

Micro- and Macro-states

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1 Probability theory and combinatorics

We have already started to argue for the occurrence 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 – developing a better understanding for irreversible processes and the associated fundamental law, the second law of thermodynamics.

We saw that irreversibility is related to the energy is distributed in a system, and not to the energy of a system itself since energy usually is conserved.

However, in order to discuss how energy is distributed and the probability for a particular distribution, we need to introduce a basic theory for probability and counting.

1.1 Probabilities

Probability theory has been developed by several of the great mathematicians – because they were all gamblers. This makes the underlying mathematical theory solid and nicely formulated.

A statistical experiment can result in an outcome.

The set of all outcomes is called the sample space.

For example, if we throw a single dice, the possible outcomes are i , where $i = 1, 2, 3, 4, 5, 6$.

We could measure what we would call the probability of this process by simple counting. We roll the dice N times and measure how many times we get i , resulting in 6 numbers, N_i .

We could then define the probability of i occurring as N_i/N when N goes to infinity.

This is a simple, operational definition that works well for many purposes.

And we can perform the measurement directly.

If all the events i are mutually exclusive, we know that

$$N_1 + N_2 + N_3 + \dots + N_k = N$$

For probabilities this means that

$$\sum P(i) = 1$$

which means that the probability is *normalized*.

In addition we know that

$$0 \leq P(i) \leq 1$$

These are usually considered the two fundamental properties of a probability.

This allows us to find the probability for throwing i on a dice. If the dice is fair, all probabilities must be the same, $P(i) = p$, and therefore

$$P(i) = p = \frac{1}{6}$$

We can generalize this principle to also account for more complicated outcomes. If we throw two dice, what are the possible outcomes?

We must specify the number of 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.

Again, we would expect each of them to be equally probable.

Then we can ask more complicated questions. Such as what is the probability for the sum of two dice to be 7? Or what is the probability for $P(i + j = Z)$ for each possible value of Z .

We call each such Z value 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.

Look at multiplicity of two-dice system.

For the two dice system we need to count the number of ways we can make a macrostate. We call this the multiplicity of the macrostate. And we need to divide by the total number of microstates to find the probability.

For example, we can divide the microstates into a set of macrostates corresponding to the sum of the two dice. The possible macrostates are then 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. What are the probabilities of the various states? We can see this by looking at a matrix representing all possible microstates.

2 Multiplicity of a spin system

Let us now move towards a more physical system – a two state system – where we can develop our understanding of micro- and macro-states better.

We start by flipping a coin: An experiment with two possible outcomes. If we flip a coin N times we can represent the possible outcomes at ± 1 for each flip. A possible outcome is therefore

$$\{1, 1, -1, 1, 1, -1, \}$$

for $N = 6$.

How many microstates are there if I flip the coin N times? (And the results are independent). For each coin there are 2 possibilities, that is the multiplicity of a single event is 2. If we look at several, independent events we can multiply the multiplicities (just as we can multiply the probabilities – but this requires independence!)

$$\Omega_{TOT} = \Omega_1 \cdot \Omega_2 \cdot \dots \cdot \Omega_N = 2 \cdot 2 \cdot \dots \cdot 2 = 2^N$$

Since all microstates are equally probable – this is how we designed this experiment – the probability of a microstate is

$$P = \frac{1}{\Omega_{TOT}} = \frac{1}{2^N}$$

Clickers - Microstates

3 Macrostates – random walk

Assume that we instead are interested in a motion described by the randomly flipping coins. The ± 1 refers to taking a step in the positive or negative x -direction. The position of such a walker – a random walker – is given as

$$X = \sum_i^N s_i$$

where $s_i = \pm 1$ is the result of a single coin flip.

The position X is a macrostate. What can we say about this macrostate?

We can illustrate this by a drawing of the process.

(Draw this on the blackboard)

What can we say about the probability of producing a specific macro-state?

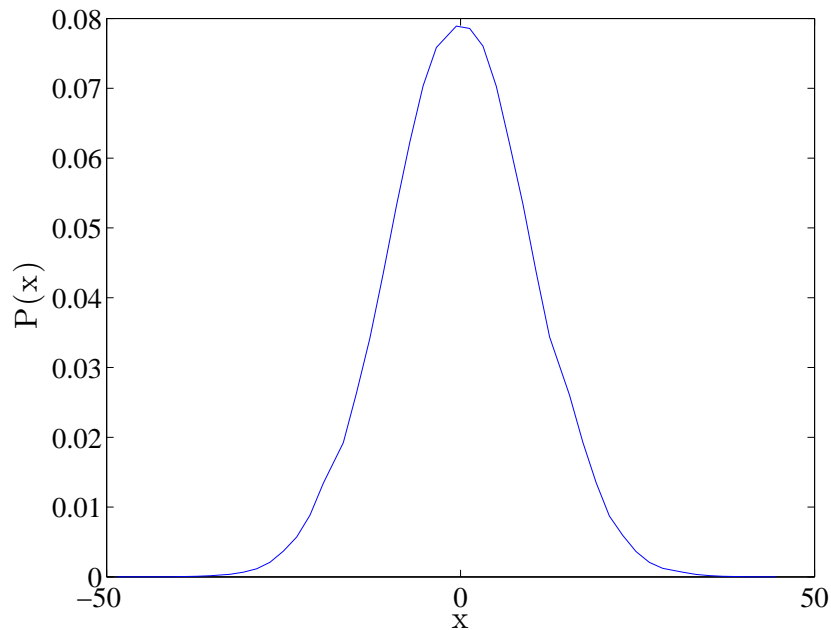
First, we can simply measure it – numerically by sampling.

We do this in matlab in the following way:

```
% A single random walk of N steps
N = 10000;
dx = 2*(randi(2,N,1)-1)-1;
x = cumsum(dx);
plot(x)

% Sampling of nsample random walks of length N
nsample = 100000;
xvalues = zeros(nsample,1);
N = 101;
for i = 1:nsample
    dx = 2*(randi(2,N,1)-1)-1;
    x = sum(dx);
    xvalues(i) = x;
end
[n,x] = hist(xvalues,100);
j = find(n~=0);
plot(x(j),n(j)/nsample)
xlabel('x')
ylabel('P(x)')
```

For $N = 101$ and sampling over $n = 10^6$ walks:



How can we calculate this distribution?

First, we notice that X only depends on the number of steps in each direction. The position is given by the number of steps in positive direction minus the number of steps in the negative direction. It does not matter in which order we step back or forth.

We therefore only need to address the probability to get $+1$ a given number of times – the remaining times will get -1 . Or with the words of the book – we only need to know the number of times we get heads – we get tails the other times. It does not matter when we get the heads.

To find the probability we need to count the number of microstate in each macrostate. The probability is then given by:

$$P = \frac{\Omega(N_+)}{\Omega_{TOT}}$$

where N_+ is the number of times we get $+1$ (or heads).

Let us start with a specific example: $N = 100$.

In this case there are 101 macrostates corresponding to $N_+ = 0, 1, 2, \dots, 100$.

We start from the simplest macrostate, $N_+ = 0$. This can only occur in one way.

What about $N_+ = 1$. This can happen 100 ways – this is the possible positions for the $+1$.

Then $N_+ = 2$. First, we need to choose the position of the first $+1$. We can do this in 100 ways. Then we choose the position of the second $+1$ and we are left with 99 ways to choose this.

But then we have overcounted the number of microstates. We could for example have chosen the first $+1$ to occur at position 45 and the second at 66. But this is the same microstate as having the first at 66 and the second at 45. We have therefore overcounted – we have counted twice as many states as are actually different.

The actual multiplicity is therefore

$$\Omega(2) = \frac{100 \cdot 99}{2}$$

Similarly, for $N_+ = 3$ we can choose the positions of the three +es in $100 \cdot 99 \cdot 98$ ways. But again, we can reshuffle the +es in $3!$ possible ways.

Generally, we get:

$$\Omega(N_+) = \frac{100 \cdot 99 \cdot \dots \cdot (100 - N_+ + 1)}{N_+!}$$

which we can write as

$$\Omega(N_+) = \frac{100!}{N_+!(100 - N_+)!} = \binom{100}{N_+}$$

We sometimes call this 100 choose N_+ – and this is indeed even what it is called in matlab, `nchoosek`.

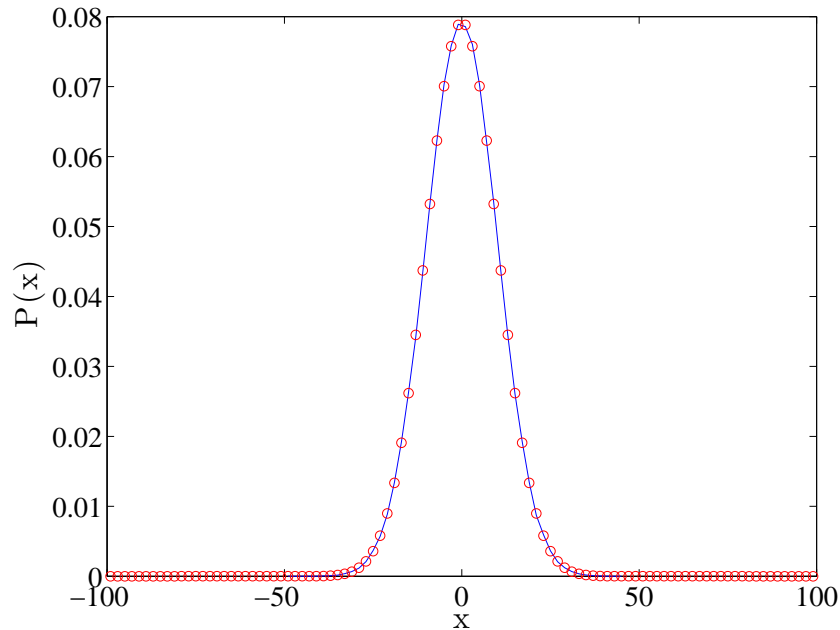
This is the number of ways to choose N_+ objects out of N when we do not care about the order they are chosen in.

This formula is fantastically useful!

Clickers - Combinatorics

We can also check if it works – how does it correspond to the results we got by random sampling?

```
% Comparing random sampling with the exact formula
nsample = 1000000;
xvalues = zeros(nsample,1);
N = 101;
for i = 1:nsample
    dx = 2*(randi(2,N,1)-1)-1;
    x = sum(dx);
    xvalues(i) = x;
end
edges = (-50.5:50.5);
n = histc(xvalues,edges);
j = find(n~=0);
plot(x(j),n(j)/nsample)
xlabel('x')
ylabel('P(x)')
hold on
% Calculate exact values
prob = zeros(N,1);
xx = prob;
for ix = 1:N
    prob(ix) = nchoosek(N,ix)/2^(101);
    xx(ix) = ix-(N-ix); % corresponding position
end
plot(xx,prob,'or');
hold off
```



This is a wonderful correspondence!

4 Spin systems

The system we have studied so far also corresponds to a two-state paramagnet (and also to the Ising system - where there are correlations!)

In a paramagnet, each particle has a small magnetic moment. In the simplest models, the magnetic moment can have two possible states, corresponding to heads or tails.

The energy of a spin parallel to an external magnetic field B is $-\mu B$ and the energy of a spin antiparallel to B is μB . The energy of a spin system in a field B - consisting of non-interacting spins - is

$$U = N_+(-\mu B) + (N - N_+)\mu B = -(2N_+ - N)\mu B$$

We can use the same approach to address the behavior of spin systems - and we will do this further on.

5 Ideal crystal

We will now address a more interesting, realistic system - the Ideal crystal also called the Einstein crystal.

The Einstein crystal consists of N independent harmonic oscillators. This is the simplest approximation we can make to a crystal: non-interacting atoms on a crystal lattice. In this case, for a three-dimension system, each atom really consists of three 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

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

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

$$\epsilon = h\nu n$$

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

An Einstein crystal is a system consisting of N such independent oscillators – with the same ν and therefore the same energy levels.

What are the possible states of such a system: It depends on the total energy U available to the system. We measure the energy in units of $h\nu = \epsilon$, and we often use the symbol q for this dimensionless energy.

q can only take on integer values.

Let us address this by looking at a simple example where $N = 4$ and $q = 2$.

What are the possible microstates of the Einstein crystal under this condition for energies $q = 0, 1, 2, 3$?

These are the possible microstates for a given number q .

Can we find a general expression for the multiplicity of a macrostate given by the value q of the total energy? What are the number of ways we can place q energy units into N boxes when we allow more than one energy unit in a given box?

There is a trick that makes this arrangement simple: Instead of specifying units and boxes, we think of arranging units and box walls along a line.

We can specify the microstate by arranging q energy units and $N - 1$ walls – in total $q + N - 1$ objects.

The number of ways we can arrange this, when we do not care about the ordering of the objects, is given by how many ways we can choose q numbers from $q + N - 1$ numbers, that is:

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

Clickers - Einstein crystal 1

6 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.

But let us try to see how the energy will be fluctuating among the individual oscillators in the system in equilibrium.

We will do that in two ways:

- We will actually look at the fluctuations – using the method that you will develop in oblig01
- And by counting microstates

Just like we did for the ideal gas in two chambers, we can always simply divide the system into two parts, A and B, that simple are subsets of the oscillators. This way, we can see what kind of internal oscillations we have.

Alternatively, we can think of this as being two initially isolated, but identical, Einstein crystals coming into thermal contact.

System A with N_A oscillators and system B with N_B oscillators.

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 .

What are the possible values of q_A ?

Clickers - Einstein crystal 2

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 .

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

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
clear all;clf;
NA = 100;
NB = 100;
q = 200;
N = NA + NB;
% Find multiplicity of all macrostates
nstate = q+1;
omegaA = zeros(nstate,1);
qAvalue = omegaA;
omegaB = omegaA;
omegaTOT = omegaA;
% Loop through all macrostates and find multiplicity
for istate = 1:nstate
    qA = istate-1;
    qAvalue(istate) = qA;
    omegaA(istate) = nchoosek(qA+NA-1,qA);
    qB = q - qA;
    omegaB(istate) = nchoosek(qB+NB-1,qB);
    omegaTOT(istate) = omegaA(istate)*omegaB(istate);
end
plot(qAvalue,omegaTOT,'-o');
%
matrix = [omegaA omegaB omegaTOT]
```

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**:

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 will span all possible microstates if you just wait long enough.

Later we will look at time variations.

Not yet – let us continue to look at the consequences of all microstates being equally probable.

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 really 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.

7 Time development of the Einstein model and heat flow

Let us develop a model for the time development of the Einstein model.

We have really defined the Einstein model without any interactions.

The other opposite is to model the full crystal lattice using either MD (or QM - with a high computational cost).

This is possible, but not really realistic because the time interval available for such simulations is small - typically on the order of microseconds.

So how can we introduce interactions into a system without interactions in a simple way? How does energy flow throughout the various oscillators in the Einstein crystal?

In this case we have to make an educated guess. We may be able to justify our guess - and we should ensure that it satisfies fundamental principles such as the principle of detailed balance – but beyond that we do not really have that many strong limitations.

We expect energy transport to be local. We could do this if all the oscillators were localized in space. But they are not in the model we have presented. (We can, and will, do this later because it is cool).

Instead we start with non-local energy transport. That means that we really lose a good physical time scale based on simple principles, but this is ok.

We assume that energy transport is random and between oscillators.

We suggest 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 may receive energy from n_1 .
- Transfer one unit of energy from i_1 to i_2 .

The resulting behavior is seen using the following program:

```
% Energy transport in an Einstein crystal
clear all;
Ly = 40; % System size y-direction
LA = 40; % Length of system A in x direction
LB = 40; % Length of system B in x direction
Lx = LA + LB;
NA = LA*Ly;
NB = LB*Ly;
qA = 3000; % Initial energy in system A
qB = 0; % Initial energy in system B
```

```

q = qA + qB; % Total energy - conserved
N = NA + NB; % Total number of oscillators
state = zeros(Lx,Ly); % 2d state matrix
% Generate initial, random states for A and B
for ia = 1:qA
    ix = randi(LA,1,1); % Rnd position from 1 to LA
    iy = randi(Ly,1,1); % Rnd position from 1 to Ly
    state(ix,iy) = state(ix,iy) + 1; % Add energy to this site
end
for ib = 1:qB
    ix = randi(LB,1,1)+LA; % Rnd pos from LA+1 to LA+LB
    iy = randi(Ly,1,1); % Rnd pos from 1 to Ly
    state(ix,iy) = state(ix,iy) + 1; % Add energy to this site
end
% Simulate state development
nstep = 10000000; % nr of simulation steps
EA = zeros(nstep,1); % Energy per oscillator in system A
EB = EA; % Energy per oscillator in system B
for istep = 1:nstep
    % Select an oscillator at random
    ix1 = randi(Lx,1,1);
    iy1 = randi(Ly,1,1);
    % Check if this oscillator has non-zero energy
    if (state(ix1,iy1)>0)
        % Find a random neighbor
        dx = 2*randi(2,1,1)-3; % +/-1 with equal prob
        ix2 = mod(ix1 + dx-1,Lx)+1; % mod for periodic boundaries
        dy = 2*randi(2,1,1)-3; % +/-1 with equal prob
        iy2 = mod(iy1 + dy-1,Ly)+1; % mod for periodic boundaries
        % Transfer energy from (ix1,iy1) to (ix2,iy2)
        state(ix2,iy2) = state(ix2,iy2) + 1;
        state(ix1,iy1) = state(ix1,iy1) - 1;
    end
    if (mod(istep,1000)==0) % Display system at regular intervals
        imagesc(state','colorbar', axis equal, axis tight, drawnow
    end
end
end

```

8 Stirling's formula

In order to estimate the behavior of combinatorial formulas we need an efficient way to calculate factorials. This is done using Stirling's formula:

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

which is ok when N is large.

When we look at the logarithm of the faculty it becomes even simpler:

$$\ln N! \simeq N \ln N - N + \frac{1}{2} \ln 2\pi N \simeq N \ln N - N$$

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

This allows us to find a simplified expression for the multiplicity of the Einstein crystal:

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

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

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

We apply Stirling's formula

$$\ln \Omega \simeq \ln(q+N)! - \ln q! - \ln N! = (q+N) \ln(q+N) - (q+N) - N \ln N + N - \ln q + q = (q+N) \ln(q+N) - N \ln N - q \ln q$$

Now we assume that $q \gg N$. We can use this to simplify $\ln(q + N)$ through:

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

Plugging this back into the equation gets rid of the $q \ln q$ terms, giving

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

The multiplicity is then

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

9 Sharpness of the multiplicity function

Now, let us apply this method to find the multiplicity of two interacting systems A and B each with N oscillators.

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

We expect the multiplicity function to have a very sharp peak at $q_A = q/2$, we therefore introduce

$$q_A = \frac{q}{2} + x$$

and

$$q_B = \frac{q}{2} - x$$

where x is a number much smaller than q (but it is still rather large).

We insert this expression back into the multiplicity

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

We simplify the logarithm

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

We plug this back into the equation for multiplicity:

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

This is a Gaussian – with a peak at $x = 0$.

The multiplicity falls to $1/e$ when

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

that is when

$$x = \frac{q}{2\sqrt{N}}$$

This may look like a large number, but not if N is 10^{20} , then it is only $1/10^{10}$ of the scale of $q/2$ where the center is.

It is very small – there are no measureable fluctuations!

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

10 Microstates of the Ideal gas

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

$$\epsilon(n_x, n_y, n_z) = \frac{h^2}{8mL^2} \vec{n} \cdot \vec{n},$$

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

$$\vec{p} = \frac{h}{2L} \vec{n}.$$

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.

10.1 Microstates of a single particle

If a single particle has energy E , we see that

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

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 $1/8$ 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:

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

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

10.2 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

Energy	Distinguishable		Fermions	
	n_1	n_2	n_1	n_2
1	1	1	0	1
		0	1	0
2	2	2	0	2
		0	2	0
		1	1	1

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

We are going to address this quantum 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.

10.3 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:

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

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

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

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

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

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

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

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

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

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

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

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

10.4 Interaction between two ideal gases

The multiplicity of a system subdivided into two systems with total energy $U = U_A + U_B$ and $N_A = N_B = N$ is the number of particles (so that the total number of particles is $2N$):

$$\Omega = \Omega_A \cdot \Omega_B = f(N_A) f(N_B) (V_A V_B)^N (U_A U_B)^N,$$

If we now look at a fluctuation $U_A = \bar{U} + u$, $U_B = \bar{U} - u$ we will again find that the multiplicity is strongly peaked and is a Gaussian, so that any fluctuation will be extremely unlikely.

11 Entropy and Temperature

We have found that a system of Ideal crystal or Ideal gas most likely is in the most likely macrostate. Any fluctuation from this most probably state will be very 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. The multiplicity of a state with energy q_A is

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

where $q = q_A + q_B$ is conserved.

We can find the extremum of this function by differentiation:

$$\begin{aligned} \frac{d}{dq_A}\Omega(N_A, q_A)\Omega(N_B, q - q_A) &= 0, \\ \frac{d\Omega(N_A, q_A)}{dq_A}\Omega(N_B, q - q_A) + \Omega(N_A, q_A)\frac{d\Omega(N_B, q - q_A)}{dq_A} &= 0, \\ \frac{\partial\Omega(N_A, q_A)}{\partial q_A}\Omega(N_B, q - q_A) - \Omega(N_A, q_A)\frac{\partial\Omega(N_B, q_B)}{\partial q_B} &= 0, \\ \frac{\partial\Omega(N_A, q_A)}{\partial q_A}\Omega(N_B, q_B) &= \Omega(N_A, q_A)\frac{\partial\Omega(N_B, q_B)}{\partial q_B}, \\ \frac{1}{\Omega(N_A, q_A)}\frac{\partial\Omega(N_A, q_A)}{\partial q_A} &= \frac{1}{\Omega(N_B, q_B)}\frac{\partial\Omega(N_B, q_B)}{\partial q_B}, \\ \frac{\partial \ln \Omega(N_A, q_A)}{\partial q_A} &= \frac{\partial \ln \Omega(N_B, q_B)}{\partial q_B}. \end{aligned}$$

We notice that it may be useful to take the logarithm of the multiplicity – this also makes the numbers more reasonable.

Since multiplicities are very large numbers it is simpler to work with the logarithm of these numbers, and we therefore usually introduce the entropy - S - as the logarithm of the multiplicity of the most probable state.

$$S = k \ln \Omega_{max},$$

12 Heat transport and Entropy

Let us look at this derivative and this equation 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 :

$$\Omega(q_A, q_B) = \Omega(N_A, q_A) \cdot \Omega(N_B, q_B)$$

where

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

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:

```
% Calculate number of microstates for two Einstein crystals in contact
NA = 300;
NB = 200;
q = 200;
multA = zeros(q,1);
multB = multA;
mult = multA;
N = NA + NB;

qvalue = (0:q);
for ik = 1:length(qvalue)
    qA = qvalue(ik);
```



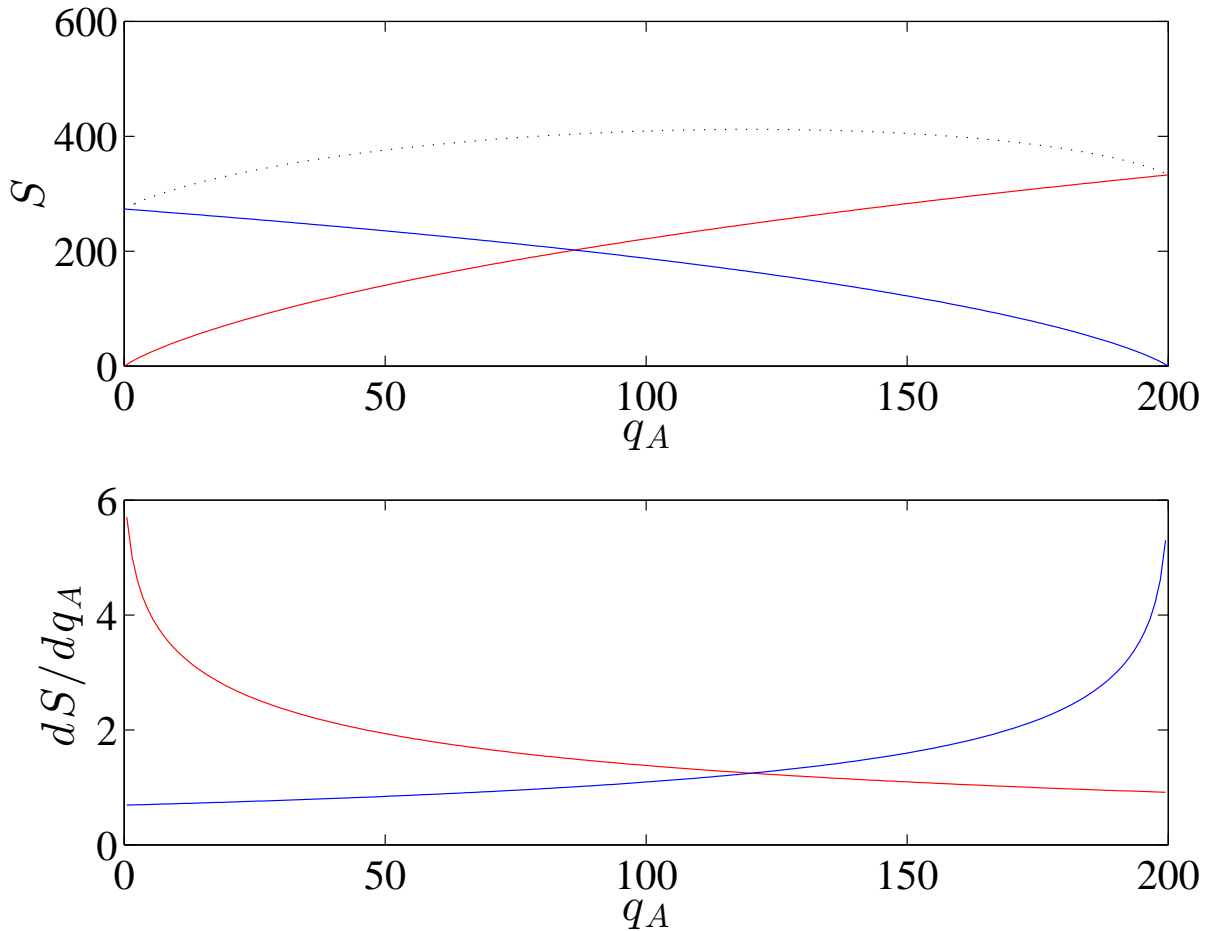
```

qB = q - qA;
multA(ik) = nchoosek(qA+NA-1,qA);
multB(ik) = nchoosek(qB+NB-1,qB);
mult(ik) = multA(ik)*multB(ik);
end
summult = sum(mult);
SA = log(multA);
SB = log(multB);
STOT = SA + SB;
subplot(2,1,1);
plot(qvalue,SA,'-r',qvalue,SB,'-b',qvalue,STOT,':k')
xlabel('q_A')
ylabel('S')
subplot(2,1,2);
dSA = diff(SA);
dSB = diff(SB);
qq = 0.5*(qvalue(2:end)+qvalue(1:end-1));
plot(qq,dSA,'-r',qq,-dSB,'-b');
xlabel('q_A')
ylabel('dS/dq_A')
legend('A','B')

```

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.

Running the program gives the plot shown in the following figure:



We can use this figure to understand better the condition for equilibrium we found above:

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

This corresponds to

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

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

We can easily find the value in the plots. What would happen in a system that was at a q_A value smaller than the equilibrium value, \bar{q}_A ? 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 the 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 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.)

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. The simplest interpretation with this property is to assume that the temperature is inversely proportional to the slope. This will indeed be how we define the temperature:

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

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

13 Entropy of ideal crystal

This allows us to start connecting the microscopic and the macroscopic worlds. We now 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

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

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

$$S = k \ln \Omega = Nk (\ln q + \ln(U/\epsilon) - \ln N) ,$$

$$S = Nk \ln U - Nk \ln(\epsilon N) + Nk .$$

And the temperature is:

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

which gives

$$U = NkT .$$

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

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

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

14 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:

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

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

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

Now, we can organize this a bit:

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

Then we take the logarithm:

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

This equation is called Sackur-Tetrode's equation.

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

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

This formula should be valid for an quasistatic, 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.

14.2 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

$$\Delta S = Nk \ln 2 ,$$

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

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

(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:

$$\Delta S_{A,B} = 2Nk \ln 2 .$$

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 .

14.3 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

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

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?

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

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

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

and the entropy of a double system would be:

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

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 raised by Gibbs, and is called Gibbs paradox.

15 Properties of the Entropy

The entropy has a few nice properties:

It is additive when the multiplicities are multiplicative.

Hence if $\Omega = \Omega_A \cdot \Omega_B$ then $S = S_A + S_B$.

16 Laws of thermodynamics

Usually, when we study thermodynamics, we start from a given number of postulates, and then the rest follows from these postulates. The nice part of statistical mechanics is that it provides a basis for the postulates (in addition to methods to calculate many of the thermodynamic functions you otherwise would have to measure).

These laws of thermodynamics are

0th law : If system A and B are in thermal equilibrium and system 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, $T_A = T_C$.

First law : The first law is the conservation of energy, where heat is introduced as thermal energy transferred between two systems.

Second law : This law can have several formulations. A formulation that comes from the statistical models we are using may be:

“If a closed system is in a configuration that is not the equilibrium configuration, the most probable consequence will be that the entropy of the system will increase monotonically with time.” (From Kittel and Kroemer).

However, the law could also be given a more thermodynamic formulation, for example, in the form of heat engines: “It is impossible for any cyclic process to occur whose sole effect is the extraction of heat from a reservoir and the performance of an equivalent amount of work” (again, Kittel and Kroemer).

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

17 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

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

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

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

The total change in entropy is therefore:

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

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:

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

combining this with the first law:

$$dU = W + Q ,$$

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

$$dS = \frac{Q}{T} .$$

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:

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

and

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

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

18 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.

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

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

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

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:

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

as the definition of pressure.

18.1 Pressure of ideal gas

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

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

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

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

and

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

which corresponds to

$$pV = NkT,$$

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

19 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 :

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

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

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

We insert these, getting:

$$dS = \frac{1}{T}dU + \frac{p}{T}dV \Rightarrow TdS = dU + p dV.$$

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

19.1 Entropy and Heat

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

$$dU = W + Q,$$

which would tempt 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.

20 Diffusive equilibrium

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

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

The corresponding condition for the number of particles is:

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

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

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

and

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

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

$$\mu_A = \mu_B .$$

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.

20.1 Thermodynamical identity

The thermodynamic identity now becomes:

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

which gives:

$$dU = TdS - pdV + \mu dN .$$

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

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

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

20.2 Chemical potential of Einstein crystal

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

$$S = Nk \ln U - Nk \ln(\epsilon N) + Nk ,$$

We find the chemical potential as

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

20.3 Chemical potential of Ideal gas

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

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

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

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

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.