Quiz 7 Polymer Properties
March 15, 2019

Guinier's Law can be derived by considering that the scattered amplitude for an isotropic system is given by,

$$A(q) = \int \rho(\underline{r}) \exp(-i\underline{qr})\, d\underline{r}$$
$$= \int \rho(\underline{r}) \left\{1 + i\underline{qr} - \tfrac{1}{2!}(\underline{qr})^2 + \ldots\right\} d\underline{r}$$
$$= \rho V \left\{1 - \frac{(\underline{qr})^2}{2}\right\}$$

Where $\underline{\boldsymbol{r}}$ is centered at the center of mass for a particle, and,

$$I(q) = A^2(q) = (\rho V)^2 \left\{1 - (\underline{qr})^2 + \frac{(\underline{qr})^4}{4}\right\} \approx (\rho V)^2 \left\{1 - (\underline{qr})^2\right\},$$

at low q. $\underline{\boldsymbol{r}}$ is a vector for an isotropic system,

$$R_g^2 = \int \rho(x) x^2 dx = \int \rho(y) y^2 dy = \int \rho(z) z^2 dz$$
$$3R_g^2 = x^2 + y^2 + z^2 = \underline{r}^2$$

Yielding,

$$I(q) \approx (\rho V)^2 \left\{1 - \left(\frac{q^2 R_g^2}{3}\right)\right\} \approx (\rho V)^2 \exp\left(-\frac{q^2 R_g^2}{3}\right)$$

The Fourier transform of Guinier's law yields,

$p(r) = \exp\left(-\frac{3r^2}{4R_g^2}\right)$ which is a Gaussian function.

a) Make a sketch of a particle that would have a pair distribution function, $p(r)$, that is a Gaussian function. Does this cartoon particle have a surface?

b) The behavior of a pair distribution function is that the linear term in "r" is $S/(4V)$, $p(r) = 1 - S/(4V)\, r + \ldots$ Use the exponential expansion, $\exp(-x) = 1 - x + x^2/2! \ldots$ to calculate the surface area of a "Gunier particle". Does this agree with your sketch in part a?

c) The derivation of Gunier's Law required using the assumption that $qr \ll 1$ in two instances. Is this consistent with parts "a" and "b"? Explain in terms of the definition of $q \sim 1/d$.

d) The radius of gyration can be calculated by $R_g^2 = \frac{\int \rho(r) r^2\, dr}{\int \rho(r)\, dr}$. Calculate the radius of gyration for a sphere, $R_g^2 = 3/5\, R^2$. Is this larger or smaller than the hydrodynamic radius for a sphere, R_H?

e) From the above derivation the normalized intensity is given by, $\frac{I(q)}{I(q=0)} = \frac{(\rho V)^2 \left\{1 - (\underline{qr})^2\right\}}{(\rho V)^2}$. From this expression what moment of size is R_g^2? What is the implication for a polydisperse sample?

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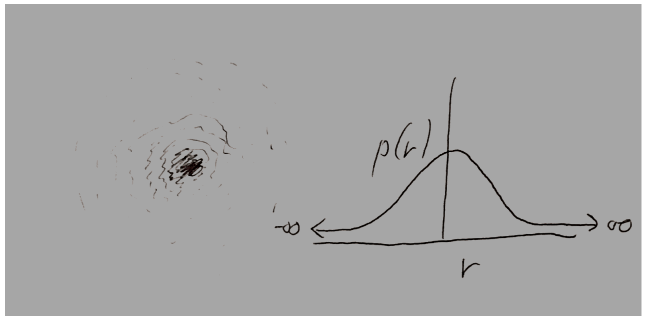
a)



b) There is no linear term I the expansion so there is no surface. This is consistent with the particle with no surface described by the correlation function.

c) At low q you cannot see the surface scattering. Since the function displays no internal structure or surface scattering the low-q approximation is appropriate.

d) Surface area of a spherical shell is $4\pi r^2$. So $R_g^2 = \frac{\int 4\pi r^2 r^2 \, dr}{\int 4\pi r^2 \, dr} = \frac{3r^5}{5r^3} = \frac{3}{5} r^2$.

e) $V \sim r^6$ so $R_g^2 \sim \langle r^8 \rangle / \langle r^6 \rangle$