Lecture 18

In the previous lecture, we derived the critical volume for a Van Der Waals gas:

$$V_{\mathrm{C}} = 3Nb$$

Using this volume and the above equations then gives

$$T_{\mathrm{C}} = \frac{8a}{27k_{\mathrm{B}}b}$$

and

$$P_{\mathrm{C}} = \frac{a}{27b^2}$$

So what happens at the critical point? Well, let's look at the isothermal compressability:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T_c}$$

We have that

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0$$

and so the isothermal compressability diverges!

So, in order to figure out what happens below the critical temperature, let's look at the Gibbs' Free energy. We're choosing this as the Gibb's function is useful for experiments which are carried out under constant temperature and constant pressure.

To get the Gibb's function, we'll first calculate the Helmholtz function for the VdW gas, which is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

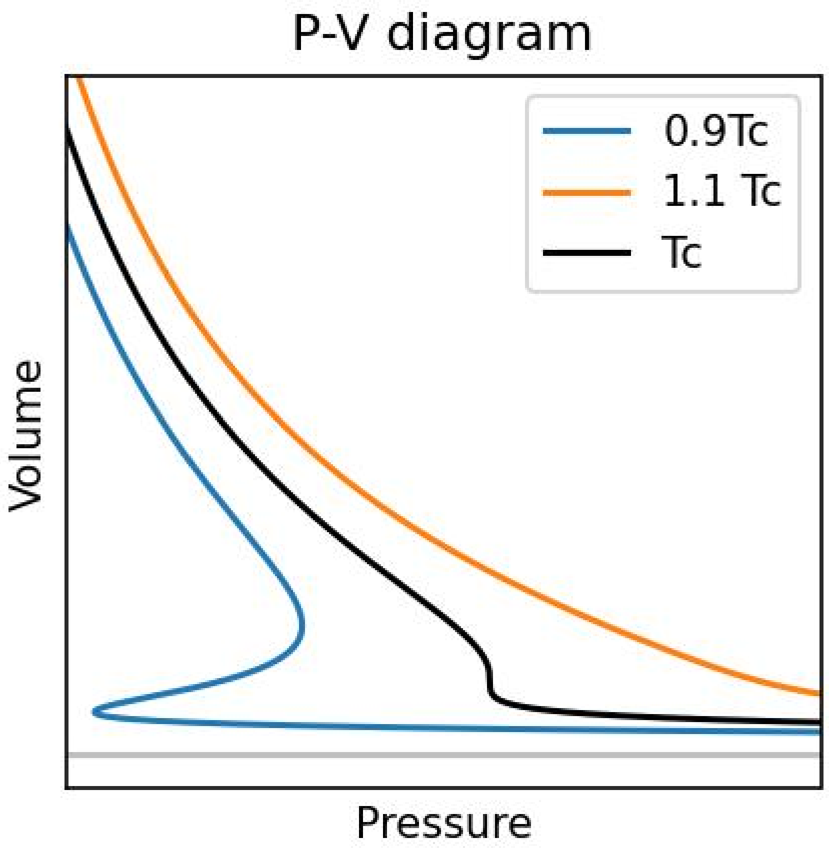
Solving for F this, and substituting P from earlier, gives

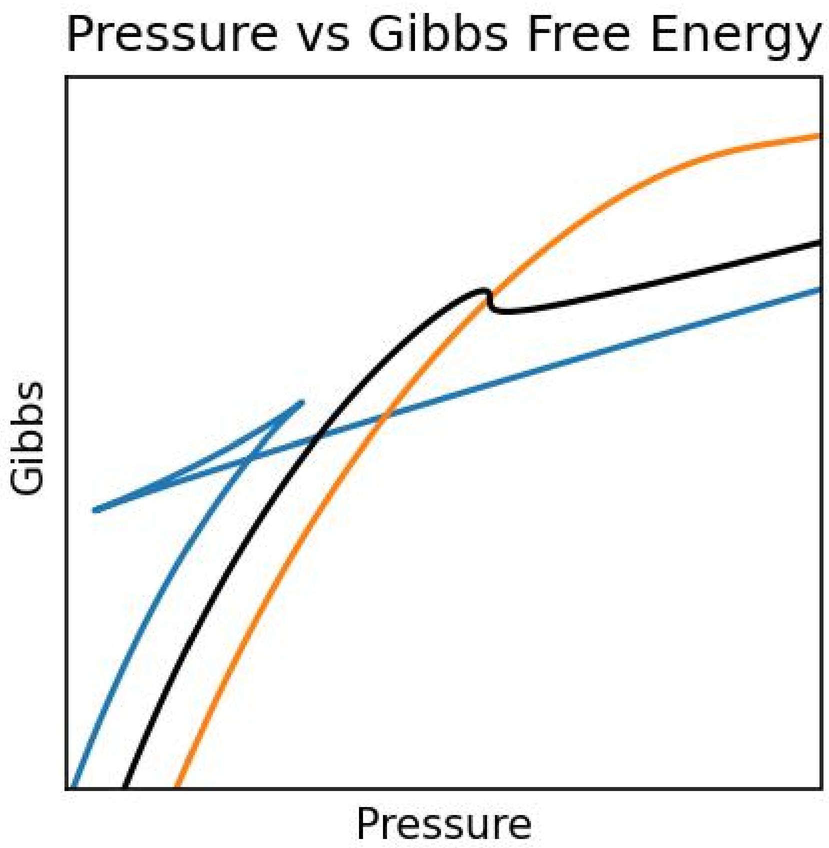
$$F = +f(T) - \left(\int \frac{Nk_{\mathrm{B}}T}{V - Nb} - \frac{aN^2}{V^2}\mathrm{d}V\right)$$
$$F = f(T) - Nk_{\mathrm{B}}\ln(V - Nb) - \frac{aN^2}{V}$$

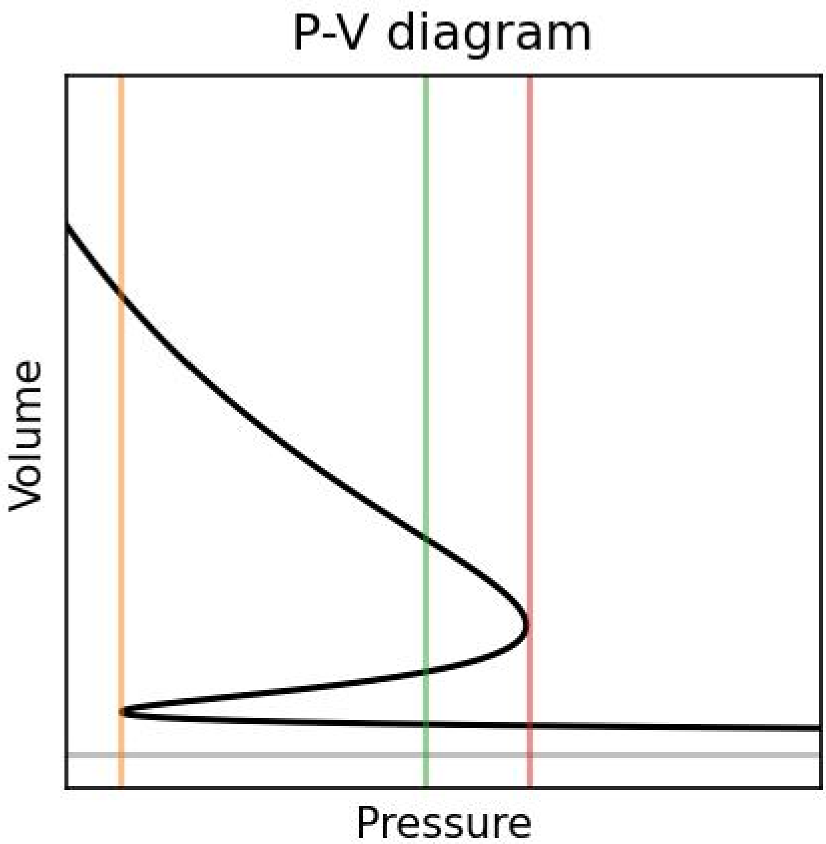
where $f(T)$ is some function of temperature that we don't really care about. This is because the Gibb's free energy is given by

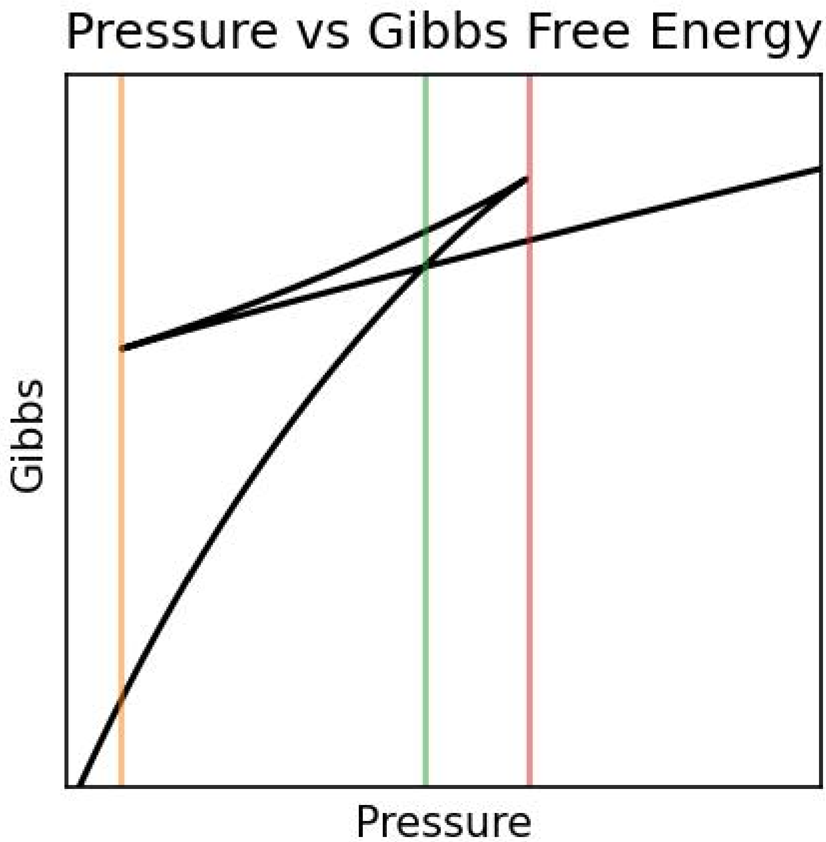
$$G = F + PV = f(T) - Nk_{\mathrm{B}}\ln(V - Nb) - \frac{aN^2}{V} + PV$$

The Volume and Gibb's functions for a VdW gas are shown below versus P for three different temperatures (one above the critical temperature, one at the critical temperature, and one below).









So what does this translate to? It means your system can be in 2 states (a low volume or high volume) state at the same time. Physically, this would mean if you had a system which started as a liquid, then at this point, your system can exist both as a liquid and a gas as the gibbs energy for both phases is the same!

The upper triangle of the Gibbs-Pressure diagram is an interesting phase space. Normally, it's very hard to get a system in there as they are states with higher Gibbs energies, but it is possible. We won't discuss these states in this course, but perhaps you will in future courses.