Physics 127b: Statistical Mechanics

Lecture 3: First Order Phase Transitions

The van der Waals equation for a gas is

$$\left[P+\frac{a}{V^2}\right][V-b]=Nk_BT. \tag{1}$$

(The variable a is proportional to N^2 and b to N, i.e. $a=N^2\bar{a}$ and $b=N\bar{b}$ with $\bar{a},\bar{b}$ constants). It can be motivated by rewriting it in the form

$$P=\frac{Nk_BT}{V-b}-\frac{a}{V^2} \tag{2}$$

The $V-b$ term comes from estimating the "free volume" available for the molecules by excluding a hard core contribution, and the a/V^2 is a reduction in the pressure proportional to the density squared, representing the attractive interaction of the molecules. In Lecture 2 we derived expressions for $\bar{a}$ and $\bar{b}$ in terms of the pair potential.

The corresponding free energy is

$$A=A_{ideal}-NkT\ln\left(1-\frac{b}{V}\right)-\frac{a}{V} \tag{3}$$

with A_{ideal} the ideal gas expression. (Actually, if we integrate $P=-(\partial A/\partial V)_{N,T}$ to get A there is an integration "constant" $f(N,T)$, and we fix this by comparing with the ideal gas expression for $V\to\infty$.) The second term is $-T$ times the *entropy correction* from the excluded volume, and the third term is the *energy correction* from the attractive potential.

For $T>T_c=(8a/27Rb)$ the $P-V$ isotherms do not look much different from those for the ideal gas. However, at $T=T_c$ the isotherm develops an inflection point at $P_c=a/27b^2$, $V_c=3b$. The point P_c, V_c, T_c defines the *critical point* of the liquid gas transition. Incidentally, in terms of variables reduced to these critical values, $P_r=P/P_c$, $V_r=V/V_c$, $T_r=T/T_c$ the van der Waals equation takes the form

$$\left(P_r+\frac{3}{V_r^2}\right)\left(V_r-\frac{1}{3}\right)=\frac{8}{3}T_r \tag{4}$$

so that all liquid gas systems should look the same in these reduced variables. This qualitative statement is known as the law of corresponding states, and is actually more general than this derivation from the van der Waals equation—it depends on the assumption of pairwise potentials, and on there being a single energy and length scale parameterization of the interaction potential.

For $T<T_c$ the $P(V)$ curve becomes non-monatomic—the isotherm for $T\simeq 0.94T_c$ is plotted in Fig. (1).

We immediately recognize that the (red) dashed portion of the curve is linearly *unstable* since $(\partial P/\partial V)>0$. As we discussed in lecture 11 last term, further constraints are given by the *convexity* requirement on the Helmholtz free energy, Fig. (2a). The dashed (red) portion of the curve, where the curvature is negative, corresponds to the obviously unstable dashed portion of the $P-V$ isotherm. But now we see that the dotted (green) portion is also unstable by the chord

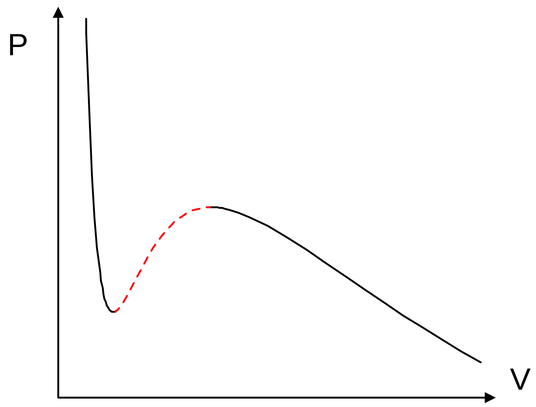

Figure 1: Isotherms of the van der Waals equation.

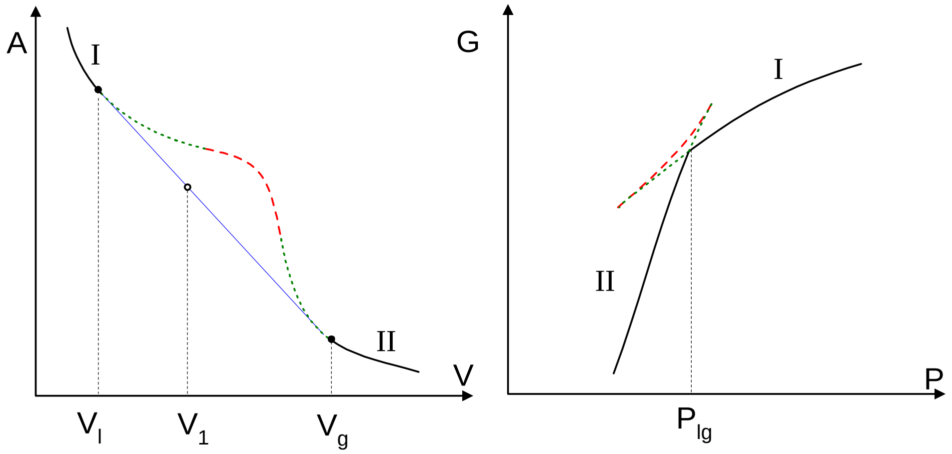

Figure 2: Thermodynamic potentials of the van der Waals system.

condition. We recognize from the discussion of the instability that the system will *phase separate* into two macroscopic regions of high density ($\rho_l = N/V_l$) liquid and low density ($\rho_g = N/V_g$) gas phase with properties given by the endpoints of the common tangent construction to the $A(V)$ curve. The fraction f_l, f_g (with $f_l + f_g = 1$) of the total number N in each phase when the system volume is at some volume V_1 in this mixed phase region is given by

$$f_l V_l + f_g V_g = V_1 \Longrightarrow f_l = \frac{V_g - V_1}{V_g - V_l}. \tag{5}$$

The free energy is $A(V_1) = f_l A(V_l) + f_g A(V_g)$ which is consistent with the physical $A(V)$ curve being given by the *common tangent* construction: the full $A(V)$ curve is given by the solid (black-blue-black) curve in the figure. It is now evidently convex, as required.

To return to the $P(V)$ curve it is useful do a Legendre transformation. Since $dA = -SdT - PdV$ the Legendre transform is

$$G(P, T) = A(V) + PV = A(V) - (-P)V. \tag{6}$$

This can be constructed by the intercept-slope interpretation of the transformation: as V varies on the $A(V)$ curve slide a ruler along to make a tangent at the point V, and read off the slope $-P$ and the intercept G. After some struggle you should be able to see that the $G(P)$ curve is as sketched in the second panel of the figure. (Portions I and II correspond in each figure, and the dashed (red) and dotted (green) of the unphysical portions also correspond.) Note that the *whole* of the common tangent part of the physical $A(V)$ curve maps into the *single* point of discontinuity of $G(P)$, defining the unique pressure for liquid-gas equilibrium at each temperature $P_{lg}(T)$. Also note that the physical portion of the $G(P)$ curve is concave, as required.

The equilibrium pressure can be identified on the $P-V$ by noting that the integral of $\partial G/\partial P$ around the loop of unphysical solutions is zero

$$\oint_{P_{lg}} \frac{\partial G}{\partial P} dP = 0 = \oint_{P_{lg}} V dP. \tag{7}$$

The final expression is the area between the $P-V$ curve and the P axis. Thus P_{lg} is identified by the *Maxwell equal area* construction (Fig. 3) —P_{lg} must be chosen so that the shaded regions (which contribute to $\oint V dP$ with opposite signs) must be equal. Thus the physical $P-V$ curve is given by the solid (black-blue-black) curve, and the unphysical portions are now shown with the same scheme as in the previous figures.

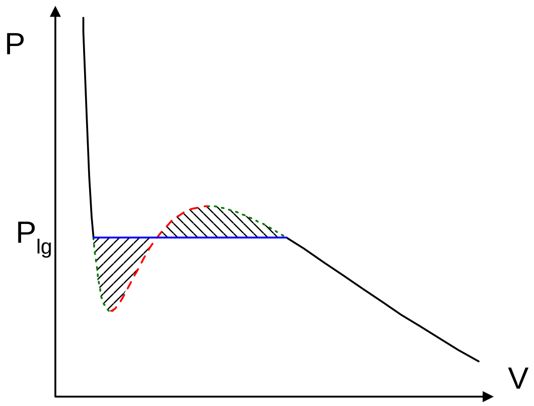

Figure 3: Maxwell construction

This type of transition is a *first order* phase transition. Notice the properties:

- The second derivative of the thermodynamic potential is *zero* (the straight portion of $A(V)$) or *infinite* (the cusp in $G(P)$).
- As a function of the extensive variable V there is a region (between V_l and V_g) of *phase coexistence*. The densities of the extensive variables of the two phases in equilibrium are *discontinuous* across the transition (e.g. the density, and also the entropy density, Helmholtz free energy density).

- On the other hand the temperature T, pressure P, and Gibbs free energy density $g = G/N$, are *continuous* across the transition. Since g is equal to the chemical potential μ, this corresponds to the usual condition between two systems in contact under exchange of energy, volume, and particles.

- The constraint that the chemical potentials are equal for the phases (labelled one and two)

  $$\mu_1(T, P) = \mu_2(T, P) \tag{8}$$

  provides a *single constraint* on the two variables T, P, i.e. two phase coexistence occurs along a line in the P, T plane—an example of the *Gibbs phase rule*. Using this expression at nearby points on the coexistence line and the thermodynamic identity

  $$d\mu = dg = -s dT + v dP \tag{9}$$

  with $s = S/N$ the entropy density and $v = V/N$ the volume per particle gives the *Clausius-Clapeyron* relation for the slope of the coexistence line

  $$\left.\frac{dP}{dT}\right|_{coexistence} = \frac{\Delta s}{\Delta v} \tag{10}$$

  with $\Delta s = s_2 - s_1$ and $\Delta v = v_2 - v_1$.

- The $G(P)$ curve (if we include the (green) dotted portions) appears to be simply the curves for two different phases (liquid and gas) that “happen” to cross, and the system switches to the curve of lower G. The dotted (green) portions are often considered as describing a “supercompressed” gas or “superexpanded” liquid (cf. supercooled water at the water-ice transition). However more careful analysis [S. Katsura, *Adv. Phys.* **12**, 416 (1963), *Physics* **3**, 255 (1967), A. F. Andreev, *JETP* **18**, 1415 (1964)] shows that this interpretation is only qualitatively correct, and in fact there is an *essential singularity* of the free energy curves at the junction point.

We thus get the picture of the phase transition shown in Fig. (4a).

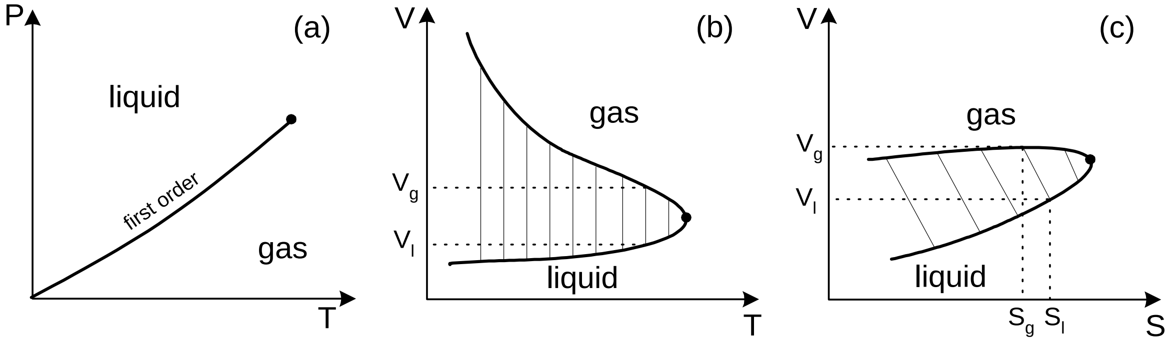

Figure 4: Liquid-gas transition in the VT, PT, and VS planes. The thin *tie lines* in the mixed phase regions link the two coexisting phases.

We can alternatively ask what happens if we maintain N particles at a fixed temperature and change the pressure rather than the volume. In this case, as the pressure is raised from the low pressure gas phase, when the pressure reached the gas-liquid equilibrium pressure there will be a *discontinuous jump* in the volume as all the gas changes to liquid at this pressure. This is sketched in Fig. (4b). Note that the two phases coexist along a *line* in the PT plane. The two coexisting phases also have different entropy densities, and so in the SV plane the transition will appear as in Fig. (4c).

The van der Waals equation predicts that the liquid-gas transition disappears above a critical temperature T_c. As T approaches T_c from below, the discontinuities in the density, entropy density etc. between the liquid and gas become smaller and smaller, and disappear at a critical temperature T_c, critical pressure P_c. It is not too hard to show that the volume difference Δv varies as $(T_c - T)^{1/2}$. Since the two phases are becoming very close in all their properties, fluctuations producing regions of one phase in the other, which in turn contain regions of the other… become important. For $T > T_c$ there is no qualitative difference between the high and low density regions. Since we can find a continuous path between regions we have identified as "gas" and "liquid", this also shows there is no qualitative difference between these two phases in general—a liquid is just a dense gas!

It is interesting to explore the consequences for the full dependence structure of the thermodynamic potentials taking into account convexity requirements e.g. $E(S, V)$ at fixed N (Fig. 5).

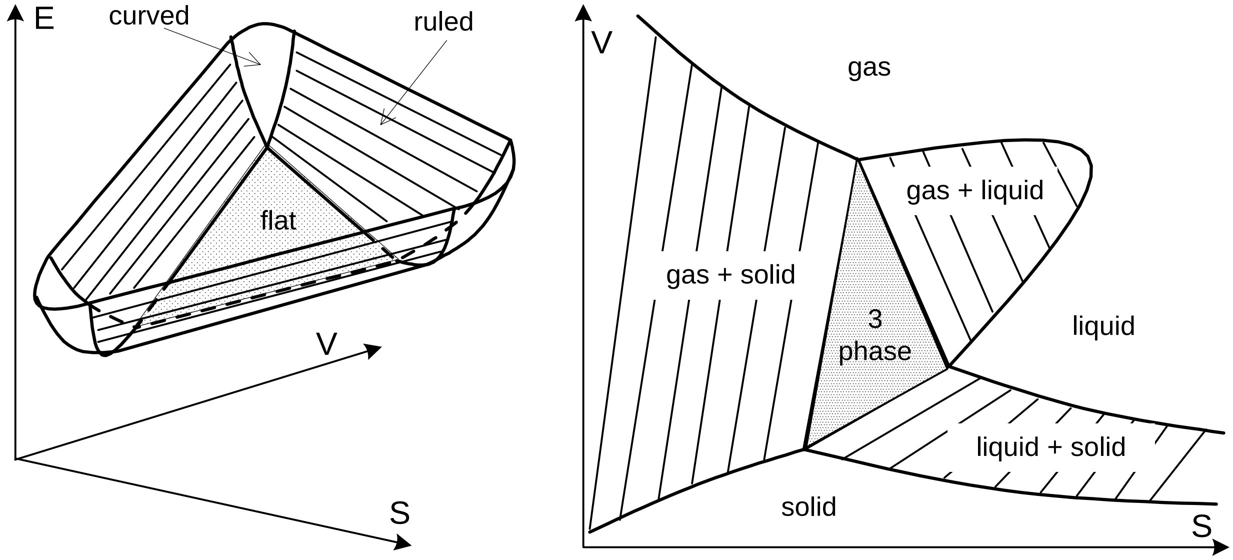

Figure 5: Plot of $E(S, V)$ obeying convexity requirement showing "ruled" regions of two phase coexistence and a planar region of three phase coexistence (the three phases correspond to the corners of the triangle.

Convexity tells us that $E(S, V)$ must have a "bowl" shape, however the bowl need not be smooth. In particular, as well as the smooth regions with (positive) curvature in both direction, there can be regions that can be ruled with straight lines (no curvature in one direction). These correspond to the two phase regions looked at above. In addition there can be planar regions. These correspond to three phase coexistence. An example (which may correspond to the gas-liquid-solid system) is shown in Fig. 5, together with its projection onto the SV plane. (Actually the figure is not quite right: the conditions of positive temperature and pressure, i.e. the derivatives of E with respect to

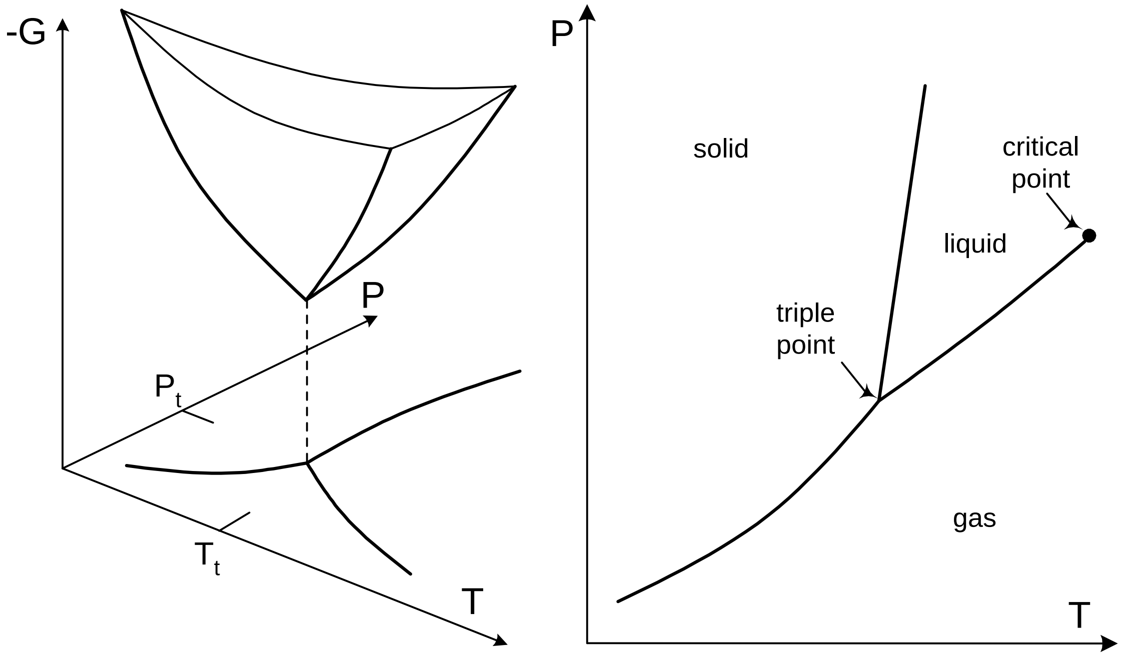

Figure 6: Gibbs potential $G(P,T)$ showing two and three phase coexistence. (Actually $-G$ is plotted.)

S and $-V$, has not been implemented—the bowl must be "tipped" to include this.)

The corresponding Gibbs free energy is shown in Fig. (6). The two phase coexistences correspond to ridges, and the three phase coexistence to a single point called the triple point (at P_t, T_t). The result that *three* phases can coexist only at a point in the P, T plane (in a single component system) is another example of the *Gibbs phase rule*.

Similar remarks will apply at other first order transitions, although the appropriate variables will be different. For example, for a first order magnetic transition, the magnetization M replaces V, and magnetic field H replaces P. Also a the appropriate free energy depending on the intensive variables H and T, will be continuous at the transition.