Chemical potential and Gibbs Distribution

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1 Chemical potential

We started from the microcanonical ensemble, where U, V, N was constant. Then we introduced the possibility for energy exchange, by looking at systems in contact with a large heat bath. But, still the number of particles were constant. But for many systems we are interested in, the number of particles is not constant: for a crystal growing, for ice melting, for chemical reactions, the number of particles are not constant. How can we extend the methods we have developed to handle non-constant particle numbers?

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

What is this X? We call it the chemical potential: If two systems are at the same temperature and only have a single chemical species and the same value of the chemical potential, there is no net flux of particles from one side to another.

But if the chemical potential is different, there will be a net flux. We have seen this example earlier, when we looked at two gases with different particle numbers in the same volume.

How can we relate the chemical potential to other quantities we know?

First, if we consider two systems A and B in contact with a heat bath at temperature T, but where there is a diffusive equilibrium between A and B. The Helmholtz free energy for this system is then

$$F = F_A + F_B \ ,$$

where $N_A + N_B = N$. Helmholtz free energy will be minium with respect to $dN_A = -dN_B$ at equilibrium, and therefore

$$\frac{\partial F}{\partial N} = \left(\frac{\partial F_A}{\partial N_A}\right)_{T,V} + \left(\frac{\partial F_B}{\partial N_B}\right)_{T,V} = 0 \ ,$$

which gives

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

at equilibrium. This severes as a good definition of chemical potential:

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

so that the differential for Helmholtz free energy is:

$$dF = -SdT - pdV + \mu dN \ .$$

The condition that $\mu_A = \mu_B$ characterizes the diffusive equilbrium between two systems in diffusive contact.

Notice that we cannot really divide particles into smaller pieces than one, so that the chemical potential should be defined as a finite difference:

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

If several chemical species are present, then each species will have its own chemical potential

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

where all the other N_j are kept constant in the derivative.

1.1 Example: Chemical potential of the Einstein crystal

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

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

and

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

which gives

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

1.2 Example: Chemical potential for Ideal gas

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

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

where $Z_1 = n_Q V$ and

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

Helmholtz free energy is therefore:

$$F = -kT \ln Z = -kt \left(N \ln Z_1 - \ln N!\right) .$$

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

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

which gives

$$F = -kT \left(\ln Z_1 - \frac{d}{dN} \ln N! \right) = -kT \left(\ln Z_1 - \ln N\right) = kT \ln(N/Z_1) .$$

We insert $Z_1 = n_Q V$, getting:

$$\mu = kT \ln(N/Vn_Q) = kT \ln(n/n_Q) .$$

(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.

2 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 a the same temperature that may exchange particles, but the two systems are not yet in diffusive. 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, for charged particles we may introduce an electric field with a voltage difference ΔV. We apply this to all particles in system A so that we raise their potential energy by $\Delta\mu$. This is done by choose the potential difference so that

$$q\Delta V = q(V_B - V_A) = \Delta\mu \ .$$

(We could also have used a difference in gravitational potential energy, mgh, or other ways to introduce a potential difference).

Let us now reanalyze the system thermodynamically. We have changed the potential energy of all particles in system A, but we have not made any changes in system B. This means that we have change the energy U_A of system A and Helmholtz free energy F_A, but we have not changed either U_B or F_B. The change in free energy in system A is by the change in internal energy, $U_A = N_A q\Delta V$ – this means that the energy of every state in system A has changed by $\Delta mu = q\Delta V$. This means that the chemcial potential in system A in the state (2) after the potential is applied, can be expressed in terms of the chemical potential in the states (1) before the potential was added:

$$\mu_A(2) = \mu_A(1) + \Delta\mu = \mu_A(1) + (\mu_B(1) - \mu_A(1)) = \mu_B(1) = \mu_B(2) \ .$$

There is therefore no longer any difference in chemical potential – and there will not be any particle flux.

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 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.

2.1 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 Earths surface. The chemical potential of a particle in a gas in a graviational field would therefore have two contributions:

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

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

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

which gives

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

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

$$pV = NkT \ \Rightarrow \ p = \frac{N}{V}kT = nkT \ ,$$

and

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

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 $z_c = 8.5$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.

2.2 Example: Batteries

(Not written yet)

2.3 Potential energy adsorbed in 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 is the consequences for Helmholtz free energy and the chemical potential?

The partition function is

$$Z' = \sum_i \exp(-\epsilon_i/kT - E_0/kT) = \exp(-E_0/kT) \sum_i \exp(-\epsilon/kT) = \exp(-E_0/kT) Z \ ,$$

Heltholtz free energy is therefore

$$F' = -kT \ln Z' = E_0 - kT \ln Z = E_0 + F \ ,$$

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

$$F = -NkT \ln Z + NE_0 \ ,$$

and that the chemical potential therefore is

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

Adding a potential energy per particle therefore corresponds to adding a potential energy to the chemical potential. We call such an addition an extenal 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.

2.4 Example: Modeling potential gradients

3 Thermodynamic relations for chemical potential

Here, we have defined the chemical potential as

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

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

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

We can rewrite this to get:

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

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

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

which means that

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

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

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

Where we now have an intuition for the chemical potential.

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

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

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:

$$U_0 = U_S + U_R \ , \ N_0 = N_S + N_R \ ,$$

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

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

Let us now look at $\ln P$:

$$\ln P(N_1, U_1) = \ln C + \ln g(N_0 - N_1, U_0 - U_1) = \ln C + S(N_0 - N_1, U_0 - U_1)/k \ ,$$

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

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

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

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

and therefore we find:

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

and where normalization now gives:

$$P(N_1, U_1) = \frac{1}{Z_G} ,$$

and

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

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:

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

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

4.1 Average number of particles

The average number of particles is given as

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

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

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

and therefore

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

4.2 Example: CO poisoning

Each hemoglobin molecule has four, independent adsorption sites, each consiting 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 $\epsilon = -0.7eV$.

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

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

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

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

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

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

which means that the probabilty to be occupied is

$$P = \frac{40}{1+40} \simeq 0.98 \ .$$

Now, what happens if CO is also present, which also can be adsorbed. Now, there are three possible states: unoccupied, occupied by O_2 or occupied by CO. The grand partition function is now

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

Now we need numbers. CO is more strongly bound, so $\epsilon_{CO} = -0.85eV$. 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 that oxygen, we would find that

$$\mu_{CO} = -kT\ln(n_Q/n_{CO}) = -kT\ln(n_Q/xn_O) = -kT\ln(n_Q/n_O) + kT\ln x \ ,$$

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

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

and therefore

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

So just a small amount of CO is devastating!

4.3 Numerical example: Vacancies

5 Gibbs Free Energy and Chemical Reactions

We introduced Helmholtz free energy, F, to describe systems with constant T, V, and N. However, in many experimental and practical situations it is not the volume that is constant, but we perform an experiment at constant pressure – this is what happens if we perform an experiment here in the lecture hall.

In this case it is useful to introduce another free energy to address the equilibrium at constant T, p, and N, **Gibbs free energy**, G:

$$G = F + pV = U - TS + pV \ .$$

We can show that Gibbs free energy is minimal in equilibrium. We consider a case where the system S is in thermal equilbrium with a heat reservoir R_1 and mechanical equilbrium with a pressure reservoir R_2. The differential for G is

$$dG = dU - TdS - SdT + pdV + Vdp \ .$$

We insert the thermodynamic identity, $TdS = dU - pdV + \mu dN$, getting:

$$dG = -SdT + Vdp + \mu dN \ ,$$

and when pressure and temperature (and N) is constant, $dp = 0$ and $dT = 0$, $dN = 0$, we get

$$dG_S = 0 \ .$$

This shows that G_S is either a maximum or a minimum. What is it? Any irreversible change in the system S will result in an increase in the entropy, $dS \geq 0$, and therefore $dG \leq 0$, which means that G is a minimum for a system in equilbrium.

From the differential in equation 5 we see that

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial N}\right)_{T,p} dN = -SdT + Vdp + \mu dN \ ,$$

which gives the following expressions:

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

We can now find three Maxwell relations – you may do this for yourself.

6 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

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

and

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

7 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

$$dS = \frac{1}{T}dU - \frac{p}{T}dV \ ,$$

then we extended to a system with N particles, getting

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

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

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

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):

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

And similarly for Gibbs free energy:

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

The thermodynamic identity then becomes

$$TdS = dU + pdV - \sum_j \mu_j dN_j \, ,$$

and the differential for G becomes

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j \, .$$

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

8 Dilute solutions

(Ikke pensum i 2013)

9 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).

We describe a chemical reaction by it stochiometric coefficients, ν_j:

$$\nu_1 A_1 + \nu_2 A_2 + \ldots + \nu_k A_k = 0 \, ,$$

where A_j describes a chemical species such as O or O_2 or H_2O. For example, the reaction

$$\mathrm{H}^+ + \mathrm{OH}^- \leftrightarrow \mathrm{H_2O} \, ,$$

is described as

$$+1\,\mathrm{H}^+ + 1\,\mathrm{OH}^- - 1\,\mathrm{H_2O} = 0 \, ,$$

that is

$$\nu_1 = 1 \, , \; A_1 = \mathrm{H}^+ \, , \; \nu_2 = 1 \, , \; A_2\mathrm{OH}^- \, , \; \nu_3 = -1 \, , \; A_3 = \mathrm{H_2O} \, .$$

Usually, we consider equilibrium in a chemical reaction at constant pressure and temperature – this is how most experiments are done, and how I would do it here in the lecture hall.

In equilibrium, Gibbs free energy must therefore be minimal, and the differential must be zero:

$$dG = \sum_j \mu_j dN_j = 0 \, .$$

Now, what are the changes in N_j in such a chemical potential? Notice, that the N_j values may not be the same – they may all be different. But for each chemical reaction that happens, the relation

$$\sum_j \nu_j A_j = 0 \; ,$$

must hold. What does that means – it means that the changes must be similarly related. If the chemical reaction happens m times, then the change in species j from before and after the reaction is $\nu_j m$. (The sign depends on what way the reaction goes the m times). This means the $dN_j = \nu_j m$, and therefore that

$$dG = \sum_j \mu_j dN_j = \sum_j \mu_j \nu_j m = \left(\sum_j \nu_j \mu_j \right) m \; ,$$

and in equilibrium we know that $dG = 0$. We therefore get a relation that is independent of m:

$$dG = \left(\sum_j \nu_j \mu_j \right) m = 0 \; \Rightarrow \; \sum_j \nu_j \mu_j = 0 \; .$$

This is the condition for chemical equilibrium. We can calculate it 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 applied to the equilibrium of reactions at constant T and V).

Notice: The chemical potential μ_j is an intensive quantity, but it does in principle depend on the other N_i values, because

$$\mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T,p,\{N_i\}} \; ,$$

where the derivative is over all $i \neq j$. But since we expect μ_j to be intensive, we may instead assume that it only depends on the fractions, $X_i = N_i/N$ of particles of species j, which does not change when we change N.

Notice also that it is usual to call the relation

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j = 0 \; ,$$

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

$$\sum_j \mu_j dN_j = -SdT + Vdp \; .$$

10 Chemical equilibrium for Ideal Gas systems

If each of the constituent can be described as ideal gases – which are non-interacting by design and therefore have no cross-dependencies in their chemical potentials, we get nice and simple results.

(How reasonable is this for example for a material in a dilute solution - you should discuss this here!)

For an ideal gas we know that

$$\mu = -kT \ln(n_Q/n) \; ,$$

which we can write as

$$\mu_j = kT \ln(n_j/n_{Q,j} Z_{j,\mathrm{int}}) = kT \left(\ln n_j - \ln c_j \right) \; ,$$

where $c_j = n_{Q,j} Z_{j,\mathrm{int}}$ depends on the temperature, but it does not depend on the concentration n_j (or any of the other concentrations n_i). Here, $Z_{j,\mathrm{int}}$ is the partition function for the other, internal degrees of freedom.

We can rewrite the equilibrium condition to be

$$\sum_j \nu_j \ln n_j = \sum_j \nu_j \ln c_j(T) \ ,$$

which we can write as

$$\sum_j \ln n_j^{\nu_j} = \sum_j \ln c_j^{\nu_j} \ ,$$

and we can write

$$\sum_j \ln n_j^{\nu_j} = \ln \prod_j n_j^{\nu_j} \ ,$$

and

$$\sum_j \ln c_j^{\nu_j} = \ln \prod_j c_j^{\nu_j} = K(T) \ .$$

which is a function of temperature, T, but not the densities n_j. We call this the equilibrium constant. Notice that we can actually calculate this for ideal gases!

We therefore get

$$\prod_j n_j^{\nu_j} = K(T) \ ,$$

which is called the **law of mass action** (massevirkningsloven).

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.

(We will see this clearly in an example later.)

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 consituents of A_2 infinitely far away from each other), we place the ground state of the composite particle (A_2) at $-\epsilon$.

10.1 Example: Disassociation of hydrogen

We start with the reaction

$H_2 \leftrightarrow 2H$

which also can be written as

H_2 - 2H = 0

The law of mass action gives:

$$\prod_j n_j^{\nu_j} = K(T) \ ,$$

where $j = 1$ corresponds to H_2, so that $\nu_1 = 1$, and $j = 2$ corresponds to H, so that $\nu_2 = -2$.

It is usual to write

$$n_{\mathrm{H}_2} as \, [\mathrm{H}_2]$$

The law of mass action is therefore

$$[\mathrm{H}_2]\,[\mathrm{H}]^{-2} = \frac{[\mathrm{H}_2]}{[\mathrm{H}]^2} = K(T) \; ,$$

This means that

$$\frac{[\mathrm{H}_2]}{[\mathrm{H}]} = \frac{1}{[\mathrm{H}_2]^{1/2}\,K^{1/2}} \; ,$$

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

What is $K(T)$? We find that

$$\ln K = \ln n_Q(\mathrm{H}_2) - 2\ln n_Q(\mathrm{H}) - F(\mathrm{H}_2)/kT \; ,$$

where spin factors are put into F. Zero of energy is for an H atom at rest.

If H_2 is more tightly bound, then the more negative if F and the higher is K. As a result there is a higher proportion of H_2 in the mixture – which is not surprising.

10.2 Example: pH and the Ionization of water

Water goes through the process

$$\mathrm{H}_2\mathrm{O} \leftrightarrow \mathrm{H}^+ + \mathrm{OH}^- \; ,$$

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

The law of mass action gives:

$$\left[\mathrm{H}^+\right]\left[\mathrm{OH}^-\right] = [\mathrm{H}_2\mathrm{O}]\,K(T) \; .$$

(We should now really have introduced dilute solutions already – but this is not currently part of the curriculum – we need to change this).

In pure water each of the concentrations are

$$\left[\mathrm{H}^+\right] = \left[\mathrm{OH}^-\right] = 10^{-7}\mathrm{mol}\,\mathrm{l}^{-1} \; .$$

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 usualy to introduce the pH through

$$\mathrm{pH} = -\log_{10}\left[\mathrm{H}^+\right] \; .$$

The pH of pure water is therefore 7.

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

10.3 Example: Kinetics, reaction rates, and catalytic processes

What if we study the process

$$\mathrm{A} + \mathrm{B} \leftrightarrow \mathrm{AB} \; ,$$

Then the rate at which the concentrations changes are related by

$$\frac{dn_{AB}}{dt} = Cn_An_B - Dn_{AB} \; ,$$

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

In equilibrium the concentrations does not change, and

$$Cn_A n_B = Dn_{AB} ,$$

which also are related by the law of mass action:

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

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

$$A + E \leftrightarrow AE \ , \ AE + B \leftrightarrow AB + E \ ,$$

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*.

10.4 Example: Dissolved Oxygen

Henry's law. Needs dilute solutions. Not part of the curriculum. May do later.

10.5 Example: Charge distribution of the Hemoglobin Molecule

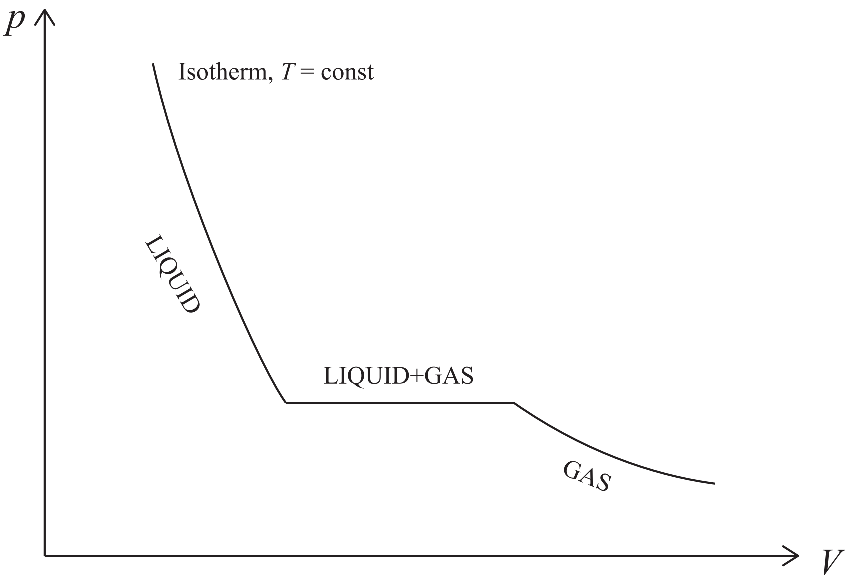
longer analytical and numerical example.

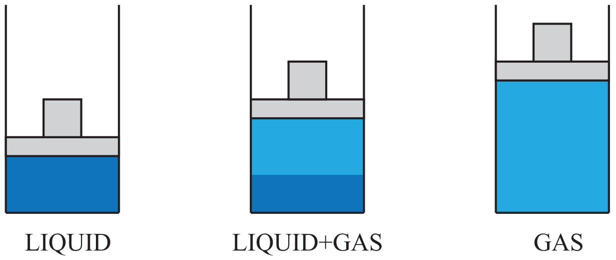
11 Phase transformations

We call the curve $P(V)$ for constant T an isotherm.

Let us sketch an isotherm for a real gas (not ideal) - such as the Lennard-Jones system we introduced.

We can have solid, liquid, and gas phases.



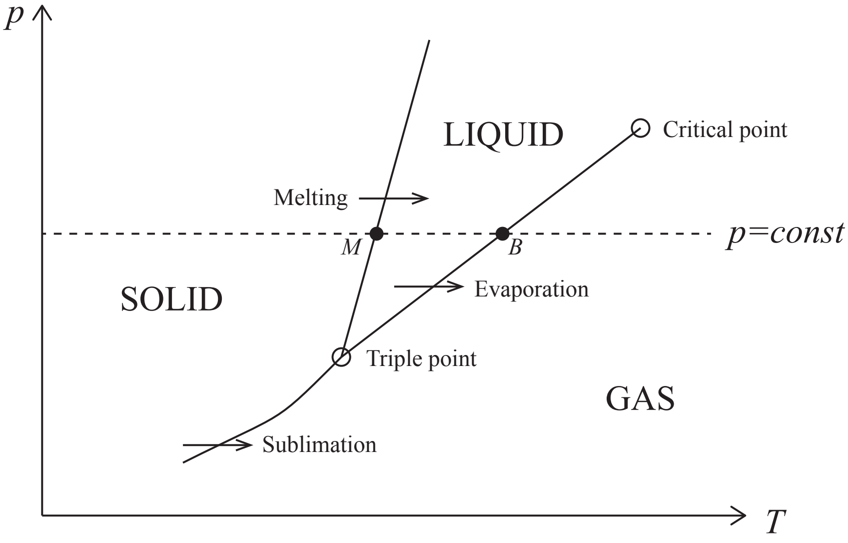


A phase is a portion of a system that is uniform in composition. (Whatever that means).

Two phases can exist at the same time. For example, an isotherm may go from a liquid to a gas, through a region where the liquid and gas coexists.

As we continue to increase the volume (pull the piston), we change the composition of gas and liquid in the same, until all is gas.

Liquid and gas (vapor) may coexist only when the isotherm is below the critical temperature. Above this, we cannot discern a liquid from its vapor, and we talk about a fluid instead.



Critical T for

O2 is 154.3 K H2O is 647.1 K CO2 is 304.2 K N2 is 126.0 K H2 is 33.2 K

What is the condition for the isotherm?

The system is in thermal equilbrium at the isotherm. Since the system is at constant p, and T, this means that Gibbs free energy for the system is minimal.

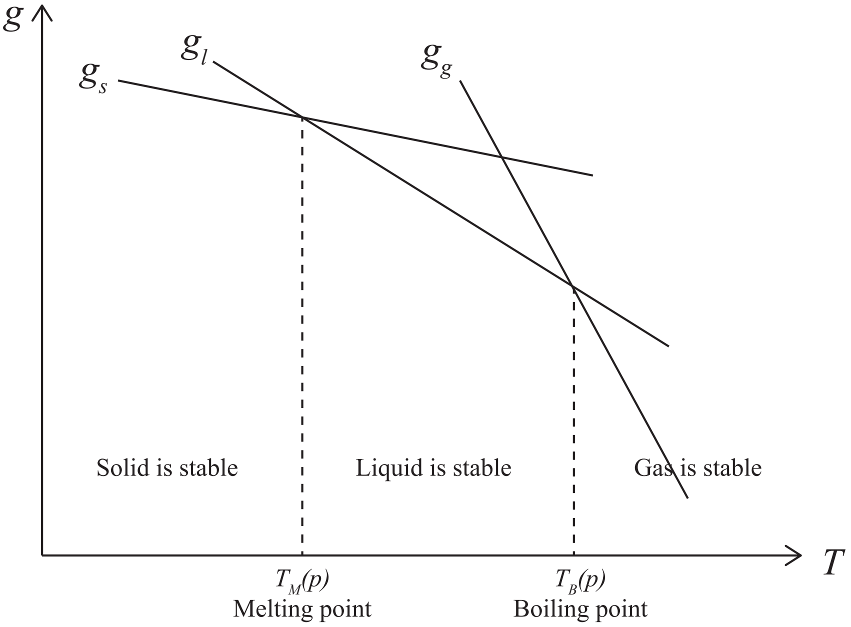
Gibbs free energy will have contributions from both the gas, liquid and solid phases, and we can write $n_g = N_g/N_0$, $n_l = N_l/N_0$ and $n_s = N_s/N_0$. The total Gibbs free energy is

$$G(n_s, n_l, n_g, p, T) = n_s g_s(p,T) + n_l g_l(p,T) + n_g g_g(p,T) \ ,$$

and

$$n = n_s + n_l + n_g = \text{const.} \ .$$

Notice that in general the three (molar) energies may have different behaviors with p, T. We have sketched their behavior for a constant p line as shown in the figure above:



The phase equilibria are characterized by

$$g_l(T, p_v(T)) = g_g(T, p_v(T)) \ ,$$

This also corresponds to $\mu_g(p,T) = \mu_l(p,T)$, but let us stay with Gibbs free energy for now.

11.1 Coexistence curve, $p(T)$

Let us find $p(T)$ for coexistence.

The condition that $g_l = g_g$ along the curve means that if we start at T_0 and then move a small distance dT along the curve, we will get

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

and

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

We subtract the two, getting

$$dg_l = g_l(p_0 + dP, T_0 + dT) - g_l(p_0, T_0) = dg_g = g_g(p_0 + dP, T_0 + dT) - g_g(p_0, T_0) \ .$$

We can now write dg_l and dg_s by the corresponding differentials

$$dg_l = -s_l dT + v_l dp \ ,$$

$$dg_g = -s_g dT + v_g dp \ ,$$

We subtract the two equations, and use that $dg_l = dg_g$, getting:

$$(s_g - s_l)dT - (v_g - v_l)dp = 0$$

and

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

What is $s_g - s_l$?

The increase in entropy when we transfer one molecule (or one mole, depending on the definition of n) from the liquid to the gas phase.

And $v_g - v_l$ is the change in volume in the system when we transfer one molecule from the liquid to the gas.

Notice that this is only true for the coexistence curve $p(T)$.

We can relate $s_g - s_l$ to the heat that must be added to the system in order to keep the temperature constant.

The heat added is

$$Q = T(s_g - s_l) \ ,$$

We introduce

$$L = T(s_g - s_l) \ ,$$

as the **latent heat** of vaporization.

We also introduce

$$\Delta v = v_g - v_l \ .$$

Then we have

$$\frac{dp}{dT} = \frac{L}{T\Delta v} \ .$$

This is called **Clausius-Clapeyrons equation**.

We can make two approximations to make it simpler.

(i) If $v_g \gg v_l$ then $\Delta v \simeq v_g$.

(ii) We assume that the ideal gas law, $pV = NkT$, applies to the gas phase, so that $\Delta v = kT/p$. Then the equation becomes

$$\frac{dp}{dT} = \frac{L}{kT^2} p \ ,$$

and

$$\frac{d}{dT} \ln p = \frac{L}{kT^2} \ .$$

Given $L(T)$, we can integrate the equation to find the curve.

If the latent heat is not dependent on T over a region, then we can find the solution:

$$\int \frac{dp}{p} = L_0 \int \frac{dT}{kT^2} \ ,$$

and

$$\ln p = -L_0/kT + \text{const} \; ,$$

and

$$p(T) = p_0 \exp(-L_0/kT) \; .$$

Triple point: All phases coexist in equilibrium.

Used to define Kelvin scale. at 0.01K above melt temp at atmospheric pressure. (0.01 deg celcius).

11.2 Latent heat and entalpy

The latent heat correspond to the difference of $H = U + pV$ between two phases when the process occurs at constant pressure p. The quantity H is called the entalpy.

Let us show this:

Along the coexistence curve we have $\mu_l = \mu_g$. The theromdynamic identity is therefore

$$TdS = dU + pdV - (\mu_g - \mu_l)\, dN \; ,$$

but since $\mu_g = \mu_l$ the last term is zero.

At constant pressure, the latent heat is the heat TdS transferred, which is

$$L = TdS = dU + pdV = dH = dU + pdV + \underbrace{V dp}_{=0} = H_g - H_l \; .$$

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

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

and

$$H = \int C_p dT \; .$$

11.3 Model system for solid-gas equilibrium

Equilibrium between ideal gas and Einstein crystal.

Energy in crystal is $n\Delta\epsilon - \epsilon_0$, where ϵ_0 is the binding energy,

The partition function for a single oscillator is

$$Z_s = \sum_i \exp(-(i\Delta\epsilon - \epsilon_0)/kT) = \frac{\exp(\epsilon_0/kT)}{1 - \exp(-\Delta\epsilon/kT)} \; .$$

and F_s is $F_s = -kT \ln Z_s$ and $G_s = F_s + pv_s = \mu_s$, where we assume that pv_s is small and we ignore it.

The activity is

$$\lambda_s = \exp(\mu_s/kT) \simeq \exp(F_s/kT) = \exp(-\ln Z_g) = \frac{1}{Z_G} = \frac{\exp(\epsilon_0/kT)}{1 - \exp(-\Delta\epsilon/kT)} \; .$$

For a zero spin ideal gas, the chemical potential is

$$\mu_g = -kT \ln Z = -kT \ln(n_Q/n) \; ,$$

and the activity is

$$\lambda_g = \frac{n}{n_Q} = \frac{p}{kTn_Q} = \frac{p}{kT}\left(\frac{2\pi\hbar^2}{MkT}\right)^{3/2} .$$

For equilibrium the two activities are equal:

$$p = kTn_Q \frac{\exp(\epsilon_0/kT)}{1-\exp(-\Delta\epsilon/kT)}$$

and we insert n_Q, getting

$$p(T) = \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} kT^5/2 \frac{\exp(\epsilon_0/kT)}{1-\exp(-\Delta\epsilon/kT)}$$

12 Modeling real gases using Lennard-Jones systems

12.1 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;
        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
```

12.2 Running MD using LAMMPS and VMD

We can simulate the same system much more efficiently using an optimized C++ code that is parallellized (and can run on GPUs). We have chosen to use the system LAMMPS.

(We can show you how to install the LAMMPS system on a Mac or a Linux box, but this does require some understanding of Linux and installation. But the results are worth it).

When you have it installed, and you know where the program is located, you can run the example “script” in

```
# in.liquidgas
# 3d Lennard-Jones liquid-gas system

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 nve
fix 1 all nvt temp 0.6 0.6 1.0

dump            id all atom 50 dump.melt

#dump           1 all image 25 image.*.jpg type type &
#               axes yes 0.8 0.02 view 60 -30
#dump_modify    1 pad 3

restart         1000 mymelt.restart1 mymelt.restart2

thermo          100
run             15000
```

using the command

```
mpirun -np 4 lmp_openmpi < in.liquidgas
```

where we now run it on 4 cores. You can run it on a single core or on more cores if you have a nice machine.

13 van der Waals equation of state

So how can we describe a real gas like the van der Waals gas?

We know that an ideal gas is described by $pV = NkT$.

How will this equation be modified for a real gas?

Let us see if we can develop a Helmholtz free energy for the real gas.

For an ideal gas we found

$$F_{IG} = -NkT\left(\ln(n_Q/n) + 1\right) \ .$$

What about the LJ gass? In this case, atoms are not allowed to be very closely packed, because of the rapidly growing potential at short interatomic distances. This means that the entire volume V is not really accessible, but only the volume except an excluded volume, V_e. How large is the excluded volume? Let us say it is b per particles, so that the actual accessible volume is $V - Nb$. We replace the colume in n with this volume:

$$F = -NkT\left(\ln(n_Q(V - Nb)/N) + 1\right) \ .$$

This is a correction for the interatomic repulsive forces.

How can we correct for interatomic attractive forces?

13.1 Mean field method

The attractive interactions are in the form of a weak, long range force between all the particles. How can be approximate the contribution from this term?

Let us write the potential energy of two atoms as $\phi(r)$, where r is the distance between the two atoms. If the concentration of atoms in the gas is (approximately) constant $n = N/V$, then the average value of the sum of the interactions from all the other atoms is

$$\int_b^\infty \phi(r)n(r)dV = n\int_b^\infty \phi(r)dV = -2na \ ,$$

where $-2a$ is the value of the integral – the sum of the potential energy over the whole volume. (The factor two is useful, as we will see later). Notice that we have excluded the volume b from the integration. We have also assumed that n is constant. We call this assumption a **mean field** assumption. This assumption ignores correlations between interacting molecules.

What is the change in (internal) energy U of the gas due to this interaction? We have this interaction $-2na$ from each particle in the gas. But – BUT – we should only include a given interaction once and not twice. We must therefore divide by 2 (see where the factor of two comes from).

$$\Delta F \simeq \Delta U = -\frac{1}{2}\left(2Nna\right) = -N^2a/V \ ,$$

(Notice that the exact number of bonds is $N(N-1)/2$, which we have approximated as $N^2/2$.)

Now, we have all terms for the Helmholtz free energy:

$$F_{\mathrm{vdW}} = -NkT\left(\ln(n_Q(V - Nb)/N) + 1\right) - \frac{N^2a}{V} \ ,$$

and the pressure is then

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

which also can be written as

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

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

How can we find b and a?

We can find them for a Lennard Jones gas by simuation. (And of course by direct insertion – since it is possible to estimate the corresponding values theoretically).

13.2 Critical point of the van der Waals gas

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

We introduce

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

We can then rewrite the vdW equation of state as:

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

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

$$\hat{p} = p/p_c \ , \ \hat{V} = V/V_c \ , \ \hat{T} = T/T_c \ .$$

and the equation becomes

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

and

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

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 = [0.8];
for i = 1:length(That)
    T = That(i);
    V = linspace(0.4,20.0,1000);
    p = 8.0/3.0*T./(V-1/3)-3.0./(V.^2);
    plot(V,p)
    hold all
end
hold off
```

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

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

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 conincides.

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

This occurs when

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

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.

13.3 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

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

which we can write as

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

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

Gibbs free energy is then

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

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

$$\hat{g} = \frac{8G}{3NkT_c} \; ,$$

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

$$\hat{g} = -3\hat{\rho} - \frac{8}{3}\hat{T}\ln\left(\frac{3}{\hat{\rho}} - 1\right) + \frac{\hat{P}}{\hat{\rho}} + C \; ,$$

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

$$\bar{\rho} = 3b\rho = 3b\frac{N}{V} \; .$$

We can plot this a function of

14 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

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

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

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

which gives

$$R_c = \frac{2\gamma}{n_l \Delta\mu} \ .$$

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 a an ideal gas – and in that case the chemical potential is

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

where p_{eq} is the equilibrium vapor pressure of the bult 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, $\gamma = 72\,10^{-3}$ N/m. This gives $R_c \simeq 10^{-8}$m = 10nm.