10.44J, 22.52 J, 8-575J **Statistical Thermodynamics of Complex Liquids**
(Spring 2004)   **Problem Set 2** (Prof. Chen)   Due April 1.

1. Starting from the general expression for the scattering field in VV geometry derived in the class:

$$\vec{E}_s(\vec{r},t) = \frac{k_v^2}{4\pi}\frac{e^{ikr}}{r}\vec{E}_0 e^{-i\omega t}\Delta\varepsilon(\vec{Q},t) \tag{1}$$

where $k_v = \dfrac{2\pi}{\lambda_0}$ is the wave no of light in vacuum, and $\Delta\varepsilon(\vec{Q},t)$ the Fourier transform of the dielectric

constant fluctuation in the fluid. We can calculate the differential cross section for the light scattering as:

$$\frac{d\sigma}{d\Omega} = \frac{\left\langle \left|\vec{E}_s(\vec{r},t)\right|^2\right\rangle r^2}{\left\langle \left|\vec{E}_i(\vec{r},t)\right|^2\right\rangle} = \frac{k_V^4}{16\pi^2}\left\langle \left|\varepsilon(\vec{Q},t)\right|^2\right\rangle. \tag{2}$$

For one-component liquids we can relate the dielectric fluctuation to the density fluctuation by:

$$\Delta\varepsilon(\vec{r},t) = \left[\frac{\partial\varepsilon}{\partial\rho}\right]_T \delta\rho(\vec{r},t) \quad \text{where } \delta\rho(\vec{r},t) = \rho(\vec{r},t) - \rho \tag{3}$$

is the number density fluctuation and $\rho = N/V$ the average number of the fluid molecules per unit
volume. We can also Fourier transform Eq.3 to obtain

$$\Delta\varepsilon(\vec{Q},t) = \left[\frac{\partial\varepsilon}{\partial\rho}\right]_T \rho(\vec{Q},t) \tag{3'}$$

(a) Show that the differential scattering cross section per unit volume can be transformed into a practical
form:

$$\left[\frac{d\Sigma}{d\Omega}\right]_{VV} \equiv \frac{1}{V}\left[\frac{d\sigma}{d\Omega}\right]_{VV} = \frac{4\pi^2}{\lambda_0^4}n^2\left[\frac{\partial n}{\partial\rho}\right]_T^2 \frac{N}{V}S(Q). \tag{4}$$

(b) Given the fluctuation theorem which states that:

$$S(Q \to 0) = \rho k_B T \chi_T = k_B T \left[\frac{\partial \rho}{\partial p}\right]_T \tag{5}$$

and the virial expansion:
$$\frac{p}{k_B T} = \rho + B_2 \rho^2, \tag{6}$$

show that

$$\left[\frac{d\Sigma}{d\Omega}\right]_{VV} = \frac{4\pi^2}{\lambda_0^4} n^2 \left[\frac{\partial n}{\partial \rho}\right]_T^2 \frac{\rho}{1 + 2B_2\rho}, \tag{7}$$

where $\left[\frac{d\Sigma}{d\Omega}\right]_{VV}$ is called the Rayleigh ratio in the literature.

For two-component liquids such as a macromolecule of molecular weight M_w and index of refraction n suspended in a solvent of index of refraction n_0, one likewise expands the $\Delta \varepsilon(\vec{Q}, t)$ in terms of the concentration fluctuation $C(\vec{Q}, t)$ as:

$$\Delta\varepsilon(\vec{Q}, t) = \left[\frac{\partial \varepsilon}{\partial C}\right]_T C(\vec{Q}, t) \tag{8}$$

so that

$$\left\langle \left|\Delta\varepsilon(\vec{Q}, t)\right|^2 \right\rangle = \left[\frac{\partial \varepsilon}{\partial C}\right]_T^2 \left\langle \left|C(\vec{Q}, t)\right|^2 \right\rangle \tag{9}$$

(c) Show that for $Q \to 0$,

$$\left\langle \left|C(\vec{Q}, t)\right|^2 \right\rangle = V^2 \left\langle \left|\Delta C\right|^2 \right\rangle \tag{10}$$

where ΔC is the average concentration fluctuation over the volume V.

(d) For the two-component system we thus have:

$$\left[\frac{d\Sigma}{d\Omega}\right]_{VV} = \frac{4\pi^2}{\lambda_0^4} \left[\frac{\partial \varepsilon}{\partial C}\right]_T^2 V \left\langle \left|\Delta C\right|^2 \right\rangle \tag{11}$$

(e) Show from thermodynamic fluctuation theory that:

$$V\left\langle |\Delta C|^2 \right\rangle = \frac{k_B TC}{\left[\dfrac{\partial \pi}{\partial C}\right]_T} \tag{12}$$

and use Vant Hoff's equation of the states

$$\Pi = \frac{N_A k_B TC}{M_W} \tag{13}$$

where N_A is Avogadro's number and C the concentration of the solute in g/ml., the differential cross section per unit volume is finally written as:

$$\left[\frac{d\Sigma}{d\Omega}\right]_{VV} = \frac{4\pi^2}{\lambda_0^4} n_0^2 \left[\frac{\partial n}{\partial C}\right]_T^2 \frac{M_W C}{N_A} = HCM_W. \tag{14}$$

where H is an experimental constant defined as:

$$H = \frac{4\pi^2}{\lambda_0^4} n_0^2 \left[\frac{\partial n}{\partial C}\right]_T^2 \frac{1}{N_A}. \tag{15}$$

An important point to observe is that for an ideal solution, the $Q = 0$ limit of the intensity is proportional to the molecular weight of the solute.

(f) Extend the cross section formula to a more general non-ideal solution case where

$$\frac{\Pi}{N_A k_B T} = \frac{C}{M_W} + B_2 C^2 \tag{16}$$

and get the often quoted formula in the literature of light scattering

$$\frac{HC}{\left[\dfrac{d\Sigma}{d\Omega}\right]_{VV}} = \frac{1}{M_W} + 2B_2 C \tag{17}$$

The left hand side quantity vs C plot at a given temperature would be a straight line giving the molecular weight from the zero intercept, and the slope of the line gives the second virial coefficient. This is called a Zimm plot in the literature.

2. Consider small angle scattering from a disordered, isotropic material. Starting from the known expression (derived in the class) for the scattering intensity per unit volume

$$I(Q) = \frac{1}{V}\left\langle \left| \sum_\ell b_\ell \exp\left(i\vec{Q} \cdot \vec{R}_\ell\right) \right|^2 \right\rangle \tag{18}$$

(A) Show that one can transform the expression to a from

$$I(Q) = \int_0^\infty dr\, 4\pi r^2 j_0(Qr) \langle \rho(0)\rho(\underline{r})\rangle, \tag{19}$$

where $\rho(r)$ is the scattering length density (sld) defined as

$$\rho(\underline{r}) = \sum_\ell b_\ell \delta(\underline{r} - \underline{R}_\ell). \tag{20}$$

We now specialize to a two-phase system. Let the scattering length density of phase 1 be $\rho_1(\approx \rho_w)$ and that of the phase 2, $\rho_2(\approx \rho_o)$, and denote by $\Delta\rho = \rho_1 - \rho_2$. The linear and square average scattering length densities of the medium are given by:

$$\overline{\rho} = \Phi_1\rho_1 + \Phi_2\rho_2 \tag{21}$$
$$\overline{\rho^2} = \Phi_1\rho_1^2 + \Phi_2\rho_2^2 \tag{22}$$

where Φ_1 and Φ_2 are the volume fractions of phase 1 and 2 respectively.

(B) From these definitions and the fact that $\Phi_1 + \Phi_2 = 1$, derive a useful relation for the mean square fluctuation of the sld in the medium:

$$\left\langle \left(\rho(r) - \overline{\rho}\right)^2 \right\rangle = \overline{\rho^2} - \overline{\rho}^2 = \Phi_1\Phi_2\left(\rho_1 - \rho_2\right)^2 = \left(\Delta\rho\right)^2\Phi_1\Phi_2 \tag{23}$$

Next, consider fluctuation of the sld $\eta(r) = \rho(r) - \overline{\rho}$

(C) Show that

$$\langle \rho(0)\rho(\underline{r})\rangle = \left\langle \left(\eta(0) + \overline{\rho}\right)\left(\eta(r) + \overline{\rho}\right) \right\rangle$$
$$= \langle \eta(0)\eta(r)\rangle + \overline{\rho}^2. \tag{24}$$

Therefore, except at Q=0, we can write:

$$I(Q) = \int_0^\infty dr\, 4\pi r^2 j_0(Qr)\langle\eta(0)\eta(r)\rangle$$

$$= \langle\eta^2\rangle \int_0^\infty dr\, 4\pi r^2 j_0(Qr)\frac{\langle\eta(0)\eta(r)\rangle}{\langle\eta^2\rangle} \tag{25}$$

where $\langle\eta^2\rangle = (\Delta\rho)^2 \Phi_1\Phi_2$ according to Eq.23. We call $\Gamma(r)$ the normalized Debye correlation function defined as:

$$\Gamma(r) = \frac{\langle\eta(0)\eta(r)\rangle}{\langle\eta^2\rangle}. \tag{26}$$

(D)   Show from Eq.25, the existence of the "invariant",

$$\langle\eta^2\rangle = \frac{1}{2\pi^2}\int_0^\infty dQ\, Q^2 I(Q). \tag{27}$$

The most important properties of the Debye correlation function of a two-phase system are:

(i) $\Gamma(r=0) = 1$, $\Gamma(r\to\infty) = 0$. \hfill (28)

The latter condition follows from the fact that at large separation $\langle\eta(0)\eta(r)\rangle \approx \langle\eta(0)\rangle\langle\eta(r)\rangle = 0$.

(ii)
$$\Gamma'(r=0) = -\frac{1}{4\Phi_1(1-\Phi_1)}\frac{S}{V}$$

$$\tag{29}$$

where S/V is the total interfacial areas per unit volume in the medium, a very important property in a micro-phase- separated system or in a porous material. Try to prove this theorem (ii) by reading the lecture notes.

There are two simple models for the Debye correlation function in a porous materials or micro-phase-separated systems which are only approximate:

(a)   Debye model (one parameter model): $\Gamma_D(r) = \exp(-r/\xi)$. \hfill (30)

(b)   Teubner-Strey model (two parameter model): $\Gamma_{TS}(r) = \exp(-r/\xi)j_0(kr)$ \hfill (31)

(E)   Calculate the scattering intensity (analytical expression) for each case and sketch its graphical form.

(F)   Relate the S/V to the model parameters in each case.

3. In the lecture notes we derive Porod's law, which is asymptotically valid for any system with smooth internal interfaces (i.e. for Q>> reciprocal of the persistence length of the surface). It can be stated as follows :

$$I(Q \to \infty) = 2\pi(\rho_1 - \rho_2)^2 \frac{S}{V} \frac{1}{Q^4}. \tag{32}$$

It was derived from consideration of the short distance behavior of $\Gamma(r)$. In the following you are asked to derive it directly from the scattering intensity formula of neutrons or x-rays from a sharp interface separating a medium with a sld ρ_1 from another medium with a sld ρ_2. Imagine a sample with a volume V, having a large, flat, internal interface of an area S. Take this interface to lie in the x-y plane. The scattering intensity for a given direction of $\vec{Q}$ (with respect to the surface normal) is, by definition,

$$I(\vec{Q}) = \frac{1}{V} |F(\vec{Q})|^2 \tag{33}$$

where the form factor is given by

$$F(\vec{Q}) = \int d^3r \, \rho(\vec{r}) e^{i\vec{Q}\cdot\vec{r}} = \int dx \int dy \int dz \exp[i(Q_x x + Q_y y + Q_z z)] \, \rho(z). \tag{34}$$

(A)   Let $\rho(z) = \rho_2$, for $z > 0$; and $\rho(z) = \rho_1$, for $z < 0$. Integrate over z first to get

$$F(\vec{Q}) = \frac{(\rho_1 - \rho_2)}{iQ_z} \int dx \int dy \exp[i(Q_x x + Q_y y)] = \frac{(\rho_1 - \rho_2)}{iQ_z} (2\pi)^2 \delta(Q_x)\delta(Q_y). \tag{35}$$

(B)   Show that

$$I(\vec{Q}) = \frac{1}{V} |F(\vec{Q})|^2 = \frac{(2\pi)^2}{V} \frac{(\rho_1 - \rho_2)^2}{Q_z^2} S\delta(Q_x)\delta(Q_y). \tag{35}$$

(C)   Now, the measured intensity distribution I(Q) is the orientational average of the above calculated $I(\vec{Q})$, namely, one has to average over all directions of the Q-vector. Take the direction of the Q-vector to be in the direction defined by polar coordinates (ϑ, φ). Then,

$$I(Q) = \langle I(\vec{Q}) \rangle = \frac{1}{V} \langle |F(\vec{Q})|^2 \rangle = \frac{(2\pi)^2}{V} \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^{\pi} d\vartheta \sin\vartheta \frac{(\rho_1 - \rho_2)^2}{Q^2 \cos^2 \vartheta} S\delta(Q_x)\delta(Q_y).$$

Show that the above integration leads to precisely the Porod's law given in the beginning of the problem.

This particularly beautiful derivation of the Porot's law was first given by P. De Genne.