**Van der Waals Gas/Liquid**

**Prologue**

Now we want to investigate how we may determine the functional form of these potentials introduced previously. We will consider for simplicity that our substance is homogeneous and obeys the scaling relations introduced in the previous lecture. Then our potentials satisfy,



It will suffice, then, to determine the heat capacity CV(T,V) and equation of state p(T,V), to construct the potentials [these basically give us S and p for the free energy F]. For instance, forming the differential of U(T,V) we have:



What are these derivatives? Well,



and,



So we have:



A similar procedure for the entropy would yield:



What are these derivatives? Well,



and,



So we have:



With U(T,V) and S(T,V), we can get F(T,V) = U(T,V) – TS(T,V) for instance, which is one of the thermodynamic potentials. So from this we can construct everything we want. And of course we can invert these equations to construct other potentials as desired.

**Van der Waal’s gas**

In the 1870’s Van der Waal proposed a model of a gas that took into account the interactions present. He proposed:



where *b* is basically the volume taken up by a gas molecule, and *a* is a parameter measuring the strength of interaction. What does this tell us about the energy, entropy, and chemical potential of the gas for instance? We have:



Integrating we get:



We can clearly see the interacting term evinced by the N2. Now let’s consider the entropy. We have:



Integrating we get:



which is the same as the ideal gas, with the only difference being the excluded volume. Why doesn’t the interaction change anything? Can we write S(U,V,N)? Seems so. Let’s solve for T again,



and plugging this into S we get:



We could get F as well,



and the chemical potential,



But it would be difficult to express this in terms of p. Let’s consider the constant pressure heat capacity.



Now ∂V/∂T is hard to evaluate so use ∂V/∂T = (∂T/∂V)-1 instead, and then substitute in what p is after fact.



Again, we are able to make the potential formulas a little prettier with some grouping of constants. First, for the internal energy, we’ll let U0 cancel those constants. Then we can say,



and the entropy,



Like before, if define Φ,



Then we can say,



or,



Note how this is exactly the same form as the ideal gas entropy; all that has changed is replacing U with the kinetic energy (by subtracting off the negative potential energy), and replacing the volume V with the actual available volume V – bN. If this is accepted, then it is very sensible equation, and it would be easy to derive the equation of state and heat capacity from such a principle. And the free energy is:



similarly here. If you accept that T is a measure of kinetic energy, then it is easy to modify the ideal F to get to the real gas F. And the Gibbs energy G = F + pV = U – TS + pV.



and the chemical potential



It would be prohibitively difficult to put these in terms of the pressure.