PC5202 Advanced Statistical Mechanics

Assignment 3 (due Tuesday 3 Mar 2020 after recess)

1. Consider molecules moving in one dimension. The molecules are modeled as rigid rods of length a, they are confined between the walls within a space of length L (larger than Na). The potential energy is 0 if the molecules do not overlap, and infinite if they overlap. The order of the molecules is maintained, i.e., they cannot pass through each other.

a. Calculate the canonical configuration partition function Q (i.e., disregard the momentum integral part) if there is only one molecule in the system.
b. Repeat the calculation if there are two molecules within the length L.
c. Generalize the results to system with an arbitrary number of N molecules.
d. Calculate the force exerted by the molecules on one of the walls for the case of one, two, or arbitrary N molecules.

2. Given the van der Waals equation:

$$P = -a\frac{N^2}{V^2} + \frac{Nk_BT}{V - Nb},$$

the Maxwell construction can also be expressed as

$$\int_{V_l}^{V_g} \left(P - \bar{P}\right) dV = f(V_g) - f(V_l) = 0,$$

where $\bar{P}$ is the value of the pressure corresponding to the cut in a Maxwell construction (the coexistence pressure in a two-phase region). Note that $\bar{P}$ also satisfies the van der Waals equation when $V = V_l$ or V_g.

(a) Find the function $f(V)$ of volume V.

(b) Using the result in (a), assuming that the liquid-gas coexistence curve is a symmetric function around the critical value V_c

$$V_g = V_c + x, \quad V_l = V_c - x, \quad V_g - V_l = 2x,$$

show that

$$x \approx 2V_c\sqrt{(T_c - T)/T_c}, \quad T < T_c$$

in the asymptotic critical region when T is close to T_c (x small).

3. (a) Drive the Helmholtz free energy of the van der Waals theory for fluid (hand-waving type is OK)

$$F = -a\frac{N^2}{V} - Nk_BT\ln(V - bN) - \frac{3}{2}Nk_BT\ln(T/c) + \text{const}.$$

The constants a, b, c, const, are independent of both volume V and temperature T. (b) Calculate the heat capacity at constant volume, C_V. (c) Calculate the heat capacity at constant pressure, C_p. (d) Give the asymptotic value as a function of temperature T for C_p near the critical point at a fixed critical pressure P_c.

Tutorial 3

8.5 (K. Huang, page 192)

Calculate the grand partition function Ξ for a system of non-interacting quantum mechanical harmonic oscillators, all of which have the same natural frequency ω_0. Do this for the following two cases:

(a) Boltzmann statistics,

(b) Bose statistics.

The system can be thought of as N identical boson particles in a harmonic potential of frequency ω_0. $N = 0, 1, 2, 3, \ldots$, is not a fixed number. [Read Sec. 8.6 page 185 to 187 of K. Huang].

4. Consider the adsorption of atoms on a crystal surface in a column-like fashion such that if the site i adsorbed n_i atoms the energy associated with the configuration is εn_i, $n_i = 0, 1, 2, 3, \ldots$, independent of the number of atoms adsorbed on other sites. There are all together N such adsorbing sites. Using grand-canonical ensemble, compute

(a) The grand-canonical partition function Ξ;

(b) The entropy S;

(c) The average number of atoms adsorbed, as functions of temperature T and chemical potential μ.

9.4-4. (Callen page 242) Show that for sufficiently low temperature the van der Waals isotherm intersects the $P = 0$ axis, predicting a region of negative pressure. Find the temperature below which the isotherm exhibits this unphysical behavior.