

# Lecture 17

## Real Gases

So, we know of particular cases when gases do not behave like an ideal gas. For example, as they cool, their heat capacities diverge from the constant that the ideal gas law predicts. So let's look at a few ways in which we can improve on an ideal gas.

Consider again the equation of state of an ideal gas:

$$PV = Nk_B T$$

This equation leads to isotherms as plotted in the left of the below figure. To try and make this equation match the observed behaviour of real gases, we can think of two simple modifications:

1. Allow for non-zero molecule size. In essence, this means that molecules are no longer free to travel anywhere within the gas - instead, the volume they can probe is reduced slightly by the volume taken up by other molecules. We can simply parameterise this as  $V \rightarrow V - Nb$ , where  $b$  is somehow related to the molecule size.
2. Allow for molecular attraction. If the density of the gas is given by  $N/V$ , then the change in energy related to  $\frac{aN^2}{V^2}dV$ . This effectively increases the pressure we should see in the gas relative to the ideal pressure by  $P = P_{\text{ideal}} + \frac{aN^2}{V^2}$

These modifications then give Van Der Waal's equation of state

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T$$

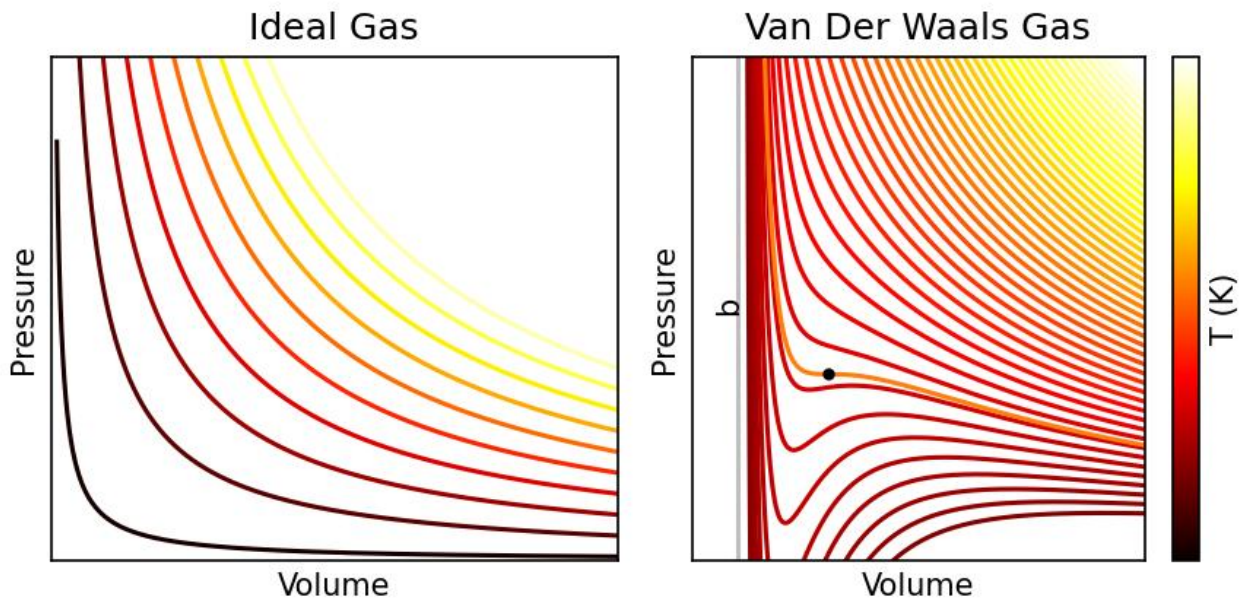
This equation leads to isotherms as plotted on the right of the below figure.

### Aside

This same equation can be arrived at in a more formal manner by considering the following. If we let the partition function for our gas be

$$Z_N = \frac{1}{N!} \left( \frac{V - Nb}{\lambda_{\text{th}}^3} \right)^N e^{-\beta(-aN^2/V)}$$

where again we've reduced the volume to account for the volume taken up by other molecules, and included an additional energy term in the partition function related to the interaction energy  $-aN^2/V$ . We can then calculate the Helmholtz free energy using  $F = -k_B T \ln(Z_N)$  and then  $P = -\left(\frac{\partial F}{\partial V}\right)_T$  to get the above equation of state.



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

For an ideal gas, this is always positive (as the last term is always negative, as the isotherms always have a negative slope). However, as we can see from the plot of the Van der Waals equation of state, at low temperatures, there are regions where  $\left( \frac{\partial V}{\partial P} \right)_T$  is positive, meaning  $\kappa_T$  becomes negative. Under such conditions, increases the pressure exerted on the gas causes the volume to increase rather than decrease. Given that this means work is done on the gas ( $W = -PdV$ ), then energy is provided to further increase the pressure - meaning this configuration is highly unstable!

There is a critical temperature whose isotherm does not have a positive gradient, but which has an inflection point - this is the critical temperature, which we'll discuss in a few lectures time.

Let's now determine the location of this critical point for a Van der Waal's gas. Solving the Van der Waal's equation for  $P$ , and assuming we're working with 1 mole, gives:

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

The inflection point occurs when

$$\left( \frac{\partial P}{\partial V} \right)_T = -\frac{Nk_B T}{(V - Nb)^2} + \frac{2aN^2}{V^3} = 0$$

and

$$\left( \frac{\partial^2 P}{\partial V^2} \right)_T = \frac{2Nk_B T}{(V - Nb)^3} - \frac{6aN^2}{V^4} = 0$$

Solving this both for  $Nk_B T$  gives

$$\frac{2aN^2(V - Nb)^2}{V^3} = Nk_B T = \frac{6aN^2(V - Nb)^3}{2V^4}$$

which gives

$$2 = \frac{3(V - Nb)}{V}$$

and thus the critical volume is

$$V_C = 3Nb$$

Using this volume and the above equations then gives

$$T_C = \frac{8a}{27k_B b}$$

and

$$P_C = \frac{a}{27b^2}$$

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 Gibbs' function is useful for experiments which are carried out under constant temperature and constant pressure.

To get the Gibbs' 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

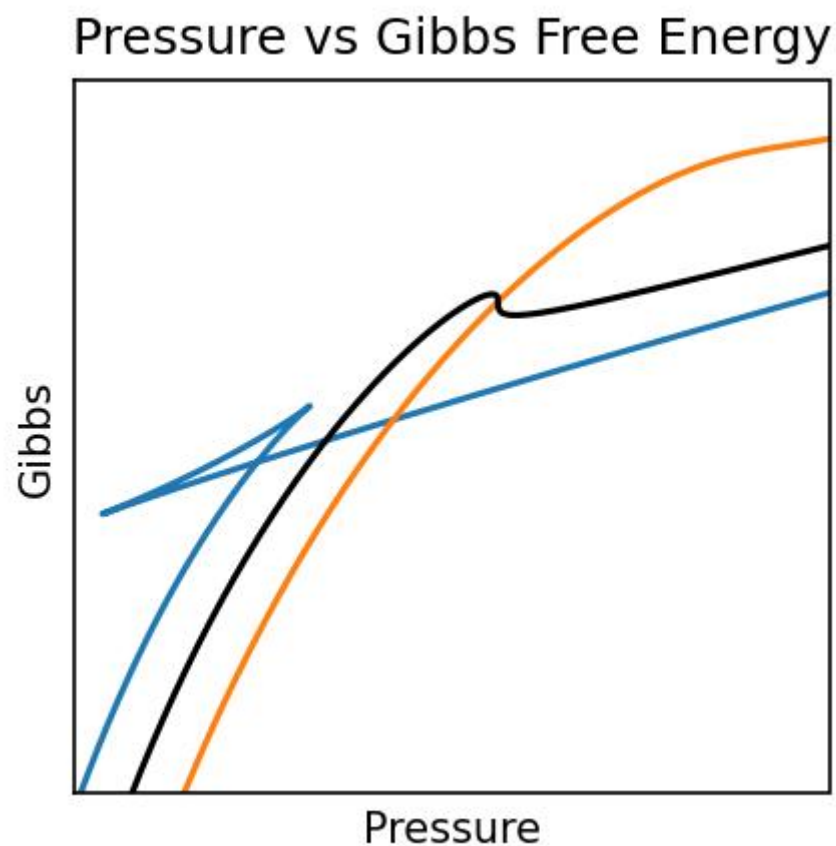
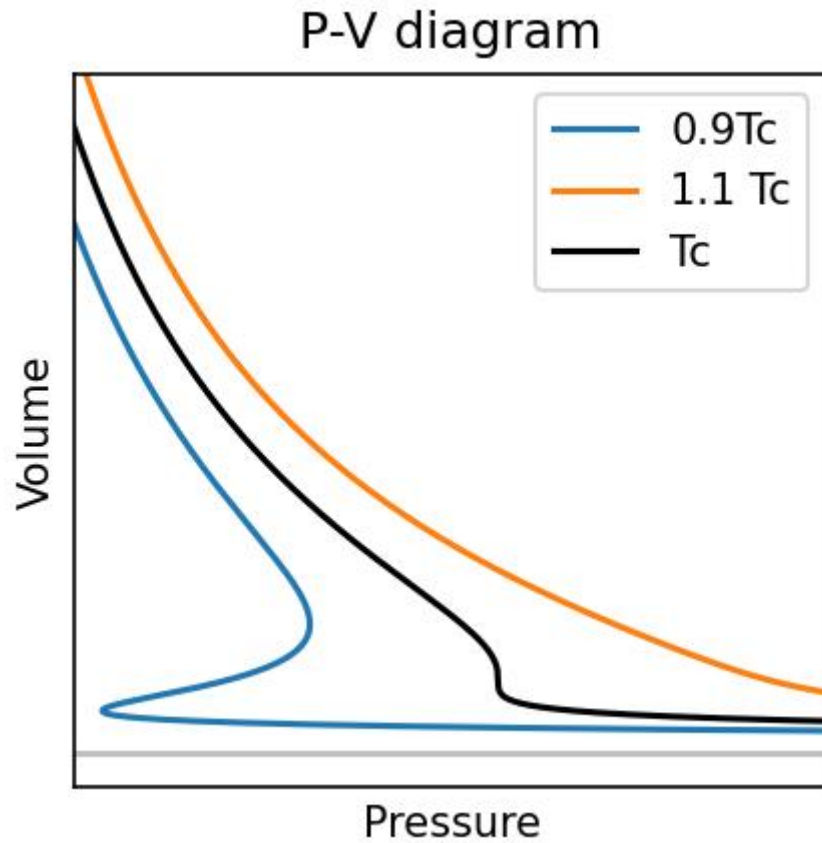
$$F = +f(T) - \left( \int \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2} dV \right)$$

$$F = f(T) - Nk_B \ln(V - Nb) - \frac{aN^2}{V}$$

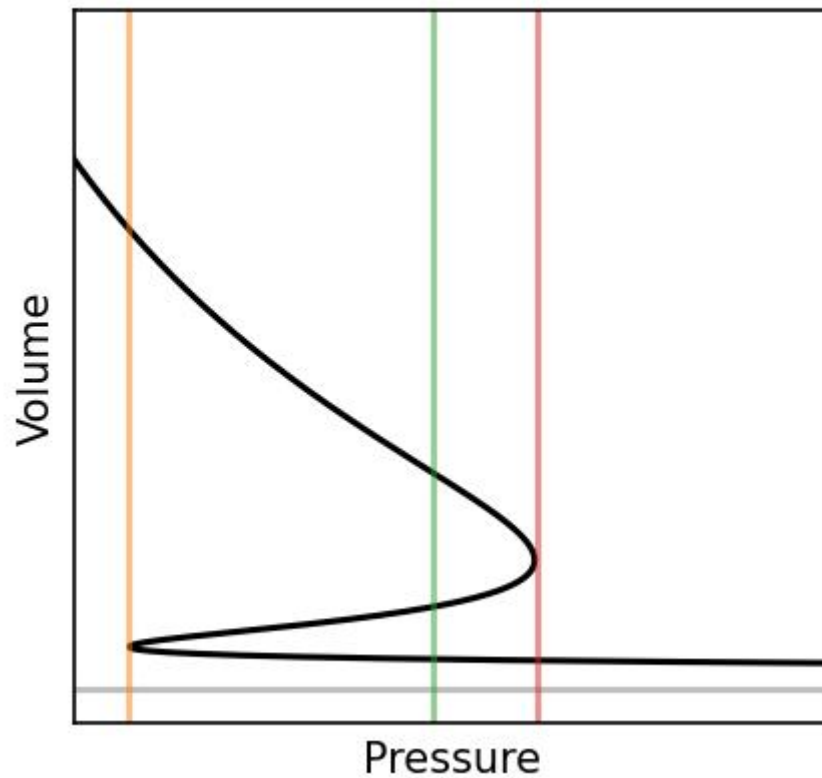
where  $f(T)$  is some function of temperature that we don't really care about. This is because the Gibbs' free energy is given by

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

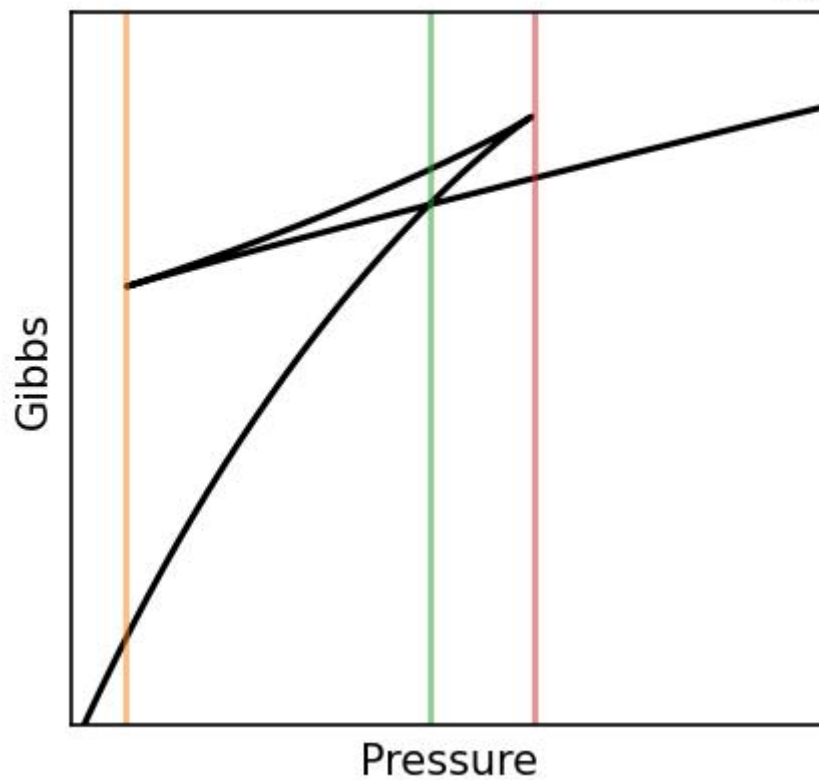
The Volume and Gibbs's functions for a VdW gas are shown below versus  $P$  for three different temperatures (one above the critical temperature, one at the critical temperature, and one below).



P-V diagram



Pressure vs Gibbs Free Energy



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.