Homework 4: Density and density fluctuations

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1. **Connection of structure factor to local density**. Density is defined as the number of particles in the system divided by volume. Local density is defined as the number of particles within some small volume, divided by that small volume. A fancy way of defining local density is

$$\rho(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i), \tag{1}$$

   where δ is the Dirac delta function in 3D. This means we are adding up a delta function at every point where there is a particle. Note that this is consistent because $\delta(\vec{r})$ has units of $1/V$.

   The Dirac delta function has the property $\int_V \delta(\vec{r} - \vec{r}_i) f(\vec{r}) dr = f(\vec{r}_i)$ and hence is normalized when you integrate over the box, $\int_V \delta(\vec{r} - \vec{r}_i) dr = 1$. The definition of $\rho(\vec{r}_i)$ is connected to the regular definition of density by:

$$\int_V \rho(\vec{r}) dr = N = \rho V \tag{2}$$

   Show that you can define the structure factor of the system $S(\vec{q}) = \frac{1}{N} \langle \rho(\vec{q}) \rho(-\vec{q}) \rangle$ where $\rho(\vec{q})$ is the Fourier transform of $\rho(\vec{r})$. ($S(\vec{q})$ is defined in Eq. 4.6.29 in Tuckerman and the Fourier transform of f is defined as $f(\vec{q}) = \int_V f(\vec{r}) e^{-i\vec{q}\vec{r}} dr$).

2. **Connection of structure factor to density fluctuations/compressibility** The isothermal compressibility $\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$. It turns out that (we may see this later) when you are at constant pressure, when the number of particles can changes, $\rho k_B T \kappa_T = \mathrm{Var}(N) / \langle N \rangle$. This is very similar to how the heat capacity is related to energy fluctuations. Interestingly, the compressibility is also connected to number fluctuations in a small volume in our constant N systems we have been discussing. We will now see how this compressibility is connected to $S(q)$ and $g(r)$.

For changing number of particles, we can redefine the two quantities above to average over changing numbers of particles

$$\rho(\vec{r}) = \left\langle \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \right\rangle, \tag{3}$$

$$S(\vec{q}) = \frac{1}{\langle N \rangle} \langle \rho(\vec{q}) \rho(-\vec{q}) \rangle, \tag{4}$$

(a) Show that with this definition, $\rho(\vec{q} = 0) = \langle N \rangle$

(b) Show that with these definitions $S(\vec{q}) = 1 + \frac{1}{\langle N \rangle} \left\langle N(N-1) e^{-i\vec{q}\cdot\vec{R}_{12}} \right\rangle$ and hence $S(0) = 1 + \frac{\langle N(N-1) \rangle}{\langle N \rangle}$ (see lecture 8 from class).

(c) Show that $\rho k_B T \kappa_T = S(\vec{q} = 0) - \rho(\vec{q} = 0)$

(d) We showed in class that $S(\vec{q}) = 1 + \rho \int_V d\vec{r} g(\vec{r}) e^{-i\vec{q}\cdot\vec{r}}$ for constant N. For fluctuating N, $\rho = \langle N \rangle / V$. Show that

$$\rho k_B T \kappa_T = 1 + \rho \int_V (g(\vec{r}) - 1) d\vec{r} \tag{5}$$

3. **Pressure for low density repulsive system** - Adapted from Tuckerman problem 4.13.
Consider a system of particles at low density interacting with the pair potential $u(r) = A/r^n$, where $A > 0$ and n is a positive integer.

(a) Compute the pressure as a function of n in the low density limit. In this limit, $g(r) \approx e^{-\beta u(r)}$ and you only need to compute the first virial coefficient $B_2(T)$ to get the pressure (i.e. pressure is given by Tuckerman Equation 4.6.73). You should express your answer in terms of the Γ function:

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt \tag{6}$$

(b) What happens to the pressure when $n = \{1, 2, 3\}$? and $n > 3$? The following properties may be useful:

- $\Gamma(x) > 0$ if $x > 0$
- $\Gamma(0) = \infty$
- $\Gamma(n) = \infty$ for integers $n < 0$
- $\Gamma(-1/2) = -2\sqrt{\pi}$