on the energy ladder, we see that for degenerate states it is actually irrelevant whether the ordinal number $\Phi(N, V, U)$ stops at the first or at the last state of that particular energy level.

2.2.2 Continuous approach: the classical limit

From quantum mechanics we know that for large systems the energy levels are usually very close together. This allows us to adopt a continuous approach to the concept of degeneracy: we define the number of states between energy U and $U + dU$ as $\Omega(N, V, U)dU$, see Fig. 2.1. We then refer to $\Omega(N, V, U)$ as the *density of states*.

Figure 2.2: One-dimensional representation of a crystal. The white particle feels its neighbours through an interaction potential (black line). For small deviations around the equilibrium position, this is approximated by a harmonic well (dashed line).



Clearly the density of states is calculated as

$$\Omega(N, V, U) = \frac{\partial \Phi}{\partial U}(N, V, U). \quad (2.4)$$

Since in the classical limit energy is a continuous variable, we need an alternative way to effectively count the number of states. This is accomplished by measuring the volume of the *phase space* obeying Eq. (2.1) in units of the “fundamental unit of $3N$ -dimensional phase space” h^{3N} . This will be substantiated in section 8.2 and the Appendix of chapter 8. The number of states with $\mathcal{H} \leq U$ is calculated by the following formula:

$$\Phi(N, V, U) = \frac{1}{h^{3N} N!} \int d^{3N} r d^{3N} p \Theta(U - \mathcal{H}(r^{3N}, p^{3N})), \quad (2.5)$$

where $\Theta(x)$ is the Heaviside step function, defined as

$$\Theta(x) = \begin{cases} 0 & (x < 0), \\ 1 & (x > 0). \end{cases} \quad (2.6)$$

Note that we integrate over all possible positions \mathbf{r} and momenta $\mathbf{p} = m\mathbf{v}$ of all N particles. The Heaviside function will pick out only those combinations of positions and momenta for which the Hamiltonian \mathcal{H} is smaller than U . Finally we need to explain the factor $N!$. According to quantum mechanics identical particles must be indistinguishable. We have therefore overestimated the number of independent states by a factor equal to the number of possible permutations of the N particles, which is $N!$

2.2.3 Example 1: degeneracy of a harmonic crystal

As a first example we will calculate the degeneracy in a crystal of N identical spherical particles. The particles are arranged in a periodic array, where each particle feels forces from neighbouring particles, see Fig. 2.2. At specific points in space (the lattice points) the sum of these forces averages out to zero. If we now expand the potential energy in the neighbourhood of each of these lattice points to

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second order in displacement we get N identical harmonic oscillators.² The energy of N quantum mechanical harmonic oscillators of characteristic frequency ω is given by

$$\begin{aligned} E_{n_1, \dots, n_{3N}} &= \hbar\omega\left(n_1 + \frac{1}{2}\right) + \dots + \hbar\omega\left(n_{3N} + \frac{1}{2}\right) \\ &= \frac{3N}{2}\hbar\omega + \hbar\omega(n_1 + \dots + n_{3N}) = \hbar\omega\left(\frac{3N}{2} + M\right) \end{aligned} \quad (2.7)$$

$$M \equiv n_1 + \dots + n_{3N}. \quad (2.8)$$

Here the n_i are non-negative integer quantum numbers. To calculate the number of states $\Omega(U)$ at a certain total energy U , it is easier to first work with $M = U/(\hbar\omega) - 3N/2$. We then need to calculate in how many ways we can partition M (the number of *quanta*) in $3N$ pieces. Suppose we mark the quanta by a cross (\times) and the end of each piece by a bar ($|$), then one possible realisation for $M = 8$ and $3N = 6$ would look like

$$\times || \times \times | \times | \times \times \times | \times |$$

In this example $n_1 = 1$, $n_2 = 0$, $n_3 = 2$, $n_4 = 1$, $n_5 = 3$, and $n_6 = 1$. We can now permute \times 's and $|$'s, except for the last one. The number of ways to do this is

$$\Omega(N, M) = \frac{(M + 3N - 1)!}{M!(3N - 1)!}. \quad (2.9)$$

This is the expression we were after. The degeneracy of a harmonic crystal is found to increase fast with increasing energy $U = \hbar\omega(3N/2 + M)$. The total number of states with an energy less than or equal to $U = \hbar\omega(3N/2 + M)$ is given by a sum over all possible values for m in the range 0 to M (see Appendix A for a derivation):

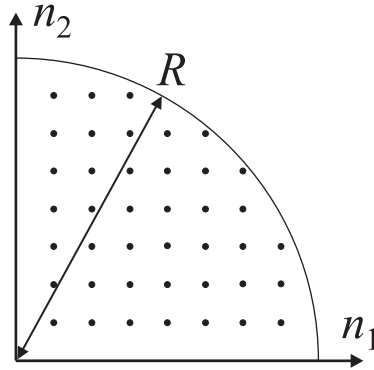
$$\begin{aligned} \Phi(N, M) &= \sum_{m=0}^M \Omega(N, m) = \frac{(3N + M)!}{(3N)!M!} \\ &\approx \left[\left(\frac{1}{M/3N} + 1 \right)^{M/N} \left(1 + \frac{M}{3N} \right)^3 \right]^N \sqrt{1 + \frac{3N}{M}} \frac{1}{\sqrt{6\pi N}} \end{aligned} \quad (2.10)$$

$$\approx \left[\left(\frac{e}{3\hbar\omega} \frac{U}{N} \right)^3 \right]^N \frac{1}{\sqrt{6\pi N}}, \quad (2.11)$$

where the last approximation is valid for not-too-low temperatures where $M \gg 3N$. Note that the main contribution is a function of U/N raised to the power N . This will be used when we discuss extensivity and entropy.

²In principle the potential energy of a particle involves the positions of the surrounding particles. Here we make the approximation that the surrounding particles are fixed to their respective lattice positions.

Figure 2.3: Each state of a system of N particles in a box can be represented by a point on a hypercubic lattice. Here we show only two axes, that of n_1 and n_2 . The number of states with energy lower than U is approximately equal to $(1/2)^{3N}$ 'th of the volume of a $3N$ -dimensional hypersphere with radius $R = \sqrt{8mL^2U/h^2}$.



2.2.4 Example 2: density of states of an ideal gas

As a second example we will calculate $\Phi(N, V, U)$ and the density-of-states $\Omega(N, V, U)$ of an ideal gas. According to quantum mechanics, the energy of an ideal gas of N particles in a box of size $V = L^3$ is given by

$$E_{n_1, \dots, n_{3N}} = \frac{h^2}{8mL^2}(n_1^2 + \dots + n_{3N}^2), \quad (2.12)$$

where the n_i are positive integer quantum numbers. To find $\Phi(N, V, U)$ we need to estimate the number of different states, i.e. the number of different combinations (n_1, \dots, n_{3N}) , which yield an energy equal or lower than U . In other words, in how many possible ways can we fulfill

$$n_1^2 + \dots + n_{3N}^2 \leq \frac{8mL^2U}{h^2}. \quad (2.13)$$

If we imagine a $3N$ -dimensional space with $3N$ orthogonal n_i axes, we may think of each state as a point on a $3N$ -dimensional hypercubic lattice, with lattice spacing 1, see Fig. 2.3. If the energy U is not too low (which is true in most practical cases), the total number of lattice points obeying Eq. (2.13) is enormous and may quite accurately be approximated by $(1/2)^{3N}$ 'th of the volume of a $3N$ -dimensional hypersphere of radius $R = \sqrt{8mL^2U/h^2}$. The factor $(1/2)^{3N}$ is necessary because only positive n_i are allowed.

There is one additional factor that needs to be taken into account: identical particles must be indistinguishable. We therefore have to correct the number of independent states by a factor $N!$. Further using the expression for the volume of a n -dimensional hypersphere (Problem 2-1), we find

$$\Phi(N, V, U) = \frac{1}{N!} \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} \left(\frac{8mL^2U}{h^2}\right)^{3N/2}. \quad (2.14)$$

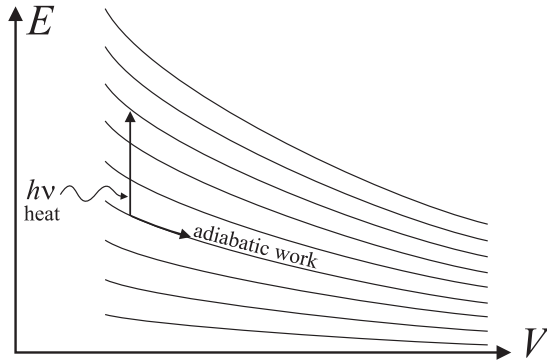


Figure 2.4: Energy levels of a system of particles in a box of volume V . The spacing between the levels is $h^2/(8mV^{2/3})$. The energy of the system can be altered by changing the volume of the box or by changing the energy level, for example by exposing the system to radiation or coupling it to a heat reservoir.

Next we use the approximation $N! \approx (N/e)^N \sqrt{2\pi N}$ (Problem 2-2) to find the number of states with energy less than U :

$$\Phi(N, V, U) = \left[\left(\frac{m}{3\pi\hbar^2} \right)^{3/2} e^{5/2} \left(\frac{U}{N} \right)^{3/2} \left(\frac{V}{N} \right) \right]^N \frac{1}{\sqrt{6\pi N}}. \quad (2.15)$$

The density of states is found by partial differentiation to U :

$$\Omega(N, V, U) = \left[\left(\frac{m}{3\pi\hbar^2} \right)^{3/2} e^{5/2} \left(\frac{U}{N} \right)^{3/2} \left(\frac{V}{N} \right) \right]^N \frac{N}{U} \sqrt{\frac{3}{8}} \frac{1}{\pi N}. \quad (2.16)$$

The number of states can also be calculated from the classical expression Eq. (2.5). In Problem 2-3 you will show that this yields the same result.

2.3 Entropy

2.3.1 Changing the energy of a system

In general, if we now consider processes in a closed system (where N is constant), Eq. (2.3) tells us that we can change the energy by changing the volume V or by changing the energy level n . If changing the volume V is done gently enough,³ the energy will change while remaining in the same energy level n . Conversely, the energy level n may be changed at constant volume by exposing the system to radiation or coupling it to a heat reservoir. Both processes are depicted in Fig. 2.4. The important point is that both n and V are independent experimental parameters that specify the energy of a closed system.

Since there is a one-to-one relation between the energy level n and the ordinal number Φ , we may just as well use Φ to specify the energy level of the system.

³The volume must be changed reversibly and adiabatically, as we will discuss later.

We can carry this idea a little further, and conclude that we can use an arbitrary monotonous function of Φ , let us call it $S = S(\Phi)$, to specify the energy level of the system. Once we have chosen a functional dependence of S on Φ , the energy is a function of N , V , and S . This is made explicit through the following notation:

$$\boxed{E_n(N, V) \equiv U(N, V, S).} \quad (2.17)$$

In thermodynamics we study the dependence of the quantities N , V , S , and U . Sofar we have considered U to be a function of N , V , and S . Obviously we can also consider S to be a function of N , V , and U .

2.3.2 Extensivity and entropy

Suppose we have two macroscopic, thermodynamically identical equilibrium systems, meaning two systems containing the the same kind of molecules, the same number of molecules N , of the same volume V , the same energy U , and the same energy level n , which we now express as “the same S ”. Suppose we combine them into one system. Schematically denoting this combination by \oplus , we find for the number of molecules, volume, energy, and function S of the combined system:⁴

$$N \oplus N = 2N \quad (2.18)$$

$$V \oplus V = 2V \quad (2.19)$$

$$U \oplus U = 2U \quad (2.20)$$

$$S \oplus S = S'. \quad (2.21)$$

We say that the number of particles, the volume, and energy are *extensive* variables, which are variables that depend linearly on the size of the system. An arbitrary function $S(\Phi)$, however, is generally not extensive, nor is Φ itself.

We may now ask the question whether it is possible to find a particular function $S = S(\Phi)$ such that $S' = 2S$? The answer is affirmative: the logarithm of Φ is extensive. Let us therefore introduce a function S called *entropy*, which we define as

$$\boxed{S = k \ln \Phi,} \quad (2.22)$$

with k some constant.

Why is $S = k \ln \Phi$ an *extensive* measure for the energy level number? For macroscopic systems, in many cases we find

$$\Phi = [\omega(v, u)]^N g(N, V, U), \quad (2.23)$$

⁴Eqs. (2.18) and (2.19) are true by definition. Eq. (2.20) is an experimental result for sufficiently large systems.

where $v = V/N$ and $u = U/N$. ω is some function monotonously increasing with increasing v and u , and

$$\lim_{N \rightarrow \infty} g(N, Nv, Nu) = C(v, u)N^\alpha, \quad (2.24)$$

with α some constant of order 1. In taking this limit v and u must be kept constant. We have already verified this explicitly for the case of a harmonic crystal, see Eq. (2.10), and for an ideal gas, see Eq. (2.15). If we accept the validity of Eq. (2.23) the rest of the proof is simple:

$$\begin{aligned} S &= k \ln \Phi = Nk \ln \omega + k \ln g \\ &= Nk \left(\ln \omega + \frac{1}{N} \ln g \right). \end{aligned} \quad (2.25)$$

In the limit of large enough N

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln g(N, Nv, Nu) = \lim_{N \rightarrow \infty} \frac{1}{N} [\alpha \ln N + \ln C(v, u)] = 0. \quad (2.26)$$

So indeed $S = k \ln \Phi = Nk \ln \omega$ is extensive. In Appendix B of this chapter we give an alternative derivation.

Actually, if Eq. (2.23) holds true, the derivative of Φ with respect to U can also be used instead of Φ in Eq. (2.22) (prove this yourself!), i.e. we may also write Eq. (2.22) in the more familiar form

$$\boxed{S = k \ln \Omega.} \quad (2.27)$$

In Appendix B of this chapter we give an additional argument for this expression.

2.4 Intensive variables

We have argued that the energy may be written as a function of N , V and S . The first two are extensive by definition and by choosing $S = k \ln \Phi$ or $S = k \ln \Omega$ the latter is also extensive. Let us see what this means for the energy of a combined system of x identical copies:

$$U(xN, xV, xS) = xU(N, V, S). \quad (2.28)$$

Differentiating to x , and setting $x = 1$ we find the interesting result

$$N \frac{\partial U}{\partial N} + V \frac{\partial U}{\partial V} + S \frac{\partial U}{\partial S} = U. \quad (2.29)$$

Because U , N , V , and S are all extensive variables, the partial derivatives occurring in Eq. (2.29) are all *intensive*. Intensive variables are independent of the size of the

problem. The intensive variables are defined thermodynamically as the temperature, pressure and chemical potential:

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_{V,N} \equiv T.} \quad (2.30)$$

$$\boxed{-\left(\frac{\partial U}{\partial V}\right)_{N,S} \equiv P.} \quad (2.31)$$

$$\boxed{\left(\frac{\partial U}{\partial N}\right)_{V,S} \equiv \mu.} \quad (2.32)$$

The minus sign in the definition of the pressure is for reason of convention: this way the pressure usually is a positive quantity. Using these definition we see that Eq. (2.29) may be written as

$$U = TS - PV + \mu N. \quad (2.33)$$

At this point we have simply *defined* the partial derivatives as temperature, pressure and chemical potential. In the next two sections we will show that the first two of these derivatives agree with our intuitive notion of temperature and pressure. The experimental importance and meaning of the chemical potential μ will be discussed in section 3.8.

If we make infinitesimally small changes in all variables N , V and S , we can formally expand $U(N, V, S)$ and use the partial derivatives μ , P and T to write the infinitesimal change in energy as

$$\boxed{dU = TdS - PdV + \mu dN.} \quad (2.34)$$

This expression is referred to as the fundamental equation of thermodynamics. From Eq. (2.33) we find

$$dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu. \quad (2.35)$$

Combining both expressions for dU we arrive at the so-called Gibbs-Duhem relation,

$$SdT - VdP + Nd\mu = 0. \quad (2.36)$$

This important result states that the three intensive variables T , P , and μ cannot be varied independently. Notice that in order to completely describe the system we need three variables. So we conclude that at least one of these variables must be extensive. This is obvious (why?).

2.5 Mono-atomic ideal gas

Let us see what our thermodynamic definitions give for a mono-atomic ideal gas of N particles in a volume V . From Eq. (2.15) we find that the entropy is given by (see Problem 2-4)

$$S = Nk \ln \left[\left(\frac{m}{3\pi\hbar^2} \right)^{3/2} e^{5/2} \left(\frac{U}{N} \right)^{3/2} \left(\frac{V}{N} \right) \right]. \quad (2.37)$$

This allows us to express the energy of an ideal gas in terms of N , V and S :

$$U = N e^{-5/3} \frac{3\pi\hbar^2}{m} e^{\frac{2S}{3Nk}} \left(\frac{N}{V} \right)^{2/3}. \quad (2.38)$$

We can now calculate the thermodynamic temperature and pressure of an ideal gas:⁵

$$kT = k \left(\frac{\partial U}{\partial S} \right)_V = \frac{2U}{3N} \quad (2.39)$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S = \frac{2U}{3V}. \quad (2.40)$$

Rewriting, we find

$$PV/N = \frac{2U}{3N} = kT \quad (\text{ideal gas}). \quad (2.41)$$

We could have derived the first equality in Eq. (2.41) directly from the energy of a system of N particles in a box (Problem 2-5).

U , V and N are all mechanical properties of the system. Once they are defined, P and kT can be calculated. Note that T only appears in the combination with the constant k , originating from Eq. (2.22). If we want to define numerical values for T , we must introduce a numerical value for k . The Kelvin scale of temperature is defined by assigning to k a value of 1.38×10^{-23} J/K. k is called the Boltzmann constant. From now on we will label it consistently as k_B . We further define the gas constant as

$$R = N_{Av} k_B = 8.314 \text{ J/K/mol}, \quad (2.42)$$

with $N_{Av} = 6.022 \times 10^{23}$ Avogadro's number.

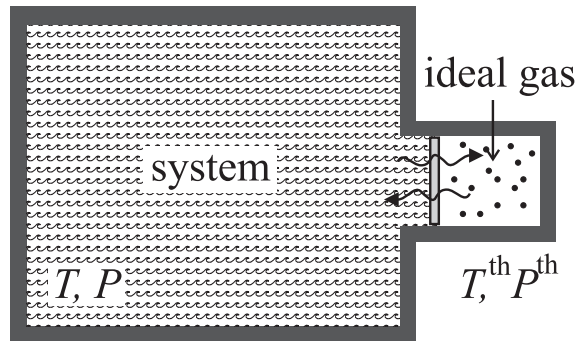
By rewriting the above equations, we find the following well-known relations for an ideal gas:

$$PV = Nk_B T \quad (2.43)$$

$$U = \frac{3}{2} PV = \frac{3}{2} Nk_B T. \quad (2.44)$$

⁵The chemical potential is not important for our arguments here and will be derived elsewhere.

Figure 2.5: We let a (non-ideal) system come into contact with a small amount of ideal gas, by means of a moveable wall which can conduct heat, but does not let through any particles. The combined system + ideal gas is surrounded by insulating walls. Equilibrium will be achieved when the pressure P and temperature T of the system are equal to the pressure P^{th} and T^{th} of the ideal gas.



2.6 Measuring temperature and pressure with an ideal gas

We can use the above results for an ideal gas to measure the temperature and pressure of any non-ideal system. Figure 2.5 shows a system which comes into contact with a small amount of ideal gas by means of a moveable wall which can conduct heat, but does not let through any particles. The combined system + ideal gas is surrounded by insulating walls. In Chapter 4 we will show that a configuration like this will tend to an equilibrium situation in which the pressure and temperature are the same in the system and in the ideal gas. If the volume of ideal gas is much lower than the volume of the system, the ideal gas will effectively attain the temperature and pressure of the system.

In the previous section we have shown that we can measure the pressure and temperature in an ideal gas, so effectively we have a way to measure the pressure and temperature of the non-ideal system too. The Boltzmann constant k_B has been chosen such that the temperature of a mixture of ice, water and water vapour in mutual equilibrium (clearly a non-ideal system!) is associated with the number $T = 273.16$ (Kelvin).

2.7 Thermodynamic processes

2.7.1 Work and heat

It is important to note that the energy of a macroscopic system in equilibrium is a *state function*. This means that no matter by which process we go from a state A , defined by the variables (N_A, V_A, S_A) , to a state B , defined by the variables (N_B, V_B, S_B) , the energy difference $\Delta U = U_B - U_A$ between these two equilibrium states will always be the same.

According to classical mechanics, if work is performed on a system while making sure that there are no other influences, let us call this *adiabatic* work w_{adiab} , then

the energy increase of the system is given by

$$(\Delta U)_{adiab} = w_{adiab}. \quad (2.45)$$

An adiabatic process is a special kind of process. In general, other influences cannot be excluded: it is possible to start from the same state (A) and end in the same state (B) by going through an entirely different process. In general, therefore, the amount of work w performed on the system may be different from the adiabatic case, even though ΔU will be the same. The difference between ΔU and the amount of work w performed on a system is *defined* as the heat Q which has flown into the system. In other words:

$$\boxed{\Delta U = Q + w.} \quad (2.46)$$

This is called the first law of thermodynamics. It is basically an expression of the law of conservation of energy.

We can see an important consequence of Eq. (2.46): if we are able to tabulate U for different values of the system's thermodynamic variables, then we are able to calculate $Q + w$ for each process leading from one set of variables to the other. We emphasise again that the amount that was added or subtracted in the form of heat relative to the amount that was added or subtracted in the form of work depends entirely on the details of the process that was used.

2.7.2 Infinitesimal reversible processes

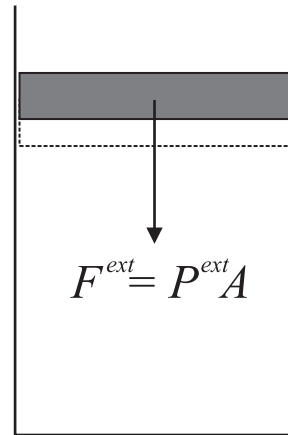
In the following we will consider a special class of processes, used in many thermodynamic considerations: *reversible* processes. From a practical point of view, reversible processes are processes that are performed in a controlled and sufficiently slow manner. One may think of a reversible process as a process which is sufficiently slow in order that the system is always in equilibrium and which can be reversed by small changes of the external forces. On reversing the process, all thermodynamic variables will undergo exactly the same changes as in the forward process, only in reverse order. This way the system and its surroundings return to their original states.

All other processes are called *irreversible* processes. These are processes that occur spontaneously in an isolated system, after an internal constraint has been removed. We will say more about irreversible processes when we treat the second law of thermodynamics in chapter 4.

Adiabatic infinitesimal reversible process

Consider the piston in Fig. 2.6. The walls of the cylinder and the piston are insulated, so changing the height of the piston amounts to performing adiabatic work.

Figure 2.6: The external pressure P^{ext} on this system of a cylinder and piston is defined as the ratio externally applied force F^{ext} and piston area A . The cylinder's volume is decreased by moving the piston down under the influence of this external force. This may be done reversibly or irreversibly. If the compression is done reversibly, at each step the external pressure P^{ext} is in equilibrium with the pressure P inside the cylinder.



According to classical mechanics, Eq. (1.41), the adiabatic work done on the system when changing the height of the piston by an infinitesimal amount ds under the influence of an external force F^{ext} is equal to

$$w_{adiab} = F^{ext} \frac{ds}{dt} dt = F^{ext} ds. \quad (2.47)$$

Mechanically, the externally applied force F^{ext} may be thought of as the product of externally applied pressure P^{ext} and the area A over which this pressure is applied,

$$F^{ext} = P^{ext} A. \quad (2.48)$$

Without heat exchange, the (infinitesimal) increase of energy dU of the system is determined solely by the total amount of *work* performed by the external force to decrease the system's volume, i.e.

$$(dU)_{rev,adiab} = P^{ext} A ds = -P^{ext} dV, \quad (2.49)$$

where we have used that the change in volume of the cylinder is given by $dV = -A ds$.

Up to this point we have considered the cylinder and piston from a mechanical point of view. Now we will approach it from a statistical mechanical point of view. First we need to ask: what does it mean to change the volume adiabatically? It means that only the external parameters (in our case only the volume V) of the quantum mechanical energy level will change, but the system will not jump from one energy level to another. According to Fig. 2.4 this means that an adiabatic process takes place at a constant energy level n , i.e. at constant entropy S . If the entropy S is constant and the number of particles N is constant, according to Eq. (2.31) the infinitesimal increase of system energy is given by

$$(dU)_{rev,adiab} = -P dV. \quad (2.50)$$

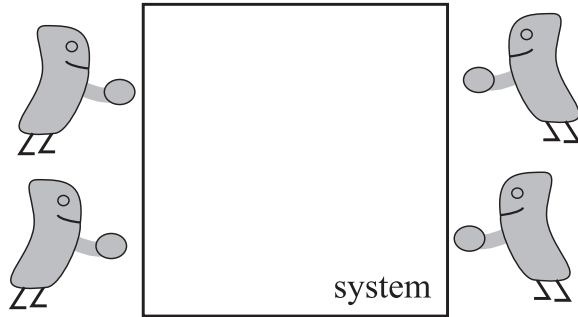


Figure 2.7: The energy is changed by giving random kicks (represented by boxers) to the boundary of the system. The boxers can also absorb energy. This is representative of coupling to a thermostat (or heat reservoir).

Comparing this with the mechanical definition Eq. (2.49), we find

$$P = P^{ext} \quad (\text{reversible}). \quad (2.51)$$

The thermodynamic pressure, defined in Eq. (2.31), has the correct physical interpretation: at each small step in an adiabatic reversible process, the pressure P of the system is in balance with the externally applied mechanical pressure P^{ext} .

Isochoric infinitesimal reversible process

A process in which the volume is kept constant is called an isochoric process. More generally, we are now going to focus on processes that change the energy level of the system without changing the external parameters. From a quantum mechanical point of view, this may be accomplished by absorption or emission of light (see Fig. 2.4). From a classical mechanical point of view, this may be accomplished by coupling the system to a thermostat (or heat reservoir), as in Fig. 2.7. The walls of the system are fixed, so the volume of the system does not change ($dV = 0$).

We slowly increase the temperature T^{th} of the thermostat, i.e. the activity of the “boxers”, in many small steps while letting the system equilibrate at each step and measuring the amount of heat q that streams into the system.⁶

Because $w = 0$, the increase of energy of the system is equal to the amount of heat that has transferred from the thermostat to the system:

$$(dU)_{rev, isoch} = q. \quad (2.52)$$

⁶This may for example be accomplished by using an ideal gas thermostat with known specific heat, $C_V = \frac{3}{2}N^{th}k_B$, and by dividing each small step into two substeps: (1) Increasing the temperature of the thermostat slightly, for example by shortly applying a current to an electric heating element embedded in the thermostat, without letting heat flow between the thermostat and the system, and (2) letting heat flow from the thermostat to the system. Before executing substep (2) we measure the temperature of the equilibrated thermostat. After substep (2) we give the system and thermostat enough time to equilibrate again to a new state and once more measure the temperature of the thermostat. The amount of heat that flown from the thermostat into the system is equal to $q = -C_V dT^{th}$. The minus sign arises because a positive q is associated with a negative temperature change dT^{th} of the thermostat.

On the other hand, if the volume V is constant and the number of particles N is constant, according to Eq. (2.31) the infinitesimal increase of system energy is given by

$$(dU)_{rev, isoch} = TdS. \quad (2.53)$$

Comparing Eqs. (2.52) and (2.53) we find that for a reversible isochoric process

$$\boxed{dS = \left(\frac{q}{T}\right)_{rev}.} \quad (2.54)$$

A reversible flux of heat into a system is associated with an increase of entropy of that system.

2.7.3 General reversible processes

For a general *finite* reversible process in a *closed* system, involving both volume and entropy changes, the increase of energy U of the system may be found by integration:

$$\Delta U = \int TdS - \int PdV. \quad (2.55)$$

We recognise two contributions to the increase of energy of the system: heat that has flown into the system and (volume) work done on the system. Both may be calculated separately:

1. In a reversible process the temperature of the system remains a well-defined quantity during all intermediate stages of the process. A reversible process may be shown as a continuous line in a temperature versus entropy plot, where the integral under the line yields the total heat supplied to the system:

$$\boxed{Q = \int TdS \quad (\text{any reversible process}).} \quad (2.56)$$

2. In a reversible process the pressure P of the system remains a well-defined quantity during all intermediate stages of the process. A reversible process may be shown as a continuous line in a pressure versus volume plot, where the integral under the line yields (minus) the volume work done on the system:

$$\boxed{w = - \int PdV \quad (\text{any reversible process}).} \quad (2.57)$$

As already stated several times, the relative contributions of work and heat in Eq. (2.55) depend very much on the details of the process leading from A to B . However, because the energy $U = U(N, V, S)$ is a state function, the total energy difference $\Delta U = U_B - U_A$ between two equilibrium states does *not* depend on the details of the process taken between states A and B , see Fig. 2.8.

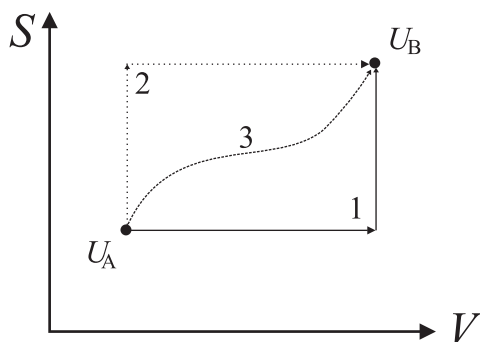


Figure 2.8: The energy U is a state function, meaning that the energy difference $U_B - U_A$ between two equilibrium states does not depend on the path taken between states A and B : the paths 1, 2, and 3 will all correspond to the same increase of energy, although the relative amounts of work and heat differ.

2.7.4 General irreversible processes

Finally, for an *irreversible* process the pressure and temperature are generally undefined, except for the equilibrium states at the beginning and the end of the process. As a consequence, it is impossible to determine the work and heat by performing the integrals in Eqs. (2.56) and (2.57). However, we have seen that for any process (whether reversible or irreversible) the work w can be calculated based on our knowledge of the external force:

$$w = - \int P^{ext} dV. \quad (2.58)$$

We can then use the first law of thermodynamics to calculate the heat Q that has flown into the system as the difference between the energy increase and the work done on the system.

2.8 Equations of state

We have seen that we can characterise a system in equilibrium by just a small number of variables. How many variables do we need to specify exactly to completely characterise a system? For a homogeneous one-component system the answer is three variables, at least one of which is extensive. In case of a closed system (where the number of particles is fixed), only two variables matter. By specifying two independent variables, the third is therefore fixed. In other words, there is a functional dependence between the three variables. For example:

$$\begin{array}{ll} \text{closed:} & P = P(V, T) \quad \text{only two independent variables} \\ \text{open:} & P = P(V/N, T) \quad \text{only two independent intensive variables.} \end{array}$$

Such functional dependences are called equations of state. We will now explore some well-known equations of state.

2.8.1 Ideal gas equation

We have already encountered the ideal gas in the previous section:

$$Pv = RT \quad (2.59)$$

$$v = V/n \quad (2.60)$$

$$n = N/N_{Av}. \quad (2.61)$$

This equation is valid for dilute gases. It is impossible to give general criteria that determine whether a gas can be considered dilute or not. As a rule of thumb we can say that for temperatures sufficiently far above the critical temperature and pressures lower than five times the critical pressure, the ideal gas equation is valid. Examples are noble gases, N_2 , H_2 , O_2 , CO and CO_2 at room temperature or higher, at pressures lower than 100 bar.

2.8.2 Virial equation

$$Pv = RT \left(1 + \frac{B(T)}{v} + \frac{C(T)}{v^2} + \dots \right). \quad (2.62)$$

B and C are independent of the volume V , but do depend on the temperature T . In this form the equation of state is v -explicit. The ρ -explicit form ($\rho = N/V$) is:

$$P = \rho k_B T \left(1 + B_2(T)\rho + B_3(T)\rho^2 + \dots \right). \quad (2.63)$$

B_2 and B_3 are called the second and third virial coefficients, respectively. Again B_2 and B_3 are temperature dependent. The virial equation cut after the second, quadratic, term is valid in a larger range of temperatures and pressures than the ideal gas equation, and is much more accurate in that range.

2.8.3 Van der Waals equation

$$P = \frac{RT}{v-b} - \frac{a}{v^2}. \quad (2.64)$$

Here b represents the diminishing of the (free) volume caused by the presence of the molecules, and a represents attractions between the molecules. With this equation it is possible to describe both the liquid and gas phase. In Fig. 2.9 we have drawn three isotherms. The isotherm with $T < T_c$ does not monotonically decrease, but has a local minimum and maximum. At high pressures the isotherm corresponds to a liquid phase and at low pressures it corresponds to a gas phase. In the intermediate area one can find, for each pressure, three different values for the volume, which is

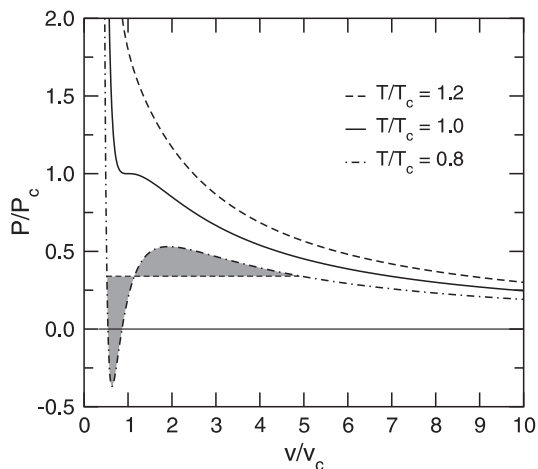


Figure 2.9: Isotherms of the van der Waals equation of state at $T/T_c = 0.8, 1.0$ and 1.2 . For $T < T_c$ there is a liquid phase at high pressure and a gas phase at low pressure. In the intermediate area, at the vapour pressure, the two phases will co-exist. The vapour pressure can be found by means of the Maxwell construction, in which the grey areas are of equal size.

of course not very realistic. Only at a certain pressure, the vapour pressure at that given temperature, the equation of state should produce two volumes, in between of which the isotherm should be horizontal. The vapour pressure can be found by finding that pressure at which both grey areas in Fig. 2.9 are of equal size. This is called the Maxwell construction. A proof will be postponed to Problem 3-4.

T_c in the above paragraph is the critical temperature, above which the distinction between a liquid and a gas disappears. The critical pressure P_c and volume v_c are defined as the pressure and volume on the critical isotherm where

$$\left(\frac{\partial P}{\partial v}\right)_T = \left(\frac{\partial^2 P}{\partial v^2}\right)_T = 0 \quad (\text{critical point}). \quad (2.65)$$

For the van der Waals equation of state these are given by (see Problem 2-6)

$$T_c = \frac{8a}{27bR}, \quad P_c = \frac{a}{27b^2}, \quad v_c = 3b.$$

In Problem 2-7 you are asked to calculate the second virial coefficient of the van der Waals equation of state and in Problem 2-8 you are asked to calculate the molar volume of methane using both the ideal gas and van der Waals equation of state.

2.8.4 Redlich-Kwong equation

There are many modifications of the van der Waals equation which are very successful. One of the simplest of these is the Redlich-Kwong equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{T^{1/2}v(v-b)}. \quad (2.66)$$

The constants a and b can again be related to the conditions at the critical point:

$$a = 0.42748R^2 \frac{T_c^{5/2}}{P_c}, \quad b = 0.08664R \frac{T_c}{P_c}.$$

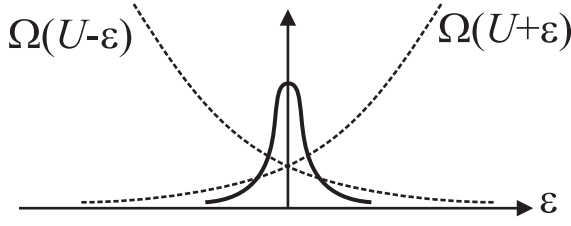


Figure 2.10: Because $\Omega(U)$ is a sharply increasing function of U , the integrand of Eq. (2.72) is a sharply peaked function around $\epsilon = 0$.

Here we have used that $N! \approx (N/e)^N \sqrt{2\pi N}$, see Problem 2-2, and written the result such that the dependence on the ratio M/N becomes clear. At not-too-low temperatures the number of available quanta is much larger than the number of oscillators, i.e. $M \gg 3N$, in which case Φ can also be written as

$$\Phi(N, M(U)) \approx e^{3N} \left(\frac{M}{3N}\right)^{3N} \frac{1}{\sqrt{6\pi N}} = \left(\frac{Ue}{3N\hbar\omega}\right)^{3N} \frac{1}{\sqrt{6\pi N}}, \quad (2.71)$$

where we have used that $\lim_{n \rightarrow \infty} (1 + x/n)^n = \exp(x)$.

Appendix B

Suppose we bring two identical systems into thermal contact. Heat is allowed to flow from one system to the other, temporarily increasing the energy of one system, while decreasing the energy of the other. The total energy, however, is always conserved. The density of states of the combined system is therefore given by

$$\Omega(2U, 2N, 2V) = \int d\epsilon \Omega(U + \epsilon, N, V) \Omega(U - \epsilon, N, V). \quad (2.72)$$

As shown in Fig. 2.10, the integrand is a sharply peaked function around $\epsilon = 0$. We can therefore write

$$\Omega(U + \epsilon) \Omega(U - \epsilon) \approx [\Omega(U)]^2 \exp(-A\epsilon^2) \quad (2.73)$$

$$\Omega(2U) = \int d\epsilon [\Omega(U)]^2 \exp(-A\epsilon^2) = [\Omega(U)]^2 \sqrt{\pi/A}, \quad (2.74)$$

with A some constant characteristic of the width of the sharply peaked function. More generally, apart from irrelevant constants such as the factor $\sqrt{\pi/A}$ above,

$$\Omega(xU) = [\Omega(U)]^x. \quad (2.75)$$

This may be used to show that $k \ln \Omega$ is the only possible extensive function of Ω .

We look for an extensive function S such that

$$\begin{aligned} S(\Omega(xU, xN, xV)) &= xS(\Omega(U, N, V)) \Rightarrow \\ S(\Omega^x) &= xS(\Omega). \end{aligned}$$

Differentiating with respect to x gives

$$\begin{aligned} S'(\Omega^x) \frac{d}{dx} \Omega^x &= S(\Omega) \\ S'(\Omega^x) \Omega^x \ln \Omega &= \frac{1}{x} S(\Omega^x) \\ \frac{S'(\Omega^x)}{S(\Omega^x)} &= \frac{1}{\Omega^x \ln \Omega^x} \\ \frac{d}{d\Omega^x} \ln S(\Omega^x) &= \frac{d}{d\Omega^x} \ln(\ln \Omega^x) \\ S(\Omega^x) &= k \ln \Omega^x. \end{aligned}$$

So, we again find $S(\Omega) = k \ln \Omega$. Note that we have ignored the possibility that S may also depend explicitly on x . Taking this into account leads to $S(\Omega(xU, xN, xV), x) = k \ln \Omega(xU, xN, xV) + cx$, where c is some constant that may be used to fix a reference state for the entropy.

Problems

2-1. Volume of an n dimensional hypersphere. A hypersphere in n dimensions consists of all points $\{x_1, \dots, x_n\}$ for which $(\sum_{i=1}^n x_i^2) \leq R^2$. Show that the volume of this hypersphere, for even n , is given by

$$V_n = \frac{\pi^{n/2}}{(n/2)!} R^n$$

(Hint: first consider the unit sphere in n dimensional space. Use polar coordinates (r, θ) for the first two coordinates. For every point (r, θ) , there is a sphere in $n - 2$ dimensions with radius $\sqrt{1 - r^2}$. Let v_{n-2} be the volume of the unit sphere in $n - 2$ dimensions. Scale by the radius, and the volume of the sphere at a distance r from the origin is $v_{n-2} \times (1 - r^2)^{\frac{1}{2}(n-2)}$. Integrate with respect to r and θ (remember that the Jacobian of polar coordinates is r) to find the volume of the unit sphere in n dimensions. The result should be

$$v_n = \frac{2\pi}{n} v_{n-2}.$$

Use a well known limiting case to iteratively generate the volumes of unit spheres in even n dimensions.)

2-2. Stirling and other approximations to $N!$

a) We can write $\ln N!$ as $\sum_{n=1}^N \ln n$. Prove that $\ln N! \approx N \ln N - N$ or $N! \approx (N/e)^N$ (this is called Stirling's approximation).

2. ENERGY OF MACROSCOPIC SYSTEMS

b) Show that $N! = \int_0^\infty dx x^N e^{-x} = \int_0^\infty dx e^{-x+N \ln x}$.

c) Expand the function $f(x) = -x + N \ln x$ around its maximum, and show that a more precise approximation for $N!$ is $(N/e)^N \sqrt{2\pi N}$.

2-3. Classical number of states in an ideal gas. Starting from the classical expression for the energy of a collection of N ideal particles in a box, and using Eq. (2.5), derive the number of states $\Phi(U)$ with an energy equal of less than U in an ideal gas. Compare your result with the quantum mechanical result derived in Eq. (2.15). (Hint: for an ideal gas the Hamiltonian is simply the sum of kinetic energies $\mathcal{H} = \sum_i p_i^2/(2m)$, and each particle is restricted to the same volume V .)

2-4. Entropy of an ideal gas. Use Eq. (2.15) to prove Eq. (2.37). Discuss why it was important to include the quantum mechanical correction $1/N!$.

2-5. Pressure of an ideal gas. The energy of an ideal gas consisting of N particles in a box of volume V (see also Problem 1-5) is given by:

$$U = E_{n_1, \dots, n_{3N}} = \frac{h^2}{8mL^2}(n_1^2 + \dots + n_{3N}^2) = \frac{1}{V^{2/3}} \frac{h^2}{8m}(n_1^2 + \dots + n_{3N}^2).$$

Show that from this equation we can already calculate the pressure of an ideal gas:

$$P = \frac{2U}{3V},$$

without explicit knowledge of the entropy S . (Hint: remember that constant entropy S implies constant energy level n .)

2-6. Critical point of the van der Waals equation of state. Prove that the critical point of the van der Waals equation of state, Eq. (2.64), is given by $T_c = 8a/(27bR)$, $P_c = a/(27b^2)$ and $v_c = 3b$.

2-7. Virial coefficient of the van der Waals equation of state. Calculate the second virial coefficient B of the van der Waals equation of state. Compare with the experimental value for methane:

$$\frac{B}{v_c} = 0.430 - 0.886 \frac{T_c}{T} - 0.694 \left(\frac{T_c}{T} \right)^2.$$

2-8. Molar volume of methane. Calculate the molar volume of methane at 250 K and 10 MPa, both with the ideal gas equation and the van der Waals equation. Given: $T_c = 190.6$ K and $P_c = 4.604$ MPa. Experimentally: $v = 0.1376$ litre/mole.

Chapter 3

Thermodynamic functions and applications

In this chapter we will treat some thermodynamic applications of the ideas developed in the previous chapter.

3.1 Work and heat for reversible processes

As we have seen, the first law of thermodynamics states that the energy of a system may be increased by adding heat Q or by performing work w on the system,

$$\Delta U = Q + w. \quad (3.1)$$

In most experimental situations we do not have control over the heat or work, but rather control the pressure and/or the temperature. For these cases we will now introduce useful thermodynamic functions.

3.1.1 Isobaric processes: the enthalpy H

Suppose a process is taking place under constant external pressure P^{ext} . If the process is done reversibly, then the pressure of the system will always be equal to the external pressure,

$$P = P^{ext} = \text{const.} \quad (3.2)$$

This is called an isobaric process. For such a process it is useful to distinguish between volume work w_{vol} and other forms of work w' performed on the system. According to Eq. (2.57) then

$$w = w' + w_{vol} = w' - P\Delta V \quad (3.3)$$

The change in energy then is

$$\begin{aligned}\Delta U &= Q + w' - P\Delta V = Q + w' - \Delta(PV) \\ \Delta H &= \Delta(U + PV) = Q + w',\end{aligned}\tag{3.4}$$

where we have defined the enthalpy H ,

$$\boxed{H \equiv U + PV.}\tag{3.5}$$

Because U , P and V are all system properties, H is also a system property. For quasi-static isobaric processes, the enthalpy is a more useful thermodynamic quantity than the energy U : by tabulating H for different values of the system parameters, we are able to calculate $Q + w'$ for each process.

3.1.2 Isothermal processes: the free energy A

For an isothermal reversible process the added heat is given by

$$Q = T\Delta S = \Delta(TS).\tag{3.6}$$

The change in energy is therefore

$$\Delta U = \Delta(TS) + w \quad (\text{isothermal}).\tag{3.7}$$

For isothermal reversible processes, the work w done on the system is given by the difference in *free energy* A :

$$\Delta A = w \quad (\text{isothermal}),\tag{3.8}$$

where A is defined as

$$\boxed{A \equiv U - TS.}\tag{3.9}$$

The free energy is sometimes also denoted as F , especially in the chemical literature.

3.1.3 Isothermal isobaric processes: the free enthalpy G

For an isothermal isobaric process the added heat and volume work are given by, respectively,

$$Q = T\Delta S = \Delta(TS)\tag{3.10}$$

$$w_{vol} = -P\Delta V = -\Delta(PV).\tag{3.11}$$

The change in energy is therefore

$$\Delta U = \Delta(TS) - \Delta(PV) + w' \quad (\text{isothermal isobaric}).\tag{3.12}$$

For isothermal isobaric processes, the work w' done by other means is given by the difference in *free enthalpy* G :

$$\Delta G = w' \quad (\text{isothermal isobaric}), \quad (3.13)$$

where G is defined as

$$\boxed{G \equiv U - TS + PV.} \quad (3.14)$$

The free enthalpy is also known as the Gibbs free energy.

3.2 Specific heat

3.2.1 Definition of specific heat

The specific heat (or heat capacity) of a system is the amount of heat that must be added in order to raise the temperature of the system by one degree Kelvin. The exact amount of heat depends on whether the heat is added under constant volume (isochoric) or constant pressure (isobaric) conditions:

$$\text{isochoric process } q_V \equiv C_V dT \quad (3.15)$$

$$\text{isobaric process } q_P \equiv C_P dT. \quad (3.16)$$

The relation to the system properties is found by writing

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ (dU)_V &= \left(\frac{\partial U}{\partial T}\right)_V dT = q_V \end{aligned} \quad (3.17)$$

and hence

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V.} \quad (3.18)$$

Similarly

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \\ (dH)_P &= \left(\frac{\partial H}{\partial T}\right)_P dT \\ (dH)_P &= q_P, \end{aligned} \quad (3.19)$$

and hence

$$\boxed{C_P = \left(\frac{\partial H}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P.} \quad (3.20)$$

For the case of an ideal gas, the energy is given by $U = \frac{3}{2}Nk_B T = \frac{3}{2}nRT$, so

$$\left(\frac{\partial U}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V \quad (3.21)$$

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + \left(\frac{\partial(PV)}{\partial T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_V + nR, \quad (3.22)$$

which implies a simple relation between C_P and C_V :

$$C_P = C_V + nR \quad (\text{ideal gas}). \quad (3.23)$$

3.2.2 Specific heat of a harmonic crystal

We will now try to calculate the specific heat of a crystal of N identical spherical particles. In section 2.2.3 we have seen that the degeneracy of a harmonic crystal of energy $U = \hbar\omega(3N/2 + M)$ is given by¹

$$\Omega(M) = \frac{(M + 3N - 1)!}{M!(3N - 1)!}. \quad (3.24)$$

The entropy is now given by

$$\begin{aligned} S(M) &= k_B \ln \Omega \\ &= k_B(3N + M - 1) \ln(3N + M - 1) \\ &\quad - k_B(3N - 1) \ln(3N - 1) - k_B M \ln M. \end{aligned} \quad (3.25)$$

In theory we can then invert this and find $M = M(S)$, i.e. $U = \hbar\omega[3N/2 + M(S)]$. In this case it is more practical, however, to express S in terms of U and use

$$dS = \frac{1}{T}dU + \frac{P}{T}dV. \quad (3.26)$$

It is then an easy task (see Problem 3-1) to calculate T and $U(T)$, from which follows

$$C_V = 3Nk_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\hbar\omega/(k_B T)}}{(1 - e^{-\hbar\omega/(k_B T)})^2}. \quad (3.27)$$

A graph of Eq. (3.27) is given in Fig. 3.1. For temperatures $k_B T \gg \hbar\omega$, the heat

¹Note that we did not need to include a quantum symmetry factor $1/(N!)$, because the particles are bound to the lattice positions, and are therefore in principle distinguishable.

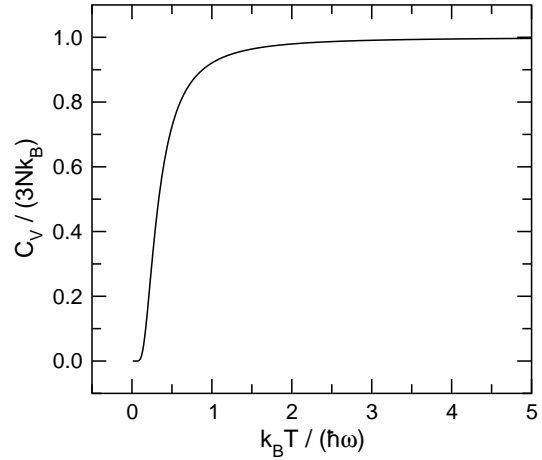


Figure 3.1: Heat capacity of the (quantum mechanical) harmonic crystal as a function of temperature. Note that $C_V \rightarrow 0$ as $T \rightarrow 0$.

capacity of a harmonic crystal is approximately $3Nk_B$, which agrees with the result in the classical limit. At low temperatures $k_B T \ll \hbar\omega$, however, $C_V(T) \rightarrow 0$. This surprising result is a consequence of our quantum mechanical treatment, in which the energy of the harmonic oscillators can only have discretized values.

3.3 Quasi-static adiabatic changes of an ideal gas

Suppose we quasi-statically (reversibly) compress or expand an ideal gas. Furthermore, we do not allow any heat to be exchanged with the surroundings, $q = 0$, i.e. we are studying an adiabatic process. Because the process is quasi-static, at each instant the energy increase or decrease is given by

$$dU = -PdV = -\frac{nRT}{V}dV. \quad (3.28)$$

On the other hand, for an ideal gas the energy is only a function of the temperature, $U = U(T)$, hence

$$dU = nc_V dT, \quad (3.29)$$

where we have defined c_V as the specific heat per mole molecules. Equating Eqs. (3.28) and (3.29) we find

$$\begin{aligned} \frac{dV}{V} &= -\frac{c_V}{R} \frac{dT}{T} \\ V &= \text{cst.} T^{-c_V/R} \\ PV &= nRT = \text{cst.} V^{-R/c_V} \\ PV^\gamma &= \text{cst.} \quad (\text{adiabatic}) \end{aligned} \quad (3.30)$$

$$\gamma = c_P/c_V. \quad (3.31)$$

γ is called the specific heat ratio. For an ideal gas, according to Eqs. (2.44) and (3.23), it is equal to 5/3. Note that $\gamma > 1$, so at any point (V_0, P_0) in a PV -diagram an adiabatic line going through (V_0, P_0) will have a larger (more negative) slope than an isothermal line going through (V_0, P_0) . In Problem 3-2 you are asked to calculate the work done on an ideal gas when it is quasi-statically and adiabatically compressed. A clever way to measure γ is described in Problem 3-3.

3.4 Entropy differences

3.4.1 Reversible processes

In section 2.7.2 we have seen that, at each point along the path of a reversible process, the entropy increase is

$$dS = \left(\frac{q}{T}\right)_{rev} \quad (\text{reversible}). \quad (3.32)$$

So, for a reversible processes from state A to B the change in entropy is

$$\text{adiabatic} \quad \Delta S = 0 \quad (3.33)$$

$$\text{isochoric} \quad \Delta S = \int \frac{C_V}{T} dT = C_V \ln \frac{T_B}{T_A} \quad (3.34)$$

$$\text{isobaric} \quad \Delta S = \int \frac{C_P}{T} dT = C_P \ln \frac{T_B}{T_A} \quad (3.35)$$

$$\text{isothermal} \quad \Delta S = \int \frac{q}{T} \quad (3.36)$$

$$\text{isothermal, ideal} \quad \Delta S = \int \frac{q}{T} = \int \frac{P}{T} dV = \int \frac{nR}{V} dV = nR \ln \frac{V_B}{V_A} = -nR \ln \frac{P_B}{P_A}. \quad (3.37)$$

In the second and third equation we have assumed that the specific heat is independent of temperature. The last equation is *only valid for an ideal gas*, where we have used $dU = q - PdV = 0$ (explain why!).

In Problems 3-4 and 3-5 you are asked to calculate the entropy increase in different combinations of reversible processes.

A reversible process may start and end in the same state point, forming a cycle in a $P - V$ diagram. When the cycle is formed by two isotherms and two adiabatics, it is called a Carnot process. In Problem 3-6 you are asked to calculate the efficiency of a Carnot process.

3.4.2 Irreversible processes

If we want to measure the entropy increase of an irreversible process, we need to construct an auxiliary reversible process from the same initial condition to the same final condition, and use Eq. (3.32) for that process.

For example, let an ideal gas expand at constant T against vacuum. Because we are dealing with an ideal gas $\Delta U = 0$ and because we are expanding against $P^{ext} = 0$ we have $w = 0$. So we conclude that $Q = 0$, i.e. heat is produced nor consumed in the process. However, we cannot conclude that $\Delta S = 0$. To calculate ΔS we expand the system reversibly and isothermal, in which case Eq. (3.37) applies: $\Delta S = nR \ln(V_B/V_A)$.

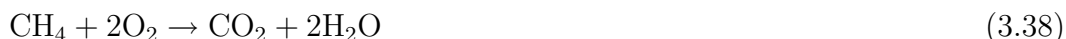
In Problems 3-7 and 3-8 we will consider the case of two bodies at different temperature coming into thermal contact, leading to irreversible flow of heat from the hotter body to the cooler body. You will discover that the entropy increase is maximal when the two bodies have reached the same temperature. This will be the topic of chapter 4.

3.5 Reference states

3.5.1 Chemical reactions and reference state

Until now we have talked about energy and enthalpy differences only. The existence of a reference state in which $U = 0$ or $H = 0$ was, in fact, irrelevant. In practice, one often chooses a reference state for H because it is easier to do experiments under constant pressure conditions.

One should beware, however, that one is not entirely free in choosing reference states when chemical reactions occur in the system. For example when burning methane



under isobaric conditions the enthalpy increase per mole is, by definition,

$$\Delta h = q_P. \quad (3.39)$$

Looking at the reaction formula, one would guess that the heat produced by this reaction is

$$q_P = h_{\text{CO}_2} + 2h_{\text{H}_2\text{O}} - h_{\text{CH}_4} - 2h_{\text{O}_2}, \quad (3.40)$$

in which case the enthalpy of the water molecules is

$$h_{\text{H}_2\text{O}} = \frac{1}{2} (h_{\text{CH}_4} + 2h_{\text{O}_2} - h_{\text{CO}_2} + q_P). \quad (3.41)$$

What this equation shows is that one cannot choose an arbitrary reference state for each component independently: the reference enthalpy of the water molecules is related to the reference enthalpies of the other molecules. Only for an independent set of substances can reference states be chosen at will.

3.5.2 Standard enthalpy and enthalpy of formation

To overcome difficulties in communicating experimental results, a convention for the standard enthalpy has been established. *The standard enthalpy is that enthalpy for which the elements in stable form at standard reference state have enthalpy equal to zero.* The standard reference state is defined as $T^0 = 298.15$ K and $P^0 = 1$ atm., where 1 atmosphere = 1.01325×10^5 Pa.

The notation for a chemical reaction, such as the one used in the previous section, is



$$\sum_i \nu_i A_i = 0. \quad (3.43)$$

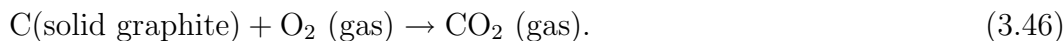
Using the stoichiometric coefficients ν_i , we can express the reaction enthalpy or change of specific heat as

$$\Delta h_r = \sum_i \nu_i h_i \quad (3.44)$$

$$\Delta c_{pr} = \sum_i \nu_i c_{pi}. \quad (3.45)$$

This is easily generalized to changes in other properties. Note that Δh_r is the reaction enthalpy per mole at the standard reference state, i.e. at $T^0 = 298.15$ K and $P^0 = 1$ atm. In order to calculate the reaction enthalpy at another temperature, it is useful to know the change of specific heat at intermediate temperatures, see Problem 3-9.

Finally, it is useful to know the enthalpy of formation Δh_f of a certain substance. *The enthalpy of formation of a substance is the reaction enthalpy of a reaction in which the particular substance is formed from its elements.* Usually tables contain Δh_f^0 , i.e. the enthalpy of formation at the standard state. For example, the standard enthalpy of formation of carbon dioxide would be the reaction enthalpy of the following reaction under standard conditions:



3.5.3 Standard entropy, absolute entropy and the third law of thermodynamics

Just as in the case of energy and enthalpy, until now we have focused on entropy differences. As long as no chemical reactions take place we can choose for each substance an arbitrary reference state. If chemical reactions do occur, we need to choose the reference states in an internally consistent manner. The simplest case is, again, by choosing the reference states for the (stable) elements. The *standard entropy* is defined by putting the entropies of the elements at standard conditions ($T^0 = 298.15$ K and $P^0 = 1$ atm.) equal to zero.

Another choice for the reference states of the elements leads to the so-called *absolute entropy*. Experimentally it is found that for all processes

$$\lim_{T \rightarrow 0} \Delta S = 0. \quad (3.47)$$

In words: near absolute zero temperature, the entropy change of any process is nearly zero. This is verified to such a good extent that it is sometimes referred to as the third law of thermodynamics. Moreover, using statistical thermodynamics it can be made very plausible. If we now set the entropy of the elements at 0 K equal to 0, Eq. (3.47) predicts that also all other substances at 0 K have an entropy equal to 0. This defines the absolute entropy. For all elements and substances the absolute entropy at a temperature T can be measured through

$$S(T) = \int_0^T \left(\frac{q}{T} \right)_{rev} + \frac{\Delta H_{tr}}{T_{tr}}. \quad (3.48)$$

The last term accounts for contributions from any phase transition that takes place between 0 K and T .

3.6 Two phase equilibrium

The (free) enthalpy function plays an important role in the study of two phase equilibrium. Suppose have a closed system with movable and heat conducting walls containing some vapour. We now slowly and isothermally decrease the volume of the system, see Fig. 3.2. At a certain pressure, P_{coex} a drop of liquid will appear. Upon further compression the system pressure will remain equal to P_{coex} , but the fraction of liquid will increase. In other words, we can let some vapour condense at constant temperature and pressure. In this process, according to Eq. (3.13),

$$\Delta G = w' = 0. \quad (3.49)$$

If we define g^l as the free enthalpy per mole of liquid, g^v the free enthalpy per mole of vapour, dn^l the increase of moles of liquid, and equivalently for the vapour dn^v ,

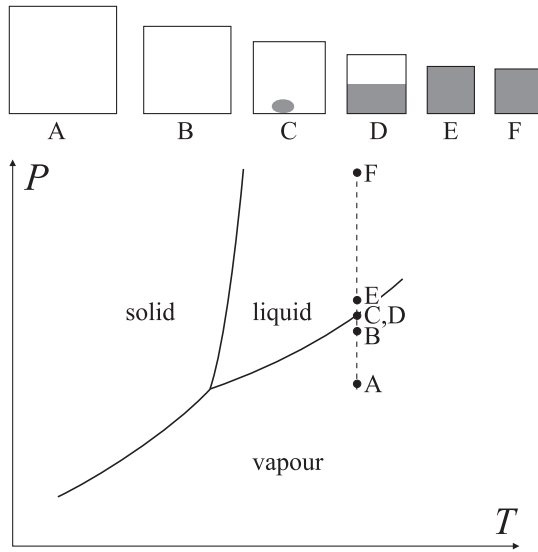


Figure 3.2: Isothermal vapour-liquid phase transition. We slowly and isothermally compress (decrease the volume of) a system containing a vapour (A,B). At a certain pressure P_{coex} a drop of liquid will appear (C). Upon further compression the system pressure will remain equal to P_{coex} , but the fraction of liquid will increase (D) until the entire system is filled with liquid. Further compression of the system will result in a rapid rise of the pressure (E,F).

we have

$$\Delta G = g^l dn^l + g^v dn^v = (g^l - g^v) dn^l = 0 \quad (3.50)$$

$$\Rightarrow g^l = g^v, \quad (3.51)$$

where we have used the law of conservation of mass in a closed system. So we find that for liquid-vapour coexistence the free enthalpy per mole of liquid must be equal to the free enthalpy per mole of vapour. For both the liquid and the vapour the free enthalpy per mole is some function of pressure and temperature, $g^v = g^v(P, T)$ and $g^l = g^l(P, T)$. The intersection of these two surfaces yields a line in the $P - T$ plane. In other words, liquid-vapour coexistence is only possible for certain values $P_{coex}(T)$ in the $P - T$ plane, see Fig. 3.2.

We can estimate the shape of this line by analysing an infinitesimal change of temperature $T \mapsto T + dT$. This will be accompanied by an infinitesimal change of free enthalpy per mole,

$$\begin{aligned} g^l &\mapsto g^l + dg^l \\ g^v &\mapsto g^v + dg^v. \end{aligned}$$

Because $g^l = g^v$ at each temperature, the differentials must also be equal:

$$\begin{aligned} dg^l &= dg^v \\ \left(\frac{\partial g^l}{\partial T}\right)_P dT + \left(\frac{\partial g^l}{\partial P}\right)_T dP &= \left(\frac{\partial g^v}{\partial T}\right)_P dT + \left(\frac{\partial g^v}{\partial P}\right)_T dP. \end{aligned} \quad (3.52)$$

In the above equation we have used the chain rule for differentiation. What are the $(\partial g/\partial T)$ and $(\partial g/\partial P)$ terms? We find the answer by using the definition of G ,

Eq. (3.14), and the fundamental equation of thermodynamics, Eq. (2.34), together yielding

$$\boxed{dG = -SdT + VdP}, \quad (3.53)$$

or in molar quantities $s = S/n$ and $v = V/n$,

$$dg = -sdT + vdP. \quad (3.54)$$

From this result we read

$$\left(\frac{\partial g^l}{\partial T}\right)_P = -s^l, \quad \left(\frac{\partial g^l}{\partial P}\right)_T = v^l, \quad (3.55)$$

and equivalently for the vapour phase. We now continue with Eq. (3.52):

$$\begin{aligned} -s^l dT + v^l dP &= -s^v dT + v^v dP \\ \Rightarrow \left(\frac{dP}{dT}\right)_{coex} &= \frac{s^v - s^l}{v^v - v^l}. \end{aligned} \quad (3.56)$$

This result is called the Clausius relation. Because $g = h - Ts$, we can write the numerator $s^v - s^l$ as

$$s^v - s^l = \frac{1}{T}(h^v - h^l) \equiv \frac{\Delta h^{vap}}{T}, \quad (3.57)$$

Δh^{vap} is the enthalpy increase associated with evaporating one mole of liquid. Far away from the critical point the molar volume of the vapour phase is usually much larger than the molar volume of the liquid phase, and can be approximated by the ideal gas equation of state, i.e.

$$v^v - v^l \approx v^v = \frac{RT}{P}. \quad (3.58)$$

The Clausius relation can then be rewritten as

$$\begin{aligned} \left(\frac{dP}{dT}\right)_{coex} &= \frac{\Delta h^{vap}}{R} \frac{P}{T^2} \\ \frac{d \ln P}{dT} &= -\frac{d}{dT} \frac{\Delta h^{vap}}{RT} \\ P_{coex}(T) &= P_\infty \exp\left(-\frac{\Delta h^{vap}}{RT}\right), \end{aligned} \quad (3.59)$$

which is called the Clapeyron equation. Note that we have assumed the the evaporation enthalpy is approximately independent of temperature.

3.7 Maxwell relations

Suppose a function $F(x, y)$ depends on x and y , its differential form then is

$$dF(x, y) = A(x, y)dx + B(x, y)dy, \quad (3.60)$$

with A and B functions depending on x and y . The partial derivatives of A and B are not independent, but are related by the interchangeability of differentiation:

$$\frac{\partial A}{\partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial B}{\partial x}. \quad (3.61)$$

Similarly, writing down differential forms of the thermodynamic functions we can find some quite surprising relations between different thermodynamic properties. Let us first write down these differentials:

$$dU = TdS - PdV \quad (3.62)$$

$$dH = TdS + VdP \quad (3.63)$$

$$dA = -SdT - PdV \quad (3.64)$$

$$dG = -SdT + VdP. \quad (3.65)$$

From these equations we can read the *Maxwell relations*

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad (3.66)$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad (3.67)$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V} \quad (3.68)$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}. \quad (3.69)$$

The Maxwell relations can be quite useful. For example, let us reconsider the two-phase equilibrium of section 3.6. Let some liquid evaporate, at constant temperature T , by means of volume work, i.e. by slightly increasing the volume V of the system. The change of entropy with volume then is given by

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{(s^l - s^v)dn^v}{(v^v - v^l)dn^v} = \frac{s^v - s^l}{v^v - v^l}. \quad (3.70)$$

The Maxwell relation Eq. (3.68) tells us that this is the same as the increase in pressure if we slightly raise the temperature by supplying heat at constant volume V . Because at coexistence the pressure is a function of the temperature only, we have

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{dP}{dT}. \quad (3.71)$$

Combining these equations we again find the Clausius relation

$$\frac{dP}{dT} = \frac{s^v - s^l}{v^v - v^l}. \quad (3.72)$$

Another example. Suppose we somehow know the entropy (per mole) as a function of temperature at some reference pressure, $s^* = s^*(P_0, T)$. Then the entropy at another pressure is given, in principle, by

$$s(P, T) = s^*(P_0, T) + \int_{P_0}^P dP \left(\frac{\partial s}{\partial P}\right)_T. \quad (3.73)$$

The entropy is not an easily measurable property, but the temperature and volume are. So, making use of Eq. (3.69), we rewrite this equation to

$$s(P, T) = s^*(P_0, T) - \int_{P_0}^P dP \left(\frac{\partial v}{\partial T}\right)_P. \quad (3.74)$$

For an ideal gas $v = RT/P$, so

$$s(P, T) = s^*(P_0, T) - \int_{P_0}^P dP \frac{R}{P} = s^*(P_0, T) - R \ln \left(\frac{P}{P_0}\right) \quad (\text{ideal gas}). \quad (3.75)$$

In Problem 3-10 you are asked to calculate $s = s(P, T)$ for a van der Waals gas. In Problem 3-11 you will need Maxwell relations to derive the so-called first and second energy relations.

3.8 Open systems: the chemical potential and the Gibbs-Duhem relation

Up to this point we have always considered closed systems, where the number of molecules (or atoms in case of chemical reactions) is considered to be constant. We will now also consider open systems, where molecules are allowed to enter from, or escape to, an external reservoir. If we denote the number of molecules (or alternatively moles) in the system as N , we can write the extensive thermodynamic

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properties U , S , and V in terms of intensive thermodynamic properties u , v , and s , which are the energy, entropy and volume *per molecule* (or per mole). Then

$$U = Nu \rightarrow dU = Ndu + udN \quad (3.76)$$

$$S = Ns \rightarrow dS = Nds + sdN \quad (3.77)$$

$$V = Nv \rightarrow dV = Ndv + vdN. \quad (3.78)$$

From these equations we find

$$\begin{aligned} dU &= N(Tds - Pdv) + udN \\ &= TdS - TsdN - PdV + PvdN + udN \\ &= TdS - PdV + (u - Ts + Pv) dN \\ &\equiv TdS - PdV + \mu dN. \end{aligned} \quad (3.79)$$

In the last line we have defined the chemical potential μ . Comparing with Eq. (3.14), we see that the chemical potential is nothing but the Gibbs free energy per molecule (or per mole):

$$\boxed{\mu = g = G/N = u - Ts + Pv.} \quad (3.80)$$

Differentials of the other thermodynamic functions are given similarly by

$$dH = TdS + VdP + \mu dN \quad (3.81)$$

$$dA = -SdT - PdV + \mu dN \quad (3.82)$$

$$dG = -SdT + VdP + \mu dN. \quad (3.83)$$

New Maxwell relations can easily be derived from these equations (Problem 3-12). We also see that the chemical potential can be calculated as

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial H}{\partial N} \right)_{S,P} = \left(\frac{\partial A}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{T,P}. \quad (3.84)$$

Writing Eq. (3.80) as $dG = d(N\mu) = Nd\mu + \mu dN$ and comparing with Eq. (3.83) we find an interesting relation:

$$\boxed{SdT - VdP + Nd\mu = 0.} \quad (3.85)$$

This important results is called the Gibbs-Duhem relation. It states that never three intensive variables (T , P , and μ) can be independent.

3.9 The chemical potential and fugacity

In section 3.6 we have seen that two phases I and II of a pure compound can only coexist if $g^I = g^{II}$, which we now write as $\mu^I = \mu^{II}$. This is the first example of an equilibrium condition, of which we will derive more in the next chapter. It is therefore useful to study the dependence of μ on P and T .

3.9.1 μ as a function of T

The easiest way to calculate μ as a function of T is to use

$$\mu(P, T) = h(P, T) - Ts(P, T). \quad (3.86)$$

Usually h and s are tabulated at standard conditions $T^0 = 298.15$ K and $P^0 = 1$ atm. (see sections 3.5.2 and 3.5.3). We can then calculate h and s at an arbitrary temperature T and at $P = P^0$ using

$$h(P^0, T) = h^0 + \int_{T^0}^T c_P dT' \quad (3.87)$$

$$s(P^0, T) = s^0 + \int_{T^0}^T \frac{c_P}{T'} dT'. \quad (3.88)$$

To calculate these integrals, we need c_P at given pressure as a function of T . Often it is sufficiently accurate to assume that c_P is independent of temperature, in which case

$$\mu(P^0, T) = \{h^0 - Ts^0\} + c_P (T - T^0) - c_P T \ln \left(\frac{T}{T^0} \right). \quad (3.89)$$

Note that $h^0 - Ts^0$ is *not* equal to $\mu^0 \equiv \mu(P^0, T^0)$. In Problem 3-15 you are asked to calculate coexistence properties of graphite and diamond.

3.9.2 μ as a function of P

Let us first focus on systems in which the pressure is so low that it behaves as an ideal gas. In that case we can write

$$\left(\frac{\partial \mu}{\partial P} \right)_T = v = \frac{RT}{P} \quad (3.90)$$

$$\mu(P, T) = \mu^*(T) + RT \ln(P/P^0). \quad (3.91)$$

In the first line we have used the Gibbs-Duhem relation Eq. (3.85). The expression $\mu^*(T)$ in principle depends on our choice of reference pressure P^0 . Usually the standard pressure is used, in which case $\mu^*(T)$ is the chemical potential of an ideal

gas at one atmosphere. $\mu^*(T)$ can be determined experimentally from a real gas by measuring μ at given T as a function of P , and plotting the result against $RT \ln P$. At low enough pressure the gas behaves ideal and the plot is approximately a straight line. Extrapolating to $P^0 = 1$ atm. yields the value of $\mu^*(T)$. Note that the actual $\mu(P^0, T)$ equals $\mu^*(T)$ only when the system behaves like an ideal gas at given temperature and at $P^0 = 1$ atm.

For an *arbitrary* system, be it a gas, liquid, or solid, we define the fugacity coefficient ϕ and the fugacity f by

$$\begin{aligned}\mu(P, T) &= \mu^*(T) + RT \ln(P/P^0) + RT \ln \phi \\ &= \mu^*(T) + RT \ln f(P/P^0, T).\end{aligned}\quad (3.92)$$

So $RT \ln \phi$ is the correction to ideal gas behaviour. In the limit $P \rightarrow 0$, ϕ will go to 1. The pressure dependence of ϕ is given by

$$\begin{aligned}\left(\frac{\partial}{\partial P} RT \ln \phi\right)_T &= v - \frac{RT}{P} \\ RT \ln \phi &= \int_0^P \left(v - \frac{RT}{P'}\right) dP'.\end{aligned}\quad (3.93)$$

This formula is only useful if one knows v as a function of P and T . Usually one knows P as a function of v and T , in which case the integral in Eq. (3.93) is difficult to evaluate. For these cases, one can derive other formulas, which we will not go into.

Now that we know μ as a function of its characteristic variables (P and T) we can easily derive other thermodynamic properties. In summary (prove these yourself!):

$$\mu(P, T) = \mu^*(T) + RT \ln P + \int_0^P \left\{v - \frac{RT}{P'}\right\} dP' \quad (3.94)$$

$$s(P, T) = s^*(T) - R \ln P - \int_0^P \left\{\left(\frac{\partial v}{\partial T}\right)_{P'} - \frac{R}{P'}\right\} dP' \quad (3.95)$$

$$h(P, T) = h^*(T) + \int_0^P \left\{v - T \left(\frac{\partial v}{\partial T}\right)_{P'}\right\} dP' \quad (3.96)$$

$$c_P(P, T) = c_P^*(T) - T \int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_{P'} dP'. \quad (3.97)$$

Note that the integrals, when applied to an ideal gas, yield zero.

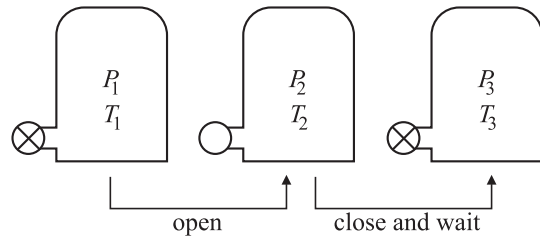


Figure 3.3: Experiment to measure the specific heat ratio.

Problems

3-1. Heat capacity of the harmonic crystal. Calculate the temperature T and then the energy $U(T)$ of the harmonic crystal. Then prove Eq. (3.27).

3-2. Work done by quasi-static adiabatic compression. An ideal gas is compressed quasi-statically and adiabatically from a state (V_1, P_1) to a state (V_2, P_2) . Show that the work done on the system is

$$w = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}.$$

3-3. Measurement of the specific heat ratio of a dilute gas. Consider the experimental setup in Fig. 3.3. An amount of gas is held in a flask at a pressure P_1 slightly higher than the pressure P_0 of the surrounding environment. The flask's walls can conduct heat, so the temperature of the gas inside the flask equals the temperature of the surrounding environment, $T_1 = T_0$. At a given moment we open the valve for a few seconds to let some gas escape until the pressure inside equals the outside pressure, $P_2 = P_0$. We notice that the temperature has dropped in the process, $T_2 < T_1$. After closing the valve, the temperature slowly increases again, until $T_3 = T_0$. We then measure a pressure P_3 .

Express $\gamma = C_p/C_v$ in terms of P_1 , P_2 , and P_3 .

(Hint: the expansion of the gas can be considered to be an adiabatic process. Define the system as the amount of gas that *eventually* remains in the flask.)

3-4. Entropy and heat. An ideal gas undergoes a process from (P_1, V_1) to (P_2, V_2) . We consider two different processes:

A. Reversibly and isothermally at T_1 until the end volume, and then reversibly and isochorically to the end state.

B. Reversibly and isochorically to T_2 , and then reversibly and isothermally to the end state.

Draw both processes in a $P - V$ diagram. Calculate the total heat added to the system $Q = \int q$, and the entropy increase $\Delta S = \int (q/T)$ for both processes. Conclusion?

3-5. Entropy in a reversible process. An ideal gas is expanded from (T_1, V_1) to (T_1, V_2) . Calculate ΔS for the following two processes:

A. A reversible isothermal expansion.

B. A reversible isochoric process followed by a reversible isobaric expansion.

Conclusion?

3-6. Carnot processes. A Carnot process is a reversible cycling process between two isotherms and two adiabatics. Suppose we have a work delivering Carnot process (i.e. w is negative) using an ideal gas between temperatures T_h and T_l . We denote the total amount of heat delivered (per cycle) at the high and low isotherm by Q_h and Q_l , respectively (note that a negative Q means the heat is flowing out of the system). We define the efficiency as

$$\epsilon = -w/Q_h.$$

a) Draw the process in a $P - V$ diagram and indicate the direction of the process.

b) Calculate Q_h/Q_l .

c) Calculate ϵ .

3-7. Entropy in an irreversible process. In an isolated system we have two copper blocks of equal mass and equal volume, with unequal temperatures T_A and T_B , separated by a rigid, thermally insulating wall. We now make the wall thermally conducting. An irreversible process will take place from (T_A, V) , (T_B, V) to (T'_A, V) , (T'_B, V) . Using conservation of energy, express T'_B in terms of (T_A, T_B, T'_A) . Calculate ΔS for this irreversible process. For what value of T'_A is ΔS maximal? You may assume that the specific heat C_V is independent of temperature.

3-8. Temperature dependent specific heat. Suppose that in the above case the specific heat depends on temperature, as

$$C_V = A + BT$$

where $A = 8 \text{ J/K}$ and $B = 2 \times 10^{-2} \text{ J/K}^2$. If the two blocks are initially at $T_A = 400 \text{ K}$ and $T_B = 200 \text{ K}$, then what is the final temperature and what is the total change in entropy?

3-9. Reaction enthalpy at miscellaneous temperature. Prove that the reaction enthalpy at temperature T and standard pressure $P^0 = 1 \text{ atm}$. is given by

$$\Delta h_r(T, P^0) = \Delta h_r(T^0 \text{ K}, P^0) + \int_{T^0}^T dT' \Delta c_{pr}(T').$$

What if phase transitions occur between $T^0 = 298.15$ K and T ?

3-10. Entropy of a van der Waals gas. Using the van der Waals equation of state Eq. (2.64), calculate the molar entropy as a function of pressure and temperature $s = s(P, T)$. You may assume that the entropy $s^*(P_0, T)$ at some reference pressure P_0 is known.

3-11. First and second energy equations. Using the Maxwell relations, derive the first and second energy equations (assume N is constant everywhere):

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T \left(\frac{\partial P}{\partial T}\right)_V - P \\ \left(\frac{\partial U}{\partial P}\right)_T &= -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T. \end{aligned}$$

These equations are very useful, because if we know the equation of state of a system (i.e. the relation between P , V , and T), we can use these equations to gain information about the internal energy U of that system.

3-12. Maxwell relation involving N . Write down the Maxwell relation for the following partial derivative:

$$\left(\frac{\partial V}{\partial N}\right)_{T,P}.$$

3-13. The Maxwell construction. In section 2.8 we have introduced the Maxwell construction to find the vapour pressure (or P_{coex}) at a certain temperature. This construction may be stated mathematically as

$$P_{coex}(T) (v^v - v^l) = \int_{v^l}^{v^v} P(v, T) dv,$$

where v^v and v^l are the vapour and liquid molar volumes at coexistence. Give a proof of this construction.

3-14. Equation of state. For a certain compound we know that

$$\begin{aligned} u(T, v) &= f_1(T) - a/v \\ s(T, v) &= f_2(T) + R \ln(v - b), \end{aligned}$$

where a and b are constants. Derive the equation of state $P = P(T, v)$.

3-15. Coexistence of graphite and diamond. Graphite and diamond are two different phases of carbon. We now give the following quantities at standard conditions ($T^0 = 298.15$ K and $P^0 = 1$ atm.):

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	s^0	μ^0	ρ
graphite	5.694 J/mol/K	-1698 J/mol	2.22 g/cm ³
diamond	2.439 J/mol/K	1167 J/mol	3.15 g/cm ³

ρ is the mass density. You may assume that the density and entropy are independent of temperature and pressure.

- At which temperature do diamond and graphite coexist at $P^0 = 1$ atm.?
- At which pressure do diamond and graphite coexist at $T = 2000$ K? (Hint: What is the slope of the phase coexistence line $P_{coex}(T)$?)

Chapter 4

Second law of thermodynamics, equilibrium, and stability

4.1 The second law of thermodynamics

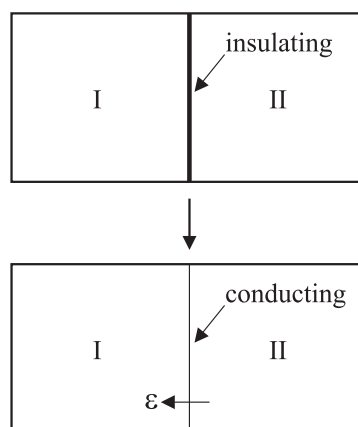
Irreversible processes take place after an internal constraint has been removed. By the very nature of a constraint, the number of accessible states must increase or remain the same,

$$\Omega^c \rightarrow \Omega^u \geq \Omega^c. \quad (4.1)$$

An example will make things clearer.

Suppose we have an adiabatically sealed system, as in Fig. 4.1. The system is composed of two compartments, separated from each other by an insulating wall. The insulating wall is an internal constraint, preventing energy to flow from compartment I to compartment II or vice versa. With each state in compartment I we can combine one state in compartment II. The total number of possible states in

Figure 4.1: Example of removing an internal constraint. An adiabatically sealed system consists of two compartments I and II, separated by an insulating wall (*top*). The wall constrains the energy in both compartments. As soon as the wall is made conducting (*bottom*) energy can flow freely from one compartment to the other.



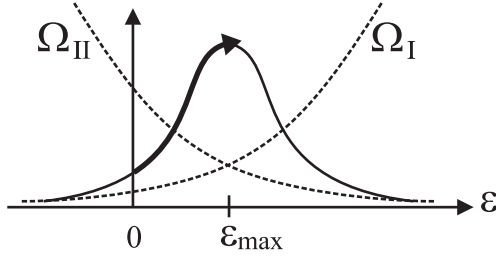


Figure 4.2: Statistical meaning of the second law of thermodynamics. After removing the internal constraint ($\epsilon = 0$), the system is free to partition its energy over the available compartments. An overwhelmingly large fraction of all possible states will be in the neighbourhood of $\epsilon = \epsilon_{max}$. The system will therefore evolve most likely (arrow) to a state in which $\epsilon = \epsilon_{max}$.

this constrained system is therefore

$$\Omega^c = \Omega_I(U_I)\Omega_{II}(U_{II}). \quad (4.2)$$

If we now suddenly remove the internal constraint, i.e., we make the insulating wall conducting, energy can be exchanged between the two systems. The total number of states in the unconstrained system is now given by a sum, or for the continuous case an integral, over all possible values for the energy exchange ϵ :

$$\Omega^u = \int d\epsilon \Omega_I(U_I + \epsilon)\Omega_{II}(U_{II} - \epsilon). \quad (4.3)$$

Note that $\Omega_I(U_I + \epsilon)$ is a fast increasing function of ϵ and $\Omega_{II}(U_{II} - \epsilon)$ a fast decreasing function of ϵ (explain why?). The integrand in Eq. (4.3) is therefore a sharply peaked function around some maximum $\epsilon = \epsilon_{max}$, see Fig. 4.2. An overwhelmingly large fraction of all possible states will be in the neighbourhood of ϵ_{max} , so the system is most likely to evolve to this value of ϵ (arrow in Fig. 4.2).

We can approximate the narrow distribution of $\Omega_I(U_I + \epsilon)\Omega_{II}(U_{II} - \epsilon)$ as a Gaussian centered around $\epsilon = \epsilon_{max}$:

$$\Omega_I(U_I + \epsilon)\Omega_{II}(U_{II} - \epsilon) \approx \Omega_I(U_I + \epsilon_{max})\Omega_{II}(U - \epsilon_{max}) \exp\{-c(\epsilon - \epsilon_{max})^2\} \quad (4.4)$$

The entropy after removing the internal constraint now reads

$$\begin{aligned} S^u &= k_B \ln \Omega_I(U_I + \epsilon_{max}) + k_B \ln \Omega_{II}(U_{II} - \epsilon_{max}) \\ &\quad + k_B \ln \int d\epsilon \exp\{-c(\epsilon - \epsilon_{max})^2\}. \end{aligned} \quad (4.5)$$

The last factor represents fluctuations around the average. It is very small compared to the other terms (as we will show in chapter 7), and will be neglected. So the entropy before and after removing the internal constraint is given by

$$S^c = k_B \ln \Omega_I(U_I) + k_B \ln \Omega_{II}(U_{II}) \quad (4.6)$$

$$S^u = k_B \ln \Omega_I(U_I + \epsilon_{max}) + k_B \ln \Omega_{II}(U_{II} - \epsilon_{max}). \quad (4.7)$$

Several interesting conclusions can be drawn on the basis of these last two equations.

1. Neglecting the fluctuations is equivalent to the thought experiment in which the system is split into two systems (separated by an insulating wall), one of entropy $k_B \ln \Omega_I(U_I + \epsilon_{max})$ and one of entropy $k_B \ln \Omega_{II}(U_{II} - \epsilon_{max})$. This is similar to the statement that the full distribution $\Omega_I(U_I - \epsilon)\Omega_{II}(U_{II} + \epsilon)$, for all practical purposes, is well represented by only its maximum.
2. Because the maximum $\Omega_I(U_I + \epsilon_{max})\Omega_{II}(U_{II} - \epsilon_{max})$ is, by definition, larger or equal to the constrained case $\Omega_I(U_I)\Omega_{II}(U_{II})$, we have $S^u \geq S^c$. In general

$$\boxed{(\Delta S)_{\text{adiab,closed}} \geq 0.} \quad (4.8)$$

This is the second law of thermodynamics. It states that the total entropy in an adiabatically sealed, closed system increases or remains the same if an internal constraint is removed.

3. After removing the internal constraint, given the remaining internal constraints, energy and mass will redistribute. This process will stop in an equilibrium state where the entropy is maximal (we emphasise again: given the remaining internal constraints). Mathematically this is expressed as

$$\begin{aligned} \left. \frac{d}{d\epsilon} \Omega_I(U_I + \epsilon)\Omega_{II}(U_{II} - \epsilon) \right|_{\epsilon=\epsilon_{max}} &= 0 \\ \Omega'_I(U_I + \epsilon_{max})\Omega_{II}(U_{II} - \epsilon_{max}) \frac{d(U_I + \epsilon)}{d\epsilon} + \\ \Omega_I(U_I + \epsilon_{max})\Omega'_{II}(U_{II} - \epsilon_{max}) \frac{d(U_{II} - \epsilon)}{d\epsilon} &= 0 \\ \frac{\Omega'_I(U_I + \epsilon_{max})}{\Omega_I(U_I + \epsilon_{max})} - \frac{\Omega'_{II}(U_{II} - \epsilon_{max})}{\Omega_{II}(U_{II} - \epsilon_{max})} &= 0 \\ (\ln \Omega_I)'|_{U_I + \epsilon_{max}} - (\ln \Omega_{II})'|_{U_{II} - \epsilon_{max}} &= 0, \end{aligned} \quad (4.9)$$

where a prime (') means taking the derivative of the function with respect to its argument. Using the definition $1/T = (\partial S / \partial U)_{V,N}$, we recognise

$$T_I|_{U_I + \epsilon_{max}} = T_{II}|_{U_{II} - \epsilon_{max}}. \quad (4.10)$$

Thus we have proved that the entropy is maximal when the temperature in both systems is equal. In the next section we will give a more traditional thermodynamic derivation.

It should be noted that the meaning of internal constraint is very broad. In fact, every non-quasistatic process can be described as taking away an internal constraint.

4.2 Equilibrium

So, the second law of thermodynamics says that the entropy is maximal in equilibrium, given the possible constraints. Can we predict more with this?

4.2.1 Homogeneous phase

Suppose we have an adiabatically sealed macroscopic system consisting of one homogeneous phase, say a liquid, in equilibrium. The system contains N particles, has a volume V and a total energy U . We can now perform the thought-experiment of dividing up the volume into $A+1$ parts labelled $0, \dots, A$. These parts are smaller than the original volume, but still macroscopically large. In principle we can redistribute the particles and energy in anyway we want. We call a particular redistribution a *trial state*. Because the entropy is maximum in our original state, for any trial state sufficiently close to our original state we must have

$$S^{trial} - S = dS^{trial} = 0. \quad (4.11)$$

Because the system is adiabatically sealed and closed we also have

$$\sum_{\alpha=0}^A dU^\alpha = 0 \quad \rightarrow \quad dU^0 = - \sum_{\alpha=1}^A dU^\alpha \quad (4.12)$$

$$\sum_{\alpha=0}^A dN^\alpha = 0 \quad \rightarrow \quad dN^0 = - \sum_{\alpha=1}^A dN^\alpha. \quad (4.13)$$

Because of the additivity of entropy, we can now rewrite dS^{trial} as

$$\begin{aligned} dS^{trial} &= \sum_{\alpha=0}^A dS^\alpha = \sum_{\alpha=0}^A \left\{ \frac{1}{T^\alpha} dU^\alpha - \frac{\mu^\alpha}{T^\alpha} dN^\alpha \right\} \\ &= \sum_{\alpha=1}^A \left\{ \left(\frac{1}{T^\alpha} - \frac{1}{T^0} \right) dU^\alpha - \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^0}{T^0} \right) dN^\alpha \right\} \\ &= 0. \end{aligned} \quad (4.14)$$

This must be valid for *any* choice of dU^α and dN^α . We must therefore conclude that

$$\frac{1}{T^\alpha} = \frac{1}{T^0}, \quad \frac{\mu^\alpha}{T^\alpha} = \frac{\mu^0}{T^0}. \quad (4.15)$$

So the temperature and chemical potential must be the same everywhere in the system if it is in equilibrium. This automatically implies that the pressure P is also the same everywhere.

The above discussion is valid as long as there are no external fields. In Problem 4-1 we will consider the case where an external field is present.

4.2.2 Two phase system, one component

The above arguments apply equally well to a system containing two phases, say a liquid and a vapour. The equilibrium conditions for liquid-vapour coexistence are therefore

$$T^l = T^v = T \quad (4.16)$$

$$P^l = P^v = P \quad (4.17)$$

$$\mu^l = \mu^v = \mu. \quad (4.18)$$

Often there is an expression for the chemical potential $\mu^l(P, T)$ of the liquid phase and $\mu^v(P, T)$ of the vapour phase. Equating these expressions learns us at which temperatures and pressures phase coexistence is possible. In fact, we have already used this in section 3.6 to derive the Clapeyron equation (note that $g = G/N = \mu$).

4.2.3 Two phase system, two components

The same argument also applies to a system containing two phases of two components, say a binary liquid of components A and B, coexisting with a binary vapour of components A and B. The conditions for coexistence are

$$T^l = T^v \quad (4.19)$$

$$P^l = P^v \quad (4.20)$$

$$\mu_A^l = \mu_A^v \quad (4.21)$$

$$\mu_B^l = \mu_B^v. \quad (4.22)$$

In combination with experimental relations for the chemical potentials, this enables us to calculate the fraction of A and B in the liquid and in the vapour phase as a function of pressure and temperature. For example, in many cases the chemical potential of the vapour phase (of a component A) is given by

$$\mu_A^v = \mu_A^*(T) + RT \ln P + RT \ln y_A, \quad (4.23)$$

where $\mu_A^*(T)$ is a function of temperature only, and y_A is the mole fraction of component A in the vapour phase. The chemical potential of the liquid phase (of component A) on the other hand is often taken to be that of a so-called ideal liquid¹

$$\begin{aligned} \mu_A^l &= \mu_A^{\text{pure } l}(T, P) + RT \ln x_A \\ &\approx \mu_A^{\text{pure } l}(T, P_A^\sigma(T)) + RT \ln x_A \\ &= \mu_A^{\text{pure } v}(T, P_A^\sigma(T)) + RT \ln x_A \\ &= \mu_A^*(T) + RT \ln P_A^\sigma(T) + RT \ln x_A. \end{aligned} \quad (4.24)$$

¹A derivation for the chemical potential in a binary liquid will be given in section 9.7.

In the first line $\mu_A^{\text{pure } l}(T, P)$ is the chemical potential of a liquid phase of pure (100%) component A, and x_A is the mole fraction of component A in the actual liquid phase. In the second line we have used the fact that the dependence on pressure of the chemical potential is much weaker in the liquid than it is in the vapour. The reason for this can be seen from $(\partial\mu/\partial P)_T = v$, and the fact that the molar volume of the liquid phase is much smaller than that of the vapour phase (if we are not close to the critical point). At phase coexistence, $\mu_A^l = \mu_A^v$, the pressure in the liquid phase will therefore be close to the saturation pressures $P_A^\sigma(T)$ of pure component A at that particular temperature. In the last line we have used Eq. (4.23) again. The same arguments apply to component B.

In Problem 4-2 you are asked to calculate the liquid-vapour coexistence lines in a pressure-composition diagram. Such diagrams are very useful to understand for example the process of distillation.

4.3 Stability

As we have seen, in equilibrium the entropy S is maximal, given the constraints. No constraint forbids a homogeneous system to split into two phases, yet it does not. From this we conclude that the entropy of the homogeneous state is larger than the entropy of the phase-separated state. This can be used to derive stability criteria for the homogeneous phase.

Suppose we split an adiabatically sealed homogeneous system in two phases. A fraction x of the particles will be in phase 1, the remaining fraction $(1 - x)$ in phase 2:

$$N_1 = xN, \quad N_2 = (1 - x)N. \quad (4.25)$$

In the two phases the energy per particle, the volume per particle, and the entropy per particle will be different. We now denote the energy of phase 1 *if it contained all N particles* by U_A , the energy of phase 2 *if that contained all N particles* by U_B , and similarly V_A and V_B for the volume and S_A and S_B for the entropy. The actual energy, volume, and entropy of phase 1 and 2 will then be:

$$U_1 = xU_A, \quad U_2 = (1 - x)U_B, \quad (4.26)$$

$$V_1 = xV_A, \quad V_2 = (1 - x)V_B, \quad (4.27)$$

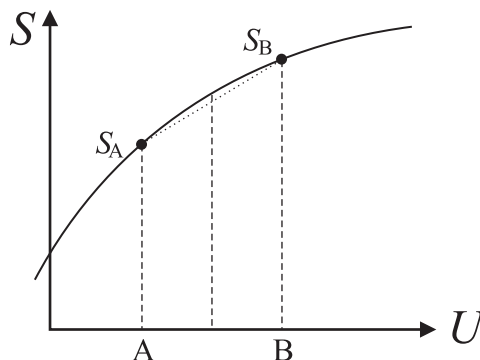
$$S_1 = xS_A, \quad S_2 = (1 - x)S_B. \quad (4.28)$$

The total energy must remain the same, so

$$U_1 + U_2 = xU_A + (1 - x)U_B = U \quad (4.29)$$

$$x = \frac{U - U_B}{U_A - U_B}. \quad (4.30)$$

Figure 4.3: A homogeneous phase is stable against phase separation if the entropy is a concave function of energy S . Any trial separation into a phase of energy A and a phase of energy B will then lead to an entropy which is lower (because it must be on the dotted line) than the entropy of the homogeneous phase.



According to the second law of thermodynamics we now demand that

$$xS_A + (1-x)S_B < S \quad (4.31)$$

$$\frac{U_B - U}{U_B - U_A}S_A + \frac{U - U_A}{U_B - U_A}S_B < S. \quad (4.32)$$

We already know that the graph of $S(U)$ must be a monotonously increasing function, because $(\partial S/\partial U) = 1/T > 0$. But from Eq. (4.32) we can learn more. The left hand side of this equation describes a straight line between $(U_A, S(U_A))$ and $(U_B, S(U_B))$. The inequality must be true for *any* U_A and U_B . Therefore the curve $S(U)$ must be above any line joining two points on its surface. In other words, it must be a concave function of U , see Fig. 4.3:

$$\boxed{\left(\frac{\partial^2 S}{\partial U^2}\right)_V < 0 \quad (\text{stability})} \quad (4.33)$$

This has consequences for the specific heat of a homogeneous system:

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = \left(\frac{\partial(1/T)}{\partial U}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V} < 0 \quad (4.34)$$

$$\Rightarrow C_V > 0. \quad (4.35)$$

From the condition of stability of the homogeneous phase we have derived that the specific heat must be positive. If it were negative, the system would not equilibrate and heat would flow from cool regions to hot regions!

A more general treatment yields other conditions on the response functions. Therefore a little digression on response functions. These are properties which represent the response of the system when you change one of the thermodynamic parameters. All of these are second derivatives of some thermodynamic function. For example second derivatives of the free enthalpy G are the specific heat at constant

pressure, the compressibility at constant temperature, and the thermal expansion coefficient at constant pressure:

$$C_P \equiv T \left(\frac{\partial S}{\partial T} \right)_{P,N} = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_{P,N} \quad (4.36)$$

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N} = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_{T,N} \quad (4.37)$$

$$\alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{P,N} = \frac{1}{V} \left(\frac{\partial^2 G}{\partial T \partial P} \right)_N. \quad (4.38)$$

Similar definitions hold for C_V and κ_S . However, there are only 3 *independent* response functions. All other response functions, i.e. second derivatives of all other thermodynamic functions, can be derived from the 3 independent ones. This is logical, because all other thermodynamic functions can be derived from any one thermodynamic function. For example, the specific heat at constant volume is given by

$$\begin{aligned} C_V &= T \left(\frac{\partial S}{\partial T} \right)_V \\ &= T \left(\frac{\partial S}{\partial T} \right)_P + T \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \\ &= C_P - T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V \\ &= C_P + T \left(\frac{\partial V}{\partial T} \right)_P \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} \\ &= C_P - TV \frac{\alpha_P^2}{\kappa_T}. \end{aligned} \quad (4.39)$$

Therefore $C_P > C_V$, as we have already seen for the ideal gas. In Problem 4-3 you are asked to show that $\kappa_S / \kappa_T = C_V / C_P$, so $\kappa_S < \kappa_T$ also.

Now back to the stability conditions. The same argument that was made for $S(U)$ may also be made for $S(V)$. In general, therefore, $S(U, V)$ must be a concave function of both U and V , see Fig. 4.4 (*top*). In many cases it is easier to swap axes, and use the fact that $U(S, V)$ must be a *convex* function of S and V , i.e. $d^2U > 0$, see Fig. 4.4 (*bottom*). Let us now analyse the consequences:

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad (4.40)$$

$$\begin{aligned} d^2U &= \left[\left(\frac{\partial^2 U}{\partial S^2} \right)_V dS + \left(\frac{\partial^2 U}{\partial V \partial S} \right) dV \right] dS + \left[\left(\frac{\partial^2 U}{\partial V \partial S} \right) dS + \left(\frac{\partial^2 U}{\partial V^2} \right)_S dV \right] dV \\ &= \left(\frac{\partial^2 U}{\partial S^2} \right)_V d^2S + 2 \left(\frac{\partial^2 U}{\partial V \partial S} \right) dS dV + \left(\frac{\partial^2 U}{\partial V^2} \right)_S d^2V > 0. \end{aligned} \quad (4.41)$$

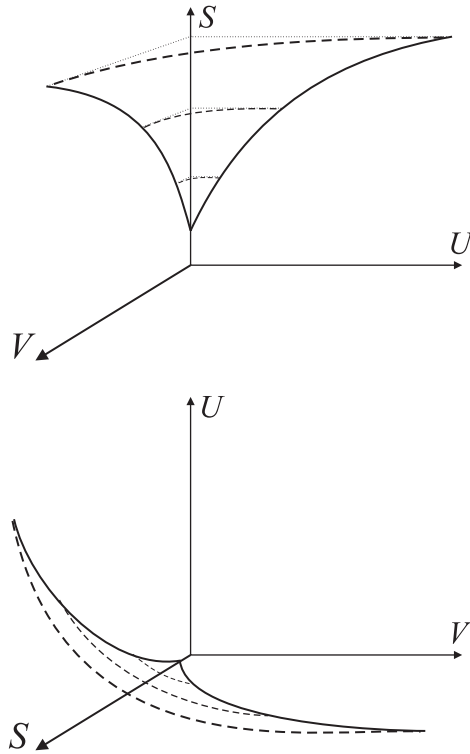


Figure 4.4: (*Top figure:*) For stability, the entropy S of a homogenous phase must be a concave function of both U and V . (*Bottom figure:*) Swapping axes, the energy U must be a convex function of both S and V . In both figures dashed lines connect points of equal entropy.

This must be true for *any* dS and *any* dV . Therefore we find the following conditions on the response functions:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V = \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V} > 0 \rightarrow C_V > 0 \quad (4.42)$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_S = -\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{V\kappa_S} > 0 \rightarrow \kappa_S > 0 \quad (4.43)$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S - \left(\frac{\partial^2 U}{\partial V \partial S}\right)^2 > 0 \rightarrow \frac{\kappa_T}{C_V} > 0. \quad (4.44)$$

Thus a stable system must have positive C_V , κ_S , and κ_T .

Problems

4-1. A liquid or vapour in an external field In this problem we will consider a closed system containing a liquid or vapour in a gravitational field g . A particle of mass m located in a cell α at height h^α has a gravitational energy of mgh^α . A particular redistribution of the particles and the energy may be therefore be written as $dU^\alpha = T^\alpha dS^\alpha + \mu^\alpha dN^\alpha + mgh^\alpha dN^\alpha$. Show that in the presence of a gravitational field:

$$T^\alpha = T^0, \quad \mu^\alpha + mgh^\alpha = \mu^0 + mgh^0,$$

(Hint: The law of conservation of energy states that the sum of internal energy and gravitational energy is constant.)

The chemical potential (per particle) may be written as $\mu(P, T) = \mu^*(T) + k_B T \ln P$. Show that the pressure in cell α relative to the pressure in cell 0 is given by

$$\frac{P^\alpha}{P^0} = \exp \left[-\frac{mg(h^\alpha - h^0)}{k_B T} \right]$$

4-2. Phase coexistence in a binary mixture. Suppose we have a binary mixture of components A and B at temperature T . In a *range* of pressures there is liquid-vapour coexistence, with varying composition of both phases; the liquid contains a mole fraction x_A of component A and therefore $x_B = 1 - x_A$ of component B. Similarly, the vapour contains a mole fraction y_A of component A and $y_B = 1 - y_A$ of component B. Calculate $P(x_B)$ (the “liquid line”) and $P(y_B)$ (the “vapour line”). Use the expressions in section 4.2.3 for the chemical potentials. Assume that the saturation pressures $P_A^\sigma(T)$ and $P_B^\sigma(T)$ of the pure components are known.

4-3. Adiabatic and isothermal compressibility. Show that

$$\frac{\kappa_S}{\kappa_T} = \frac{C_V}{C_P}$$

(Hint: Consider the differential of the entropy as a function of V and P , and next the differential of the temperature as a function of V and P .) Can you explain why it is easier to compress a system when it is coupled to a heat bath than when it is compressed adiabatically?

4-4. Isobaric and isochoric specific heat. Show that

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P.$$

Using this formula, evaluate $C_P - C_V$ for an ideal gas and for a van der Waals gas.