Assignment 3

Problem 1: Number Fluctuations and Isothermal compressibility

For the derivation of the compressibility equation we needed the relation between the fluctuations in the number of particles and the isothermal compressibility:

$$\frac{\overline{N^2} - \overline{N}^2}{\overline{N}} = \rho k T \kappa \quad \text{with} \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N},$$

where κ is called the isothermal compressibility.

A) The first step is to express the number fluctuations as some partial derivative. Later you can relate that derivative to $\left(\frac{\partial V}{\partial P}\right)_{T,N}$ by using thermodynamic relations. The average of a function $A(N, j)$ in a grand canonical ensemble is

$$\overline{A} = \sum_{N,j} A(N, j) P_{N,j},$$

where j labels the energy state, and

$$P_{N,j} = \frac{e^{-\beta E_{N,j} + \beta\mu N}}{\Xi(V, \beta, \mu)} \quad \text{and} \quad \Xi(V, \beta, \mu) = \sum_{N,j} e^{-\beta E_{N,j} + \beta\mu N}.$$

Show that

$$\overline{N^2} = kT\left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V} + \overline{N}^2.$$

So that in the thermodynamic limit

$$\overline{N^2} - \overline{N}^2 = kT\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

B) The number fluctuations are now expressed using a derivative with respect to the chemical potential, but we want a derivative with volume and pressure with constant T and N. So we need to change the derivative with respect to the chemical potential to a derivative with respect to the pressure, and then we can use the cyclic rule for partial derivatives to relate $\left(\frac{\partial N}{\partial P}\right)_{T,V}$ to the desired derivative.
The thermodynamic potential corresponding to the grand canonical ensemble is the grand potential:

$$\Omega = -PV \equiv A - \mu N,$$

where A is the Helmholtz free energy. Use this to show that

$$\left(\frac{\partial N}{\partial \mu}\right)_{T,V} = \frac{N}{V}\left(\frac{\partial N}{\partial P}\right)_{T,V}.$$

C) Show that

$$\left(\frac{\partial N}{\partial \mu}\right)_{V,T} = -\rho^2 \left(\frac{\partial V}{\partial P}\right)_{N,T},$$

and use it to show that

$$\frac{\overline{N^2} - \overline{N}^2}{\overline{N}} = -\frac{kT\rho}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}.$$

You can use the cyclic property of partial derivatives,

$$\left(\frac{N}{P}\right)_{V,T}\left(\frac{V}{N}\right)_{P,T}\left(\frac{P}{V}\right)_{N,T} = -1,$$

and $V = vN_aN$, where v is the molar volume (the volume of one mole of gas at a given T and P) and N_a is Avogadro's number.

Problem 2: Fourier transformation of the Ornstein-Zernike Equation

Fourier transform the Ornstein-Zernike equation,

$$h(|\mathbf{r}_1 - \mathbf{r}_2|) = c(|\mathbf{r}_1 - \mathbf{r}_2|) + \rho \int d\mathbf{r}_3 c(|\mathbf{r}_1 - \mathbf{r}_3|) h(|\mathbf{r}_2 - \mathbf{r}_3|),$$

and show that

$$\hat{C}(\mathbf{k}) = \frac{\hat{H}(\mathbf{k})}{1 + \rho \hat{H}(\mathbf{k})} \quad \text{and} \quad \int d\mathbf{r} h(|\mathbf{r}|) = \hat{H}(0).$$

Use the following definition of the Fourier transformation of a function $f(\mathbf{r})$ with $r \in \mathbb{R}^3$:

$$\hat{F}(\mathbf{k}) = \int d^3r \ e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}) \qquad f(\mathbf{r}) = \int \frac{d^3k}{(2\pi)^3} \ e^{-i\mathbf{k}\cdot\mathbf{r}} \hat{F}(\mathbf{k}).$$

Problem 3: The equation of state of hard spheres

Use the pressure equation,

$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT}\int_0^\infty dr 4\pi r^3 u'(r) g(r),$$

to derive the equation of state for hard spheres:

$$\frac{P}{kT} = \rho - \frac{2\pi\rho^2\sigma^3}{3} g(\sigma_+),$$

where $\sigma_+ = \lim_{\delta \to 0} \sigma + \delta$. The hard sphere potential is

$$u_{hs} = \begin{cases} \infty, & \text{if } r < \sigma \\ 0\ , & \text{if } r > \sigma. \end{cases}$$

Note that neither of the cases contains $r = \sigma$ because only the limiting cases are well defined. So, for example, $\lim_{r \to \sigma_+}$ belongs to the $r > \sigma$ case.
The problem with the integral is the derivative of the potential because the potential has an infinite discontinuity at σ. It is possible to write the integrant as some function times a derivative of an other function which has a finite discontinuity at σ. To do this you need to define two new functions:

$$\begin{aligned} y(r) =& e^{\beta u(r)} g(r), \\ e(r) =& e^{-\beta u(r)}. \end{aligned}$$