

8.575J,10.44J, 22.52J **Statistical Thermodynamics of Complex Liquids (2004)**  
**Quiz 2 (Prof. Chen)**

**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  $\rho \rightarrow 0$ , the pair correlation function  $g(r)$  is given simply by

$$g(r) = e^{-\beta u(r)} \quad (1)$$

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  $Q \rightarrow 0$  limit,

$$S(0) = 1 - 8\phi \quad (2)$$

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:

$$R(\text{Rayleigh Ratio}) = KCMS(Q \rightarrow 0) \quad [\text{cm}^{-1}] \quad (3)$$

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  $Q \rightarrow 0$  limit of the structure factor is related to the thermodynamic quantity of the solution through the “compressibility theorem”.

- (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

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

The attached figure shows the  $\log(CK/R)$  vs polymer concentration (in weight fraction) of Pluronic P104 tri-block copolymers dissolved in  $D_2O$ . 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 d 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

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

(A) (10%) Show that

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

where  $\frac{1}{\tau} = \frac{12\Delta}{R} e^{\Omega}$ , for  $\frac{\Delta}{R} \ll 1$ . (7)

Interpret the physical meaning of the two terms in Eq.6.