Part II.

1. It is shown in chapter V of the class notes that the Ornstein-Zernike equation which is the starting point for the theoretical computation of the total correlation function \( h(r) \) in liquids is an equation which connects \( h(r) \) to the direct correlation function \( c(r) \). In order to solve the O-Z equation, it is essential to give another relation which connects \( c(r) \), \( h(r) \) and the inter-particle pair potential function \( u(r) \). This latter relation is called the closure relation.

(a) (5%) Write down two closure relations that you know and use them to justify that in the limit the number density \( \rho \to 0 \), the pair correlation function \( g(r) \) is given simply by

\[
\begin{align*}
g(r) &= e^{-\beta u(r)} \\
\beta &= \frac{1}{k_B T}
\end{align*}
\]

where \( \beta = 1/k_B T \). This is the exact low density limit of the pair correlation function.

(b) (3%) Consider the case of a hard sphere system where \( \sigma \) is the hard sphere diameter of the particles. Sketch the pair correlation function in this limit. What exact features of \( g(r) \) does this approximation capture?

(c) (10%) Use the relation between \( S(Q) \) and \( g(r) \) to calculate the analytical form of \( S(Q) \). and show that in the \( Q \to 0 \) limit,

\[
S(0) = 1 - 8\phi
\]

where \( \phi \) is the volume fraction of the hard spheres. Is this an exact result to the first order in \( \phi \)?

2. It was shown in the class notes that light scattering intensity from a mono-dispersed micellar system can be written as:

\[
R(\text{Rayleigh Ratio}) = KCMS( Q \to 0 ) \ [\text{cm}^{-1}] 
\]

where \( K \) is an optical constant, \( C \) the concentration of the surfactant in solution, in g/ml, and \( M \) the effective molecular weight of the colloidal particle (a micelle in this case) in unit of g/Mol. It is important to know that \( Q \to 0 \) limit of the structure factor is related to the thermodynamic quantity of the solution through the “compressibility theorem”.

\[
S(0) = 1 - 8\phi
\]
(a) (5%) Write down the compressibility theorem for the case of a colloidal solution. Use the virial expansion to cast Eq. (3) into a form involving the second virial coefficient.

(b) (5%) Use the equation derived above to illustrate the Debye Plot applicable for dilute colloidal solutions. What useful quantities can you extract from the Debye plot?

(c) (5%) One can show from Carnahan-Stirling equation of state for hard spheres that

\[
\frac{1}{S(0)} = \frac{1 + 4\eta + 4\eta^2 - 4\eta^3 + \eta^4}{(1 - \eta)^4} \approx \exp(8\eta) .
\] (4)

The attached figure shows the log(CK/R) vs polymer concentration (in weight fraction) of Pluronic P104 tri-block copolymers dissolved in D$_2$O. It is known that the copolymer and heavy water have the same density. It is also known that in the temperature and concentration ranges studied, the copolymers form mono-disperse micelles, each of which has a dry PPO core and a hydrated corona region.

By examining the zero concentration intercept of the line, what can you conclude about the aggregation number of the micelle when the temperature rises?

(d) (10%) Give the specific property of the micelle that one can extract from the slope of the line, assuming that one can approximate the inter-micellar interaction to be hard-sphere-like.

3. The second virial coefficient can be measured easily by a light scattering experiment, so it is useful to calculate it theoretically. In class we showed that given an inter-particle pair potential function $u(r)$, one can calculate the second virial coefficient $B_2(T)$. You are asked to calculate $B_2(T)$ for the adhesive sphere system. The adhesive sphere model is defined by a dimensionless inter-particle potential function

\[
\beta u(r) = \begin{cases} 
\infty & \text{if } r < R - \Delta \\
-\Omega & \text{if } R - \Delta < r < R \\
0 & \text{if } r > R 
\end{cases}
\] (5)

(A) (10%) Show that

\[
B_2(T) = \frac{2}{3} \pi R^3 \left(1 - \frac{1}{4\tau}\right)
\] (6)

where \[
\frac{1}{\tau} = \frac{12\Delta}{R} e^\Omega, \quad \text{for } \frac{\Delta}{R} \ll 1 .
\] (7)
Interpret the physical meaning of the two terms in Eq.6.