Problem Set 7 (Due Fri March 3)

Problem 1 (30)

Starting with the Mayer cluster expansion for the grand canonical partition function compute 3 first terms in the expansion of fugacity $z(\rho)$ as a function of density $z(\rho)$ leaving the answer in terms of the cluster coefficients, b_i.

Problem 2 (40)

Develop cluster expansion for the 2-particle distribution function $n(r_1, r_2)$ as a function of density. A good starting point is the 2-particle distribution in the grand canonical ensemble

$$n(r_1, r_2) = \sum_{N=2}^{\infty} P_N n_N(r_1, r_2) \tag{1}$$

where $P_N = \mathcal{Z}_G^{-1} z^N Q_N$ is the probability of finding exactly N particles within the GC ensemble and

$$n_N(r_1, r_2) = \frac{1}{(N-2)!} \int d^3\vec{r}_3 ... \int d^3\vec{r}_N e^{-\beta \sum_{i>j} \phi(r_{ij})} \tag{2}$$

is the 2-particle distribution in the Canonical ensemble of N-particles.

Use this definition to calculate $n(r_1, r_2)$ perturbatively, correct to the 4th order in density (i.e. including the ρ^3 term). I.e.

$$n(r_1, r_2) = e^{-\beta\phi(r_{12})}[\rho^2 + C(r_1, r_2)\rho^3 + D(r_1, r_2)\rho^4 ...] \tag{3}$$

what is C? Cluster diagram representation for D will suffice.

Problem 3 (30)

Derive expressions for thermodynamic energy of a multi-component system, namely

$$U = \frac{3}{2} N\beta^{-1} + 2\pi\rho \sum_{i,j} x_i x_j \int_0^{\infty} dr r^2 g_{ij}(r) \phi_{ij}(r) \tag{4}$$

where x_i is the mole fraction of component i and $\phi_{ij}(r)$ is the interaction energy between molecules of type i and j separated by distance r. $g_{ij}(r)$ is the radial distribution fn for type i and j.