

8.575J, 10.44J, 22.52J **Statistical Thermodynamics of Complex Liquids**

Problem Set 3 (Prof. Chen)

Due May 11, 2004

1. The simplest way of taking into account the excluded volume effect on the structure factor of a system of colloidal particles is to take the following approximate form of $g(r)$:

$$g(r) = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma \end{cases} \quad (1)$$

where σ is the equivalent hard sphere diameter of the particles. This is called a “correlation hole” approximation.

(A) What exact features of $g(r)$ does the correlation hole approximation capture?

(B) Use the relation between $S(Q)$ and $g(r)$ to calculate the analytical form of $S(Q)$.

(C) Show that in the $Q \rightarrow 0$ limit,

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

where ϕ is the volume fraction of the hard spheres. This is an exact result to 1st order in ϕ . Give a plausible reason that a drastic approximation such as Eq.(1) gives correct $S(0)$ to first order in ϕ .

2. Fourier’s transformation of the direct correlation function of a sticky hard sphere model is given in an analytical form in the end of Chapter VI of the lecture note. This expression contains two parts: the first part, which is the purely hard sphere part and the second part, which comes from the stickiness. This latter part contains a parameter λ which is the smaller root of eq.(6.36).

(a) Show that the resulting structure factor $S(Q)$, where $Q = kd$, can be expressed in a closed analytical form with a set of auxiliary equations. It is functions of two basic parameters, the volume fraction ϕ and the stickiness $1/\tau$.

$$\frac{1}{S(Q)} - 1 = 24\phi \left[\alpha f_2(Q) + \beta f_3(Q) + \frac{1}{2} \phi \alpha f_5(Q) \right] + 2\phi^2 \lambda^2 f_1(Q) - 2\phi \lambda f_0(Q) \quad (3)$$

Where various functions are defined as: $f_0(x) = \sin(x)/x$; $f_1(x) = (1 - \cos(x))/x^2$; $f_2(x) = (\sin(x) - x \cos(x))/x^3$; $f_3(x) = [2x \sin(x) - (x^2 - 2) \cos(x) - 2] / x^4$; $f_5(x) = [(4x^3 - 24x) \sin(x) - (x^4 - 12x^2 + 24) \cos(x) + 24] / x^6$, and

$$\alpha = \frac{(1+2\phi-\mu)^2}{(1-\phi)^4}, \quad \beta = -\frac{3\phi(2+\phi)^2 - 2\mu(1+7\phi+\phi^2) + \mu^2(2+\phi)}{2(1-\phi)^4} \quad (4)$$

$$\mu = \lambda \phi(1-\phi), \quad \lambda = \frac{6(\Delta - \sqrt{\Delta^2 - \Gamma})}{\phi}, \quad \Gamma = \frac{\phi(1+\phi/2)}{3(1-\phi)^2}, \quad \Delta = \tau + \frac{\phi}{1-\phi} \quad (5)$$

The hard sphere limit is obtained by setting $1/\tau \rightarrow 0$, $\lambda \rightarrow 0$, $\mu \rightarrow 0$.

(b) Calculate and plot the structure factor $S(Q)$ at volume fraction $\phi = 0.1213$ and at two stickiness parameters: $1/\tau = 1.0$ and $1/\tau = 10$. Compare the first case with the pure hard sphere case at the same volume fraction. Discuss the small Q feature of the second case.

3. This problem concerns the interpretation of light scattering data from a colloidal suspension. It was stated in problem set 2 that the Rayleigh ratio at 90° scattering angle can be written as:

$$R_{90} = K \frac{cRT}{\left[\frac{\partial \pi}{\partial c} \right]_{T,P}} \quad (6)$$

where $R = N_A k_B$, c is the concentration of the solute in g/ml and

$$K = \frac{4\pi^2 n^2}{N_A \lambda_0^4} \left[\frac{\partial n}{\partial c} \right]_T^2 \quad (7)$$

If the colloidal particle is made of a spherical aggregate of polymers with total molecular weight M (molecular weight of the polymer times the average aggregation no. of polymers per colloidal particle, i.e. $M = M_w \bar{N}$) and, to the first approximation, we can treat it as a hard sphere of diameter σ . Then show that Canahan-Stirling formula for the pressure of a hard sphere system can be written as:

$$\pi = \frac{cRT}{M} f_1(c) \quad (8)$$

where

$$f_1(c) = \frac{1 + qc + q^2 c^2 - q^3 c^3}{(1 - qc)^3}, \quad q = \frac{\pi}{6} \sigma^3 \frac{N_A}{M}. \quad (9)$$

Calculate the Rayleigh ratio and plot it as a function of c in the range 0 to 0.4 g/ml. Take K as a constant and $\sigma = 100 \text{ \AA}$ and $M = 310 \text{ KD}$.

If there is an attractive interaction with the potential $u(r)$, in addition, one can use the perturbation theory described in the lecture notes

$$\frac{\beta A}{N} = \frac{\beta A_{\text{HS}}}{N} + \frac{1}{2} \beta \rho \int_0^\infty dr 4 \pi r^2 u(r) g_{\text{HS}}(r) \quad (10)$$

to show that

$$\begin{aligned} \pi &= \pi_{\text{HS}} + \left[\frac{c N_A}{M} \right]^2 \frac{\partial}{\partial c} \left[2 \pi c \int_0^\infty dr r^2 u(r) g_{\text{HS}}(r) \right] \\ &= \frac{cRT}{M} f_1(c) + f_2(c) \end{aligned} \quad (11)$$

If the attractive potential is very long-ranged, we can make an approximation,

$$2 \pi \int_0^\infty dr r^2 u(r) g_{\text{HS}}(r) = 2 \pi \int_\sigma^\infty dr r^2 u(r) g_{\text{HS}}(r) = -a \quad (12)$$

where a is called the van der Waal constant. Then,

$$\pi = \frac{cRT}{M} f_1(c) - a \left[\frac{N_A}{M} \right]^2 c^2 \quad (13)$$

Take $\frac{a}{k_B T} = 1.33 \times 10^{-18} \text{ cm}^3$ and $T = 293 \text{ K}$. Recalculate R_{90} and compare with the hard sphere result.

4. Show that for a co-polymer solution of concentration c (in unit of g/ml), where the co-polymer molecules are known to self-associate into spherical micelles of diameter σ , the general expression for the Rayleigh ratio at finite k can be written as:

$$R_\theta = K C M \bar{P}(k) S(k) \quad (14)$$

In this equation, K is the constant defined already in problem 3, $C=c$ - c.m.c. (in unit of g/ml), M the average molecular weight of the micelles (in unit of g/Mol), $\bar{P}(k)$ the normalized particle structure factor and $S(k)$ the inter-micellar structure factor. Assuming that the micellar size σ is much smaller compared to wave length of light so that effectively $\bar{P}(k)=1$ and one can take $k = 0$ limit of $S(k)$ to obtain

$$R_{\theta} = KCMS(0). \quad (15)$$

A. show that for a hard sphere system

$$\frac{1}{S(0)} = \frac{1 + 4\phi + 4\phi^2 - 4\phi^3 + \phi^4}{(1 - \phi)^4} = 1 + 8\phi + 30\phi^2 + 72\phi^3 + 140\phi^4 + \dots \quad (16)$$

where ϕ is the volume fraction of hard spheres.

B. Show by plotting $\text{Ln}(1 / S(k))$ vs ϕ , for ϕ from 0 to 0.5, that $\frac{1}{S(0)} \approx \exp(8\phi)$ to a very good approximation.

C. We can put Eq.15 into a form

$$\text{Ln} \left[\frac{KC}{R_{90}} \right] = \text{Ln} \left[\frac{1}{M} \right] + \text{Ln} \left[\frac{1}{S(k)} \right]. \quad (17)$$

According to the result of section B, if one plot $\text{Ln} \left[\frac{KC}{R_{90}} \right]$ vs C , one would obtain a straight line for a range of C from 0 to 20 weight % of polymer or so. Considering that there is about 50% of hydration in a co-polymer micelle, this would amount to a range of micellar volume fraction ϕ from 0 to 40%. Find out what information you can extract from this plot. This is a generalized "Zimm plot" which is well known in light scattering literature.

D. An example is given in the following from a light scattering investigation of a Pluronic tri-block copolymer P104 [(PEO₂₇ PPO₆₁ PEO₂₇), MW = 5900 DT] in water at 45°C (Y.C. Liu, S.H. Chen, J.S. Huang, Light Scattering Studies of Concentrated Copolymer Solutions, *Macromolecules* **31**, 6226-6233 (1998)). It is known that the density of Pluronic polymers is 1.0 g/ml to a good approximation. Calculate the hydrated volume fraction and the aggregation number of the micelle.