

## Chapter 7

### The canonical ensemble

#### 7.1 Boltzmann statistics

We have so far studied systems with constant  $N$ ,  $V$ , and  $E$  - systems in the microcanonical ensemble. Such systems are often used in dynamic simulations, such as in molecular dynamics simulations, and we can use the principle of conservation of energy to argue for how energy is redistributed in a system with constant energy.

However, studies of systems in the microcanonical ensemble require the calculations of multiplicities, which often is not that simple in more complicated situations. Also, we may be interested in answering questions that are not directly answered in the microcanonical ensemble. For example, if we look at a single harmonic oscillator – a single atom in a lattice of atoms – we may be interested in the possible states this single oscillator may take: What is the probability for the oscillator to be in a particular state  $i$  when it is in contact with a large reservoir – a large system – kept at a constant temperature?

##### *7.1.1 Einstein crystal – numerical example*

This is a system we already know how to study. We even have an exact solution to the behavior of the Ideal/Einstein crystal. Previously, we have studied an Einstein crystal divided into two parts, A and B, and we characterized the macrostate of the system by the energy,  $q_A$ , of system A. But the argument we used was valid for any distribution of particles between system A and B, also for the case where system A consists of  $N_A = 1$  oscillator, and system B consists of  $N_B = N - 1$  oscillators. In this case, the total system, consisting of system A and system B, is isolated so that  $N_A + N_B = N$ ,  $V_A + V_B = V$  and  $q_A + q_B = q$ . In this case, we can find the probability for system A to have energy  $q_A$ , which is the same as the probability for system A to be in the state  $q_A$ , since for this particular system, there is one state per energy.

The possible values of  $q_A$  is from 0 to  $q$ . We know that the probability to find system A in state  $q_A$  is

$$P(q_A) = \frac{\Omega(q_A, N_A) \Omega(q_B, N_B)}{\Omega_T}, \quad (7.1)$$

where  $\Omega(q_A, N_A)$  is the multiplicity of an Einstein crystal with  $N_A$  oscillators and  $q_A$  energy, and is given by

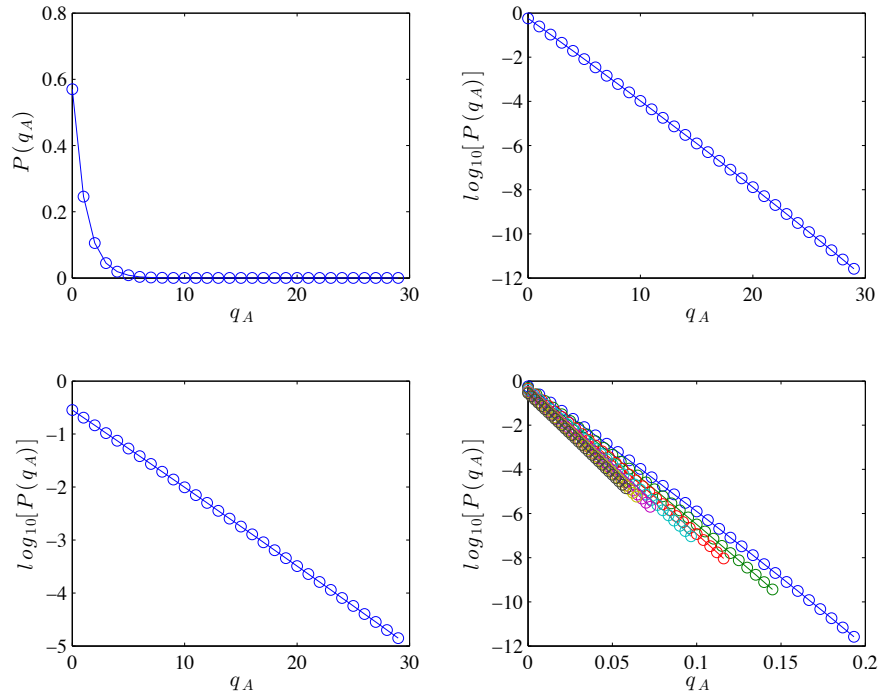
$$\Omega(q_A, N_A) = \binom{q_A + N_A - 1}{q_A}. \quad (7.2)$$

The total multiplicity  $\Omega_T$  is the sum of all the multiplicities for different values of  $q_A$ .

We can calculate and plot the probability  $P(q_A)$  using the following program. The resulting plot in fig. (7.1) shows that the probability falls off very rapidly.

```
% Einstein solid NA - NB probability
clear all; clf;
NA = 1;
NB = 199;
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
PA = omegaTOT/sum(omegaTOT);
j = find(qAvalue<40);
hold all
%plot(qAvalue(j), PA(j), '-o');
plot(qAvalue(j), log10(PA(j)), '-o');
xlabel('q_A')
ylabel('log_{10}P(q_A)')
```

How can we characterize the functional form of  $P(q_A)$ ? There are several tricks from experimental and observational physics to try to learn about the underlying functional form. Based on ideas from statistics we could expect it to be of an exponential or a power-law form. An exponential form, means that the function  $P(q_A)$  will be on the form



**Fig. 7.1** Probability  $P(q_A, N_A = 1)$  for the Einstein oscillator with  $q = 200$ ,  $N = 200$ .

$$P(q_A) = Ce^{-q_A/q^*}, \quad (7.3)$$

where  $C$  and  $q^*$  are constants. How can we test if the measured distribution has this form? We notice (and this is a common trick that it is useful for you to learn) that if we take the logarithm of the theoretical expression for  $q_A$ , we get

$$\ln P(q_A) = \ln C - \frac{q_A}{q^*}, \quad (7.4)$$

which is a linear function of  $q_A$ . This means that if we plot  $\ln P$  along the  $y$ -axis and  $q_A$  along the  $x$ -axis, we expect the plot to be linear if the functional form in eq. 7.1.1 is correct. Fig. (7.1) shows the resulting plot. Indeed, the curve is approximately linear – our theory seems to be reasonable.

Maybe our theory becomes better if we increase  $q$  and therefore the number of possible values for  $q_A$ ? We try this by plotting curves for  $P(q_A)$  for several values of  $q$  using the following program:

```
% Einstein solid NA - NB probability
% Random sampling compared with exact values
clear all;clf;
NA = 1;
NB = 199;
```

```

qq = [150 200 250 300 400 450 500];
nqq = length(qq);
for iqq = 1:nqq
    q = qq(iqq);
    %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
    PA = omegaTOT/sum(omegaTOT);
    j = find(qAvalue<40);
    subplot(2,1,1)
    hold all
    plot(qAvalue(j),log10(PA(j)),'-o');
    xlabel('q_A')
    ylabel('log_{10} [P(q_A)]')
    subplot(2,1,2)
    hold all
    plot(qAvalue(j)/q,log10(PA(j)),'-o');
    xlabel('q_A/q')
    ylabel('log_{10} [P(q_A)]')
end

```

The resulting curves for  $\ln P(q_A)$  are shown in fig. (??). Hmmm. Interesting. The slope of the curves, and therefore the  $q^*$  value, apparently depends on the total energy  $q$  in the system. How is this dependence? We could measure the slope and plot it as a function of  $q$  to find out that it appears that  $q^*$  appears to be proportional to  $q$ . And we can again check this hypothesis by plotting  $\ln P(q_A)$  as a function of  $q_A/q$ . If  $q^*$  is proportional to  $q$  we would then expect all the curves for various  $q$ -values to fall onto a common curve. The resulting plot in fig. (??) shows that this is approximately the case. You can convince yourself that this is indeed the case by redoing the plot for larger values of  $N$  and  $q$ .

Now, we have shown how  $P(q_A)$  depends on the total energy  $q$  in the system. But if we think of the system as a single oscillator – oscillator A – in contact with a large system of oscillators, we can think of the rest of the oscillators as a large reservoir with a given temperature  $T_B$  describing system B. Previously, we found that that the temperature of an Einstein crystal in the limit when  $q$  and  $N$  is large is given by  $E = q\Delta\epsilon = NkT$ , so that the temperature is proportional to  $q$ .

We can therefore sum up the results of our numerical study and the approximate theoretical model we have introduced to describe the results:

$$P(q_A) = C e^{-\frac{q_A}{cT}}, \quad (7.5)$$

where  $C$  and  $c$  are constants.

Now, let us see if we can make a theory for this behavior.

### 7.1.2 Einstein crystal in heat bath – theory

We have a complete methodology from the microcanonical ensemble which we can use to address such a problem: What is the probability for a single oscillator to be in a particular state  $|i\rangle$  with energy  $\varepsilon_i$ ?

We consider a big system, the reservoir or heat bath  $R$  – for example an Einstein crystal consisting of many oscillators – in contact with the system  $S$  – here consisting of a single oscillator. (We called the system  $A$  and the reservoir  $B$  in the numerical example above). We will assume that the reservoir is so large that it is not affected by the system: If we place a hot cup of water in the auditorium, it will cool down to the temperature of the auditorium without increasing the temperature significantly. The air and other materials in the auditorium is an example of a large heat bath.

The composite system consisting of the system and reservoir is isolated and is characterized by constant  $U$ ,  $V$ , and  $N$ . The composite system is therefore a microcanonical system and all microstates in this system are equally probable. If the system  $S$  is in a state with energy  $\varepsilon_i$  the reservoir has energy  $U_0 - \varepsilon_i$  so that the total energy is  $U = \varepsilon_i + (U_0 - \varepsilon_i) = U_0$ .

What is the probability for the system to be in the state  $|i\rangle$ ? The probability is given by the multiplicity of the whole system, consisting of both system  $S$  and reservoir  $R$ :

$$P(i) = \frac{\Omega_S \Omega_R}{\sum_i \Omega_S \Omega_R}, \quad (7.6)$$

where the sum is for normalization of the probability (to ensure the sum of probabilities of all possible states is 1 – the system must be in one of the possible states).

Since the system  $S$  is in the state  $|i\rangle$  the multiplicity of this state is 1: We have specified the state so it is only one way it can be in this state. (Note that state here is not the same as the energy, because several states can have the same energy and still be separate states. It is therefore important to remember that we here consider states and not only the energy.)

What is the multiplicity of the reservoir? For a given microstate  $|i\rangle$  of the system, the reservoir can be in many microstates. We call this  $\Omega(U_0 - \varepsilon_i)$ , where  $U_0$  is the total energy of the system.

The probability is therefore

$$P(i) = \frac{\Omega_S \Omega_R}{\sum_i \Omega_S \Omega_R} = C \cdot (1 \times \Omega_R) , \quad (7.7)$$

Let us work with the logarithm of the probability:

$$\ln P(i) = \ln C + \ln \Omega_R(U_0 - \varepsilon_i) . \quad (7.8)$$

We can expand  $\ln \Omega_R$  around  $U_0$  since  $\varepsilon_i \ll U_0$  (the heat bath is large):

$$\ln \Omega_R(U_0 - \varepsilon_i) = \ln \Omega(U_0) + \left( \frac{\partial \ln \Omega_R(U)}{\partial U} \right)_{U_0} (-\varepsilon_i) + \mathcal{O}(\varepsilon_i^2) , \quad (7.9)$$

Where we can now use that  $S = \ln \Omega$  for the reservoir, and we then recognize that

$$\left( \frac{\partial \ln \Omega_R(U)}{\partial U} \right)_{U_0} (-\varepsilon_i) = - \left( \frac{(1/k) \partial S}{\partial U} \right)_{U_0} \varepsilon_i = - \frac{\varepsilon_i}{kT} , \quad (7.10)$$

where we have used that in equilibrium:

$$\left( \frac{\partial S}{\partial U} \right) = \frac{1}{T} . \quad (7.11)$$

We put this back into the probability and find that

$$P(i) = C \exp \left( - \frac{\varepsilon_i}{kT} \right) . \quad (7.12)$$

What is the constant  $C$ ? It is given by the summation rule:

$$\sum_i P(i) = 1 = C \sum_i \exp \left( - \frac{\varepsilon_i}{kT} \right) . \quad (7.13)$$

and therefore

$$C = \frac{1}{Z} \quad (7.14)$$

where

$$Z = Z(N, V, T) = \sum_i \exp \left( - \frac{\varepsilon_i}{kT} \right) , \quad (7.15)$$

is called the partition function.

The system  $Z$  comes from the German “Zustandsumme” – sum of all *states*. The probability is therefore

$$P(i) = \frac{1}{Z} e^{-\frac{\varepsilon_i}{kT}} , \quad (7.16)$$

for the system to be in state  $|i\rangle$  when it is in equilibrium with a heat bath with temperature  $T$ .

This discussion is completely general and can be applied to any system with a given state  $|i\rangle$ , not only an oscillator system.

### 7.1.3 Comparison with numerical model

This theory is only valid for large reservoirs. We can therefore compare the theory with our numerical results for the Einstein crystal from above, but we will only expect the match to be good when  $N$  and  $q$  are large. We notice that the function we found to represent the numerical data was

$$P(q_A) = Ce^{-\frac{q_A}{cT}}. \quad (7.17)$$

The state in a system with a single harmonic oscillator is described by the state  $i$ , so that the energy levels are  $\varepsilon_i = \Delta \varepsilon i$ , where we see that the states can be enumerated by  $i$  or by  $q_A$ . The theoretical results for the probabilities for Boltzmann statistics is therefore:

$$P(q_A) = \frac{1}{Z} e^{-\frac{q_A \Delta \varepsilon}{kT}}. \quad (7.18)$$

Where we see that the constant  $c = k/\varepsilon$  and that the prefactor  $C$  is  $Z$  (which also is a function of  $T$ , but it does not depend on  $q_A$ ). The theory therefore both explains the observed numerical results, and provides us with a better understanding for the behavior of the system.

### 7.1.4 Alternative derivation of Boltzmann statistics

We may derive the Boltzmann statistics in a different way that is instructive using a variational method.

### 7.1.5 Average values and fluctuations

How can we use this new theory to connect the microscopic description of the system given in the probabilities for the states with the macroscopic description of the system given in thermodynamics? We can do this by calculating averages of the thermodynamic quantities.

We call a system with constant  $N, V, E$  a **microcanonical** system, and a system with constant  $N, V, T$  – that is a system in contact with a large heat reservoir of temperature  $T$  – a **canonical** system. In the microcanonical system the total energy is given, and we can measure the temperature  $T$ . The temperature  $T$  will fluctuate: If we measure temperature in a molecular dynamics simulation, we will get a temperature that varies in time,  $T(t)$ . However, we also found that for realistic values of  $N$  – which typically is  $10^{20}$  – the values for  $T$  are very sharp: Deviations beyond  $10^{-10}$  of its average value are very unlikely. For a canonical system, the temperature  $T$  is constant, but the energy  $E$  will fluctuate. We can therefore find the average value

(and later the fluctuations) in the energy and use this to connect the microscopic theory of Boltzmann statistics with the macroscopic theory of thermodynamics.

We find the average energy from the definition of the average

$$\bar{E} = \langle E \rangle = \sum_i \epsilon_i P(\epsilon_i) , \quad (7.19)$$

where the sum is over all states  $|i\rangle$  of the system  $S$ . Since we have an expression for  $P(i)$  we can simplify this expression to:

$$\bar{E} = \sum_i \epsilon_i \frac{1}{Z} e^{-\epsilon_i/kT} . \quad (7.20)$$

Here, we will employ a common trick, which is to introduce  $\beta = 1/(kT)$ . The equation then becomes

$$\bar{E} = \frac{1}{Z} \sum_i \epsilon_i e^{-\beta \epsilon_i} . \quad (7.21)$$

The trick is now to recognize that the sum is the derivative of a sum which is simpler to calculate:

$$\sum_i \epsilon_i e^{-\beta \epsilon_i} = -\frac{d}{d\beta} \sum_i e^{-\beta \epsilon_i} = \frac{dZ}{d\beta} . \quad (7.22)$$

The average energy then becomes:

$$\bar{E} = -\frac{1}{Z} \frac{d}{d\beta} Z = -\frac{d \ln Z}{d\beta} . \quad (7.23)$$

We will find that it is often easier to work with this expression, which allows us to calculate the energy  $E$  directly from the sum over the microstates of the system.

Now we have the tools to connect the microscopic and the macroscopic also in systems with constant  $N$ ,  $V$ , and  $T$ . Let us look at some example applications.

### 7.1.6 Example: Two-state system

Let us start with a very simple case – the two state system. We have an atom/molecule that may be in two states with energies  $\epsilon_0$  and  $\epsilon_1$  in contact with a thermal bath with temperature  $T$ . What is the internal energy and the heat capacity of this system?

We start – and you should always do this – by finding the partition function,  $Z$ . We may choose our base energy level as we like, so let us choose  $\epsilon_0 = 0$ .

$$Z = \sum_i e^{-\epsilon_i/kT} , \quad (7.24)$$

where the sum is over all the *states*. In this case, all the states corresponds to all the energies.



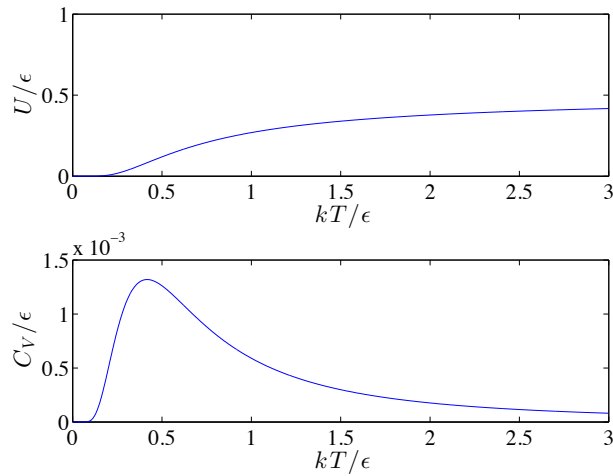
$$Z = \exp(0) + \exp(-\epsilon/kT) = 1 + \exp(-\epsilon/kT), \quad (7.25)$$

The average energy is

$$\begin{aligned} U = \bar{E} &= \frac{1}{Z} \sum_i \exp(-\epsilon_i/kT) \epsilon_i \\ &= \frac{1}{Z} (0 \cdot \exp(0) + \epsilon \cdot \exp(-\epsilon/kT)) \\ &= \epsilon \frac{\exp(-\epsilon/kT)}{1 + \exp(-\epsilon/kT)} \end{aligned} \quad (7.26)$$

The energy as a function of temperature is plotted using the following program and the resulting plot of  $E(T)$  is shown in fig. 7.2.

```
% Two state system
clear all; clf
x = linspace(0,3,1000);
U = exp(-1./x) ./ (1+exp(-1./x));
subplot(2,1,1)
plot(x,U)
xlabel('kT/\epsilon');
ylabel('U/\epsilon');
subplot(2,1,2)
CV = diff(U)/(x(2)-x(1));
xx = 0.5*(x(2:end)+x(1:end-1));
plot(xx,CV);
xlabel('kT/\epsilon');
ylabel('C_V/\epsilon');
%
%mysavefig('tmp.pdf')
```



**Fig. 7.2** Heat capacity of two-state system.

We can also check the two limits analytically. What happens when  $T \rightarrow \infty$ ? In this case, the term  $\exp(-\varepsilon/kT) \rightarrow 0$ . In this case, the probabilities for both state are equal and equal to  $1/2$ , and the average energy is  $\varepsilon/2$ . At low temperatures, the only possible state is the state with the lowest energy,  $P(1) = 1$  and  $P(2) = 0$ , and the average energy is also zero.

Finally, we can find the heat capacity,  $C_V$ , at constant  $V$  from

$$C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V}, \quad (7.27)$$

either by numerical derivation of the  $E(T)$  curve, or by analytical derivation of

$$C_V = \varepsilon \frac{\partial}{\partial T} \frac{1}{\exp \varepsilon/kT + 1}. \quad (7.28)$$

We can use a trick similar to what we introduced above to find the average energy: We introduce  $\beta = 1/kT$ , so that

$$U = \frac{1}{1 + \exp(\beta\varepsilon)}, \quad (7.29)$$

now we can write

$$\frac{\partial}{\partial T} = \frac{\partial}{\partial \beta} \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \frac{-1}{kT^2}. \quad (7.30)$$

This makes it easier to do the derivative:

$$\begin{aligned} C_V &= \varepsilon \frac{\partial}{\partial T} \frac{1}{\exp \varepsilon/kT + 1} = -\frac{\varepsilon}{kT} \frac{\partial}{\partial \beta} \frac{1}{1 + \exp \beta\varepsilon} \\ &= k\varepsilon\beta^2 \varepsilon \exp \beta\varepsilon \frac{1}{(1 + \exp \beta\varepsilon)^2} \\ &= k \left( \frac{\varepsilon}{kT} \right)^2 \frac{\exp(\varepsilon/kT)}{(\exp(\varepsilon/kT) + 1)^2}, \end{aligned} \quad (7.31)$$

### 7.1.7 Example: Fluctuations and heat capacity

There is a general result, which is interesting from a computational perspective, which allows us to calculate the heat capacity from the fluctuations in the energy. First, let us find the average energy:

$$\begin{aligned}
\bar{U} &= \frac{1}{Z} \sum_s \epsilon_s \exp(-\beta \epsilon_s) \\
&= \frac{1}{Z} \sum_s -\frac{\partial}{\partial \beta} \exp(-\beta \epsilon_s) \\
&= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_s \exp(-\beta \epsilon_s) \\
&= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta} \ln Z,
\end{aligned} \tag{7.32}$$

Similarly, we can express the heat capacity as the derivative of  $U$ :

$$\begin{aligned}
C_V &= \frac{\partial \bar{U}}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial \bar{U}}{\partial \beta} \\
&= \frac{1}{kT^2} \left( \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \right).
\end{aligned} \tag{7.33}$$

Now, we see that

$$\bar{U}^2 = \sum_s \epsilon_s^2 \exp(-\beta \epsilon_s) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}, \tag{7.34}$$

and we get the very nice relation:

$$C_V = \frac{1}{kT} \left( \bar{U}^2 - \bar{U}^2 \right). \tag{7.35}$$

This means that if we can measure the fluctuations in  $U$  we can use this to find the heat capacity – nice. This is particularly useful if we study a molecular/atomic system!

### 7.1.8 Sharpness of the canonical ensemble

Based on this result from the fluctuations, we can also determine the sharpness of the thermodynamic averages in the canonical ensemble.

Above, we found that the variation in the energy of a system,  $\Delta U$ , is proportional to the square root of the heat capacity:

$$\Delta U = \sqrt{\bar{U}^2 - (\bar{U})^2} = \sqrt{C_V kT}, \tag{7.36}$$

Now, we expect both the energy and the heat capacity (which is the derivative of energy with temperature) to be **extensive** properties – properties that are proportional to the number of particles  $N$ . This means that the relative fluctuation in  $U$  is given

as

$$\frac{\Delta U}{\bar{U}} \propto \frac{\sqrt{N}}{N} \propto (N)^{-1/2} . \quad (7.37)$$

In the limit of realistic  $N$  – typically on the order of  $10^{20}$  – we see that the relative error is  $10^{-10}$ , which is generally not measurable. The thermodynamic properties are therefore sharp.

### 7.1.9 Example: Einstein crystal

We can use the new formalism to address the behavior of the Einstein crystal. We can find the probability for a single oscillator to be in a given state, and we can find the average energy of a single oscillator. The states of an harmonic oscillator are

$$\varepsilon_i = \varepsilon_0 + i\Delta\varepsilon , \quad (7.38)$$

where  $\varepsilon_0 = \hbar\omega/2$  and  $\Delta\varepsilon = \hbar\omega$ . We choose the energy level so that  $\varepsilon_0 = 0$ , which is simply a small shift in energy, so that the energy levels are

$$\varepsilon_i = i\Delta\varepsilon , i = 0, 1, 2, \dots . \quad (7.39)$$

The partition function is then given as the sum over all states:

$$Z = \sum_{i=0}^{\infty} \exp\left(-\frac{\varepsilon_i}{kT}\right) . \quad (7.40)$$

We can simplify the notation by introducing a frequently used short-cut: We write  $\beta = 1/(kT)$ . The partition function is then:

$$Z = \sum_i \exp(-\beta\varepsilon_i) = \sum_{n=0}^{\infty} \exp(-\beta\Delta\varepsilon n) , \quad (7.41)$$

which is a geometric series, with sum

$$Z = \frac{1}{1 - \exp(-\beta\Delta\varepsilon)} . \quad (7.42)$$

We find the average energy either directly from the sum or – as we will do here – from the expression we found above:

$$\begin{aligned} \bar{U} &= -\frac{\partial}{\partial\beta} \ln Z = \varepsilon \frac{1}{1 - \exp(-\beta\Delta\varepsilon)} \exp(-\beta\Delta\varepsilon) \\ &= \Delta\varepsilon \frac{1}{\exp(\beta\Delta\varepsilon) - 1} . \end{aligned} \quad (7.43)$$

We can rewrite this now, introducing  $\beta = kT$  getting:

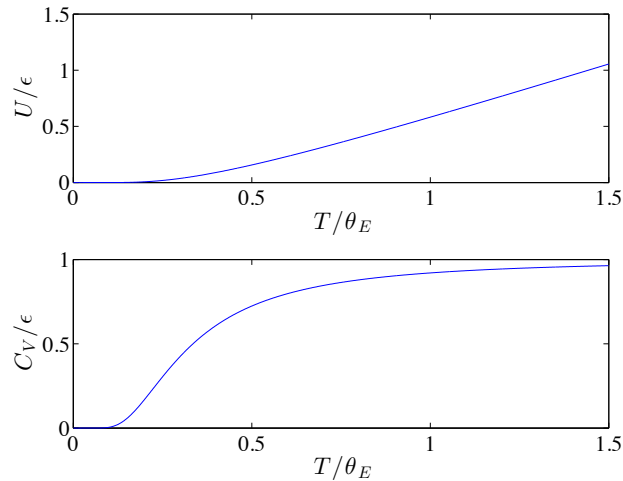
$$\bar{U} = \Delta\epsilon \frac{1}{\exp(\Delta\epsilon/kT) - 1} . \quad (7.44)$$

we can introduce the characteristic temperature  $\theta_E = \Delta\epsilon/k$  – the Einstein temperature for the oscillator, which is a constant for a given  $\Delta\epsilon$  – getting:

$$\bar{U} = \epsilon \frac{1}{\exp(\theta_E/T) - 1} . \quad (7.45)$$

It is illustrative to plot this expression as a function of  $T/\theta_E$  using:

```
% Einstein crystal energy and heat capacity
% U(T/T_E) - variables U/epsilon and x = T/T_E
clear all; clf
x = linspace(0,1.5,1000);
U = 1./ (exp(1./x)-1);
subplot(2,1,1)
plot(x,U)
xlabel(' $T/\theta_E$ ');
ylabel(' $U/\epsilon$ ');
subplot(2,1,2)
CV = diff(U) / (x(2)-x(1));
xx = 0.5*(x(2:end)+x(1:end-1));
plot(xx,CV);
xlabel(' $T/\theta_E$ ');
ylabel(' $C_V/\epsilon$ ');
%
%mysavefig('tmp.pdf')
```



**Fig. 7.3** Heat capacity in the Einstein crystal.

(I leave it for you to find an analytic expression for the heat capacity.)

It is interesting to notice the behavior of the heat capacity for a single harmonic oscillator now – this would be the contribution to the heat capacity for the vibration of a diatomic molecule. Notice that when  $T \ll T_E$  there is no contribution from the oscillations, whereas when  $T \gg T_E$  (or about at  $T_E$ ), there is a contribution from the oscillations. This allows us to sketch the expected effects of oscillations on the behavior of a diatomic ideal gas – where the behavior goes from  $3/2NkT$  to  $5/2NkT$  at around  $T_E$  for the corresponding oscillation. A nice prediction.

### 7.1.10 Example: Spin system

We can now apply these methods to address the behavior of a paramagnetic system. For a single dipole in a magnetic field, there are two possible states, one state with spin up and energy  $-\mu B$  and one state with spin down and energy  $\mu B$ .

The partition function for a single spin is therefore:

$$\begin{aligned} Z &= \sum_s \exp(-\beta \epsilon_s) \\ &= \exp(-\beta \mu B) + \exp(\beta \mu B) \\ &= 2 \cosh(\beta \mu B) . \end{aligned} \tag{7.46}$$

That was easy! We can find the average energy,  $\bar{U}$ , from:

$$\begin{aligned} \bar{U} &= -\frac{\partial}{\partial \beta} \ln Z \\ &= -\frac{1}{\cosh(\beta \mu B)} (\sinh(\beta \mu B) \mu B) \\ &= \mu B \tanh(\beta \mu B) , \end{aligned} \tag{7.47}$$

and, as you will see further down, to get the result for  $N$  independent spins we simply multiply by  $N$ .

This was very simple compared with the long calculation you had to do in the microcanonical ensemble!

### 7.1.11 Example: Ising spin system

However, this does become more complicated when we introduce interactions among the spins. For example, we may introduce the Ising model, where the interactions between two neighboring spins are given by the interaction energy:

$$-J s_i s_j , \tag{7.48}$$

where  $s_i = \pm 1$  and  $s_j = \pm 1$  describes the states of spin  $i$  and spin  $j$  – where  $i$  and  $j$  are nearest neighbors. This means that the energy contribution from this interaction is low ( $-J$ ) if the two spins are pointing in the same direction, and it is relatively high ( $+J$ ) if the two spins are pointing in opposite directions. This spin interaction will therefore lead to a situation where all the spins point in the same direction – given by the external field – in the lowest energy configuration. However, as temperature increases, fluctuations will arise, and it is not so clear what happens.

In addition, each spin interacts with the external magnetic field,  $B$ . The total energy of the system is therefore

$$\mathcal{E}_s = - \sum_{i,j} J s_i s_j - \mu B \sum_i s_i , \quad (7.49)$$

where the sum is over all the neighbors  $i, j$  in the system.

How would we find the partition function now?

- You may solve the 1d model – Ising did this.
- You may be *very* smart. Onsager solved the 2d Ising model. Nobody has solved the 3d Ising model – it may indeed not be solvable in 3d.
- You may have a computer!

Let us pursue the last option – what if we have a computer? We may then use a simple method to sample the space of lattice configuration. Let us sketch a method here, called heat-bath Monte Carlo, and we will discuss the basis of this method at the end of the chapter.

In general, we want to simulate the behavior of a system that is in equilibrium with a heat reservoir of temperature  $T$ . In the microcanonical ensemble, we know that all microstates are equally probable, but in the canonical ensemble, the probability of a microstate is given by the Boltzmann factors. How can we sample from the microstates, and ensure that we have this particular distribution?

We could generate a sequence of microstates by changing the microstates at random – such as by flipping a spin at random. However, since these microstates are not equally probable, we need to weigh their contributions accordingly when we calculate averages from this sequence of microstates: Each microstate  $n = 1, \dots, M$  of energy  $E_n$  should be weighted with its probability,  $\exp(-E_n/kT)/Z$ . This allows us to calculate the average energy of a system by

$$\bar{E} \simeq \frac{1}{Z} \sum_{n=1}^M E_n \exp(-E_n/kT) . \quad (7.50)$$

Unfortunately, we do not know  $Z$ , but we could estimate the normalization condition by the measured sum of all states, so that the sum of probabilities for all the states are normalized:

$$Z \simeq \sum_{n=1}^M \exp(-E_n/kT) , \quad (7.51)$$

and the estimator for the energy becomes:

$$\bar{E} \simeq \frac{\sum_{n=1}^M E_n \exp(-E_n/kT)}{\sum_{n=1}^M \exp(-E_n/kT)}. \quad (7.52)$$

While this is a reasonable suggestion, it is generally a very slow method. Why? Because many of the  $M$  states will typically have high energy and thus have very small probabilities.

A useful way to avoid this problem is to introduce *importance sampling* – we generate microstates with probabilities according to their weight  $\exp(-E_n/kT)$ . This ensures that we generate the microstates with the largest probabilities. The most common method for *importance sampling* is the *Metropolis algorithm*. In this algorithm we use the ratio of probabilities of two states to estimate the transition probability from one state to another. If we are at step  $n$  with energy  $E_n$  in the sequence of states, we first find a small perturbation to this state, we find the energy of this state,  $E'_n$ , and then we determine if this transition occurs or not based on the probability for the transition. If the energy is lower,  $\Delta E = E'_n - E_n < 0$  then we accept the change since this will move the system to a more probable state. If the energy is higher in the new state,  $\Delta E = E'_n - E_n > 0$ , then we accept the change with a probability given as  $\exp(-\Delta E/kT)$ . This process generates a sequence of states that we can use as a basis for averaging to determine the thermodynamic properties.

We can implement this algorithm to generate a sequence of states for the Ising system using the following algorithm:

- Choose a random site  $i$
- Find the energy of this site if  $s_i = 1$  and if  $s_i = -1$ ,  $E_+$  and  $E_-$ .
- Set the spin up with probability  $\exp(-\beta E_+)/C$  and down with probability  $\exp(-\beta E_-)/C$  with  $C = \exp(-\beta E_+) + \exp(-\beta E_-)$ .
- Repeat.

How do we find the energy of the site? We calculate it from the energy function. We therefore need to know  $m_i = \sum_j s_j$  for the neighbors of size  $i$  and calculate  $E_+ = -Jm_i - H$  and  $E_- = Jm_i + H$ , where  $H = \mu B$ .

We can do this for one site  $i$  at a time – and this is done in the following script.

```
% Heat bath Monte Carlo Ising model one spin at a time
clear all; clf;
nstep = 100; % Number of lattice changes
N = 100; % System size in x and y direction
Jdivk = 2.0/3.0; % Interaction
Hdivk = 0.0; % External field
T = 0.1; % Dimensionless temperature
JdivkT = Jdivk/T;
HdivkT = Hdivk/T;
% Make initial random spin configuration
spins = randi(2,N,N)*2-3;
sizespins = size(spins);
N2 = N*N;
% Evolve system
for istep = 1:nstep
    for jstep = 1:N2
```



```

    posx = randi(N,1);
    posy = randi(N,1);
    neighbors = [sub2ind(sizespins,mod(posx+1-1,N)+1,posy) ...
                sub2ind(sizespins,mod(posx-1-1,N)+1,posy) ...
                sub2ind(sizespins,posx,mod(posy+1-1,N)+1) ...
                sub2ind(sizespins,posx,mod(posy-1-1,N)+1)];
    sumneigh = sum(spins(neighbors));
    thisspin = spins(posx,posy);
    DeltaE = -JdivkT*thisspin*sumneigh - HdivkT*thisspin;
    change = (rand(1,1)<exp(DeltaE))*(-2)+1;
    spins(posx,posy) = spins(posx,posy)*change;
    imagesc(spins); axis square; drawnow;
end
imagesc(spins); axis square; drawnow;
end

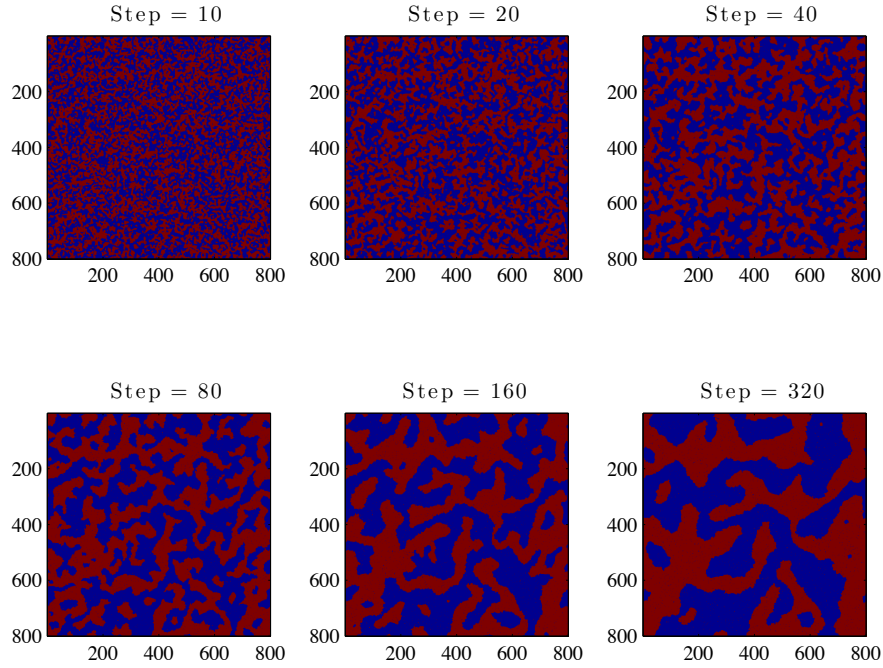
```

Unfortunately, this method is very slow in Python/matlab. We can speed it up by doing it for all states each step. Now, we cannot really do it for all sites at the same time – because if we change both  $i$  and one of its neighbors  $j$  at the same time, we do not really know how the energy changed. Instead, what we can do is to change half of the lattice each time, to ensure that there are no ambiguities. This is implemented in the following program. Resulting simulation patterns are shown in fig. 7.4.

```

% Heat bath Monte Carlo Ising model half lattice at a time
clear all; clf;
nstep = 320; % Number of lattice changes
noutput = [10 20 40 80 160 320];
N = 800; % System size in x and y direction
T = 0.8; % Dimensionless temperature
JdivkT = 1.0/T; % Interaction
HdivkT = 0.0/T; % External field
% Make initial random spin configuration
spins = randi(2,N,N)*2-3;
% Find half-matrix of sites for spin change
half lattice = zeros(N,N);
half lattice(1:2:N,2:2:N)=1;
half lattice(2:2:N,1:2:N)=1;
% Evolve system
for istep = 1:nstep
    sumneighbors = circshift(spins,[0 1]) + ...
                  circshift(spins,[0 -1]) + ...
                  circshift(spins,[1 0]) + ...
                  circshift(spins,[-1 0]);
    DeltaEdivkT = -spins.*(JdivkT*sumneighbors+HdivkT);
    pboltzmann = exp(DeltaEdivkT);
    changespin = -2*(rand(N,N)<pboltzmann).*half lattice+1;
    spins = spins.*changespin; % Flip spins
    half lattice = 1-half lattice; % Other half is next
    imagesc(spins); axis square; drawnow;
end

```



**Fig. 7.4** Illustration of spins in the Ising model for  $T = 0.8$ .

### 7.1.12 Degenerate states

Notice – and this is important – that the sum in the partition function is over all the *states* of a system. Not over all the possible energies, but over all the states. What is the difference? Several states may have the same energy!

We can group microstates with the same energies together. Each such state will contribute a term  $\exp(-\beta \epsilon_i)$  to the sum. Instead of summing over all the states  $i$ , we can sum over all the energies, but then we need to include how many states there are for a particular energy  $\epsilon$ :

$$Z = \sum_{\text{states } i} \exp(-\beta \epsilon_i) = \sum_{\text{energy levels } n} \Omega(E_n) \exp(-\beta E_n). \quad (7.53)$$

We will use this distinction many times, also when the sum is difficult to calculate.

### 7.1.13 Example: System with degenerate states

For example, we could have studied a system where the number of states with the same energy increases with the energy:

$$\varepsilon_i = \varepsilon(1, 2, 2, 3, 3, 3, 4, 4, 4, 4) \quad (7.54)$$

In this case the multiplicity of energy  $\varepsilon$  is 1, of  $2\varepsilon$  is 2, of  $3\varepsilon$  is 3 and so on.

The partition function in this case is

$$Z = \sum_i \exp(-\beta \varepsilon_i) = \sum_n \Omega(\varepsilon_n) \exp(-\beta \varepsilon_n), \quad (7.55)$$

where  $\Omega(1) = 1$ ,  $\Omega(2) = 2$ ,  $\Omega(3) = 3$  and  $\Omega(4) = 4$ . The sum is therefore:

$$Z = 1 \cdot \exp(-\beta \varepsilon) + 2 \cdot \exp(-2\beta \varepsilon) + 3 \cdot \exp(-3\beta \varepsilon) + 4 \cdot \exp(-4\beta \varepsilon), \quad (7.56)$$

And the mean energy, we find in the same way:

$$\bar{U} = \sum_i \varepsilon_i \exp(-\beta \varepsilon_i) = \sum_n \Omega(n) \varepsilon_n \exp(-\beta \varepsilon_n), \quad (7.57)$$

where the sum over  $i$  is over all the states, and the sum over  $n$  is over all the energies.

The average energy is therefore:

$$\bar{U} = \varepsilon \frac{1 \cdot \exp(-\beta \varepsilon) + 2 \cdot 2 \exp(-2\beta \varepsilon) + 3 \cdot 3 \exp(-3\beta \varepsilon) + 4 \cdot 4 \exp(-4\beta \varepsilon)}{Z}. \quad (7.58)$$

## 7.2 Thermodynamics in the canonical ensemble

In the microcanonical ensemble, all microstates have the same probability,  $P(i) = 1/\Omega$ , whereas in the canonical ensemble, the probability of a microstate is weighted with its energy,  $\varepsilon_i$ , according to the Boltzmann factor  $P(i) = (1/Z) \exp(-\varepsilon_i/kT)$ . In the microcanonical ensemble, the coupling between the microscopic models and the macroscopic thermodynamics, occurs through  $S(E, V, N) = k \ln \Omega(E, V, N)$ . Can we find a similar simple relation between the microscopic and the macroscopic for the canonical system where  $(T, V, N)$  are constants?

First, we have already found one such connection: We found that we can calculate the (average) energy  $\bar{E}$  in the system from:

$$\bar{E} = \sum_i \varepsilon_i P(i) = -\frac{\partial}{\partial \beta} \ln Z, \quad (7.59)$$

where  $\beta = 1/(kT)$ . We will now use this relation as a basis for the coupling between the microscopic and the macroscopic.

### 7.2.1 Helmholtz free energy

For the microcanonical ensemble, entropy is a function of  $E, V, N$ ,  $S = S(E, V, N)$ , and the thermodynamic identity is

$$TdS = dE + pdV - \mu dN , \quad (7.60)$$

We can rewrite this equation to be the energy as a function of  $S, V, N$ :

$$E = E(S, V, N) , \quad (7.61)$$

and we can find the corresponding differential relations by rearranging the thermodynamic identity:

$$dE = TdS - pdV + \mu dN . \quad (7.62)$$

Indeed, from this rearrangement we see that when  $E$  is a function of  $S, V, N$ , we can find the  $T$ ,  $p$  and  $\mu$  from various derivatives of  $E = E(S, V, N)$ .

Now, to describe the canonical system, we would like to have a similar differential to  $dE$ , but with the differentials  $dT$ ,  $dV$ , and  $dN$ . We would like to have a relation like:

$$dA = ()dT + ()dV + ()dN , \quad (7.63)$$

where we need to find the unknown functions/variables shown as  $()$  in the differential. Also – we need to figure out how we can construct  $A$  to have these properties. There is a formal way to do this – using Legendre transforms – which is robust (meaning that it always works) and we will introduce it later. For now, we will motivate the Legendre transform by observing that the differential for  $E$  almost got us there, we only need to replace the  $dS$  term with some  $dT$  term. We need to subtract the  $TdS$  term and then get a new  $XdT$  term with the  $T$  dependence. We see that if we subtract  $d(TS)$  on both sides of the thermodynamic identity, we get

$$\begin{aligned} dE - d(TS) &= TdS - d(TS) - pdV + \mu dN \\ &= TdS - TdS - SdT - pdV + \mu dN \\ &= -SdT - pdV + \mu dN , \end{aligned} \quad (7.64)$$

which has exactly the right form! This is the quantity we were looking for. It is an energy – it has units energy – it is a function of  $T$ ,  $V$ , and  $N$ . We call this quantity  $F$ , Helmholtz free energy:

**Helmholtz free energy:**  $F(T, V, N) = E - TS$

The differential for  $F$  is:

$$dF = -SdT - pdV + \mu dN . \quad (7.65)$$

This allow us to find the entropy,  $S$ , the pressure  $p$ , and the chemical potential  $\mu$  if we have an expression for Helmholtz free energy:

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad p = - \left( \frac{\partial F}{\partial V} \right)_{T,N}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}. \quad (7.66)$$

This means that if we know Helmholtz free energy, we can calculate the remaining thermodynamical properties of the system. However, to do this we need an expression for  $F(V, T, N)$  either from experiments, simulations, or theory. We have already found how we can connect the energy  $E$  to the microscopic theory through the use of the partition function  $Z(T, V, N)$ . How can we relate  $F$  to the partition function and thus complete the coupling between the microscopic and the macroscopic also for the canonical system?

### 7.2.2 A microscopic expression for Helmholtz free energy

We have already found that the energy  $E$  can be related to the microscopic description of the system through the partition function:

$$\bar{E} = - \frac{\partial \ln Z(T, V, N)}{\partial \beta}, \quad (7.67)$$

We can therefore find the energy if we know the partition function. However, for the canonical ensemble, we would also like to be able to calculate quantities such as the entropy, the pressure or the chemical potential. We would therefore like to have an expression for Helmholtz free energy, because, as we saw above, we can then find all quantities of interest from partial derivatives of  $F$ . We know that Helmholtz free energy,  $F$ , is

$$F = E - TS, \quad (7.68)$$

We already know  $E$ , but we do not know  $S$  – yet. However, we know that  $dF = -SdT - pdV + \mu dN$  and therefore we know that

$$S = \left( \frac{\partial F}{\partial T} \right)_{V,N}, \quad (7.69)$$

which we can insert back into eq. 7.68, giving

$$F = E + T \left( \frac{\partial F}{\partial T} \right)_{V,N}. \quad (7.70)$$

We recognize this as a differential equation for  $F$ .

$$F = - \frac{\partial \ln Z(V, T, N)}{\partial \beta} + T \left( \frac{\partial F}{\partial T} \right)_{V,N}. \quad (7.71)$$

We can find the solutions to this differential equation, by starting from a good guess – which of course is correct. A solution to this differential equation is

$$F = -kT \ln Z(V, T, N) . \quad (7.72)$$

We can demonstrate that this is a solution by substitution. First, we find the derivative of  $F$  with respect to  $T$ :

$$\begin{aligned} \left( \frac{\partial F}{\partial T} \right)_V &= \frac{\partial}{\partial T} (-kT \ln Z) \\ &= -k \ln Z - kT \frac{\partial \ln Z}{\partial T} \\ &= -k \ln Z - kT \frac{U}{kT^2} . \end{aligned} \quad (7.73)$$

Then we insert this into the differential equation above, and find that

$$E + T (-k \ln Z - (E/T)) = -k \ln Z , \quad (7.74)$$

which proves that  $F = -kT \ln Z$  is one possible solution to the differential equation. However, there may in addition be a constant term  $F = -kT \ln Z + aT$ . To address the  $aT$  term, we need to invoke the *third law of thermodynamics*, which states that the entropy of a system approaches a small number or zero as the temperature approaches zero. This is because as the temperature approaches zero, the system will be frozen into the lowest possible energy configurations, and the entropy will only be the possible degeneration of the lowest energy, which will typically be a small number. Since the entropy is the derivative of  $F$  with respect to  $T$ , we see that the entropy only will approach zero or a small number if  $a$  is zero or a small number, that is, is  $a \simeq 0$ .

We have therefore proven the fundamental relationship between thermodynamics and the microscopic models for the canonical ensemble:

$$F = -kT \ln Z . \quad (7.75)$$

I find the equation beautiful. It is simple. It connects the microscopic and the macroscopic worlds. It allows all types of calculations of  $S$ ,  $p$  and  $\mu$  from the partition function. We can now apply this to find all thermodynamic properties of systems described in the canonical ensemble.

### 7.2.3 Helmholtz free energy is minimal in equilibrium

For the micro-canonical ensemble we have seen how the system develops towards equilibrium and what characterizes the equilibrium state: The system evolves towards the most likely macrostate – that is, towards the macrostate with most mi-

crostates – equivalently the system evolves towards maximum entropy:

$$\Delta S \geq 0. \quad (7.76)$$

This condition also characterizes the equilibrium state: The entropy is a maximum for the equilibrium state.

For example, for the Einstein crystal, divided the system into two parts, A and B. We saw that the total entropy of the system  $S = S_A + S_B$  increases with time, and that the total entropy is maximal at equilibrium. This is indeed what characterizes the equilibrium state in the system.

Do we have similar principles for the canonical system? Does the entropy increase for a canonical system? Does the energy increase? Or is there some other principle that we do not yet know? We can study this in the Einstein crystal. We make a system consisting of two parts, a small part A, which is the system, and a large part B, which is the reservoir. We can make a system with  $N_A = 10$  and  $N_B = 990$ . This should ensure that system B is so large that the temperature in this system does not change – it is constant and equal to the reservoir temperature  $T_B = T_R$ . The total energy is  $q = q_A + q_B$ . We can simulate the dynamics of this system using the monte-carlo method we developed previously. This would allow us to simulate the time dynamics of the system as it develops through a sequence of microstates. This is done by the following program:

```
% MC for a two part Einstein crystal
clear all; clf;
NA = 10;
NB = 990;
qA = 300;
qB = 9700;
q = qA + qB; % Total energy
N = NA + NB;
nstep = 1000000;
nbetween = 1000;
state = zeros(N,1);
% Generate initial, random state
placeA = randi(NA,qA,1);
for ip = 1:length(placeA);
    i = placeA(ip);
    state(i) = state(i) + 1;
end
placeB = randi(NB,qB,1);
for ip = 1:length(placeB);
    i = placeB(ip)+NA;
    state(i) = state(i) + 1;
end
% Simulate state development
EA = zeros(nstep,1);
EB = zeros(nstep,1);
TBSA = zeros(nstep,1);
TB = zeros(nstep,1);
for istep = 1:nstep
```

```

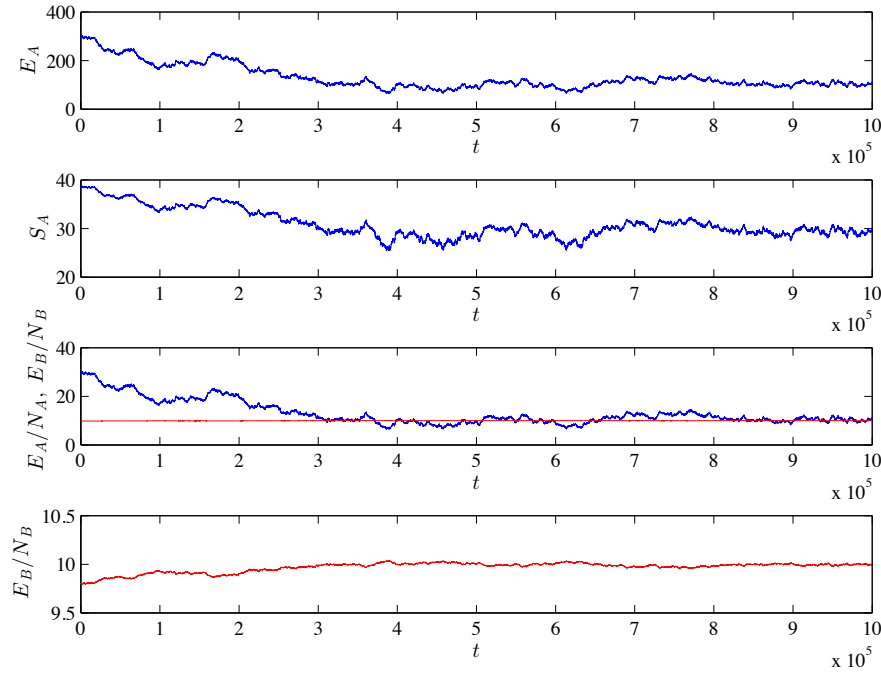
i1 = randi(N,1,1); % Select oscillator at random
if (state(i1)>0) % Check if it has energy
    i2 = randi(N,1,1); % Then find other oscillator
    state(i2) = state(i2) + 1;
    state(i1) = state(i1) - 1;
end
% Calculate T_B S_A
EA(istep) = sum(state(1:NA));
EB(istep) = sum(state(NA+1:end));
qA = EA(istep);
qB = EB(istep);
omegaA = nchoosek(NA+qA-1,qA);
TB(istep) = qB/NB;
TBSA(istep) = TB(istep)*log(omegaA);
if (mod(istep,nbetween)==0)
    subplot(4,1,1) % State
    bar((1:NA),state(1:NA),'b'), hold on
    bar((NA+1:N),state(NA+1:end),'r'), hold off
    a = axis(); a(2) = N; axis(a);
    xlabel('i'); ylabel('n_i'); drawnow;
    subplot(4,1,2); % Avg energy in each system
    plot((1:istep),EA(1:istep)/NA,'-r',...
        (1:istep),EB(1:istep)/NB,'-b');
    drawnow, xlabel('t'); ylabel('q_A/N_A , q_B/N_B')
    subplot(4,1,3) % Plot T_B
    plot((1:istep),EB(1:istep)/NB,'-b')
    xlabel('t'); ylabel('T_B'); drawnow
    subplot(4,1,4)
    plot((1:istep),EA(1:istep),'-r',...
        (1:istep),TBSA(1:istep),'-b',...
        (1:istep),EA(1:istep)-TBSA(1:istep),'-k')
    xlabel('t'); ylabel('E');
    legend('E_A','T_B*S_A','E_A-T_B*S_A');
    drawnow
end
end

```

We need to decide on the initial distribution of energy in the system. We try to alternatives: First, we try the case where system A has a large amount of the energy than an even distribution, we choose  $q_A = 300$ , and  $q_B = 9700$ , giving  $q = 10000$ . In this case, the average energy per oscillator in system A is 30 and the average energy per oscillator in system B is 9.8. We measure the entropy,  $S_A(t)$  and energy  $q_A(t)$  of system A,  $S_A(t)$ , as a function of time  $t$ . Fig. 7.5 shows the development of  $E_A(t)$  and  $E_B(t)$ . We see that the energy in system A decreases with time and reaches an approximately constant level – corresponding to the equilibrium state of the system. We see that in the equilibrium state – after a long time – the energy is evenly distributed throughout the system, and the average energy per oscillator in system A and system B,  $E_A/N_A$  and  $E_B/N_B$  become the same value, close to the average of the total energy per oscillator,  $q/N$ , in the system. This is not surprising. We expect the average energy per oscillator to be related to the temperature, and we know that in equilibrium the temperatures in the two systems will be the same.

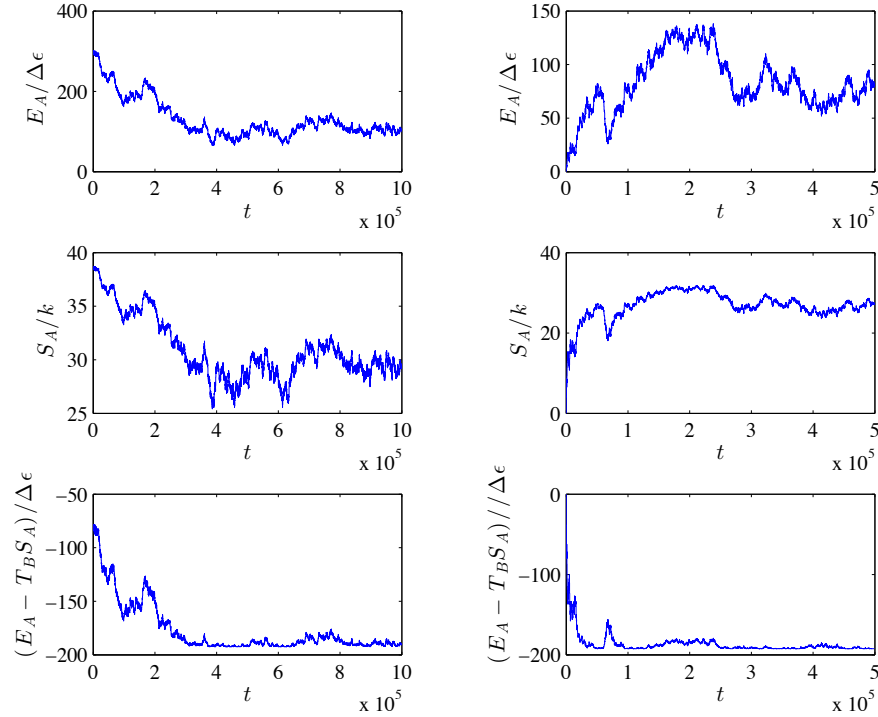


We also see that system B is indeed large. In the plot that shows both  $E_A/N_A$  and  $E_B/N_B$  we see that the change in  $E_B/N_B$  is very small compared with the change in system A. This is what we mean when we call a reservoir *large* – it is so large that the temperature does not change significantly. There are, however, changes in  $E_B/N_B$  as well, as evident from the plot of  $E_B/N_B$  alone, but these fluctuations are small.



**Fig. 7.5** Time development of the energies in two systems A with  $N_A = 10$  and B with  $N_B = 990$  in thermal contact.

The energy in system A clearly decreases with time in this system. What about the entropy? We can measure the entropy in system A through the formula  $S_A = k \ln \Omega_A(q_A, N_A)$ , which we have developed previously. Now,  $q_A$  will change with time, and therefore as will  $S_A$ . This measurement was implemented in the program above. Fig. 7.6 shows both the energy and the entropy for system A. We see that the entropy in system A decreases in time and approaches an approximately stationary value. We expect the fluctuations to become smaller for larger systems and the entropy to become sharp. These observations suggest that in equilibrium – which is what we reach after a long time – the system has reached a minimum in entropy and a minimum in energy. Hmm. That was surprising – the entropy is decreasing in this system. (Convince yourself that this is not unphysical and that the second law of thermodynamics still is valid).



**Fig. 7.6** Time development of the energies and entropies for an Einstein system with  $N_A = 10$  and  $N_B = 990$  for two different initial distributions of energy. In the left figures the system start with  $q_A = 300$ ,  $q_B = 9700$  and in the right figures the system start with  $q_A = 0$  and  $q_B = 10000$ .

Let us try the same simulation, but from a different starting point – the case where system A initially has less energy than the average energy,  $q_A = 0$  and  $q_B = 10000$ . We expect the same equilibrium state in this system as in the previous since the number of oscillators is the same and the total energy in the system is the same. How does it develop in time? Fig. 7.6 shows that the entropy,  $S_A(t)$ , and energy,  $q_A(t)$ , of system A in this case both increase, and then reach a stationary value which is a maximum of both entropy and energy? Hmmm. Now it is not easy to see what kind of rule would determine the behavior of the system: Should the entropy be a maximum or a minimum? Should the entropy increase or decrease?

It is time to revisit the theory and develop a better theoretical understanding of this process. We know that the whole system, system A and system B, is thermally isolated and therefore described as a microcanonical system with  $E$ ,  $V$ , and  $N$  constant. For this system, the energy is constant  $E_A + E_B = E$  and the total entropy must be increasing:

$$\Delta S = \Delta S_A + \Delta S_B \geq 0. \quad (7.77)$$

The change in entropy in system A is indeed what we observed in the simulations – it could be both positive or negative. This is what we want to develop a theory

for. What about the development of system B? Since system B is very large, we will now assume that system B is very close to equilibrium – so close that we can assume that system B is in equilibrium. In this case, we know that we can describe the behavior of system B with the thermodynamic identity:

$$TdS = dE + pdV - \mu dN, \quad (7.78)$$

where  $dV$  and  $dN$  is zero for system B – there is no change in volume or the number of oscillators. We therefore get  $T_B \Delta S_B = Q_B = \Delta E_B$ , where the change in energy in system B comes from the thermal energy  $Q_B$  transferred from system A to system B, which again corresponds to  $\Delta E_B = -\Delta E_A$ , and therefore we have  $\Delta S_B = -\Delta E_A/T_B$ , which we insert back into eq. 7.77, getting:

$$\Delta S = \Delta S_A - \frac{\Delta E_A}{T_B} \geq 0. \quad (7.79)$$

We rearrange, getting

$$T_B \Delta S_A - \Delta E_A \geq 0, \quad (7.80)$$

where we can now assume that  $T_B$  does not change – it is (approximately) constant during this process, and we can write this as the change in  $(E_A - T_B S_A)$ :

$$\Delta(T_B S_A - E_A) \geq 0, \quad (7.81)$$

or

$$-\Delta(E_A - T_B S_A) \geq 0, \quad (7.82)$$

giving, finally:

$$\Delta(E_A - T_B S_A) \leq 0. \quad (7.83)$$

We have now found a criterion for how the system should develop in time, and a criterion for the equilibrium. In equilibrium, we expect  $E_A - T_B S_A$  to be minimal and we expect  $E_A - T_B S_A$  to decrease with time and approach a minimal value.

In equilibrium,  $T_A = T_B$ , and we therefore know that in equilibrium

$$\Delta(E_A - T_A S_A) \geq 0, \quad (7.84)$$

where we recognize this as Helmholtz free energy,  $F_A = E_A - T_A S_A$  for system A. We have therefore found a new principle, valid for a canonical system with  $T, V, N$  constant: For this system, Helmholtz free energy will always decrease  $\Delta F \leq 0$ , and the equilibrium state is characterized as a minimum for Helmholtz free energy,  $F$ .

First, let us check if this indeed is the case in the simulations we performed above. We have already found  $E_A$  and  $S_A$  as part of the simulations. How can we find  $T_B$  from the simulations? The simplest approach would be to notice that system B is large, so that the high temperature and large system size approximation for the energy of an Einstein crystal can be used,  $E_N \simeq N_B k T_B$ , which we can use to find the temperature through  $T_N = E_N/(N_B k)$ . We are now able to calculate  $E_A - T_B S_A$ , but we should now check that the units we use are ok. In the program, we calculate

$q_A$ ,  $q_B$  and  $\ln \Omega$  for  $S_A$ . We know that  $E_A = q_A \varepsilon$  and  $E_B = q_B \varepsilon$ , where  $\varepsilon$  is the characteristic energy (the energy level spacing) for the harmonic oscillator in the Einstein crystal. We therefore get:

$$\begin{aligned} E_A - T_B S_A &= \varepsilon q_A - (\varepsilon q_B) / (N_B k) k \ln \Omega(q_A, N_A) \\ &= \varepsilon (q_A - (q_B / N_B) \ln \Omega(q_A, N_A)) , \end{aligned} \quad (7.85)$$

which shows that we can use  $q_A (q_B / N_B) \ln \Omega$  to characterize  $F_A$  in the simulations. Fig. ?? shows  $F_A(t)$  for the two simulated models. We see that even if  $S_A$  and  $E_A$  are increasing for one system and decreasing in the other system, Helmholtz free energy  $F_A$  is decreasing in both cases, and approaches a stationary value as time increases, corresponding to the equilibrium value of  $F_A$ . Indeed, the theory we have developed describes the system we have studied, and provides us with additional insight: Helmholtz free energy is minimal in equilibrium.

This means that Helmholtz free energy plays a similar role in canonical systems ( $T, V, N$  constant) as the entropy did for the microcanonical system ( $E, V, N$  constant). We call the principle that the free energy is minimal in equilibrium a minimum free energy principle, and we will see later that such principles are very useful and will allow us to calculate equilibrium states in for example fluid or solid mixtures, and for both biological, geological and meteorological systems of interest.

Where does the word **free** energy come from? We see that if  $T$  and  $N$  is constant, then the work that is performed by a canonical system is

$$(\Delta F)_T = -p \Delta V = -\Delta W , \quad (7.86)$$

so that the work  $\Delta W$  done on the environment by the system at constant temperature and  $N$  is equal to the loss in free energy for the system: Hence the name *free energy*. (This is only true for reversible processes).

### 7.2.4 Helmholtz free energy is a minimum in equilibrium

We can also show that Helmholtz free energy is not only an extremum value, but it is actually a minimum:

The total energy is  $U = U_S + U_R$ . The total entropy is

$$\begin{aligned} S &= S_R + S_S \\ &= S_R(U - U_S) + S_S(U_S) \\ &\simeq S_R(U) - U_S \cdot \left( \frac{\partial S_R}{\partial U_R} \right)_{V,N} + S_S(U_S) . \end{aligned} \quad (7.87)$$

Where we also know that

$$\left( \frac{\partial S_R}{\partial U_R} \right)_{V,N} = \frac{1}{T} , \quad (7.88)$$

and therefore we get

$$S = S_R(U) - \frac{1}{T} F_S, \quad (7.89)$$

where  $F_S = U_S - TS_S$  is the free energy of the system. Now  $S_R(U)$  is a constant. We also know that  $S = S_R + S_S$  is maximum with respect to  $U_S$  in equilibrium. There  $F_S$  must be a minimum.

### 7.2.5 Maxwell relations

We can now find a new group of relations – thermodynamic relations – based on the second derivative of Helmholtz free energy: If the energy is continuous in its variables, we know that the order of derivatives for the second derivative is not important, therefore:

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}, \quad (7.90)$$

we can use this to find that

$$\frac{\partial p}{\partial T}_V = \frac{\partial S}{\partial V}_T. \quad (7.91)$$

We will find more such relations later as we introduce more variables. (There are three possible permutations in this case, but the other two involve the chemical potential, which we are not familiar with yet).

### 7.2.6 Example: Composite systems

Before we do the ideal gas of many, identical particles, let us start by studying systems of identical and non-identical particles.

Let us start by a system consisting of two different particles, each described independently by the quantum states  $\epsilon_{1,i}$  and  $\epsilon_{2,j}$ .

The partition function is

$$\begin{aligned} Z &= \sum_i \sum_j \exp(-\beta \epsilon_{1,i}) \exp(-\beta \epsilon_{2,j}) \\ &= \left( \sum_i \exp(-\beta \epsilon_{1,i}) \right) \left( \sum_j \exp(-\beta \epsilon_{2,j}) \right) \\ &= Z_1 \cdot Z_2. \end{aligned} \quad (7.92)$$

For two non-interacting systems, with distinguishable particles, the partition function is the product of the partition functions!

Now, what if the two particles are not distinguishable?

In that case, we have included too many elements in the sum, because we have included both

$$\exp(-\beta(\epsilon_{2,j} + \epsilon_{1,i})) \quad (7.93)$$

and

$$\exp(-\beta(\epsilon_{2,i} + \epsilon_{1,j})) , \quad (7.94)$$

but these two states are the same, and should only be counted once.

We should therefore divide by 2:

$$Z_{TOT} = \frac{1}{2} Z_1 Z_2 , \quad (7.95)$$

and this is almost correct, but I have then also divided the terms

$$\exp(-\beta(\epsilon_{2,i} + \epsilon_{1,i})) , \quad (7.96)$$

by two – and these terms have not been double counted. However, the mistake we make by this will be small as long as there are few of such states.

Generalized to  $N$  particles we get:

$$Z = Z_1 Z_2 \dots Z_N , \quad (7.97)$$

for distinguishable particles, and

$$Z = \frac{Z_1 Z_2 \dots Z_N}{N!} = \frac{Z_1^N}{N!} , \quad (7.98)$$

for identical particles.

### 7.2.7 Example: Ideal gas in the canonical ensemble

We would therefore like to find  $Z_1$  for one particle in a box to find the partition function for an ideal gas.

But even for a single particle, there can be several, independent degrees of freedom, and each of these would be considered independent states, and therefore independent partition function. For a diatomic gas we may have translation, vibration and rotation, and the corresponding partition function for a single particle is then:

$$Z_1 = Z_{\text{trans}} \cdot Z_{\text{rot}} \cdot Z_{\text{vib}} , \quad (7.99)$$

and if there are further internal degrees of freedom we should include these as well.

Let us now address the partition function for a single atom (particle) in a box of size  $L$  (and volume  $V$ ). Again, we know that the states of the system are given by  $n_x, n_y, n_z$  for the particle, with

$$\epsilon_n = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) . \quad (7.100)$$

The partition function is given by the sum over all the states  $n_x, n_y, n_z$ :

$$Z = \sum_{n_x} \sum_{n_y} \sum_{n_z} \exp \left( -\beta \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \right) , \quad (7.101)$$

which is the product of three identical sums,  $\xi$ , so that:

$$Z = (\xi)^3 , \quad (7.102)$$

where

$$\xi = \sum_{n=0}^{\infty} \exp(-\lambda^2 n^2) , \quad (7.103)$$

where we have introduced  $\lambda$  as

$$\lambda^2 = \beta \frac{h^2}{8mL^2} . \quad (7.104)$$

For small values of  $\lambda$  we can approximate the sum by the integral:

$$\xi \simeq \int_0^{\infty} \exp(-\lambda^2 n^2) , dn = \frac{\sqrt{\pi}}{2\lambda} . \quad (7.105)$$

The partition function is therefore given by:

$$Z = \frac{\pi^{3/2}}{8} \left( \frac{2mL^2}{\beta \hbar^2 \pi^2} \right)^{3/2} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} V . \quad (7.106)$$

It is usual to introduce the *quantum density*  $n_Q$  through:

$$n_Q = \left( \frac{m}{2\pi \hbar^2 \beta} \right)^{3/2} , \quad (7.107)$$

and the partition function is then

$$Z = V n_Q = \frac{n_Q}{n} , \quad (7.108)$$

where  $n = 1/V$  is the density of particles.

The average particle energy is given by:

$$\bar{U} = \langle \epsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} kT . \quad (7.109)$$

This is in correspondence with the equipartition principle.

Notice the effect of adding in addition internal degrees of freedom, this would correspond to adding in addition products in  $Z$ , which would give additional addends in the sums in  $\bar{U}$  and in  $F$ . We can therefore indeed add in the effect of rotations and vibrations in both the energy and in the free energy – as we did to address the heat capacity of a vibrating atom in an ideal gas.

### 7.3 Transformation between ensembles

We introduced Helmholtz free energy,  $F$ , as a function with the natural variables  $T$ ,  $V$ ,  $N$ . The method we used to develop  $F$  from  $E$  is a general method, that we can use to gain a very useful insight into the relation between the various *free energies* that we will use in thermodynamics. The various free energies may often seem unmotivated – you may remain with the impression that they were dreamed up or that we arrived at them in some unspecified way. Not so – they are all derived in a very natural way.

Let us start from the microcanonical system. This system is thermally isolated and described by the state variables  $E$ ,  $V$ ,  $N$ . These three state variables provide the complete state of the system. From these state variables – and from the relation  $S = S(E, V, N)$ , we can calculate other state variables such as  $T$ ,  $p$ , and  $\mu$  for the system.

From a thermodynamic perspective – where  $S(E, V, N)$  is a sharp function of  $E$ ,  $V$ , and  $N$  – we could instead describe the system with the variables  $S$ ,  $V$ , and  $N$ , and then find the energy  $E$  from a relation  $E = E(S, V, N)$ . We can use the thermodynamic identity to see how we can gain all the thermodynamic properties from  $E(S, V, N)$  in this case:

$$TdS = dE + PdV - \mu dN \Rightarrow dE = TdS - PdV + \mu dN . \quad (7.110)$$

We use these differential forms to find what are the variables describing the system. Here is it  $S$ ,  $V$ , and  $N$ , since these are the variables for  $dE$ . And we can also use this identity to read out the partial derivatives of  $E$ :

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -P, \quad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu . \quad (7.111)$$

Now, we would like to describe the system with the variables  $T$ ,  $V$ , and  $N$  instead of  $S$ ,  $V$ , and  $N$ , just as we did for the canonical ensemble. What is then the quantity corresponding to  $E$  – the quantity  $A$  that when we take the differential of  $A$  we end up with  $T$ ,  $V$ , and  $N$  as the free variables. We want to develop a function  $A = A(T, V, N)$  so that

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,N} dT + \left(\frac{\partial A}{\partial V}\right)_{T,N} dV + \left(\frac{\partial A}{\partial N}\right)_{T,V} dN . \quad (7.112)$$



How can we create such a function and what would the partial derivatives be? Fortunately, there is a general theory in the form of Legendre transforms that allow us to transform a function  $E(S, V, N)$  into a new function  $A(T, V, N)$ , where  $T$  is the partial derivative of  $E$  with respect to  $S$ . This transform is called the Legendre transform. In general, if we have a function  $f = f(x, y, z)$  and we want to replace  $x$  with its *partial derivative conjugate*,  $t$ :

$$t = \left( \frac{\partial f}{\partial x} \right)_{y,z} . \quad (7.113)$$

This is achieved by the Legendre transform:

$$\mathcal{L}f(x, y, z) = g(t, y, z) = f(x(t, y, z), y, z) - xt . \quad (7.114)$$

This is what we do for the transformation between the microcanonical and the canonical ensemble: We move from a description of the system in terms of  $E(S, V, N)$  to  $A(T, V, N)$ , by introducing

$$A(T, V, N) = E(S(T, V, N), V, N) - S(T, V, N) \left( \frac{\partial E}{\partial S} \right)_{V,N} = E - TS , \quad (7.115)$$

and this is what we called the Helmholtz free energy. Let us check that this free energy indeed has the correct dependent variables by finding the differential for  $F$  using the thermodynamic identity:

$$\begin{aligned} dF &= d(E - TS) \\ &= dE - TdS - SdT = dE - (dE + pdV - \mu dN) - SdT \\ &= -SdT - pdV + \mu dN , \end{aligned} \quad (7.116)$$

which indeed shows that the dependent variables – the variables occurring in the differentials on the right hand side,  $dT$ ,  $dV$ , and  $dN$  – are indeed  $T$ ,  $V$ , and  $N$  as we wanted.

Now, we are ready to examine other possible combinations of state variables. What if we want to study a system where the volume is no longer constant – so that we want to replace  $V$  with its partial derivative conjugate. What is the conjugate of  $V$ ? It is  $-p$ :

$$-p = \left( \frac{\partial E}{\partial V} \right)_{S,N} . \quad (7.117)$$

We can now use the Legendre transform to generate the potential

$$H = E - V \left( \frac{\partial E}{\partial V} \right)_{S,N} = E - V(-p) = E + pV . \quad (7.118)$$

This potential is called the **enthalpy** of the system. Let us check that it has the correct dependent variables by finding the differential for  $H$ :

$$\begin{aligned}
dH &= d(E + pV) \\
&= dE + pdV + Vdp \\
&= (TdS - pdV + \mu dN) + pdV + Vdp \\
&= TdS + Vdp + \mu dN .
\end{aligned} \tag{7.119}$$

Indeed, the dependent variables are  $S$ ,  $p$ , and  $N$ .

Let us look at two further systems that we will introduce later on. What if we want to study systems at constant  $T, p, N$  – that is, we want to replace  $V$  with  $p$  in  $F$ ? In that case, we apply the transform to  $F$ , getting

$$G = F + pV = E - TS + pV , \tag{7.120}$$

which is called **Gibbs free energy**.

Similarly, we will want to study chemical reactions in open systems with constant  $T$ ,  $V$ , and  $\mu$ , but where  $N$  may vary. This corresponds to changing from  $N$  to  $\mu$  in  $F$ , again applying the transform we get

$$\Phi = F - \mu N , \tag{7.121}$$

which is called the **Grand potential**.

It is also useful to develop an interpretation of *free energy as the energy needed to generate a system out of nothing*. For the microcanonical ensemble, the energy  $E$  is the energy we need to generate the system.

For the canonical system, we also need to generate the energy  $E$  of the system, but now we do this while in equilibrium with a large reservoir with temperature  $T$  – we therefore get some energy for free from the reservoir, in the form of heat transfer from the reservoir. This corresponds to  $TS$ . The energy needed to create a canonical system with  $T$ ,  $V$ , and  $N$  is therefore given by Helmholtz free energy,  $F = E - TS$ . This is also the energy we would be able to get out of the system if we annihilated the system – again we would gain the energy  $E$ , but we would now lose the energy  $TS$  to the reservoir.

For a system at constant  $E$ ,  $p$ ,  $N$  – corresponding to the microcanonical system, but at constant pressure instead of constant volume, we need to generate the energy  $E$ , but in addition we need to make room for the volume  $V$  of the system, which requires work done by the system on the environment, and this work is  $pV$ . The energy needed to create the system is therefore  $H = E + pV$ , the **enthalpy** of the system.

For a system in equilibrium with a heat bath with temperature  $T$  and in an atmosphere/environment with pressure  $p$ , we need to generate the energy  $E$  and we need to do a work  $pV$  to make room for the system, but since we are in equilibrium with a heat bath, we get a thermal energy of  $TS$  from the reservoir. The total energy needed is therefore  $G = E - TS + pV$ , which is the **Gibbs free energy** of the system.

We therefore see that the free energies are the energies needed to generate a system in various conditions. Tables of free energies are therefore useful tools to determine the energy needed to create various systems or to go from one system to

another system through chemical reactions or physical transformations, as demonstrated by the following examples.

### 7.3.1 Example: Fuel cell

Fuel cells are used in cars, such as the BMW 750Hl. In a fuel cell hydrogen and oxygen is combined to form water:



What is the energy produced in this reaction, if it occurs at constant temperature  $T = 298\text{K}$  and constant pressure?

In this case, we know that the energy we get from creating 1 mole of water, while removing 1 mole of hydrogen and half a mole of oxygen, is given by the Gibbs free energy. The energy from the reaction will be

$$\Delta G = \Delta G(\text{H}_2\text{O}) - \Delta G(\text{H}_2) - \frac{1}{2}\Delta G(\text{O}_2) . \quad (7.123)$$

In the table for the Gibbs free energy for water in Schroder, it is the total  $\Delta G$  which is listed. We find that for water  $\Delta G = -237\text{kJ}$  per mole. It is negative, because to generate water from its basic compounds, we gain energy.

Since this process occurs at constant temperature corresponding to room temperature, we know that Gibbs free energy has two components, one component from the change in enthalpy and one component from the change in entropy:

$$\Delta G = \Delta H - T\Delta S , \quad (7.124)$$

We therefore lose some of the energy to heat. How much energy is converted to heat? We can estimate this in two ways: (i) We can simply use the change in enthalpy tabulated in Schroder – this gives us the total energy produced in a system that is not in thermal contact with a heat bath; or (ii) We can calculate the changes in entropy also based on entropy values from Schroder.

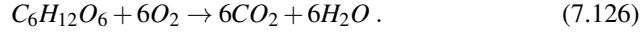
The change in enthalpy for the reaction is

$$\Delta H = -286\text{kJ} . \quad (7.125)$$

This means that the entropy change, due to heat, is  $\Delta G = \Delta H - T\Delta S$ , giving  $T\Delta S = Q = \Delta H - \Delta G = -286\text{kJ} + 237\text{kJ} = -49\text{kJ}$ , where the negative sign means that the heat is transferred from the system to the environment/reservoir in the process. This means that the efficiency of this process is  $237/286$ , which is 0.83, which is very high!

### 7.3.2 Example: Muscle cell

We can think of a muscle cell as a fuel cell, but using different chemicals than the hydrogen fuel cell, of course. The general form of reaction in the muscle cell is to use glucose to generate water and  $\text{CO}_2$ :



If we assume that the reaction occurs at room temperature and at one atm pressure, what is the enthalpy and Gibbs free energy for this reaction?

How can we find  $\Delta H$  and  $\Delta G$  for such compound processes? In the tables in Schroder, and in other sources, the values for  $\Delta H$  and  $\Delta G$  for each compound, such as for glucose, is the enthalpy or Gibbs free energy when the compound is made from each component in its most elemental, stable form. For glucose, we assume that it is made from  $\text{C}$  (graphite),  $\text{O}_2$  and  $\text{H}_2$ . We can therefore find the  $\Delta H$  or  $\Delta G$  for the reaction, by first converting each compound into their elemental forms and then converting from the elemental forms and into the new compound – the result of the chemical reaction. We can therefore find what it would take to turn the left side into its basic components, which is the negative of what it would take to create the left side from its basic components. We call the enthalpy and Gibbs free energy of the left side  $\Delta H_L$  and  $\Delta G_L$  respectively – the energies needed to create the left side. Similarly,  $\Delta H_R$  and  $\Delta G_R$  are the energies needed to create the right side from its basic components:

$$\Delta H_L = \Delta H_{\text{C}_6\text{H}_{12}\text{O}_6} + \Delta H_{6\text{O}_2} = -1273\text{kJ} + 6 \cdot 0\text{kJ} = -1272\text{kJ} , \quad (7.127)$$

$$\Delta G_L = \Delta G_{\text{C}_6\text{H}_{12}\text{O}_6} + \Delta G_{6\text{O}_2} = -910\text{kJ} + 6 \cdot 0\text{kJ} = -910\text{kJ} . \quad (7.128)$$

Similarly, for the right hand side:

$$\Delta H_R = \Delta H_{6\text{CO}_2} + \Delta H_{6\text{H}_2\text{O}} = 6 \cdot -393\text{kJ} + 6 \cdot -286\text{kJ} = -4074\text{kJ} , \quad (7.129)$$

$$\Delta G_R = \Delta G_{6\text{CO}_2} + \Delta G_{6\text{H}_2\text{O}} = 6 \cdot -394\text{kJ} + 6 \cdot -237\text{kJ} = -3786\text{kJ} . \quad (7.130)$$

The change in enthalpy occurs by creating the right side and removing the left side, thus

$$\Delta H = \Delta H_R - \Delta H_L = -4074\text{kJ} + 1272\text{kJ} = -2802\text{kJ} , \quad (7.131)$$

and the change in Gibbs free energy is similar:

$$\Delta G = \Delta G_R - \Delta G_L = -3786\text{kJ} + 910\text{kJ} = -2876\text{kJ} . \quad (7.132)$$

Gibbs free energy is negative, meaning that this is the energy available for mechanical work done by the muscle on the environment.

We see that the magnitude of Gibbs free energy is larger than the magnitude of the enthalpy. What does this imply? Since  $\Delta G = \Delta H - TS = \Delta H - Q$ , where  $Q$  is the heat transferred into the muscle from the environment due to the energy in the

thermal bath, we see that in this case:

$$Q = \Delta H - \Delta G = -2802\text{kJ} + 2876\text{kJ} = 74\text{kJ} . \quad (7.133)$$

which is the heat dumped from the environment to the muscle (to help it do work at the same temperature).

## 7.4 Additional material (not exam relevant)

### 7.4.1 Derivation of pressure in the canonical systems

What happens if we change the volume of a system in a microstate  $\epsilon_s$ ? Generally, we expect the energy to be a function of the volume, but we assume that the volume change is so small that the system remains in the same quantum state, only the energy of the states. If we now change the volume slowly (reversibly) from  $V$  to  $V + \Delta V$  by an external force. The energy of state  $s$  after the reversible volume change is

$$\epsilon_s(V + \Delta V) = \epsilon_s(V) + \frac{d\epsilon_s}{dV}\Delta V + \dots . \quad (7.134)$$

Now, if the change in volume corresponds to changing all the walls with  $\Delta x$ ,  $\Delta y$ , and  $\Delta z$ , then the volume change is  $\Delta V = A(\Delta x + \Delta y + \Delta z)$ . The work done by this volume change is

$$W = -p_s A(\Delta x + \Delta y + \Delta z) = -p_s \Delta V , \quad (7.135)$$

Since we have assumed that the change in volume is without any changes to the energy states of the system, the change is without any change in entropy and hence also without any heat (when the system is changed reversibly, quasistatically). The work therefore corresponds to the change in energy:

$$dU = Q + W = -p_s \Delta V , \quad (7.136)$$

and we can now recognize that

$$p_s = -\frac{d\epsilon_s}{dV} . \quad (7.137)$$

Now, if we introduce the average pressure of the system as:

$$\bar{P} = \sum_s p_s P(s) = -\sum_s \frac{d\epsilon_s}{dV} P(s) = -\frac{d}{dV} \sum_s \epsilon_s P(s) = -\left(\frac{\partial U}{\partial V}\right)_S , \quad (7.138)$$

where we have written that  $S$  must be constant. It may be tempting to also write that  $T, N$  is constant, and thus refer it to the Canonical ensemble that this calculation was done in. This is correct, while not properly proven here.

We could also express the sum in eq. 7.138 directly from the partition function, and in that case we find that:

$$\bar{P} = \sum_s \frac{d\epsilon_s}{dV} \frac{1}{Z} \exp(-\beta\epsilon_s) = kT \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N}, \quad (7.139)$$

since for the derivation of the partition function and  $P(s) = (1/Z) \exp(-\beta\epsilon_s)$  we assumed constant  $N, V, T$ , and now we are allowing  $V$  to change.

### 7.4.2 Statistical entropy

From the average energy we get:

$$\bar{U} = \sum_s \epsilon_s P(s), \quad (7.140)$$

Now, the total change in energy is therefore:

$$dU = \sum_s \epsilon_s dP(s) + \sum_s P(s) d\epsilon_s, \quad (7.141)$$

Where we can write the second term as:

$$\sum_s P(s) d\epsilon_s = \sum_s P(s) \frac{d\epsilon_s}{dV} dV = -\bar{P} dV, \quad (7.142)$$

and therefore the change in energy is:

$$d\bar{U} = \sum_s \epsilon_s dP(s) - \bar{P} dV. \quad (7.143)$$

If we compare with the thermodynamic identity, we see that we can interpret:

$$TdS = \sum_s \epsilon_s dP(s), \quad (7.144)$$

This expressions can be (with some tricks) be related to another expression for the entropy – which we could instead have started from:

$$TdS = \sum_s \epsilon_s dP(s) = -kT \sum_s \ln Z dP(s) - kT \sum_s \ln P(s) dP(s) \quad (7.145)$$

where we have used that

$$P(s) = (1/Z) \exp(-\epsilon_s/kT), \quad (7.146)$$

and therefore that

$$\varepsilon_s = -kT(\ln Z + \ln P(s)) . \quad (7.147)$$

Notice that  $\sum_s dP(s) = d\sum_s P(s) = d(1) = 0$ . We therefore get:

$$dS = -k \sum_s \ln P(s) dP(s) = -k \sum_s d(P(s) \ln P(s)) , \quad (7.148)$$

and

$$S = -k \sum_s P(s) \ln P(s) , \quad (7.149)$$

which is a general expression for the entropy. This relation also holds in the microcanonical ensemble, since then  $P_s = 1/\Omega$  for all states and therefore we find  $S = k \ln \Omega$  after summing.

### 7.4.3 Equipartition theorem

Let us look at a general result for systems with an energy that has a quadratic shape:

$$\varepsilon(q) = cq^2 , \quad (7.150)$$

where  $q$  is a degree of freedom, such as the position, the velocity, the angular velocity, or any other.

We will assume that the states are densely, but discretely placed in  $q$ -space (but that they are not degenerate), so that there are states every  $\Delta q$ . The partition function is therefore

$$Z = \sum_q \exp(-\beta cq^2) , \quad (7.151)$$

which we will approximate by the integral over all  $q$ -values:

$$Z = \frac{1}{\Delta q} \sum_q \exp(-\beta cq^2) \Delta q = \frac{1}{\Delta q} \int \exp(-\beta cq^2) dq , \quad (7.152)$$

we change variable to  $x = \sqrt{\beta c} q$ , so that  $dx = \sqrt{\beta c} dq$ , and

$$Z = \frac{1}{\Delta q} \frac{1}{\sqrt{\beta c}} \int_{-\infty}^{\infty} e^{-x^2} dx , \quad (7.153)$$

where the integral is simply a numerical value (which we do not need to know) – we call it  $b$ .

$$Z = \frac{1}{\Delta q \sqrt{\beta c}} b = C \beta^{-1/2} . \quad (7.154)$$

(Notice that we are here only concerned with the scaling with  $\beta$  of this function – not the exact functional form.)

The energy is then found from:

$$\bar{U} = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right) = \frac{1}{C\beta^{-1/2}} (-1/2) C\beta^{-3/2} = \frac{1}{2}\beta = \frac{1}{2}kT, \quad (7.155)$$

and we have proved the equipartition theorem – which is true as long as the states are spaced in  $q$ -space with no degeneracy.

This is ok as long as the spacing between levels is much smaller than  $kT$  – which is not true for quantum systems at low energies.

## 7.5 Numerical modeling in the canonical ensemble

The canonical ensemble lends itself to modeling. Indeed, the Monte Carlo method is widely used as a numerical/computational method to gain insight into real systems – biological, technological, geological.

We saw a first version of the Monte Carlo method above – the heat bath Monte Carlo. For the Ising system with energy:

$$\varepsilon = \sum_i \left( S_i \sum_{j:i} -JS_j - H \right), \quad (7.156)$$

we picked a spin at random and replaced it with a spin  $S'_i$  with probabilities  $P(E_1) \propto \exp(-\beta E_1)$  and  $P(E_2) \propto \exp(-\beta E_2)$  for the two possible energies  $E_1$  and  $E_2$  of the spin in the system – thus trying to ensure that the system is consistent with Boltzmann statistics.

### 7.5.1 Monte Carlo estimates of integrals

This method is an example of a Monte Carlo algorithm. Monte Carlo methods can be used for many things – not only physics, but also to solve mathematical problems. For example, we could use Monte Carlo methods to find an area or to solve an integral.

We can use the “hit or miss” algorithm to calculate the definite integral of a function:

$$y = \int_{x_0}^{x_1} f(x) dx. \quad (7.157)$$

This integral can be interpreted as the integral under the curve  $f(x)$  from  $x_0$  to  $x_1$ . To estimate this we choose a box from  $y = 0$  to some  $y_1 > f(x)$  for all  $x$  on the interval. We then select  $N$  points randomly in the interval  $x_0$  to  $x_1$  and  $y_0 = 0$  to  $y_1$ . We can then estimate the integral by the fraction of points falling below the curve  $f(x)$  multiplied by the area of the box:



$$y \simeq \frac{N_{\text{below}}}{N} (y_1 - y_0) (x_1 - x_0) . \quad (7.158)$$

We expect this to become a better and better estimate as  $N$  goes to infinity.

We can use this method to estimate the area of a circle and thereby estimate the value of  $\pi$ . The method is as follows: We select  $N$  points on the interval 0 to 1 for both  $x$  and  $y$  and count how many times the points are close to the origin than 1, that is, we count when  $x^2 + y^2 \leq 1$ . (Notice that we compare the square – we do not take the square root since this is computationally inefficient!). The number of point inside is  $N_{\text{below}}$  and the estimate for  $\pi$  is:

$$\frac{1}{4}\pi \simeq \frac{N_{\text{below}}}{N} , \quad (7.159)$$

and therefore

$$\pi \simeq 4 \frac{N_{\text{below}}}{N} . \quad (7.160)$$

This is done in the following program:

```
% Monte Carlo estimate of pi
N = 100000;
N0 = 0;
piest = zeros(N,1);
for i = 1:N
    x = rand(1,1);
    y = rand(1,1);
    r2 = x*x+y*y;
    N0 = N0 + (r2<=1);
    piest(i) = 4*N0/i;
    if (mod(i,1)==0)
        plot((1:i),piest(1:i),'-r',[i i],[pi pi],'o')
        drawnow
    end
end
piest = 4*N0/N
```

### 7.5.2 Metropolis Algorithm

This method is not that efficient. It corresponds to the most direct method for simulating the canonical ensemble. If we simulate an Einstein crystal, we could simulate the model by choosing an oscillator at random and randomly changing the energy by  $\pm 1$ . We will then generate a sequence of microstates, and from this sequence we could estimate for example the average energy by:

$$\bar{U} = \frac{\sum_i \epsilon_i \exp(-\beta \epsilon_i)}{\sum_i \exp(-\beta \epsilon_i)} , \quad (7.161)$$

where  $\epsilon_i$  is the energy of state  $i$  of the Einstein crystal, and the sum is over all the states we have generated – not all possible states.

Unfortunately, this method, just like the integration method above is not very efficient. We may end up with many microstates that are unlikely, and therefore do not contribute much the sum. Instead, we could choose microstates in a way that ensures that we have many states that contributed to the sum – we could choose microstates according to their importance. Such as method is called importance sampling, and one of the simples importance sampling methods is called the *Metropolis Algorithm*.

In the Metropolis Algorithm we generate a sequence of states, but the transition between the states depends on the transition probability from one state to another. This generates a sequence of states which we call a Monte Carlo path.

How do we select the transition probabilities between the states  $\epsilon_i$  of the system?

Since the probability for a state with energy  $\epsilon_i$  is

$$P(\epsilon_i) = \frac{1}{Z} \exp(-\beta \epsilon_i), \quad (7.162)$$

we could use this – but we do not know  $Z$ !

However, we can avoid this problem if we are only interested in the probability for a transition from one state  $\epsilon_i$  to another state with energy  $\epsilon_j$  – for example by changing a single spin at a time in the Ising system or if we move energy from one oscillator to another in the Einstein crystal. In this case, it is only the relative probabilities that matter (this will become clearer when you are introduced to Markov chains in a later course).

The change in energy when we go from state  $i$  to state  $j$  is  $\Delta E$ , and the relative probability for the states are:

$$P(i)/P(j) = \exp(-\beta \Delta E). \quad (7.163)$$

We may interpret this ratio as the transition probability from state  $i$  to state  $j$ , and this is indeed what is done in the first method developed – the Metropolis algorithm. In this case, the transition probability (rate) is chosen to be

$$W = \begin{cases} \exp(-\Delta E/kT), & \Delta E > 0 \\ 1, & \Delta E < 0 \end{cases} \quad (7.164)$$

We can therefore implement the algorithm using the following steps:

1. Choose an initial microstate – for example random spins in the Ising magnet or random energies for each oscillator in the Einstein crystal.
2. Make a random change in the microstate – a trial change. Calculate the change of energy going from the old state to the new state,  $\Delta E$ . For example, for the Ising system we may choose a spin at random and see what happens if we flip it; for the Einstein crystal choose an oscillator at random and change its energy by  $\pm 1$ .
3. Generate a random number,  $r$ , between 0 and 1
4. if  $r \leq \exp(-\Delta E/kT)$  accept the change. (This formulation means that we will always accept a change where  $\Delta E > 0$ .)

### 5. Repeat

This generates a sequence of states that you can now make measurements on.

We can use this method to study the Ising system as well. This is implemented in the following program. It is not that different from the heat bath Monte Carlo method – but there are small differences.

### 7.5.3 Detailed balance

Are there any limits to what kinds of rules we can choose for the transitions? Could we invent any rule we like?

No! The transition rates must satisfy a principle called detailed balance. What is this.

What do we want to model? We want to model a sequence of microstates for the system – like a time development of microstates. Let us write the states as  $|j\rangle$ : The possible states of the system is  $|1\rangle, |2\rangle, |3\rangle$ , etc. If the system is in state  $|i\rangle$  at time  $t$  we can write this as  $|i\rangle(t)$ .

We want to find the next state,  $|j\rangle(t + \Delta t)$ . Then, we need the probability to get to state  $|j\rangle$  for all possible configurations at time  $t$ . And not only that – in general we may consider that case that the probability to be in state  $|j\rangle$  at time  $t + \Delta t$  depends not only on the state the system was in at a time  $t$ , but also all the previous states at earlier time. Hmmm. That was a lot of information. We can simplify the problem if we remove the history dependence – if we assume that the probability to be in a state  $|j\rangle(t + \Delta t)$  only depends on the state  $|i\rangle(t)$  it was in at time  $t$  and not on what happened before that. We can think of this as implying that the state  $|i\rangle(t)$  contains all the relevant information about the system and determines what new states can occur. If the state only depends on the previous state and not on the history we call the sequence of states a Markov chain.

What we need is the probability  $P(j, t + \Delta t)$  to be in state  $|j\rangle$  for each possible state  $|i\rangle$  at  $t$ . And we need this probability for all states  $|j\rangle$  and  $|i\rangle$ . We call the probability to go from state  $|i\rangle$  at  $t$  to state  $|j\rangle$  at  $t + \Delta t$  the transition probability:

$$W_{ij} = W(i \rightarrow j) = P(j(t + \Delta t) | i(t)) , \quad (7.165)$$

where the symbol  $|$  means “given than” – it is a conditional probability.

We know that  $W_{ij} \geq 0$  and that  $\sum_j W_{ij} = 1$ : Starting from state  $|i\rangle$  at time  $t$  we know that it must end up in some state  $|j\rangle$  at time  $t + \Delta t$ .

The probability  $P(j, t + \Delta t)$  is therefore:

$$P(j, t + \Delta t) = \sum_i P(j, t + \Delta t | i, t) = \sum_i W_{ij} P(i, t) . \quad (7.166)$$

What determines how this system develops? The master equation – a cool name – which is given as

$$\frac{dP(j,t)}{dt} = -\sum_i W_{ji}P(j,t) + \sum_i W_{ij}P(i,t) . \quad (7.167)$$

(Not finished)