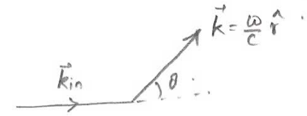
Set 39

Light scattering off polymers

① Scattering amplitude for light scattering off a polarizable atom/molecule in the Rayleigh approximation is:

$$\vec{F}_0(\theta,\phi) = -\alpha_0 \frac{\omega^2}{c^2} \hat{r}\times(\hat{r}\times\vec{E}_0)\, e^{-i(\vec{k}-\vec{k}_{in})\cdot\vec{r}_0}$$



$\vec{r}_0$ is the position of the molecule.

② We found that

$$|\vec{F}_0(\theta,\phi)|^2 = \alpha^2 \frac{\omega^4}{c^4} E_0^2 \begin{cases} 1, & \perp \text{ pol.}, \\ \cos^2\theta, & \parallel \text{ pol.}, \\ \frac{1+\cos^2\theta}{2}, & \text{unpolarized light.} \end{cases}$$

③ For scattering off N particles we have

$$|F(\theta,\phi)|^2 = \left| \sum_{m=1}^{N} F_m(\theta,\phi) \right|^2,$$

which leads to interference effects. Crystallography involves the case when the N molecules are orderly positioned. Here we shall study scattering off a polymer chain whose position is known as a probability distribution.

(4) Polymer is, to the first approximation, modelled as a Brownian motion in 3+1 space-time dimensions.

Let us consider Brownian motion in 1+1 space-time dimensions:

a — length of each step → starts at origin.

x — distance from origin.

s — total distance travelled.

$p(x,s)$ — probability of finding the particle at x at time t. Note s is a measure of t.

(5) We observe that

$$p(x, s+a) = \frac{1}{2}\left[p(x+a, s) + p(x-a, s) \right]$$

Taylor expanding and keeping only the leading terms,

$$p(x,s) + a\frac{\partial}{\partial s}p(x,s) = \frac{1}{2}\Big[p(x,s) + a\frac{\partial}{\partial x}p(x,s) + \frac{a^2}{2}\frac{\partial^2}{\partial x^2}p(x,s) + \ldots$$
$$+ p(x,s) - a\frac{\partial}{\partial x}p(x,s) + \frac{a^2}{2}\frac{\partial^2}{\partial x^2}p(x,s) + \ldots \Big]$$

$$a\frac{\partial}{\partial s}p(x,s) = \frac{a^2}{2}\frac{\partial^2}{\partial x^2}p(x,s)$$

This is the diffusion equation in 1+1 dimensions.

6 This idea can be generalized to 3+1 dimensions to derive the diffusion equation in 3+1 dimen.

$$\frac{\partial}{\partial s} p(\vec{r}, s) = \frac{a^2}{6} \nabla^2 p(\vec{r}, s)$$

For the initial condition

$$p(\vec{r}, 0) = \delta^{(3)}(\vec{r})$$

we have the solution

$$p(\vec{r}, s) = \left(\frac{3}{2\pi a s}\right)^{\frac{3}{2}} e^{-\frac{3r^2}{2\pi a s}}$$

which satisfies

$$\int d^3r \, p(\vec{r}, s) = 1.$$

7 The quality

$$\langle r^2 \rangle = \int d^3r \, r^2 \, p(\vec{r}, s)$$

$$= a s$$

is a measure of the square of polymer radius.

8 Let

$L = Na.$

$R^2 = \langle r^2 \rangle = N a^2. \Rightarrow R = \sqrt{N} a.$

$R_g^2 = \frac{1}{6} N a^2 \rightarrow$ gyration radius.

(9) The scattering amplitude off each monomer in the polymer is $\vec{q} = \vec{k} - \vec{k}_{in}$

$$F_m(\theta,\phi) = -\alpha(\vec{R}_m)\,\frac{\omega^2}{c^2}\,\hat{r}\times(\hat{r}\times\vec{E}_0)\,e^{-i\vec{q}\cdot\vec{R}_m}$$

$\vec{R}_m$ — position of monomer

Let $\alpha(\vec{R}_m) = \alpha$

(10) Total scattering amplitude is

$$F(\theta,\phi) = \sum_{m=1}^{N} F_m(\theta,\phi)$$

$$= -\alpha\,\frac{\omega^2}{c^2}\,\hat{r}\times(\hat{r}\times\vec{E}_0)\sum_{m=1}^{N} e^{-i\vec{q}\cdot\vec{R}_m}$$

(11) $$|F(\theta,\phi)|^2 = \alpha^2\,\frac{\omega^4}{c^4}\,|\hat{r}\times(\hat{r}\times\vec{E}_0)|^2\sum_{m=1}^{N}\sum_{n=1}^{N} e^{i\vec{q}\cdot(\vec{R}_n-\vec{R}_m)}$$

Scattering cross section

$$= \alpha^2\,\frac{\omega^4}{c^4}\,E_0^2\,\frac{1+\cos^2\theta}{2}\sum_{m=1}^{N}\sum_{n=1}^{N} e^{i\vec{q}\cdot(\vec{R}_n-\vec{R}_m)}$$

(12) For a polymer the scattery cross sech needs to be averaged with the probability amplitude.

$$\left\langle |F(\theta,\phi)|^2 \right\rangle = \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2}$$

$$\times \sum_{m=1}^{N} \sum_{n=1}^{N} \int d^3(\vec{R}_m - \vec{R}_n)\; p(\vec{R}_m - \vec{R}_n)\; e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_m)}$$

$$= \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} \int d^3(\vec{R}_m - \vec{R}_n) \left(\frac{3}{2\pi|n-m|a^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}_n - R_m)^2}{2|n-m|a^2}}\; e^{i\vec{q}\cdot(\vec{R}_n - \vec{R}_m)}$$

$$\vec{b} = \vec{q}\sqrt{\frac{2|n-m|a^2}{3}}$$

$$= \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} \left(\frac{1}{\sqrt{\pi}}\right)^3 \int d^3\vec{t}\; e^{-t^2 + i\vec{a}\cdot\vec{t}}$$

$$= \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} \left(\frac{1}{\sqrt{\pi}}\right)^3 \int d^3\vec{t}\; e^{-\left(\vec{t} - \frac{i\vec{a}}{2}\right)^2}\; e^{\left(\frac{i\vec{a}}{2}\right)^2}$$

$$= \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} e^{-\frac{b^2}{4}}$$

$$= \alpha^2 \frac{\omega^4}{c^4} E_0^2 \frac{1+\cos^2\theta}{2} \sum_{m=1}^{N} \sum_{n=1}^{N} e^{-\frac{1}{6} q^2 a^2 |n-m|}$$

13 $$\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-\frac{1}{6}q^2a^2|n-m|} = \int_0^L \frac{dx}{a}\int_0^L \frac{dx'}{a}\, e^{-\frac{1}{6}q^2a|x-x'|}$$

$x = na$

$x' = ma$.

$$= \left(\frac{6}{q^2a^2}\right)^2 \int_0^{\frac{1}{6}q^2aL} dt \int_0^{\frac{1}{6}q^2aL} dt'\, e^{-|t-t'|}$$

$t = \frac{1}{6}q^2ax$.

$dt = \frac{q^2a^2}{6}\frac{dx}{a}$.

14 $$\int_0^c dt\int_0^c dt'\, e^{-|t-t'|} = \int_0^c dt\int_0^t dt'\, e^{-(t-t')} + \int_0^c dt\int_t^c dt'\, e^{-(t'-t)}$$

$$= \int_0^c dt\, e^{-t}(e^t-1) + \int_0^c dt\, e^t(e^{-t}-e^{-c})$$

$$= \int_0^c dt\,(1-e^{-t}) + \int_0^c dt\,(1-e^{-c}e^t)$$

$$= c + (e^{-c}-1) + c - e^{-c}(e^c-1)$$

$$= 2c - 2 + 2e^{-c}$$

$$= 2\left(e^{-c}+c-1\right)$$

$R_g^2 = \frac{aL}{6}$

$= \frac{1}{6}Na^2$.

15 Using 14 in 13

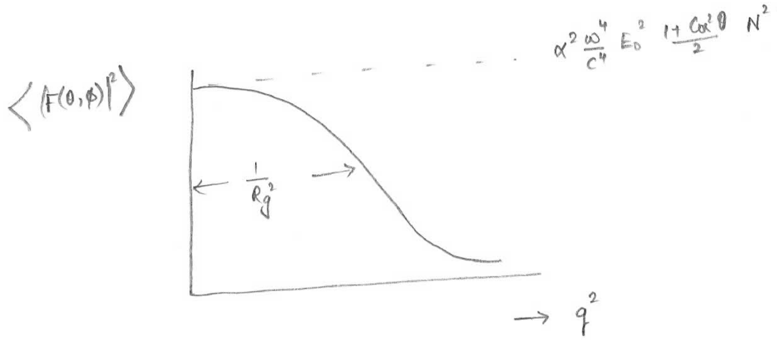
$$\sum_{m=1}^{N}\sum_{n=1}^{N} e^{-\frac{1}{6}q^2a^2|n-m|} = \left(\frac{6}{q^2a^2}\right)^2 2\left[e^{-\frac{q^2aL}{6}} + \frac{q^2aL}{6} - 1\right]$$

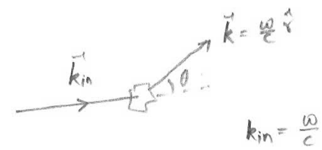
$$= \left(\frac{N}{q^2R_g^2}\right)^2 2\left[e^{-q^2R_g^2} + q^2R_g^2 - 1\right]$$

16 Using 15 in 12 we have.

$$\left\langle |F(\theta,\phi)|^2 \right\rangle = \alpha^2 \frac{\omega^4}{c^4} E_0^2 \, \frac{1+\cos^2\theta}{2} \, N^2 \, \frac{2}{(q^2 R_g^2)^2} \left[e^{-q^2 R_g^2} + q^2 R_g^2 - 1 \right]$$

17
$$\frac{2}{x^4}\left(e^{-x^2} + x^2 - 1\right) = \begin{cases} 1 & x \ll 1. \\ \dfrac{2}{x^2} & 1 \ll x. \end{cases}$$





Note that
$$\begin{aligned} q^2 &= (\vec{k} - \vec{k}_{in})^2 \\ &= k^2 + k^2 - 2\,\vec{k}\cdot\vec{k}_{in} \\ &= 2k^2(1-\cos\theta) \\ &= 4k^2 \sin^2\frac{\theta}{2}. \\ &= 4\frac{\omega^2}{c^2} \sin^2\frac{\theta}{2}. \end{aligned}$$

Thus, angular variation is equivalent to varying q^2.