## Quiz 9 Polymer Properties March 29, 2019

Guinier and Fournet (1955, p. 42) Refer to Yvon and Green's equation of state for a fluid (derived separately),

$$p = \frac{kT}{v_1} - \frac{1}{6v_1^2} \int_0^\infty P(r) \Phi'(r) 4\pi r^2 dr$$
(61)

Where  $v_1$  is the specific volume available to a colloidal particle or a liquid molecule (inverse of the density), P(r) is the normalized binary correlation function for the arrangement of particles such that at large r, P(r) goes to 1,  $P(r) \sim \exp(-\mathcal{P}(r)/kT)$  ((1-P(r)) is the transform of scattered intensity related to the structure factor by equation (53)),  $\mathcal{P}(r)$  is the potential between particles in units of kT and r is the separation distance between particles. Debye worked out the following expression for scattered intensity (the sin term is the Fourier transform for isotropic particles),

$$I(q) = I_e(q) \left\{ \overline{F^2(q)} - \frac{\left(\overline{F(q)}\right)^2}{v_1} \int_0^\infty \frac{\sin qr}{qr} \left[1 - P(r)\right] 4\pi r^2 dr \right\}$$
(53)

- a) Show that the ideal gas law and the scattering law for a single particle correspond to the same condition by inspecting equations (61) and (53).
- b) As particles approach each other, at higher concentration, P(r) can be written as a Taylor series in the volume available to a particle  $P(r) = P_0(r) + v_1 P_1(r) + \dots$

series in the volume available to a particle, 
$$v_1$$
,  $(r) = 0$ ,  $r = 1$ ,  $r = 1$ , where  
 $P_0(r) = \exp\left(\frac{-\Phi(r)}{kT}\right)$  and looking at only the first term of the expansion the equation of  
 $pv_1 = kT \left[1 - \frac{(2\pi)^{3/2}}{2} \frac{\beta(0)}{2}\right]$ 

state becomes,  $[ (where \beta(0) )$  is related to the second virial coefficient) and the scattered intensity from equation (53) becomes,

$$I(q) = \overline{N}I_e(q)F^2(q)\left\{1 + \frac{(2\pi)^{\frac{3}{2}}}{v_1}\beta(q)\right\} \text{ where } \beta(q) = \frac{2}{q\sqrt{2\pi}}\int_0^\infty \left(e^{-\frac{\Phi(r)}{kT}} - 1\right)\sin(qr)rdr$$

Debye (while at Cornell) worked out this equation for hard spheres such that P(r) = 0 for 0 < r < 2R (excluded volume) and P(r) = 1 for r > = 2R,

$$I(q) = NI_{e}(q)\varphi^{2}(qR)\{1 - p\varphi(2qR)\} \qquad p = \frac{8v_{0}}{v_{1}}$$
(66)

 $\psi(qr)$  is the sphere scattering amplitude function. *p* is the packing factor and  $v_0$  is the occupied volume of the sphere,  $v_1$  is the available volume. This equation accounts for

binary interactions but not higher order interactions (c(r) in the Ornstein Zernike equation but not  $\gamma(r)$ ).

Explain what the terms  $v_0$  and  $v_1$  correspond to in a sketch of a collection of spheres. How would the two parameters depend on concentration. What is the value for *p* for FCC or HCP structure where space is filled to about 74%.

- c) Raman (1924) (the Raman scattering Raman) believed that the solution of question "b" was exact and general for higher concentrations. Explain, based on the Ornstein-Zernike-Prins equation and ideas about dogs barking at night why this is not true at higher concentrations.
- d) Guinier states that "the more complete theories of Born and Green (and Yvon) (done in separate papers) lead to the following result",

$$I(q) = \overline{N}I_{e}(q) \left\{ \overline{F^{2}(q)} - \frac{\beta(q)(\overline{F(q)})^{2}}{v_{1}(2\pi)^{-3/2} - \beta(q)} \right\}$$
(67)

Under the assumption of spherically symmetric particles this becomes,

$$I(q) = \overline{N}I_e(q)F^2(q) \left\{ \frac{v_1}{v_1 - (2\pi)^{\frac{3}{2}}\beta(q)} \right\}$$
(68)

For a polymer in a solvent the scattering can be described by the RPA equation which is

of the form,  $\frac{\phi}{I(q)} \sim \frac{\phi_0}{I_0(q)} - \phi A_2$ . Show that equation (68) is basically the RPA equation for a polymer in solution.

e) Fournet used a Leonard-Jones potential and equation (68) to model diffraction from argon gas at high densities using,

$$I(q) = \overline{N}I_{e}(q)\varphi^{2}(qR)\left\{\frac{1}{1+p\varphi(2qR)}\right\} \sim \overline{N}I_{e}(q)F^{2}(q)\left\{\frac{1}{1+p\varphi(q\xi)}\right\}$$
(75)

Where the latter approximation is due to Beaucage I believe, and assumes that odd shaped, but spherically symmetric particles described by a dilute scattering function,  $F^2(q)$ , can correlate in a roughly spherical manner, i.e. in disordered spherical shells of radius  $\xi$ . This function has been applied to colloidal suspensions and polymer/filler systems with some success.

Equation (75) transforms a thermodynamic description of interactions, equation (68), to a structural interpretation of interactions (75). This is similar to the relationship between the equation of state (61) and the scattering function (53). Explain in your own words how structure relates to thermodynamics for disordered systems in this context.

f) Equation (68) (and (75)) have a resemblance to the geometric series:

$$rac{1}{1-x} = 1+x+x^2+...=\sum_{k=0}^{\infty}x^k$$

How might this relate to questions "b" and "c"?

Guinier A, Fournet G. *Small-Angle Scattering of X-rays*, John Wiley & Sons NY (1955) (Translated by Walker CB).

## Answers: Quiz 9 Polymer Properties March 29, 2019

- a) When the potential function equals 0 the equation of state becomes the ideal gas law and the scattering function becomes scattering from a single particle  $F^2(q)$ .
- b)

As concentration increases  $v_0$  remains the same but  $v_1$  drops, so p

increases.

c) Binary interactions do not alone describe the impact of closer packing on interactions. Binary interactions can be impacted by interactions of other particles. This is similar to if your dog barks, he is influenced by the barking of other dogs. Two supposedly independent dogs barking at each other will influence your dogs barking despite not having a direct interaction.

$$I(q) = \overline{N}I_e(q)F^2(q)\left\{\frac{v_1}{v_1 - (2\pi)^{\frac{3}{2}}\beta(q)}\right\}$$

d) If you look at the inverse of intensity for

$$\phi/I(q) = \phi_0/I_0(q) - \phi \beta(q)/I_0(q)$$

Which compares with  $\frac{\phi}{I(q)} \sim \frac{\phi_0}{I_0(q)} - \phi A_2$ .  $\beta(q=0)/I_0(q=0) = A_2$ . The two functions are the same if at low-q

e)

$$I(q) = \overline{N}I_{e}(q)\varphi^{2}(qR)\left\{\frac{1}{1+p\varphi(2qR)}\right\} \sim \overline{N}I_{e}(q)F^{2}(q)\left\{\frac{1}{1+p\varphi(q\xi)}\right\}$$
$$I(q) = \overline{N}I_{e}(q)F^{2}(q)\left\{\frac{v_{1}}{v_{1}-(2\pi)^{\frac{3}{2}}\beta(q)}\right\}$$

 $\beta(q)$  is a thermodynamic potential function, while  $\psi(q\xi)$  is a geometric function for a sphere that is calculated