Problem Sheet 5

I. SOLID-LIQUID-GAS PHASE DIAGRAM

Sketch the $p-V-T$ and its projection on the $p-T$, $p-V$ and $V-T$ planes for a substance which can be in the solid, liquid or gas phase. Pay attention to the regions where two phases coexist, and to the tricritical point.

How does the phase diagram of water differ from that of most other substances? Ice melts upon applying pressure! Can you infer that from Clausius-Clapeyron relation,

$$\frac{dP_c(T)}{dT} = \frac{\Delta s}{\Delta v} \tag{1.1}$$

and other commonly known properties of water?

Remark: A common tale is that ice-skating works because the pressure exerted by the skates melts the ice. You can check by using explicit numbers for water that this explanation is not valid: Estimate the reduction of the melting temperature by the pressure exerted by a typical skater!

II. REAL GASES: THE VIRIAL EXPANSION

In real gases, the interactions and the finite volume of gas particles lead to corrections in the equation of state (as compared to that of an ideal gas). One naturally expects the corrections to be small at low density. Convince yourself that it is natural to expect that the pressure should have a Taylor expansion in the density, and that its most general form should look like:

$$P = T(n + B_2(T)n^2 + B_3(T)n^3...). \tag{2.1}$$

for small n. This form of the equation of state is known as the virial expansion.

One can indeed devise a systematic expansion in the small density n. However, note that one should never expand in a dimensionful quantity. Argue that the small parameter (let's call it x) in which one can expect a well-behaved expansion, is $x = nr_0^3$, where r_0 is the typical range of the interactions between atoms!

e) **Challenge**: Find (by yourself, or with the help of some literature) the explicit expression

$$B_2 = \frac{1}{2}\int d^3r(1 - \exp(-\beta V_{int}(r))) \tag{2.2}$$

for the second virial coefficient.

Guide: Write the free energy as

$$\begin{aligned} F &= -T \log Z, \\ Z &= \frac{1}{N!} \int d^{3N} p d^{3N} q \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \frac{1}{2}\beta \sum_{i \neq j=1}^{N} V_{int}(q_i - q_j) \right]. \end{aligned} \tag{2.3}$$

Do the momentum integral. Find a way to expand the q-integration in the partition function: Namely, write $\exp[-\beta V_{int}(q_1 - q_2)] = 1 + (\exp[-\beta V_{int}(q_1 - q_2)] - 1)$, and expand the product of such terms in powers of factors $(\exp[-\beta V] - 1)$, retaining only zeroth and first orders of the latter. Obtain the ideal gas equation from the term of zeroth order! (Express the pressure as a derivative of F!). Finally, determine the first order correction, rewrite it as an exponential (this needs careful reflection!) and obtain B_2! Can you convince yourself that this gives a systematic expansion in nr_0^3?

Can you find even the next virial term?