

## Reading

Finish K&K chapter 10.

## Phase Transitions and the van der Waals Equation of State

Last time, we discussed the van der Waals equation of state. Note that we didn't derive the equation of state. We simply showed how it might plausibly come from a plausible model of the interaction energy between molecules. The van der Waals corrections to the ideal gas equation of state are really the first terms in a Taylor expansion. Higher order terms are needed to accurately model a real gas.

Our goal is not accurate modeling of a gas, but a model for a phase transition and that's what we will consider here. Recall that the van der Waals equation of state is

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

where  $b$  is a volume related to the short range "hard sphere" repulsion of the molecules and  $a$  is a volume times an energy related to the longer range attraction between molecules.

We put the van der Waals equation of state into dimensionless form with the definitions

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

and the equation of state becomes

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

In fact it's convenient to work in the dimensionless variables

$$\hat{p} = \frac{p}{p_c}, \quad \hat{V} = \frac{V}{V_c}, \quad \hat{\tau} = \frac{\tau}{\tau_c},$$

in which the equation of state becomes

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

A plot of the isotherms on a  $pV$  diagram showed that for  $\hat{\tau} \gg 1$  and  $\hat{V} \gg 1/3$ , they look very much like the ideal gas isotherms. In the neighborhood of  $\hat{\tau} = 1$ , the curves develop a "wiggle," and for small  $\hat{\tau}$ , the volume is a multivalued (there are three roots) function

of the temperature. We can get a little more insight by differentiating the pressure with respect to the volume at fixed temperature:

$$\hat{p} = +\frac{8\hat{\tau}}{3\hat{V}-1} - \frac{3}{\hat{V}^2},$$

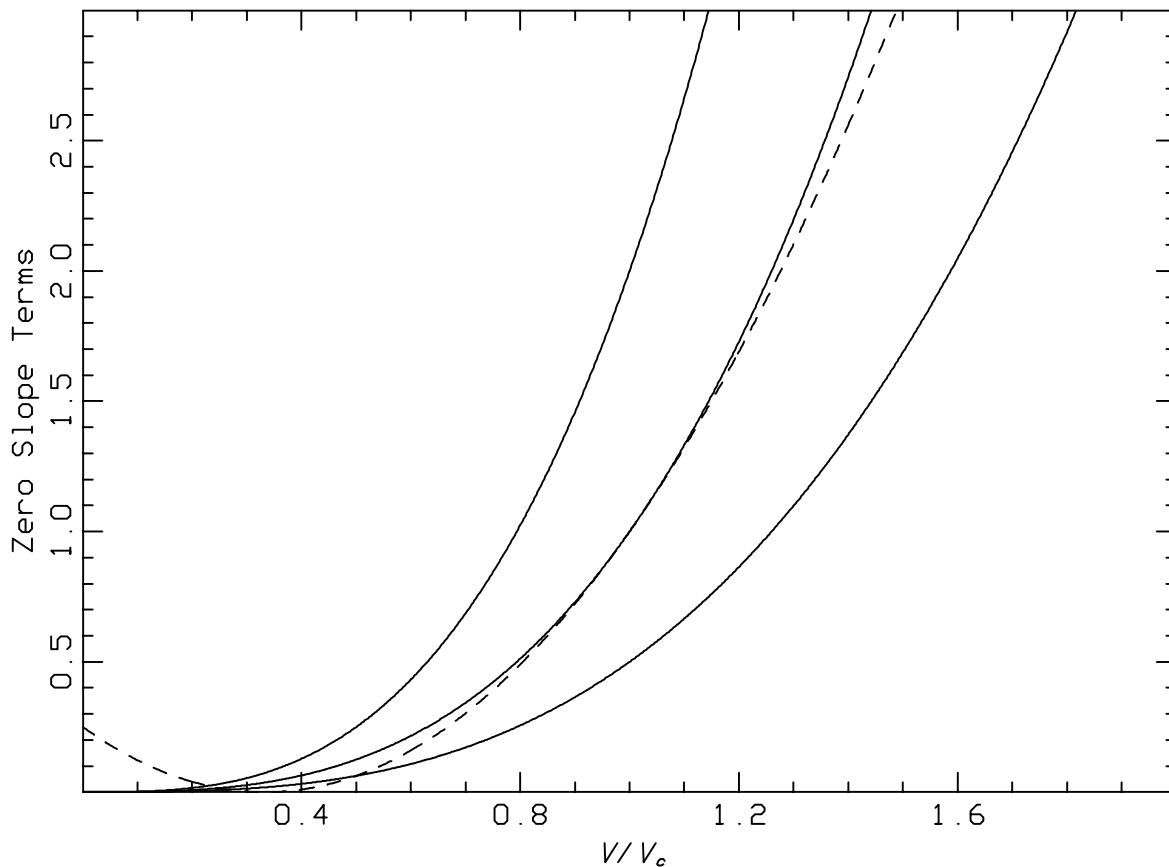
$$\frac{d\hat{p}}{d\hat{V}} = -\frac{24\hat{\tau}}{(3\hat{V}-1)^2} + \frac{6}{\hat{V}^3},$$

$$\frac{d^2\hat{p}}{d\hat{V}^2} = +\frac{144\hat{\tau}}{(3\hat{V}-1)^3} - \frac{18}{\hat{V}^4},$$

The extrema of the pressure along an isotherm occur when  $d\hat{p}/d\hat{V} = 0$  which gives the condition

$$\hat{\tau}\hat{V}^3 = \frac{1}{4}(3\hat{V}-1)^2.$$

The right hand side of this equation is plotted as the dashed line in the figure. Solid



curves show the left hand side for  $\hat{\tau} = 2, 1,$  and  $1/2$  from left to right. The curves always have an intersection at  $\hat{V} < 1/3$ , since  $\hat{V} = 1/3$  is the point at which the right hand side goes to zero. However, the volume cannot be as small as or less than  $\hat{V} = 1/3$  as this corresponds to the hard spheres in contact and a singularity in the pressure. This means that the entire region of this diagram with  $\hat{V} \leq 1/3$  is unphysical and does not correspond

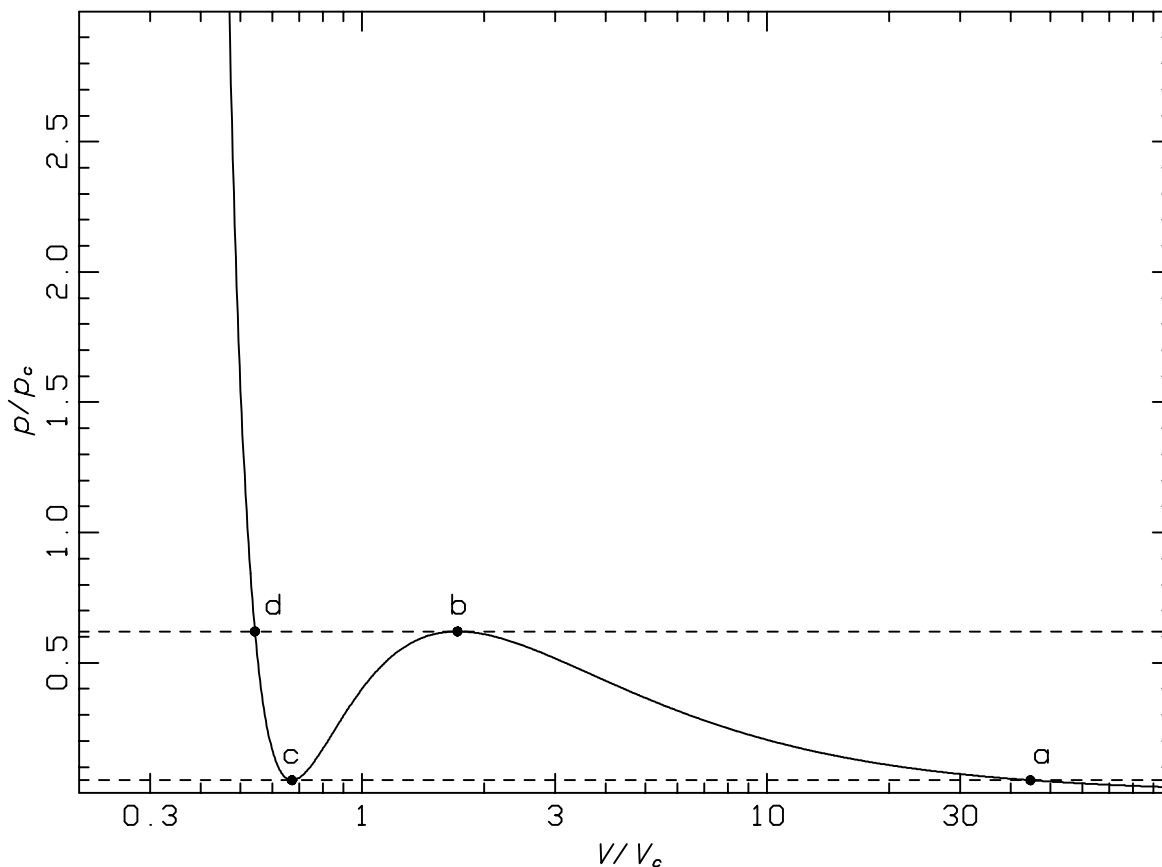
to real solutions. If the temperature is high enough, the unphysical root is the only root of the equation, the volume is a single valued function of temperature, and there is no phase transition. An example is the  $\hat{\tau} = 2$  curve on the diagram. If the temperature is low enough, there are two roots in the physical region, the isotherm has a wiggle, and  $\hat{V}$  is a triple valued function of  $\hat{p}$  for  $\hat{p}$  between the two roots. This case is illustrated by the  $\hat{\tau} = 1/2$  curve in the figure. There is a root just past  $\hat{V} = 1/3$  and another outside the figure up and to the right (the cubic curve eventually catches up to the quadratic curve). This case corresponds to a phase transition. The dividing line between the two cases occurs when the cubic curve just touches (is tangent to) the quadratic curve. This is illustrated by the  $\hat{\tau} = 1$  curve. This case corresponds to the critical point which divides the phase transition region from the no phase transition region. Since the slope of the isotherm is 0, but  $\hat{V}$  remains a single valued function of  $\hat{p}$ , this point must be a horizontal ( $d\hat{p}/d\hat{V} = 0$ ) inflection point. At an inflection point, the second derivative is 0. In other words, in this case we find the critical point by setting both the slope and the second derivative to zero. If we do this, we find

$$\hat{p} = 1, \quad \hat{V} = 1, \quad \hat{\tau} = 1,$$

which is what motivated the definition of  $p_c$ ,  $V_c$ , and  $\tau_c$  in the first place!

Now consider an isotherm for a temperature less than  $\tau_c$ , for example,  $\hat{\tau} = 0.85$  as shown in the figure. Note that the plot has a logarithmic volume axis in order to get everything in but still be able to see what's happening at the "wiggle." The dashed lines delimit the lower ( $\hat{p} = 0.0496$ ) and upper ( $\hat{p} = 0.6206$ ) pressures for which  $\hat{V}$  is triple valued on this isotherm. The labeled points show the intersections of these lines with the isotherm. We suppose our van der Waals gas is in a cylinder topped by a piston with a weight on it to provide the pressure. The cylinder is in contact with a thermal reservoir to maintain constant  $\hat{\tau}$ . Suppose we start with a big volume and low pressure—that is, to the right of point  $a$  on the isotherm. We slowly and carefully add a bit of weight to the piston. This increases the pressure and the volume decreases in response. Some mechanical work was done on the gas and some heat was transferred to the heat reservoir. We moved left along the isotherm. We continue increasing the pressure and moving left along the isotherm. Once we pass point  $a$ , we have to be extremely careful that the gas doesn't condense into a liquid. Suppose we are careful and we get to point  $b$ . At point  $b$ , we add just a tiny bit more weight to the top of the cylinder. What happens? Once we get to the left of point  $b$  decreasing the volume lowers the pressure the gas can support, this means the volume decreases even more which means the pressure decreases even more, etc. No point on the isotherm between  $b$  and  $c$  is stable! Anywhere in this region, a slight lowering of the pressure, causes a runaway collapse. Once we get to point  $b$ , and we continue to increase the pressure, we will wind up at point  $d$ . If we start to the left of point  $d$ , with the system a liquid, and slowly remove weight to lower the pressure, and we get to point  $c$ , we can't lower the pressure any further. If we try, we will wind up at point  $a$ .

We've just shown that all points between  $b$  and  $c$  are mechanically unstable. However, there are points to the right of  $b$  and the left of  $c$  where the Gibbs free energy is not a

van der Waals Isotherm with  $\tau/\tau_c = 0.85$ 

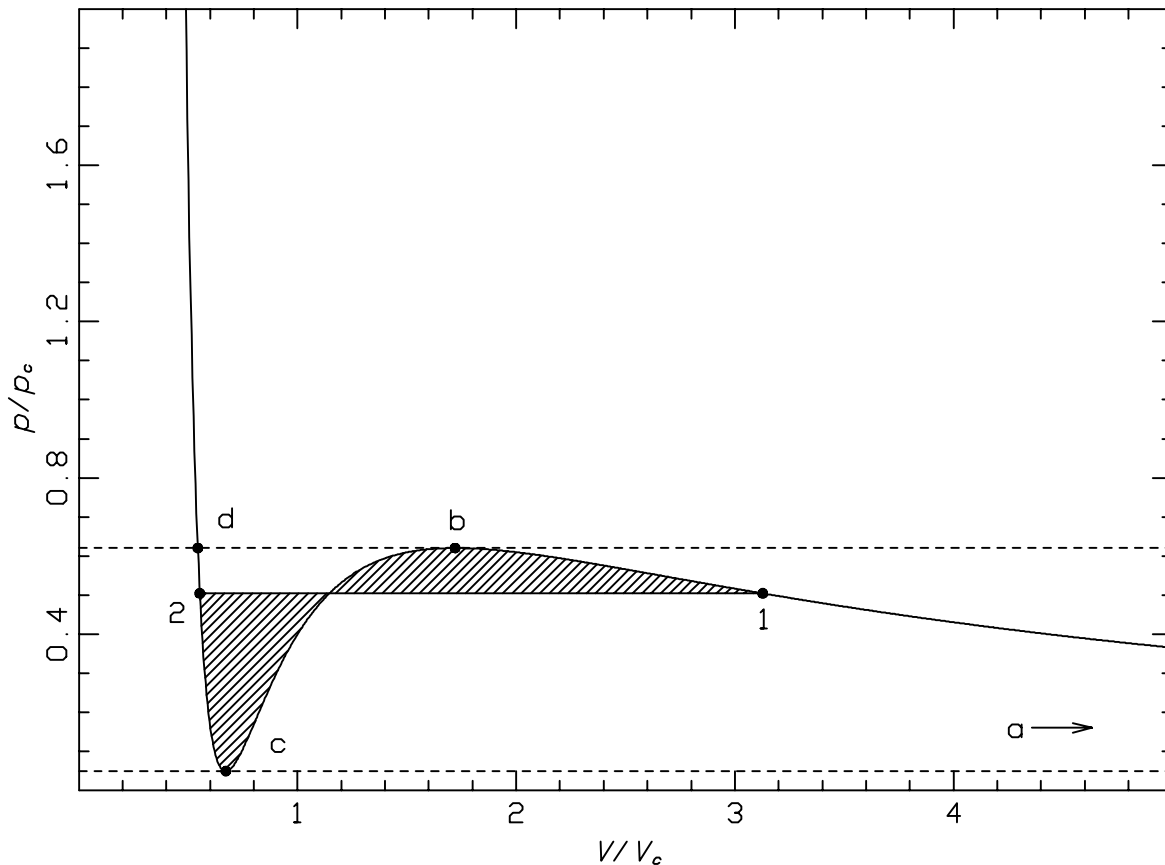
minimum when on the isotherm. How can this be? Again, we start to the right of  $a$  and follow the isotherm. Since the number of particles isn't changing and the temperature isn't changing, we have

$$G(\tau, p, N) = N\mu(\tau, p) = \int_{p_0}^p V dp + N\mu(\tau, p_0),$$

where  $p_0$  is the pressure where we start. As we go along the isotherm to the left, the Gibbs free energy increases ( $V > 0$  and  $dp > 0$ ) until we reach point  $b$ . At this point, it starts to decrease and continues to decrease until we reach point  $c$ . But, when we get to point  $c$ , it's not as low as it was at point  $a$ , because the volume is smaller on  $b \rightarrow c$  than it was on  $a \rightarrow b$ . After point  $c$ , the free energy increases again. At point  $d$ , the free energy still isn't as large as it was at point  $b$  (for the same reason as before). So what does all this tell us? First of all, for a given pressure between the two dashed lines, we can be on the  $a \leftrightarrow b$  or  $c \leftrightarrow d$  segment of the isotherm. The  $b \leftrightarrow c$  segment is excluded because it's unstable. Near  $a$  or  $c$ , the  $a \leftrightarrow b$  segment has the lowest free energy and will be the equilibrium phase. Near  $b$  or  $d$ , the  $c \leftrightarrow d$  segment has the lowest free energy and will be the equilibrium

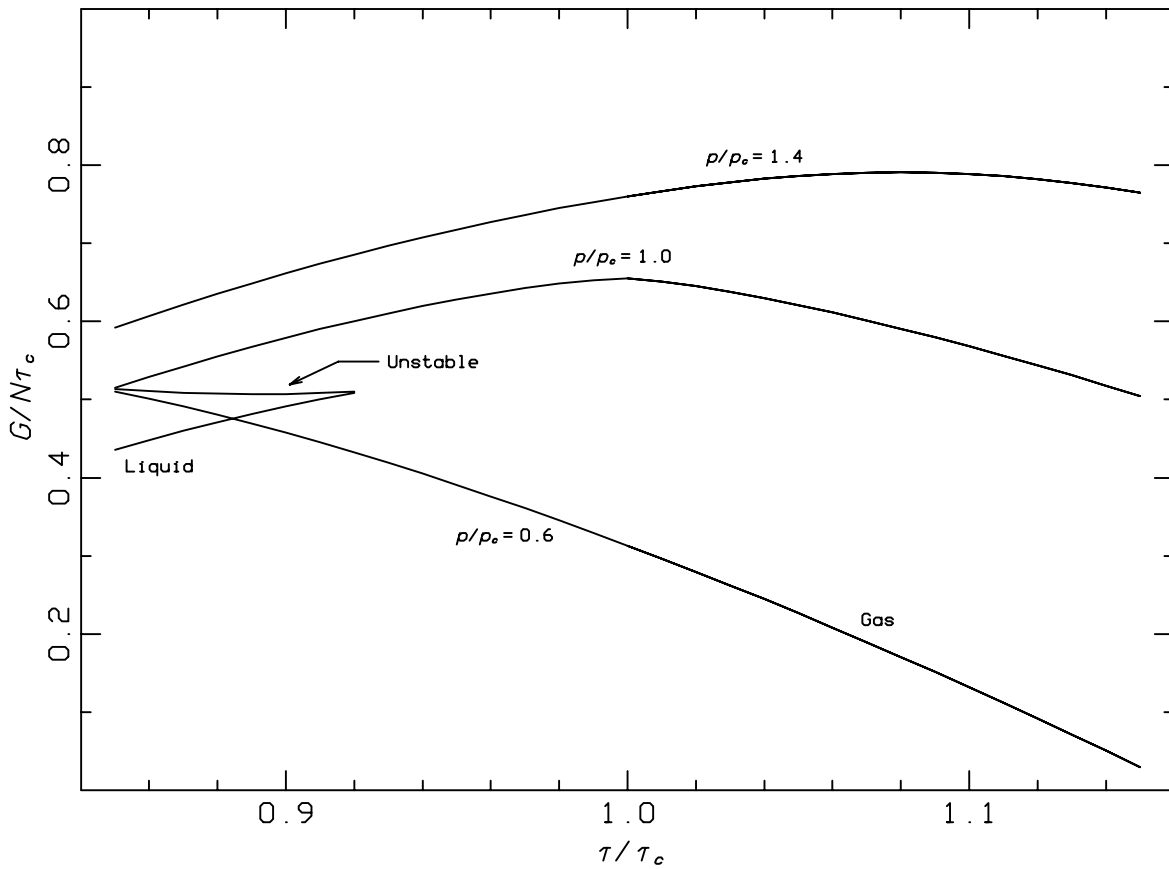
phase. For some pressure between the two dashed lines, the free energies of the two phases are equal and at this pressure, the equilibrium is a mixture of the two phases with the amounts of the two phases determined by the volume. The pressure is determined by the requirement that the areas of the two hatched regions shown in the figure should be

van der Waals Isotherm with  $\tau/\tau_c = 0.85$



equal. Note that this figure has a linear volume axis so that the areas appear correctly. Numerical calculations are used to determine that for  $\hat{\tau} = 0.85$ ,  $\hat{V}_1 = 3.1276$ ,  $\hat{V}_2 = 0.5534$ , and  $\hat{p}_1 = \hat{p}_2 = 0.5045$ . The equilibrium isotherm starts at the far right, goes through point *a*, comes to point 1, follows the constant pressure segment to point 2, goes through point *d*, and out the top left. It's possible, under very carefully controlled conditions, to have the system on the segment  $1 \leftrightarrow b$ , where it would be considered a supercooled gas. The system can also be on segment  $2 \leftrightarrow c$ , where it would be considered a superheated liquid. The system can never be on the  $b \leftrightarrow c$  segment. On the  $1 \leftrightarrow 2$  segment, part of the system is at 1, as a gas, and part of the system is at 2, as a liquid. The relative amounts of gas and liquid determine the total volume of the system and just where along the  $1 \leftrightarrow 2$  segment the system appears.

Gibbs Free Energy versus Temperature



The Gibbs free energy for the van der Waals gas is

$$G(\tau, V, N) = \frac{N\tau V}{V - Nb} - \frac{2N^2 a}{V} - N\tau \log \left( \frac{n_Q(V - Nb)}{N} \right) - N\tau.$$

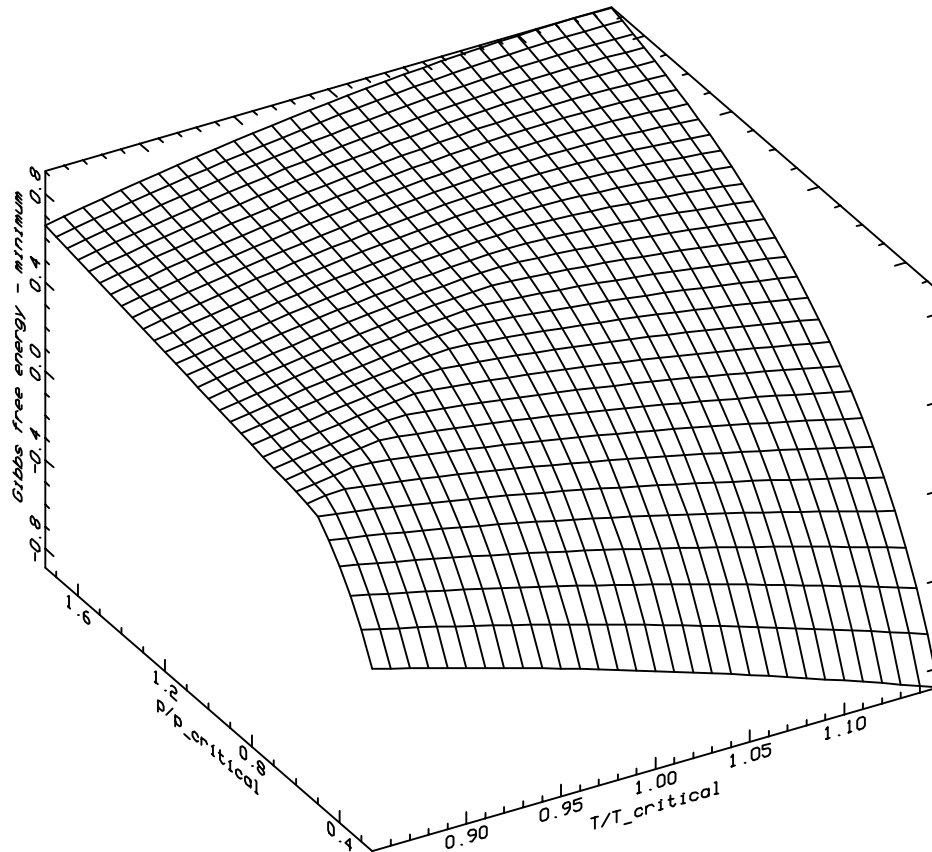
We can convert this to dimensionless variables by making the same substitutions as before. The result is

$$\frac{G}{N\tau_c} = \frac{\hat{\tau}\hat{V}}{\hat{V} - 1/3} - \frac{9}{4\hat{V}} - \hat{\tau} \log \left( 3bn_Q(\tau_c)\hat{\tau}^{3/2}(\hat{V} - 1/3) \right) - \hat{\tau}.$$

In this expression,  $n_Q(\tau_c)$  is the quantum concentration evaluated at  $\tau_c$ . The temperature dependence of  $n_Q$  is explicitly shown as the  $\hat{\tau}^{3/2}$  factor in the logarithm. We want  $G(\tau, p, N)$ . It turns out that there is no analytic solution for  $V$  in terms of  $\tau$  and  $p$ , so we can't write down an expression for  $G$  in terms of the desired variables. Instead, we can evaluate  $G$  numerically. For this purpose, we've taken  $\log(3bn_Q(\tau_c)) = -2$ . The actual value of this factor changes the overall slope of  $G$  versus  $\hat{\tau}$ , but does not change any of the

details. The particular slope we've chosen helps fit things on the plots. Since  $V$  is a triple valued function of pressure for some temperatures,  $G$  will also be a triple valued function. (This is one of the reasons we can't come up with an analytic form for  $G$ .) The figure shows  $G/N\tau_c$  versus  $\hat{\tau}$  for three pressures: the critical pressure, 1.4 times the critical pressure, and 0.6 times the critical pressure. The first two are smooth (continuous first derivative) curves. The curve for  $0.6p_c$  is the triple valued curve. There are branches corresponding to the gas phase, the liquid phase, and the unstable phase. The minimum, comprising part of the gas curve and part of the liquid curve, is the equilibrium phase.

The next figure shows the a surface plot of the Gibbs free energy versus both tem-



perature and pressure. The critical point is in the center of the diagram. It's not very pronounced, but perhaps you can spot the ridge line which separates the liquid and gas phases at low pressures and temperatures.

## Droplets

Suppose we have a system with a temperature and pressure that are close to the values where gas and liquid can co-exist, but they slightly favor the liquid. Suppose the system exists as a gas (it might have been warmer but has cooled down, such as a rising air mass on a hot day). If the system is to condense into a liquid, it's not likely to do it all at once. Instead, small droplets form and grow. But do they? Let's consider the Gibbs free energy of a droplet and see under what conditions growing a droplet would decrease the free energy of a system.

So, we let  $\Delta\mu$  be the difference in chemical potential between the vapor phase and the "bulk" liquid phase. That is

$$\Delta\mu = \mu_v - \mu_l > 0,$$

where the inequality holds since we postulated that pressure and temperature favor the liquid phase. You'll notice that we said "bulk" liquid. What's the difference between bulk liquid and droplets? Answer: the relative contribution of the surface energy. In a liquid, molecules have neighbors with which they have an attractive interaction and the interaction energy is negative. It's this overall negative contribution to the energy that's responsible for the wiggle in the van der Waals isotherms and the phase transition to a liquid. A molecule at the surface of a liquid is missing some neighbors (compared to a molecule in the interior), so it costs energy to have a surface. A liquid configuration minimizes its energy by minimizing its surface area. This is why droplets and bubbles are round! (What about bubbles on special frames?)

The tendency to minimize surface area leads to a force known as surface tension. This is a force per unit length which acts perpendicular to any small length lying in a surface. Just like pressure is a force per unit area which acts perpendicular to any small area embedded in a fluid. Of course, pressure is repulsive while surface tension is attractive. The surface tension of a given liquid can depend on what's dissolved in it and what gases are on the other side of the surface. For water in air, the surface tension varies from about 76 dyne cm<sup>-1</sup> at 0°C to about 59 dyne cm<sup>-1</sup> at 100°C. At room temperature (20°C) it's 72.8 dyne cm<sup>-1</sup>.

Suppose you have a rectangular surface with sides  $a \times b$ . You grab the  $b$  edge and pull it a distance  $da$ . The force required is  $\gamma b$ , where  $\gamma$  is the surface tension. The work done is  $\gamma b da = \gamma dA$ , where  $dA$  is the change in area of the surface. So a change in surface area requires an energy input to the system of  $\gamma\Delta A$ . This is very much like  $-p\Delta V$  work. With surface tension, we have a positive sign since it's a tension rather than a pressure, and we have an area rather than a volume since it's a force per unit length rather than a force per unit area. The upshot of all this is that a surface of area  $A$  requires an energy  $\gamma A$  to produce. Also,  $\gamma$  can equally well be expressed as energy per unit area. So for water at room temperature,  $\gamma = 72.8$  erg cm<sup>-2</sup>.

Back to the droplets. Suppose we imagine removing some molecules from the vapor phase and making a spherical droplet with them. What is the change in Gibbs free energy? Answer

$$\Delta G = G_l - G_v = -N\Delta\mu + 4\pi R^2\gamma = -\frac{4\pi}{3}R^3n_l\Delta\mu + 4\pi R^2\gamma,$$

where  $N$  is the number of molecules in the droplet,  $R$  is the radius of the droplet, and  $n_l$  is the concentration of the liquid in the droplet. The first term in this expression accounts for the decrease in energy of going from vapor to bulk liquid. The second term adds a correction for the surface of the droplet.

Here's the interesting point. For small enough  $R$ , the quadratic surface energy term wins over the cubic volume energy term. A small drop lowers the free energy by evaporating. If  $R$  is big enough, the cubic term wins and this size drop can lower the free energy by growing. The dividing line is found by setting  $d\Delta G/dR = 0$  which gives the critical radius

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

at which point the change in Gibbs free energy is

$$\Delta G_c = \frac{16\pi\gamma^3}{3(n_l\Delta\mu)^2}.$$

In dimensionless units we have

$$\frac{\Delta G}{\Delta G_c} = -2\left(\frac{R}{R_c}\right)^3 + 3\left(\frac{R}{R_c}\right)^2,$$

which is plotted in the figure. Approximating water vapor as an ideal gas, we have  $\Delta\mu = \tau \log(p/p_{\text{vapor}})$ , where  $p_{\text{vapor}}$  is the equilibrium vapor pressure of the water. Recall (lecture 11) that the chemical potential for an ideal gas can be written as  $\mu = \tau \log(n/n_Q) = \tau \log(N/Vn_Q) = \tau \log(p/\tau n_Q)$ . If the pressure were the same as the vapor pressure, then the vapor and bulk liquid would have the same chemical potentials. So the difference in chemical potentials depends on  $p/p_{\text{vapor}}$ , as indicated. If we assume a value for this ratio, then we know everything to estimate  $R_c$ . If we follow K&K and take  $p/p_{\text{vapor}} = 1.1$ ,  $T = 293$  K, then  $R_c = 110$  Å, quite small, but still about 70 molecules in diameter! Do you suppose this has anything to do with cloud formation and seeding as a technique to get clouds to form?

