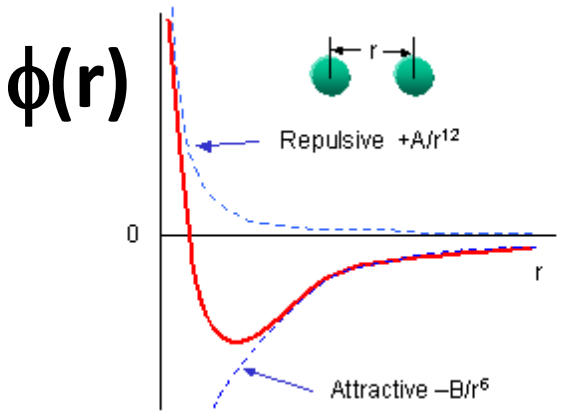
Lecture 27

Physics 404

How do we understand the origins of phase transformations? The ideal gas law can be modified to include interactions between particles that lead to phase transformations. Start with the Helmholtz free energy for an ideal gas: $F = U - \tau\sigma = -N\tau\left[log\left(\frac{n_Q}{n}\right) + 1\right]$. We will modify this in two ways. The inter-molecular potential energy of most substances looks like this:



At short distances there is a strong inter-molecular repulsion due to Coulomb interaction and the Pauli exclusion principle between the electron clouds. This shows up as the strong upturn to positive values of the inter-molecular potential. At larger separations there is a weak attractive interaction between the molecules. This attraction can lead to clustering and clumping of the molecules at low temperatures, and the development of a condensed phase (liquid or solid).

We include the effects of short range repulsion by reducing the volume by the excluded volume per molecule, which we call "b". Thus the volume that appears in the free energy above will be replaced by the value $V - Nb$, for a system of N particles. The value of b is expected to be on the order of a few cubic Angstroms or so.

The attractive potential will reduce the energy of a single particle by an amount $\Delta u = \int_b^\infty \varphi(r)n(r)dV$, where $\varphi(r)$ is the intermolecular potential, $n(r)$ is the number of particles per unit volume at distance r from the molecule, and the integral is taken over the attractive part of the potential. This integral is hard to carry out because it requires knowledge of the structure of the fluid to calculate $n(r)$. We shall use the "mean field approximation" and ignore these details, replacing $n(r)$ with it's overall average $n = N/V$. Then the integral is just a property of the intermolecular potential: $2a \equiv -\int_b^\infty \varphi(r)dV$, so that $\Delta u = -2na$. If we do this calculation for all the atoms, one introduces a factor of $N/2$, since each atom is included in N such integrals exactly twice. The energy to be added to the free energy above is $\Delta U = \frac{N}{2}(-2na) = -\frac{N^2}{V}a$.

With these two changes, the modified free energy of an ideal gas with interactions is: $F_{new} = -N\tau\left[log\left(\frac{n_Q}{N}(V-Nb)\right)+1\right] - \frac{N^2}{V}a$. The equation of state of this new and improved gas is obtained from the calculation of pressure: $P = -\frac{\partial F}{\partial V}|_{\tau,N} = \frac{N\tau}{V-Nb} - \frac{N^2}{V^2}a$. Re-arranging, we come up with the van der Waals equation of state: $\left(P + \frac{N^2}{V^2}a\right)(V-Nb) = N\tau$. Note that this reduces to the ideal gas law when $a = b = 0$. The parameter "a" effectively adds an additional pressure on the gas due to attractive forces it creates between the molecules. Typical values for a are 2.5 eVÅ^3 for N_2, 10 eVÅ^3 for H^2O, and 0.063 eVÅ^3 for He.

Define the "critical" pressure, volume and temperature as $P_c \equiv \frac{a}{27\,b^2}$, $V_c \equiv 3Nb$, $\tau_c \equiv \frac{8a}{27\,b}$, and the vdW equation of state becomes prettier: $\left(\frac{P}{P_c} + 3\left(\frac{V_c}{V}\right)^2\right)\left(\frac{V}{V_c} - \frac{1}{3}\right) = \frac{8}{3}\frac{\tau}{\tau_c}$. The isotherms of this equation of state are shown on the class web site. It is found that for $\frac{\tau}{\tau_c} > 1$ that the $P\ vs.\ V$ curves are monotonically decreasing. For $\frac{\tau}{\tau_c} < 1$ it is found that there are two points on the $P(V)$ curves where the derivative $\frac{\partial P}{\partial V}|_\tau = 0$, called "spinodal points". In between these points on the isotherm the slope of the $P(V)$ curve is positive, which is un-physical. We will fix this problem later. There is one special isotherm at $\frac{\tau}{\tau_c} = 1$ for which there is a single point at which both $\frac{\partial P}{\partial V}|_\tau = 0$ and $\frac{\partial^2 P}{\partial V^2}|_\tau = 0$. This occurs precisely at the point $P = P_c$, $V = V_c$, and $\tau = \tau_c$, which is the critical point identified in the last lecture. Hence the vdW equation of state describes the liquid/vapor phase transition and the associated critical point.

By calculation, one finds that $\frac{P_c V_c}{N\tau_c} = \frac{3}{8} = 0.375$ for the vdW model. Real gases show values for this quantity ranging from 0.277 for CO_2 up to 0.327 for He, showing that the vdW model is not too far off the mark.

The van der Waals equation of state can be interpreted as a "law of corresponding states": $\left(\hat{p} + \frac{3}{\hat{v}^2}\right)\left(\hat{v} - \frac{1}{3}\right) = \frac{8}{3}\hat{\tau}$, with the definitions of the dimensionless quantities $\hat{p} = \frac{P}{P_c}$, $\hat{v} = \frac{V}{V_c}$, and $\hat{\tau} = \frac{\tau}{\tau_c}$. This law is 'universal' in the sense that it applies to the liquid-vapor transformation of all materials. The details of each particular material are "scaled away" in the critical parameters (P_c, V_c, τ_c) to create a material-independent equation of state. The universal properties of the gas depend only on how far away the system is from its critical values of pressure, volume and temperature. The class web site (slide 2) shows experimental data from a variety of materials that have been scaled onto universal curves using the law of corresponding states.

The unphysical part of the vdW isotherms where the slope of the $P(V)$ curve is positive can be eliminated using the "Maxwell construction". One observes that in coexistence of vapor and fluid the chemical potential (hence the Gibbs free energy per particle, G/N) of these two phases must be equal, and on an isotherm with a fixed total number of particles $dG = VdP$, hence $\int_{Liq}^{Vap} dG = G_{vap} - G_{Liq} = \int_{Liq}^{Vap} VdP = 0$. In other words, we expect the Gibbs free energies to be equal on either end of the coexistence isotherm in the $P-V$ plane. One can choose a certain constant pressure P and carry out this process to see in the integral $\int_{Liq}^{Vap} VdP = 0$ or not. There will be one value of pressure for a given isotherm that satisfies this equation. That pressure becomes the coexistence pressure for that

particular temperature. This process is repeated for each temperature below τ_c to create a final $P - V$ phase diagram describing the liquid-vapor phase transition, as shown on the class web site (see slide 3).