PH4211 Statistical Mechanics

Problem Sheet 3

3.1 Show that the Joule-Kelvin coefficient is zero for an ideal gas.

3.2 Derive the second virial coefficient expression for the Joule-Kelvin coefficient

$$\mu_{J} = \frac{2T}{5k}\left\{\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T}\right\}$$

and find the inversion temperature for the square well potential gas.

3.3 For the van der Waals gas show that $T_B = \dfrac{a}{bk}$ and $T_I = \dfrac{2a}{bk}$.

3.4 Show that for a van der Waals fluid the critical parameters are given by

$V_c = 3Nb, \ p_c = \dfrac{a}{27b^2}, \ kT_c = \dfrac{8a}{27b}$. Express these critical quantities in terms of the

microscopic interaction (Lennard-Jones) parameters ε and σ.

3.5 Show that, for a van der Waals fluid, the combination of critical parameters P_cV_c/NkT_c takes the universal value 3/8.

3.6 Show that for the Dieterici fluid the critical parameters are given by

$V_c = 2Nb, \ p_c = \dfrac{a}{4b^2e^2}, \ kT_c = \dfrac{a}{4b}$, and the universal combination P_cV_c/NkT_c has the

value $2/e^2 = 0.271$.

3.7 Show that the partition function for an interacting gas may be expressed as

$$Z = Z_{id}\frac{1}{V^N}\int e^{-\sum_{i<j}U(q_i,q_j)/kT}\,d^{3N}q$$

where Z_{id} is the partition function for a non-interacting gas. In terms of this expression explain why the partition function of a *hard sphere* gas might be approximated by.

$$Z = Z_{id}\left(\frac{V - Nb}{V}\right)^N.$$

3.8 Show that the approximate partition function for the hard sphere gas in the previous question leads to the equation of state $p(V - Nb) = NkT$. This is sometimes called the Clausius equation of state. Give a physical interpretation of this equation.

Show that the first few virial coefficients are given by $B_2(T) = b, B_3(T) = b^2$, $B_4(T) = b^3$, etc. These virial coefficients are independent of temperature. Discuss whether this is a fundamental property of the hard sphere gas, or whether it is simply a consequence of the *approximated* partition function.

3.9 For a general interatomic interaction potential $U(r)$ we may define an effective hard core dimension d by $U(d) = kT$. What is the significance of this definition? Show that for the Lennard-Jones potential of Section 3.2.4, d is given by

$$d = \sigma \left\{ \frac{2}{1 + \sqrt{1 + kT/\varepsilon}} \right\}^{1/6}.$$

Plot this to demonstrate that d is a very slowly varying function of temperature.

If you have access to a symbolic mathematics system such as *Mathematica* or *Maple*, show that at low temperatures

$$d \sim \sigma \left(1 - \frac{1}{24} \frac{kT}{\varepsilon} + \frac{19}{1152} \left(\frac{kT}{\varepsilon} \right)^2 - \ldots \right).$$

So how high must the temperature be so that d differs appreciably from its zero temperature value?

How does d vary for the hard core and the square well potentials of Sections 3.2.2 and 3.2.3?

3.10 The one dimensional analogue of the hard sphere gas is an assembly of rods constrained to move along a line (the Tonks model). For such a gas of N rods of length l confined to a line of length L, evaluate the configuration integral Q_N. Show that in the thermodynamic limit the equation of state is

$$f(L - Nl) = NkT$$

where f is the force, the one dimensional analogue of pressure.

Comment on the similarities and the differences from the hard sphere equation of state mentioned in Problem 3.8 (Clausius equation) and the van der Waals equation of state.

3.11 Compare the square well and the van der Waals expressions for the second virial coefficient. Show that they become equivalent when the range of the square well potential tends to infinity while its depth tends to zero.