8.575J , 10.44J, 22.52J **Statistical Thermodynamics of Complex Liquids**
(Spring 2004) **Problem Set 1** (Prof. Chen) Due March 18.

1. Given the following table for the scattering lengths of common elements:

Isotope	Hydrogen	Deuterium	Carbon	Nitrogen	Oxygen
b_{coh} (10^{-12} cm)	-0.37423	0.6674	0.66484	0.936	0.5805

estimate the molecular volume (from the molecular weight and density) and then calculate the scattering length densities of the following molecules, in unit of10^{10} cm^{-2}: H_2O, D_2O, Octane, Deuterated octane, and Pluronic P-84, a tri-block co-polymer, $[(PEO)_{19}(PPO)_{43}(PEO)_{19}]$, where PEO = $-(CH_2)_2O-$, having a molecular volume 72.4 Å^3, and PPO = $-(CH_2)_3O-$, having a molecular volume 95.4 Å^3.

2. Show that the form factor of a spherical particle with an internal core of radius R_1 and a scattering length density (sld) ρ_1, surrounded by a shell with an outer radius R_2 and sld ρ_2, immersed in a solvent of sld ρ_s, is given by:

$$F_{2-shell}(Q) = \frac{4}{3}\pi R_1^3(\rho_1 - \rho_2)\left[\frac{3j_1(QR_1)}{QR_1}\right] + \frac{4}{3}\pi R_2^3(\rho_2 - \rho_s)\left[\frac{3j_1(QR_2)}{QR_2}\right]$$

Use this result to calculate and plot the normalized particle structure factor $\overline{P}(Q)$ of a co-polymer micelle having an inner core radius R_1 and an outer radius R_2. In a core-shell model of the micelle [Y.C. Liu et al, Phys. Rev. E 54, 1698 (1996)], the inner and outer radii can be determined from the aggregation (N) and hydration (H) numbers of the micelle. Plot the $\overline{P}(Q)$ for the case of N = 63 and H = 290.

3. Show that the form factor of a randomly oriented prolate spheroid, with semi-major and minor axes of a and b, is given by:

$$F_{ellipsoid}(Q) = \frac{4\pi}{3}ab^2(\Delta\rho)\int_0^1 d\mu\left[\frac{3j_1(u)}{u}\right] \qquad (2)$$
$$u = Q\sqrt{a^2\mu^2 + b^2(1-\mu^2)}$$

where $(\Delta\rho)$ is the contrast between the particle and the solvent, μ the cosine of the angle between the major axis of the spheroid and the Q-vector.

4. Derive a normalized particle structure factor $\bar{P}(Q)$ of a uniform cylindrical particle of radius R and length L. Assuming that the particle is randomly oriented with respect to the $\vec{Q}$ vector.

(A) Show that:

1

$$\bar{P}(Q) = \left\langle \left| \frac{1}{V_p} \int_{V_p} e^{i\vec{Q}\cdot\vec{r}} d^3 r \right|^2 \right\rangle = \frac{1}{2} \int_{-1}^{1} d\mu \left[\frac{\sin QL\mu/2}{QL\mu/2} \right]^2 \left[\frac{2J_1(QR\sqrt{1-\mu^2})}{QR\sqrt{1-\mu^2}} \right]^2 . \quad (3)$$

In Eq.3, V_p denotes the volume of the particle, $\vec{r}$ the position vector of an arbitrary point in the interior of the particle, and μ the cosine of the angle between the axis of the cylinder and the Q-vector. The bracket means that we are considering an average over random orientations of the particle.

(B) Show that for a long and thin cylinder, one has asymptotic formulae:

$$\bar{P}(Q) \underset{QL>2\pi}{\longrightarrow} \frac{\pi}{QL} \left[\frac{2J_1(QR)}{QR} \right]^2 \underset{QR<1}{\longrightarrow} \frac{\pi}{QL} e^{-\frac{1}{4}Q^2R^2} \quad (4)$$

(C) Show that for a flat particle (a lamellar) of QR>>1,

$$\bar{P}(Q) \underset{QR>>1}{\longrightarrow} \frac{2}{Q^2R^2} \left[\frac{\sin QL/2}{QL/2} \right]^2 \underset{QL<1}{\longrightarrow} \frac{2}{Q^2R^2} e^{-\frac{1}{12}Q^2L^2} \quad (5)$$

where L is the thickness of the flat plate.

(D) From Eq.4 and 5, one can conclude that for a long rod a ln[QI(Q)] vs Q^2 plot, and for a flat disk, a ln[Q^2I(Q)] vs Q^2 plot, will result in a straight line at large Q with slopes proportional to $R^2/4$ and $L^2/12$ respectively. Explore additional system parameters you can extract from the intercept at Q = 0.

(E) In polymer literature, another approximate formula is often used. It is the limit when R goes to zero, the so called "stiff thin rod" limit. Show that:

$$\bar{P}(Q) \underset{R\to 0}{=} \int_0^1 d\mu \left[\frac{\sin QL\mu/2}{QL\mu/2} \right]^2 = \int_0^1 d\mu \left[\frac{\sin x\mu}{x\mu} \right]^2 = \frac{1}{x} \int_0^{2x} \frac{\sin u}{u} du - \left(\frac{\sin x}{x} \right)^2 . \quad (6)$$

Explore graphically the difference between approximations of the last equation and Eq. 3

5. **(This problem is added for your interest only. Your answer is optional. In case you solve it, you will get a bonus points of 20/100)**

Scattering intensity of a Gaussian chain. Consider a flexible polymer chain of a contour length L =Na, where N is the no. of segments and a is the Kuhn length. If the chain makes a random walk in space, then the mean square end-to-end distance is $R^2 = Na^2$. For this chain, the distribution of distances between two links (i,j) is Gaussian, namely,

2

$$P(R_{ij})dR_{ij} = \left[\frac{3}{2\pi\langle R_{ij}^2\rangle}\right]^{3/2} 4\pi R_{ij}^2 \exp\left[\frac{-3R_{ij}^2}{2\langle R_{ij}^2\rangle}\right] dR_{ij}\ , \text{ where } \langle R_{ij}^2\rangle = |i-j|a^2 . \qquad (7)$$

In order to calculate the normalized particle structure factor of such chain. (a) Start from the definition:

$$\overline{P}(Q) = \frac{1}{N^2}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} e^{i\vec{Q}\cdot(\vec{R}_i - \vec{R}_j)} \right\rangle = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle e^{i\vec{Q}\cdot\vec{R}_{ij}}\right\rangle_{gaussian} \qquad (8)$$

so that we can evaluate the Gaussian average by integrating the exponential phase factor using the distribution function given by Eq.7. (b) Show first that :

$$\overline{P}(Q) = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp[-\frac{1}{6}\langle R_{ij}^2\rangle] = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\exp[-\frac{1}{6}Q^2a^2|i-j| \qquad (9)$$

(c) Prove a theorem: For an arbitrary function f(x),

$$\sum_{i=1}^{N}\sum_{j=1}^{N} f(|i-j|) = Nf(0) + 2\sum_{n=1}^{N-1}(N-n)f(n) \qquad (10)$$

(d) Use the theorem to show that the sum in Eq.9 can be evaluated as:

$$\overline{P}(Q) = \frac{1}{N^2}\left[N + 2\frac{(N-1)\alpha - N\alpha^2 + \alpha^{N+1}}{(1-\alpha)^2}\right] \qquad (11)$$

where $\alpha = \exp(\frac{1}{6}Q^2a^2) \approx 1 - \frac{1}{6}Q^2a^2$, because Qa is much smaller than unity in practice.

(e) Show that in the limit $N \to \infty$, $\overline{P}(Q)$ approach the Debye function

$$\overline{P}(Q) = \frac{2}{x^2}(x - 1 + e^{-x}),\ \text{where } x = \frac{1}{6}Q^2R^2 = \frac{1}{6}Q^2a^2N \qquad (12)$$

(f) Discuss the small and large Q behavior of Eq.12. In particular, show that:

$$\lim_{x\to\infty}\frac{1}{P(Q)}=\frac{1}{2}+\frac{1}{12}Q^2R^2 \quad (13)$$