

Chapter 6

Micro- and Macro-states

We have seen that a gas develops towards a state where the number of particles is uniform throughout the gas. We measured the number of particles on the left side of the gas, and found that the system naturally evolves towards a state with a uniform distribution. While the number of particles in one half of the gas is fluctuating, the fluctuations becomes very small compared with the number of particles, and the number of particles increases. The behavior we observed for the gas is not a special case, but a very general behavior in all systems with many particles — the system will develop towards an equilibrium state. So far, we have only analyze the number of particles — or the density — in a part of a system. In this chapter we will extend this analysis to address *thermal fluctuations*, fluctuations in energy, *mechanical fluctuations*, fluctuations in volume, and *density fluctuations*, fluctuations in the number of particles in a system.

Our plan is to follow the same strategy as we introduced for the gas: We will study an isolated system — in molecular dynamics the number of particles, the total energy and the volume is constant, which means that the system is completely isolated. To understand what happens inside this isolated system we will divide the system in two, and study how the energy, the volume or the number of particles are distributed between the two halves, just like we have done for the gas system.

Already for the gas, we saw that the system evolved towards an *equilibrium* state, which corresponded to the most probable value for n , and that the development was *irreversible* when we started from a state that was far from the equilibrium state. Here, we will develop a better understanding for irreversible processes and the associated fundamental law, the second law of thermodynamics. We will also study the conditions for the *equilibrium* state.

However, the most important new concepts introduced in this chapter occurs in the coupling between the microscopic and the macroscopic. We will demonstrate how we can use our microscopic models to determine the macroscopic behavior of systems. We will be able to *predict* quantitative features of macroscopic systems such as the equation of state for an ideal gas or the heat capacity for a gas or a solid. This is made possible by a coupling from the microscopic to the macroscopic — a major achievement in physics. Using this coupling we will introduce the concepts of

entropy, temperature, pressure, and chemical potential, which are the essential components of thermodynamics — the theory of the thermal behavior of macroscopic objects.

We start from our description of a gas — a description of both the microscopic and the macroscopic state.

6.1 States of the model gas

We described the gas on several levels: In the molecular dynamics model we described the detailed dynamics of all the particles. But this was too detailed. Instead, we introduced a simplified model where we described the position of each particle using a binary number, n_i , which shows if the particles is on the left side ($n_i = 1$) or not ($n_i = 0$). We call such a description a microscopic description, and we can describe the state of the system by providing the set of n_i values, $(n_1, n_2, n_3, \dots, n_N)$. We call this set of numbers a *microstate* for the gas.

Given the microstate, that is the set of n_i for every particle i , we could calculate the number of particles on the left side, $n = \sum_i n_i$. We call the value of n a *macrostate* of the system. We found that there are many possible microstates that give the same result for n , that is, there are many possible microstates for a given macrostate.

6.1.1 Micro- and macro-states for two dice

If we throw two six-sided dice, the set of possible outcomes is the set of pairs or numbers, $(1, 1)$, $(1, 2)$, $(1, 3)$ etc. representing the number on dice 1 and dice 2 respectively. That is, the number of possible states of the two-dice system is given by (n_1, n_2) , where $n_1 = 1, 2, \dots, 6$ and $n_2 = 1, 2, \dots, 6$. These are the *microstates* of the two-dice system. How many microstates are there? This is problem from combinatorics and for two independent dice, there are $6 \times 6 = 36$ such (ordered) two-number states.

The *macrostates* of this system represent a group of microstates. There are many possible ways to divide the total set of outcomes into various groups — various macrostates. For example, we could introduce a set of macrostates corresponding to the sum, $n = n_1 + n_2$, of the two dice. In this case, the macrostate n can vary from 2 to 12. Each unique value of Z represents a macrostate. But there can be many microstates corresponding to a macrostate.

We call the number of microstates that give the same macrostate the *multiplicity* of the macrostate. For the two-dice system, all the microstates — all the possible pairs of numbers (n_1, n_2) are equally probable since the dice are fair and the two throws are independent of each other. The multiplicity of macrostate can therefore be used to find the probability of a macrostate: The probability of the macrostate is the number of microstates in the macrostate divided by the total number of mi-

crostates. If we introduce the notation $\Omega(n)$ for the multiplicity, then the probability for state n is

$$P(n) = \frac{\Omega(n)}{\Omega_{TOT}} = \frac{\Omega(n)}{\sum_{n=2}^{12} \Omega(n)}, \quad (6.1)$$

where we have used that the total number of microstates is the sum of the number of microstates for each of the possible values of n . Fig. 6.1 illustrates the number of states for each of the macrostates, and you should now be able to find the probability for each macrostate simply by counting the number of microstates.

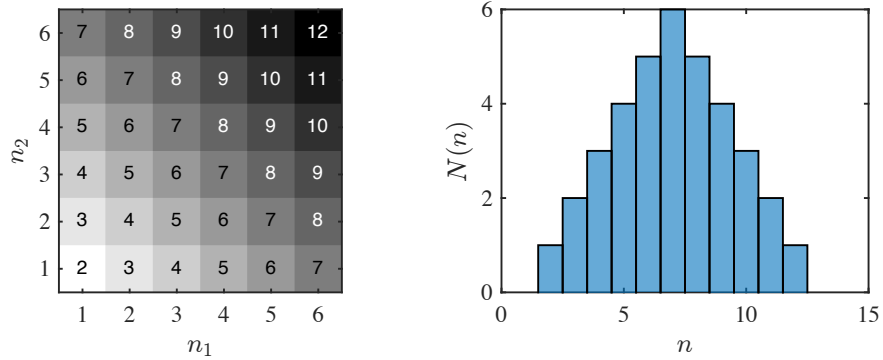


Fig. 6.1 *Left* Illustration of the microstates of two dice. The microstates that are part of the same macrostate $n = n_1 + n_2$ are given the same color. *Right* Plot of the histogram of the number of microstates for each macrostate n for two dice.

6.1.2 Definition of micro- and macro-states

A **microstate** is a microscopic description of the degrees of freedom of the system on some level of precision. Typically, but not always, we can specify the microstate by specifying the state of each of the N elements in the system, (n_1, n_2, \dots, n_N) .

A **macrostate** is a set of microstates. Usually, the macrostate is specified by a number which can be computed directly from the microstate. We call this number the *macrovariable*. Each microstate belongs to one and only one macrostate. The set of all possible macrostates therefore span all the possible microstates of the system.

The **multiplicity** $\Omega(N, z)$ of a macrostate described by the macrovariable Z , is the number of microstates in the macrostate characterized by the value z .

6.1.3 Multiplicity of the macrostate of the gas

We have already studied a particular macrostate of the ideal gas: The number of particles, n , on the left side of a box. For each possible value of n we found that there were an enormous amount of microstates. In order to make our concepts and the notation very clear, we introduce a more consistent notation: In our theoretical description of the system, the microstates was a sequence of numbers describing the position of each atom. Each atom may be on the left side ($n_i = 1$) or on the right side ($n_i = 0$) for $i = 1, \dots, N$. The total number of atoms on the left side was

$$n = \sum_{i=1}^N n_i, \quad (6.2)$$

We found that the probability distribution for n was given by the binomial distribution

$$P(N, n) = \Omega(N, n) 2^{-N}, \quad (6.3)$$

where the *multiplicity* $\Omega(N, n)$ represents the number of microstates that give the value n for n . We call this the number of microstates in macrostate n .

Sharpness of the multiplicity. The multiplicity for the number of particles on the left side of an ideal gas was given as

$$\Omega(N, n) = \binom{N}{n}. \quad (6.4)$$

We also found that this probability, and hence also the multiplicity, was very sharp around its average value. Indeed, the average value \bar{n} and the standard deviation σ_n are given as

$$\bar{n} = \frac{N}{2}, \quad \sigma_n = \sqrt{\frac{N}{4}}. \quad (6.5)$$

From this result we see that the standard deviation becomes very small compared with the average:

$$\frac{\sigma_n}{\bar{n}} = \frac{\sqrt{N}}{N} = N^{-1/2}, \quad (6.6)$$

which means that for a litre of gas at room temperature and atmosphere pressure, where N is of the order of 10^{23} we see that the standard deviation is 10^{-10} of the

average value, which is well beyond the resolution of most measurement methods. This means that for all practical purposes the number of particles n is a constant.

Most probable macrostate. For the ideal gas system, we expect the system to cycle through all possible microstates: They are all equally probable. However, we also found that the initial state where all the atoms were on the left hand side did not appear spontaneously. Why? In principle, all values of n are possible. In practice, there are most states near the average value of n . So many more states that if we move a few standard deviations away from the average, which is 10^{-11} of the average value, the probability to find such a state becomes negligible. This is the reason why we find the return to the initial state comic — it is extremely unlikely to happen.

The development of the system away from $n = N$, where we started the simulation previously, towards $n = N/2$ is therefore effectively *irreversible*, because there are so many more states near $\bar{n} = N/2$ than near $n = N$ or $n = 0$. This also means that the system develops towards a macrostate where the number of particles per volume (the number density) is the same on each side (if the two sides are equally large). The system develops towards a homogeneous density.

Fluctuations in particle number. When we study the number of particles on the left side of the gas, we are addressing the variations, of the *fluctuations*, in the number of particles inside the system. Alternatively, we could say that there are fluctuations in the number of particles per unit volume, since the volume does not change, that is, there are fluctuations in the density of the gas.

These fluctuations are related to transport of particles: If the number of particles on the left side changes by Δn : $n(t + \Delta t) = n(t) - \Delta n$, the number on the right hand side increases by the same amount: The particles Δn are transported from the left hand side to the right hand side. This can occur because the systems are open to particle transport: There is no wall between the two halves.

Other fluctuations. Ok, we have a good description of the fluctuations of the number of particles, or the density, inside an isolated gas. However, we may be interested in variations in other macroscopic properties as well. For example, if the two halves of the system can transfer energy between each other, what are the fluctuations in energy in the two halves of the system? However, if we want to address fluctuations in energy, we would like to single out this fluctuation alone. We would therefore like to have a system where the number of particles on each side of the system is the same — identically the same — but where the total energy can be distributed in many ways between the two parts of the isolated system. This is the motivation to start working with other model system such as solids, where the particles do not move around significantly, but energy is free to flow throughout the system. We will therefore first address the fluctuations of energy in a simplified solid — in the Einstein crystal.

6.2 Behavior of a solid — Observations

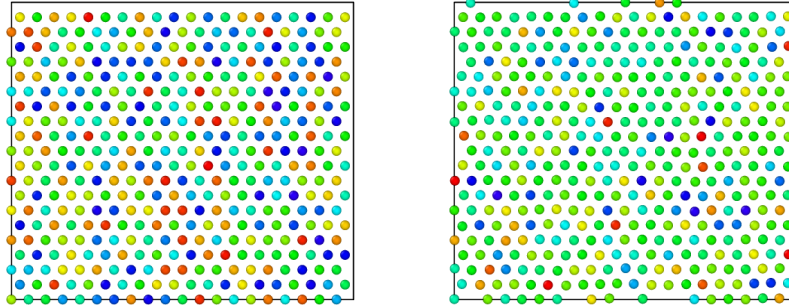


Fig. 6.2 Visualization of a solid of Argon atoms modelled using the Lennard-Jones potential at two different times. The colors indicate the velocities in the x -direction.

For a solid, the atoms are approximately fixed in space, but still vibrating. For this system energy is free to flow, but particles will remain in place. The solid is therefore well suited to study fluctuations and transport of energy.

Running a molecular dynamics simulation of a solid. Let us first start from a molecular model of a solid. We can address the behavior of a solid using the same model we used for the Argon system, but with smaller initial velocities and a smaller volume so that we ensure that the system is in its solid phase. You find reasonable input parameters for a simulation in `in.solidstat02`¹:

```
# 2d Lennard-Jones solid
units      lj
dimension  2
atom_style atomic
lattice    hex 1.05
region     box block 0 20 0 10 -0.1 0.1
create_box 1 box
create_atoms 1 box
mass       1 1.0
velocity   all create 0.5 87287
pair_style lj/cut 2.5
pair_coeff  1 1 1.0 1.0 2.5
neighbor   0.3 bin
neigh_modify every 20 delay 0 check no
fix        1 all nve
dump 1 all custom 100 solidstat02.lammpstrj id type x y z vx vy vz
thermo     100
run        500000
```

You can run the simulation using

¹<http://folk.uio.no/malthe/fys2160/in.solidstat02>

```
lammmps < in.solidstat02
```

The resulting atomic configuration is shown in Fig. 6.2. The atoms are organized in a regular lattice, a triangular lattice, which corresponds to the (equilibrium) crystal structure of the two-dimensional system. (It should here be noted that a two-dimensional system is somewhat unphysical, but it is simple to visualize. You can easily run all simulations in 3d without changing any of the general aspects of the results).

Measuring energy in the solid. Based on these simulations, we can measure the kinetic energy of the particles on the left side of the model. This does not represent the total energy for a crystal, since the potential energy part is non-negligible. But it does give a picture similar to what we had for the gas simulations. We read the data from the simulations into Python, find all the particles on the left side, find the sum of the kinetic energies of all these particles, and plot the result using the script `solidplotkt02.py`²:

```
from pylab import *
d = dump("solidstat02.lammpstrj") # Read output states
t = d.time()
n = size(t)
Ktot = zeros(n,float) # Kinetic energy
# Get information about simulation box
tmp_time,box,atoms,bonds,tris,lines = d.viz(0)
halfsize = 0.5*box[3] # Box size in x-dir
# Loop over all timesteps
for i in range(n):
    x = array(d.vecs(t[i],"x"))
    vx = array(d.vecs(t[i],"vx"))
    vy = array(d.vecs(t[i],"vy"))
    # Find list of all atoms in left half
    jj = find(x<halfsize)
    k = sum(0.5*(vx[jj]*vx[jj]+vy[jj]*vy[jj]))
    Ktot[i] = k
plot(t,Ktot),xlabel('t'),ylabel('n(t)'),show()
```

Fluctuations in the kinetic energy. The kinetic energy $K(t)$ as a function of time t is shown in Fig. 6.3. This plot looks similar what we saw for $n(t)$ for the gas — there are fluctuations around a clear average value. We can characterize the size of the fluctuations by looking at the probability distribution $P(K)$ of the kinetic energy of the left-hand half of the system, which is also shown in Fig. 6.3. This plot suggests that the fluctuations also may be described by a Gaussian distribution. We will look more closely at this as we develop a theory for the behavior in the following, when we introduce the ideal crystal model for the behavior of a solid.

Towards equilibrium of the solid. We can also use this simulation framework to address how the system approaches equilibrium. We start a simulation where the

²<http://folk.uio.no/malthe/fys2160/solidplotkt02.py>

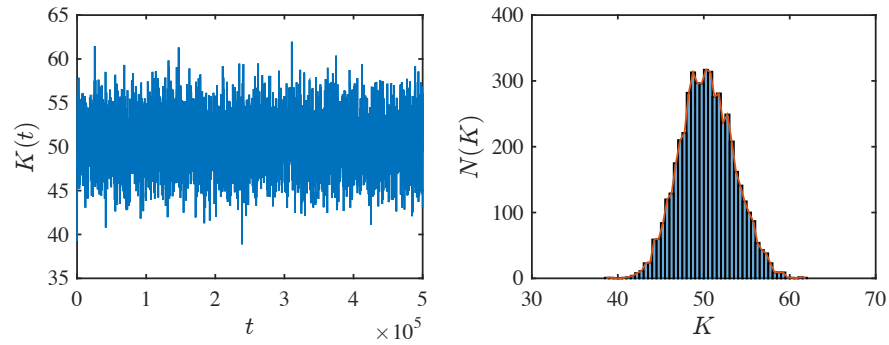
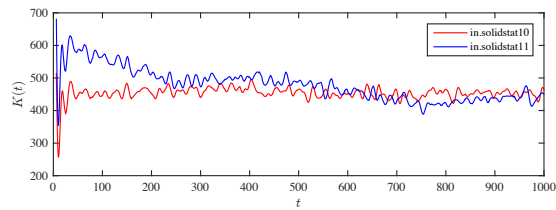


Fig. 6.3 *Left* Plot of the kinetic energy of the left-half of the Argon solid. *Right* Histogram of the kinetic energy K for the Argon system.

Fig. 6.4 Plot of $K(t)$ for added velocity (Black) and for the control simulation with no change (Red).



left half of the system have a different average initial kinetic energy than the right half of the system. This is done by the input file `in.solidstat10`³:

```
# 2d Lennard-Jones gas
units      lj
dimension  2
atom_style atomic
lattice    hex 1.05
region     box block 0 40 0 20 -0.5 0.5
create_box 1 box
create_atoms 1 box
region     2 block 0 20 0 20 -0.5 0.05
group      leftatoms region 2
mass       1 1.0
velocity   all create 0.5 87287
velocity   leftatoms create 1.5 282772
pair_style lj/cut 2.5
pair_coeff  1 1 1.0 1.0 2.5
neighbor   0.3 bin
neigh_modify every 20 delay 0 check no
fix        1 all nve
# Define output to file
dump       1 all custom 1 ss10.lammpstrj id type x y z vx vy vz
thermo     10
run        1000
```

³<http://folk.uio.no/malthe/fys2160/in.solidstat10>

The resulting plot of $K(t)$ is shown in Fig. 6.4. Again, we see that the system approaches a stationary state, corresponding to an equilibrium state, after a short transient. The system has a clear direction of time. What characterizes the equilibrium state? To answer this we need to develop a theory for the behavior of the solid.

6.3 Behavior of a solid — Theory

Let us now build a simplified model of the solid, inspired by the model for the ideal gas. Fig. 6.5 illustrates atomic arrangements in a solid, liquid and gas system. In the simulated solid, and in a real crystal where all the atoms are spaced regularly on a lattice, the atoms are fixed into a position on a lattice through the interactions with the other atoms in the crystal. The lattice configuration is a stable configuration as long as none of the atoms gain enough energy to break out of the local potential well they are situated in. A reasonable description of such a system would be that each atom vibrates around the minimum in an energy landscape, where the potential energy is due to the interactions with the other atoms. For simplicity, we can assume that the atoms do not directly interact, they only interact through their average potential field, but the potential does not vary as the atom vibrates. In this simplified picture, which is our theoretical approximation to the system, each atom in the lattice is affected by a local potential, and we can describe the vibrations around the minimum of this potential by the lowest-order approximation, as illustrated in Fig. 6.5, where each atom is affected by a set of springs, and therefore acts as if it affected by a spring force. This corresponds to the most basic vibration system — the harmonic oscillator.

6.3.1 *Einstein crystal model*

Our model for an ideal crystal therefore contains the following components:

- The atoms in the crystal do not interact directly
- Each atom acts as a harmonic oscillator in a three-dimensional potential
- The total system consists of N such atoms
- The atoms in the system share the total energy in the system

This model is called the **Ideal crystal** or the **Einstein crystal**. This model is going to be our basic model for a solid, and it is going to be equally versatile as the ideal gas description of a gas.

Harmonic oscillator system. For a three-dimension system, each atom consists of three independent oscillators in the x , y , and z directions so that a system with N oscillators really only consists of $N/3$ atoms. Each harmonic oscillator is subject to a potential

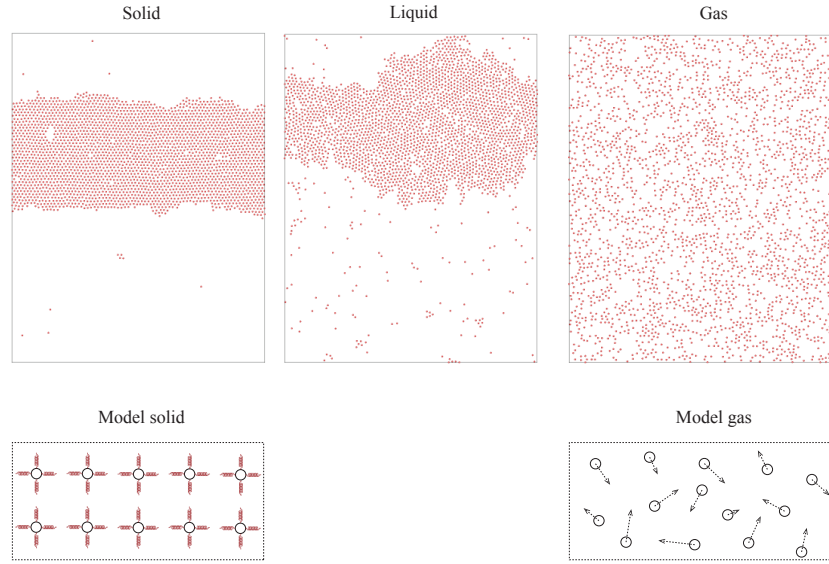


Fig. 6.5 Snapshots from simulations of a solid, a liquid, and a gas using the molecular dynamics model. Illustrations of the corresponding model systems.

$$V(x) = \frac{1}{2}kx^2. \quad (6.7)$$

where k is the “spring constant” and x is the deviation from the equilibrium position.

Quantized harmonic oscillator. From quantum mechanics we know that the energies of such a system is quantized, with possible values

$$\varepsilon = h\nu n. \quad (6.8)$$

where $n = 0, 1, 2, \dots$ can only take integer values.

Energy in a system of harmonic oscillators. An Einstein crystal is a system consisting of N such independent oscillators, where each oscillator has the same ν and therefore the same energy levels. What are the possible states of such a system of N oscillators? It depends on the total energy U available to the system. We measure the energy in units of $h\nu = \varepsilon$, and we often use the symbol q for this dimensionless energy. Notice that the number q can only take *integer values*.

Four-oscillator system. Let us address a simplified system with $N = 4$ and $q = 2$. What are the possible states of the whole system under these conditions? We describe the states using a simple illustration where we have drawn the possible energy levels for the $N = 4$ oscillators in Fig. 6.6. There are generally two possibilities: (case A) One oscillator may be in energy level 2, and the other in energy level 0; or (case B) two oscillators may be in energy level 1 and the others in energy level 0. But how many possible ways can this occur in? We can describe the possible

configurations by a sequence (n_1, n_2, n_3, n_4) where $n_i = 0, 1, 2, \dots$ describes the state of oscillator i . For case A, the oscillator in energy level 2 can be placed in $N = 4$ possible places: $(2, 0, 0, 0)$, $(0, 2, 0, 0)$, $(0, 0, 2, 0)$, and $(0, 0, 0, 2)$. There are therefore 4 possible states of the system with one oscillator in energy level 2 and the rest in energy level 0. For case B, the two oscillators in level 1 can be placed in 6 possible configurations. You may be tempted to use the following argument to count the number of possible configurations: We can choose the first oscillator from 4 positions and the second from 3 positions, hence the total number of possibilities are $4 \cdot 3 = 12$. However, this would be wrong, since we have then counted all the actual configurations twice. If we place the first energy unit in oscillator one and the second in oscillator two, we get the state $(1, 1, 0, 0)$, but this is the same state we would get if we place the first energy unit in oscillator two and the second in oscillator one: $(1, 1, 0, 0)$. The total number of possible states are therefore only $4 \cdot 3/2 = 6$: $(1, 1, 0, 0)$, $(1, 0, 0, 1)$, $(0, 0, 1, 1)$, $(1, 0, 1, 0)$, $(0, 1, 0, 1)$, and $(0, 1, 1, 0)$.

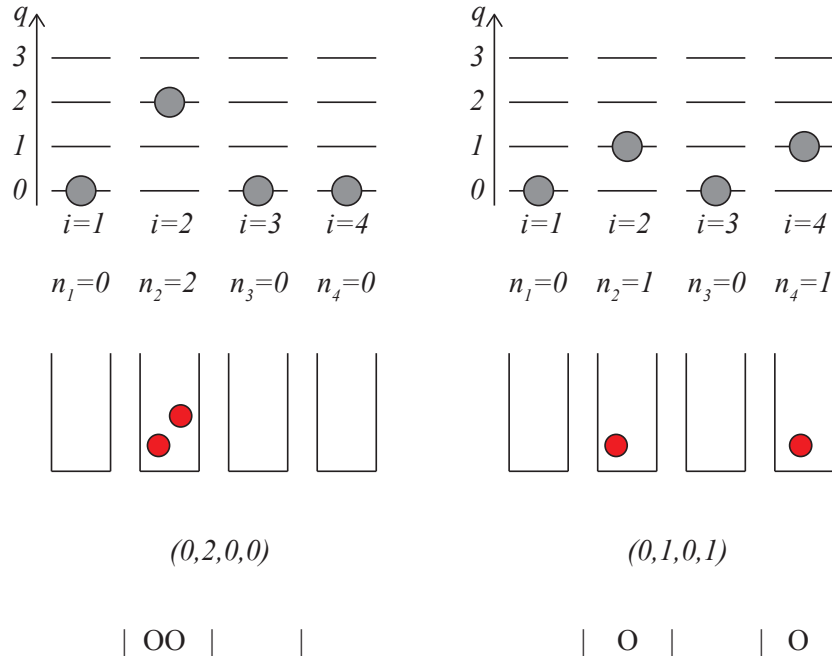


Fig. 6.6 Illustration of the Einstein crystal model.

Energy level diagram. It is customary to illustrate the states in an energy level diagram. Fig. 6.6 shows an illustration of the state $(0, 2, 0, 0)$ and $(0, 1, 0, 1)$. Another way to think about what states are possible is to think of q as the total number of energy units and N as the total number of boxes they can be placed in. The two states

(0,2,0,0) and (0,1,0,1) is also illustrated in this way in Fig. 6.6 – by the number of energy units shown as balls in the boxes.

Microstates in the Einstein crystal. We call each sequence (n_1, n_2, \dots, n_N) a microstate of the Einstein crystal. The energy level or box representation in Fig. 6.6 therefore provides a basis for counting the number of possible microstates for a given set of oscillators N and a given total energy q of the system. However, there is an even better way to represent the states that makes counting simpler, illustrated in the bottom of Fig. 6.6. We can represent the microstate by a sequence of energy units, 0, and walls, 1. If we only include the internal walls (the outer walls of the boxes cannot change position) we can list all possible microstates by listing all possible orderings of $N - 1$ walls and q energy units. The two states (0,2,0,0) and (0,1,0,1) then get the following representation 10011 and 10110. Now, we have mapped the problem onto a problem we already know the answer to. (This is a very common method in physics — to find some smart way to map an unsolved problem onto a well-known and solved problem). We know how to count how many possible configurations we can have of q zeroes and $N - 1$ ones: This corresponds to the number of ways we can place q zeros in $q + N - 1$ positions. The number of microstates for the Einstein crystal with q energy units and N oscillators is therefore given as

$$\Omega(N, q) = \binom{N - 1 + q}{q} = \frac{(N - 1 + q)!}{q!(N - 1)!}, \quad (6.9)$$

We call this the multiplicity of the Einstein crystal with N oscillators and energy q .

Question

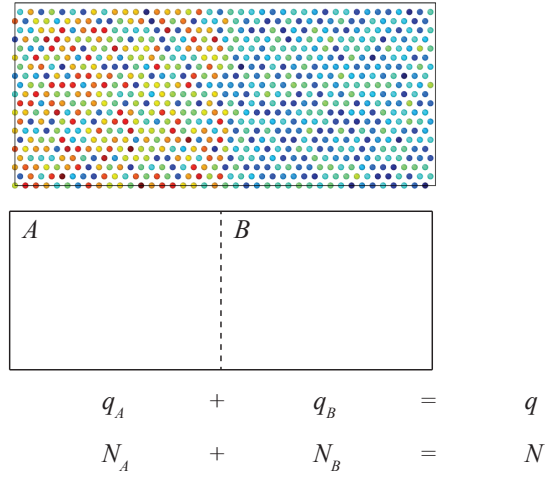
Clickers: Einstein crystal 1

6.3.2 Two Einstein crystals in contact

Now we know how to count microstates. But with only a single Einstein crystal, the macrostate, the energy, q , in this case, is not that interesting. In the numerical simulations, we saw how the energy was fluctuating between two halves in a crystal. Can we apply the theory we have developed of the microstates in a model crystal to address this behavior?

Fig. 6.7 illustrates the kinetic energy in the molecular dynamics system. We divide the system into two parts, or two subsets of the oscillators, A and B. For example, we may choose part A to be the left half and part B as the right half as illustrated. We can now measure the energy, q_A , directly, and calculate the energy in system B, $q_B = q - q_A$. How can we make a model of the exchange between system A and B?

Fig. 6.7 Illustration of two parts A and B of an Einstein crystal.



In our simulations, the two parts of the solids were connected. In the model, there are no direct interactions between the oscillators. However, all the oscillators in a crystal share the total energy: If one oscillator in a crystal gets more energy, another oscillator gets less. Now, let us model systems A and B as two separate Einstein crystals with N_A and N_B oscillators and q_A and q_B units of energy in system A and B respectively. Given N_A, q_A we have found how to calculate the multiplicity of system A, and similarly for system B. However, we will also assume that the whole system (A and B together) is isolated so that the total energy, the total volume and the total number of particles is constant — this was also the underlying assumption for the molecular dynamics simulations.

Multiplicity of macrostate $q_A, q_B = q - q_A$. The total system therefore consists of two Einstein crystals sharing the total energy q so that $q = q_A + q_B$. The macrostate of this system is the energy q_A in system A. This is similar to the gas system, where the macrostate was the number of particles on the left side. Our plan is now to find the probability of a macrostate by counting the number of microstates for macrostate q_A and divide by the total number of microstates. But how can we find the multiplicity of macrostate q_A of the whole system?

First, we notice that if the system is in macrostate q_A for system A, it must be in macrostate $q_B = q - q_A$ in system B. It is therefore sufficient to provide q_A to describe the macrostate of the whole system. We already know how to find the number of microstates for Einstein crystals A and B respectively. What about the combined system? We can now use another assumption about the system: System A and system B are independent of each other. This means that if I know the microstate of system A, which must be consistent with an energy q_A , I cannot predict what the microstate of system B is, except that it must be consistent with the energy q_B . This means that for each microstate in A, system B can be in any of its microstates. This means that the total number of microstates is the number in system A multiplied by

the number in system B. If we call the multiplicity of system A, $\Omega_A(N_A, q_A)$, and the multiplicity of system B, $\Omega_B(N_B, q_B)$, then the multiplicity of the whole system in macrostate q_A is $\Omega = \Omega_A(N_A, q_A) \Omega_B(N_B, q_B)$.

Question

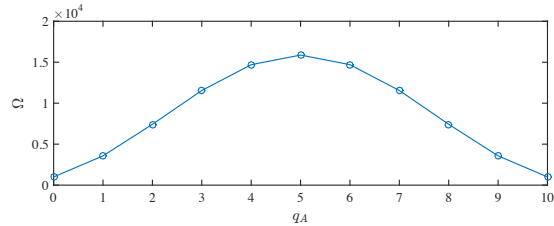
Clickers - Einstein crystal 2

We can calculate the multiplicities Ω_A , Ω_B and Ω for all the possible values of q_A numerically. For example, if $N_A = N_B = 5$, and $q = 10$, the the possible values of q_A are $0, 1, 2, \dots, 10$. The multiplicities are calculated and plotted in the following script.

```
# Einstein solid NA - NB multiplicity
from pylab import *
from scipy.misc import comb
NA = 100
NB = 100
q = 200
N = NA + NB
# Find multiplicity of all macrostates
omegaA = zeros(q+1)
qAvalue = zeros(q+1)
omegaB = zeros(q+1)
omegaTOT = zeros(q+1)
# Loop through all macrostates and find multiplicity
for istate in range(0,q):
    qA = istate
    qAvalue[istate] = qA
    omegaA[istate] = comb(qA+NA-1, qA)
    qB = q - qA
    omegaB[istate] = comb(qB+NB-1, qB);
    omegaTOT[istate] = omegaA[istate]*omegaB[istate];
plot(qAvalue, omegaTOT, '-o')
xlabel('q'), ylabel('W')
show()
#
#matrix = [omegaA omegaB omegaTOT]
```

The resulting number of microstates are show in Fig. 6.8 and in the following table. We notice that the the multiplicity $\Omega = \Omega_A \Omega_B$ has a maximum for $q_A = q/2 = 5$. But how can we use the *multiplicities* to find the *probability* of a macrostate?

Fig. 6.8 Plot of Ω_{tot} as a function of q_A for an two Einstein crystals A and B in contact with $N_A = N_B = 5$ and $q = q_A + q_B = 10$.



q_A	q_B	Ω_A	Ω_B	Ω_{tot}
0	10	1	1001	1001
1	9	5	715	3575
2	8	15	495	7425
3	7	35	330	11550
4	6	70	210	14700
5	5	126	126	15876
6	4	210	70	14700
7	3	330	35	11550
8	2	495	15	7425
9	1	715	5	3575
10	0	1001	1	1001

Fundamental assumption of statistical mechanics. To find the probability of a macrostate, we need more information about the microstates. Are the microstates equally probable, as we assumed for a dice, or are there some microstates that are more probable than others? We need another assumption about the microstates — we need the *fundamental assumption of statistical mechanics*:

Fundamental assumption of statistical mechanics: In an isolated system in thermal equilibrium, all accessible microstates are equally probable.

We cannot prove this assumption here, but we can understand where it comes from: At the microscopic level we expect any process that takes the system from state X to Y to be reversible, so that the probability for the reverse process is the same. This assumption, or aspect of physics, is called **the principle of detailed balance**. Another idea is that the system, as it is evolving in time like in our simulation, will span all possible microstates if you just wait long enough. For now, we will simply assume that the fundamental assumption is correct, and that all microstates have the same probability.

Probabilities of the macrostate $q_A, q_B = q - q_A$. Now we can find the probability of a macrostate by simply summing the probabilities of all the microstates in the macrostates. How many microstates are there in a macrostate? This is the multiplicity $\Omega_A \Omega_B$ of the macrostate. What is the probability of a microstate? It is $p = 1/\Omega$, where Ω is the total number of microstates. And what is the total number of mi-

crostates? This is the number of microstates for each possible value of q_A , which also corresponds to the number of microstates in the whole system, which the multiplicity of an Einstein crystal with N oscillators and q units of energy:

$$\Omega = \sum_{q_A=0}^q \Omega_A(N_A, q_A) \Omega_B(N_B, \underbrace{q - q_A}_{q_B}) = \Omega(N, q). \quad (6.10)$$

The probability for macrostate q_A is therefore

$$P(q_A) = \frac{\Omega_A(N_A, q_A) \Omega_B(N_B, q - q_A)}{\sum_{q_A=0}^q \Omega_A(N_A, q_A) \Omega_B(N_B, q - q_A)}. \quad (6.11)$$

The probability of macrostate q_A is proportional to $\Omega_A \Omega_B$, we can therefore also interpret the plot of $\Omega_A \Omega_B$ in Fig. 6.8 as a plot of the probabilities. We observe that the macrostates are not equally probable. For example, the $q_A = 0$ macrostate is clearly much more unlikely than $q_A/N_A = q_B/N_B$. How can we use such a result to interpret the development of an Einstein crystal with time? Let us address this by introducing a simplified model for the dynamics of an Einstein model, and by a theoretical argument based on the probabilities of macrostates

6.3.3 Time development of the Einstein crystal — Monte Carlo model

The Einstein crystal does not include any description of how the system developing in time, whereas the molecular dynamics simulation only shows how the system develops in time. To include dynamics, we need to add further assumptions to the model. When we defined the Einstein crystal we assumed that there were no interactions between the individual oscillators, whereas for the molecular dynamics simulations, the atoms had both specific positions in the crystal and they interacted with their neighbors. Let us see how we can extend the Einstein crystal model to include both simplified interactions and the relative positions of the atoms, so that we can model energy flow without including the full dynamics.

Global dynamics in the Einstein crystal. We can make a small modification to the Einstein crystal model to include some of these effects. The system consists of two parts, A and B, so that each atom/oscillator belongs to either A or B. The first step, will be to introduce some simplified interaction between the oscillators. As a first approximation, we simply move from one microstate to another in a random manner while conserving the total energy. We can do this by the following algorithm:

- Select an oscillator (particle) at random, i_1 . Let us attempt energy transport from this oscillator.
- Select another oscillator (particle) at random, i_2 . This oscillator may receive energy from n_1 .

- We transfer one unit of energy from i_1 to i_2 , if oscillator i_1 has at least one unit of energy.

The resulting behavior is seen using the following program:

```
# Two coupled Einstein crystals
NA = 100 # Nr of oscillators in A
NB = 100 # Nr of oscillators in B
qA = 300 # Initial energy in A
qB = 0    # Initial energy in B
q = qA + qB # Total energy
N = NA + NB # Total oscillators
state = zeros(N,float)
ion() # Interactive plotting ON
# Generate initial, random state
placeA = randint(0,NA,(qA,1))
for ip in range(len(placeA)):
    i = placeA[ip]
    state[i] = state[i] + 1
placeB = randint(0,NB,(qB,1))
for ip in range(len(placeB)):
    i = placeB[ip]
    state[i] = state[i] + 1
# Simulate state development
nstep = 100000
EA = zeros(nstep,float)
EB = zeros(nstep,float)
for istep in range(nstep):
    i1 = randint(0,N) # Select osc. i1
    if (state[i1]>0): # Has it any energy ?
        i2 = randint(0,N) # Select osc. i2
        state[i2] = state[i2] + 1 # Transfer
        state[i1] = state[i1] - 1 # energy
    # Output and display result dynamically
    subplot(2,1,1)
    plot(r_[0:NA-1],state[0:NA-1],'b',r_[0:NB-1]+NA,state[NA:NA+NB-1],'r')
    xlabel('i'); ylabel('n_i'); draw()
    subplot(2,1,2) # Avg energy in each system
    EA[istep] = sum(state[0:NA-1])/NA
    EB[istep] = sum(state[NA:])/NB
    plot(r_[0:istep],EA[0:istep],'-r')
    plot(r_[0:istep],EB[0:istep],'-b');
    xlabel('t'); ylabel('q_A/N_A , q_B/N_B'); draw()
```

Fig. 6.9 shows the resulting dynamics. Notice that all the energy starts on the left hand side, and that it gradually is transferred to an equal distribution — as expected.

Local dynamics in the Einstein crystal. We could add another level of complexity to the model, by introducing local interactions. All oscillators are placed on a square, two-dimensional grid. Oscillator i will be at position x_i, y_i . We follow the same algorithm as above: We select an oscillator at random, and transfer energy to another oscillator — if possible. However, we now only allow the oscillator to transfer energy to one of its neighbors. We select the neighbor at random from the four

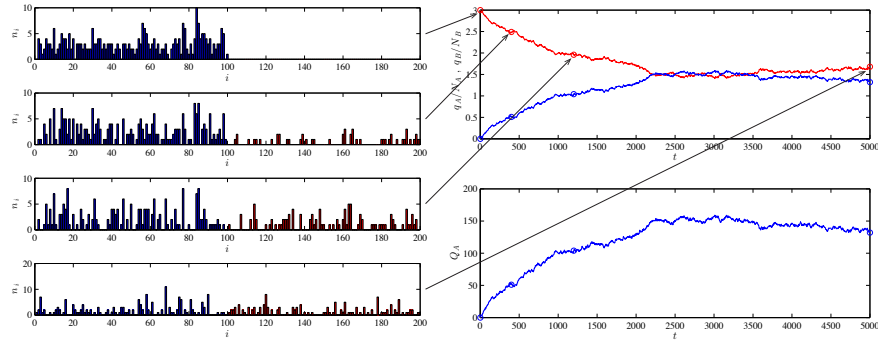


Fig. 6.9 Illustration of the time development of two Einstein crystals in thermal contact.

nearest neighbors $x_i + 1, y_i$, $x_i - 1, y_i$, $x_i, y_i + 1$, and $x_i, y_i - 1$. This results in local energy transport as illustrated in Fig. 6.10. You can use the following program to study heat conduction in this simple model of thermal behavior in a solid.

```
# Energy transport in an Einstein crystal
Ly = 40 # System size y-direction
LA = 40 # Length of system A in x direction
LB = 40 # Length of system B in x direction
Lx = LA + LB
NA = LA*Ly
NB = LB*Ly
qA = 3000 # Initial energy in system A
qB = 0 # Initial energy in system B
q = qA + qB # Total energy - conserved
N = NA + NB # Total number of oscillators
state = zeros((Lx, Ly), float) # 2d state matrix
# Generate initial, random states for A and B
for ia in range(qA):
    ix = randint(0, LA) # Rnd position from 1 to LA
    iy = randint(0, Ly) # Rnd position from 1 to Ly
    state[ix, iy] = state[ix, iy] + 1 # Add energy to this site
for ib in range(qB):
    ix = randint(0, LB) + LA # Rnd pos from LA+1 to LA+LB
    iy = randint(0, Ly) # Rnd pos from 1 to Ly
    state[ix, iy] = state[ix, iy] + 1 # Add energy to this site
# Simulate state development
nstep = 10000000 # nr of simulation steps
EA = zeros(nstep, float) # Energy per oscillator in system A
EB = zeros(nstep, float) # Energy per oscillator in system B
ion() # Interactive drawing ON
for istep in range(nstep):
    # Select an oscillator at random
    ix1 = randint(0, Lx)
    iy1 = randint(0, Ly)
    # Check if this oscillator has non-zero energy
    if (state[ix1, iy1] > 0):
```

```

# Find a random neighbor
dx = 2*randint(0,2)-1 # +/-1 with equal prob
ix2 = mod(ix1 + dx-1,Lx) # mod for periodic boundaries
dy = 2*randint(0,2)-1 # +/-1 with equal prob
iy2 = mod(iy1 + dy-1,Ly) # mod for periodic boundaries
# Transfer energy from (ix1,iy1) to (ix2,iy2)
state[ix2,iy2] = state[ix2,iy2] + 1
state[ix1,iy1] = state[ix1,iy1] - 1
if (mod(istep,1000)==0): # Display system at regular intervals
    imshow(state)
    draw()

```

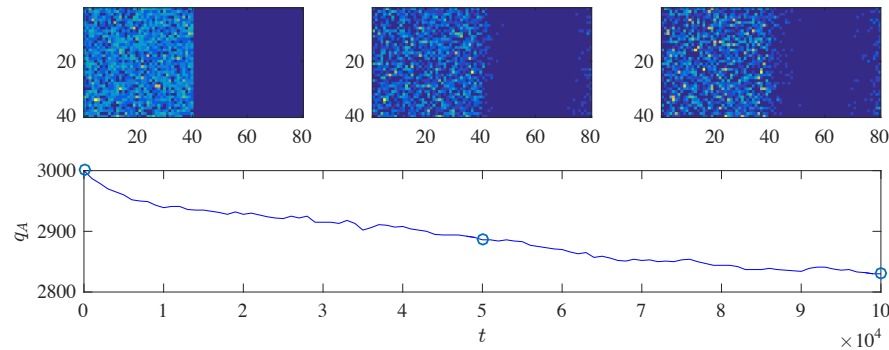


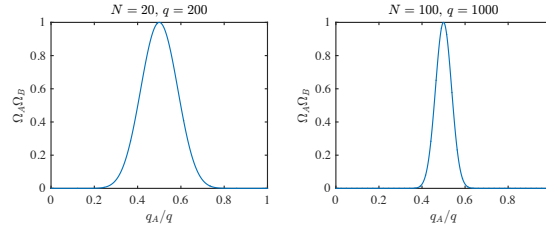
Fig. 6.10 Illustration of the time development of two two-dimensional Einstein crystals in thermal contact.

Both of these models show that the Einstein crystal will approach a stationary state with a uniform distribution of energy per oscillator: $q_A/N_A = q_B/N_B$. This corresponds to the macrostate with the maximum multiplicity. Why is that? How is this observation of the dynamics explained by the probabilities of the macrostates?

6.3.4 Time development of the Einstein crystal — Theoretical argument

How can we interpret the time development of the Einstein crystal using the probabilities of a macrostate in *equilibrium*? The probabilities we have found an expression for are the probabilities of a macrostate when the system have reached equilibrium. If the system starts with all the energy in system A, $q_A = q$, $q_B = 0$, we know that this state is very unlikely in equilibrium. If we just leave the system to itself, it seems reasonable that it will develop from one microstate to another, exploring the space of all possible microstates. (This is actually another fundamental hypothesis called the ergodicity hypothesis). If we then observe the system after some time, when it has forgotten about its initial microstate, it will be in some ran-

Fig. 6.11 Plot of $\Omega(q_A; q, N) \Omega_B$ as a function of q_A for **a** $N_A = N_B = 10, q = 200$ **b** $N_A = N_B = 50, q = 1000$. Notice that the multiplicity becomes sharper for larger systems.



dom microstate. But since there are so many more microstates in the most probable macrostates than in the initial macrostate, it is much more likely that the system after a while will be in the most probable macrostates. And it will be very unlikely to find the system in the initial macrostate. The behavior therefore corresponds to an *irreversible* processes. Not because it is impossible to go back to the initial macrostate, but just because it is very unlikely to happen.

This also means that if the system starts with a much higher energy per oscillator in system A than in system B, $q_A/N_A \gg q_B/N_B$, energy will flow spontaneously from A to B, but not the other way around. (Except for small fluctuations). This is an explanation of *heat* — the flow of thermal energy from one side to another.

We have here essentially found the second law of thermodynamics: the law of increased multiplicity. The system develops towards a state of maximum (or increased) multiplicity. Simply because this is the most probable behavior. And as the system size increases it becomes increasingly more probable to be in the most probable macrostate and the probability for all other states goes to zero. But to gain insights into the probability of a macrostate for a large system, we need an improved expression for the multiplicity of macrostate q_A , an expression we can analyze mathematically.

6.3.5 Approximate multiplicities using Stirling's formula

Fig. 6.11 show the multiplicities of the macrostates q_A for two systems with $N_A = N_B = 10, q = 200$, and $N_A = N_B = 50, q = 1000$. In both cases, the maximum of the multiplicity occurs at $q_A = q_B = q/2$, but we see that for the system with larger N (and larger q) the multiplicity is sharper relative to the position of the maximum. But how sharp is it and how does the function look like around its peak? The multiplicity of macrostate q_A of the two-part Einstein crystal is $\Omega(q_A) = \Omega_A(q_A) \Omega_B(q_B)$ and the probability of the macrostate is $P(q_A) = \Omega(q_A) / \Omega_{TOT}$, where the multiplicity $\Omega_A(q_A) = (q_A + N_A - 1)! / (q_A! (N_A - 1)!)$. Unfortunately, it is difficult to discuss this expression because of the factorials. Instead, we would like an approximative formula which we can address using the tool-box of calculus. How can we find this approximative formula? We will do this in two stages, first we will find an approximative expression for the multiplicity using Stirling's approximation, and then we will find an approximative expression for the probability of a macrostate.

Theoretical argument: Approximation for the multiplicity. The multiplicity of an Einstein crystal is

$$\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}, \quad (6.12)$$

How can we approximate this expression? First, we employ the common trick of working with the logarithm of the multiplicity. Life becomes simpler when all the multiplications then become additions.

$$\ln \Omega(N, q) = \ln(q + N - 1)! - \ln q! - \ln(N - 1)!, \quad (6.13)$$

To simplify the factorials, we introduce Stirling's approximation for the factorial, which is good when the argument of the factorial is large:

$$\ln x! = x \ln x - x + \frac{1}{2} \ln 2\pi x, \quad (6.14)$$

which for large values of x can be further approximated to

$$\ln x! = x \ln x - x. \quad (6.15)$$

This is a good starting point to simplify the multiplicity. We can apply Stirling's approximation to each of the factorials in (6.12) if each of the factorials are large. That is, if q and N are large. In the limit of (very) large q and N we can also assume that $N - 1 \simeq N$. With these approximations we get:

$$\ln \Omega(N, q) = \ln(q + N - 1)! - \ln q! - \ln(N - 1)! \quad (6.16)$$

$$\simeq \ln(q + N)! - \ln q! - \ln N! \quad (6.17)$$

$$\simeq (q + N) \ln(q + N) - (q + N) - q \ln q + q - N \ln N + N \quad (6.18)$$

$$= (q + N) \ln(q + N) - q \ln q - N \ln N, \quad (6.19)$$

Now we assume that the number of units of energy is very large compared to the number of oscillators: $q \gg N$, which corresponds to assuming that we are in the classical limit where the quantum resolution into discrete energy levels are not important. We can then simplify $\ln(q + N)$ through:

$$\ln(q + N) = \ln \left[q \left(1 + \frac{N}{q} \right) \right] = \ln q + \ln \left(1 + \frac{N}{q} \right) \simeq \ln q, \quad (6.20)$$

where we have used the approximation $\ln(1 + x) \simeq 0$, which is valid when $x \ll 1$. Plugging this back into the relation for $\ln \Omega$ gets rid of the $q \ln q$ terms, giving

$$\ln \Omega \simeq (q + N) \ln q - N \ln N - q \ln q \quad (6.21)$$

$$= q \ln q + N \ln q - N \ln N - q \ln q = N \ln \frac{q}{N}. \quad (6.22)$$

The multiplicity is then

$$\Omega \simeq e^{N \ln(q/N)} = \left(\frac{q}{N}\right)^N \quad (q \gg N), \quad (6.23)$$

This is the multiplicity of the Einstein crystal. We will see further on that this is a very useful expression since we can use it to calculate macroscopic properties of the Einstein crystal. Now, we will use this formula to show that the multiplicity function is indeed very sharp.

Sharpness of the multiplicity function. Armed with this approximation for the multiplicity, we are ready to find an approximate expression for the multiplicity and probability of a macrostate for an Einstein crystal divided into two parts, A and B, that are in thermal contact. The multiplicity for the two-part system is

$$\Omega = \Omega_A(N_A, q_A) \Omega_B(N_B, q_B) = \left(\frac{q_A}{N_A}\right)^{N_A} \left(\frac{q_B}{N_B}\right)^{N_B} \quad (6.24)$$

For simplicity, let us address the case where $N_A = N_B$. The multiplicity is then

$$\Omega_A \Omega_B = \left(\frac{q_A}{N}\right)^N \left(\frac{q_B}{N}\right)^N = \left(\frac{q_A q_B}{N^2}\right)^N. \quad (6.25)$$

We saw in Fig. 6.11 that the multiplicity is sharp around $q_A = q/2$, we therefore express both q_A and q_B as small deviations from $q/2$ by introducing

$$q_A = \frac{q}{2} + x, \quad q_B = \frac{q}{2} - x, \quad (6.26)$$

where x is a number much smaller than q (but it is still rather large). We insert this expression back into the multiplicity, getting

$$\Omega = \Omega_A \Omega_B = \left(\frac{q_A q_B}{N^2}\right)^N = N^{-2N} \left[\left(\frac{q}{2} + x\right) \left(\frac{q}{2} - x\right)\right]^N \quad (6.27)$$

$$= N^{-2N} \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N. \quad (6.28)$$

Again, it is easier to work with the logarithm of this expression

$$\ln \Omega = \ln N^{-2N} + \ln \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N. \quad (6.29)$$

We simplify the second part of this expression by pulling $(q/2)^2$ outside the parenthesis

$$\ln \left[\left(\frac{q}{2}\right)^2 - x^2\right]^N = N \ln \left[\left(\frac{q}{2}\right)^2 \left(1 - \left(\frac{2x}{q}\right)^2\right)\right] \quad (6.30)$$

$$= N \ln \left(\frac{q}{2}\right)^2 + N \ln \left(1 - \left(\frac{2x}{q}\right)^2\right). \quad (6.31)$$

Where $2x/q \ll 1$ and we can therefore use the approximation $\ln(1+u) \simeq u$ (when $u \ll 1$):

$$\ln \left[\left(\frac{q}{2} \right)^2 - x^2 \right]^N \simeq N \ln \left(\frac{q}{2} \right)^2 - N \left(\frac{2x}{q} \right)^2. \quad (6.32)$$

The total multiplicity is therefore

$$\Omega = N^{-2N} e^{N \ln(q/2)^2} e^{-N(2x/q)^2} = \Omega_{\max} e^{-N(2x/q)^2} = \Omega_{\max} e^{-\left(\frac{x}{q/(2\sqrt{N})} \right)^2}, \quad (6.33)$$

This is the multiplicity for the macrostate $q_A = q/2 + x$, and the probability for this macrostate is simply the multiplicity multiplied by a constant. The probability $P(q_A)$ is therefore a similar function

$$P(q_A) = \Omega_A \Omega_B / \Omega_{TOT} = P_{\max} e^{-\left(\frac{x}{q/(2\sqrt{N})} \right)^2}, \quad (6.34)$$

We have found that the multiplicity and the probability is a Gaussian with a peak at $x = 0$, that is for $q_A = q/2$. This function falls off rapidly for both positive and negative x . How rapidly? The multiplicity has fallen to a value of $1/e$ when $N(2x/q)^2 = 1$, that is, when $x = q/(2\sqrt{N})$. It might appear that this value of x is a large number, since q is a large number. However, for realistic systems $N = 10^{22}$, which means that the multiplicity has fallen to $1/e$ after a deviation $x = q/(2 \cdot 10^{11})$, which is very small compared with the value of q . If the full graph, that is with the full range of possible q_A values from 0 to q , spanned from here to the Moon, the multiplicity of a system with would have fallen to $1/e$ over a distance of $3.86 \cdot 10^8 \text{ m} / (2 \cdot 10^{11}) = 19 \text{ mm}$. This also means that it is very unlikely to observe a value of q_A which is far away from $q/2$. The relative variations of q_A are extremely small in realistic systems — in practice these fluctuations are not measureable at all.

We call the limit when there are no measureable fluctuations away from the most likely macrostate **the thermodynamic limit**.

Comparison of exact and approximate results. We can test this approximation by comparing it with directly calculated values of the multiplicity. Fig. 6.12a shows plots of the multiplicity $\Omega(q_A; N, q) / \Omega_{\max}$ for $N = 10, 20, 40, 80$ and $q = 10N$. Fig. 6.12a shows direct plots of the multiplicity rescaled by its maximum value. Otherwise the systems with larger N and q would completely dominate the plot. The multiplicities have a clear maximum value and decay approximately symmetrically from each side of the maximum. The q_A value that gives maximum multiplicity increases as we increase N and q . We expect the maximum to be at $q_A = q/2$. Indeed, in Fig. ??b we see that if we plot Ω_{\max} as a function of $q_A - q/2$, the distributions are centered around zero. However, the widths of the distributions are also changing when we change q and N . How wide is the distribution compared to the average or typical value of q_A ? This is shown in Fig. 6.12, which shows Ω_{\max} as a function of $(q_A - q/2)/(q/2)$. Here, it is clear that the multiplicity becomes more and more narrowly distributed as N and q increases — the multiplicity is becoming sharper, and deviations from the average value for q_A are becoming less and less likely.

How good is the approximation we found in (6.33)? First, we replot the multiplicities according to the theory in (6.33): We plot Ω/Ω_{\max} as a function of $(q_A - (q/2))/(2\sqrt{N})$ in Fig. 6.12d. Yes! All the curves now fall onto the same curve, corresponding to the Gaussian form in (6.33). We call such a plot a data-collapse, and we often use such plots to demonstrate/validate our theories. Now, we can even compare with the Gaussian curve, we plot $\exp((q_A - q/2)/(2\sqrt{N}))$ in the same plot in Fig. 6.12d, and indeed the theoretical curve fits nicely with the observed curve — the approximation we have developed seems sound.

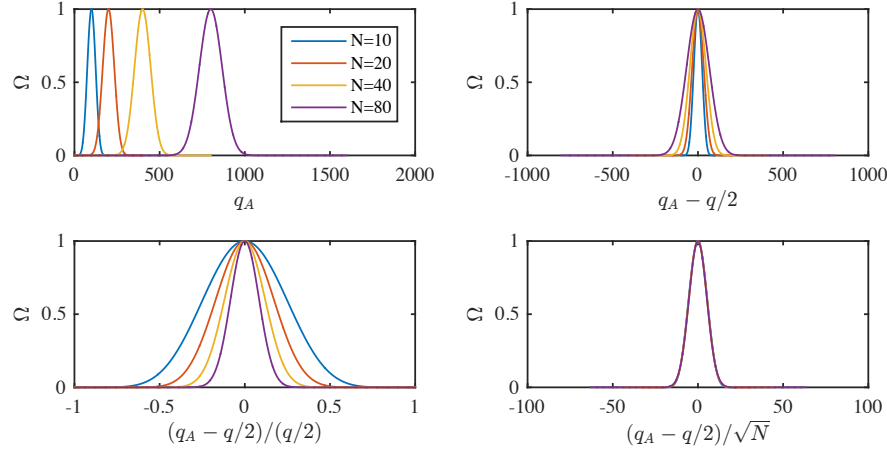


Fig. 6.12 Plot of $\Omega(q_A; q, N)/\Omega_{\max}$ as a function of **a** q_A , **b** $q_A - q/2$, **c** $(q_A - q/2)/(q/2)$, **d** $(q_A - q/2)/(2\sqrt{N})$.

6.4 The ideal gas — Theory

The main observations and conclusions we have made so far are valid for most systems in thermal contact or for fluctuations in parts within the system. The multiplicity function will typically be very sharp for large systems, meaning that the system will only have a reasonable probability to be in a very small fraction of the macrostates. Here, we will demonstrate in detail that this is also the case for an ideal gas — a simplified model of a gas.

Ideal gas. An ideal gas consists of N atoms (or molecules) in a box of size $L \times L \times$ as illustrated in Fig. ???. We assume that if the gas is thin, that is if the particles typically are far from each other, they do not interact much, except when they collide. As a first approximation, we will assume that the particles do not interact at all. This is our gas model, called an ideal gas, consisting of a set of particles moving inside a box without interactions. However, we do assume an implicit interaction — the

atoms may exchange energy, but in such a way that the total energy of the system is conserved. In addition to this, we will encounter a two quantum mechanical features. First, if the particles are Fermions, then two particles cannot be in the same energy state. We will see what consequences this has further on. Second, the particle cannot be discerned, and therefore we cannot discern two states where we only have exchanged two atoms. This will have consequences for how many states there are for the system.

The **ideal gas** model consists of the following assumptions

- The gas consists of N particles
- The particles are confined to an $L \times L \times L$ box of volume V
- The particles do not interact directly
- The total energy of the gas is E , but the distribution of energy within the gas is not prescribed
- The particles are identical and cannot be discern from one another

To describe the ideal gas, we will start from a single particle, then discuss two particles, before finally moving to a system of N particles. Our goal is to find the multiplicity of the ideal gas and to show that the multiplicity function indeed is sharp also for the ideal gas.

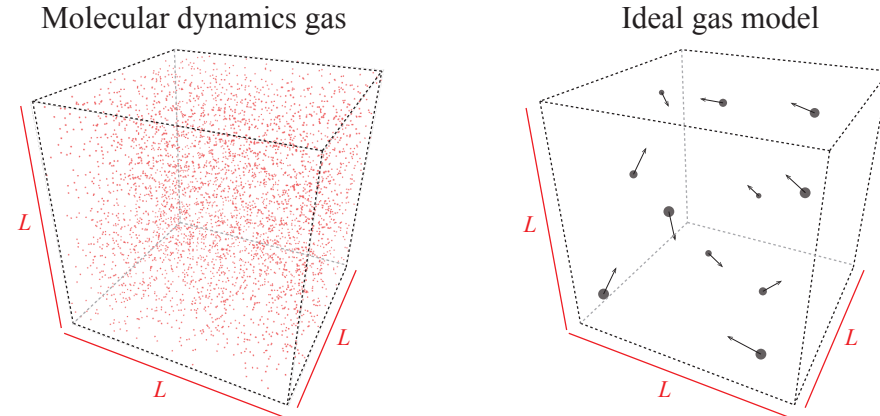


Fig. 6.13 (Left) Illustration of a molecular dynamics simulation of a thin gas. **Right** Illustration of the ideal gas model consisting of N non-interacting, identical particles in a $L \times L \times L$ box.

6.4.1 Microstates of a single particle

We start by addressing the multiplicity of a single particle in a three-dimensional box. What are the possible states of a single particle? From quantum mechanics we know that the possible states of a particle in a $L \times L \times L$ box are quantized with energy levels

$$\varepsilon(n_x, n_y, n_z) = \frac{h^2}{8mL^2} \mathbf{n} \cdot \mathbf{n} = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2), \quad (6.35)$$

where m is the mass of the particle, L is the length of the box and $\mathbf{n} = (n_x, n_y, n_z)$ is related to the momentum

$$\mathbf{p} = \frac{h}{2L} \mathbf{n}. \quad (6.36)$$

Each of the numbers n_x, n_y, n_z represents state for the motion in the x, y , and z -direction respectively, and they are all positive integers. We can illustrate the possible states in a three-dimensional space with n_x, n_y, n_z along the axes as illustrated in Fig. 6.14. Each point such as $(1, 1, 1)$ or $(2, 3, 2)$ represent a state for system. In the \mathbf{n} space there is a constant *density of states* corresponding to one state per unit volume. (Each $1 \times 1 \times 1$ volume has one state). We also see that because the energy depends on n^2 , $E = (h^2/8mL^2)n^2$, all states that have the same distance to the origin in n -space have the same energy.

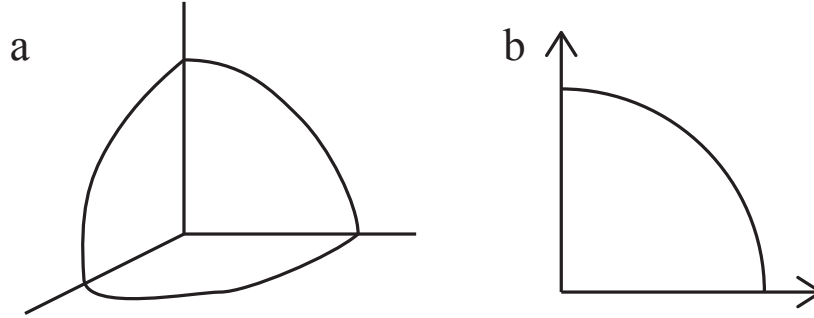


Fig. 6.14 Illustration of the states of a single particle in a three-dimensional box.

How can we use this to count the number of states in an ideal gas with a given total energy E , but with only one particle, $N = 1$? In this case, all the states with the same energy is on the surface of sphere with radius n in \mathbf{n} -space. What is this radius? It is found from the relation between n and E for the system consisting of a single particle in three dimensions:

$$E = \frac{h^2}{8mL^2} n^2 \Rightarrow n = \frac{2L}{h} \sqrt{2mE} \quad (6.37)$$

How can we count the corresponding number of states with this energy? We need to find the surface area of the corresponding sphere in \mathbf{n} -space, remembering to include only $1/8$ of this surface since we only address positive n -values. This is simple for the 3d system. The surface area is $4\pi n^2$, so that the number of states is:

$$\Omega_1 = \frac{1}{8}4\pi n^2 = \frac{1}{8}4\pi \frac{8mL^2}{h^2}E = \frac{4\pi L^2}{h^2}E = \frac{4\pi}{h^2}v^{2/3}E. \quad (6.38)$$

We notice that this result is a function of E and V as it should, and a function of N , but $N = 1$ here. How can we generalize this result to more particles?

6.4.2 Microstates of two non-interacting particles

What happens if we have more than one particle, for example, two particles? Let us address this in the simplest case — a one-dimensional system. In this case each particle is described by a single quantum state n_i , n_1 for particle 1 and n_2 for particle 2, so that the state of the system can be written as the pair (n_1, n_2) . When the total energy of the system is E , the possible states of the system is therefore all the states so that $E = h^2/(8mL^2)(n_1^2 + n_2^2) = E_0(n_1^2 + n_2^2)$, and we call this the multiplicity $\Omega_2(E)$ of the two-particle system. This means that for a total energy of $E = 4E_0$ there are two possible states, $(2, 0)$, and $(0, 2)$, and therefore $\Omega_2(4E_0) = 2$. Or is it? We have overlooked an important quantum mechanical effect!

Indistinguishable particles. This result is true if the particles are *distinguishable* from each other. They are distinguishable if we can place a label on each of them so that we can see that particle 1 is in state 2 whereas particle 2 is in state 0. However, for a gas of identical particles (atoms, molecules), the particles are *indistinguishable*. We cannot discern the state $(2, 0)$ from the state $(0, 2)$ because the molecules are identical. This means that we have counted too many states! We should not count all the possible ways that we can interchange the two particles. In general we know that for N particles, there are $N!$ possible ways to interchange them. For two particles, there are $2! = 2$ ways to interchange them. The correct multiplicity is therefore $\Omega_2(4E_0) = 2/2! = 1$.

Fermions or Bosons. In addition, we should also reflect on whether the particles are Fermions or Bosons. Why? Because if the particles are Fermions, there are additional restrictions. Two particles cannot be in the same state. This means that the state $(4, 4)$ is not a possible state for the two-particle system. We will return to this case later. For now, we will simply assume that we are in the limit when the energy is large, so that there are many more possible states available than there are particles, so that the number of restricted states for Fermions is negligible. These considerations will be more explicit in Chap. 7.

6.4.3 Microstates of N non-interacting particles

Distinguishable particles. For N independent, *distinguishable* particles all in a box of size $V = L \times L \times L$ the energy of the system is given as:

$$E = \frac{h^2}{8mL^2} \sum_{i=1}^N (n_{xi}^2 + n_{yi}^2 + n_{zi}^2) = \frac{h^2}{8mL^2} \sum_{i=1}^{3N} n_i^2. \quad (6.39)$$

Here, the sum is over $3N$ values of n_i . This means that we write N particles with 3 degrees of freedom as $3N$ particles with 1 degree of freedom. This expression reproduces the result for $N = 1$. We see that the energy E depends on the radius n in the $3N$ -dimensional \mathbf{n} -space:

$$E = (h^2/(8mL^2)) n^2 \Rightarrow n = (2L/h) \sqrt{2mE} \quad (6.40)$$

We can use the same approach as for a single particle to find the number of states with this energy. The density of states in the $3N$ -dimensional \mathbf{n} -space is still 1: There is one state for each $1 \times 1 \times \dots \times 1$ ($3N$ times) volume.⁴ We can therefore estimate the number of states by estimating the “area” of a sphere with radius n in $3N$ dimensions. (We must also remember to only include positive values for all the n_i in $\mathbf{n} = (n_1, n_2, n_3, \dots, n_{3N})$).

The general formula for the surface area of a d -dimensional sphere is:

$$A = \frac{2\pi^{d/2}}{(\frac{d}{2} - 1)!} r^{d-1}. \quad (6.41)$$

We use this expression with $d = 3N$. In addition, we also need to ensure that only the n_i -values in the first “octant” ($3N$ -tant) are used, that is we must divide by the number of “quadrants” $= 2^d = 2^{3N}$:

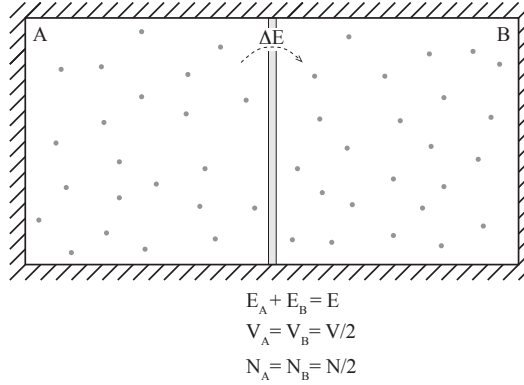
$$\Omega_{\text{disting}} = \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} \left(\frac{2L}{h} (2mE)^{1/2} \right)^{3N-1}, \quad (6.42)$$

Indistinguishable particles. This the number of states of a system of N distinguishable particles. However, an ideal gas consists of N *indistinguishable* particles? How should the multiplicity be modified? Based on our argument for two-particles above, we realize that we have counted too many states. We must therefore divide by the number of ways we can rearrange the N particles between the states, which is $N!$. The multiplicity for a gas of indistinguishable particles is therefore

$$\Omega = \Omega_{\text{indisting}} = \frac{1}{N!} \Omega_{\text{disting}} = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} \left(\frac{2L}{h} (2mE)^{1/2} \right)^{3N-1}. \quad (6.43)$$

⁴This is true if we do not include spin. For particles with spin $1/2$ there will be two states per such volume, one state with spin up and one state with spin down. We will return to this effect in Chap. ??.

Fig. 6.15 An isolated ideal gas is divided into two equal-sized parts, A and B. The two parts are separated by a partition that allows energy to pass through, but it is immobile (so that the volumes do not change), and impermeable (so that the number of particles on each side is constant).



We can simplify this expression by using that for very large N , $3N - 1 \simeq 3N$. However, in the first few examples, we will only be interested in the V and E dependence of this expression, which is simple:

$$\Omega = f(N) V^N E^{3N/2} . \quad (6.44)$$

6.4.4 Interaction between two ideal gases

We have now found the multiplicity for an ideal gas of N atoms, volume V , and energy E . We can use this expression to address the macrostate of two ideal gases in equilibrium, or equivalently, to find the distribution of energy inside an ideal gas.

Just like we did for the ideal crystal, we can divide the system into two parts A and B as illustrated in Fig. 6.15. The whole system is isolated, but the two parts are not thermally insulated. This means that the sum of the energies in A and B is constant, $E_A + E_B = E$. We assume that the two parts cannot change shape and that there is no transport of particles from one part to the other. Thus, the number of particles and the volumes of each of the two parts are constant and equal to N_A , N_B and V_A and V_B . For simplicity we assume that the system is divided into two equal parts: $N_A = N_B = N/2$ and $V_A = V_B = V/2$.

The question we want to answer is: What is the multiplicity of the macrostate described by E_A , $\Omega(E_A)$? In general, the multiplicity of the combined system is the product of the multiplicities of each of the systems:

$$\Omega(E_A; E, N, V) = \Omega_A \Omega_B = f(N_A) f(N_B) (V_A V_B)^N (E_A E_B)^N , \quad (6.45)$$

The only variation occurs in E_A and $E_B = E - E_A$. Just like we did for the Einstein crystal, we can develop a theory for this variation for small fluctuations in the energy. Let us look at a variation

$$E_A = \bar{E}_A + \Delta E , \quad E_B = \bar{E}_B - \Delta E , \quad (6.46)$$

where $\bar{E}_A = \bar{E}_B = E/2$ when $N_A = N_B$ and $V_A = V_B$. The two systems are then equal, and we would expect each system to have the same equilibrium energy given by \bar{E}_A and \bar{E}_B . We insert $E_A = E/2 + \Delta E$ and $E_B = E/2 - \Delta E$ into the multiplicity, getting

$$\Omega(\Delta E) = C \left(\left(\frac{E}{2} \right)^2 - \Delta E^2 \right)^N, \quad (6.47)$$

To simplify the algebra, we work on the logarithm of $\Omega(\Delta E)$, getting

$$\begin{aligned} \ln \Omega(\Delta E) &= \ln C + N \ln \left(\left(\frac{E}{2} \right)^2 - \Delta E^2 \right) \\ &= \ln C + N \ln \left(\frac{E}{2} \right)^2 \left(1 - \left(\frac{2\Delta E}{E} \right)^2 \right) \\ &= \ln C + 2N \ln(E/2) - N \left(\frac{2\Delta E}{E} \right)^2, \end{aligned} \quad (6.48)$$

which gives that

$$\Omega(\Delta E) = \Omega_m e^{-\left(\frac{\sqrt{N}\Delta E}{(E/2)} \right)^2} = \Omega_m e^{-\left(\frac{\Delta E}{(E/\sqrt{N})} \right)^2}, \quad (6.49)$$

This is Gaussian form for the multiplicity function, just like we found for the Einstein crystal. This means that also for the ideal gas, the multiplicity function is very sharp. Just as we found for the Einstein crystal, the width of the multiplicity function is proportional to \sqrt{N} while the average value is proportional to E which is proportional to N , hence the relative value of the width goes like $1/\sqrt{N}$. For realistic values of N , such as $N = 10^{20}$, this relative width becomes a very small number, typically 10^{-10} , which means that we cannot discern the actual value of the energy E_A in the ideal gas from its average value $E/2$ unless we can measure E_A to a precision of 10^{-10} , which is practically impossible.

This means that it is very unlikely to find the system in a state that is significantly different from $E/2$, where the multiplicity is at its maximum. If the system started away from this value, for example by having much more energy in part A than in part B, the system would evolve towards the most probable macrostate, where $E_A = E/2$. This is an example of a general principle, the second law of thermodynamics.

6.5 Thermal equilibrium, Entropy and Temperature

We have found that for the two models system we have addressed, the ideal gas and the ideal (Einstein) crystal, the most likely macrostate is very sharp and any fluctuation away from the most likely macrostate is extremely unlikely. If we start from a microstate that corresponds to a macrostate that is away from the most likely

macrostate the system will develop toward the most likely macrostate, and therefore toward a state with higher multiplicity — simply from the laws of probability.

This is what we call **the second law of thermodynamics**: The multiplicity of a system increases. What characterizes the state it evolves towards? The system evolves towards the macrostate with the largest multiplicity, and this state corresponds to the stationary state or the **equilibrium state** of the system.

Characteristics of the equilibrium state. What characterizes this equilibrium state — the state with maximum multiplicity? Let us find the maximum of the multiplicity for two Einstein crystals in contact. The multiplicity of a macrostate with energy q_A is

$$\Omega(N_A, q_A)\Omega(N_B, q_B) = \Omega(N_A, q_A)\Omega(N_B, q - q_A) \quad (6.50)$$

where $q = q_A + q_B$ is conserved. We can find the extremum of this function by differentiation with q_A :

$$\frac{d}{dq_A} \Omega(N_A, q_A)\Omega(N_B, q - q_A) = 0, \quad (6.51)$$

$$\frac{d\Omega(N_A, q_A)}{dq_A} \Omega(N_B, q - q_A) + \Omega(N_A, q_A) \frac{d\Omega(N_B, q - q_A)}{dq_A} = 0, \quad (6.52)$$

$$\frac{\partial \Omega(N_A, q_A)}{\partial q_A} \Omega(N_B, q - q_A) - \Omega(N_A, q_A) \frac{\partial \Omega(N_B, q_B)}{\partial q_B} = 0, \quad (6.53)$$

$$\frac{\partial \Omega(N_A, q_A)}{\partial q_A} \Omega(N_B, q_B) = \Omega(N_A, q_A) \frac{\partial \Omega(N_B, q_B)}{\partial q_B}, \quad (6.54)$$

$$\frac{1}{\Omega(N_A, q_A)} \frac{\partial \Omega(N_A, q_A)}{\partial q_A} = \frac{1}{\Omega(N_B, q_B)} \frac{\partial \Omega(N_B, q_B)}{\partial q_B}, \quad (6.55)$$

$$\frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} = \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B}. \quad (6.56)$$

$$\frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} = \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B}. \quad (6.57)$$

Definition of Entropy. This equation, (6.56), suggests an interesting relation between the logarithms of the multiplicities for the q_A -value that corresponds to the maximum multiplicity, that is, for the macrostate that is most probable. We introduce the term **entropy** to describe the logarithm of the multiplicity of the system:

Entropy: The entropy of an isolated system with given N , V , and E is given as

$$S = k \ln \Omega(N, V, E), \quad (6.58)$$

where k is called the Boltzmann constant, $k = 1.3806488(13) \cdot 10^{-23} \text{ J/K}$, and $\Omega(N, V, E)$ is the multiplicity of the system.

Relation between a microscopic and a macroscopic description. The definition of entropy relates the *microscopic description* of the world, given in the form of the multiplicity function, with the *macroscopic description* in the form of entropy. This definition of the entropy will allow us to calculate the macroscopic, thermodynamic properties of a system from a microscopic theory of the system.

Entropy and the second law of thermodynamics. We have seen that isolated systems will develop so that the multiplicity increases and they will develop toward a state with maximal multiplicity. We can now reformulate this law in terms of entropy: Isolated systems will develop so that the entropy increases, and in equilibrium the system will be in a macrostate with maximum entropy.

Properties of the Entropy. We see from the definition of the entropy that it is **additive**: Since the entropy is defined as the logarithm of the multiplicities, the entropy of two independent systems are the sums of their individual entropies, because the total multiplicity is the product of the individual multiplicities:

$$S = S_A + S_B \text{ when } \Omega = \Omega_A \cdot \Omega_B . \quad (6.59)$$

6.5.1 Equilibrium of the Einstein crystal

Let us see how the concept of entropy is related to the equilibrium of a system through an example we already know in detail — the Einstein crystal. For this system we know the multiplicity for a macrostate q_A , where q_A of the energy is in part A of the system and $q_B = q - q_A$ is in part B. The multiplicity for the macrostate q_A is

$$\Omega(q_A) = \Omega(N_A, q_A) \Omega(N_B, q_B) = \frac{(q_A + N_A - 1)!}{q_A! (N_A - 1)!} \frac{(q_B + N_B - 1)!}{(q_B! (N_B - 1)!)} . \quad (6.60)$$

And the entropy of the system when it is in macrostate q_A is therefore

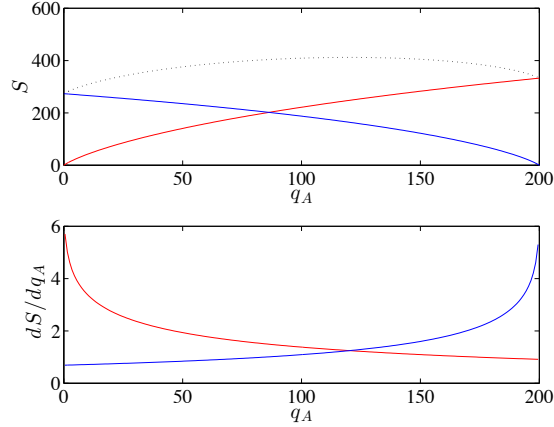
$$S(q_A) = \ln \Omega(q_A) = \ln \frac{(q_A + N_A - 1)!}{q_A! (N_A - 1)!} \frac{(q_B + N_B - 1)!}{(q_B! (N_B - 1)!)} . \quad (6.61)$$

We have already plotted the multiplicity of this system in Fig. 6.8, and we found that it had a sharp maximum. Let us redo this, but instead plot the Entropy $S(q_A)$ of the system as a function of the macrostate q_A . This is done using the a similar program, but we now take the logarithm of the multiplicity. The following program find the multiplicity and the entropy as a function of q_A for two Einstein crystals in thermal contact with $N_A = 300$ and $N_B = 200$ and $q = 100$ ⁵

```
from pylab import *
```

⁵We have here chosen N_A and N_B not to be equal so that the position of the maximum is not at the center of the figure. This makes the arguments clearer.

Fig. 6.16 Plot of the entropies S_A and S_B of two coupled Einstein crystals, and plots of the derivatives of the entropies with respect to q_A .



```
from scipy.misc import comb
NA = 300
NB = 200
q = 200
multA = zeros(q+1,float)
multB = zeros(q+1,float)
mult = zeros(q+1,float)
N = NA + NB
qvalue = array(range(q+1))
for ik in range(len(qvalue)):
    qA = qvalue[ik]
    qB = q - qA
    multA[ik] = comb(qA+NA-1, qA)
    multB[ik] = comb(qB+NB-1, qB)
    mult[ik] = multA[ik]*multB[ik]
SA = log(multA), SB = log(multB), STOT = SA + SB
plot(qvalue, SA, '-r', qvalue, SB, '-b', qvalue, STOT, '-k')
xlabel('q_A'), ylabel('S')
```

The resulting entropies of system A, $S_A(q_A)$, system B, $S_B(q - q_A)$, and of the total system, $S_{TOT}(q_A) = S_A(q_A) + S_B(q - q_B)$, is plotted in Fig. 6.16.

Entropy and equilibrium. We can use the plot of $S_{TOT}(q_A)$ and $S_A(q_A)$ in Fig. 6.16 to better understand the condition for equilibrium. Equilibrium occurs at the q_A -value where the entropy (and therefore the multiplicity) is maximum. This point is easily recognized in Fig. 6.16a. However, we can also find the equilibrium from the equilibrium condition in (??):

$$\frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} = \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B}, \quad (6.62)$$

which we can we translate into a condition for the entropies

$$\frac{\partial S(N_A, q_A)}{\partial q_A} = \frac{\partial S(N_B, q_B)}{\partial q_B}, \quad (6.63)$$

that is, the derivatives of the entropies of the two subsystems are the same when in equilibrium.

The derivatives of the entropies are shown in Fig. 6.16b. How can we interpret the condition in (6.112)? We can use the plot of $\partial S_A / \partial q_A$ to see what happens if system A is in a macrostate with a q_A -value that is smaller than the equilibrium value, such as the point marked with a circle in Fig. 6.16b. In this case, we see from the plot of $\partial S_A / \partial q_A$ that if we increase q_A by one, S_A increases and S_B decreases. However, we also see from the two curves that S_A increases more than S_B decreases, because the slope of $S_A(q_A)$ is steeper than that of $S_B(q_A)$, that is

$$\frac{\partial S(N_A, q_A)}{\partial q_A} > \frac{\partial S(N_B, q_B)}{\partial q_B}, \quad (6.64)$$

in this point. A small increase in q_A by Δq : $q_A \rightarrow q_A + \Delta q$, therefore results in an increase in the total entropy of the system

$$\Delta S_{TOT} = \Delta S_A + \Delta S_B = \frac{\partial S_A}{\partial q_A} \Delta q_A + \frac{\partial S_B}{\partial q_B} \Delta q_B = \left(\frac{\partial S_A}{\partial q_A} - \frac{\partial S_B}{\partial q_B} \right) \Delta q \quad (6.65)$$

since $\Delta q_A = \Delta q$ and $\Delta q_B = -\Delta q_A = -\Delta q$ since $q_B = q - q_A$ and q is a constant when the small amount Δq of energy is transferred from part B to part A. Since the entropy must increase as the system evolves towards equilibrium, we see that a small transfer of energy from part B to part A will occur when q_A is smaller than the equilibrium value.

Test your understanding: See if you can formulate a similar argument when q_A is larger than the equilibrium value.

It is first when the two slopes are equal that the system is in equilibrium. What does the slope of S_A tell us? It tells us how much the entropy (or multiplicity) changes when we add a small amount of energy. It tells us which way the system will develop, because it will develop toward larger entropy (multiplicity). For $q_A < \bar{q}_A$ the system will gain more entropy (multiplicity) by increasing q_A and decreasing q_B . Since the system, most likely, develops towards larger entropy (multiplicity) it will develop this way. Not always, but most probably.

6.5.2 Temperature in the Einstein crystal

Now, we can interpret the slope, $\partial S_A / \partial q_A$. This is what is equal when two systems are in thermal equilibrium. Since we also know that the temperature is equal in two systems in thermal equilibrium, it means that this relation is related to the temperature. How is it related to the temperature? The simplest assumption would be that it is a simple function of temperature. (If we look at the dimensions, we would get a

strong hint, but this, does, of course depend on how we have chosen the dimensions of k_B , which means that this argument becomes circular.)

When the slope, $\partial S/\partial q$, of the entropy as a function of energy is larger in system A than in system B, $\partial S_A/\partial q_A > \partial S_B/\partial q_B$, energy will spontaneously flow from system B to system A, since this will lower the total energy. Since we also know that thermal energy tends to flow from a system with high temperature to a system with low temperature, we expect the temperature to be low when the slope is high. One possible functional relationship with this behavior is to assume that the temperature is inversely proportional to the slope. This will indeed be how we define the temperature:

Temperature in an isolated system — a system with given (N, V, E) :

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}, \quad (6.66)$$

where we have included the N and V to show that we keep them constant as we are changing E .

This is our definition of temperature. We will in the following see that this is indeed consistent with our other possible definitions of temperature, such as from the average kinetic energy per particle in an ideal gas.

Connection between the microscopic and the macroscopic. We now have all the tools we need to connect the microscopic theories we have developed and the measurements we have done with macroscopic properties such as temperature, energy, and heat. This allows us to connect between the microscopic and the macroscopic worlds. This is the coupling between *statistical mechanics* and *thermodynamics*. Thermodynamics is the rules and laws we use to describe thermal and mechanical properties of macroscopic systems, whereas statistical mechanics is the theory that allows us to calculate and prove thermodynamic principles, laws and properties from a microscopical foundation.

We will in the following use this coupling to calculate the entropy of a system, $S(N, V, E)$ from a microscopic model: It may be from a theoretical model where we can count all the states or from a numerical simulation such as a molecular dynamics simulation. As soon as we have the function $S(N, V, E)$ we can start applying thermodynamics to this function, to understand relations between energy, temperature, volume, pressure, and the number of particles in our system. For this development, for the application of thermodynamics, it is not important how we have found $S(N, V, E)$, we just need this function as a starting point for our calculations. Let us therefore see how we can use the theories we have developed to find entropies, temperatures and energies for the ideal gas and the ideal crystal systems.

Microscopic.

- Multiplicity: $\Omega(N, V, E)$

- An isolated system develops towards larger multiplicity
- In equilibrium, an isolated system is in the macrostate with maximum multiplicity

Macroscopic.

- Entropy: $S = k_B \ln \Omega(N, V, E)$
- An isolated system develops towards larger entropy
- In equilibrium, an isolated system is in the macrostate with maximum entropy
- Temperature: $(1/T) = (\partial S / \partial E)_{N, V}$

6.5.3 Example: Entropy and energy of the Einstein crystal

We can now start connecting the microscopic and the macroscopic worlds. We have developed methods to find the multiplicity of an ideal gas and an Einstein crystal for a system with given N , V , and E . From this we can calculate the entropy, and from the entropy we can calculate the temperature.

The multiplicity of the Einstein crystal is

$$\Omega = \left(\frac{eq}{N} \right)^N, \quad (6.67)$$

in the limit when q and N is large, and $q \gg N$. The internal energy, E , is related to q by $E = q\varepsilon$, where ε is the energy unit for the energy states of the harmonic oscillator. The entropy is

$$S = k \ln \Omega = Nk (\ln q + \ln(E/\varepsilon) - \ln N), \quad (6.68)$$

$$S = Nk \ln E - Nk \ln(\varepsilon N) + Nk. \quad (6.69)$$

And the temperature is:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right) = \frac{Nk}{E}, \quad (6.70)$$

which gives

$$E = NkT. \quad (6.71)$$

This is what we would expect from the **equipartition theorem**, since N is the number of oscillators, and each oscillator has two degrees of freedom, hence, in equilibrium the energy is kT per oscillator and NkT in total.

From this we can also predict the **heat capacity**. The heat capacity is the amount of thermal energy, heat, which we need to transfer to a system in order to increase its temperature by one unit (Kelvin), which is given as the derivative of the energy with respect to temperature:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} (NkT) = Nk. \quad (6.72)$$

We call this the heat capacity at constant volume, since we keep both the volume and the number of particles constant when we take the partial derivative.

What we have found here now is a theoretical prediction of the heat capacity of a solid. The prediction is that it only depends on the number of oscillators, N , in the solid. This result can be compared with experimental or simulational results to check its validity.

6.5.4 Example: Entropy and energy of the ideal gas

We can perform a similar calculation for the ideal gas. In this case the multiplicity was a bit more complicated:

$$\Omega = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \left(\frac{2L}{h} (2mE)^{1/2} \right)^{3N-1}. \quad (6.73)$$

Here, we will assume that N is very large, so that $N - 1 \simeq N$, which simplifies the expression to:

$$\Omega \simeq \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \left(\frac{2L}{h} (2mE)^{1/2} \right)^{3N}. \quad (6.74)$$

This is further simplified to

$$\Omega = 2 \frac{1}{N! \left(\frac{3}{2}N\right)!} \left(\frac{2\pi mEL^2}{h^2} \right)^{3N/2}. \quad (6.75)$$

And the entropy is

$$\begin{aligned} \frac{S}{k} &= \ln \Omega \\ &= -(N \ln N - N) - \left(\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \right) + N \ln \left(\frac{2\pi mEL^2}{h^2} \right)^{3/2} \\ &= N \left(-(-1) - \left(-\frac{3}{2} \right) + \ln \left(\frac{V}{N} \right) + \ln \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} \right) \\ &= N \left(\ln \frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} + \frac{5}{2} \right). \end{aligned} \quad (6.76)$$

This equation is called Sackur-Tetrode's equation.

Sackur-Tetrode's equation for the entropy of an ideal gas:

$$S = N k_B \ln \left(\ln \frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} + \frac{5}{2} \right) . \quad (6.77)$$

We can use this to find the energy E of the ideal gas, by finding the temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} . \quad (6.78)$$

Since N and V are constants in this derivative, we only need to include the terms that include the energy:

$$S(N, V, E) = g(N, V) + N k \ln E^{3/2} = g(N, V) + \frac{3}{2} N k \ln E , \quad (6.79)$$

where $g(N, V)$ contains all the factors that do not depend on E . It is now easy to find the temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{3}{2} N k \frac{1}{E} , \quad (6.80)$$

which gives

$$E = \frac{3}{2} N k T . \quad (6.81)$$

Again, this corresponds to the **equipartition principle**. The ideal gas has N atoms, and each atom has three degrees of freedom: classically this corresponds to three independent directions for the velocities, and quantum-mechanically this corresponds to the three independent quantum number n_x, n_y, n_z we used to characterize the states of the ideal gas. Each degree of freedom contributes with $kT/2$, which gives $3NkT/2$ for the whole gas of N gas atoms.

6.5.5 Example: Entropy of expansion

We can use Sackur-Tetrode's equation to gain more insight into the behavior of the ideal gas. First, let us look at what happens if we allow an ideal gas to expand without changing its energy or the number of particles as illustrated in Fig. 6.17. We only change the volume. You can think of an isolated box of size V_2 , where the gas initially is confined to a smaller part, V_1 , of the box. Then an internal barrier is removed, and the gas is allowed to fill the entire volume, while the total energy and the total number of particles is conserved since the whole system is isolated. The change (increase, as always) in entropy in this case by going from a volume V_1 to a volume V_2 is:

$$\Delta S = Nk (\ln V_2 - \ln V_1) = Nk \ln \frac{V_2}{V_1}. \quad (6.82)$$

In this case, the expansion of the system was *isoenergetic* — done at constant energy of the whole system. However, since for an ideal gas, the energy and the temperature are related by $E = (3/2)NkT$, we see that when the number of particles is constant, having a constant energy corresponds to having a constant temperature. In this particular case, the change in entropy we have found therefore also corresponds to an *isothermal* expansion — an expansion done at constant temperature. (*Iso* here means *at the same* or constant).

In this case, the process is clearly also *irreversible* because the entropy of the isolated system increases during the processes. Indeed, we would be very surprised if we placed the dividing wall back into the system, and all the gas particles spontaneously concentrated in the initial volume, V_1 , by itself. Such a process in an isolated system would be violating the second law of thermodynamics, because entropy would decrease, and also appears to violate our basic intuitions about valid or probable processes in the world.

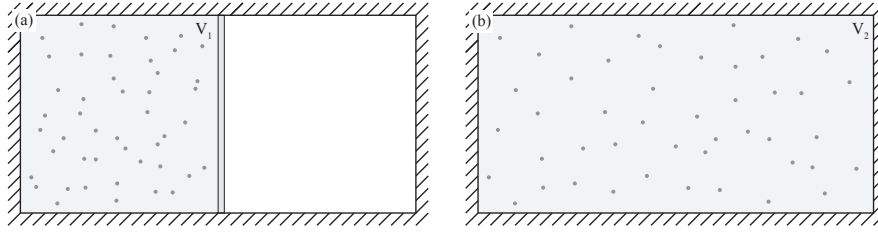


Fig. 6.17 Illustration of an expansion of an ideal gas while the gas is in an isolated box. The system is isolated, and the gas expands from V_1 to V_2 after the internal wall was removed from the system.

6.5.6 Example: Entropy of mixing

What if we take two gases, A and B, each initially occupying a volume V , and then allow the two gases to mix? Let us assume that the two gases are inside a common, isolated system, so that their total number of particles, energy and volumes are conserved. Then an internal barrier between the two gases is removed, so that gas A can move into the volume originally occupied by gas B and vice versa as illustrated in Fig. 6.18. If the two gases are not interacting, and the two gases are not the same, we can consider each process independently. First gas A expands into twice its volume, leading to an entropy change

$$\Delta S_A = N_A k \ln \frac{V_{A,2}}{V_{A,1}}, \quad (6.83)$$

and similarly for gas B:

$$\Delta S_B = N_B k \ln \frac{V_{B,2}}{V_{B,1}}, \quad (6.84)$$

If $N_A = N_B = N$ and $V_2 = 2V_1$ for both A and B, we get

$$\Delta S_A = Nk \ln 2, \quad \Delta S_B = Nk \ln 2, \quad (6.85)$$

and the total entropy change is

$$\Delta S_{TOT} = \Delta S_{\text{mix}} = \Delta S_A + \Delta S_B = 2Nk \ln 2, \quad (6.86)$$

where we have used the additive property of entropies. This entropy is called the *entropy of mixing* of the system.

Notice that we here assumed that the two gases were different. Otherwise, nothing would happen — there would not be any change in entropy if we open a separation between two equal gases each of volume V .

We also clearly see that this process is *irreversible* for this isolated system since the entropy is increasing. We would be very surprised if, after the system was completely mixed, gas A spontaneously segregated into the left side and gas B segregated into the right side. Indeed, such as processes in an isolated system would violate the second law of thermodynamics, since the total entropy of the isolated system would increase. Your intuition is therefore perfectly aligned with the second law of thermodynamics in this case.

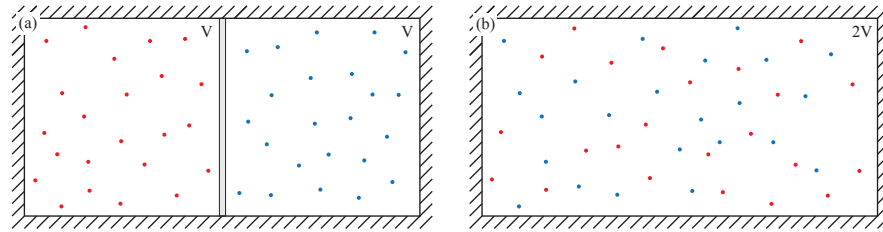


Fig. 6.18 Illustration of the mixing of two gases A and B, each with initial volume V .

6.5.7 Example: *Gibb's paradox*

Sackur-Tetrode's equation is carefully constructed to ensure that the entropy does not change if we mix two identical gases. What is the change in entropy if we have two identical gases each with N particles and volume V and at the same energy, E , and then we remove the barrier between them?

If the gases were different, we know that the change in entropy would correspond to the entropy of mixing. If the gases are identical, there should not be any change in entropy. What does the Sackur-Tetrode equation give us?

Before the partition is removed, the entropy of each part is $S(N, V, E)$ so that the total entropy of the system is $2S(N, V, E)$. After the partition is removed, the system consists of a gas with $2N$ particles, $2V$ volume and $2E$ energy with entropy $S(2N, 2V, 2E)$. According to Sackur-Tetrode's equation the entropy is

$$S(2N, 2V, 2E) = (2N)k \left(\ln \frac{2V}{2N} \left(\frac{4\pi m(2E)}{3(2N)h^2} \right)^{3/2} + \frac{5}{2} \right). \quad (6.87)$$

We see that the two ratios $2V/2N = V/N$ and $2E/2N = E/N$, and that the total entropy therefore is

$$S(2N, 2V, 2E) = 2Nk \left(\ln \frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} + \frac{5}{2} \right) = 2S(N, V, E). \quad (6.88)$$

Sackur-Tetrode's equation therefore correctly predicts that there is no change in entropy when we remove such an internal barrier between two identical gases. However, in order for this to be the case, it was essential to include the $N!$ -term in the multiplicity, because it is this term that ends up as the N in the V/N term. Without the $N!$ -term, we would instead have

$$S(N, V, U) = Nk \left(\ln \left(V \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} \right) + \frac{3}{2} \right). \quad (6.89)$$

and the entropy of a double system, $S(2N, 2V, 2E)$, would be:

$$S(2N, 2V, 2E) = 2Nk \left(\ln \left(2V \left(\frac{4\pi m2E}{3N2h^2} \right)^{3/2} \right) + \frac{3}{2} \right) \quad (6.90)$$

The difference between $2S(N, V, E)$ and $S(2N, 2V, 2E)$ would then be $2Nk \ln 2$, which is the entropy of mixing. The Sackur-Tetrode equation is therefore carefully made to ensure that this does not occur. This issue was first raised by Gibbs, and is called *Gibbs paradox*.

We notice that the entropy scales in a simple way when we change all the variables with a factor b : $S(bN, bV, bE) = bS(N, V, E)$. We call quantities that scale in such a simple way *extensive quantities*.

6.6 The laws of thermodynamics

We now have the basis for the two first laws of thermodynamics, and we have both a microscopic and a macroscopic interpretation of the laws of thermodynamics.

In the *microscopic view*, we know that a system with constant N , V , and E has constant energy. This is indeed how we have set the system up. On an atomic scale, the total energy is the sum of the kinetic and potential energies of all the atoms in the system, and this energy is conserved. This corresponds to the **first law of thermodynamics** – the conservation of energy.

In the microscopic view, we characterize a system by the multiplicity $\Omega(N, V, E)$, which we have been able to calculate for simple systems such as the ideal gas and the ideal crystal. We have also found two basic laws:

- The system develops in time to the macrostate with the maximum multiplicity
- In equilibrium, the system in the macrostate with the maximum multiplicity

We have found that we can characterize a system by its microstates. We assume that all microstates are equally probable. There are much more microstates for some macrostates, and these most likely macrostates will be the most likely observed macrostates in the system. Indeed, for realistic system sizes — i.e. $N = 10^{20}$ — deviations from the maximum values of the macrostates are extremely unlikely. The standard deviation of the distribution of macrostates is about 10^{-10} of the value at the maximum. These distributions are therefore so sharp that we can characterize the system by the value of the most likely macrostate alone.

These two laws are called the second law of thermodynamics. Here, they have a microscopic formulation. How can we formulate similar laws on the macroscale?

The first law of thermodynamics is easily transferrable. The total energy of the system is conserved. We call this the internal energy U or E . Any change in the internal energy must come from an external source: In the form of mechanical work W performed on the system or in the form of thermal energy Q transferred into the system. Hence, we can formulate the first law of thermodynamics:

First law of thermodynamics:

$$\Delta E = W + Q, \quad (6.91)$$

Macroscopically, we have introduced the quantity S for the entropy of the system, and entropy is related to the multiplicity of the system with constant N , V , and E by

$$S = k \ln \Omega(N, V, E). \quad (6.92)$$

The two microscopic laws that (i) the system evolves towards larger multiplicity and (ii) that in equilibrium the system has maximum multiplicity therefore corresponds to

The second law of thermodynamics:

An isolated system with constant N , V , E develops towards larger entropy, $\Delta S \geq 0$, and in equilibrium, the entropy is at its maximal value.

These are the fundamental laws we need to understand the macroscopic world. We can use our microscopic understanding to understand the foundation of the macroscopic laws, and to calculate the relationships for quantities such as the entropy.

In addition, we usually supplement with two additional laws:

The zeroth law of thermodynamics:

If systems A and B are in thermal equilibrium and systems B and C are in thermal equilibrium, then system A and C are also in thermal equilibrium.

This follows from the equation for thermal equilibrium - and temperature: If $T_A = T_B$ and $T_B = T_C$ then, indeed, $T_A = T_C$.

In addition, we will later also introduce a third law of thermodynamics, which allows us to set an absolute scale for the entropy.

The third law of thermodynamics: The entropy of a system approaches a constant as the temperature approaches zero.

These are the fundamental laws of thermodynamics. From these laws we will be able to develop the complete theory of thermodynamics. We will now use these laws, along with our microscopic theory that allows us to calculate the entropy and the temperature of an isolated system, in order to address the behavior of realistic, macroscopic systems.

6.6.1 Example: Entropy and heat

Let us now use the laws of thermodynamics to discuss a process without resorting to a microscopic description. Let us address the entropy change for a real process where thermal energy, heat, is transferred from one system to another.

First, we need to be precise in how we define the system we study. We start with an isolated system that consists of two subsystems, A and B. Initially, the two systems have temperatures T_A and T_B , energies E_A and E_B , and entropies, S_A and S_B . The systems are also isolated from each other. But what happens if we now transfer a small amount of thermal energy, ΔE , from A to B, so that the total energy in the

system is conserved as illustrated in Fig. ?? . This means that the change of energy in system A is $\Delta E_A = -\Delta E$ and the change of energy in system B is $\Delta E_B = \Delta E$.

Change in entropy. The entropy change in the whole system is

$$\begin{aligned}\Delta S &= \Delta S_A + \Delta S_B \\ &= \left(\frac{\partial S_A}{\partial E_A} \right)_{N_A} \Delta E_A + \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B} \Delta E_B \\ &= \left(\frac{\partial S_A}{\partial E_A} \right)_{N_A} (-\Delta E) + \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B} \Delta E\end{aligned}\quad (6.93)$$

We can now use the general relation between temperature and the derivative of the entropy for each of the two systems:

$$\frac{1}{T_A} = \left(\frac{\partial S_A}{\partial E_A} \right)_{N_A}, \quad \frac{1}{T_B} = \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B}. \quad (6.94)$$

The total change in entropy is therefore:

$$\Delta S = \Delta S_A + \Delta S_B = \left(-\frac{1}{T_A} + \frac{1}{T_B} \right) \Delta E. \quad (6.95)$$

Because the whole system is isolated, the total entropy must increase (or be the same) in this process. This means that T_A must be larger than T_B for this process to be thermodynamically possible. (Meaning probable: Any other process would be very unlikely). This is, of course, in perfect alignment with our intuition: Heat is transferred from objects with high temperature to objects with lower temperature and not the opposite way.

Heat and entropy change. How is the heat transferred between the two systems related to the entropy change in the systems? Since there is no other energy transfer than heat between systems A and B, we know that the change in energy corresponds to heat transferred. From the first law of thermodynamics we know that $\Delta E_A = Q_A + W_A$, and since $W_A = 0$, we see that $Q_A = \Delta E_A$. Similarly, for system B, $Q_B = \Delta E_B$. It is now simple to relate the entropy change and the change in energy for each of the systems. As long as the systems do not change volume or particle number, we can use the definition of temperature to find the change in entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} \Rightarrow dS = \frac{dE}{T}. \quad (6.96)$$

This means that we can estimate the change in entropy from the heat:

$$dS = \frac{Q}{T}. \quad (6.97)$$

or we can estimate the heat from the change in entropy:

$$Q = TdS. \quad (6.98)$$

Numerical example. For example, if a hot object, A, at $T_A = 1500\text{ K}$ is put in contact with a cold object, B, at $T_B = 300\text{ K}$, and the thermal energy transferred during 60 s is 150 J, then we can calculate the changes in entropy through:

$$\Delta S_A = \frac{-150\text{ J}}{1500\text{ K}} = -0.1\text{ J/K}, \quad (6.99)$$

and

$$\Delta S_B = \frac{150\text{ J}}{300\text{ K}} = 0.5\text{ J/K}. \quad (6.100)$$

We see that the total change in entropy is indeed positive, as it must for this process to be possible according to the second law of thermodynamics.

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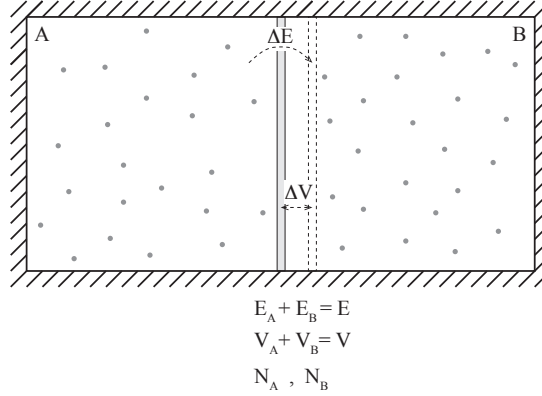
6.7 Mechanical equilibrium — Pressure

So far we have developed a theory for a fluctuation in the energy of a system: We divided an isolated system into two parts, and allowed a small amount of energy, ΔE , to be transported from one part to another, and found the equilibrium state as a function of the derivative of the entropy. Now, let us see if we can expand this argument also to systems where we allow also the volume of the system to vary and further on, also the number of particles to vary. But we will now use a thermodynamics argument without resorting to the microscale. Can we pull this off?

We address the behavior of an isolated system divided into two parts A and B. The systems are divided by a piston: A wall that can transfer thermal energy and mechanical energy by moving. The wall is not permeable, so the number of particles is constant on each side of the wall. The total energy and volume is conserved: $E_A + E_B = E$ and $V_A + V_B = V$, as well as the number of particles in each subsystem N_A, N_B , as illustrated in Fig. ??.

Intuitively, what would we expect to determine the equilibrium in such a system? We already know that for thermal equilibrium to occur, the two systems must have the same temperature, otherwise we could increase entropy by transferring some energy from one part to another. But what would determine mechanical equilibrium? We would expect the piston to be in equilibrium only if the force acting from each part of the system on the piston sum to zero, so that the net force on the piston is zero. This occurs only if the pressure in each of the parts are the same, since the force from part A on the piston is $F_A = p_A A_A$, where F_A is the force and p_A is the pressure, and similarly for part B, $F_B = p_B A_B$. Here, the areas on each side

Fig. 6.19 Illustration of an isolated system divided into two parts by a piston so that thermal energy and volume may be exchanged between the systems, but the total energy and volume is conserved.



of the piston are the same, so that the pressures also must be the same. Equilibrium would therefore require equal pressures.

What are the equilibrium condition from a thermodynamical perspective? We know from the second law of thermodynamics, that an isolated system — the whole system including both part A and B — is in equilibrium when the entropy of the whole system is maximum. The total entropy is the sum of the entropies of each subsystem:

$$S_{TOT} = S_A(N_A, V_A, E_A) + S_B(N_B, V_B, E_B), \quad (6.101)$$

where $V_A + V_B = V$, $E_A + E_B = E$, and N_A and N_B are constants, so that $V_B = V - V_A$ and $E_B = E - E_A$. The entropy is therefore a function of the macrostate described by E_A and V_A , and we want to find the macrostate that maximizes the entropy. This corresponds to finding the maximum of a two-dimensional function, which occurs as a maximum along both axes, as illustrated in Fig. 6.20. The maximum (or extremum) occurs when $dS = 0$, that is, when

$$dS = dS_A + dS_B = \left(\frac{\partial S_A}{\partial E_A} \right)_{N_A, V_A} dE_A + \left(\frac{\partial S_A}{\partial V_A} \right)_{N_A, E_A} dV_A \quad (6.102)$$

$$+ \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B} dE_B + \left(\frac{\partial S_B}{\partial V_B} \right)_{N_B, E_B} dV_B = 0, \quad (6.103)$$

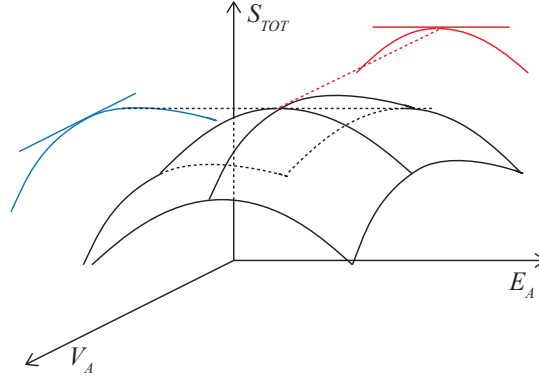
where we now insert that $dE_B = -dE_A$ and $dV_B = -dV_A$ (from $E_A + E_B = E = \text{const.}$ and $V_A + V_B = V = \text{const.}$), getting:

$$dS = \left(\left(\frac{\partial S_A}{\partial E_A} \right)_{N_A, V_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B} \right) dE_A \quad (6.104)$$

$$+ \left(\left(\frac{\partial S_A}{\partial V_A} \right)_{N_A, E_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{N_B, E_B} \right) dV_A = 0. \quad (6.105)$$

For this to be true for any small dE_A and dV_A , we get the two conditions:

Fig. 6.20 Illustration of the entropy as a function of E_A and V_A . The maximum of the entropy occurs where the derivatives with respect to both E_A and to V_A are zero.



$$\left(\frac{\partial S_A}{\partial E_A}\right)_{N_A, V_A} = \left(\frac{\partial S_B}{\partial E_B}\right)_{N_B, V_B}, \quad \left(\frac{\partial S_A}{\partial V_A}\right)_{N_A, E_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{N_B, E_B}. \quad (6.106)$$

The first condition is the same condition we found for a purely thermal contact: The temperatures in the two parts must be the same in equilibrium. We guess that the second term is related to the pressures in the two parts. But how is it related to the pressure? We can gain some insight into this by looking at the units of this expression: dS/dV . We notice that entropy has dimensions $\text{J/K} = \text{Nm/K}$, V has dimensions m^3 , and pressure has dimensions N/m^2 . The derivative of S with respect to V therefore has dimensions $(\text{Nm/K})/\text{m}^3$, that is $(\text{N/m}^2)/\text{K}$. We must therefore multiply (dS/dV) by a temperature to get dimension pressure. Since T is the same in both systems in equilibrium we can multiply with T , getting to a definition of pressure:

Definition of pressure in an isolated system:

$$p = T \left(\frac{\partial S}{\partial V} \right)_{E, N}, \quad (6.107)$$

This is not the only way to define pressure. We could for example also have included a multiplicative or an additive constant, but we will see below that this definition of pressure does reproduce the correct ideal gas law and other known features of the systems we are interested in.

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6.7.1 Example: Pressure of ideal gas

We are now in a position to calculate the pressure of a system, given that we know the entropy. For an ideal gas, we found that the entropy was given by Sackur-Tetrode's equation:

$$S = Nk \ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3N h^2} \right)^{3/2} + \frac{5}{2} \right) . \quad (6.108)$$

However, we only need the volume dependence to find the pressure:

$$S = Nk \ln V + f(N, E) . \quad (6.109)$$

From (6.107) the pressure in the ideal gas is:

$$p = T \left(\frac{\partial S}{\partial V} \right)_{E, N} = T \frac{Nk}{V} \quad (6.110)$$

which corresponds to

$$pV = NkT , \quad (6.111)$$

which indeed is the ideal gas law. This also shows we should not include any other factors in the definition of the pressure in (??) — it reproduces the correct ideal gas law at it is.

6.8 The thermodynamic identity

We now know enough to develop a differential for the entropy: We would like to see how the entropy S changes with a change in E and V . We do this by writing out the differential for the change dS :

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V, N} dE + \left(\frac{\partial S}{\partial V} \right)_{E, N} dV + \left(\frac{\partial S}{\partial N} \right)_{E, V} dN . \quad (6.112)$$

We have not looked at changes in particle number yet. Let us therefore for now assume that $dN = 0$. The other two expressions we now know

$$\left(\frac{\partial S}{\partial E} \right)_{V, N} = \frac{1}{T} , \quad \left(\frac{\partial S}{\partial V} \right)_{E, N} = \frac{1}{T} p . \quad (6.113)$$

We insert these into the differential in (6.112):

$$dS = \frac{1}{T} dE + \frac{p}{T} dV \Rightarrow T dS = dE + p dV . \quad (6.114)$$

This equation is true for any infinitesimal change in any system, as long as p and T are well defined and N is constant. It is a fundamental equation in thermodynamics, which we will use many times throughout this book. It is called

The thermodynamic identity:

$$T dS = dE + p dV - \mu dN . \quad (6.115)$$

(We have not yet allowed N to vary or introduced the chemical potential μ , but we write the equation in this form for completeness. When N is constant, $dN = 0$, and the last term disappears).

6.8.1 The thermodynamic identity and partial derivatives

This equation, in combination with the first and second law of thermodynamics will be our main tool to address thermodynamic processes, as we will see in examples and problems. However, this equation is also a very compact way to remember the various derivatives of the entropy. From (6.115) we can easily find the various partial derivatives by applying simple algebra to the differentials. Let us demonstrate by examples.

First, what is the derivative of S with respect to E when V and N are constant? We can see this directly from the thermodynamic identity, using that $dV = 0$ and $dN = 0$:

$$T dS = dE + p \underbrace{dV}_{dV=0} - \mu \underbrace{dN}_{dN=0} \quad (6.116)$$

$$\frac{dS}{dE} = \frac{1}{T} . \quad (6.117)$$

which gives us:

$$\left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{1}{T} . \quad (6.118)$$

Similarly, we find the derivative of S with respect to V when E and N are constants? In this case, $dE = 0$ and $dN = 0$, which we insert into the thermodynamic identity in (6.115), getting

$$T dS = \underbrace{dE}_{dE=0} + p dV - \mu \underbrace{dN}_{dN=0} \quad (6.119)$$

$$\frac{dS}{dV} = \frac{p}{T} . \quad (6.120)$$

which gives us:

$$\left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{p}{T} . \quad (6.121)$$

This is a very useful technique, which we will use again and again in various disguised throughout this text. Learn and practice it, and you will only have to remember a very few definitions and laws in order to master all of thermodynamics.

6.8.2 Entropy, Heat and Work

If we compare the thermodynamic identity

$$T dS = dE + p dV - \mu dN , \quad (6.122)$$

which when $dN = 0$ can be rewritten as

$$dE = T dS - p dV , \quad (6.123)$$

with the first law of thermodynamics

$$dE = Q + W , \quad (6.124)$$

We recognize that the work done on a system, such as a piston, with a pressure p , when the piston is moved so that the volume changes by a small amount dV , is $W = p dV$. Notice the sign! The work W in the first law is the work done *on* the system. If the pressure inside the system is p and the piston expands so the $dV > 0$, the system inside the piston does a positive work $p dV$ on the environment, whereas the work done on the system is the negative of this, $W = -p dV$.

Similarly, if there is no mechanical work done on the system, then the change in energy corresponds to the heat, Q , transferred into the system. Therefore, we may conclude that $Q = T dS$ in this case.

However, these results are only correct when the processes we consider are sufficiently close to the equilibrium, that is, when the processes are *quasistatic*. Let us now briefly review how we can describe various thermodynamic processes.

6.8.3 Process description

We describe thermodynamic systems by the macrostate variables of the system, such as by S , E , V , N , T , and p . Various thermodynamic processes are described by how we change these variables and by how we change the system.

We discern between **reversible** and **irreversible** processes. A reversible process is a process that may go both ways — backward and forward. That is, the process has time symmetry. This means that the entropy change for a reversible process in

an isolated system must be zero. If it was positive, then the reverse process cannot occur since it would lead to a reduction in entropy.

If we always keep a system very close to its equilibrium state, we call the process **quasistatic**. This is an ideal case, where the process occurs infinitely slowly so that the system always has time to reach thermodynamic equilibrium between each time the system is changed.

In addition, we will introduce various words to describe processes where some of the thermodynamic variables are constant. Usually, we will use the prefix *iso* for the constant variable. For example, a process at constant temperature is called *isothermal*, whereas a process at constant pressure is called *isobaric*. The various processes are

- **quasistatic processes** where the system is changed so slowly that it is at equilibrium at each step
- **adiabatic processes** where there is no thermal energy (heat) transferred to the system
- **isentropic processes** = adiabatic + quasistatic processes
- **isobaric processes** = processes at constant pressure
- **isochoric processes** = processes at constant volume
- **isothermal processes** = processes at constant temperature
- **isoenergetic processes** = processes at constant energy

Most of the theory we develop will be for quasistatic processes. Just be careful about what happens when a process is not quasistatic, then we may have a change in entropy that is larger than what you would expect from work or heat alone.

6.9 Diffusive equilibrium — Chemical potential

We have now seen that two systems that are in *thermal contact*, that is they are allowed to exchange energy, are in equilibrium when the temperatures are the same. If the two systems also are in *mechanical contact*, that is they are allowed to exchange volume, they are in equilibrium when also the pressures are the same. What if we also allow the two systems to exchange particles — what is the equilibrium condition then?

Two systems that are allowed to exchange particles are said to be in *diffusive contact*. We divide an isolated system into two parts, A and B, so that the total energy, volume and particle number is conserved:

$$E_A + E_B = E \Rightarrow E_A = E - E_B \quad dE_A = -dE_B \quad (6.125)$$

$$V_A + V_B = V \Rightarrow V_A = V - V_B \quad dV_A = -dV_B \quad (6.126)$$

$$N_A + N_B = N \Rightarrow N_A = N - N_B \quad dN_A = -dN_B \quad (6.127)$$

This system is in equilibrium for the macrostate (E_A, V_A, N_A) that makes the total entropy maximum, which occurs when $dS_{TOT} = 0$, where the differential is

$$dS = \left(\frac{\partial S_A}{\partial E_A} \right)_{N_A, V_A} dE_A + \left(\frac{\partial S_A}{\partial V_A} \right)_{N_A, E_A} dV_A + \left(\frac{\partial S_A}{\partial N_A} \right)_{E_A, V_A} dN_A \quad (6.128)$$

$$+ \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B} dE_B + \left(\frac{\partial S_B}{\partial V_B} \right)_{N_B, E_B} dV_B + \left(\frac{\partial S_B}{\partial N_B} \right)_{E_B, V_B} dN_B = 0, \quad (6.129)$$

which gives

$$dS = \left(\left(\frac{\partial S_A}{\partial E_A} \right)_{N_A, V_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B} \right) dE_A \quad (6.130)$$

$$+ \left(\left(\frac{\partial S_A}{\partial V_A} \right)_{N_A, E_A} - \left(\frac{\partial S_B}{\partial V_B} \right)_{N_B, E_B} \right) dV_A \quad (6.131)$$

$$+ \left(\left(\frac{\partial S_A}{\partial N_A} \right)_{E_A, V_A} - \left(\frac{\partial S_B}{\partial N_B} \right)_{E_B, V_B} \right) dN_A = 0, \quad (6.132)$$

which again gives the following conditions:

$$\left(\frac{\partial S_A}{\partial E_A} \right)_{N_A, V_A} = \left(\frac{\partial S_B}{\partial E_B} \right)_{N_B, V_B}, \quad (6.133)$$

$$\left(\frac{\partial S_A}{\partial V_A} \right)_{N_A, E_A} = \left(\frac{\partial S_B}{\partial V_B} \right)_{N_B, E_B}, \quad (6.134)$$

$$\left(\frac{\partial S_A}{\partial N_A} \right)_{V_A, E_A} = \left(\frac{\partial S_B}{\partial N_B} \right)_{V_B, E_B}. \quad (6.135)$$

We introduce this new condition as the chemical potential, μ , which has units of energy and must be the same in both systems when the two systems are in equilibrium:

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{E, V}. \quad (6.136)$$

For two systems in diffusive equilibrium, the chemical potential is the same in both systems:

$$\mu_A = \mu_B. \quad (6.137)$$

We will build more intuition for the chemical potential in Chap. 9. Here we have simply introduced it for consistency.

Notice that the minus sign ensures that particles flow from systems with high chemical potential to systems with low potential. We can see this from $\partial S / \partial N$. The system with the largest value for this will gain the most entropy by adding particles. Hence, when we use minus this value we ensure that particles flow from high to low chemical potential.

6.9.1 Thermodynamical identity

With this new definition, all the quantities in the thermodynamic identity are now fully introduced. The thermodynamic identity therefore becomes:

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_{V,N} dE + \left(\frac{\partial S}{\partial V} \right)_{E,N} dV + \left(\frac{\partial S}{\partial N} \right)_{E,V} dN \\ &= \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN, \end{aligned} \quad (6.138)$$

which gives:

$$T dS = dE + p dV - \mu dN, \quad (6.139)$$

and

$$dE = T dS - p dV + \mu dN. \quad (6.140)$$

This expression allows us to gain new intuition into the interpretation of the chemical potential. For a process where S and V is fixed, we see that

$$dE = \mu dN, \quad (6.141)$$

which tells us that

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V}. \quad (6.142)$$

The chemical potential therefore is change in energy per particle added to the system, when the particle is added so that the volume and the entropy of the system does not change. We will return to better, and more intuitive definitions of the chemical potential in Chap. 9.

6.9.2 Example: Chemical potential of the Einstein crystal

When we know the entropy of a system, $S = S(N, V, E)$, we can use this to find the chemical potential using (6.136). For the Einstein crystal, we found that the entropy was

$$S = Nk \ln E - Nk \ln(\epsilon N) + Nk. \quad (6.143)$$

The chemical potential is therefore

$$\begin{aligned} \mu &= -T \left(\frac{\partial S}{\partial N} \right)_{E,V} \\ &= -T (k \ln E + k - k \ln(\epsilon N) - k) \\ &= -T (k \ln E - k \ln \epsilon N) \\ &= -kT \ln \frac{E}{N} \epsilon. \end{aligned} \quad (6.144)$$

6.9.3 Example: Chemical potential of the ideal gas

Similarly, we can find the chemical potential for the ideal gas from the Sackur-Tetrode equation for the entropy:

$$\begin{aligned} S &= Nk \left(\frac{V}{N} \left(\frac{4\pi mE}{3h^2 N} \right)^{3/2} + \frac{5}{2} \right) \\ &= Nk \left(\ln V \left(\frac{4\pi mE}{3h^2} \right)^{3/2} - \ln N^{5/2} + \frac{5}{2} \right). \end{aligned} \quad (6.145)$$

We take the derivative with respect to N to find the chemical potential:

$$\begin{aligned} \mu &= -T \left(\frac{\partial S}{\partial N} \right)_{E,V} \\ &= -Tk \left(\ln V \left(\frac{4\pi mE}{3h^2} \right)^{3/2} - \ln N^{5/2} + \frac{5}{2} \right) - TNk \frac{5}{2} \frac{1}{N} \\ &= -Tk \left(\ln \frac{V}{N} \left(\frac{4\pi mE}{3Nh^2} \right)^{3/2} \right) \\ &= -Tk \left(\ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right) \end{aligned} \quad (6.146)$$

where we have inserted that $E = (3/2)NkT$ for the ideal gas. We see that the chemical potential depends on the density: Increasing the density (N/V) while keeping T constant would mean that (V/N) becomes smaller, so that the chemical potential becomes larger — the system becomes more willing to give away particles.

Question

Clickers: Heat capacities

Summary

- The **multiplicity** of a macrostate is the number of microstates in the macrostate
- The **Einstein crystal** is a simple model for a solid where the atoms do not interact and where each atom acts as a harmonic oscillator in three dimensions
- For two Einstein crystals in contact we describe the systems by the energy distribution between the two systems, described by the energy q in one of the systems.

- The macrostates for the two Einstein crystals do not have the same number of microstates — some of the macrostates have vastly more number of microstates than others.
- A system develops towards the most probable macrostate

Exercises

Exercise 6.1. Entropy

In a generic system with N particles the multiplicity is given as $\Omega(E, N) = CE^{3N/2}$, where C is a constant.

- Show that $E = (3/2)NkT$.
- Show that

$$\left(\frac{\partial^2 S}{\partial E^2} \right)_N < 0, \quad (6.147)$$

and discuss what this means.

Exercise 6.2. Gas in one- and two-dimensions

- Find an expression for the multiplicity of an ideal gas of N indistinguishable atoms, where each atom only can move along a one-dimensional tube, such as along a narrow nanotube.
- Find an expression for the multiplicity of an ideal gas of N indistinguishable atoms, where each atom only can move along a two-dimensional flat sheet, such as for electrons in a graphene sheet.

Exercise 6.3. Micro- and Macrostates in the Einstein Crystals

In this project we will address the micro- and macro-states of an Einstein crystal. You will learn how to represent and count microstates in a simple model of a crystal consisting of a set of independent oscillators, you will learn how to find the probability of a macrostate for two Einstein crystals in thermal contact, and to find the time evolution of the Einstein crystal using a Monte Carlo simulation technique.

A simple model for a crystal that still captures surprisingly many of the important features of the statistical physics of a crystal is the Einstein crystal. A real crystal consists of a set of atoms in a periodic configurations interacting through interatomic interactions that include both short range and longer ranged forces. As a result, individual atoms will oscillate around an equilibrium position while interacting mostly with its nearest neighbors. As a simplified model for this system we consider each atom, i , to behave like an independent harmonic oscillator with a potential energy U_i :

$$U_i(\mathbf{r}_i) = \frac{1}{2}k_x(x_i - x_{i,eq})^2 + \frac{1}{2}k_y(y_i - y_{i,eq})^2 + \frac{1}{2}k_z(z_i - z_{i,eq})^2, \quad (6.148)$$

From quantum mechanics, we know that the energy of a harmonic oscillator i is

$$\varepsilon_i = n_i \Delta \varepsilon, \quad (6.149)$$

where n_i is an integer describing the state of oscillator i . We can therefore describe the state of a crystal with N independent (meaning non-interacting) oscillators by the states n_i for $i = 1, \dots, N$. The total energy of the crystal in this simplified model is then:

$$U = \sum_{i=1}^N \varepsilon n_i. \quad (6.150)$$

For simplicity we will measure energy in units of ε :

$$q = \frac{U}{\varepsilon} = \sum_{i=1}^N n_i, \quad (6.151)$$

For a system with a given total energy, the sum of all the n_i is constant, but we can still change how the energy is distributed in the system. We can think of the energy as a given number of energy units that we are free to distribute between the oscillators. Any distribution is allowed as long as we do not change the total energy.

We describe a microstate of this system by the numbers n_i for each oscillator:

$$\{n_1, n_2, \dots, n_N\} \quad (6.152)$$

For example, for a system with $N = 4$ and $q = 4$, a possible microstate is $\{1, 0, 2, 1\}$, that is $n_1 = 1$, $n_2 = 0$, $n_3 = 2$, and $n_4 = 1$.

We will now find the various microstates of this system:

- a) For a system with $N = 2$ oscillators and $q = 3$, list all the possible microstates.
- b) For a system with $N = 3$ oscillators and $q = 3$, list all the possible microstates.
- c) For a system with $N = 4$ oscillators and $q = 3$, list all the possible microstates.

The general formula for the number of microstates for N oscillators with q units of energy is:

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!}. \quad (6.153)$$

- d) Check that the results you found above are consistent with this formula.

We can now list and count the number of microstates for an Einstein crystal, and we are ready to address what happens if two Einstein crystals come in contact. First, we start by looking at a system consisting of two isolated Einstein crystals, system A with N_A oscillators and energy q_A and system B with N_B oscillators and energy q_B . Each system is surrounded by an insulating, rigid and impermeable outer wall so that its energy, volume and number of oscillators (particles) is constant. The total system consists of system A and system B, so that $N = N_A + N_B$ and $q = q_A + q_B$. However, the systems are initially isolated – meaning that they are independent systems with constant energy, volume and number of particles.

e) For a system consisting of subsystem A with $N_A = 2$ and $q_A = 5$ and subsystem B with $N_B = 2$ and $q_B = 1$ list all possible microstates of the system.

The two systems are put in thermal contact, so that they can exchange energy, but the number of particles and the volume of each subsystem does not change. The total energy $q = q_A + q_B = 6$ is constant, but the energy can now be freely distributed between the two systems. Let us now count the number of possible microstates for each possible value of q_A and q_B .

f) For $N_A = 2$, $N_B = 2$, and $q = 6$ what are the possible values of q_A and q_B ? We call a state with a given q_A (and therefore also a given $q_B = q - q_A$) a macrostate for the system.

g) For each possible macrostate q_A find the number of compatible microstates.

h) Compare the total number of microstates available to the system before and after the systems came in thermal contact. Comment on the result. What aspects of this result do you think is general?

i) If all microstates have the same probability, what are the probability of each of the macrostates?

j) What is the probability of the initial macrostate before the two systems came in contact?

k) What is the probability of finding all the energy in system A?

l) What is the probability of finding exactly half the energy in system A?

We will now address larger systems numerically. You therefore need to write a script/program to find the number of macrostates and the probability of the macrostates. We start from the system we had above, but you will need to write a general program you can use for any value of N_A , N_B , q , and q_A .

m) For $N_A = N_B = 2$ and $q = 6$ write a program to find the number of microstates for each macrostate q_A and the probability $P(q_A) = \Omega(N_A, q_A)\Omega(N_B, q_B)/\Omega_{TOT}$ for each macrostate. Compare with your results from above. Plot the probability $P(q_A)$ as a function of q_A .

We will now address a larger system with $N_A = 50$, $N_B = 50$ and $q = q_A + q_B = 100$.

n) Plot the probability $P(q_A)$ as a function of q_A for all possible values of q_A .

o) What is the most probable macrostate? What is the probability of the system being in the most probable macrostate compared to all other macrostates in the system? Comment on the result.

p) We start from a system with $q_A = 0$ and $q_B = 100$ before the systems come in thermal contact. What is the probability of being in this state after the system has reached equilibrium?

The microstate of the system is given by the energy of each oscillator given as n_i for each of the oscillators. We start by studying a single system with N oscillators

and energy q . You can generate the initial state by placing each energy unit in a random oscillator. (Some oscillators may receive more than one energy units and some may receive none). At each timestep we attempt a transfer of energy from one oscillator to another oscillator using the following algorithm. Select an oscillator n_1 at random. If the oscillator has zero energy, do nothing, if the oscillator has a positive energy, select another oscillator n_2 at random and transfer one unit of energy from n_1 to n_2 . Repeat the process for as many “timesteps” as you want.

q) Write a program to generate the initial microstate and the “time” development of the microstate. Plot the initial state and the state after 100 flips.

r) Divide your system into two parts, each part having $N/2$ oscillators. We call the first $N/2$ oscillators system A corresponding to oscillators $i = 1, N/2$, and the second $N/2$ oscillators system B, corresponding to oscillators $i = N/2 + 1, N$. Plot q_A/N_A and q_B/N_B as a function of time. Comment on the result.

s) Initialize the system with all the energy in the system A only. Plot the average energy per oscillator (q_A/N_A and q_B/N_B) as a function of time and comment on the result.

t) Starting from an equilibrium configuration (either by starting from a random configuration or by running a non-random configuration for a long time before starting measurements) plot the probability of the macrostates. Comment on the results.

Exercise 6.4. Equilibrium fluctuations in a spin system

In this project we will characterize micro- and macro-states in a spin system and address fluctuations between two thermally coupled spin systems. You will learn how to calculate fluctuations analytically and numerically and how to relate the multiplicities to entropy and temperature of the system.

In a paramagnetic system with binary spins, each particle can be in two possible states, $S = +1$ or $S = -1$. We call such a “particle” a spin — since it is only the spin we are interested in. The energy of a single spin depends on the orientation of the spin relative to an external magnetic field B . If the spin is parallel (or antiparallel) to the external field, the energy is $E = -S\mu B$, where $S = +1$ corresponds to a spin parallel to the field and $S = -1$ corresponds to a spin antiparallel to the field.

The simplest system we can consider consists of N independent spins, S_i . (Independent here means that the spins do not interact, just like for an ideal gas or an Einstein crystal).

a) What is the number of microstates of the N -spin system?

We introduce S_+ as the number of spins with value $+1$ and S_- as the number of spins with value -1 . We call $2s = S_+ - S_-$ the spin excess or the net spin.

b) Express the total energy using the net spin, $2s$.

c) Generate 10000 microstates for a $N = 50$ system randomly – assuming that all microstates are equally likely - and plot the energy as the number of the trial. Plot a histogram of the energies using for example `hist` in matlab.

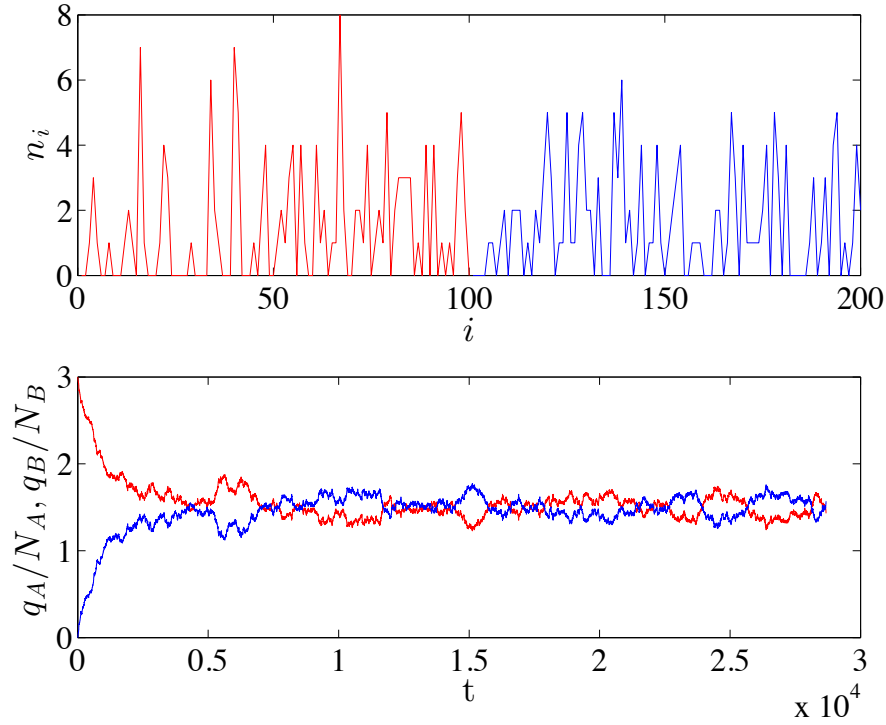


Fig. 6.21 Example state (top) and time development of the average energy per oscillator for a system divided into two parts A and B.

d) Show that the multiplicity of a state with S_+ spins pointing up is

$$\Omega(N, S_+) = \frac{N!}{S_+! S_-!} . \quad (6.154)$$

e) Show that the multiplicity can be written as a function of the net spin, s , on the following form:

$$\Omega(N, s) = \frac{N!}{(\frac{1}{2}N + s)! (\frac{1}{2}N - s)!} , \quad (6.155)$$

Since the multiplicity is a very large number when N is large, you may in the following want to work using the logarithm of the multiplicity.

f) (This problem requires some algebra — you may skip it without loss of continuity). Show that the multiplicity can be written as

$$\Omega(N, s) = \Omega(N, 0) \exp(-2s^2/N) , \quad (6.156)$$

using Stirling's formula:

$$N! \simeq (2\pi N)^{1/2} N^N e^{-N} , \quad (6.157)$$

g) Compare this analytical result with the histogram you generated of the microstates.

We will now study a system consisting of two spin systems each with N_1 and N_2 spins. The net spin in the whole system is $2s = N_+ - N_-$ and $2s_1$ and $2s_2$ in each of the subsystems. The total energy (and therefore the total net spin) is conserved, but the two subsystems may exchange energy.

You can assume that $N_1 = N_2 = 10^{22}$ and that the multiplicities therefore have the sharp, Gaussian form:

$$\Omega_1(N_1, s_1) = \Omega_1(N_1, 0) \exp(-2s_1^2/N_1), \quad (6.158)$$

and similarly for s_2 .

h) What are the possible values of s_1 (or $2s_1$ if your prefer). What are the possible energies U_1 of system 1? We call each such a state (with a given energy U_1 in system 1) a macrostate of the coupled system.

i) Show that the multiplicity of the macrostate s_1, s_2 is

$$\Omega_1(N_1, 0) \Omega_2(N_2, 0) \exp\left(-\frac{2s_1^2}{N_1} - \frac{2s_2^2}{N_2}\right). \quad (6.159)$$

j) (This requires some algebra, but is fully possible). Show that in the most probable macrostate we have \hat{s}_1 and \hat{s}_2 where

$$\frac{\hat{s}_1}{N_1} = \frac{\hat{s}_2}{N_2} = \frac{s}{N}. \quad (6.160)$$

We will now return to a single system with N spins and S_+ spins parallel to the magnetic field.

k) Find the entropy as a function of N and S_+ .

l) Find an expression for the temperature of the system.

(Hint: $\partial S / \partial U = (\partial S / \partial S_+) (\partial S_+ / \partial U) = (\partial S / \partial S_+) (\partial S_+ / \partial U)$.)

Exercise 6.5. Vacancies in a crystal

In this project⁶ we will address micro- and macro-states of vacancies in a crystal using the machinery we have developed for the microcanonical ensemble.

In crystalline matter the atoms are organized into a regular pattern — a crystal lattice as shown in Fig. 6.22. When the temperature is zero and the system is in perfect equilibrium all the atoms are in their minimum energy configurations and the lattice is perfectly ordered. However, at finite temperatures the lattice will no longer be perfectly ordered, because thermal fluctuations will introduce imperfections in the lattice. The atoms will oscillate around their average positions (this occurs even at zero temperature), but at finite temperatures the atoms may leave their lattice position and move to a different position. This may leave a vacancy - an empty

⁶This project is inspired by an exercise developed by Terje Finstad for Fys114.

space in the lattice - formed as an atom leaves its equilibrium position and migrates to the surface of the crystal. We do not here specify the migration mechanisms, but introduce an energy cost $\Delta\epsilon$ associated with the formation of a vacancy: We assume that the energy of the system increases by $\Delta\epsilon$ when an atom is moved from an interior position to the surface, forming a vacancy in the process.

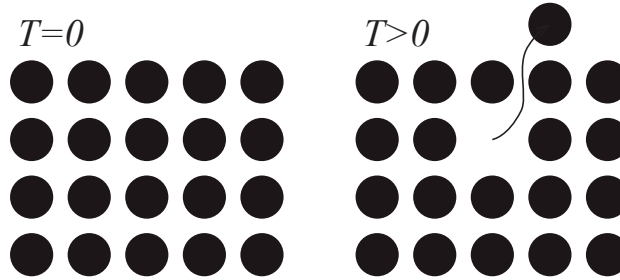


Fig. 6.22 Illustration of a crystal with a vacancy.

- a) Find the multiplicity of a crystal with N atoms and n vacancies.
- b) Find the entropy $S = S(n, N, V)$.
- c) Find an approximation for the entropy without any factorials when $n \ll N$ and $N \gg 1$.
- d) What is the temperature of the crystal when it contains n vacancies.
- e) Find an expression for the number of vacancies as a function of T . Discuss if this is a fluctuating value in this system.
- f) How many vacancies are there in the limit when $T = 0$?
- g) If we assume that $\Delta\epsilon = 1\text{eV}$. Plot the concentration of vacancies as a function of T .
- h) Assume that $n \ll N$. Find an expression for the heat capacity as a function of temperature. Plot the heat capacity as a function of temperature from $T = 0$ to $T = 1000$ for this system. Comment.
- i) (Discussion question for class discussion): A real crystal will have several contributions to its entropy. Vacancies are one possibility. Interstitial atoms - atoms that occupy places in between the regular lattice spaces - are another. In addition we must include the base vibrations of the crystal. Discuss the contributions of the various effects to the entropy and to the heat capacity of a crystal.

Exercise 6.6. Micro- and Macrostates of a polymer

Polymer materials consists of long molecular strands that can be tangled into a complex configurations with many possible microstates. The entropic contribution

to the mechanical properties of polymers are important. In this project we will introduce a simplified model of a polymer to understand how entropy affects mechanical properties of a polymer and how mechanical behavior can affect the thermal state of a polymer.

We will start with a one-dimensional model for a polymer chain. The chain consists of N links of length ΔL corresponding to the basic monomer components of the polymer. The polymer may bend at the “hinges” between the monomer links of length ΔL . In a one-dimensional model, the polymer consists of a sequence of links, where each link can point to the left or to the right. We describe the macro-state of the polymer chain by its net length L .

- a) Find an expression for the multiplicity of the macrostate in terms of N and N_R , the number of links pointing to the right.
- b) Find how L is related to N and N_R .
- c) Find the entropy as a function of L and N .
- d) For the one-dimensional system, the work done on the polymer from an external (tension) force F when the polymer is extended a distance dL is $W = FdL$. Show that the thermodynamic identity for this system is $TdS = dE - FdL$.
- e) Use the thermodynamic identity to find an expression for the force F as a partial derivative of the entropy. Find the tension F in terms of L , T , N , and ΔL for the system.
- f) Show that Hooke’s law is valid, that is, when $L \ll N\Delta L$ show that F is proportional to L .
- g) Discuss the temperature dependence of F . How does F change if you increase or decrease the temperature? Does this make sense to you?
- h) If you hold a relaxed rubber band and suddenly stretch it, would you expect the temperature of the band to increase or decrease? Explain your answer. (You can try this experimentally by placing a rubber band on your tongue and pulling it. Your tongue is quite sensitive to changes in temperature.)