Physics 114 Statistical Mechanics Spring 2018
Seminar 13

Overview:

This week's assignment is made up of three parts. First, we study systems which have interparticle interactions which can't be neglected (which can thus make a system undergo a phase transition). The potential energy, $u(r_i, r_j)$ between particles i and j thus factors into a fluid's statistical properties. We will learn how to write *virial series* for pressure (and other quantities like free energy). These are *series with the density N/V as the expansion parameter.* A virial series is used when a gas is not dilute enough to be ideal, but not dense enough to be a liquid.

Second, we have several presentations in each of our 3 sections.
Wed A: David, Noah R, Sarah
Wed B: Jimmy, Emma, Davy
Thurs: Noah L, Sam, Jaron
If you have reached out to me for good references, I will respond to you over the weekend. Please make this talk as informative, interactive, and polished (slides?!) as you can. Aim for 10 minutes, but if your talk lasts 15 minutes it will be OK.

Finally, I am assigning an Honors Exam from the past. I hope everyone will attempt it. Please bring solutions, partial solutions, ideas, ... and we will go over as much as we can!

Reading:

G&T Sections

- 8.1-8.3
- *optional 8.4.1 - 8.4.4 Diagrammatic expansion of free energy*

B&B Section

- 26.3

Concept checklist from readings:

- **Virial coefficients** Suppose we have a classical gas that is dense enough for interparticle interactions to matter, but insufficiently dense or cold for transition to a liquid. Now pressure can be written as a *virial expansion.* B&B are fond of writing expressions *per mole* so framed this way, for one mole with molar volume V_m:

$$\frac{pV_m}{RT} = 1 + \frac{B(T)}{V_m} + \frac{C(T)}{V_m^2}$$

In G&T language, this would be

$$P/kT = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + ...$$

- G&T and B&B go on to justfy this virial series in similar ways (though B&B is a lot shorter and just fine for our purposes). Recall the general form for the partition function:

  $$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \int ... \int d\mathbf{r_1},...,d\mathbf{r_N}\, d\mathbf{p_1},...,d\mathbf{p_N}\, e^{-\beta U(\mathbf{r_1},....\mathbf{r_N},\mathbf{p_1},....\mathbf{p_N})}$$

  For much of seminar, we've been dealing with an ideal gas, so U was wholly kinetic: $U = U_K \equiv \Sigma_i p_i^2/2m$. In this case, the partition function was:

  $$Z(T,V,N) = Z_{ideal}(T,V,N) = \frac{1}{N!}V^N(\frac{\sqrt{2\pi mkT}}{h})^N$$

- Now we will assume there is potential energy as well as kinetic. So $U = U_K + U_P$. We find that we can write the partition function as a product $Z = Z_{KE}Z_{PE}$ where $Z_{KE} = Z_{ideal}$ and Z_{PE} is often seen written as Z_c. This is because Z_c is called the "configuration integral" - it depends on the spatial configuration $\mathbf{r_1},...,\mathbf{r_N}$. We thus have

  $$Z_{PE} = Z_c = \frac{1}{V^N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} e^{-\beta U_P(\mathbf{r_1}....\mathbf{r_N})}$$

- *Notice* the V^N in the denominator! We need it! Otherwise, $U = 0$ would not lead to $Z = Z_{ideal}$.

- Two approximations: i) We use *pair potentials* - so two particles contribute to U_p via $u(\mathbf{r_i},\mathbf{r_j})$, no matter where the other particles in the system are located. ii) It is only the *scalar distance between particles i and j* that determines their potential energy. Thus

  $$U_P = \Sigma_{i<j}u(|\mathbf{r_i} - \mathbf{r_j}|) \equiv \Sigma_{i<j}u(r_{ij})$$

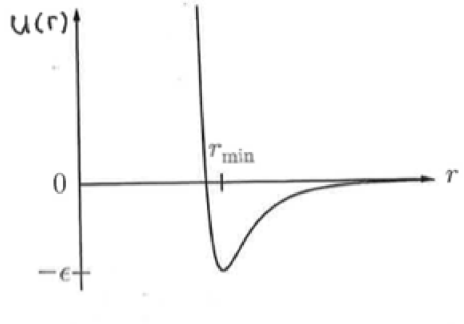
  where the sum is over all distinct pairs of particles. This leads to

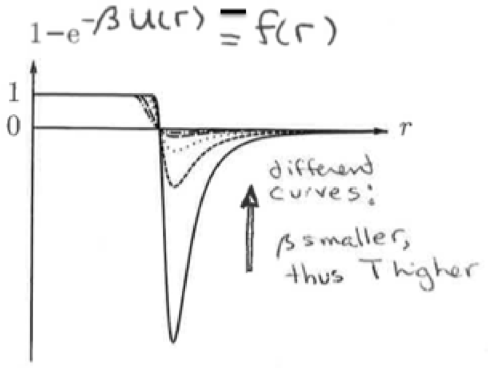
  $$Z_c = V^{-N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} \;\; \Pi_{i<j}e^{-\beta u(r_{ij})}$$

- Now comes a notation that B&B doesn't use but G&T, and most other people do. We frame Z_c in terms of the *Mayer f functions* $f(r_{ij}) = e^{-\beta u(r_{ij})} - 1$. See the figure below ...

- The $f(r)$ functions go quickly to zero as soon as a pair of particles are separated by r greater than the range of their interactions. These are "molecule-sized" functions. By definition,

  $$Z_c = V^{-N} \int ... \int d\mathbf{r_1}...d\mathbf{r_N} \;\; \Pi_{i<j}[1 + f(r_{ij})]$$





- From here, one expands out the infinite product. Note that $f(r)$ is small when βu is small ... i.e. when interactions between particles are not too important on a scale of kT. If we truly expect f to be small enough to ignore for all pairs of particles, we have $Z_c = 1$. This is an ideal gas.

- If we can't ignore these factors of f, we have the issue of calculating terms in the product.

$$Z_c = \frac{1}{V^N}\int ... \int d\mathbf{r_1}...d\mathbf{r_N}[1+\Sigma_{pairs\ i<j} f(r_{ij}) + \Sigma_{distinct\ pairs\ i<j,\ k<l}\ f(r_{ij})f(r_{kl})+...]$$

- It is at this point that we say that we are stopping only at the very first sum above ... only one power of $f(r)$. This is like saying that our gas is dilute enough that it is rare to have a triplet (or quadruplet or ...) of particles close to each other at any one time. We can make the usual N large approximation

$$Z_c = 1 + \frac{N^2}{2V}\int d\mathbf{r} f(r)$$

We now integrate over angle space for the one remaining 3d coordinate, $\mathbf{r}$, to arrive at

$$Z_c = 1 - \frac{NB_2(T)}{V} \quad where \;\; B_2(T) = -2\pi \int_0^\infty r^2 f(r) dr$$

- Last steps ... use $F = -kTlnZ$ and $P = -(\frac{\partial F}{\partial V})_T$ to get our first term in the virial expansion for free energy and pressure:

$$F = F_{ideal} + \frac{N}{V}kT\ B_2(T)\ ; \quad \frac{PV}{NkT} = 1 + \frac{N}{V}B_2(T)$$

- **Quantum gasses at high temperatures ...** In the context of Virial expansions, I'm asking you to do G&T problem 6.60 on finding $P(T)$ for the ideal Fermi gas and G&T 6.61 for the ideal Bose gas. Though these are ideal gasses, they are nonclassical ones. As a result, there is a correction to $PV = NkT$ so long as the deBroglie wavelength is not negligible compared to the average spacing between particles. As you will derive in these problems, this correction is *positive* for Fermions, raising the pressure from the classical result:

  $$PV = NkT\ [1 + \frac{\lambda_{th}}{2^{7/2}}\ (\frac{N}{V})\ + ...]$$

  and is *negative* for Bosons, lowering the pressure:

  $$PV = NkT\ [1 - \frac{\lambda_{th}}{2^{5/2}}\ (\frac{N}{V})\ + ...]$$

Warmup Problems: *None!*

Regular problems:

1: Virial coefficients:
G&T Problem 8.30 parts (a) and (b)

2: VdW virial coefficients:
Begin with the vdW equation of state:

$$(P + a\left(\frac{N}{V}\right)^2)\ (V - Nb) = NkT$$

Expand the equation of state for low density $\rho = N/V$ and thus find the second virial coefficient, $B(T)$ for a vdW gas. The temperature at which $B(T) = 0$ is called the "Boyle temperature". Why is this a special temperature?

3: Ideal Fermi Gas at high T:
G&T Problem 6.60

4: Ideal Bose Gas at high T:
G&T Problem 6.61