Chapter 5

A thermodynamical example

Abstract We have now seen how a system approaches equilibrium using both molecular dynamics modeling and algorithmic modeling, but what characterizes the equilibrium of a system? Here, we briefly introduce the thermodynamic principles of equilibrium for an ideal gas. We measure the ideal gas law in molecular simulations and develop a simplified theory for the equation of state for the gas. We also quickly introduce a few key concepts that will reappear with full force later in the book.

We start with a quick introduction to thermodynamcis with emphasis on an example – the ideal gases. Here, we will focus of on a few key concepts of the gas — in particular on the concept of temperature. What do we know about temperature? Not much, yet, because we have not introduced it rigorously. We do know that temperature is what we measure with a thermometer. However, this is not that useful. We might expect it to be related to energy. If all the atoms in a gas move faster — so that the average or total kinetic energy increases — we may expect the gas to have a higher temperature.

The typical definition of temperature is that temperature is the *thing* that is equal when two systems are in thermal equilibrium. If a highly agitated gas comes in contact with a less agitated gas, we expect the two gases to becomes equally agitated over time. We expect the temperature to become the same over time. And in the process the system with a lot of kinetic energy will tranfer it to the system with less kinetic energy.

However, notice that even though temperature is related to energy, it is not the same as energy. We can see that from two though experiments:

- If we increase the velocity of all particles we do not expect the temperature to increase.
- If we lift all the particles upwards in a gravitational field, increasing their energy, we do not expect the temperature to increase.

Temperature is not directly releated to energy, but it rather related to the distribution of energy. One of our goals for this course is to develop a good understanding of

temperature. Here, we will start from a simple example — how is the energy in a gas related to other properties of the gas?

5.1 Ideal gas

We start by addressing a few real systems in more detail. First, we discuss the properties of an ideal gas, which is going to be our model system for many, non-interacting particles. An ideal gas is a gas that has so low density that there are no interactions between the particles. It is simply a box filled with non-interacting particles (atoms or molecules). We assume that we can model an ideal gas using molecular dynamics by looking at a system with very low density. We start from such as simulation.

5.1.1 Ideal gas — Results from simulations

We can also use the molecular dynamics simulations to learn about the ideal gas. We can, for example, determine how the pressure in the gas depends on other properties of the system?

The pressure is a property we can measure in the gas and which may vary or at least fluctuate with time — just as we have seen the number of particles in the left half to vary. The volume and the total energy on the other hand, are values we determine when we start the simulations, and we typically do not allow them to vary throughout the simulation: Total energy is conserved when the particles move in conservative force fields, and we keep the size of the box, and hence the volume, constant.

If the gas is very dilute, all the particles are far away from each other most of the time, and the interaction energies from the interatomic potentials will be very small (since it decays rapidly with the distance between atoms). We may therefore approximate the total energy by the kinetic energy of the atoms instead. We will come back later to how to measure the pressure in a molecular dynamics simulation, but let us here assume that it is measured from the average force on the walls of the system. We introduce reflective walls in both the *x* and the *y* direction to contain the system.

We can set up a two-dimensional simulation of a dilute gas, just as we did before, and measure the volume $V = L_x \cdot L_y$, the pressure P, as measured by the simulation program, and the total kinetic energy

$$K = \sum_{i=1}^{N} \frac{1}{2} m_i \left(v_{xi}^2 + v_{yi}^2 \right) , \qquad (5.1)$$

which is also measured directly in the simulation program.

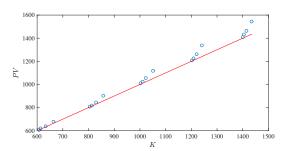
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To characterize the behavior of a gas, we perform simulations and record measurements for various values of the initial velocities of the system — which determines the initial energy of the system — and for various values of the volume V of the system. We do this by changing the input file used by the simulation program. We then run the simulation, and extract the volume from the actual size of the box used in the simulation. We measure the pressure in the simulation and we measure the total kinetic energy, K, in the final time-step of the simulation. This is implemented in the program findeqstategas01.py¹:

```
from pylab import *
import re
pressarr = array([]) # Store pressures
volarr = array([]) # Store volumes
Karr = array([]) # Store kinetic energies
myvelocities = array([1.5, 2.0, 2.5, 3.0, 3.5])
myvolumes = array([0.010, 0.020, 0.040, 0.080])
for ivel in range(0, size(myvelocities)):
     for ivol in range(0, size(myvolumes)):
          # Change the word mydensity to myvolumes[ivol]
infile = open("in.gasstatistics30",'r')
          intext = infile.read()
          infile.close()
          replacestring = "%f" % (myvolumes[ivol])
          intext2=intext.replace('mydensity',replacestring)
          # Change the word myvelocity to myvelocities[ivel]
replacestring = "%f" % (myvelocities[ivel])
          intext3=intext2.replace('myvelocity', replacestring)
infile = open("in.tmp",'w')
          infile.write(intext3)
          infile.close()
          # Run the simulator
          print "Executing lammps < in.tmp"</pre>
          os.system("lammps < in.tmp") # Run lammps
          # Extract data from trajectory of simulation
d = dump("tmpdump.lammpstrj") # Read sim states
          tmp_time, simbox, atoms, bonds, tris, lines = d.viz(0)
          dx = simbox[3] - simbox[0]
          dy = simbox[4] - simbox[1]
vol = dx*dy # Volume of box
          t = d.time(), n = size(t)
          # Calculate total kinetic energy of last timestep
         vx = array(d.vecs(n-1,"vx"))
vy = array(d.vecs(n-1,"vy"))
          K = 0.5*sum(vx*vx+vy*vy) # Sum of kinetic energy
          # Read pressures calculated in simulation
          l = logfile("log.lammps")
          # Find pressure averaged over all timesteps
press = average(l.get("Press"))
          # Store calculated values in arrays
          pressarr = append(pressarr,press)
          volarr = append(volarr, vol)
          Karr = append(Karr, K)
# Plot the results
pvarr = pressarr*volarr
plot(Karr, pvarr, 'o'), xlabel("K"), ylabel("PV"), show()
```

http://folk.uio.no/malthe/fys2160/findeqstategas01.py

Fig. 5.1 Plot of the histogram for n(t) from the simulation and n_i from a binomial distribution.



Notice the use of regular expressions to change the volume (really density) and initial velocities in a default file, and write the resulting text into a new file which is read by the simulation. Notice also how we can run a program from the command line from Python. This script runs a sequence of 20 molecular dynamics simulations, and the result is shown in Fig. 5.1.

The plot shows PV as a function of K. It is not easy to know how to plot such data to find general relationships — often we have to make guesses and test them out – but you might have guessed it by dimensional analysis: We see that both PV and K have units of energy. However, when we plot the data in this way, we see that PV is approximately linearly dependent on K — indeed they are directly proportional with a factor of one:

$$PV = K (5.2)$$

We may rewrite K as N(K/N), where N is the number of atoms in the simulation. The kinetic energy per particle may be used as a measure of how energetic the gas is, and we could define the this to be the temperature, or proportional to the temperature with some factor of proportionality k_B to ensure that temperature has reasonable values for the melting point of water and the boiling point of water, since these are important scales for us. We therefore, for now, introduce the temperature T through $K/N = k_B T$, where k_B is called Boltzmann's constant:

$$k_B = 1.3806488(13) \cdot 10^{-23} \text{J/K} = 8.6173324(78) \cdot 10^{-5} \text{eV/K} .$$
 (5.3)

We can therefore rewrite the equation of state for the two-dimensional dilute gas as

$$PV = Nk_BT (5.4)$$

This form of the result is general and true also in one and three dimensions. Indeed, what we have found here is the **ideal gas law**, or the **equation of state** for the ideal gas. An **ideal gas** is a gas that is so dilute there are no collisions (no interactions) between the atoms.

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5.1.2 Ideal gas — Results from theory

We have now observed the ideal gas law in our simulations. Can we also develop a theoretical understanding and a theoretical argument for the ideal gas law? We can do that by making a simplified, microscopic model.

Let us start by addressing the motion of a single atom bouncing in a volume $V = L^3$. How can we find the pressure P on the walls of the container?

We can find the force on the wall from the change in momentum of the particle as it bounces off the wall. We assume that each bounce is conservative, and that the only change in momentum is in the direction normal to the wall. The velocity in the direction normal to the wall is reversed in each collision: $v_x \to -v_x$. We can use this assumption to find the force acting on the particle – and from that we can find the reaction force which is acting on the wall. The force on the wall is $F_X = m\Delta v_x/\Delta t$, where Δt is the time interval we are averaging over. The typical time between two collisions corresponds to the time between each time the particle hits the wall. This is twice the time it takes for a particle to travel from one side and to the other side of the box. We use this as the typical time between collisions: $\Delta t = 2L/v_x$. In addition we know that $\Delta v_x = 2v_x$, since the particles reverses its velocity in each collision. This gives

$$P = \frac{F}{A} = \frac{-m(-2v_x)}{A2L/v_x} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V}.$$
 (5.5)

Similarly, for the other particles we find:

$$PV = Nmv_x^2 . (5.6)$$

We recognize this from the ideal gas law, which we could measure, which gives PV = NkT. Therefore we have related temperature to the velocity of a particle:

$$\frac{1}{2}kT = \frac{1}{mv_x^2} \,. {(5.7)}$$

We find similar results in the y and z direction, so that in total we have

$$K = \frac{3}{2}kT \ . \tag{5.8}$$

5.1.3 Ideal gas — equipartition principle

The result we found above:

$$\langle E_{k,x} \rangle = \frac{1}{2}kT \,, \tag{5.9}$$

is more general, as we will prove later, and it is valid not only for the kinetic energy, but for all terms in the energy that are quadratic in position or velocity. We will call this principle the **equipartition principle**:

Equipartition principle: In equilibrium, every (quadratic) term in the sum for the energy of a system has an energy which is (1/2)kT

ams 1: We may here discuss vibration and rotation.

This simple principle can be applied to provide insight into the two fundamental model system for gases and solids:

Simplfied model for a gas — **ideal gas.** An ideal gas where there are no interactions between the atoms/molecules. This means that the particles only have kinetic energy and no (internal) potential energy due to interparticle interactions. The total number of quadradic terms in the energy sum is therefore 3N — there are three quadratic terms for each particles. The equipartition principle therefore tells us that

$$U = \frac{3}{2}NkT \,, \tag{5.10}$$

If there are more degrees of freedom, such as from rotation or vibrations of molecules, these must also be included by including f, the number of degrees of freedom into the expression, and the expression for the energy of the gas becomes

$$U = \frac{f}{2}NkT \,, \tag{5.11}$$

where f is:

- f = 3 if the only degree of freedom per particle are motion along the three orthogonal directions.
- f = 5 if we include rotation in a diatomic gas. (Two new degrees of freedom to describe rotation).
- f = 7 if we also include vibration in a diatomic gas. (Two additional degrees of freedom to describe vibration).

Simplified model for a solid — ideal solid. In the simplest model for a solid, each particle in the solid can move in three directions. A solid with N atoms therefore have 6 degrees of freedom for each atom, three degrees of freedom for their positions relative to their equililibrium positions and three degrees of freedom for their velocities. This gives: 3

$$U = 3NkT (5.12)$$

for a solid.

Clickers - Equipartition

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Summary

- An ideal gas is described by the ideal gas law PV = NkT.
- Each degree of (quadratic) freedom for a system contributes an amount (1/2)kT to the total energy in equilibrium.

Exercises

Chapter 6 Micro- and Macro-states

We have already started to argue for the occurence of irreversibility. When we started with a gas separated in two chambers we saw that the system developed towards an equilibrium state. Here we will continue this discussion and develop a better understanding for irreversible processes and the associated fundamental law, the second law of thermodynamics.

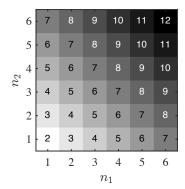
We saw that irreversibility is related to how energy is distributed in a system, and not to the energy of a system itself since energy usually is conserved. How can we describe the state of a system, including both the energy and how energy is distributed? We describe a system on a microscopic scale, through a microstate, and on a macroscopic scale, through a macrostate.

6.1 Microstates

We have already seen several examples of **microstates**. If we throw two six-sided dice, what are the possible outcomes? We must specify the number on dice 1 and on dice 2. How many such states do we have? We would call such states microstates in physics. We can easily list them all: There are 36 of them. We specify them by a two-number set: (1,1), (1,2), (1,3) etc. Similarly, if we flip a coin N times, the microstates consist of all possible results, each given as a sequence of flips $(1,0,1,1,0,1,0,\ldots,1)$.

Macrostates represent a group of microstates. For example, the sum Z = i + j of two dice can produce the numbers from 2 to 12. Each such value of Z represents a macrostate. Notice that for each microstate there is a unique macrostate. But there can be many microstates corresponding to a macrostate.

If all the microstates are equally probable, we can estimate the probability of the macrostate by counting the number of microstates corresponding to a macrostate. We call the number of microstates in a given macrostate the multiplicity of the macrostate.



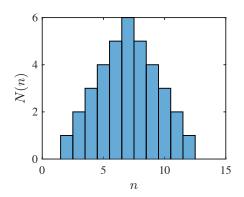


Fig. 6.1 Left Illustration of the microstates of two dice. The microstates that are part of the same macrostate $n = n_1 + n_2$ are given the same color. Right Plot of the histogram of the number of microstates for each macrostate n for two dice.

For example, for the two dice system we find the probability of a macrostate by counting the number of microstates in a macrostate and divide by the total number of microstates. We can use this to find the probabilities P(n), where $n = n_1 + n_2$ is the sum of two dice. Fig. 6.1 illustrates the number of states for each of the macrostates simply by counting the microstates.

Now, let us see how we can use the concept of micro- and macro-states to characterize various model system that represent simplified, but real, physical systems.

6.2 Model systems

Here, we will address three main model systems that we will understand in depth:

- The ideal gas: A gas where the particles are not interacting
- The ideal solid: A solid where the atoms are not interacting
- The ideal spin system: A set of magnetic moments that are not interacting

These systems all have in common that the individual elements are not interacting directly. In real systems, the particles are interacting, but as a first approximation we will disregard this interaction.

6.2.1 Multiplicity of the macrostate

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

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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 ($x_i = 1$) or on the right side ($x_i = 0$) for i = 1, ..., N. The total number of atoms on the left side was

$$Z = \sum_{i=1}^{N} x_i \,, \tag{6.1}$$

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

$$P(N,z) = \Omega(N,z)2^{-N}$$
, (6.2)

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

Multiplicity: The multiplicity $\Omega(N,z)$ is the number of microstates in the macrostate characterize by the value z for the macrovariable Z.

6.2.2 Multiplicity of the number of particles in an ideal gas

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

$$\Omega(N,z) = \binom{N}{z} \ . \tag{6.3}$$

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

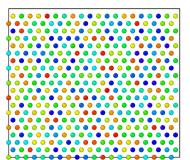
$$\bar{z} = \frac{N}{2} , \sigma_z = \sqrt{\frac{N}{4}} . \tag{6.4}$$

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

$$\frac{\sigma_z}{\bar{z}} = \frac{\sqrt{N}}{N} = N^{-1/2} \,, \tag{6.5}$$

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.

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 z are possible. In practice,



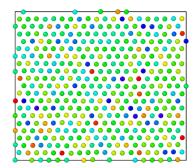


Fig. 6.2 Visualization of a solid of Argon atoms modelled using the Lennard-Jones potential at two different times. The colors indicate the velocities in the *x*-direction.

there are most states near the average value of z. 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 intial state comic – it is extremely unlike to happen.

The development of the system away from z = N, where we started the simulation previously, towards z = N/2 is therefore effectively irreversible, because there are so many more states near $\bar{z} = N/2$ than near z = N or z = 0.

Fluctuations. Previously, we studied fluctuations in the number of particles in an ideal 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 halfes. We will discuss fluctuations in several properties of a system. We have now started by addressing fluctuations in the number of particles, and we will return to this later. We will also discuss fluctuations in the energy and in the volumes of the systems, to mention a few. First, we will address fluctuations in energy. We can, of course, easily measure fluctuations in energy in the simulated gas system. But the theoretical discussion of energy fluctuations in an ideal gas is slightly more complicated than for a solid, where there is no transport of particles, but only of energy. We will therefore first address the behavior of a simplified crystal.

6.3 Behavior of a solid — Modeling

While the gas system is a good starting point to model the fluctuations and flow of particles, it is not similarly suitable to model the fluctuations in energy within a system, because both energy and particles are continuously transmitted throughout the system. It is therefore difficult to separate the effects of particle transport from

the effects of energy transport. Instead, we will focus on a system where we can study the fluctuations and flow of energy alone. This can be done in a solid. If the atoms are approximately fixed in space, but still vibrating, then energy is free to flow, but particles will remain approximately fixed in space. We model a solid in the molecular dynamics model using the same model we used for the Argon system, but with smaller initial velocities and a smaller system. You find reasonable input parameters for a simulation in in.solidstat02¹:

```
# 2d Lennard-Jones gas
units
            lj
            2
dimension
atom_style
           atomic
lattice 
                   hex 1.05
                  box block 0 20 0 10 -0.1 0.1
region
create_box 1 box
create_atoms 1 box
                1 1.0
mass
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
               1 all nve
fix
dump 1 all custom 100 solidstat02.lammpstrj id type x y z vx vy vz
thermo
                  100
            500000
run
```

You can run the simulation using

```
lammps < in.solidstat02</pre>
```

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 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).

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.py²:

```
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)
```

http://folk.uio.no/malthe/fys2160/in.solidstat02

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

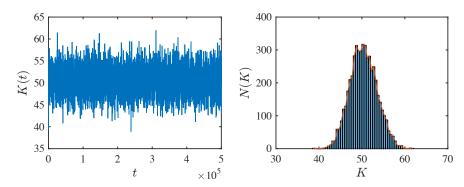
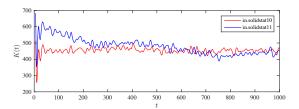


Fig. 6.3 *Left* Plot of the kinetic energy of the left-half of the Argon solid. *Right* Histogram of the kinetic energy *K* for the Argon system.

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



```
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()</pre>
```

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 by described by a normal 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.

6.3.1 Towards equilibrium in the solid

We can also use this simulation framework to address how the system approaches equilibrium. We start a simulation where the 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.solidstat10³:

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

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.

6.4 Behavior of a solid — Theory

Let us now build a simplified model of the solid, inspired by the model for the ideal gas. In the simulated system, 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 land-scape – 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

http://folk.uio.no/malthe/fys2160/in.solidstat10

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: The harmonic oscillator.

We are therefore left with the following simplified model:

- The atoms in the crystal do no interact directly
- Each atom acts as a harmonic oscillator in a three-dimensional potential
- The total system consist of N such atoms

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.

For 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

$$V(x) = \frac{1}{2}kx^2 \,. \tag{6.6}$$

where k is the "spring constant" and x is the deviation from the equilibrium position. From quantum mechanics we know that the energies of such a system is quantized, with possible values

$$\varepsilon = h v n . ag{6.7}$$

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

An Einstein crystal is a system consisting of N such independent oscillators, where each oscillator has the same v 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 $hv = \varepsilon$, and we often use the symbol q for this dimensionless energy. Notice that the number q can only take *integer values*.

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. 6.5. 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 $n_i = 0, 1, 2, ...$ 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 $4 \cdot 3 = 12$.

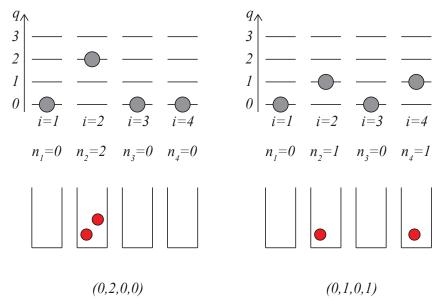


Fig. 6.5 Illustration of the Einstein crystal model.

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).

It is customary to illustrate the states in an energy level diagram. Fig. ?? 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. 6.5 – by the number of energy units shown as balls in the boxes.

We call each sequence $(n_1, n_2, ..., n_N)$ a microstate of the Einstein crystal. The energy level or box representation in Fig. 6.5 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. 6.5. 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

$$\Omega(N,q) = \binom{N-1+q}{q} = \frac{(N-1+q)!}{q!(N-1)!},$$
(6.8)

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

Clickers - Einstein crystal 1

6.4.1 Two Einstein crystals in contact

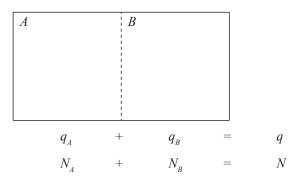
Now we know how to count microstates. But with only a single Einstein crystal the macrostate, the energy in this case, is not that interesting. In the numerical simulations, we saw how the energy was fluctuating between two halves in a crystal. Can we apply the theory we have developed of the microstates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

We divide the system into two parts, A and B, that simply are subsets of the oscillators. This way, we can observe the fluctuations between the two parts of the system. In our simulations, the two parts of the solids were connected. In our model system, there are no direct interactions between the oscillators. However, they do share the same total energy, so that if one oscillator gets more energy, another oscillator will have to get less. We can therefore think of the two systems A and B as two Einstein crystals with N_A and N_B atoms and with q_A and q_B of energy – where each system is described as an Einstein crystal – but the systems are in thermal contact which simply means that their total energy is conserved $q = q_A + q_B = \text{const.}$ This system is illustrated in Fig. 6.6.

Before they are in contact, the systems have energy q_A and q_B . After contact, the total system have energy $q = q_A + q_B$ which is a constant, but q_A and q_B will generally not be constant. We will characterize the macrostate by the value q_A . This description is similar to the description we used to describe the number of particles on the left side of the ideal gas. What are the possible values of q_A ? q_A may vary from 0 – meaning that all the energy is in system B, to q – meaning that all the energy is in system A.

Clickers - Einstein crystal 2

Fig. 6.6 Illustration of two parts *A* and *B* of an Einstein crystal.



Let us look at the probability of the system being in macrostate q_A . We can calculate the multiplicity of A with energy q_A and the multiplicity of B with energy q_B finding the total multiplicity for these particular values of q_A and q_B .

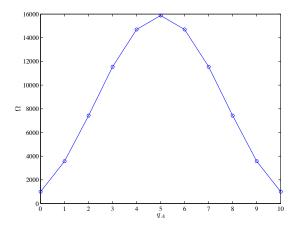
$$\Omega_{AB} = \Omega_A \cdot \Omega_B \tag{6.9}$$

for each microstate in A consistent with q_A there are Ω_B microstates in system B. We can do this for a small system with $N_A = N_B = 5$ and q = 10 numerically.

```
# 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. 6.7 and in the following table.

Fig. 6.7 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

So the number of microstates is given. However, we need an assumption to find the probability of a macrostate. We need to assume that all the microstates are equally probable! This is called 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 really prove this assumption, but we can understand where it comes from: At the microscopic level we expect that any process that takes the system from state X to Y is 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.

All macrostates are clearly not equally probable. We can plot the probabilities using the same program. And the $q_A=0$ macrostate is clearly much more unlikely than $q_A/N_A=q_B/N_B$. So if it starts at this macrostate, the system will evolve and end up in a different macrostate - with very high probability it will end up in the most probable macrostate! This corresponds to an *irreversible* behavior. Energy flows spontaneously from B to A, 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 now 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 - the probability for all other states goes to zero.

6.4.2 Time development of the Einstein crystal

We can examine the behavior of the Einstein crystal model in more detail by introducing a model that also include the time dynamics inside 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. 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.

We can make a small modification to the Einstein crystal model to include some of these effects. First, we start by dividing the model into to 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
```

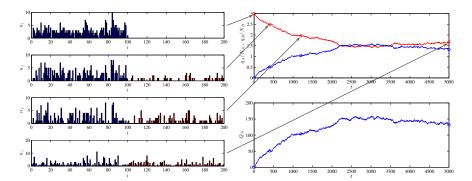


Fig. 6.8 Illustration of the time development of two Einstein crystals in thermal contact.

```
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.

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 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. 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 * Lv
NB = LB * Ly
qA = 3000 # Initial energy in system A
qB = 0  # Initial energy in system B
\vec{q} = \vec{q}A + \vec{q}B # 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(gA):
    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
         dy = 2*randint(0,2)-1
         # Transfer energy from (ix1, iy1) to (ix2, iy2)
         state[ix2, iy2] = state[ix2, iy2] + 1
         state[ix1,iy1] = state[ix1,iy1] -
    if (mod(istep,1000) == 0): # Display system at regular intervals
         imshow(state)
         draw()
```

Both of these models show that the Einstein crystal will approach a stationary state with uniform distribution of energy per oscillator between the two parts. This corresponds to the macrostate with the maximum multiplicity. This is indeed another example of the second law of thermodynamics: Systems move towards the state with the maximum multiplicity and the equilibrium state is the state with maximum multiplicity. Let us now look at the multiplicity of the Einstein crystal model, and find an explicity expression for how sharp the multiplicity function is.

6.4.3 Approximate multiplicities using Stirling's formula

The combinatoric formulas we have found so far typically includes the factorial function. While this function is useful in combinatorics, we do not know how to treat this function in analysis – we do not know how to integrate it or take the derivative of it. It is therefore useful to use an approximation of the factorial that allows us to use the analytical machinery we know so well from mathematics. Enter Stirling's formula – a useful approximation for the factorial that allows us to rewrite the combinatorial formulas in an analytical formula. Stirling's formula is the approximation:

$$N! \simeq N^N e^{-N} \sqrt{2\pi N} \,, \tag{6.10}$$

which is ok when *N* is large. When we look at the logarithm of the faculty it becomes even simpler:

$$\ln N! \simeq N \ln N - N + \frac{1}{2} \ln 2\pi N \simeq N \ln N - N,$$
 (6.11)

(You can find the derivation of Stirling's formula in Appendix B).

Stirling's formula allows us to find a simplfied expression for the multiplicity of the Einstein crystal:

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

We will in the following assume that N is a very large number, so that $N \simeq N-1$ and $q+N-1 \simeq q+N$.

Let us look at the logarithm of the multiplicity - it is easier to handle for such very large numbers:

$$\ln \Omega = \ln \left(\frac{(q+N-1)!}{q!(N-1)!} \right) \simeq \ln \left(\frac{(q+N)!}{q!N!} \right)$$
(6.13)

We apply Stirling's formula to N! and (q+N)!, getting:

$$\begin{split} \ln \Omega &\simeq \ln(q+N)! - \ln q! - \ln N! \\ &\simeq (q+N) (\ln(q+N) - 1) - q (\ln q - 1) - N (\ln N - 1) \\ &= (q+N) \ln(q+N) - (q+N) - q \ln q + q - N \ln N + N \\ &= (q+N) \ln(q+N) - N \ln N - q \ln q \;. \end{split} \tag{6.14}$$

Now we assume that the number of units of energy is very large compared to the number of oscillators: $q \gg N$. That is, we assume that quantum effects are not important. We can use this to simplify $\ln(q+N)$ through:

$$\ln(q+N) = \ln\left[q\left(1 + \frac{N}{q}\right)\right] = \ln q + \ln\left(1 + \frac{N}{q}\right) \simeq \ln q + \frac{N}{q}, \quad (6.15)$$

where we have used the approximation $\ln(1+x) \simeq x$, 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

$$\ln \Omega \simeq (q+N) \left(\ln q + \frac{N}{q} \right) - N \ln N - q \ln q$$

$$\simeq q \ln q + N \ln q + N + \frac{N^2}{q} - N \ln N - q \ln q$$

$$= N \ln \frac{q}{N} + N + \frac{N^2}{q} .$$
(6.16)

The multiplicity is then

$$\Omega \simeq e^{N\ln(q/N)}e^N = \left(\frac{eq}{N}\right)^N, \tag{6.17}$$

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.

6.4.4 Sharpness of the multiplicity function

Now, let us apply this result to find a simplified formula for the multiplicity of two interacting ideal crystals A and B, each with N oscillators: $N_A = N_B = N$. Above, we calculated and plotted the multiplicity of this system, and we found that the multiplicity had a very sharp maximum for $q_A = q_B = q/2$ (when $N_A = N_B$). Can we now use Stirling's formula to get an idea about how sharp this function is?

The total multiplicity of both the A and B system is

$$\Omega = \left(\frac{eq_A}{N}\right)^N \left(\frac{eq_B}{N}\right)^N = \left(\frac{e}{N}\right)^{2N} (q_A q_B)^N \tag{6.18}$$

Now, we will use what we know about the solution to help simplify this expression. We expect the multiplicity function to have a very sharp peak at $q_A = q/2$, we therefore introduce q_A and q_B as values with small deviations around this maximum value:

$$q_A = \frac{q}{2} + x \,, \tag{6.19}$$

and

$$q_B = \frac{q}{2} - x \,, \tag{6.20}$$

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

$$\Omega = \left(\frac{e}{N}\right)^{2N} \left[\left(\frac{q}{2}\right)^2 - x^2 \right]^N , \qquad (6.21)$$

We simplify the logarithm

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

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

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

$$\simeq N \left[\ln\left(\frac{q}{2}\right)^{2} - \left(\frac{2x}{q}\right)^{2}\right]$$
(6.22)

and we plug this back into the equation for the multiplicity:

$$\Omega = \left(\frac{e}{N}\right)^{2N} e^{N\ln(q/2)^2} e^{-N(2x/q)^2}$$

$$= \Omega_{max} \cdot e^{-N(2x/q)^2}$$

$$= \Omega_{max} e^{-\left(\frac{x}{q/(2\sqrt{N})}\right)^2},$$
(6.23)

This is a Gaussian - with a peak at x = 0. We see that the multiplicity falls to 1/e of its maximum when $x = q/(2\sqrt{N})$. This may look like a large number, but if N is 10^{20} , then it is only $1/10^{10}$ of q/2. The relative fluctuations in q_A are therefore extremely small in realistic systems – in practice such 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**.

We can test this theory by comparing with the directly calculated values of the multiplicity. Fig. (??) shows plots of the multiplicity $\Omega(q_A;N,q)$ for N=10,20,40 and q=5N. The left figure shows the direct plot of the multiplicity rescaled with its maximum value: $\Omega(q_A;N,q)/\Omega(q/2;N,q)$ for a case where $N_A=N_B=N/2$ so that the maximum occurs are $q_A=q/2$. We see that both the average and the width of the distribution increases as N increases. We can see that the theory for the width of the distribution found above indeed is correct by plotting Ω/Ω_m as a function of $(q_A-q/2)/\sqrt{N}$. According to the theory above, all the plots should then fall onto the same curve. We call such a plot a data-collapse, and we often use such plots to demonstrate/validate our theories.

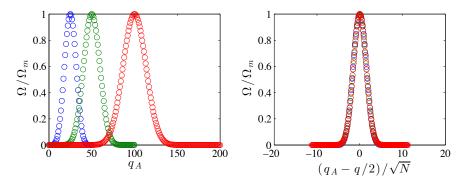


Fig. 6.9 Plot of $\Omega(q_A;q,N)/\Omega_m$ as a function of q_A and as a function of $(q_A-q/2)/\sqrt{N}$).

6.5 Behavior of a gas – Theory

We know from quantum mechanics that the state of a particle in a cubic box of size $L \times L \times L$ is quantized, and that the energy is

$$\varepsilon_{(n_x, n_z, n_z)} = \frac{h^2}{8mL^2} \mathbf{n} \cdot \mathbf{n} , \qquad (6.24)$$

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

$$\mathbf{p} = \frac{h}{2L}\mathbf{n} \,. \tag{6.25}$$

Here n_i are positive integers.

How can we use this to count the number of states in an ideal gas?

Our strategy will consist of two parts: First we address the number of states of a single particle in a volume. We use this to gain insight into how to count the states of a set of non-interacting particles.

6.5.1 Microstates of a single particle

If a single particle has energy E, we see that

$$E = \frac{h^2}{8mL^2}n^2 \Rightarrow n = \frac{2L}{h}\sqrt{2mE}$$
 (6.26)

How can we count the corresponding number of states with this energy?

The simplest approach would be to find the surface area of the corresponding sphere in n-space and only include 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:

$$\Omega_1 = \frac{1}{8} 4\pi n^2 = \frac{1}{8} 4\pi \frac{8mL^2}{h^2} E = \frac{4\pi L^2}{h^2} E = \frac{4\pi}{h^2} v^{2/3} E.$$
 (6.27)

It is a function of E and V (and N, but N = 1 here).

6.5.2 Microstates of two non-interacting particles

What happens if we have more than one particle? We address this in the simplified case of a one-dimensional system. In this case each particle is described by a single quantum state n, n_1 for particle 1 and n_2 for particle 2.

However, we now have to consider several effects from quantum mechanics.

First, the particles are indistinguishable: We cannot discern the state where particle 1 is in state 1 and particle 2 is in state 2 from the state where particle 1 is in state 2 and particle 2 in state 1: The states of the two-particle system are identical and should only be counted once. This is not too difficult to handle: We can simply count all the states assuming that the particle can be distinguished and then remove the double countings by dividing by the number of possible ways we can arrange N identical particles, which is N!.

Second, particles can be either fermions or bosons. For fermions we also have the condition that no to particles can be in the same quantum state. What are the consequences of this? It means that if we look at the two-particle ideal gas system (particle in 1d box system really) we have the following possible states for to distinguishable particle and for fermions

Engrav	Dicting	uichoblo	Form	ione
Energy	Disting-	uishable	гепп-	IOHS
	n_1	n_2	n_1	n_2
1	1	0	1	0
	0	1	0	1
2	2	0	2	0
	0	2	0	2
	1	1		

(We have not listed bosons - we come back to this later)

We are going to address this quantumm effect later. Here, we will assume we are in what we call the semi-classical limit where the limitations of fermions are not important. What does that mean? It means that the number of possible states is very large compared to the number of particles - in that case the number of states affected by the fermion condition will be small compared with the overall number of states and the error we make when we also count the states where two fermions are in the same quantum state will be small.

In this case - in the semiclassical limit - we can simply count the number of states for N independent particles and divide by N! to account for the indistinguishability of the particles.

6.5.3 Microstates of many non-interacting 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:

$$E = \frac{h^2}{8mL^2} \sum_{i=1}^{N} N(n_{xi}^2 + n_{yi}^2 + n_{zi}^2) = \frac{h^2}{8mL^2} \sum_{i=1}^{3N} n_i^2.$$
 (6.28)

This means that we can write *N* particles with 3 degrees of freedom as 3*N* particles with 1 degree of freedom. The energy is related to the radius *R* in the 3*N* dimensional *n*-space:

$$R = \frac{2L}{h}\sqrt{2mE} \tag{6.29}$$

Again, we can estimate the number of states by the "area" of the sphere in 3N dimesions. We must also remember that we also look at only positive n values.

The area of a *d*-dimensional sphere is given as:

$$A = \frac{2\pi^{d/2}}{\left(\frac{d}{2} - 1\right)!} r^{d-1} . \tag{6.30}$$

we use this with d = 3N. However, we also need to ensure that only the *n*-values in the first "octant" (3*N*-tant) are used, that is we must divide by the number of "quadrants" = $2^d = 2^{3N}$:

$$\Omega = \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{(\frac{3N}{2} - 1)!} \left(\frac{2L}{h} (2mE)^{1/2}\right)^{3N - 1}, \tag{6.31}$$

This was the expression for distinguishable particles. What if we have indistinguishable particles? We must also divide by N!, getting:

$$\Omega = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \left(\frac{2L}{h} (2mE)^{1/2}\right)^{3N-1} , \qquad (6.32)$$

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

$$\Omega = f(N)V^N E^{3N/2} \,, \tag{6.33}$$

6.5.4 Interaction between two ideal gases

Just like we did for the ideal crystal, we can divide the system into two parts A and B. The two parts are not thermally insulated, so that we only know that he sum of the

energies in A and B is constant, $E_A + E_B = E$, but let us assume that 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 $N_A = N_B = N/2$ and $V_A = V_B = V/2$. What is the multiplicity of the macrostate described by E_A ?

In general, the multiplicity of the combined system is the product of the multiplicities of each of the systems:

$$\Omega(E_A; E, N, V) = \Omega_A \cdot \Omega_B = f(N_A) f(N_B) (V_A V_B)^N (E_A E_B)^N , \qquad (6.34)$$

The only variation occurs in E_A and $E_B = E - E_A$. We can again develop a theory for this variation for small fluctuations. Let us look at a variation

$$E_A = \bar{E}_A + \Delta E , E_B = \bar{E}_B - \Delta E , \qquad (6.35)$$

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 .

Now, we can use the same approach as for the Einstein crystal. We insert $E_A = E/2 + \Delta E$ and $E_B = E/2 - \Delta E$ into the multiplicity, getting

$$\Omega(\Delta E) = C\left(\left(\frac{E}{2}\right)^2 - \Delta E^2\right)^N, \qquad (6.36)$$

We address the logarithm of $\Omega(\Delta E)$ to simplify the *N*-dependence, getting

$$\ln \Omega(\Delta E) = \ln C + N \ln \left(\left(\frac{E}{2} \right)^2 - \Delta E^2 \right)$$

$$= \ln C + N \ln \left(\frac{E}{2} \right)^2 \left(1 - \left(\frac{2\Delta E}{E} \right)^2 \right)$$

$$= \ln C + 2N \ln(E/2) - N \left(\frac{2\Delta E}{E} \right)^2,$$
(6.37)

which gives that

$$\Omega(\Delta E) = \Omega_m e^{-\left(\frac{\sqrt{N}\Delta E}{(E/2)}\right)^2} = \Omega_m e^{-\left(\frac{\Delta E}{(E/\sqrt{N})}\right)^2},$$
(6.38)

This is indeed a Gaussian form for the multiplicity function, just like we found for the Einstein crystal. 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 E, hence the relative value of the width goes like $1/\sqrt{N}$. For realistic values of E, such as E = E 1020, this relative width becomes a very small number, typically E 10-10, which means that we cannot discern the actual value of the energy E in the

ideal gas from its average value E/2 unless we can measure E_A is a precision of 10^{-10} .

6.6 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.

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

$$\Omega(N_A, q_A)\Omega(N_B, q_B) = \Omega(N_A, q_A)\Omega(N_B, q - q_A)$$
(6.39)

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

$$\frac{d}{dq_A}\Omega(N_A, q_A)\Omega(N_B, q - q_A) = 0, \qquad (6.40)$$

$$\frac{d\Omega(N_A,q_A)}{dq_A}\Omega(N_B,q-q_A) + \Omega(N_A,q_A)\frac{d\Omega(N_B,q-q_A)}{dq_A} = 0, \qquad (6.41)$$

$$\frac{\partial \Omega(N_A, q_A)}{\partial q_A} \Omega(N_B, q - q_A) - \Omega(N_A, q_A) \frac{\partial \Omega(N_B, q_B)}{\partial q_B} = 0, \qquad (6.42)$$

$$\frac{\partial \Omega(N_A, q_A)}{\partial q_A} \Omega(N_B, q_B) = \Omega(N_A, q_A) \frac{\partial \Omega(N_B, q_B)}{\partial q_B} , \qquad (6.43)$$

$$\frac{1}{\Omega(N_A, q_A)} \frac{\partial \Omega(N_A, q_A)}{\partial q_A} = \frac{1}{\Omega(N_B, q_B)} \frac{\partial \Omega(N_B, q_B)}{\partial q_B} , \qquad (6.44)$$

$$\frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} = \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B}.$$
 (6.45)

This suggests an interesting relation between the logarithms of the multiplicities. We introduce the term **entropy** to describe the logarithm of the multiplicity of the system:

$$S = k \ln \Omega(N, V, E) , \qquad (6.46)$$

where *k* is called the Boltmann constant, $k = 1.3806488(13) \cdot 10^{-23} \text{J/K}$.

This formula 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 formula will allow us to calculate the macroscopic, thermodynamic properties of a system from a microscopic theory of the system.

Entropies are **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:

$$S = S_A + S_B$$
 when $\Omega = \Omega_A \cdot \Omega_B$. (6.47)

6.6.1 Entropy in the Einstein crystal

Let us address the concept of entropy in more detail through the example we already have developed extensively - the Einstein crystal. For two Einstein crystals, A and B, in thermal contact, we have found the multiplicities of states with energies q_A and q_B :

$$\Omega(q_A, q_B) = \Omega(N_A, q_A) \cdot \Omega(N_B, q_B) \tag{6.48}$$

where

$$\Omega(N_A, q_A) = \frac{(q_A + N_A - 1)!}{q_A!(N_A - 1)!}.$$
(6.49)

To address this system for a large system, for example a system with $N_A = 300$ and $N_B = 200$ and q = 100, we can calculate the multiplicities using the following program:

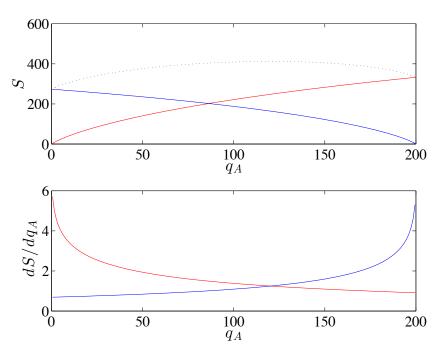


Fig. 6.10 Plot of the entropies S_A and S_B of two coupled Einstein crystals, and plots of the derivatives of the entropies with respect to q_A .

```
xlabel('q_A'), ylabel('S')
subplot(2,1,2)
dSA = diff(SA)
dSB = diff(SB)
qq = 0.5*(qvalue[1:]+qvalue[0:-1])
plot(qq,dSA,'-r',qq,-dSB,'-b');
xlabel('q_A'), ylabel('dS/dq_A')
legend(('A','B')), show()
```

In order to visualize the multiplicities, it is easier to address the logarithm of the multiplicity - which we now call the entropy of the system. The entropies of system A and system B as a function of q_A are shown in Fig. 6.10.

We can use the plot of $S_A(q_A)$ in Fig. 6.10 to better understand the condition for equilibrium. Equilibrium occurs when:

$$\frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} = \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B} . \tag{6.50}$$

which formulated for the entropies correspond to

$$\frac{\partial S(N_A, q_A)}{\partial q_A} = \frac{\partial S(N_B, q_B)}{\partial q_B} , \qquad (6.51)$$

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

We can use the plot to see what happens if system A is in a state with a q_A that is smaller than the equilibrium value. In this case, we see from the curve that if we increase q_A by one, S_A would increase and S_B would decrease. However, we also see from the curve that S_A would increase more than S_B decreases, because the slope of $S_A(q_A)$ is steeper than that of $S_B(q_A)$. 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 multiplicity or the entropy changes when we add a small piece of energy.

So it tells us which way the system will develop - because it will develop toward larger multiplicity. For $q_A < \bar{q}_A$ the system will gain more entropy (multiplicity) by increasing q_A . Since the system, most likely, develops towards larger multiplicity it will develop this way. Not always, but most probably.

Now, we can interpret the slope, $\partial S_A/\partial q_A$. This is what is equal when two systems are in thermal equilibrium.

This means that it 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 because circular.)

6.6.2 Temperature in the Einstein crystal

We see that when the slope is large, energy tends to flow into the system. Therefore we would expect the temperature to be low when the slope is high, since we would expect energy to flow into a system with low temperature. 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:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{NV},\tag{6.52}$$

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

This is going to be 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.

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. We will in the following use this coupling to develop theories for S(V, E, N) from a microscopic view – it may be from a theoreti-

cal 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(V,E,N) 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 thermodynamics – it is not important how we have found S(V,N,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.

6.6.3 Example: Entropy and energy of the ideal 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 U. From this we can calculate the entropy, and from the entropy we can calculate the temperature.

Let us now use the results we have found for the ideal gas and the Einstein crystal. The multiplicity of the Einstein crystal is

$$\Omega = \left(\frac{eq}{N}\right)^N,\tag{6.53}$$

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

$$S = k \ln \Omega = Nk \left(\ln q + \ln(U/\varepsilon) - \ln N \right) , \qquad (6.54)$$

$$S = Nk \ln U - Nk \ln(\varepsilon N) + Nk. \tag{6.55}$$

And the temperature is:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right) = \frac{Nk}{U},\tag{6.56}$$

which gives

$$U = NkT. (6.57)$$

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

From this we can also predict the **heat capacity** - which is given as the derivative of the energy:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T} (NkT) = Nk.$$
 (6.58)

6.6.4 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:

$$\Omega = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} \left(\frac{2L}{h} (2mU)^{1/2}\right)^{3N-1} . \tag{6.59}$$

Here, we will assume that $N-1 \simeq N$, which simplifies the expression somewhat:

$$\Omega = \frac{1}{N!} \frac{1}{2^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \left(\frac{2L}{h} (2mU)^{1/2}\right)^{3N} . \tag{6.60}$$

Now, we can organize this a bit:

$$\Omega = 2\frac{1}{N! \left(\frac{3}{2}N\right)!} 2\pi m U L^2 h^2)^{3N/2} . \tag{6.61}$$

Then we take the logarithm:

$$\begin{split} \frac{S}{k} &= \ln \Omega \\ &= -(N \ln N - N) - \left(\frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2}\right) + N \ln \left(\frac{2\pi m U L^2}{h^2}\right)^{3/2} \\ &= N \left(-(-1) - \left(-\frac{3}{2}\right) + \ln \left(\frac{V}{N}\right) + \ln \left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right) \\ &= N \left(\ln \frac{V}{N} \left(\frac{4\pi m U}{3Nh^2}\right)^{3/2} + \frac{5}{2}\right) \end{split}$$
(6.62)

This equation is called Sackur-Tetrode's equation.

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

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V}.$$
(6.63)

Since N and V are constants in this derivative, we can simplify the relation for the entropy to:

$$S(N,V,U) = g(N,V) + Nk \ln U^{3/2} = g(N,V) + \frac{3}{2}Nk \ln U, \qquad (6.64)$$

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

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{3}{2}Nk\frac{1}{U}, \qquad (6.65)$$

which gives

$$U = \frac{3}{2}NkT \ . \tag{6.66}$$

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.

6.6.5 Example: Entropy of expansion

We can use the Sackur-Tetrode 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 - we only change the volume. The change (increase, as always) in entropy in this case by going from a volume V_1 to a volume V_2 is:

$$\Delta S = Nk \left(\ln V_2 - \ln V_1 \right) = Nk \ln \frac{V_2}{V_1} . \tag{6.67}$$

This formula should be valid for an quasistic, isothermal expansion (but we need to be careful, since isothermal is not necessarily the same as isoenergetic). It is also valid for free expansion. In this case there is not done any work, but the gas still enters a larger volume and changes its entropy: No change in energy and no work done, but still a change in entropy.

6.6.6 Example: Entropy of mixing

What if we take two gases, each initially occupying a volume V, and then allow the two gases to mix. If the two gases are not interacting, and the two gases are distinguishable particles, we can consider each process independently. First gas A expands into twice its volume, leading to an entropy change

$$\Delta S = Nk \ln 2 \,, \tag{6.68}$$

and similarly for gas B, leading to a total entropy change of

$$\Delta S_{A,B} = \Delta S_A + \Delta S_B \tag{6.69}$$

(Notice the nice use of adding entropies of two systems. The entropy of system A and B is the sum of their entropies). That is:

$$\Delta S_{AB} = 2Nk \ln 2. \tag{6.70}$$

Notice that this does require the two gases to be different. Otherwise it would not matter - there would not be any change in entropy if we open a separation between two equal gases each of volume V.

6.6.7 Example: Gibb's paradox

Sackur-Tetrode's equation is carefully made 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, 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 a large change in entropy. What does the Sackur-Tetrode equation give us?

Before the partition was removed, the total entropy is

$$S = 2N \left(\ln \frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} + \frac{5}{2} \right)$$
 (6.71)

After the partition is removed, we have a system with double the number of particles, double the volume, and double the energy. What is the entropy of this system?

$$S = 2N \left(\ln \frac{2V}{2N} \left(\frac{4\pi m2U}{3 \cdot 2Nh^2} \right)^{3/2} + \frac{5}{2} \right)$$
 (6.72)

This is indeed the same as we found above.

However, if we had not included the N! term in the multiplicity, the entropy would have been

$$S(N,V,U) = Nk \left(\ln \left(V \left(\frac{4\pi mU}{3Nh^2} \right)^{3/2} \right) + \frac{3}{2} \right). \tag{6.73}$$

and the entropy of a double system would be:

$$S(2N, 2V, 2U) = 2Nk \left(\ln \left(2V \left(\frac{4\pi m2U}{3N2h^2} \right)^{3/2} \right) + \frac{3}{2} \right)$$
 (6.74)

The difference is therefore $2Nk \ln 2$, which is indeed the entropy of mixing, which should not have been included. The Sackur-Tetrode equation is therefore carefully made to ensure that this does not occur.

This issue was first raided by Gibbs, and is called *Gibbs paradox*.

6.7 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 interpretations.

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 converved. 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:

$$\Delta E = W + Q \,, \tag{6.75}$$

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

$$S = k \ln \Omega(N, V, E) . \tag{6.76}$$

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, $\Delta S \ge 0$, 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, $T_A = T_C$.

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

6.7.1 Example: Entropy and heat

What is the entropy change for a real process?

We start with two systems, A and B, where A has an initial temperature T_A and B T_B . (Initial energies are U_A and U_B , and entropies S_A and S_B).

What happens if we transfer an amount ΔU of energy from A to B? In this case the entropy change of the whole system is

$$\Delta S = \Delta S_A + \Delta S_B
= \left(\frac{\partial S_A}{\partial U_A}\right)_{N_A} \Delta U_A + \left(\frac{\partial S_B}{\partial U_B}\right)_{N_B} \Delta U_B
= \left(\frac{\partial S_A}{\partial U_A}\right)_{N_A} (-\Delta U) + \left(\frac{\partial S_B}{\partial U_B}\right)_{N_B} \Delta U$$
(6.77)

Now, these derivatives correspond to the temperatures of the respective systems:

$$\frac{1}{T_A} = \left(\frac{\partial S_A}{\partial U_A}\right)_{N_A} \,. \tag{6.78}$$

The total change in entropy is therefore:

$$\Delta S = \left(-\frac{1}{T_A} + \frac{1}{T_B}\right) \Delta U \ . \tag{6.79}$$

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).

We can also relate this to the heat - the thermal energy input or output from the systems.

If the system does not change volume and no other work is done on the system, then we can estimate the change in entropy from:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,V} \Rightarrow dS = \frac{dU}{T} , \qquad (6.80)$$

combining this with the first law:

$$dU = W + Q, (6.81)$$

where we assumed no work, W = 0, we see that we can relate the change in entropy to the heat Q:

$$dS = \frac{Q}{T} \,. \tag{6.82}$$

We can use this just as we used the expression with ΔU above.

For example, if a hot object, A, at $T_A = 500K$ is put in contact with a cold object, B, at $T_B = 300K$. If the thermal energy transferred during 10s is 1500J, then we can calculate the changes in entropy through:

$$\Delta S_A = \frac{-1500J}{500K} = -3J/K, \qquad (6.83)$$

and

$$\Delta S_B = \frac{1500J}{300K} = 5J/K. \tag{6.84}$$

(Example from Schroder). We see that the total change in entropy is positive - just as we sketched when we discussed the Einstein crystal.

6.8 Mechanical equilibrium – Pressure

Now, we will try to make a quick stab at more thermodynamic laws without developing the full microscopic models for them. This will be somewhat floating -

without real contact with a microscopic foundation - but it does give an interesting initial contact with thermodynamics.

First, we will address a system with an internal piston that ensures that two parts of a system are in both thermal and mechanical equilibrium.

We have found that a transfer of energy between the two systems is determined by the temperature: thermal energy flows from high to low temperatures. What would happen with a change in volume? We would expect such a change to be determined by the pressure: the change should go from large to smaller pressures.

We know that in equilibrium the system must be at a maximum in multiplicity and therefore also entropy, both with respect to a change in energy and with respect to a change in volume.

$$\frac{\partial S_{tot}}{\partial U_A} = 0 \,, \, \frac{\partial S_{tot}}{\partial V_A} \,. \tag{6.85}$$

The first condition leads to the definition of temperature. What does the second condition lead to? It leads to:

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \,. \tag{6.86}$$

and we would therefore expect this derivative to be related to the pressure? How? We could guess based on the dimensions, S has dimensions J/K=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 $(Nm/K)/m^3$, that is $(N/m^2)/K$. We must therefore multiply by a temperature to get dimension pressure. Since T is the same in both systems in equilibrium we can multiply with T, getting:

$$p = T \left(\frac{\partial S}{\partial V}\right)_{U,N},\tag{6.87}$$

as the definition of pressure.

6.8.1 Example: Pressure of ideal gas

For the ideal gas we found that the entropy was given by Sackur-Tetrode equation:

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

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

$$S = Nk \ln V + f(N, U) , \qquad (6.89)$$

and

$$p = T \left(\frac{\partial S}{\partial V}\right)_{U.N} = T \frac{Nk}{V} \tag{6.90}$$

which corresponds to

$$pV = NkT (6.91)$$

which indeed is the ideal gas law. This also shows we should not include any other factors in the definition of the pressure.

6.9 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 U and V. We do this by writing out the differential for the change dS:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{VN} dU + \left(\frac{\partial S}{\partial V}\right)_{UN} dV + \left(\frac{\partial S}{\partial N}\right)_{UV} dN, \qquad (6.92)$$

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

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} , \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T} p . \tag{6.93}$$

We insert these, getting:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV \implies TdS = dU + p dV.$$
 (6.94)

This equation is true for any infitesimal change in any system, as long as p and T are well defined and N is constant.

6.9.1 Entropy and Heat

It may seem that this formula looks like the first law:

$$dU = W + Q, (6.95)$$

which would temp us to write W = -pdV and Q = TdS. And this is ok as long as the change in volume is quasistatic, so that the pressure is the same throughout. If this is the only work performed, we indeed find that Q = TdS (for a quasistatic process!).

There are now more processes to consider:

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

Just be careful 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.

6.10 Diffusive equilibrium – Chemical potential

We have now seen what determines when two systems are

- allowed to exchange energy. In equilibrium their temperatures are the same
- allowed to exchange volume. In equilibrium their pressures are the same

What happens if two systems are allowed to exchange particles: That is if there is diffusion (or transport) between the two systems?

We have two systems A and B that can exchange energy and particles. The particles are the same (identical type) in A and B. Again, we get exactly the same procedure as before, leading to

$$\frac{\partial S_{tot}}{\partial U_A} = 0 , \frac{\partial S_{tot}}{\partial N_A} . \tag{6.96}$$

The corresponding condition for the number of particles is:

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \,. \tag{6.97}$$

Completely from the blind we are going to introduce this as the chemical potential, μ :

$$-T\frac{\partial S_A}{\partial N_A} = -T\frac{\partial S_B}{\partial N_B}.$$
 (6.98)

and

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)_{U,V} . \tag{6.99}$$

This is the quantity that is the same on each side when there is exchange of particles

$$\mu_A = \mu_B . \tag{6.100}$$

Not very helpful when we have no other insight into the chemical potential.

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.

6.10.1 Thermodynamical identity

The termodynamic identity now becomes:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$

$$= \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dN,$$
(6.101)

which gives:

$$dU = TdS - pdV + \mu dN. (6.102)$$

This allows us to find easier ways to determine the chemical potential. For example, for a process with dU=0 and dV=0 we regain the original definition of the chemical potential. But a new insight is gained from setting S and V fixed, then we see that $dU=\mu dN$ and

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{6.103}$$

This is a useful expression to calculate the chemical potential for particular systems.

6.10.2 Chemical potential of Einstein crystal

We find the chemical potential from the expression for the entropy:

$$S = Nk \ln U - Nk \ln(\varepsilon N) + Nk, \qquad (6.104)$$

We find the chemical potential as

$$\begin{split} \mu &= -T \left(\frac{\partial S}{\partial N} \right)_{U,V} \\ &= -T \left(k \ln U + k - k \ln(\varepsilon N) - k \right) \\ &= -T \left(k \ln U - k \ln \varepsilon N \right) \\ &= -kT \ln \frac{U}{N} \varepsilon \;, \end{split} \tag{6.105}$$

6.10.3 Example: Chemical potential of Ideal gas

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

$$S = Nk \left(\frac{V}{N} \left(\frac{4\pi mU}{3h^2 N} \right)^{3/2} + \frac{5}{2} \right)$$

$$= Nk \left(\ln V \left(\frac{4\pi mU}{3h^2} \right)^{3/2} - \ln N^{5/2} + \frac{5}{2} \right) ,$$
(6.106)

which we take the derivative of to find the chemical potential:

$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$$

$$= -Tk \left(\ln V \left(\frac{4\pi mU}{3h^2}\right)^{3/2} - \ln N^{5/2} + \frac{5}{2}\right) - TNk \frac{5}{2} \frac{1}{N}$$

$$= -Tk \left(\ln \frac{V}{N} \left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right)$$

$$= -Tk \left(\ln \frac{V}{N} \left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right)$$
(6.107)

We see that the chemical potential depends on the density: Larger densities (N/V) while keeping T constant would mean that the number becomes smaller, so that the chemical potential becomes larger – the system becomes more willing to give away particles.

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 that others.
- A system develops towards the most probably 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.

- a) Show that E = (3/2)NkT.
- **b**) Show that

$$\left(\frac{\partial^2 S}{\partial E^2}\right)_N < 0 \,, \tag{6.108}$$

and discuss what this means.

Exercise 6.2. 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 :

$$U_i(\mathbf{r}_i) = \frac{1}{2}k_x(x_i - x_{i,eq})^2 + \frac{1}{2}k_y(y_i - y_{i,eq})^2 + \frac{1}{2}k_z(z_i - z_{i,eq})^2,$$
 (6.109)

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

$$\varepsilon_i = n_i \Delta \varepsilon \,, \tag{6.110}$$

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, ..., N. The total energy of the crystal in this simplified model is then:

$$U = \sum_{i=1}^{N} \varepsilon \, n_i \,. \tag{6.111}$$

For simplicity we will measure energy in units of ε :

$$q = \frac{U}{\varepsilon} = \sum_{i=1}^{N} n_i \,, \tag{6.112}$$

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 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:

$$\{n_1, n_2, \dots, n_N\} \tag{6.113}$$

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:

$$\Omega(N,q) = \binom{q+N-1}{q} = \frac{(q+N-1)!}{q!(N-1)!} . \tag{6.114}$$

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?
- I) 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.

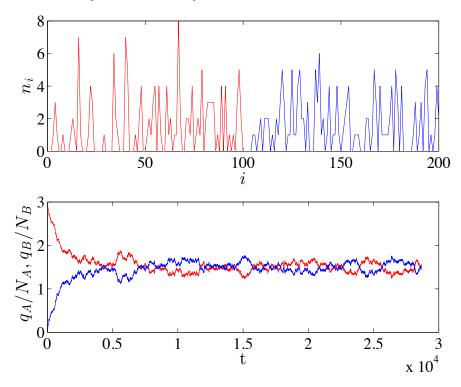


Fig. 6.11 Example state (top) and time development of the average energy per oscillator for a system divided into two parts A and B.

- **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 $(q_A/N_A \text{ and } q_B/N_B)$ as a function of time and 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.