

Chapter 9

Chemical potential and Gibbs Distribution

9.1 Chemical potential

We have now developed the microscopic understanding and the thermodynamics for systems that are closed to all transport: isolated systems with E , V , and N , and for systems that are only open to thermal transport, systems with T , V , and N constant. We started with an isolated, closed system, and then opened the possibility for energy transport.

For the microcanonical system, we found that the link between the microscopic and the macroscopic follows from $S = k \ln \Omega(E, V, N)$ and we found that the multiplicity, and hence entropy, of such a system must increase and equilibrium is obtained when the multiplicity, and hence entropy, is at its maximum.

For the canonical system, we found that the microscopic description is given by the Boltzmann factors and the partition function, $Z = Z(T, V, N)$, and that the macroscopic state is found through $F = -kT \ln Z$. The thermodynamic principle that determines the behavior of this system is that the system develops towards a minimum in Helmholtz free energy, F , and that the equilibrium is characterized by a minimum in F .

There are, however, many systems of interest that are open to particle transport. For example, how can we determine the equilibrium state of an ideal gas in the atmosphere – where the particles are free to flow; the equilibrium state of electrons in a voltage field; or the equilibrium state of a gas-water mixture? If we pour water into an empty container of a given volume and keep the temperature constant, how much of the water will be water, how much will be ice and how much will be vapor? And what principle determines this equilibrium? Similar questions could be asked about chemical reaction, such as the reaction between hydrogen and oxygen to form water – what are the equilibrium concentrations of each component? To answer such questions, we need to extend our microscopic and thermodynamic framework to also address systems that are open to transport. We call such systems diffusional open or open to diffusion.

We would need a principle similar to what we have seen previously. We have seen that:

- If two systems have the same temperature there is no net energy flow between them.
- If two systems have the same pressure, there is no net change of volumes
- If two systems have the same X , there is no net flow of particles

We need to identify this X . Let us do this by expanding gradually from systems we already know how to treat. Let us start with a system S that is in thermal contact with a large reservoir with temperature T , but otherwise of constant particle number and constant volume: This system is described by the canonical ensemble. We take this system and divide it into two parts A and B that are in diffusional contact. For example, if the system is a gas, we simply divide the container into two parts and call one part A and the other part B . Particles will then be allowed to pass from A to B and the other way. This is similar to the molecular dynamics model for the ideal gas where half the system was empty. (Similar, but not identical, since our molecular dynamics model was for constant energy and not constant temperature!). We can characterize this system by N the total number of particles in the system, where $N_A + N_B = N$ is constant, but N_A and N_B may vary.

This system is a canonical system, and we know that it will develop towards minimum Helmholtz free energy and that the equilibrium is characterized by a minimum of the Helmholtz free energy. What is the Helmholtz free energy for this system? It is the sum of the energy for the components: $F = F_A + F_B$. What happens if we look at a small change in this system – a small transfer dN_A of particles from A to B ? In this case, there is no change in the temperature or volume of systems A and B , only in the number of particles, and the change in Helmholtz free energy is

$$dF = dF_A + dF_B = \left(\frac{\partial F_A}{\partial N_A} \right)_{V,T} dN_A + \left(\frac{\partial F_B}{\partial N_B} \right)_{V,T} dN_B. \quad (9.1)$$

Since $N = N_A + N_B$ is constant, we know that $dN_A = -dN_B$:

$$\begin{aligned} dF &= \left(\frac{\partial F_A}{\partial N_A} \right)_{V,T} dN_A - \left(\frac{\partial F_B}{\partial N_B} \right)_{V,T} dN_A \\ &= \left(\left(\frac{\partial F_A}{\partial N_A} \right)_{V,T} - \left(\frac{\partial F_B}{\partial N_B} \right)_{V,T} \right) dN_A. \end{aligned} \quad (9.2)$$

In equilibrium, F is minimal, and this change must be zero. Therefore we find that in equilibrium

$$\left(\frac{\partial F_A}{\partial N_A} \right)_{V,T} = \left(\frac{\partial F_B}{\partial N_B} \right)_{V,T}. \quad (9.3)$$

This looks very similar to what we found for the canonical system – this is the quantity related to particle transport which must be the same for the two systems to be in **diffusive equilibrium**. This is the X we were talking about.

We call this quantity the chemical potential. Indeed, we will use this as the definition of the chemical potential:

$$\mu(T, V, N) = \left(\frac{\partial F}{\partial N} \right)_{V, T}, \quad (9.4)$$

and the condition for diffusive equilibrium between the two systems A and B (that are in thermal equilibrium) is then

$$\mu_A = \mu_B. \quad (9.5)$$

It may seem strange to define a derivative in N , which is essentially a discrete quantity – the number of particles. We could therefore instead have used the definition

$$\mu = F(N+1, V, T) - F(N, V, T), \quad (9.6)$$

which is the same for large N . This definition also emphasizes that the chemical potential is related to the change in Helmholtz free energy when we add one particle to the system, keeping the temperature and volume constant.

We can also use the minimization of Helmholtz free energy to determine the direction of transport in the system. The change in Helmholtz free energy is

$$\begin{aligned} dF &= \left(\frac{\partial F_A}{\partial N_A} \right)_{V, T} dN_A - \left(\frac{\partial F_B}{\partial N_B} \right)_{V, T} dN_A \\ &= \mu_A dN_A - \mu_B dN_A = (\mu_A - \mu_B) dN_A. \end{aligned} \quad (9.7)$$

If the system is out of diffusive equilibrium, we know that the change in N_A will result in a lower value of F as the system approaches equilibrium, hence $dF \leq 0$. We therefore see that if $\mu_A > \mu_B$ then $dN_A < 0$ for dF to be negative, hence the flux is from A to B when μ_A is larger than μ_B : **The flux is from large to small chemical potential.** Indeed, this makes intuitive sense since taking a particle from a system with large chemical potential and transferring it to a system with lower chemical potential will reduce the total Helmholtz free energy and therefore move the system towards equilibrium.

Thermodynamic identity for diffusive systems. We can now extend the thermodynamic identity to also include changes in N . We already found that $dF = -SdT - pdV + XdN$ for Helmholtz free energy. Previously we did not have a good intuition for X , but now we have defined this X as the chemical potential. The potential for Helmholtz free energy is therefore

$$dF = -SdT - pdV + \mu dN, \quad (9.8)$$

and we can use this to find the thermodynamic identity

$$TdS = dE + pdV - \mu dN. \quad (9.9)$$

Chemical potential for multi-particle systems. If several chemical species are present, then each species will have its own chemical potential

$$\mu_j(T, V, N) = \left(\frac{\partial F}{\partial N_j} \right)_{T, V, N_k}, \quad (9.10)$$

where all the other $N_k, k \neq j$, are kept constant in the derivative.

9.1.1 Example: Chemical potential of the Einstein crystal

We found the Helmholtz free energy for the Einstein crystal to be

$$Z = \left(\frac{1}{1 - \exp(-\beta \epsilon)} \right)^N, \quad (9.11)$$

and

$$F = -kT \ln Z = NkT \ln(1 - \exp(-\beta \epsilon)), \quad (9.12)$$

which gives

$$\mu = \left(\frac{\partial F}{\partial N} \right) = kT \ln(1 - \exp(-\beta \epsilon)). \quad (9.13)$$

9.1.2 Example: Chemical potential for Ideal gas

For an ideal gas, the partition function can be written as:

$$Z = \frac{1}{N!} (Z_1 Z_{\text{vib}} Z_{\text{rot}})^N, \quad (9.14)$$

where $Z_1 = n_Q V$ and

$$n_Q = \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2}. \quad (9.15)$$

Helmholtz free energy is therefore:

$$F = -kT \ln Z = -kT (N \ln Z_1 - \ln N!). \quad (9.16)$$

We use Stirling's approximation $\ln N! \simeq N \ln N - N$, getting:

$$\frac{d}{dN} \ln N! = \frac{d}{dN} (N \ln N - N) = \ln N + 1 - 1 = \ln N, \quad (9.17)$$

which gives

$$\begin{aligned}
 F &= -kT \left(\ln Z_1 - \frac{d}{dN} \ln N! \right) = -kT (\ln Z_1 - \ln N) \\
 &= kT \ln(N/Z_1) .
 \end{aligned}
 \tag{9.18}$$

We insert $Z_1 = n_Q V$, getting:

$$\mu = kT \ln(N/Vn_Q) = kT \ln(n/n_Q) . \tag{9.19}$$

(We could also have found this by using $\mu = F(N) - F(N-1)$, and we would then not have had to use Stirling's approximation. The result would have been the same).

We see that the chemical potential increase with the density n of particles: Particles flow from systems with high n to systems with low n .

For classical concentrations - that is when $n/n_Q \ll 1$, the chemical potential of an ideal gas is always negative.

9.1.3 Potential energy and the chemical potential

We can better understand the chemical potential by looking at a system with a difference (or a gradient) in potential energy. The simplest example is a potential step.

Let us look at two systems A and B at the same temperature that may exchange particles, but the two systems are not yet in diffusive equilibrium. We assume that we start from $\mu_B > \mu_A$ so that particles will flow from B to A. The difference in chemical potential is $\Delta\mu = \mu_B - \mu_A$.

Let us now introduce a difference in potential energy between the two systems. For example, if the particles have masses, we may lift system A up in the gravitational field compared with system B. Let us see how high we would need to lift it to stop particles from flowing from system B to system A? (We assume that systems are connected somehow, for example by a tube). What happens when we lift the system? It corresponds to adding an external, extra potential energy to all particles in system A. The increase in energy is $mg\Delta z$ or simply $u = mg\Delta z$, where u is the change in potential energy per particle in system A. The change in the energy of system A is then simply

$$E_{A,1} = E_{A,0} + N_A u , \tag{9.20}$$

where $E_{A,1}$ is the energy after lifting the system, and $E_{A,0}$ is the energy before lifting the system. Lifting the system only corresponds to adding a constant energy u to all the energy levels of system A – there is no other change in the distribution of energy levels. This simply introduces a multiplicative constant in the partition constant and a constant in the Helmholtz free energy. Put another way: changing the energy levels by adding a constant does not change the entropy of the system – only the energy, E . Therefore, the Helmholtz free energy of system A after adding the potential is

$$F_{A,1} = F_{A,0} + N_A u , \tag{9.21}$$

and the new chemical potential is

$$\mu_{A,1} = \left(\frac{\partial F_{A,1}}{\partial N_A} \right)_{V,T} = \left(\frac{\partial F_{A,0}}{\partial N_A} \right)_{V,T} + u = \mu_{A,0} + u . \quad (9.22)$$

The effect of adding a potential energy to system A – such as by lifting it in a gravitational field – is to increase the chemical potential by the potential energy per particle, u .

We can therefore stop the flux of particles from system B to system A by increasing the potential energy per particle in system A by $u = \Delta\mu$ so that

$$\mu_{A,1} = \mu_{A,0} + u = \mu_B , \quad (9.23)$$

This can be done by adding a gravitational field, but for charged particles, it could also be done by adding an electrical field with a potential energy u per particle.

This means that:

The difference in chemical potential between two systems A and B corresponds to the potential energy difference needed in order to establish diffusional equilibrium.

We could use this to measure the chemical potential: We apply a potential difference and determine at what potential difference net particle flow stops.

It is useful to discern between the internal and the external chemical potential. The **external chemical potential** is the potential energy per particle in an external field, and the **internal chemical potential** energy is the chemical potential that would be present without the external field.

9.1.4 Example: Barometric pressure formula

Let us assume that the atmosphere in the Earth is at the same temperature T . The potential energy of a gas particle would be mgz , where we may place the zero in potential energy at the Earth's surface. The chemical potential of a particle in a gas in a gravitational field would therefore have two contributions:

$$\mu = \mu_{\text{gas}} + \mu_{\text{grav}} = kT \ln(n/n_Q) + mgz . \quad (9.24)$$

In equilibrium there should be no differences in chemical potential, hence

$$kT \ln(n(z)/n_Q) + mgz = kT \ln(n(0)/n_Q) , \quad (9.25)$$

which gives

$$n(z) = n(0) \exp(-mgz/kT) . \quad (9.26)$$

What does that mean for the pressure of an ideal gas? If the temperature does not depend on height, the pressure is

$$pV = NkT \Rightarrow p = \frac{N}{V}kT = nkT , \quad (9.27)$$

and

$$p(z) = p(0) \exp(-mgz/kT) = p(0) \exp(-z/z_c) , \quad (9.28)$$

where $z_c = kT/mg$ is a characteristic height.

This depends on the mass of the gas molecules! For N_2 the mass of a molecule is 28 which gives $z_c = 8.5\text{km}$. Lighter molecules will extend further up - and will mostly have escaped from the atmosphere. Notice that T is not really constant, and $n(z)$ is generally more complicated. And also notice that various gases have different m , and will therefore have different values of z_c - which means that the composition of the air will change with distance z as well.

9.1.5 Example: Batteries

(Not yet done)

9.1.6 Potential energy and F

We can also directly see how a potential energy enters the various expressions.

Assume that we have a system with energy states ϵ_i . Let us assume that we add a potential energy E_0 to the system, so that the new levels are $\epsilon_i + E_0$.

What are the consequences for Helmholtz free energy and the chemical potential?

The partition function is

$$\begin{aligned} Z' &= \sum_i \exp(-\epsilon_i/kT - E_0/kT) \\ &= \exp(-E_0/kT) \sum_i \exp(-\epsilon_i/kT) \\ &= \exp(-E_0/kT) Z , \end{aligned} \quad (9.29)$$

Helmholtz free energy is therefore

$$F' = -kT \ln Z' = E_0 - kT \ln Z = E_0 + F , \quad (9.30)$$

which corresponds to a change in Helmholtz free energy.

If this is the energy for each particle, we expect that the energy for N particles (or that $Z_N = Z'^N$), is

$$F = -NkT \ln Z + NE_0 , \quad (9.31)$$

and that the chemical potential therefore is

$$\mu' = \left(\frac{\partial F'}{\partial N} \right)_{V,T} = E_0 + \mu . \quad (9.32)$$

Adding a potential energy per particle therefore corresponds to adding a potential to the chemical potential. We call such an addition an external chemical potential if it is due to an external field, as compared to the internal chemical potential which is due to the statistical physics of the system without the external potential.

9.1.7 Example: Modeling potential gradients

Fig. 9.1 shows a system with a gradient in the chemical potential. The system stretches from $x = 0$ to $x = L$, and within the system the chemical potential is $\mu(x)$. Is this system in equilibrium? What potential energy must you add in order to make the system be in equilibrium?

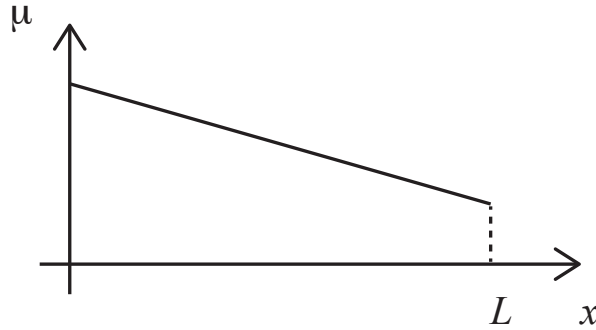


Fig. 9.1 Plot of the chemical potential $\mu(x)$ as a function of x in a system.

Clearly, the system is not in equilibrium. Because if it were in equilibrium the chemical potential would be the same everywhere. Since the chemical potential is not the same, there will be a flow of particles from regions with high chemical potential to regions with small chemical potential. We can make this argument more quantitative. Let us assume that the whole system is at a constant temperature T , that diffusion is possible inside the system, but not across the boundaries at $x = 0$ and $x = L$. This system has T , V , and N constant, and its equilibrium is determined from the minimum of Helmholtz free energy. We can find Helmholtz free energy of the whole system by dividing the system into small parts from x to $x + \Delta x$, where Helmholtz free energy of this small part is $F(x)$. If each part is independent – that is, if the energy levels in each part are independent – then each part will have its

separate sum over states in the partition function and Helmholtz free energy will be the sum of the free energies for each part. The total free energy is then

$$F_{tot} = \sum_x F(x) . \quad (9.33)$$

We can use this to discuss how the chemical potential must develop as the system approaches equilibrium. If the chemical potential is not constant, as sketched in the figure, we can reduce the total Helmholtz free energy by moving a particle from a position with high chemical potential to a position with low chemical potential. When we remove a particle from a point, the decrease in F is the chemical potential at that point, and, similarly, when we add the same particle to another point, the increase in F is the chemical potential. If we remove a particle from a region with high chemical potential and place it in a region with low chemical potential, we therefore remove more from Helmholtz free energy than we put back, hence the free energy is reduced. This process will continue until the chemical potential is equal everywhere.

Another alternative to obtain equilibrium is to add an external potential, so that the total chemical potential is constant. For example, we can add the external potential $u(x)$ given as $u(x) = u_0 - \mu_0(x)$, where u_0 is a constant and $\mu_0(x)$ is the initial chemical potential. The total chemical potential is then:

$$\mu(x) = \mu_0(x) + u(x) = \mu_0(x) + u_0 - \mu_0(x) = u_0 , \quad (9.34)$$

which is a constant. In practice, we may not add any potential, but only simple potentials such as a linear potential in the case of an electrical potential difference for charged particles or a gravitational field for particles with non-negligible masses.

Clicker question on $\mu(x)$ as introduction.

9.1.8 Thermodynamic relations for chemical potential

Here, we have defined the chemical potential as

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V,T} . \quad (9.35)$$

How does this relate the the thermodynamic identity and to the relations we introduced, but did not pursue, for the microcanonical ensemble?

From the microcanonical ensemble we introduce the entropy, $S(U, V, N)$, and we argued that

$$\begin{aligned}
dS &= \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV + \left(\frac{\partial S}{\partial N} \right)_{U,N} dN \\
&= \frac{1}{T} dU - \frac{p}{T} dV + \left(\frac{\partial S}{\partial N} \right)_{U,N} dN .
\end{aligned} \tag{9.36}$$

We can rewrite this to get:

$$TdS = dU - pdV + T \left(\frac{\partial S}{\partial N} \right)_{U,N} dN . \tag{9.37}$$

In addition, we know that $F = U - TS$ so that $dF = dU - TdS - SdT$, which is therefore

$$\begin{aligned}
dF &= dU - TdS - SdT = dU - (dU - pdV + T \left(\frac{\partial S}{\partial N} \right)_{U,N} dN) - SdT \\
&= -SdT - pdV - T \left(\frac{\partial S}{\partial N} \right)_{U,N} dN
\end{aligned} \tag{9.38}$$

which means that

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = -T \left(\frac{\partial S}{\partial N} \right)_{U,N} . \tag{9.39}$$

We have therefore related the two expressions for the chemical potential, and found that what we earlier called the chemical potential indeed corresponds to what we now call the chemical potential - and what we now are starting to build an intuition for. Good! We are on the right way.

We can therefore also write the thermodynamic identity as

$$TdS = dU - pdV + \mu dN . \tag{9.40}$$

Where we now have an intuition for the chemical potential.

9.2 Gibbs factor and Gibbs sum

Now - let us see how we can treat systems where the number of particles may change from a microscopic point of view.

For a system in thermal equilibrium with a large heat bath, we found that the probability for the system to be in state $|i\rangle$ could be expressed as

$$P(i) = \frac{\exp(-\epsilon_i/kT)}{Z} , \tag{9.41}$$

where the partition function Z is a normalization constant.

How can we generalize this to a system S in contact with a reservoir R - but where the contact allows both exchange of energy and exchange of particles?

Let us look at a composite system which consists of the system S and a reservoir R. The system S and reservoir R can exchange energy and particles, but the total composite system (S+R) is thermally isolated (it has constant energy) and has constant number of particles:

$$U_0 = U_S + U_R, \quad N_0 = N_S + N_R, \quad (9.42)$$

are both constant. Let us now look at a particular case where system S is in a state 1 with energy U_1 and number of particles N_1 . What is the probability for this state?

Since S is in state 1, the multiplicity of S is 1. The multiplicity g of the whole system (R+S) is therefore the multiplicity of R, which depends on U_1 and N_1 , and the probability for the system S to be in state 1 characterized by U_1 and N_1 is therefore

$$P(N_1, U_1) = \frac{g(N_0 - N_1, U_0 - U_1)}{\sum g(N_0 - N_1, U_0 - U_1)}. \quad (9.43)$$

Let us now look at $\ln P$:

$$\begin{aligned} \ln P(N_1, U_1) &= \ln C + \ln g(N_0 - N_1, U_0 - U_1) \\ &= \ln C + S(N_0 - N_1, U_0 - U_1)/k, \end{aligned} \quad (9.44)$$

where we can now expand S around N_0, U_0 to first order, getting:

$$S(N_0 - N_1, U_0 - U_1) = S(N_0, U_0) - N_1 \left(\frac{\partial S}{\partial N} \right)_{U_0} - U_1 \left(\frac{\partial S}{\partial U} \right)_{N_0}, \quad (9.45)$$

where we now recognize the two partial derivatives of S as $1/T$ and $-\mu/T$, giving:

$$S(N_0 - N_1, U_0 - U_1) = S(N_0, U_0) + \frac{N_1 \mu}{T} - \frac{U_1}{T}, \quad (9.46)$$

and therefore we find:

$$P(N_1, U_1) = C' \exp((N_1 \mu - U_1)/kT), \quad (9.47)$$

and where normalization now gives:

$$P(N_1, U_1) = \frac{1}{Z_G} \exp((N_1 \mu - U_1)/kT), \quad (9.48)$$

and

$$Z_G = \sum_N \sum_{s(N)} \exp((N \mu - \epsilon_{s(N)})/kT). \quad (9.49)$$

This sum is called Gibbs sum or the grand sum or the grand partition function. Notice that the sum is over all the states of the system for each particle number N , starting from $N = 0$.

Again, we find averages by sums of the probabilities:

$$\langle X \rangle = \sum_N \sum_{s(N)} X(N, s) P(N, s), \quad (9.50)$$

Notice that both the energy and the number of particles now are fluctuating quantities!

9.2.1 Average number of particles

The average number of particles is given as

$$\langle N \rangle = \frac{1}{Z_G} \sum_N \sum_{s(N)} N \exp((N\mu - \epsilon_s)/kT). \quad (9.51)$$

we can again use the “derivative trick” we used earlier, but now take the derivative with respect to μ :

$$N \exp((N\mu - \epsilon_s)/kT) = kT \frac{d}{d\mu} \exp((N\mu - \epsilon_s)/kT), \quad (9.52)$$

and therefore

$$\langle N \rangle = kT \frac{1}{Z_G} \frac{d}{d\mu} Z_G = kT \frac{\partial \ln Z_G}{\partial \mu}. \quad (9.53)$$

9.2.2 Example: CO poisoning

Each hemoglobin molecule has four, independent adsorption sites, each consisting of a Fe^{2+} ion, and each site can couple to one O_2 molecule. The system therefore has two possible states, occupied by oxygen and not occupied by oxygen, with energies 0 (unoccupied) and ϵ (occupied), where $\epsilon = -0.7\text{eV}$.

In this case, we analyze the system using the grand partition function.

$$Z_G = 1 + \exp(-(\epsilon - \mu)/kT), \quad (9.54)$$

What is μ in this case? Near the lungs, we assume the blood is in diffusive equilibrium with the air in the lungs, and we can therefore use the chemical potential for an ideal gas:

$$\mu = -kT \ln(n_Q/n) \simeq -0.6\text{eV}, \quad (9.55)$$

when $T = 310\text{K}$, which is the temperature in your body. This gives

$$\exp(-(\epsilon - \mu)/kT) \simeq \exp(0.1\text{eV}/kT) \simeq 40, \quad (9.56)$$

which means that the probability to be occupied is

$$P = \frac{40}{1+40} \simeq 0.98 . \quad (9.57)$$

Now, what happens if CO is also present, which also can be adsorbed. Now, there are three possible states: unoccupied, occupied by O₂ or occupied by CO. The grand partition function is now

$$Z_G = 1 + \exp(-(\epsilon_O - \mu_O)/kT) + \exp(-(\epsilon_{CO} - \mu_{CO})/kT) . \quad (9.58)$$

Now we need numbers. CO is more strongly bound, so $\epsilon_{CO} = -0.85\text{eV}$. But what is the chemical potential? We could still use the expression for the ideal gas, but with the concentration n of CO in air. If CO is x times less abundant than oxygen, we would find that

$$\begin{aligned} \mu_{CO} &= -kT \ln(n_Q/n_{CO}) \\ &= -kT \ln(n_Q/xn_O) \\ &= -kT \ln(n_Q/n_O) + kT \ln x , \end{aligned} \quad (9.59)$$

where $kT \ln 100 = 0.12\text{eV}$, so that $\mu_{CO} = 0.72\text{eV}$. This gives for the new Gibbs factor:

$$\exp(-(\epsilon_{CO} - \mu_{CO})/kT) = 120 , \quad (9.60)$$

and therefore

$$P(O) = \frac{40}{1+40+120} = 0.25 . \quad (9.61)$$

So just a small amount of CO is devastating!

9.2.3 Diffusive equilibrium in the Einstein crystal

9.3 Gibbs Free Energy

9.3.1 Equilibrium between an ideal gas and an ideal crystal

We started out by saying that we wanted to study diffusive equilibrium because we were interested in processes such as the equilibrium between different phases of a material and chemical reactions that transform one material to another. Now, we have introduced the concept of chemical potential. Let us see how we can use this concept to address the equilibrium between phases of a material.

The basic phases of matter are solid, liquid and gas (and plasma). A phase equilibrium is an equilibrium between two or several phases of a material. If I hold a cup of water in the lecture room, and place a lid on the cup, I have a system with water molecules in a given volume, at a given temperature (the temperature in the room is the temperature of the heat reservoir), and a given number of molecules – particles

– of water. Inside the cup, there will be a given number of water molecules. What determines how much of the water is a solid, how much is a liquid and how much is a gas. If the cup contained water at room temperature, we expect the closed cup to contain some water and some water vapor. How can we determine the amount of particles in each phase and how can we determine the state of the phases, such as the pressure in the vapor?

To address this situation, we will discuss phase equilibrium in a simplified model in which we can understand all the processes in detail. We will address equilibrium between a solid – a crystal of a given particles type – and a gas of the same particle. Such as an equilibrium between ice and water vapor at sub-zero temperatures. We will model this system – a cup with water molecules – as a system with a given temperature, T , volume, V , and number of particles, N . The system consists of two subsystems: a gas system (subindex g) of N_g gas particles in the gas phase; and a solid system (subindex s) of N_s solid particles. The gas will be modelled as an ideal gas and the solid as an Einstein crystal. The system is illustrated in fig. 9.2.

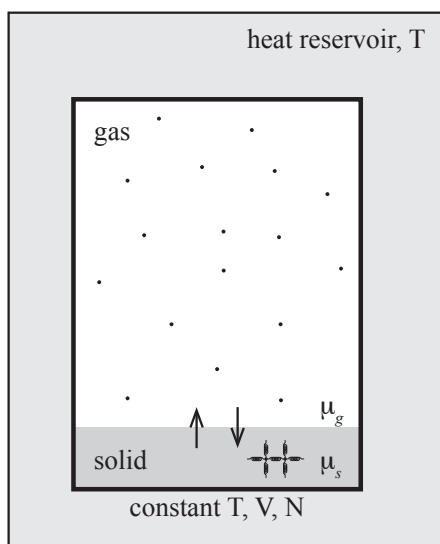


Fig. 9.2 Illustration of a system with phase equilibrium between a solid and a gas phase of the same particles.

Our plan is to find the chemical potential for each of the two subsystems. In equilibrium, the chemical potentials must be equal, otherwise there would be a flow of particles from the part of the system with high chemical potential towards the part with a low chemical potential. (You can see that such a change would make the total Helmholtz free energy of the system smaller: If you remove a particle from a region with high chemical potential and place it in a region with low chemical potential, Helmholtz free energy would be reduced more from removing the particles than from adding it, and hence F would decrease, and the system would move closer to

equilibrium.) We can calculate the chemical potentials from Helmholtz free energy, which in turn can be found from the partition functions for each of the two systems.

We have found previously that Helmholtz free energy for a gas in a volume V_g is

$$F_g = -N_g kT \left(\ln \frac{n_Q}{n_g} + 1 \right), \quad n_Q(T) = \left(\frac{2\pi m kT}{h^2} \right)^{3/2}, \quad (9.62)$$

where $n_g = N_g/V_g$ is the density of the gas. Similarly, the Helmholtz free energy for the Einstein crystal is

$$F_c = N_{osc} kT \ln(1 - \exp(-\Delta\epsilon/kT)). \quad (9.63)$$

If we are to compare these two energies, we need to ensure that we have the same reference level for energies. For a particle in a gas, we have assumed that the particle has zero energy when at rest. Similarly, for the crystal, we have assumed that the lowest energy level is at zero energy. However, we know that the particles in a crystal are bound to the crystal, and that we need to add an energy to such a particle to pull the particle from the crystal and make it part of the gas. This energy added corresponds to the binding energy, ϵ_0 , of a particle in the crystal. This means that a particle in the lowest energy level in the crystal has an energy $-\epsilon_0$ compared with an energy at rest in the gas, we must therefore add a term $-N_c \epsilon_0$ to Helmholtz free energy for the crystal:

$$F_c = N_{osc} kT \ln(1 - \exp(-\Delta\epsilon/kT)) - N_c \epsilon_0. \quad (9.64)$$

Also notice that we have written N_{osc} in the expression for F_c . This is because the energy is for a given number of *oscillators* and not a given number of *particles*. For a three-dimensional system, each particle can oscillate in three different, independent directions (x , y , and z), and the number of oscillators is therefore $N_{osc} = 3N_c$, where N_c is the number of particles in the solid. Helmholtz free energy is therefore:

$$F_c = 3N_c kT \ln(1 - \exp(-\Delta\epsilon/kT)) - N_c \epsilon_0. \quad (9.65)$$

Finally, we will assume that temperatures are high compared with $\Delta\epsilon$, we can therefore approximate F_c with its high temperature limit, which corresponds to the limit of the equipartition principle with $1/2kT$ per degree of freedom, and 2 degrees of freedom per oscillator, and 6 degrees of freedom per particle:

$$F_c \simeq 3N_c kT - N_c \epsilon_0. \quad (9.66)$$

The chemical potentials can now be found from F :

$$\mu_g(V_g, T, N_g) = \left(\frac{\partial F_g}{\partial N_g} \right)_{V_g, T} = kT \ln \frac{n_g}{n_Q(T)}, \quad (9.67)$$

and

$$\mu_c(V_c, T, N_c) = \left(\frac{\partial F_c}{\partial N_c} \right)_{V_c, T} = 3kT - \epsilon_0 . \quad (9.68)$$

In equilibrium we assume that the two chemical potentials are the same. We also assume that the volume of the gas is almost the same as the volume of the whole system, $V_g \simeq V$, that is, that the volume of the crystal is negligible. (We will return with an improved model without this assumption further down.). In equilibrium we therefore have:

$$\mu_g(V, T, N_g) = kT \ln \frac{n_g}{n_Q(T)} = \mu_c(V, T, N_c) = 3kT - \epsilon_0 . \quad (9.69)$$

This allows us to find $n_g = N_g/V$ in equilibrium for the gas. This is not a very practical way to characterize the state of the gas. Instead, we use the ideal gas law to characterize the gas with its pressure, p :

$$pV_g = N_g kT \Rightarrow n_g = \frac{N_g}{V} = \frac{p}{kT} , \quad (9.70)$$

which gives

$$kT \ln \frac{p}{kT n_Q(T)} = 3kT - \epsilon_0 , \quad (9.71)$$

which we solve for p :

$$\frac{p}{kT n_Q(T)} = e^{3-\epsilon_0/kT} , \quad (9.72)$$

$$p(T) = kT n_Q(T) e^{3-\epsilon_0/kT} . \quad (9.73)$$

This result tells us that inside the closed cup, there will be both a solid and a gas, and the pressure of the gas will be given by $p(T)$. We call this the vapor pressure of the system and the curve $p(T)$ is called the coexistence curve. We have illustrated $p(T)$ in fig. 9.3. What does this curve tell us? In this form, it only describes the state inside the closed system. Let us see if we can use the model and the chemical potentials to understand what would happen if we instead of doing the experiment at constant volume, did the experiment at constant pressure: Instead of doing the experiment with a closed cup, we do the experiment inside a piston, where the outside of the piston has a pressure corresponding to the pressure in the lecture room. What would happen if we start the system on the $p(T)$ curve described by the model, and then increase the pressure? In the model, it is only the chemical potential of the gas that depends on the pressure. And the chemical potential of the gas will increase if we increase the pressure and decrease if we decrease the pressure. At $p(T)$ the chemical potential in the gas and the solid is the same. If we increase the pressure from this state, the chemical potential in the gas will increase while the chemical potential in the solid remains constant (this is in our model, not necessarily in the actual, physical system). As a result particles will diffuse from the gas and into the solid – until all the particles are in the solid. This means that the region above the $p(T)$ curve in the $p-T$ diagram corresponds to a region where the whole system is a solid. If we decrease the pressure, the chemical potential in the gas will decrease

while the chemical potential in the solid will remain constant, hence all the particles will diffuse to the gas. The region below $p(T)$ in the $p - T$ diagram hence corresponds to a gas. The phase coexistence curve is therefore the border between the solid and the gas phases!

Now, there are a few problems with this argument. Primarily, the problem is that we have described the system in terms of T , V , and N , but the system we have sketched with the piston is not a system with constant V , but rather a system with constant p . We therefore need to introduce methods to address systems with constant T , p , N – including methods to find the equilibrium states in such systems. We will therefore introduce the T, p, N ensemble and the corresponding free energy – Gibbs free energy – before we return to the model system to complete the discussion of the phase coexistence curve.

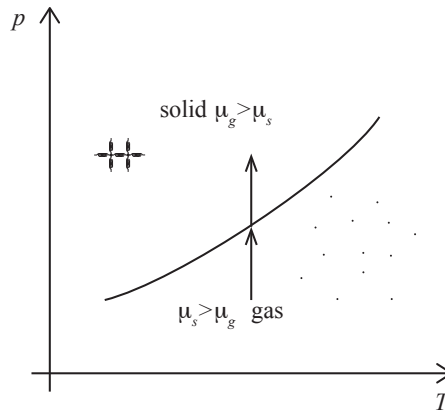


Fig. 9.3 Plot of the phase coexistence curve $p(T)$ for the ideal gas - ideal crystal model system.

9.3.2 Gibbs Free Energy

We need to develop a theory to address systems where T, p, N are constant – corresponding to a system in a piston in a large reservoir with a given temperature and pressure. This corresponds to many laboratory situations or many natural situations where systems are in a surrounding gas or liquid and therefore in equilibrium with an external pressure. How can we develop such a theory?

We have already found that for the micro-canonical system, we characterize the energy by E , the internal energy, and the development of the system toward equilibrium is determined by the second law of thermodynamics, $\Delta S \geq 0$. Based on this we developed Helmholtz free energy through a Legendre transformation: We exchanged the variable S with the conjugate variable T (conjugate because $(\partial E / \partial S)_{V, N} = T$). This was done by introducing

$$F = E - \left(\frac{\partial E}{\partial S} \right)_{V,N} = E - TS . \quad (9.74)$$

Now, we want to introduce a new free energy with the natural variables T , p , N . We know that F has the variables T , V , and N and the differential

$$dF = -SdT - pdV + \mu dN . \quad (9.75)$$

We would now like to replace pdV by some term which depends on dp . We see that we can do this by adding pV to F , because the new differential of $d(F + pV)$ will then not contain pdV , but instead a term Vdp . If we introduce $G = F + pV$ then

$$\begin{aligned} dG &= d(F + pV) \\ &= dF + pdV + Vdp \\ &= -SdT - pdV + \mu dN + pdV + Vdp \\ &= -SdT + Vdp + \mu dN . \end{aligned} \quad (9.76)$$

We see that G has T , p , and N as natural variables.

We could also have found this by applying the Legendre transform. We could define G by replacing V by p in $F(T, V, N)$:

$$G = F - V \left(\frac{\partial F}{\partial V} \right)_{T,N} = F - V(-p) = F + pV , \quad (9.77)$$

which is the same as we found above.

Minimum Free Energy principle. We can also demonstrate a minimization principle for Gibbs free energy. We address a closed, isolated system – a microcanonical system – that contains a small system which is in thermal and mechanical (pressure) equilibrium with a large bath. For the whole system we know that the entropy must increase:

$$\Delta S = \Delta S(bath) + \Delta S(system) \geq 0 , \quad (9.78)$$

The change in internal energy in the bath is related to the heat and work done on the bath:

$$\begin{aligned} \Delta E(bath) &= \Delta Q(bath) + \Delta W(bath) \\ &= T_0 \Delta S(bath) - p_0 \Delta V(bath) . \end{aligned} \quad (9.79)$$

Since the total system is closed, we know that

$$\Delta E(bath) = -\Delta E(system) = -\Delta E , \quad (9.80)$$

$$\Delta V(bath) = -\Delta V(system) = -\Delta V . \quad (9.81)$$

This gives us that

$$\begin{aligned}
T_0 \Delta S(bath) &= \Delta E(bath) + p_0 \Delta V(bath) \\
&= -\Delta E(system) - p_0 \Delta V(system) \\
&= -\Delta E - p_0 \Delta V .
\end{aligned} \tag{9.82}$$

We insert this into eq. 9.78, getting

$$T_0 \Delta S(system) - \Delta E - p_0 \Delta V \geq 0 , \tag{9.83}$$

or

$$\Delta (E - T_0 S + p_0 V) \leq 0 . \tag{9.84}$$

This demonstrates that Gibbs free energy always decreases and is minimum in equilibrium. This principle will turn out to be a very powerful theoretical and practical tool as we will see below.

Gibbs free energy and the chemical potential. Gibbs free energy is an extensive quantity, so that Gibbs free energy for a system of N particles is

$$G(T, p, N) = N g(T, p) , \tag{9.85}$$

where $g(T, p)$ is the Gibbs free energy per particle (or we could with a slightly different definition define it to be Gibbs free energy per mole).

Notice that since T and p are intensive, this means that

$$g(T, p) = \frac{G(T, p, N)}{N} = \left(\frac{\partial G}{\partial N} \right)_{T, p} = \mu(T, p) . \tag{9.86}$$

Notice that this is true for G , but it is not true for F !

9.3.3 Phase coexistence in a T, p, N system

We have now developed the basic tools needed to discuss the behavior of a system at constant T , p , and N . This corresponds to the case where we have a system of a given number of particles inside a box, but where the volume of the box is varying while the pressure outside (and inside) the box is constant. This is what we would call a piston. Now, we can ask the same question as we did above for the T, V , and N system – what is the state of the system inside the piston for a given set of T , p , and N values?

We can use the same approach as we did before. In our simplified model the system consists of N particles, of which N_g are in a gas phase and N_c are in a crystal phase. The state of the system is determined by the minimum of the total Gibbs free energy of the entire system, consisting of both gas and crystal particles. The equilibrium of this system can be found either as a minimum of the Gibbs free energy, or as the state when the chemical potential in the two phases are the same.

We find Gibbs free energy for each part of the system. For the crystal, we find Gibbs free energy from

$$G_c(T, p, N_c) = F_c(T, V_c, N_c) + pV_c, \quad (9.87)$$

where V_c is the volume of the crystal. The volume does not appear in F_c , but we will need an expression for V_c for the pV_c term. We will therefore make a small addition to the ideal crystal (Einstein crystal) model – we will assume that there is a volume v_0 associated with each crystal particle, so that the volume of the crystal is $V_c = N_c v_0$. We insert the approximation $F_c(T, V_c, N_c) = 3N_c kT - N_c \epsilon_0$ from our calculations above and find:

$$G_c(T, p, N_c) = 3N_c kT - N_c \epsilon_0 + pN_c v_0, \quad (9.88)$$

and $g_c(T, p) = \mu_c(T, p)$ is

$$g_c(T, p) = \mu_c(T, p) = \frac{G_c}{N_c} = 3kT - \epsilon_0 + pv_0. \quad (9.89)$$

We see that the chemical potential for the crystal is modified by the term pv_0 compared with the expression we have above to the T, V, N system.

Similarly, we find Gibbs free energy for the gas:

$$\begin{aligned} G_g(T, p, N_g) &= F_g(T, V_g, N_g) + pV_g \\ &= -N_g kT \left(\ln \frac{n_Q}{n_g} + 1 \right) + pV_g. \end{aligned} \quad (9.90)$$

We can now apply the ideal gas law, $pV_g = N_g kT$ and $p = (N_g/V_g)kT = n_g kT$, which gives $n_g = p/(kT)$, giving:

$$\begin{aligned} G_g(T, p, N_g) &= -N_g kT \left(\ln \frac{n_Q kT}{p} + 1 \right) + N_g kT \\ &= N_g kT \ln \frac{p}{n_Q kT}. \end{aligned} \quad (9.91)$$

which gives

$$g_g(p, T) = \mu_g(p, T) = kT \ln \frac{p}{n_Q kT}. \quad (9.92)$$

(This is exactly the same result for μ_g as we would get if we inserted $n_g = p/(kT)$ into the result for $\mu_g(T, V)$ from our previous discussion.)

Phase equilibrium occurs for the p_e, T_e pair when $\mu_c(p_e, T_e) = \mu_g(p_e, T_e)$, which is given by

$$\mu_g = kT_e \ln \frac{p}{n_Q(T_e)kT_e} = \mu_c = 3kT_e - \epsilon_0 + p_e v_0. \quad (9.93)$$

Unfortunately, this equation is not simple to solve, since p_e occurs both in the logarithm and directly in the equation. However, if $p_e v_0$ is much smaller than kT , we

may neglect the $p_e v_0$ term and the resulting $p_e(T_e)$ curve will be the same as we found above.

However, this representation of the problem provides us with a richer description and a richer understanding of the phase equilibrium than this. The total system consists of both gas and crystal particles. The total Gibbs free energy is therefore

$$G_{tot} = G_c + G_g = N_c g_c + N_g g_g, \quad (9.94)$$

Fig. 9.4 illustrates g_c and g_g as a function of T for a given value of p . We see that since g_g is proportional to kT (except for a logarithmic dependency on T which is weaker), and g_c is proportional to $3kT$, the slope of g_c with T is higher. For small values of T , $g_c < g_g$, up to $T = T_e$ corresponding to the phase equilibrium curve, $p_e(T_e)$. This means that the system has a minimum of Gibbs free energy if all the particles are in the crystal phase and no particles are in the gas phase, $N_c = N$, and $N_g = 0$. However, for $T > T_e$, $g_c > g_g$, and the system will have a minimum in the total Gibbs free energy if all the particles are in the gas phase and no particles are in the crystal phase, $N_g = N$, $N_c = 0$. This is illustrated in the figure.

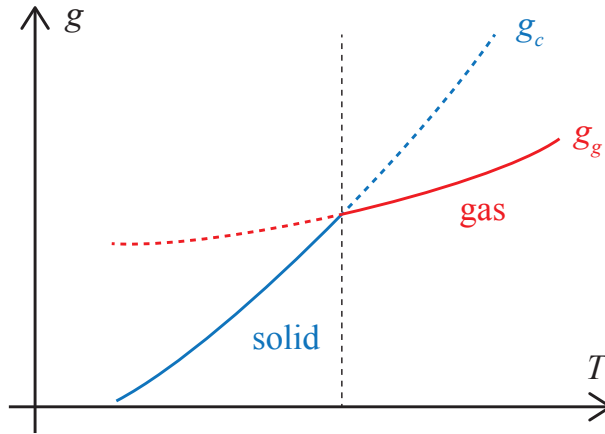


Fig. 9.4 Plot of the Gibbs free energies per particles for the gas and the crystal. The dashed regions indicate where the other phase has a lower Gibbs free energy, the solid lines show the minimum of the total Gibbs free energy and hence the actual behavior of the system.

For this system, the $p_e(T_e)$ represents a singular region. It is only when the pressure and temperature are exactly on this curve that there is co-existence between the two phases in the system. If the system starts at the co-existence curve, and we increase the temperature in the system, then the chemical potential in the gas will be lower than the chemical potential of the crystal (or, similarly, the Gibbs free energy per particle will be lower in the gas than in the crystal), and the system will only contain gas particles. If we lower the temperature from $p_e(T_e)$, all the particles will be in the crystal phase.

So what happens in the system if we start with all the particles in the solid phase, that is we start at a temperature lower than the phase coexistence curve, and then we gradually (and slowly) increase the temperature in the bath? As long as $T < T_e$, the Gibbs free energy of the crystal will be lower than the Gibbs free energy of the solid, and all the particles will be in the solid phase until we reach $T = T_e$. At this point, the number of particles in the crystal and the gas phases are not known – they are not determined by the minimum in Gibbs free energy. Any choice of N_c and N_g (consistent with the condition that $N_g + N_c = N$) will give the same Gibbs free energy

$$G_{tot} = N_g g_g + N_c g_c , \quad (9.95)$$

because $g_g = g_c$ when $p = p_e(T_e)$. So what determines N_c and N_g ? The history! How we have come to this state. If we came to the state from $T < T_e$ then $N_g = N$ and $N_c = 0$. But how can we change N_g and N_c ? We can do this by transferring thermal energy – heat – into the system. This will not lead to a change in temperature in the system – since the system will remain on the phase coexistence curve as long as there are particles in both the crystal and gas phases in the system. Instead, the heat will take particles from the crystal phase and into the gas phase. We realize that this does require energy, because the particles in the crystal are bound with a binding energy ϵ_0 . But there are other contributions as well.

What is the heat needed to transfer one particle (atom or molecule) from the solid to the gas? We can analyze this using the first law for thermodynamics. The change in state of the system when $N_g \rightarrow N_g + 1$ and $N_c \rightarrow N_c - 1$ is

$$\Delta E = \Delta Q + \Delta W , \quad (9.96)$$

where the work done on the system by the environment is $\Delta W = -p\Delta V$. The heat transferred into the system therefore goes into work done by the system on the environment and a change in internal energy in the system:

$$\Delta Q = \Delta E + p\Delta V . \quad (9.97)$$

The situation is illustrated in fig. ???. If a particle is transferred from the solid to the gas, the volume of the solid decreases by v_0 , the volume per particle in the solid, and the volume in the gas increases by $v_g = V_g/N_g$, the volume per particle in the gas:

$$\Delta V = v_g - v_s = v_g - v_0 . \quad (9.98)$$

If $v_0 \ll v_g$ we can use the approximation, $\Delta V \simeq v_g$.

Material	Critical T
O ₂	154.3 K
H ₂ O	647.1 K
CO ₂	304.2 K
N ₂	126.0 K
H ₂	33.2 K

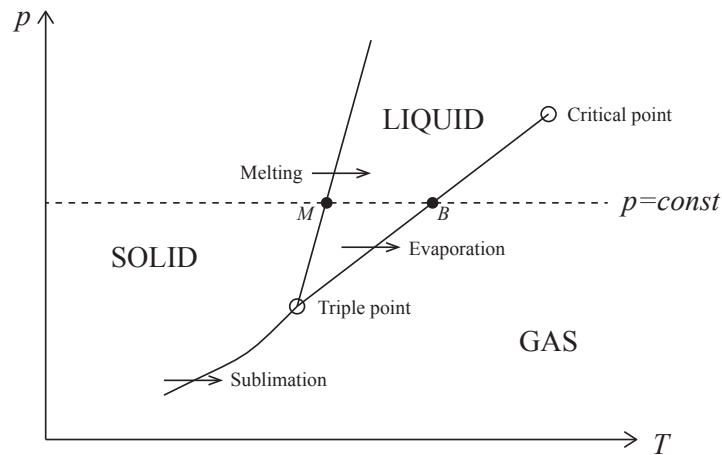


Fig. 9.5 Phase plot in P - T space.

For water, the phase coexistence curve between the solid and the liquid phase has a negative slope – this is due to density differences between ice and water: Ice has a lower density than water. For most other materials, the coexistence curve will have a positive slope.

For the simplified model, we discussed the behavior for processes at constant temperature or constant pressure. An isotherm crossing from the liquid phase at high pressures to the gas phase at lower pressures is illustrated in fig. 9.5. How does this process look like in a P - V -diagram? We have illustrated an isotherm across the phase boundary in fig. 9.6. Let us assume that the system starts at a high pressure (and low volume). The system is fully in the liquid phase: The whole system is a liquid. If we gradually decrease the pressure (without changing the temperature), the system will eventually reach the phase coexistence pressure p_e for this system. The behavior is then similar to what we observed in the simplified model. We must add energy – in the form of heat – to the system to vaporize the particles in the liquid so that they form a gas. This occurs at constant pressure p_e , but the volume increases in the process. Indeed, the system does work on the environment in this process, and the energy for this work comes from the added heat. When all the liquid is transformed into gas. We could think of this process as a process where we gradually change the volume: We pull on the piston slowly, and observe the internal state of the system. This will result in the same behavior illustrated in the figure, and heat will also in this case flow into the system from the thermal bath in order to keep the system at the same temperature while the system is expanding and particles evaporate. Notice that the pressure is a function of the volume, but that the volume is not a function of pressure: There are many possible volumes for the pressure p_e .

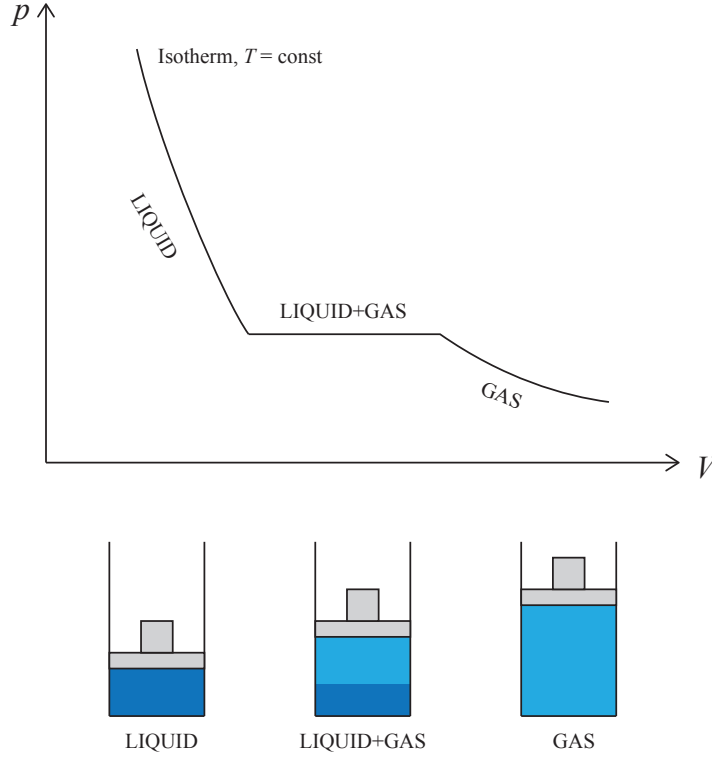


Fig. 9.6 Illustration of an isothermal process crossing the liquid-gas phase boundary plotted in P - V space.

9.3.4 Phase coexistence and Gibbs free energy

The equilibrium state of a system at constant T , p , and N is determined by the minimum of the Gibbs free energy of the system. For a system with three phases: gas (g), liquid (l), and solid (s), the total Gibbs free energy can be written as

$$\begin{aligned} G_{tot} &= G_g(N_g, p, T) + G_l(N_l, p, T) + G_s(N_s, p, T) \\ &= N_g g_g(p, T) + N_l g_l(p, T) + N_s g_s(p, T) , \end{aligned} \quad (9.99)$$

where g_g , g_l , and g_s are the Gibbs free energy per particles for the gas, liquid and solid phases, and $N_g + N_l + N_s = N$ are the particles in the gas, liquid and solid phases respectively. In general, the three free energies will have different dependencies of p and T . In fig. 9.7 we have sketched the behavior of the Gibbs free energies for a sample system. Just like for the simplified model, we see that the system will be in the phase with the minimum Gibbs free energy per particle. Phase coexistence occurs where the Gibbs free energies per particle are equal: The evaporation transition (e) from gas to liquid occurs for the p_e, T_e values where $g_g(p_e, T_e) = g_l(p_e, T_e)$; and

the melting (m) transition from liquid to solid occurs where $g_l(p_m, T_m) = g_s(p_m, T_m)$. This provides us with a method to calculate the phase coexistence curves if we know the Gibbs free energies for the various phases in the system. Let us see how we can find the shape of the $p(T)$ curve without knowing all the details of the underlying system.

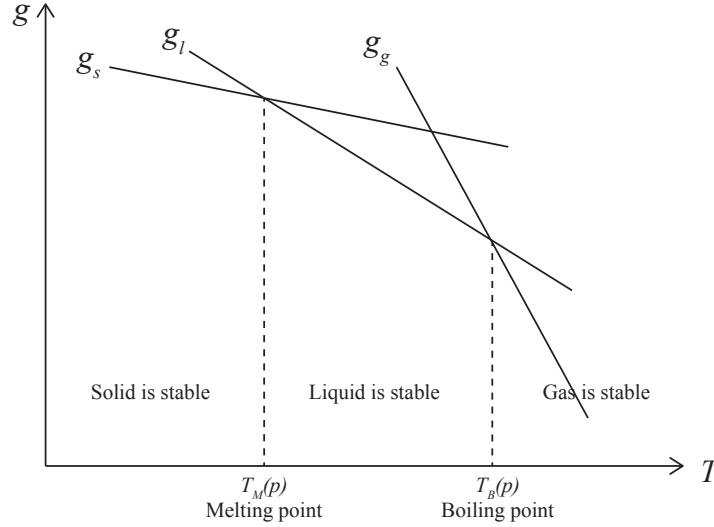


Fig. 9.7 Illustration of the gibbs free energies per particle as a function of temperature at constant pressure for the solid (s), liquid (l), and gas (g) phases.

9.3.5 Phase coexistence curve

Let us find a general expression for the coexistence curve, $p_e(T_e)$, using the liquid-gas transition as an example. Coexistence occurs when the Gibbs free energy per particle in the liquid and gas phases are the same:

$$g_l(p, T) = g_g(p, T) . \quad (9.100)$$

This means that if we start at a point p_0, T_0 on the coexistence curve, and make a small change dT to $T_0 + dT$ we must also make a change dp in the pressure to still remain on the curve:

$$g_l(p_0, T_0) = g_g(p_0, T_0) , \quad (9.101)$$

and

$$g_l(p_0 + dp, T_0 + dT) = g_g(p_0 + dp, T_0 + dT) . \quad (9.102)$$

We subtract the two equations, getting

$$\begin{aligned} dg_l &= g_l(p_0 + dp, T_0 + dT) - g_l(p_0, T_0) \\ &= dg_g = g_g(p_0 + dp, T_0 + dT) - g_g(p_0, T_0) . \end{aligned} \quad (9.103)$$

We can now Taylor-expand g_l and g_g around p_0, T_0 :

$$g_l(p_0 + dp, T_0 + dT) \simeq g_l(p_0, T_0) + \left(\frac{\partial g_l}{\partial p} \right)_T dp + \left(\frac{\partial g_l}{\partial T} \right)_p dT , \quad (9.104)$$

and similarly for $g_g(p, T)$. We recognize the partial derivatives as

$$\left(\frac{\partial g_l}{\partial p} \right)_T = v_l , \quad \left(\frac{\partial g_l}{\partial T} \right)_p = -s_l . \quad (9.105)$$

We insert this into eq. 9.103, getting

$$dg_l = v_l dp - s_l dT = dg_g = v_g dp - s_g dT . \quad (9.106)$$

We rearrange to find an equation for dp/dT :

$$(v_l - v_g)dp = (s_l - s_g)dT , \quad (9.107)$$

and the coexistence curve $p(T)$ is therefore determined by the equation:

$$\left(\frac{dp}{dT} \right)_{\text{along curve}} = \frac{s_g - s_l}{v_g - v_l} . \quad (9.108)$$

How can we interpret the two differences $\Delta s = s_g - s_l$ and $\Delta v = v_g - v_l$? We see that Δs is the increase in entropy when we transfer one molecule from the liquid to the gas phase. Similarly, Δv is the change in volume when we transfer one molecule from the liquid to the gas. We can relate Δs to the heat added to the system:

$$\Delta Q = T \Delta s = T (s_g - s_l) = \ell , \quad (9.109)$$

which is called the **latent heat** of evaporation. It is common to describe the latent heat by the latent heat for the evaporation of one mole and not one particle. The molar latent heat $L = T(s_g - s_l)$, where s_g and s_l are the entropies of one mole of gas and liquid phase of the molecules. (If we use molar values for the entropy or latent heat, we also need to use molar values for the volumes v .) Notice that the latent heat is generally dependent on temperature: $L = L(T)$. We can now rewrite eq. 9.108 as

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{T \Delta s}{T \Delta v} = \frac{L(t)}{T \Delta v} . \quad (9.110)$$

This equation is called **Clausius-Clapeyron's equation**.

For the liquid-gas transition, we can simplify the expression because $v_g \gg v_s$, so that $\Delta v = v_g - v_s \simeq v_g$, and in addition, the gas phase can be described approximately by the ideal gas law, so that $v_g = p/kT$ (or if we use molar values, $v_g = p/RT$, where $R = N_A k$, where N_A is Avogadro's number). The equation for the coexistence curve then becomes

$$\frac{dp}{dT} = \frac{L(T)}{T\Delta v} \simeq \frac{L(T)p}{kT^2}, \quad (9.111)$$

and

$$\frac{dp}{p} = \frac{L(t)dT}{kT^2}. \quad (9.112)$$

Given an expression for $L(T)$ we can integrate this equation to find $p(T)$. If the latent heat $L(T) \simeq L_0$ is approximately constant over a range of temperatures T , we can find an analytical solution:

$$\int_{p_0}^p \frac{dp}{p} = \int_{T_0}^T \frac{L(T)dT}{kT^2} \simeq L_0 \int_{T_0}^T \frac{dT}{kT^2}, \quad (9.113)$$

which gives

$$\ln p - \ln p_0 = -\frac{L_0}{kT} + \frac{L_0}{kT_0}, \quad (9.114)$$

and

$$p(T) = p'_0 e^{-\frac{L_0}{kT}}. \quad (9.115)$$

9.3.6 Example: Transition from graphite to diamond

9.3.7 Latent heat and enthalpy

We can use thermodynamic tables that list enthalpies to find the latent heat for a transition. The latent heat correspond to the difference of the enthalpy, $H = E + pV$, between two phases when the process occurs at constant pressure p .

This is simple to demonstrate, because along the coexistence curve we know that $\mu_l = \mu_g$. The thermodynamic identity is therefore

$$TdS = dE + pdV - (\mu_g - \mu_l)dN, \quad (9.116)$$

but since $\mu_g = \mu_l$ the last term is zero. At constant pressure, the latent heat is the heat TdS transferred, which is

$$L = TdS = dE + pdV = dH = dE + pdV + \underbrace{Vdp}_{=0} = H_g - H_l. \quad (9.117)$$

We can find the values of H by integrating the heat capacity at constant pressure:

$$C_P = T \left(\frac{dS}{dT} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p . \quad (9.118)$$

and

$$H = \int C_P dT . \quad (9.119)$$

9.3.8 Van der Waals fluid model

We have so far used the ideal gas model as our canonical model for a gas. But the model is limited – it does not contain any interactions between the gas particles. How well does this model really describe a real gas or a real liquid? We can test this by studying the behavior of a real, although simulated, fluid using the molecular dynamics simulation method we introduced previously. In a molecular simulation we can include any type of interactions between the molecules in the system. We could include a model of real water (we will do this later in the chapter for comparison), but most of the properties of gases and fluids are well captured by a simpler model, such as the Lennard-Jones model used to describe the Argon system.

In the Lennard-Jones model, the interatomic potential is

$$U_{LJ}(r) = 4\epsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right) . \quad (9.120)$$

This potential has a strong repulsive interaction at short ranges, described by a potential with a r^{-12} dependency, and a weak attractive interaction at long distances, described by a dipole-dipole interaction with a r^{-6} dependency. The Lennard-Jones system therefore contain both repulsive and attractive interactions. The Lennard-Jones system can describe all the three phases of the Argon system: a solid, a liquid, and a gas, depending on the pressure, density and temperature in the system.

We can use molecular simulations to study a phase equilibrium directly. We can model a microcanonical system with constant E , V , and N . In this system, if the energy is low enough, there will always be an equilibrium between a gas and a liquid phase. If we start the simulation from a regular pattern of atoms with random velocities, the system will quickly coalesce and coarsen: Droplets of liquid will spontaneously nucleate and grow, and the regions between the droplets will be filled with a gas with much lower density than the solid. Fig. 9.8 shows a sequence of snap-shots from a simulation with the following initialization file for the LAMMPS simulator:

```
# 3d Lennard-Jones coalescence
units          lj
atom_style     atomic
lattice        fcc 0.2
region         box block 0 20 0 20 0 20
create_box     1 box
create_atoms   1 box
```

```

mass      1 1.0
velocity  all create 0.1 87287
pair_style lj/cut 2.5
pair_coeff 1 1 1.0 1.0 2.5
neighbor  0.3 bin
neigh_modify every 20 delay 0 check no
fix 1 all nvt temp 0.6 0.6 1.0
dump      id all atom 100 vdw-coalesce01.lammpstrj
thermo    100
run       20000

```

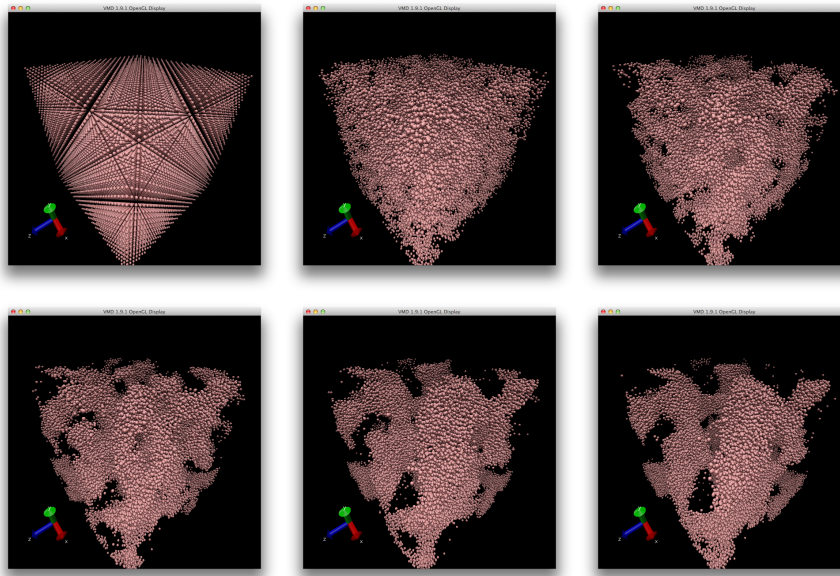


Fig. 9.8 Snapshots from simulations of a Lennard-Jones system at a low temperature, $T = 0.1T^*$, show coalescence and phase coexistence between a liquid and a gas phase.

In this case, the simulated system is at a constant temperature. We can also model systems at a constant pressure using special techniques that change the volume of the system to keep the pressure (approximately) constant. We have made a short script to generate a set of simulations to find the equation of state, $p(T)$, for the Lennard-Jones system. We use the following program

```

from pylab import *
# Generate sequence of parameters
pressarr = array([]) # Store pressures
volarr = array([]) # Store volumes
temparr = array([]) # Store temperatures
# Sequence of parameters to probe
myvelocities = array([3.0,3.5,4.0,4.5,5.0,5.5,6.0])

```

```

myvolumes = array([0.020])
# Calculation loop
for ivel in range(0,size(myvelocities)):
    for ivol in range(0,size(myvolumes)):
        # Setup simulation file in.tmp
        os.system("cp in.gasstatistics30 in.tmp2")
        # Change the word mydensity to myvolumes[ivol]
        runstring = "sed \"s/mydensity/%f/\" in.tmp2 > in.tmp1"
        os.system(runstring)
        # Change the word myvelocity to myvelocities[ivel]
        runstring = "sed \"s/myvelocity/%f/\" in.tmp1 > in.tmp"
        os.system(runstring)
        # Run the simulator
        os.system("lammmps < in.tmp") # Run lammmps
        os.system("rm in.tmp1 in.tmp2") # Clean up
        # Extract data from trajectory of simulation
        d = dump("tmpdump.lampstrj") # Read simulated states
        tmp_time,simbox,atoms,bonds,tris,lines = d.viz(0)
        dx = simbox[3]-simbox[0]
        dy = simbox[4]-simbox[1]
        dz = simbox[5]-simbox[2]
        vol = dx*dy*dz # Volume of box
        # Read pressures calculated in simulation
        l = logfile("log.lammmps")
        # Find pressure averaged over all timesteps
        press = average(l.get("Press"))
        temp = average(l.get("Temp"))
        # Store calculated values in arrays
        pressarr = append(pressarr,press)
        volarr = append(volarr,vol)
        temparr = append(temparr,temp)
# Plot the results
pvarr = pressarr*volarr
plot(temparr,pressarr,'o')
xlabel("T"),ylabel("P")
show()

```

and the file used by the program is

```

# 3d Lennard-Jones gas
units      lj
dimension  3
atom_style atomic
lattice     fcc 0.1
region      box block 0 10 0 10 0 10
create_box  1 box
create_atoms 1 box
mass        1 1.0
velocity    all create myvelocity 87287
pair_style   lj/cut 2.5
pair_coeff   1 1 1.0 1.0 2.5
neighbor     0.3 bin
neigh_modify every 20 delay 0 check no
fix         1 all nve

```

```

dump      1 all custom 100 tmp.lammpstrj id type x y z vx vy vz
thermo    100
run       5000

```

These molecular simulations allow us to test the precision of the ideal gas law, and maybe we can also learn how we can modify the ideal gas law to better represent the material in the simulations. The ideal gas law states that $pV = NkT$, which gives us a functional form for $p = NkT/V$. We can measure and plot p as a function of T for a given number N of atoms and for a given volume V and test the accuracy of the model. Fig. 9.9 shows the measured $p(T)$ from molecular simulations and the corresponding curve $p = NkT/V$. The ideal gas law is clearly decent, but not a very good approximation. The law seems to be wrong in two ways: There is an additional constant in the actual data:

$$p = p_0 + \frac{NkT}{V}, \quad (9.121)$$

and in addition, the slope of the $p(T)$ curve is not given by NkT/V , but is somewhat adjusted.

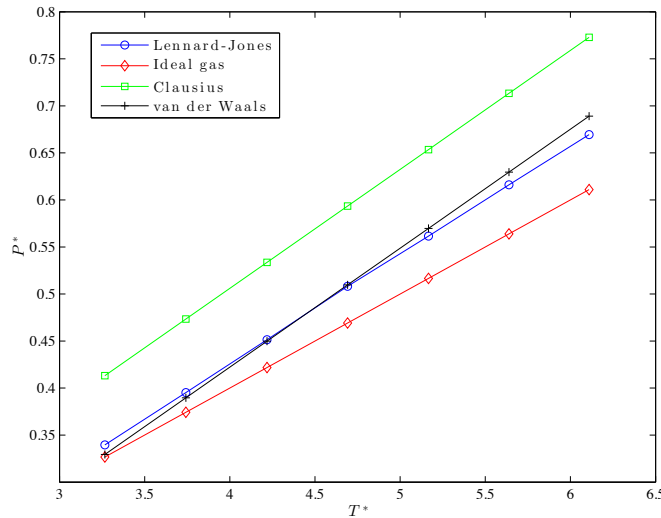


Fig. 9.9 Plot of $p(T)$ as measured in molecular dynamics simulations using the Lennard-Jones potential, for the ideal gas law, and for various modifications of the ideal gas law.

What can be the origin of these differences? What effects in the Lennard-Jones model have not been included in the ideal gas law? There are two main interaction in the Lennard-Jones potential: A repulsion at short distances and an attraction at long distances. Neither are included in the ideal gas law. How can we include these effect in a simple modification?

First, how can we include the repulsion at short distances? The repulsion means that atoms will not be very close to each other. When the atoms are far apart –

for low densities – this does not matter much. But as the atoms are pressed closer together, we will notice that a significant part of the volume is not available for motion because it is too close to other atoms: We have a region of excluded volume. We can make a simple model for this by assuming that each atom has a small volume b associated with it, so that the excluded volume is Nb . The volume that is actually available for the atoms are then $V - Nb$ and not V . This will lead to a modification of the ideal gas law. However, we do not only want to modify the ideal gas law, we want to develop a new theory for a more realistic gas. This means that we would need expressions not only for the pressure, but also for the entropy and the chemical potential – which can be found from Helmholtz free energy. Let us therefore see how we can modify the free energy. For an ideal gas (IG), the Helmholtz free energy is

$$F_{IG} = -NkT \left(\ln \frac{n_Q(T)}{n} + 1 \right) = -NkT \left(\ln \frac{V n_Q(t)}{N} + 1 \right). \quad (9.122)$$

In this equation, the volume only occurs once, and we can include the excluded volume by replacing $V \rightarrow V - Nb$:

$$F_C = -NkT \left(\ln \frac{(V - Nb)n_Q(t)}{N} + 1 \right). \quad (9.123)$$

This model for a gas is called the Clausius model, and the corresponding equation of state is found by calculating p as a derivative of F :

$$p_C = - \left(\frac{\partial F_C}{\partial V} \right)_{T,N} = \frac{NkT}{V - Nb}. \quad (9.124)$$

This equation is called Clausius law. It is an improvement of the ideal gas model, as seen in fig. 9.9, but it does not include the correct shift, p_0 , in pressure. We therefore need an addition term. Based on the plot in fig. 9.9 we see that the additional term must reduce the effective pressure – the actual pressure must be lower than the pressure predicted by Clausius law. What physical effect may cause this? Attraction between the particles! We therefore need to include the effect of the attractive part of the Lennard-Jones model. This will give rise to a binding energy – a reduction in the energy and in Helmholtz free energy – when the density is high.

Let us construct a simplified model for the attractive interaction between the atoms. An atom in the gas will experience attractive interactions from all the other atoms. The potential energy of this interaction is the sum of the potential energies for all the other atoms. The potential energy of atom i is

$$u_i = \sum_{j \neq i} U_{LJ}(r_{ij}), \quad (9.125)$$

where r_{ij} is the distance from atom i to atom j . However, since the potential energy only depends on the distance, we can instead sum over distances, but then we need to include how many atoms are at each distance, which corresponds to the density of atoms measured around atom i , $n_i(r)$ times the volume element dV :

$$u_i = \int_V U_{LJ}(r) n_i(r) dV . \quad (9.126)$$

For each atom, the actual $n_i(r)$ will vary in time as all the other atoms move about. Instead of calculating this integral for each atom, we will assume that all atoms experience the same, average density $n(r)$ as a function of distance to the atom, and that this average density can be written as $n(r) = n\phi(r)$, where n is the average density of the system and $\phi(r)$ gives the variations relative to the average density. The potential energy of atom i is then:

$$u_i = \int_V U_{LJ}(r) n\phi(r) dV = n \underbrace{\int_V U_{LJ}\phi(r) dV}_{=-2a} = -2an . \quad (9.127)$$

The integral does not depend on N or V and we have therefore called it $-2a$. (You will see below why we have introduced the factor 2). The theory can be made even simpler by assuming that $\phi(r)$ is constant in space, but this is not important for our argument.

The potential energy of one atom is u_i . What is the potential energy of the whole gas? The gas consists of N atoms, and it may therefore be tempting to simply multiply u_i by N . But this is not correct, because we should only include the potential energy for each pair of particles once, and the number of pairs is $N(N-1)/2$ and not N^2 . Since u_i already includes the interactions from N atoms, we must multiply u_i by $N/2$ to find the total potential energy: $u_{tot} = (N/2)(-2an) = -anN$. This potential energy must be added to the Helmholtz free energy without interactions to find the (approximative) Helmholtz free energy with attractive interactions:

$$\begin{aligned} F_{vdw} &= -NkT \left(\ln \frac{n_Q(T)}{n} + 1 \right) - anN \\ &= -NkT \left(\ln \frac{Vn_Q(T)}{N} + 1 \right) - a \frac{N^2}{V} . \end{aligned} \quad (9.128)$$

This model is called the van der Waals model of an ideal gas. The model was introduced in the doctoral dissertation of Johannes Diderik van der Waals (1837-1923; Nobel 1910). The equation of state for the van der Waals gas is found from the pressure:

$$p = - \left(\frac{\partial F_{vdw}}{\partial V} \right)_{T,N} = \frac{NkT}{V - Nb} - \frac{N^2 a}{V^2} , \quad (9.129)$$

which also can be written as

$$\left(p + \frac{N^2 a}{V^2} \right) (V - Nb) = NkT , \quad (9.130)$$

which is called the **van der Waals equation of state**.

9.3.9 Parameters for the Lennard-Jones system

How can we determine the values of b and a for an actual gas? We can find these either from experimental data, by simulations for more complicated fluids such as water, or by theoretical considerations for simple fluids such as a Lennard-Jones system. The actual values of a and b will be different for different substances, and they may even vary for the same substance, but at different conditions because the model is only approximative.

For the Lennard-Jones system we may estimate the values of a and b . The excluded volume corresponds to a volume that is not available for motion. This must be related to σ , the characteristic length of the potential. We could assume that the excluded volume starts where the potential is zero, that is for a volume of radius σ in the Lennard-Jones potential. However, this is too large, since the atoms often may be compressed into this zone. Instead, we will guess that the excluded volume is one half of the volume corresponding to σ , that is

$$b = v_{ex} = (1/2)(4\pi/3)\sigma^3 = (2\pi/3)\sigma^3. \quad (9.131)$$

We can estimate a from the integral of the potential, assuming that the density is constant, $n(r) = n$ ($\phi(r) = 1$):

$$a \simeq \int_{\sigma/2^{1/3}}^{\infty} -\frac{\sigma^6}{r^6} 4\pi r^2 dr = \frac{8\pi}{3}\sigma^3. \quad (9.132)$$

This set of values are plotted in fig. 9.9, and the resulting model fits excellently to the data measured in molecular dynamics simulations of the Lennard-Jones model.

9.3.10 Properties of the van der Waals system

9.3.11 Critical point of the van der Waals gas

Let us start from a trick - since we know the answer here.

We introduce

$$p_c = \frac{a}{27b^2}, \quad V_c = 3Nb, \quad kT_c = \frac{8a}{27b}. \quad (9.133)$$

We can then rewrite the vdW equation of state as:

$$\left(\frac{p}{p_c} + \frac{3}{(V/V_c)^2} \right) \left(\frac{V}{V_c} - \frac{1}{3} \right) = \frac{8kT}{3kT_c}. \quad (9.134)$$

We can then plot p/p_c as a function of V/V_c for different values of kT/kT_c . It is useful to plot this for T near T_c , for example for $T/T_c = 1.05, 1.0, 0.95, 0.9$.

We could introduce the quantities

$$\hat{p} = p/p_c, \hat{V} = V/V_c, \hat{T} = T/T_c. \quad (9.135)$$

and the equation becomes

$$\left(\hat{p} + \frac{3}{\hat{V}^2}\right) \left(\hat{V} - \frac{1}{3}\right) = \frac{8}{3}\hat{T}, \quad (9.136)$$

and

$$\hat{p} = \frac{\frac{8}{3}\hat{T}}{\hat{V} - \frac{1}{3}} - \frac{3}{\hat{V}^2}. \quad (9.137)$$

This is called the **law of corresponding states**.

When we plot the equation of state in terms of these quantities, all gases/liquids look the same.

This has been done by the following program, where we can vary the temperature \hat{T} .

```
% Plot vdW
clear all; clf;
That = [0.9 0.95 1.0 1.05];
for i = 1:length(That)
    T = That(i);
    V = linspace(0.5, 2.0, 1000);
    p = 8.0/3.0*T./(V-1/3)-3.0./(V.^2);
    plot(V,p)
    hold all
end
hold off
xlabel('V/V_c')
ylabel('p/p_c')
a = axis(); a(4) = 1.5; axis(a);
```

What happens if we plot $p(V)$ for \hat{T} less than 1? In this case, we find that \hat{P} has a local maximum for some value of V . Hmmm. This is a bit worrying?

Why is this problematic? Because near the maximum, we see that an increase in the volume would lead to smaller pressure, which is an unstable situation.

This is usually analyzed in terms of the compressibility of the gas

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}, \quad (9.138)$$

and the compressibility must always be larger than or equal to one – otherwise the gas is unstable. The condition that $\kappa \geq 0$ corresponds to the condition that dP/dV is always smaller than zero: The $p(V)$ curve must be decreasing.

This equality is satisfied as long as $\hat{T} > 1$ - corresponding to the temperature where we have an inflection point - a point where the curve $\hat{p}(\hat{V})$ has a horizontal point of inflection. This means that the maximum and minimum of the $p - V$ curve coincide.

(This means that there is no separation between gas and liquid – although we have not shown this yet).

This occurs when

$$\left(\frac{\partial \hat{p}}{\partial \hat{V}}\right)_{\hat{T}} = 0, \quad \left(\frac{\partial^2 \hat{p}}{\partial \hat{V}^2}\right)_{\hat{T}} = 0 \quad (9.139)$$

which occurs for $\hat{p} = 1$, $\hat{V} = 1$, and $\hat{T} = 1$. We call these values the critical values - the critical pressure, volume and temperature.

9.3.12 Behavior above and below T_C

How can we understand what happens above and below T_c ?

Above T_C there are no problems with the solution. In this case, there is a unique solution - a unique volume for a given pressure.

Below T_C there are three possible volumes that give the same pressure. And there is a range of values where we have a negative compressibility.

In this range the vdW equation of state is not a good approximation to the behavior of the gas. But we can fix this by a simple fix - so that we still get physically reasonable results - by including the effect of phase separation into the equation. However, we need to do this “manually”.

Let us gain more insight into the behavior by studying Gibbs free energy for the system.

We know that Helmholtz free energy for the system is

$$F = -NkT (\ln(n_Q(V - Nb)/N) + 1) - \frac{N^2 a}{V}, \quad (9.140)$$

which we can write as

$$F = -NkT \ln(V - Nb) - \frac{N^2 a}{V} + NkT c(T), \quad (9.141)$$

where the form of the function $c(T)$ is not important for our calculation now.

Gibbs free energy is then

$$G = F + pV = -NkT \ln(V - Nb) - \frac{aN^2}{V} + pV + NkT c(T). \quad (9.142)$$

We now write Gibbs free energy in dimensionless form - by a convenient, but not obvious non-dimensionalization:

$$\hat{g} = \frac{8G}{3NkT_c}, \quad (9.143)$$

and we can then rewrite (after some algebra) gibbs free energy to be

$$\hat{g} = -3\hat{p} - \frac{8}{3}\hat{T} \ln\left(\frac{3}{\hat{p}} - 1\right) + \frac{\hat{p}}{\hat{p}} + C, \quad (9.144)$$

where the term C - which is just a constant - does not include any terms that involve $\hat{\rho}$ or \hat{P} . We have also introduced the dimensionless density,

$$\bar{\rho} = 3b\rho = 3b\frac{N}{V}. \quad (9.145)$$

We can plot this as a function of

9.3.13 Example: Nucleation theory

We introduce $\Delta\mu = \mu_g - \mu_l$ as the difference in chemical potential between the vapor surrounding a liquid droplet and the liquid in bulk - that is for a very large drop (no surface effects).

If $\Delta\mu > 0$ it means that the liquid has lower free energy than the gas/vapor - and liquid droplets may spontaneously form.

However, we must also include the surface free energy, because this tends to increase the energy of the liquid.

For a very small droplet, with a very small radius of curvature, the surface energy will be dominating and the drop can be unstable with respect to the gas/vapor.

Let us study this by addressing Gibbs free energy when a droplet of radius R forms. We introduce

$$\Delta G = G_l - G_g = -(4\pi/3)R^3 n_l \Delta\mu + 4\pi R^2 \gamma, \quad (9.146)$$

where n_l is the number density of the liquid (the concentration), and γ is the energy it costs to form a surface - per area.

The liquid drop will grow when $G_l < G_g$.

There is a maximum at

$$\frac{d\Delta G}{dR} = 0 = -4\pi R^2 n_l \Delta\mu + 8\pi R \gamma, \quad (9.147)$$

which gives

$$R_c = \frac{2\gamma}{n_l \Delta\mu}. \quad (9.148)$$

We call this the **critical radius of nucleation**.

When the radius is smaller than R the drop will grow smaller - and disappear.

When the radius is larger than R the drop will continue to grow larger and larger.

We may (or maybe not?) assume that the gas is an ideal gas - and in that case the chemical potential is

$$\Delta\mu = kT \ln(p/p_{eq}), \quad (9.149)$$

where p_{eq} is the equilibrium vapor pressure of the bulk liquid.

We can use realistic values then to estimate R_c for water at 300K and $p = 1.1 p_{eq}$. In addition, we need a value for γ , which we can find from tables, $\gamma = 72 \cdot 10^{-3} \text{ N/m}$. This gives $R_c \simeq 10^{-8} \text{ m} = 10 \text{ nm}$.

9.4 Binary mixtures

9.5 Dilute Solutions

Dilute solutions are mixtures where one of the components are so dilute that they do not affect the energy of the other component. Typical examples are trace gases in air or dilute solutions in water. When we discuss solutions, we call the component that is dissolved the **solute**. The substance it is being dissolved in is called the **solvent**. And the resulting product is called the **solution**. For example, salt water is a *solution*, made from a *solvent*, water, and a *solute*, salt.

While solutions in general may include complex interactions – dilute solutions are simple, since the interactions between the solvent and the element that is dissolved primarily is through the entropy of mixing term. Let us start by looking at mixed, ideal gases – often called ideal mixtures.

9.5.1 Ideal mixture

An ideal mixture is a mixture with many of the properties from mixtures of ideal gases. We therefore start by studying the properties of a mixture of ideal gases. Since the gases are ideal, there are no interactions between the particles in the gas. The behavior of one species is therefore largely independent of the behavior of another species in the gas. For an ideal gas of c components $i = 1, \dots, c$, the total number of particles is

$$N = \sum_{i=1}^c N_i, \quad (9.150)$$

and the pressure is

$$p = \frac{NkT}{V} = \sum_{i=1}^c \frac{N_i kT}{V} = \sum_{i=1}^c p_i, \quad (9.151)$$

where

$$p_i = \frac{N_i kT}{V}, \quad (9.152)$$

is called the partial pressure of component i . We would like to develop an expression for the chemical potential for each of the components of the mixed, ideal gases, and we will do this through the Gibbs free energy for the whole system. Gibbs free energy for the gas will be the sum of Gibbs free energy for each of the gas

components – as they would be without the other components since there are no interactions – but it must also include term due to the mixing of the gases:

$$G(p, T, \{N_i\}) = \sum_{i=1}^c N_i \mu_i^0(p, T) - TS_{mix} , \quad (9.153)$$

where Gibbs free energy of component i without the other components present is $G_i = N_i \mu_i^0$. Here the superscript 0 shows that this is the chemical potential when there are no other components present.

What is the entropy of mixing for a c -component gas? We find it from the multiplicity for the c -component system, which is

$$\Omega(\{N_i\}) = \frac{N!}{N_1! N_2! N_3! \dots N_c!} , \quad (9.154)$$

which is a generalization of the expression for two components. We find an approximate expression for the mixing entropy using Stirling's formula, $\ln N! = N \ln N - N$:

$$\begin{aligned} S = k \ln \Omega &= N \ln N - N - \sum_{i=1}^c (N_i \ln N_i - N_i) \\ &= k \sum_{i=1}^c N_i \ln N - \sum_{i=1}^c N_i \ln N_i \\ &= -k \sum_{i=1}^c N_i \ln \frac{N_i}{N} . \end{aligned} \quad (9.155)$$

We insert into Gibbs free energy, finding

$$G(p, T, \{N_i\}) = \sum_{i=1}^c N_i \mu_i^0(p, T) + kT \sum_{i=1}^c N_i \ln \frac{N_i}{N} . \quad (9.156)$$

And we can find the chemical potential for component i through the partial derivative

$$\begin{aligned} \mu_i &= \left(\frac{\partial G}{\partial N_i} \right)_{p, T, \{N_j\}} \\ &= \mu_i^0(p, T) + \left(\frac{\partial}{\partial N_i} \sum_{r=1}^c N_r \ln x_r \right)_{p, T, \{N_j\}} \\ &= \mu_i^0(p, T) + kT \ln x_i + \sum_{r=1}^c N_r \frac{1}{x_r} \frac{\partial x_r}{\partial N_i} \\ &= \mu_i^0(p, T) + kT \ln x_i + N \frac{\partial x_r}{\partial N_i} \underbrace{\sum_{r=1}^c x_r}_{=1} \\ &= \mu_i^0(p, T) + kT \ln x_i . \end{aligned} \quad (9.157)$$

The chemical potential for component i is therefore only dependent on $x_i = N_i/N = n_i/n = m_i$, and not on the other x_j values. The only dependence on the other atoms is through the N in the denominator of $x_i = N_i/N$. We can check the consistency of the expression by noticing that for $x_i = 1$ we only have the pure substance, and $\mu_i = \mu_i^0$ – as it should.

This simple expression for the chemical potential is an approximation to general mixtures. We call this approximation the **ideal mixture** approximation. This approximation is versatile. While we here started by assuming that we studied an ideal gas, there are many systems for which the ideal mixture approximation is reasonable. In general, it is better the more similar the molecules are. It is well demonstrated the the ideal mixture approximation is:

- almost exact for mixtures of isotopes
- good for mixtures of similar molecules
- very good for the *solvent* in dilute solutions
- reasonably good for use in chemical equilibriums

9.5.2 Chemical potential for the solvent in dilute solution

A dilute solution corresponds to a solution where the solute does not interact strongly with the solvent, so that $N_B \ll N_A$. We can describe the solution by $x = N_B/N$, the amount of the dissolved material. What is the chemical potential for the solvent when the solute B is present? We start from the expression for the chemical potential for component A in an ideal mixture:

$$\mu_A(p, T) = \mu_A^0(p, T) + kT \ln \frac{N_A}{N} = \mu_A^0(p, T) + kT \ln(1 - x), \quad (9.158)$$

when $x \ll 1$, we can approximate $\ln(1 - x) \simeq -x$, getting:

$$\mu_A(p, T) = \mu_A^0(p, T) - kT \ln x, \quad (9.159)$$

where $\mu_A^0(p, T)$ was the chemical potential of the solvent before the solute was added.

9.5.3 Chemical potential for the solute in dilute solutions

9.5.4 Example: Osmotic pressure

We can use our newfound theory for dilute solutions to find the osmotic pressure of a solution. Biological membranes ensure that the chemistry inside and outside of

the membrane can be different – thus ensuring the machinery of life inside a cell, while living in a potentially hostile environment. Membranes can be made to allow the transport of a solvent such as water while restricting the transport of a solute, such as salt. Fig. 9.10 illustrates a membrane with pure solvent on one side and a solution on the other side. The membrane allows the solvent to move from one side to another, but not the solute.

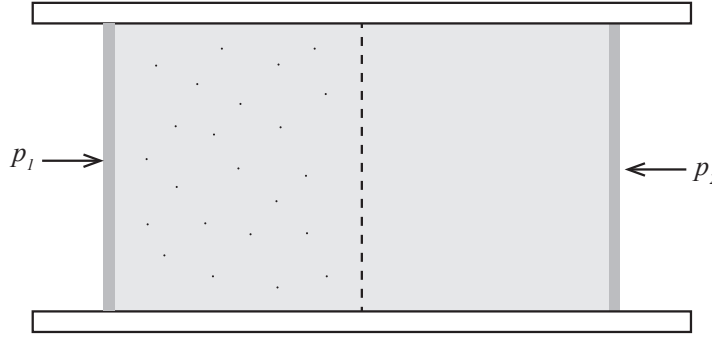


Fig. 9.10 Illustration of a solution (left) and a pure solvent (right) separated by a membrane that is permeable to the solvent, but not to the solute.

If the system starts in this situation, with a pure solvent on one side and a solution on the other, the system will clearly not be in thermodynamic equilibrium, because the chemical potentials are not the same on each side of the membrane. The chemical potential in the solvent is $\mu_2(p, T) = \mu_s^0(p, T)$, while the chemical potential in the (dilute) solution is approximately $\mu_1(p, T) = \mu_s(p, T) = \mu_s^0(p, T) - kT \ln x$. Transport will therefore occur from the side with the solvent to the side with the solution. However, we can stop the transport by increasing the pressure in the solution until the chemical potentials are equal. This occurs when the pressure in the solution is p_1 and the pressure in the solvent is p_2 . The chemical potentials are then

$$\mu_2(p_2, T) = \mu_s^0(p_2, T) = \mu_1(p_1, T) = \mu_s^0(p_1, T) - kT \ln x. \quad (9.160)$$

If the pressure difference $\Delta p = p_2 - p_1$ is small compared with p_1 , we can approximate $\mu_s^0(p_2, T)$ with the Taylor expansion around $p = p_1$:

$$\mu_s^0(p_2) \simeq \mu_s^0(p_1) + (p_2 - p_1) \left(\frac{\partial \mu_s^0}{\partial p} \right)_{T, N, x}. \quad (9.161)$$

We can find the derivative of the chemical potential from the derivative of Gibbs free energy, because $\mu_s^0 = G_s^0/N$, and therefore

$$\left(\frac{\partial \mu_s^0}{\partial p} \right)_{T, N, x} = \frac{1}{N} \left(\frac{\partial G_s^0}{\partial p} \right)_{T, N, x} = \frac{V}{N} = v_s^0, \quad (9.162)$$

that is, the volume per particle in the pure solute. This gives

$$\mu_s^0(p_2) \simeq \mu_s^0(p_1) + \frac{V}{N} \Delta p \quad (9.163)$$

which we can insert into eq. 9.160, getting

$$\mu_s^0(p_2) \simeq \mu_s^0(p_1) + \frac{V}{N} \Delta p = \mu_s^0(p_1, T) - kTx, \quad (9.164)$$

and therefore

$$\Delta p = -\frac{NkTn}{V} = -\frac{NkTN_B}{VN} = -\frac{N_B kT}{V}, \quad (9.165)$$

where B represent the solute. This pressure difference is called the **osmotic pressure**. And the equation describing the osmotic pressure of a dilute solution is called van't Hoff's formula. This means that the pressure difference needed corresponds to the pressure in an ideal gas with the concentration N_B/V of the solute.

This pressure can be quite significant for realistic, biological systems. For example, for a cell there are about 200 water molecules for every molecule of some other type – this is therefore a dilute solution. Since the atomic weight of water is 18u, the number of water molecules in a liter of water (1 kg) is

$$N_s = \frac{1\text{kg}}{18 \cdot 1.66 \cdot 10^{-27}\text{kg}}, \quad (9.166)$$

and the pressure in a gas of $N_s/200$ particles in 1 liter is

$$\begin{aligned} p &= \frac{NkT}{V} = \frac{(1/200)N_s kT}{0.001\text{m}^3} \\ &= \frac{1.38 \cdot 10^{-23}\text{J/K} \cdot 300\text{K}}{200 \cdot 18 \cdot 1.66 \cdot 10^{-27} \cdot 0.001\text{m}^3} = 6.9\text{N/m}^2. \end{aligned} \quad (9.167)$$

The pressure difference between the inside and the outside of a cell in equilibrium with pure water is therefore approximately 7 atm – which is high!

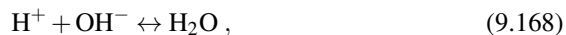
If the pressure difference is smaller than the osmotic pressure, molecules from the pure solvent will flow through the membrane and into the solution. However, if the pressure difference is larger than the osmotic pressure, the pressure will drive the solvent from the solution and into the pure solvent. This process is, not surprisingly, called **reverse osmosis** and currently represents one of the best techniques for desalination (removing salt from seawater) to make freshwater. Making good membranes for this process is an area of great current technological and industrial interest.

9.5.5 Example: Vapor pressure over dilute solution

9.6 Chemical reactions

We now have what we need to address chemical reactions - how some species are transformed into other species without changing the total number of atoms. (The total number of particles may change).

Let us analyze chemical reactions from an example: The formation of water from hydrogen and oxygen.



It is common to describe chemical reactions by its stoichiometric coefficients, v_j :

$$v_1 A_1 + v_2 A_2 + \dots + v_k A_k = 0 , \quad (9.169)$$

where A_j describes a chemical species such as O or O₂ or H₂O. The reaction above would then be described as

$$+1 \text{H}^+ + 1 \text{OH}^- - 1 \text{H}_2\text{O} = 0 , \quad (9.170)$$

that is

$$v_1 = 1 , A_1 = \text{H}^+ , v_2 = 1 , A_2 = \text{OH}^- , v_3 = -1 , A_3 = \text{H}_2\text{O} . \quad (9.171)$$

What characterizes the equilibrium of a system with hydrogen, oxygen and water present? Typically, we will consider equilibrium at constant pressure and temperature, $dp = dT = 0$, which corresponds to typical laboratory conditions. In this case, thermodynamic equilibrium occurs when Gibbs free energy is minimal, that is, when $dG = 0$. In general, we have that

$$dG = -SdT + Vdp + \sum_{i=1}^c \mu_i dN_i = 0 , \quad (9.172)$$

which for $dT = dp = 0$ simplifies to

$$dG = \sum_{i=1}^c \mu_i dN_i = 0 . \quad (9.173)$$

We have equilibrium when one more chemical reaction – one transformation from the left to the right or opposite – does not change Gibbs free energy. For the chemical reaction at hand, the changes in N_i are not arbitrary – they are linked by the coefficients v_i of the reaction. For a single reaction, $dN_j = v_j$. We therefore have that in equilibrium:

$$dG = \sum_j \mu_j dN_j = \sum_j \mu_j v_j = 0 . \quad (9.174)$$

We can determine this condition for any reaction if we only know the chemical potential μ_j for each of the species. (Notice that this relation is derived for constant p and T , but it also applies to the equilibrium of reactions at constant T and V).

Gibbs-Duhem relation. Notice that it is usual to call the relation

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j = 0, \quad (9.175)$$

(which it is in equilibrium) the **Gibbs-Duhem relation** when rewritten as

$$\sum_j \mu_j dN_j = -SdT + Vdp. \quad (9.176)$$

9.6.1 Chemical equilibrium for Ideal Gas systems

For a multi-component ideal mixture, such as a system of ideal gases or any other system well described as an ideal mixture, the chemical potential of component i is

$$\mu_i = \mu_i^0 + kT \ln x_i, \quad (9.177)$$

where $x_i = N_i/N$ and μ_i^0 is the chemical potential of the pure gas – without any other gases present. The equilibrium condition from eq. 9.174 then gives

$$\sum_i \mu_i \nu_i = \sum_i \mu_i^0 \nu_i + \sum_i kT \ln x_i = 0, \quad (9.178)$$

which gives

$$kT \sum_i \ln x_i = - \sum_i \mu_i^0 \nu_i. \quad (9.179)$$

If we now multiply by Avogadro's number, N_A , in each side we get

$$RT \sum_i \nu_i \ln x_i = -N_A \sum_i \mu_i^0 \nu_i = -\Delta G^0, \quad (9.180)$$

where ΔG^0 is the change in Gibbs free energy for the reaction – which is the hypothetical change in G when one mole of H_2 reacts with one mole of OH^- , forming one mole of water at 1 bar. This value of ΔG^0 you can usually find in reference tables. If we take the exponential on both sides, we find

$$\prod_i x_i^{\nu_i} = e^{-\frac{\Delta G^0}{RT}} = K(T), \quad (9.181)$$

where $K(T)$ is only a function of T – and you can often find the value of ΔG^0 in chemical tables. The constant K is usually known as the equilibrium constant – and

we see that we can actually calculate the value of $K(T)$ if we know the chemical potentials μ_i^0 for all the components in the reaction.

For ideal gases, the relation can be rewritten in terms of the concentrations, $n_i = N_i/V$, instead:

$$\begin{aligned} \prod_i x_i^{v_i} &= \prod_i \left(\frac{N_i}{N} \right)^{v_i} = \prod_i \left(\frac{N_i kT}{NkT} \right)^{v_i} \\ &= \prod_i \left(\frac{N_i kT}{pV} \right)^{v_i} = \prod_i \left(\frac{N_i}{V} \right)^{v_i} \left(\frac{kT}{pV} \right)^{v_i} = K(T), \end{aligned} \quad (9.182)$$

which gives

$$\prod_i \left(\frac{N_i}{V} \right)^{v_i} = \frac{K(T)}{\prod_i \left(\frac{kT}{pV} \right)^{v_i}} = K_1(p, T). \quad (9.183)$$

These equations are called the **law of mass action**

Notice that when we calculate $K(T)$ we must be very careful to choose a consistent value for all the energies - we need to select the zero level in the same way for all the particles. One way to define energies that are internally consistent can be explained through a disassociation reaction, where a molecule A_2 disassociates into $2A$. In this case, we should choose the zero level of each composite particle (A_2) to be the energy of the disassociated particles (A) at rest. That is, if the binding energy for A_2 is ε (this is the energy needed to place the two constituents of A_2 infinitely far away from each other), we place the ground state of the composite particle (A_2) at $-\varepsilon$.

9.6.2 Example: Disassociation of hydrogen

We start with the reaction



which also can be written as

$$H_2 - 2H = 0, \quad (9.185)$$

The law of mass action gives:

$$\prod_j n_j^{v_j} = K(T), \quad (9.186)$$

where $j = 1$ corresponds to H_2 , so that $v_1 = 1$, and $j = 2$ corresponds to H , so that $v_2 = -2$. It is usual to write

$$n_{H_2} \text{as } [H_2] \quad (9.187)$$

The law of mass action is therefore

$$[\text{H}_2] [\text{H}]^{-2} = \frac{[\text{H}_2]}{[\text{H}]^2} = K(T) , \quad (9.188)$$

This means that

$$\frac{[\text{H}_2]}{[\text{H}]} = \frac{1}{[\text{H}_2]^{1/2} K^{1/2}} , \quad (9.189)$$

so that the relative concentration of hydrogen is inversely proportional to the concentration of H_2 .

9.6.3 Example: pH and the Ionization of water

Water goes through the process



when in liquid form. This process is called the disassociation of water.

The law of mass action gives:

$$[\text{H}^+] [\text{OH}^-] = [\text{H}_2\text{O}] K(T) . \quad (9.191)$$

In pure water each of the concentrations are

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{mol l}^{-1} . \quad (9.192)$$

We can change this concentration by introducing a proton donor. This increases the number of H^+ ions and decreases the number of OH^- ions to ensure the product of the concentrations is constant.

It is common to introduce the pH through

$$\text{pH} = -\log_{10} [\text{H}^+] . \quad (9.193)$$

The pH of pure water is therefore 7.

Strong acids have low pH values. An apple has pH around 3.

9.6.4 Example: Kinetics, reaction rates, and catalytic processes

What if we study the process



Then the rate at which the concentrations changes are related by

$$\frac{dn_{AB}}{dt} = Cn_A n_B - Dn_{AB} , \quad (9.195)$$

where C describes how AB is formed in collisions and D is the reverse process.

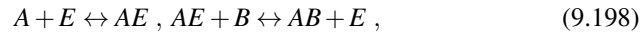
In equilibrium the concentrations does not change, and

$$Cn_A n_B = Dn_{AB} , \quad (9.196)$$

which also are related by the law of mass action:

$$\frac{n_A n_B}{n_{AB}} = \frac{D}{C} = K(T) . \quad (9.197)$$

Now, what if AB is not formed by collisions between A and B , but in a two step process involving a catalyst E :



where E is returned to its original state after the reaction.

What is the point of E ? It may increase the rates significantly?

How? The rates are not only determined by the energy of the final configuration, but also by an energy barrier. The rate is determined by the height of the energy barrier and the temperature (Arrhenius processes). However, by introducing E we may lower the energy barrier in each step, increasing the rate of the reaction.

Now, if the process is rapid so that E is short lived, then AE does not form a significant quantity of A . Then the ratio $n_A n_B / n_{AB}$ is the same as we found above - it is given by the law of mass action. The route taken by the reaction is not important - the end result is the same.

In equilibrium, the direct and the inverse reaction rates must be the same - what we assumed above - is called the *principle of detailed balance*.

9.6.5 Example: Dissolved Oxygen

Henry's law.

9.6.6 Example: Charge distribution of the Hemoglobin Molecule

Longer analytical and numerical example.

9.7 Old Stuff

9.7.1 Intensive, Extensive Variables, and G

We take two identical systems - for example two system of ideal gas or two systems of the einstein crystal - and put them together, forming a system with double the number of particles.

Some variable will change and some will not in this process.

We call the variable that dot not change **intensive variables**. They are p, T, μ .

Other variables are linear in N : They double when the system doubles. We call these variables **extensive variables**. Examples are U, S, V, N, F, G .

If G is directly proportional to N , we can write $G = Ng(p, T)$, where $g = G/N$. What is g ? It is simply

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{T,p} = g, \quad (9.199)$$

and

$$G(T, p, N) = N\mu(T, p). \quad (9.200)$$

9.7.2 Multi-component systems

How can we generalize all our results to multi-component systems?

Originally, we introduced the thermodynamic identity from the microcanonical ensemble, and we found that we could write the entropy, S as a function of U and V , which gave us the differentiale

$$dS = \frac{1}{T}dU - \frac{p}{T}dV, \quad (9.201)$$

then we extended to a system with N particles, getting

$$dS = \frac{1}{T}dU - \frac{p}{T}dV - \frac{\mu}{T}dN. \quad (9.202)$$

This can now directly be extended to a system with $j = 1, \dots, k$ different species by introducing a term related to the diffusive equilibrium for each of the species, resulting in (review the original introduction if you are in doubt):

$$dS = \frac{1}{T}dU - \frac{p}{T}dV - \sum_j \frac{\mu_j}{T}dN_j. \quad (9.203)$$

Similarly, we can generalize the chemical potential we found from Helmholtz free energy (which is the same as the one we found from the entropy):

$$\mu_j = \left(\frac{\partial F}{\partial N_j} \right)_{T,V,\{N_j\}}. \quad (9.204)$$

And similarly for Gibbs free energy:

$$G(T, p, \{N_j\}) = \sum_j N_j \mu_j. \quad (9.205)$$

The thermodynamic identity then becomes

$$TdS = dU + pdV - \sum_j \mu_j dN_j, \quad (9.206)$$

and the differential for G becomes

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j. \quad (9.207)$$

We will use this to address reactions between different chemical components - by introducing the fundamental laws of chemistry.

9.7.3 Matlab MD script

```
% LJ MD calculation
clear all; clf;
L = 10; % Number of atoms = L^2
N = L*L;
rho = 0.8; % reduced density
Temp = 0.1; % reduced temperature
nsteps = 10000;
dt = 0.02;
printfreq = 1;
% Initial coordinates on cubic grid
r = zeros(N,2);
v = zeros(N,2);
[x y] = meshgrid((0:L-1),(0:L-1));
r(:,1) = x(:); r(:,2) = y(:);
% Rescale to wanted rho
L = L*(1.0/rho^2); r = r*(1.0/rho^2);
% Initialize with wanted T
v = sqrt(Temp)*randn(N,2);
% Internal variables
dt2 = dt*dt;
force = zeros(N,2);
epot = zeros(N,1); ekin = epot; t = epot;
% Integrate motion
for i = 1:nsteps
    % Velocity-Verlet - part 1
```

```

    r = r + v*dt + 0.5*force*dt2;
    r = r + (r<0.0)*L - (r>L)*L; % Periodic
    v = v + 0.5*force*dt;
    % Find forces/accelerations
    [force,energy] = LJforce(r,L);
    % Velocity-Verlet - part 2
    v = v + 0.5*force*dt;
    % Store energies
    epot(i) = energy/N;
    ekin(i) = 0.5*sum(sum(v.*v))/N;
    t(i) = i*dt;
    % Plot
    if (mod(i,printfreq)==0)
        tit = sprintf('Timesteps = %d',i);
        plot(r(:,1),r(:,2),'o');
        title(tit);
        axis equal, axis([0 L 0 L])
        drawnow
    end
end
%%
figure
ii = (1:i-1);
plot(t(ii),ekin(ii),'-r',t(ii),ekin(ii)+epot(ii),'k');
xlabel('t')
ylabel('E');
legend('K','E_{TOT}');

```

```

function [force,energy] = LJforce(r,L);
% Calculate the force on each particle and the
% potential energy of a Lennard-Jones system
% with potential energy for each pair:
%  $V(r) = 4*U0*((\sigma/dr)^{12}-(\sigma/dr)^6)$ 
% Variables in: r(1:N,3) coordinates
%               L system size
% Notice: lengths measured in units of sigma
%         energies measured in units of U0
s = size(r);
npart = s(1); dim = s(2);
L2 = L*0.5; mL2 = -L2;
ff = zeros(npart,dim); % forces
en = 0;
for i = 1:npart
    ri = r(i,:);
    for j = i+1:npart
        rj = r(j,:);
        rij = (ri-rj);
        rij = rij + (rij<mL2)*L - (rij>L2)*L;
        r2 = sum(rij.*rij);
        ir2 = 1.0/r2;
        ir6 = ir2*ir2*ir2;
        ir12 = ir6*ir6;
        % Calculate force from i-j interaction
        fij = (2*ir12-ir6)*rij*ir2;
    end
    ff(i,:) = ff(i,:) + fij;
    energy = energy + 0.5*sum(fij.*rij);
end

```

```
        ff(i,:) = ff(i,:) + fij;  
        ff(j,:) = ff(j,:) - fij;  
        % Calculate energy from i-j interaction  
        enij = (ir12-ir6);  
        en = en + enij;  
    end  
end  
en = en*4;  
energy = en;  
ff = ff*24;  
force = ff;  
return
```