

First Order and Second Order Phase Transitions

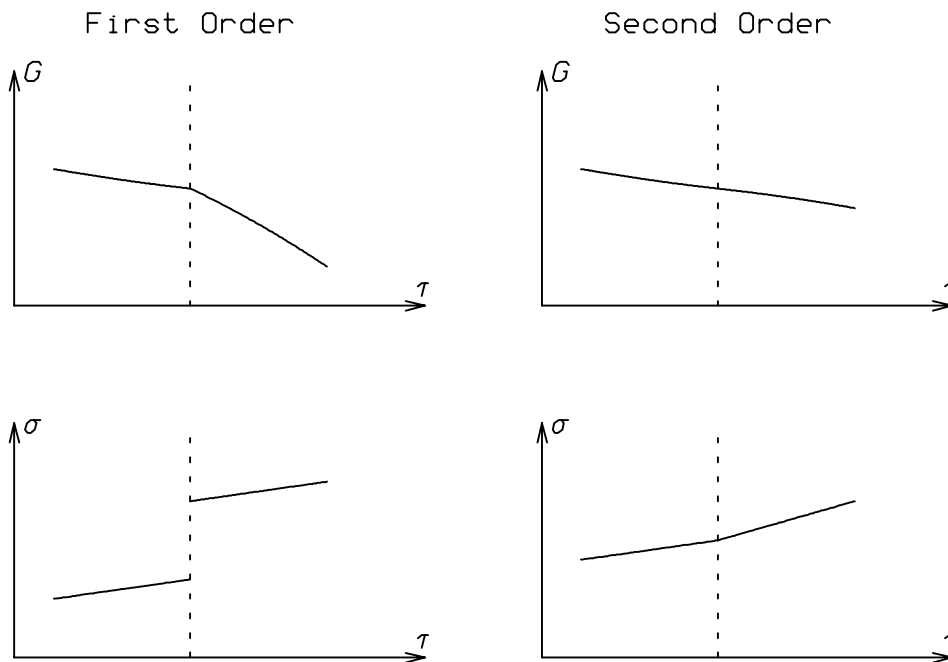
In the phase diagram we've been discussing, as we cross a coexistence curve, G is continuous, but its slope changes discontinuously. This is true whether we cross the curve by changing temperature or by changing pressure. This means that the entropy and volume have step discontinuities. Recall,

$$dG = -\sigma d\tau + V dp + \mu dN ,$$

so

$$\sigma = - \left(\frac{\partial G}{\partial \tau} \right)_{p,N} , \quad V = + \left(\frac{\partial G}{\partial p} \right)_{\tau,N} , \quad \mu = + \left(\frac{\partial G}{\partial N} \right)_{p,\tau} .$$

The situation is sketched in the left pair of plots in the figure which shows the change in entropy resulting from the phase transition. Such a transition is called a first order



transition—the first derivatives of G have discontinuities.

Second order transitions have discontinuities in the second derivatives. So things like the entropy and volume are continuous, but their slopes change suddenly. This is illustrated in the righthand pair of plots.

Since there is a discontinuous change in the entropy in a first order transition, heat must be added, and

$$\Delta\sigma = L/\tau ,$$

where L is the heat required for the system to go from completely liquid to completely vapor at temperature τ . This is called the heat of vaporization (or sometimes the latent

heat of vaporization). Similarly, there are heats of melting (fusion) and sublimation. In a first order transition, the heat capacities $dQ/d\tau$ are δ -functions!

The Clausius-Clapeyron Equation

Now we are going to return to a first order transition, like the liquid–vapor transition in water and see if we can say something about the functional form of the coexistence curve. The vapor pressure curve is given by

$$\mu_l(p, \tau) = \mu_v(p, \tau).$$

Let's move a short distance along the curve in which τ changes by $d\tau$ and p changes by dp . As we move along the curve, the chemical potentials change as well. If we remain on the curve, the change in both chemical potentials must be the same. We have

$$\begin{aligned} d\mu_l(p, \tau) &= d\mu_v(p, \tau), \\ \left(\frac{\partial\mu_l}{\partial p}\right)_\tau dp + \left(\frac{\partial\mu_l}{\partial\tau}\right)_p d\tau &= \left(\frac{\partial\mu_v}{\partial p}\right)_\tau dp + \left(\frac{\partial\mu_v}{\partial\tau}\right)_p d\tau, \\ + \left(\frac{\partial\mu_v}{\partial p}\right)_\tau dp - \left(\frac{\partial\mu_l}{\partial p}\right)_\tau dp &= - \left(\frac{\partial\mu_v}{\partial\tau}\right)_p d\tau + \left(\frac{\partial\mu_l}{\partial\tau}\right)_p d\tau, \\ \frac{dp}{d\tau} &= \frac{- \left(\frac{\partial\mu_v}{\partial\tau}\right)_p + \left(\frac{\partial\mu_l}{\partial\tau}\right)_p}{+ \left(\frac{\partial\mu_v}{\partial p}\right)_\tau - \left(\frac{\partial\mu_l}{\partial p}\right)_\tau}. \end{aligned}$$

Now, what are all these partial derivatives?

$$\begin{aligned} - \left(\frac{\partial\mu_v}{\partial\tau}\right)_p &= - \left(\frac{\partial G_v/N_v}{\partial\tau}\right)_{p, N_v}, \\ &= - \frac{1}{N_v} \left(\frac{\partial G_v}{\partial\tau}\right)_{p, N_v}, \\ &= + \frac{1}{N_v} \sigma_v = \frac{\sigma_v}{N_v} = s_v, \end{aligned}$$

where s_v is the entropy per particle in the vapor phase. The other partial derivative in the numerator gives the entropy per particle in the liquid phase, s_l , while the partials in the denominator give the volumes per particle in the vapor and liquid phases, v_v and v_l , respectively. Altogether, we have

$$\frac{dp}{d\tau} = \frac{s_v - s_l}{v_v - v_l}.$$

This is called the *Clausius-Clapeyron equation*.

Some comments on this equation are in order. First of all, $dp/d\tau$ is the slope of the vapor pressure curve (it has nothing directly to do with the equation of state of the substance). Secondly, we have the entropy per particle and the volume per particle. Since we have a ratio, the equation remains true if we use the entropy per mole and volume per mole, or the entropy per gram and volume per gram, etc. In words, the equation says the slope of the vapor pressure curve is the ratio of the change in specific entropy to the change in specific volume between the vapor and liquid phases. A similar equation applies to each coexistence curve. We just need to put in the right quantities. For example, the melting curve would have

$$\frac{dp}{d\tau} = \frac{s_l - s_s}{v_l - v_s}.$$

A final comment is that the specific entropies and volumes are to be evaluated at the temperature and pressure at the point on the coexistence curve for which the slope is desired.

The Clausius-Clapeyron equation is often written in other forms. In particular, the change in entropy can be immediately related to the latent heat.

$$\frac{dp}{d\tau} = \frac{\ell}{\tau \Delta v},$$

where ℓ is the specific latent heat and Δv is the change in specific volume. We can apply this to the melting of ice and the change in melting temperature with pressure. We start with what happens at 1 atm and $0^\circ\text{C} = 273.15\text{ K}$. The specific latent heat of fusion is $3.35 \times 10^9\text{ ergs g}^{-1}$. The specific volumes of ice and liquid water are

$$v_s = 1.09070\text{ cm}^3\text{ g}^{-1}, \quad v_l = 1.00013\text{ cm}^3\text{ g}^{-1}.$$

Remember, water expands as it freezes! The result is

$$\frac{dp}{dT} = -1.35 \times 10^8\text{ dyne cm}^{-2}\text{ K}^{-1} = -134\text{ atm K}^{-1}.$$

The slope is negative! This accounts for the fact that the melting curve of water leaves the triple point headed up and slightly to the left. Most materials (which expand on melting!) have a melting curve which leaves the triple point headed up and slightly to the right. That is, a large positive slope instead of a large negative slope. This unusual property of water is often said to be the reason why we can have figure skating and ice hockey and why glaciers can flow. As a glacier meets up with an obstruction, the pressure at the point of contact with the obstruction increases until the ice melts and the liquid water can flow around the obstruction and refreeze on the other side. Similarly, ice skates can melt ice and the liquid water helps lubricate the skate. This sounds good, but the numbers don't work out. For example, one needs about 10 meters of ice to generate a pressure of one atmosphere; to get a 10 degree change in melting temperature, we would need a 13 km thick glacier. A 50 kg skater on a pair of 20 cm by 0.1 mm (very sharp) skates would produce about a 1 degree

change in melting temperature. Although this effect may play a role, it is probable that surface effects are more important. For example, a water molecule on the surface forms bonds with fewer neighbors than a molecule in the interior of the solid. Also, it may be attracted to the material in contact with the surface making it easier to “melt.”

Now let’s look at what happens at the normal boiling point of water and the liquid–vapor transition. This occurs at 1 atm and $100^\circ\text{C} = 373.15\text{ K}$. The latent heat of vaporization is $2.257 \times 10^{10}\text{ ergs g}^{-1}$ and the specific volumes of the liquid and the vapor are

$$v_l = 1.043\text{ cm}^3\text{ g}^{-1}, \quad v_v = 1673\text{ cm}^3\text{ g}^{-1}.$$

This gives

$$\frac{dp}{dT} = 3.62 \times 10^4\text{ dyne cm}^{-2}\text{ K}^{-1} = 0.036\text{ atm K}^{-1}.$$

On Mauna Kea in Hawaii at an altitude of about 14,000 ft, the pressure is about 60% of sea level pressure. That is, the pressure has decreased by 0.4 atm. Using the slope we just calculated, we find that the boiling point of water decreases by 11°C to 89°C .

Up to this point, we haven’t made any approximations in dealing with the Clausius-Clapeyron equation. When we deal with the vapor pressure curve, we can usually neglect the volume of the liquid compared to the gas (as we’ve just seen). Also, we can use the ideal gas law to get volume in terms of the pressure and temperature (of course, if the substance is making the transition between liquid and gas, the ideal gas law may not apply all that well!). Recall, we need the specific volume, so if we have the latent heat per unit mass, then we can write $v = RT/pM$, where R is the gas constant (per mole) and M is the molecular weight (mass per mole). Then we have

$$\frac{dp}{dT} = \frac{\ell}{T(RT/pM)} = p \frac{M\ell}{RT^2}.$$

This is yet another form of the Clausius-Clapeyron equation. Note that if we evaluate the slope at the normal boiling point with this expression, we get

$$\frac{dp}{dT} = 3.54 \times 10^4\text{ dyne cm}^{-2}\text{ K}^{-1} = 0.035\text{ atm K}^{-1},$$

within 3% of what we had with the exact expression.

We can rewrite the approximate form of the Clausius-Clapeyron equation as

$$\frac{dp}{p} = \frac{M\ell}{R} \frac{dT}{T^2}.$$

If we now assume that the ℓ does not depend on temperature or pressure, we can integrate this expression.

$$\log p = -\frac{M\ell}{RT} + \text{constant},$$

or

$$p = p_0 e^{-M\ell/RT} .$$

What this says is that a semi-log plot of the vapor pressure against T^{-1} should be a straight line. K&K figure 10.3 shows that this is not all that bad of an approximation. Of course, we know that the latent heat isn't constant and it goes to zero at the critical point. Part of the reason the plot in K&K doesn't look all that bad is that the scale is very coarse and covers 8 orders of magnitude in pressure. Even though the latent heat isn't constant, it's a good approximation to assume it is for a small range of the curve and for a small range, the pressure is well approximated by an exponential of $1/\tau$. (One can think of the integration constant, p_0 , as changing from one small range to the next.)

The van der Waals Equation of State

If we want to have an atomic model for a liquid–vapor transition, we will need to model the gas as something more than non-interacting point particles. A reasonably successful approach models the gas molecules as having an attractive force for separations larger than some distance (roughly the equilibrium separation in the solid). The attractive force gets weaker and goes to zero as the separation is increased. If the molecules get too close, a strong repulsive force arises. We can approximate this force by thinking of the molecules as “hard spheres” which can get as close as twice their radii, but no closer. K&K, figure 10.7 shows a schematic of the potential energy curve of the interaction between two molecules. (Remember the force is the negative of the slope of this curve.) Fortunately, we don't need to know the details of this curve. It's only described to this extent in order to motivate the van der Waals equation of state.

The van der Waals equation of state is

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

where a and b are constants that depend on the gas molecules. b is related to the hard sphere repulsion and a is related to the longer range attraction. This equation of state can be obtained by starting with the Helmholtz free energy of an ideal gas and making corrections to account for these effects.

The ideal gas free energy is

$$F = -N\tau (\log(n_Q/n) + 1) .$$

If each molecule occupies a volume b then the effective volume available is $V - bN$, so the concentration should be replaced by $N/(V - bN)$. Of course, this is not entirely legitimate, but if each molecule has a volume b , then you would expect the pressure to diverge if the density reaches 1 molecule per volume b . This is exactly what this correction provides.

Since there is an attractive force between the molecules, there is a net negative contribution to the energy produced by every pair of molecules. We will evaluate this in an approximate way. Suppose $\phi(r)$ is the potential energy between two molecules separated by r . The potential energy of one molecule due to its interactions with all the other molecules is

$$u = \int_{r_{\min}}^{\infty} n(r)\phi(r) dV ,$$

where r_{\min} corresponds to the minimum distance set by b and $n(r)$ is the concentration at distance r from the given molecule. The simplest thing we can do is to assume $n(r) = n = \text{const}$. This is called the mean field approximation. We assume that each molecule moves in the average field of all the other molecules and does not affect the density of the other molecules. Of course, since there is an attractive force, the concentration of molecules around any given molecule will be higher than it is at a randomly chosen point. That is, the molecular positions are correlated. The mean field approximation ignores these correlations. So, we have

$$u = n \int_{r_{\min}}^{\infty} \phi(r) dV = -2na ,$$

which is really just the definition of a . The factor of two is included for computational convenience. Due to its interactions with all the other molecules, a given molecule has, on the average, a change to its energy of $-2na$. There are N molecules, so the total change in energy due to the attractive part of the van der Waals interaction is

$$\Delta U = -2a \frac{N^2}{V} ,$$

However, this double counts the interaction energy since each molecule is counted twice: once while contributing to the mean field and once while being acted upon by the mean field. So we need to divide by a factor of two (why we put 2 in to start with!). So

$$\Delta U = \Delta F = -a \frac{N^2}{V} .$$

Our final approximate expression for the free energy of a van der Waals gas is

$$F = -N\tau \left(\log \frac{n_Q(V - bN)}{N} + 1 \right) - a \frac{N^2}{V} .$$

We differentiate with respect to the volume to get the pressure,

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

which can be rearranged to

$$\left(p + a \frac{N^2}{V^2} \right) (V - bN) = N\tau .$$

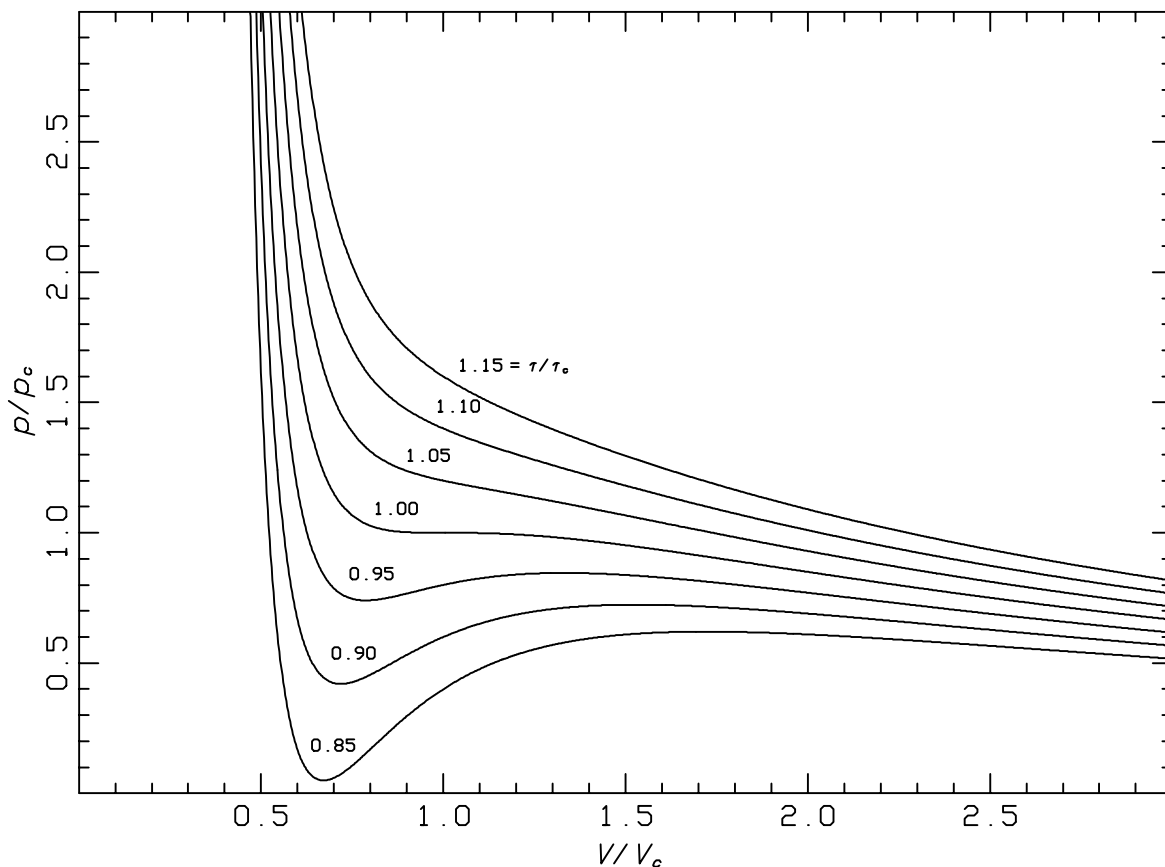
We can put the van der Waals equation of state into dimensionless form if we define

$$p_c = a/27b^2, \quad V_c = 3bN, \quad \tau_c = 8a/27b.$$

Then

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

This equation is plotted for several values of τ in the figure. For large τ , it approaches
van der Waals Isotherms



the ideal gas equation of state, but for small τ there are large deviations from the ideal gas equation of state. We will explore these deviations and see what they have to do with phase transitions next time!