1 Introduction

"Scattering" is an experimental method of probing structure (and, potentially, dynamics) of polymers and other soft-matter systems. This part of the course is aimed at introducing you to some background theory for the majority of scattering experiments. Normally, scattering experiments are set up to give weak scattering (the scattered radiation only scatters once off the material, not multiple times) and look at the far field scattering (i.e. we don't need to worry about interference between incoming and outgoing radiation). The theory looks pretty much the same whether you are dealing with neutron, or X-ray, or light scattering (although each technique measures a slightly different quantity and probes different lengthscales). BUT - this theory is NOT appropriate for the acoustic scattering experiments you will see within this module (the far field assumption breaks down). A rough outline of what we will try to cover is:

- Geometry of a scattering experiment
- Definition of density variables
- Bragg-law
- Structure factor and form factor
- Calculations for dilute polymers
- Porod law

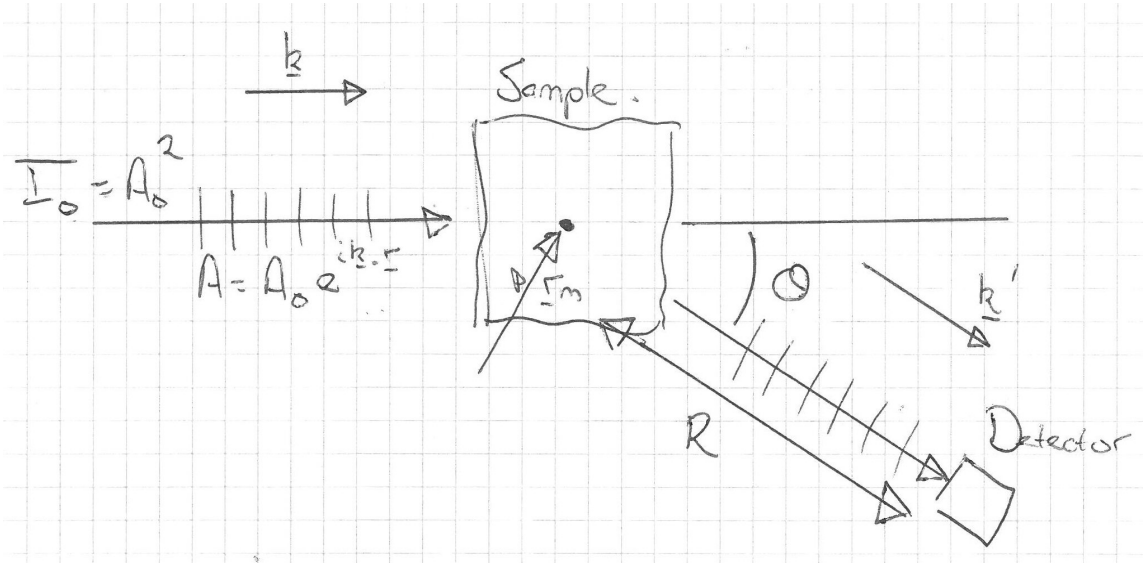
In these notes there are also section on the following, though i defintiely won't have time to cover them!

- Multicomponent systems and incompressibility
- Labelling of components in a melt
- Random Phase Approximation and Phase Separation.

2 Geometry of a scattering experiment

Most scattering experiments have the geometry shown in the figure above. An incoming beam with intensity I_0 (intensity is related to amplitude A of the wave as $I = |A|^2$) and wavelength λ hits the sample we are measuring, and whatever is in the sample scatters some of the beam though an angle θ, where it is picked up at a detector a distance R from the sample. We define the *wavevector* $\mathbf{k}$ of the incoming beam as a vector with magnitude $\frac{2\pi}{\lambda}$ and pointing in the direction of the incoming beam. Similarly, the wavevector $\mathbf{k}'$ of the scattered beam has the same magnitude (here we deal with elastic scattering only) but points in the direction of the scattered beam. Then, the *amplitude* of the incoming beam at a position $\mathbf{r}$ can be written as

$$A = A_0 \exp\left(i\mathbf{k} \cdot \mathbf{r}\right).$$



I'm hoping you're happy with using the complex form $\exp(i\mathbf{k}\cdot\mathbf{r})$ to describe a wave! The mathematics can be done using the trigonmetric functions sin and cos but it is much more long-winded! Roughly, what you need to do is to explicitly include the time-dependence of the oscillations:

$$A = A_0 \cos(\mathbf{k}\cdot\mathbf{r} - \omega t)$$

and then you go through the mathematics below, using double angle trigonometric formulae and finally (at the end) average over the time variable. This method is presented, for example, in Rubinstein and Colby's Polymer Physics book (pages 79-88). So, it can be done, but it is quite clumsy. I'm going to stick with the complex numbers, but will try to explain the practical implications of the physics as we go along.

2.1 Particle-level description of scattering

Sometimes it is useful to think of the scattering as arising from a set of particles. For simplicity, let's suppose that the thing doing the scattering is a set of identical particles (these could be atoms, monomers, etc....) with the mth particle at position $\mathbf{r}_m$. Then, the scattered wave from the mth particle has amplitude

$$A_m = A_0 \frac{\tilde{b}_m}{R} \exp(i\mathbf{k}\cdot\mathbf{r}_m) \exp(i\mathbf{k}'\cdot(\mathbf{x}-\mathbf{r}_m))$$

where

- The factor $\frac{1}{R}$ gives the drop off in intensity due to the distance from sample to detector.
- $\tilde{b}_m$ is known as the "scattering length" of the particle (unfortunately for polymer scientists, b gets used both for scattering length and for Kuhn length - it is rare, though, to find a situation where these will be confused).
- The factor $\exp(i\mathbf{k}\cdot\mathbf{r}_m)$ gives the phase shift of the wave from souce to the particle.

- The factor $\exp\left(i\mathbf{k}'\cdot\left(\mathbf{x}-\mathbf{r}_m\right)\right)$ gives the phase shift from paricle to detector.

This amplitude can be rewritten as

$$\begin{aligned} A_m &= A_0\frac{\tilde{b}_m}{R}\exp\left(i\left(\mathbf{k}-\mathbf{k}'\right)\cdot\mathbf{r}_m\right)\exp\left(i\mathbf{k}'\cdot\mathbf{x}\right) \\ &= A_0\frac{\tilde{b}_m}{R}\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)\exp\left(i\mathbf{k}'\cdot\mathbf{x}\right) \end{aligned}$$

where $\mathbf{q}=\mathbf{k}-\mathbf{k}'$ is the "scattering wavevector" which describes the overall effect that changes in particle position has on the phase of the scattered wave. It is easy to show (exercise for the lecture) that:

$$q=|\mathbf{q}|=\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right).$$

The wavevector $\mathbf{q}$ depends only on the geometry of the scattering experiment and the wavelength of the incident light. As a general rule, scattering probes structure of the material in the direction of $\mathbf{q}$ with lengthscale $\frac{2\pi}{q}$.

The total scattering amplitude from the sample can be found by summing up the scattering contribution from all the particles in the sample, i.e.

$$\begin{aligned} A &= \sum_m A_m \\ &= \frac{A_0}{R}\exp\left(i\mathbf{k}'\cdot\mathbf{x}\right)\sum_m \tilde{b}_m\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right). \end{aligned} \tag{1}$$

By summing over the different phase factors $\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)$ coming from each particle, we can get interference between the scattered waves, which leads to the interesting and useful patterns we see in scattering. **The detector measures the scattered intensity**, which is found using $I=|A|^2$ where $|A|^2=A\times A^*$ (A^* is the complex conjugate of A).

$$\begin{aligned} I &= \frac{I_0}{R^2}\sum_m \tilde{b}_m\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)\sum_l \tilde{b}_l\exp\left(-i\mathbf{q}\cdot\mathbf{r}_l\right) \\ &= \frac{I_0}{R^2}\sum_{m,l}\tilde{b}_m\tilde{b}_l\exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_m-\mathbf{r}_l\right)\right). \end{aligned}$$

Usually, we expect that the scattering is proportional to the volume V of the sample, and so experimenalists report the quantity

$$I_{abs}=\frac{IR^2}{I_0V} \tag{2}$$

which has units of inverse length, and removes all factors to do with experimental set-up from the reported *absolute scattering*. For our simple particle scattering.

$$\begin{aligned} I_{abs} &= \frac{1}{V}\sum_m \tilde{b}_m\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)\sum_l \tilde{b}_l\exp\left(-i\mathbf{q}\cdot\mathbf{r}_l\right) \\ &= \frac{1}{V}\sum_{m,l}\tilde{b}_m\tilde{b}_l\exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_m-\mathbf{r}_l\right)\right). \end{aligned} \tag{3}$$

2.1.1 Brief note on coherent and incoherent scattering

It would be nice to assume that all identical particles scatter with exactly the same amplitude. Life is not so simple, and (for example) with neutron scattering, the scattering length depends upon the relative spins of neutron and atomic nucleus. Using $\langle \ldots \rangle$ to denote an average over different spin states, we define the *coherent* and *incoherent* scattering lengths as

$$\begin{aligned} \tilde{b}_{\text{coh}} &= \left\langle \tilde{b}_m \right\rangle \\ \tilde{b}_{\text{inc}}^2 &= \left\langle \tilde{b}_m^2 \right\rangle - \left\langle \tilde{b}_m \right\rangle^2 . \end{aligned}$$

Then, averaging over spins and assuming that each particle spin behaves independently, we arrive at

$$I_{abs} = \frac{1}{V} \sum_{m'} \tilde{b}_{\text{inc}}^2 + \frac{1}{V} \sum_{m,l} \tilde{b}_{\text{coh}}^2 \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_m - \mathbf{r}_l\right)\right).$$

The incoherent scattering just comes from same-particle terms, and provides a constant background (it is more useful in dynamic experiments). The coherent scattering contains all the inter-particle correlations, and is the most interesting part for static scattering experiments. **From now on, we will just look at the coherent scattering**, and use $\tilde{b}$ to mean the coherent scattering length. Thus, if all the scattering particles are identical then:

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2}{V} \sum_{m} \exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right) \sum_{l} \exp\left(-i\mathbf{q}\cdot\mathbf{r}_l\right) \\ &= \frac{\tilde{b}^2}{V} \sum_{m,l} \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_m - \mathbf{r}_l\right)\right). \end{aligned} \tag{4}$$

2.2 Density level description of scattering

At other times, it is useful to think of scattering as coming from variations in density or composition of the material. This way of thinking should give exactly the same results as the particle-level description! To make the link, let us suppose we have a particle density variable $\rho(\mathbf{r})$ which describes the number of particles per unit volume. Then, the number of particles within a small volume ΔV is just $\rho(\mathbf{r})\,\Delta V$. If this volume is small, then all the particles in that volume will scatter with the same phase (i.e. the factor $\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)$ will be the same for all these particles) and the contribution of these particles to the scattered amplitude is

$$A_{\Delta V} = A_0 \frac{\tilde{b}}{R} \rho(\mathbf{r})\,\Delta V \exp\left(i\mathbf{q}\cdot\mathbf{r}\right) \exp\left(i\mathbf{k}'\cdot\mathbf{x}\right).$$

We get the total amplitude by summing up the contributions from all the little volumes ΔV through the sample

$$\begin{aligned} A &= \sum_{\Delta V \text{ in } V} A_{\Delta V} \\ &= \sum_{\Delta V \text{ in } V} A_0 \frac{\tilde{b}}{R} \rho(\mathbf{r}) \Delta V \exp(i\mathbf{q}\cdot\mathbf{r}) \exp(i\mathbf{k}'\cdot\mathbf{x}) \end{aligned}$$

and then we make the usual theoretician's trick of replacing a sum by an integral:

$$\sum_{\Delta V \text{ in } V} \Delta V \equiv \int_V dV$$

and so

$$A = A_0 \frac{\tilde{b}}{R} \exp(i\mathbf{k}'\cdot\mathbf{x}) \int_V dV \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}). \tag{5}$$

Turning this into an absolute scattered intensity, $I_{abs} = \frac{IR^2}{I_0 V}$, we get

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2}{V} \int_V dV \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) \int_V dV' \rho(\mathbf{r}') \exp(-i\mathbf{q}\cdot\mathbf{r}') \\ &= \frac{\tilde{b}^2}{V} \int_V dV \int_V dV' \rho(\mathbf{r}) \rho(\mathbf{r}') \exp(i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')) \end{aligned} \tag{6}$$

So, we can see that the scattering relates to the density $\rho(\mathbf{r})$ though the quantity

$$\rho(\mathbf{q}) = \int_V dV \rho(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}).$$

Those of you who have done a significant amount of mathematics at University level will recognise this as the *Fourier transform* of the density $\rho(\mathbf{r})$. This measures the amount of structure in the material in the direction of $\mathbf{q}$ and at a lengthscale $\frac{2\pi}{q}$. In terms of $\rho(\mathbf{q})$ the scattering is just

$$I_{abs} = \frac{\tilde{b}^2}{V} \rho(\mathbf{q}) \rho(-\mathbf{q}). \tag{7}$$

Now, we see that for expressions such as (4) and (7) to be consistent with each other, it must be true that

$$\rho(\mathbf{q}) = \sum_m \exp(i\mathbf{q}\cdot\mathbf{r}_m), \tag{8}$$

i.e. the density variable $\rho(\mathbf{q})$ just sums over the phase factors from all the particles. Those of you who are more mathematically minded will realise that this is equivalent to

$$\rho(\mathbf{r}) = \sum_m \delta(\mathbf{r} - \mathbf{r}_m)$$

i.e. we place a delta-function at the position of each particle to obtain the "density". Integrating $\rho(\mathbf{r})$ over a given volume will count the number of particles in that volume.

2.3 Summary

You can think of scattering from a set of particles either by summing over the phase factors arising from the positions of each particle, or as coming from density variations of the particles through the material. These two pictures are related by using the density variable

$$\rho(\mathbf{q}) = \sum_m \exp(i\mathbf{q}\cdot\mathbf{r}_m)$$

so that the absolute scattering intensity is

$$I_{abs} = \frac{\tilde{b}^2}{V}\rho(\mathbf{q})\,\rho(-\mathbf{q}).$$

Usually in polymers and soft matter we average over the distributions of conformations or orentation of particles (this can be thought of either as a time or space average), and so

$$I_{abs} = \frac{b^2}{V}\langle\rho(\mathbf{q})\,\rho(-\mathbf{q})\rangle \tag{9}$$

where $\langle ...\rangle$ represents an average.

3 Bragg law and crystal scattering

Probably the first time you were told about scattering, it was referring to crystal scattering. Crystals contain planes of atoms, and if there is a set of planes which have separation d then this will give a contribution to $\rho(\mathbf{q})$ for wavevector $\mathbf{q}$ such that $\mathbf{q}$ is directed perpendicular to the crystal lattice planes, and :

$$q = \frac{2\pi}{d}.$$

There will, most likely, also be contributions to $\rho(\mathbf{q})$ for wavevectors which are integer multiples of this, i.e.

$$q = \frac{2\pi n}{d}$$

(If you know about Fourier series, what we are doing is taking a Fourier series of the scattering density profile through the crystal lattice planes). So, then, the scattering angle can be found from

$$\frac{4\pi}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{2\pi n}{d}$$
$$2d\sin\left(\frac{\theta}{2}\right) = n\lambda.$$

This is known as Bragg's law.

The set of scattering planes within a particular crystal structure depend on the structure, and symmetry, of the crystal, so the angles at which you see scattering can be used to determine what kind of crystal structure you have. So, for example, in block

copolymers, you get scattering at multiples of the lowest scattering vector corresponding to:

$$1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5} \ldots \text{ for body centred cubic}$$
$$1, \sqrt{3}, \sqrt{4}, \sqrt{7} \ldots \text{ for hexagonally packed cylinders}$$
$$1, 2, 3, 4 \ldots \text{ for parallel lamellar structure.}$$

However, often in soft matter the material is not arranged in nice neat crystal structures, and yet scattering can still tell us useful information about the material. The next sections deal with scattering from less ordered materials.

4 "Structure factor" and "form factor"

The terms "structure factor" and "form factor" are common in the scattering literature. Here's a brief explanation as to what they mean.

Supose we have a set of identical particles, α, with centres at $\mathbf{r}_\alpha$, each providing a density (electrons or scattering length) $\rho_{\mathrm{P}}(\mathbf{r} - \mathbf{r}_\alpha)$ above some fixed background ρ_0 (these might, for example, be colloidal particles in a solution). Then

$$\rho(\mathbf{r}) = \rho_0 + \sum_\alpha \rho_{\mathrm{P}}(\mathbf{r} - \mathbf{r}_\alpha)$$

and

$$\begin{aligned}
\rho(\mathbf{q}) &= \int d^3\mathbf{r} \left[\rho_0 + \sum_\alpha \rho_{\mathrm{P}}(\mathbf{r} - \mathbf{r}_\alpha)\right] \exp(i\mathbf{q}\cdot\mathbf{r}) \\
&= \sum_\alpha \int d^3\mathbf{r} \rho_{\mathrm{P}}(\mathbf{r} - \mathbf{r}_\alpha) \exp(i\mathbf{q}\cdot\mathbf{r}) \\
&= \sum_\alpha \left[\int d^3\mathbf{r}' \rho_{\mathrm{P}}(\mathbf{r}') \exp(i\mathbf{q}\cdot\mathbf{r}')\right] \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha) \qquad \text{where } \mathbf{r}' = \mathbf{r} - \mathbf{r}_\alpha \\
&= \rho_{\mathrm{P}}(\mathbf{q}) \sum_\alpha \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha) \qquad \text{where } \rho_{\mathrm{P}}(\mathbf{q}) = \int d^3\mathbf{r}' \rho_{\mathrm{P}}(\mathbf{r}') \exp(i\mathbf{q}\cdot\mathbf{r}').
\end{aligned}$$

Then the scattered intensity is

$$\begin{aligned}
I_{abs} &= \frac{\tilde{b}^2}{V} \rho(\mathbf{q}) \rho(-\mathbf{q}) \\
&= \frac{\tilde{b}^2}{V} \sum_\alpha \exp(i\mathbf{q}\cdot\mathbf{r}_\alpha) \sum_{\alpha'} \exp(-i\mathbf{q}\cdot\mathbf{r}_{\alpha'}) \rho_{\mathrm{P}}(\mathbf{q}) \rho_{\mathrm{P}}(-\mathbf{q}) \\
&= \tilde{b}^2 S(\mathbf{q}) P(\mathbf{q})
\end{aligned}$$

where the "structure factor" is

$$S(\mathbf{q}) = \frac{1}{V} \sum_{\alpha,\alpha'} \exp(i\mathbf{q}\cdot(\mathbf{r}_\alpha - \mathbf{r}_{\alpha'})) = \frac{1}{V} \rho_{\mathrm{C}}(\mathbf{q}) \rho_{\mathrm{C}}(-\mathbf{q}).$$

Here we have defined a density of particles $\rho_{\mathrm{C}}(\mathbf{r}) = \sum_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)$. The "structure factor" contains contributions to the scattering from correlations between particles.

The "form factor" is

$$P(\mathbf{q}) = \rho_{\mathrm{P}}(\mathbf{q})\,\rho_{\mathrm{P}}(-\mathbf{q})$$

and this gives the contribution to the scattering from the particle itself.

Example 1: If the particles are randomly distributed through space (e.g. in dilute solution), then the structure factor $S(\mathbf{q})$ is a constant (independent of the wavevector), and since each particle is independent we can average $S(\mathbf{q})$ as

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{V}\left\langle \sum_{\alpha,\alpha'} \exp\left(i\mathbf{q}\cdot(\mathbf{r}_\alpha - \mathbf{r}_{\alpha'})\right)\right\rangle \\ &= \frac{n_p}{V} \end{aligned}$$

where n_p is the number of particles (each particle is independent!). Then the scattering is simply proportional to the particle form factor:

$$I_{abs} = \frac{\tilde{b}^2 n_p}{V} P(\mathbf{q})\,.$$

Example 2: If the particles are arranged on a regular crystal lattice (i.e. spheres of block copolymers in a body-centred cubic arrangement) then the structure factor $S(\mathbf{q})$ will consist of a set of scattering peaks corresponding to the Bragg reflection angles (the crystal planes). The form factor, $P(\mathbf{q})$, then simply varies the amplitude of those peaks - i.e. some peaks will be more intense than others.

Example 3: Form factor for a sphere. For a sphere of radius a and density ρ we can write:

$$\begin{aligned} \rho_{\mathrm{P}}(\mathbf{q}) &= \int d^3\mathbf{r}\,\rho_{\mathrm{P}}(\mathbf{r})\exp(i\mathbf{q}\cdot\mathbf{r}) \\ &= \rho\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{a} dr\, r^2 \sin\theta \exp(i\mathbf{q}\cdot\mathbf{r}) \\ &= 2\pi\rho\int_0^{a} dr \int_{-1}^{1} dx\, r^2 \exp(iqrx) \;\text{ where } x = \cos\theta \\ &= 4\pi\rho\int_0^{a} dr\, r^2 \frac{\sin(qr)}{qr} \\ &= \frac{4\pi\rho}{q^3}\left(\sin(qa) - qa\cos(qa)\right) \\ &= \frac{4\pi\rho a^3}{Q^3}\left(\sin(Q) - Q\cos(Q)\right) \end{aligned}$$

where $Q = qa$ is a dimensionless wavevector. Then, the form factor is

$$P(\mathbf{q}) = \frac{(4\pi\rho a^3)^2}{Q^6}\left(\sin(Q) - Q\cos(Q)\right)^2.$$

4.1 Rotational averaging in the form factor

Very often, in dilute suspensions, the particles might not be spherically symmetric themselves, but they might well be present in all orientations. In such cases, it is appropriate to average the form factor over all orientations (and if the particles can change shape, e.g. if they are polymer molecules, then you would average over their configurations too). Then we write:

$$\begin{aligned} P(\mathbf{q}) &= \langle \rho_{\mathrm{P}}(\mathbf{q}) \rho_{\mathrm{P}}(-\mathbf{q}) \rangle \\ &= \left\langle \int d^3\mathbf{r} \rho_{\mathrm{P}}(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) \int d^3\mathbf{r}' \rho_{\mathrm{P}}(\mathbf{r}') \exp(-i\mathbf{q}\cdot\mathbf{r}') \right\rangle \\ &= \left\langle \int d^3\mathbf{r} \int d^3\mathbf{r}' \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \exp(i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')) \right\rangle \end{aligned}$$

Now the trick: we can treat the average over *particle orientations* as the same as an average over *wavevector orientations*. And we know:

$$\begin{aligned} &\langle \exp(i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')) \rangle \\ &= \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \exp(iq|\mathbf{r}-\mathbf{r}'|\cos\theta) \\ &= \frac{\sin(q|\mathbf{r}-\mathbf{r}'|)}{q|\mathbf{r}-\mathbf{r}'|} \end{aligned}$$

which gives

$$P(\mathbf{q}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \rangle \frac{\sin(q|\mathbf{r}-\mathbf{r}'|)}{q|\mathbf{r}-\mathbf{r}'|}.$$

4.2 Radius of gyration

For small values of q, we can do a Taylor expansion:

$$\frac{\sin(q|\mathbf{r}-\mathbf{r}'|)}{q|\mathbf{r}-\mathbf{r}'|} = 1 - \frac{q^2|\mathbf{r}-\mathbf{r}'|^2}{6} + ...$$

and so we can write:

$$P(\mathbf{q}) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \rangle \left[1 - \frac{q^2|\mathbf{r}-\mathbf{r}'|^2}{6} + ... \right]$$

$$P(\mathbf{q}) = P(0) \left[1 - \frac{q^2}{3} R_g^2 \right]$$

where the form factor at zero angle is

$$P(0) = \int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \rangle$$

and the scattering radius of gyration R_g is found from

$$R_g^2 = \frac{\int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \rangle |\mathbf{r}-\mathbf{r}'|^2}{2 \int d^3\mathbf{r} \int d^3\mathbf{r}' \langle \rho_{\mathrm{P}}(\mathbf{r}) \rho_{\mathrm{P}}(\mathbf{r}') \rangle}.$$

So, the radius of gyration is the *root mean square separation of scattering density* within the particle! This shows how scattering is used to measure the size of objects - what is done is to extrapolate the scattering signal down to zero concentration of particles and towards small angles, with the radius of gyration obtained from the coefficient of q^2 in the scattering signal.

$$P(\mathbf{q}) = P(0)\left[1 - \frac{q^2}{3}R_g^2\right]$$

This is usually achieved using a "Zimm plot" (see powerpoint, and also Johan Mattsson's lectures).

Example For a sphere, the form factor is

$$P(\mathbf{q}) = \frac{\left(4\pi\rho a^3\right)^2}{Q^6}\left(\sin(Q) - Q\cos(Q)\right)^2.$$

Doing a Taylor expansion gives:

$$\begin{aligned} P(\mathbf{q}) &= \left(\frac{4\pi\rho a^3}{3}\right)^2\left[1 - \frac{Q^2}{5} + ...\right] \\ &= \left(\frac{4\pi\rho a^3}{3}\right)^2\left[1 - \frac{q^2}{3}\frac{3a^2}{5} + ...\right]. \end{aligned}$$

Hence, the radius of gyration of a sphere is $\sqrt{3a^2/5}$.

5 Scattering from dilute polymers

Let's consider a veryspecific example: scattering in a dilute polymer solution. Suppose we have in our scattering volume n polymer chains, each with exactly the same number of Kuhn monomers N. We number the chains with variable $\alpha = 1..n$ and the monomers on a chain with $m = 1..N$. Then, treating each Kuhn monomer as our scattering particle, or bead:

$$\rho(\mathbf{q}) = \sum_{\alpha}\sum_{m}\exp\left(i\mathbf{q}\cdot\mathbf{r}_{\alpha,m}\right)$$

and

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2}{V}\left\langle\rho(\mathbf{q})\,\rho(-\mathbf{q})\right\rangle \\ &= \frac{\tilde{b}^2}{V}\left\langle\sum_{\alpha}\sum_{m}\exp\left(i\mathbf{q}\cdot\mathbf{r}_{\alpha,m}\right)\sum_{\beta}\sum_{l}\exp\left(-i\mathbf{q}\cdot\mathbf{r}_{\beta,l}\right)\right\rangle \\ &= \frac{\tilde{b}^2}{V}\sum_{\alpha,\beta}\sum_{m,l}\left\langle\exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{\alpha,m} - \mathbf{r}_{\beta,l}\right)\right)\right\rangle \end{aligned}$$

where we replace the average of a sum with the sum of an average. Now, since each chain is free to explore the whole volume of the sample, and assuming the polymers are sufficiently dilute that interactions between them can be ignored, then there is no correlation between

the positions of any two polymer chains. So we can assume $\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{\alpha,m}-\mathbf{r}_{\beta,l}\right)\right)\rangle = 0$ for $\alpha \neq \beta$ because the phase factor from each chain will be completely uncorrelated and average to zero. So, since each chain is identical

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2}{V}\sum_{\alpha}\sum_{m,l}\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{\alpha,m}-\mathbf{r}_{\beta,l}\right)\right)\rangle \\ &= \frac{\tilde{b}^2 n}{V}\sum_{m,l}\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{m}-\mathbf{r}_{l}\right)\right)\rangle \end{aligned} \tag{10}$$

the sum over m and l being now restricted to a single chain.

You can think of this as being in the form

$$I_{abs} = \tilde{b}^2 S\left(\mathbf{q}\right) P\left(\mathbf{q}\right)$$

where

$$S\left(\mathbf{q}\right) = \frac{n}{V}$$

is the (featureless) structure factor for dilute particles, and

$$P\left(\mathbf{q}\right) = \sum_{m,l}\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{m}-\mathbf{r}_{l}\right)\right)\rangle$$

is the form factor for the polymer chains.

5.1 Small angle limit

Expanding the exponential for small $\mathbf{q}$ we find (assuming chains are isotropic)

$$\begin{aligned} \sum_{m,l}\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{m}-\mathbf{r}_{l}\right)\right)\rangle &= \sum_{m,l}\left\langle 1 + i\mathbf{q}\cdot\left(\mathbf{r}_{m}-\mathbf{r}_{l}\right) - \tfrac{1}{2}\left[\mathbf{q}\cdot\left(\mathbf{r}_{m}-\mathbf{r}_{l}\right)\right]^2 + ...\right\rangle \\ &= N^2 - \tfrac{1}{2}\sum_{m,l}\left(q_x^2\left\langle\left(x_m-x_l\right)^2\right\rangle + q_y^2\left\langle\left(y_m-y_l\right)^2\right\rangle + q_z^2\left\langle\left(z_m-z_l\right)^2\right\rangle\right) + ... \\ &= N^2\left(1 - \frac{q^2}{3}\frac{1}{2N^2}\sum_{m,l}\left\langle\left(\mathbf{r}_m-\mathbf{r}_l\right)^2\right\rangle + ...\right) \end{aligned}$$

where we used the result, for isotropic chains, that $\left\langle\left(x_m-x_l\right)^2\right\rangle = \frac{1}{3}\left\langle\left(\mathbf{r}_m-\mathbf{r}_l\right)^2\right\rangle$. So, the radius of gyration is (here) defined as

$$R_g^2 = \frac{1}{2N^2}\sum_{m,l}\left\langle\left(\mathbf{r}_m-\mathbf{r}_l\right)^2\right\rangle$$

and so

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2 n N^2}{V}\left(1 - \frac{q^2 R_g^2}{3} + ...\right) \\ &= \tilde{b}^2 C_{\text{mon}} N\left(1 - \frac{q^2 R_g^2}{3} + ...\right) \end{aligned}$$

where C_{mon} is the concentration of monomers. Thus, through scattering at small angles we are able to measure both the degree of polymerisation N and the radius of gyration R_g. This is the theoretical basis of using light scattering to characterise polymers (e.g. in GPC-MALLS).

5.2 Debye function for ideal chain scattering

For an ideal linear chain, the components of $\mathbf{r}_m - \mathbf{r}_l$ are Gaussian random variables, with zero mean and

$$\left\langle (x_m - x_l)^2 \right\rangle = \left\langle (y_m - y_l)^2 \right\rangle = \left\langle (z_m - z_l)^2 \right\rangle = \frac{b^2}{3} |l - m| .$$

We also know that, for a Gaussian variable X, with zero mean

$$\langle \exp(\alpha X) \rangle = \exp\left(\tfrac{1}{2}\alpha^2 \left\langle X^2 \right\rangle\right)$$

(the proof is a straightforward integration over the probability distribution, involving completing the square in the exponential) and so

$$\begin{aligned}
\langle \exp(i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_l)) \rangle &= \langle \exp(iq_x(x_m - x_l)) \rangle \langle \exp(iq_y(y_m - y_l)) \rangle \langle \exp(iq_z(z_m - z_l)) \rangle \\
&= \exp\left(\frac{1}{2}\left(q_x^2 + q_z^2 + q_z^2\right) \times \frac{b^2}{3}|l - m|\right) \\
&= \exp\left(-\frac{1}{6}q^2 b^2 |l - m|\right).
\end{aligned}$$

So

$$I_{abs} = \frac{\tilde{b}^2 n}{V} \sum_{m,l} \exp\left(-\frac{1}{6}q^2 b^2 |l - m|\right).$$

Replacing the sum by integrals

$$\begin{aligned}
I_{abs} &= \frac{\tilde{b}^2 n}{V} \int_0^N dl \int_0^N dm \exp\left(-\frac{1}{6}q^2 b^2 |l - m|\right) \\
&= 2\frac{\tilde{b}^2 n}{V} \int_0^N dl \int_0^l dm \exp\left(-\frac{1}{6}q^2 b^2 (l - m)\right)
\end{aligned}$$

we find

$$\begin{aligned}
I_{abs} &= \frac{\tilde{b}^2 n N^2}{V} g_{\text{D}}\left(Q^2\right) \\
&= \tilde{b}^2 C_{\text{mon}} N g_{\text{D}}\left(Q^2\right)
\end{aligned}$$

where we have defined a scaled wavevector $Q^2 = \frac{q^2 b^2 N}{6}$ and the Debye function

$$g_{\text{D}}(x) = \frac{2}{x^2}\left(\exp(-x) - 1 + x\right).$$

The Debye function has the asymptotic properties

$$g_{\mathrm{D}}(x) \approx \frac{2}{x} \text{ for large } x.$$
$$g_{\mathrm{D}}(x) \approx 1 - \frac{x}{3} \text{ for small } x.$$

So, in the limit of small angle scattering:

$$g_{\mathrm{D}}\left(Q^2\right) \approx 1 - \frac{Q^2}{3} = 1 - \frac{q^2}{3}\frac{Nb^2}{6} \Longrightarrow R_g^2 = \frac{Nb^2}{6} \text{ and } Q^2 = q^2 R_g^2.$$

6 Porod scattering

If a material consists of two phases with particle densities ρ_1 and ρ_2, and with *sharp interfaces between the phases*, then for for wavevectors much larger than 1/(particle size) the scattering will be:

$$I_{abs} = 2\pi \frac{\tilde{b}^2 S}{V} \left(\rho_1 - \rho_2\right)^2 \frac{1}{q^4}$$

where the ratio S/V is the surface area of interface, per unit volume. The characteristic $1/q^4$ form arises from scattering from interfaces, and is known as Porod's law. A derivation is given in the handwitten notes.

Example. For a dilute suspension of hard spheres, from above:

$$I_{abs} = \frac{\tilde{b}^2 n}{V} \frac{\left(4\pi\rho a^3\right)^2}{Q^6} \left(\sin(Q) - Q\cos(Q)\right)^2.$$

For large Q this gives

$$I_{abs} = \frac{\tilde{b}^2 n}{V} \frac{\left(4\pi\rho a^3\right)^2}{Q^4} \cos^2(Q).$$

Unless the spheres are very monodisperse, each will have a very slightly different size, so we can average the oscillating function $\cos^2(Q)$ to give $\frac{1}{2}$. Then:

$$\begin{aligned} I_{abs} &= \frac{\tilde{b}^2 n}{V} \frac{\left(4\pi\rho a^3\right)^2}{2q^4 a^4} \\ &= 2\pi \frac{\tilde{b}^2 n}{V} 4\pi a^2 \rho^2 \frac{1}{q^4} \\ &= 2\pi \frac{\tilde{b}^2 S}{V} \rho^2 \frac{1}{q^4}. \end{aligned}$$

7 Multicomponent systems and incompressibility

For multicomponent systems, there are different kinds of "particles" I =A,B,C etc. each with their own scatering length $\tilde{b}_{\mathrm{A}}$, $\tilde{b}_{\mathrm{B}}$, $\tilde{b}_{\mathrm{C}}$ etc. The above scattering formulae generalise

by summing over the scattered amplitude from each component, so that

$$\begin{aligned} A &= \frac{A_0}{R}\left(\tilde{b}_{\mathrm{A}}\rho_{\mathrm{A}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{B}}\rho_{\mathrm{B}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{C}}\rho_{\mathrm{C}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{D}}\rho_{\mathrm{D}}\left(\mathbf{q}\right)+....\right) \\ &= \frac{A_0}{R}\rho_{\mathrm{s}}\left(\mathbf{q}\right) \end{aligned}$$

where

$$\rho_{\mathrm{A}}\left(\mathbf{q}\right)=\sum_{m\in\mathrm{A}}\exp\left(i\mathbf{q}\cdot\mathbf{r}_m\right)$$

is a sum over all the phase factors from particles of type A etc, and the *scattering density* is

$$\rho_{\mathrm{s}}\left(\mathbf{q}\right)=\left(\tilde{b}_{\mathrm{A}}\rho_{\mathrm{A}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{B}}\rho_{\mathrm{B}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{C}}\rho_{\mathrm{C}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{D}}\rho_{\mathrm{D}}\left(\mathbf{q}\right)+....\right)=\sum_I\tilde{b}_I\rho_I\left(\mathbf{q}\right).$$

Then, the absolute scattering is

$$\begin{aligned} I_{abs} &= \frac{1}{V}\left\langle\rho_{\mathrm{s}}\left(\mathbf{q}\right)\rho_{\mathrm{s}}\left(-\mathbf{q}\right)\right\rangle \\ &= \frac{1}{V}\left\langle\left(\tilde{b}_{\mathrm{A}}\rho_{\mathrm{A}}\left(\mathbf{q}\right)+\tilde{b}_{\mathrm{B}}\rho_{\mathrm{B}}\left(\mathbf{q}\right)+....\right)\left(\tilde{b}_{\mathrm{A}}\rho_{\mathrm{A}}\left(-\mathbf{q}\right)+\tilde{b}_{\mathrm{B}}\rho_{B}\left(-\mathbf{q}\right)+....\right)\right\rangle \\ &= \frac{1}{V}\sum_{IJ}\tilde{b}_I\tilde{b}_J\left\langle\rho_I\left(\mathbf{q}\right)\rho_J\left(-\mathbf{q}\right)\right\rangle. \end{aligned}$$

Note that the scattered intensity contains contributions from both same-particle type terms such as $\left\langle\rho_{\mathrm{A}}\left(\mathbf{q}\right)\rho_{\mathrm{A}}\left(-\mathbf{q}\right)\right\rangle$ as well as different particle type terms such as $\left\langle\rho_{\mathrm{A}}\left(\mathbf{q}\right)\rho_{\mathrm{B}}\left(-\mathbf{q}\right)\right\rangle$.

When dealing with blends of different chemistries, it is often useful to define a reference monomer volume v_0, and define the "monomer" for each kind of polymer as being that part of the polymer chain which occupies volume v_0 (we neglect non-idealities such as volume changes upon mixing etc here). A monomer defined in this way need not be the chemical monomer unit, nor the Kuhn monomer. Now, we can invoke the concept of "incompressibility". Nothing is completely incompressibile, but it is often the case for melts and solutions that fluctuations in total monomer density (which are penalised by the bulk modulus) are much smaller than fluctuations in the density of individual components (penalised by the osmotic "modulus" for each component). To good approximation we can assume the incompressible limit in which (at coarse-grained lengthscales $\gg v_0^{1/3}$) the total monomer density remains constant:

$$\rho_{\mathrm{A}}\left(\mathbf{r}\right)+\rho_{\mathrm{B}}\left(\mathbf{r}\right)+\rho_{\mathrm{C}}\left(\mathbf{r}\right)+\rho_{\mathrm{D}}\left(\mathbf{r}\right)+....=\frac{1}{v_0}=\text{constant}$$

and so

$$\rho_{\mathrm{A}}\left(\mathbf{q}\right)+\rho_{\mathrm{B}}\left(\mathbf{q}\right)+\rho_{\mathrm{C}}\left(\mathbf{q}\right)+\rho_{\mathrm{D}}\left(\mathbf{q}\right)+....=0.$$

This allows us to eliminate one of the densities from our calculation.

7.1 Two component incompressible system

In particular, where there are just two components A and B, we have

$$\begin{aligned}\rho_{\mathrm{A}}(\mathbf{r})+\rho_{\mathrm{B}}(\mathbf{r}) &= \frac{1}{v_0}\\ \rho_{\mathrm{A}}(\mathbf{q})+\rho_{\mathrm{B}}(\mathbf{q}) &= 0 \qquad \text{for } \mathbf{q}\neq\mathbf{0}.\end{aligned}$$

Hence we have

$$\begin{aligned}\rho_{\mathrm{s}}(\mathbf{q}) &= \tilde{b}_{\mathrm{A}}\rho_{\mathrm{A}}(\mathbf{q})+\tilde{b}_{\mathrm{B}}\rho_{\mathrm{B}}(\mathbf{q})\\ &= \left(\tilde{b}_{\mathrm{A}}-\tilde{b}_{\mathrm{B}}\right)\rho_{\mathrm{A}}(\mathbf{q})\end{aligned}$$

and our scattering intensity is

$$\begin{aligned}I_{abs} &= \frac{1}{V}\left\langle\rho_{\mathrm{sl}}(\mathbf{q})\,\rho_{\mathrm{sl}}(-\mathbf{q})\right\rangle \qquad (11)\\ &= \frac{\left(\tilde{b}_{\mathrm{A}}-\tilde{b}_{\mathrm{B}}\right)^2}{V}\left\langle\rho_{\mathrm{A}}(\mathbf{q})\,\rho_{\mathrm{A}}(-\mathbf{q})\right\rangle.\end{aligned}$$

i.e. the amount of scattering depends upon the *contrast* between A and B monomers, $\left(\tilde{b}_{\mathrm{A}}-\tilde{b}_{\mathrm{B}}\right)$. In section 2 above, where we were dealing with very dilute systems, we should really have used the difference between polymer and solvent scattering lengths, i.e. $\tilde{b}=\tilde{b}_{\mathrm{polymer}}-\tilde{b}_{\mathrm{solvent}}$, in the calculations.

So, a scattering calculation usually aims to calculate, using statistical mechanics, quantities of form $s_{\mathrm{AA}}=\left\langle\rho_{\mathrm{A}}(\mathbf{q})\,\rho_{\mathrm{A}}(-\mathbf{q})\right\rangle$. Note that incompressibility for a two component system implies

$$s_{\mathrm{AA}}=s_{\mathrm{BB}}=-s_{\mathrm{AB}}$$

since $\rho_{\mathrm{A}}(\mathbf{q})=-\rho_{\mathrm{B}}(\mathbf{q})$.

7.2 Polymer melts with partial labelling

A useful experiment (particularly in neutron scattering) is to scatter off a polymer melt in which a fraction of the chains are labelled (usually these are hydrogen labelled in a matrix of deuterium labelled chains). Let's analyse what information we can obtain from this experiment.

In the scattering volume, we have n chains, of which n_{H} are hydrogen labelled and n_{D} are deuterium labelled (i.e. a fraction ϕ_{H} and ϕ_{D} of each). Each chain contains N monomers. We assume the chains are otherwise identical in all interactions (not entirely true - there are usually slight differences in interaction energies: see next section). Now, let us define two "structure factors":

$$\begin{aligned}P(\mathbf{q}) &= \frac{1}{N^2}\sum_{l,m\in\text{same chain}}\left\langle\exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_l-\mathbf{r}_m\right)\right)\right\rangle\\ Q(\mathbf{q}) &= \frac{V}{v_0N^2}\sum_{l,m\in\text{two different chains}}\left\langle\exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_l-\mathbf{r}_m\right)\right)\right\rangle.\end{aligned}$$

The factor of $\frac{V}{v_0}$ (the total number of monomers in the scattering volume) in $Q(\mathbf{q})$ is used because we anticipate that the correlation between two different chains, randomly placed in the (large) scattering volume, should decrease with the volume of the system. With these definitions, we have

$$\begin{aligned} s_{\mathrm{HH}} &= \langle \rho_{\mathrm{H}}(\mathbf{q}) \rho_{\mathrm{H}}(-\mathbf{q}) \rangle \\ &= n_{\mathrm{H}} N^2 P + n_{\mathrm{H}}(n_{\mathrm{H}} - 1) \frac{v_0 N^2}{V} Q \\ &= \frac{V}{v_0} N \left[\phi_{\mathrm{H}} P + \phi_{\mathrm{H}}^2 \frac{Q}{N} \right] \end{aligned}$$

where we have used $\phi_{\mathrm{H}} = n_{\mathrm{H}} N v_0 / V$. Similarly

$$\begin{aligned} s_{\mathrm{DD}} &= \langle \rho_{\mathrm{D}}(\mathbf{q}) \rho_{\mathrm{D}}(-\mathbf{q}) \rangle = \frac{V}{v_0} N \left[\phi_{\mathrm{D}} P + \phi_{\mathrm{D}}^2 \frac{Q}{N} \right], \\ s_{\mathrm{HD}} &= \langle \rho_{\mathrm{H}}(\mathbf{q}) \rho_{\mathrm{D}}(-\mathbf{q}) \rangle = \frac{V}{v_0} N \left[\phi_{\mathrm{H}} \phi_{\mathrm{D}} \frac{Q}{N} \right]. \end{aligned}$$

Now, due to incompressibility, we insist upon $s_{\mathrm{HH}} = s_{\mathrm{DD}} = -s_{\mathrm{HD}}$. This gives two equations, for eliminating structure factors, but we shall only need one, e.g. $s_{\mathrm{HH}} = -s_{\mathrm{HD}}$. Using $\phi_{\mathrm{H}} + \phi_{\mathrm{D}} = 1$ gives

$$\begin{aligned} \phi_{\mathrm{H}} P + \phi_{\mathrm{H}}^2 \frac{Q}{N} &= -\phi_{\mathrm{H}} \phi_{\mathrm{D}} \frac{Q}{N} \\ P + \phi_{\mathrm{H}} \frac{Q}{N} &= -\phi_{\mathrm{D}} \frac{Q}{N} \\ NP &= -Q. \end{aligned}$$

Remarkably, in this simple incompressible system, the inter-chain structure factor is directly related to the single chain structure factor, giving

$$s_{\mathrm{HH}} = s_{\mathrm{DD}} = -s_{\mathrm{HD}} = \frac{V}{v_0} N \phi_{\mathrm{H}} \phi_{\mathrm{D}} P.$$

Hence, the scattering intensity is

$$\begin{aligned} I_{abs} &= \frac{\left(\tilde{b}_{\mathrm{H}} - \tilde{b}_{\mathrm{D}} \right)^2}{V} s_{\mathrm{HH}} \\ &= \frac{\left(\tilde{b}_{\mathrm{H}} - \tilde{b}_{\mathrm{D}} \right)^2}{v_0} N \phi_{\mathrm{H}} \phi_{\mathrm{D}} P(\mathbf{q}) \end{aligned}$$

and the experiment measures just the single chain scattering function $P(\mathbf{q})$. Note that we have not specified anything about the statistics of the polymer chains, e.g. whether or not they are stretched out of equilibrium.

Melts with many different chain types - how to obtain the single chain scattering off a single component Suppose now you have a complicated melt, but that you were interested in the configuration of a single part of it: this might be a subsection of some of the molecules e.g. the backbone of some combs. What you do is to arrange to do more than one experiment. Label all the other chains in the system identically (including parts of the combs you are not interested in). This will be called the "matrix". For the bits of chain you are interested in, label a fraction f differently to the matrix, and the rest label identically to the matrix. You will need to do more than one experiment (at least 2), with different values of f.

Supposing in the scattering volume there are n_{A} chains which contain the part of interest, and that the interesting part comprises N_{A} monomers on each chain. Then, we can define

$$P(\mathbf{q}) = \frac{1}{N_{\mathrm{A}}^2} \sum_{\substack{l,m\in\mathrm{A} \\ \text{on same chain}}} \langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_l - \mathbf{r}_m\right)\right)\rangle$$

$$Q(\mathbf{q}) = \frac{V}{v_0 N_{\mathrm{A}}^2} \sum_{\substack{l,m\in\mathrm{A} \\ \text{on two different chains}}} \langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_l - \mathbf{r}_m\right)\right)\rangle .$$

Then, if the matrix is deutrium labelled and some of the A sections are hydrogen labelled we have

$$\begin{aligned} s_{\mathrm{HH}} &= \langle \rho_{\mathrm{H}}(\mathbf{q})\, \rho_{\mathrm{H}}(-\mathbf{q})\rangle \\ &= f n_{\mathrm{A}} N_{\mathrm{A}}^2 P + f n_{\mathrm{A}}\left(f n_{\mathrm{A}} - 1\right)\frac{v_0 N_{\mathrm{A}}^2}{V} Q \\ &= \frac{V}{v_0} N_{\mathrm{A}}\left[f\phi_{\mathrm{A}} P + f^2\phi_{\mathrm{A}}^2 \frac{Q}{N_{\mathrm{A}}}\right] \end{aligned}$$

where $\phi_{\mathrm{A}} = n_{\mathrm{A}} N_{\mathrm{A}} v_0/V$ is the volume fraction of "interesting material". We know, due to incompressibility, that the scattering intensity is proportional to s_{HH}. What the above result tells us is that, on varying f, the single-chain structure factor P appears at linear order in f, whilst Q (interchain correlations) appears to quadratic order. One always has to work at finite values of f, but (if background corrections are done properly) one only needs to do two experiments to obtain P and Q.

In a many-component melt, you might be interested in the configuration of more than one component, in which case the number of experiments required increases. For an x component system, there are x single-chain structure factors, and x same-component, different-chain structure factors. There are *at least* $x(x-1)/2$ different component structure factors (more if some components are part of the same chain). Incompressibility gives two equations ($s_{\mathrm{HH}} = s_{\mathrm{DD}} = -s_{\mathrm{HD}}$) which allows the elimination of just two of these structure factors - the rest must be determined by independent experiments (if you want the lot).

8 Random Phase Approximation and Phase Separation

If the different components of the melt have really different chemistries, then (obviously) their interactions are different, and very often phase separation occurs (and, in fact, even deuterium labelling can produce small differences in interaction energy and possibly phase separation). Because scattering measures variations in composition (i.e. density variations through the material) there is a close link between theory for scattering and phase separation.

The theoretical framework used for scattering calculations and the instability point for onset of phase separation in polymer mixtures is called the Random Phase Approximation. There is not time for a detailed derivation, but for a rough outline of the derivation, for the case of a two-component system (A and B monomers) is as follows.

- The density functions $\rho_{\mathrm{A}}(\mathbf{q})$ and $\rho_{\mathrm{B}}(\mathbf{q})$ involve a sum over a large number of random variables (the monomer positions) and so we expect them, to first approximation, to be Gaussian random variables (using the Central Limit Theorem). In the absence of particle-particle interacations, we would therefore expect them to have a probability distribution:

$$\Psi_0\left(\{\rho_{\mathrm{A}}(\mathbf{q}),\rho_{\mathrm{B}}(\mathbf{q})\}\right) \sim \exp\left(-\frac{1}{2}\sum_{\mathbf{q}}\left(\begin{array}{cc}\rho_{\mathrm{A}}(-\mathbf{q}) & \rho_{\mathrm{B}}(-\mathbf{q})\end{array}\right)\cdot\mathbf{M}^{-1}\cdot\left(\begin{array}{c}\rho_{\mathrm{A}}(\mathbf{q})\\ \rho_{\mathrm{B}}(\mathbf{q})\end{array}\right)\right)$$

  where $\mathbf{M}$ is the matrix of correlation functions calculated in the absence of interactions,

$$\mathbf{M}=\left[\begin{array}{cc}S_{0\mathrm{AA}} & S_{0\mathrm{AB}}\\ S_{0\mathrm{AB}} & S_{0\mathrm{BB}}\end{array}\right]$$

$$\mathbf{M}^{-1}=\frac{1}{S_{0\mathrm{AA}}S_{0\mathrm{BB}}-S_{0\mathrm{AB}}^2}\left[\begin{array}{cc}S_{0\mathrm{BB}} & -S_{0\mathrm{AB}}\\ -S_{0\mathrm{AB}} & S_{0\mathrm{AA}}\end{array}\right].$$

  The correlation functions

$$\begin{aligned}S_{0\mathrm{AA}} &= \langle\rho_{\mathrm{A}}(\mathbf{q})\,\rho_{\mathrm{A}}(-\mathbf{q})\rangle_0\\ S_{0\mathrm{AB}} &= \langle\rho_{\mathrm{A}}(\mathbf{q})\,\rho_{\mathrm{B}}(-\mathbf{q})\rangle_0\\ S_{0\mathrm{BB}} &= \langle\rho_{\mathrm{B}}(\mathbf{q})\,\rho_{\mathrm{B}}(-\mathbf{q})\rangle_0\end{aligned}$$

  are calculated from the polymer structures, assuming no interactions between chains (this is the meaning of the subscript 0). In writing the above equations, we have made use of the property of *translational symmetry* of the system, which means that all correlation functions of form $\langle\rho(\mathbf{q}_1)\,\rho(\mathbf{q}_2)\rangle_0$ are zero unless $\mathbf{q}_1+\mathbf{q}_2=0$.

- We now introduce two types of interaction. Firstly, we assume incompressibility, that is we insist on the constraint

$$\rho_{\mathrm{A}}(\mathbf{q}) = -\rho_{\mathrm{B}}(\mathbf{q}) = \tilde{\rho}(\mathbf{q}).$$

This reduces the above probability distribution to

$$\Psi_{\rm inc}\left(\{\tilde{\rho}\left(\mathbf{q}\right)\}\right) \sim \exp\left(-\frac{1}{2}\sum_{\mathbf{q}}\tilde{\rho}\left(\mathbf{q}\right)\tilde{\rho}\left(-\mathbf{q}\right)\left(\frac{S_{0\rm AA}+S_{0\rm BB}+2S_{0\rm AB}}{S_{0\rm AA}S_{0\rm BB}-S_{0\rm AB}^2}\right)\right).$$

- Secondly, we introduce different interactions between monomers of different types. It is a useful property of the density variables that two-body interactions between particles can be written as quadratic terms in the density variables, i.e. if we have an interaction energy

$$U = \frac{1}{2}\sum_{m,l}\psi\left(\mathbf{r}_m - \mathbf{r}_l\right)$$

(where the sum is taken over all particle pairs, and the factor 2 accounts for double-counting of pairs) then this can be rewritten as

$$U = \frac{1}{2V}\sum_{\mathbf{q}}\psi\left(\mathbf{q}\right)\rho\left(\mathbf{q}\right)\rho\left(-\mathbf{q}\right)$$

where $\psi\left(\mathbf{q}\right)$ is the Fourier transform of the function $\psi\left(\mathbf{r}\right)$ [this is an exercise for those skilled in Fourier transforms to attempt!]. The result generalises to multicomponent systems. In the present case, in addition to incompressibility we introduce an interaction energy which favours increases in $\tilde{\rho}\left(\mathbf{q}\right)$, of form

$$\frac{U}{k_{\rm B}T} = -\frac{1}{2}\sum_{\mathbf{q}}\frac{2\chi v_0}{V}\tilde{\rho}\left(\mathbf{q}\right)\tilde{\rho}\left(-\mathbf{q}\right)$$

where χ is the Flory interaction parameter. This modifies the probability distribution of $\rho\left(\mathbf{q}\right)$ by a Boltzmann factor, to

$$\Psi\left(\{\tilde{\rho}\left(\mathbf{q}\right)\}\right) \sim \exp\left(-\frac{1}{2}\sum_{\mathbf{q}}\tilde{\rho}\left(\mathbf{q}\right)\tilde{\rho}\left(-\mathbf{q}\right)\left(\frac{S_{0\rm AA}+S_{0\rm BB}+2S_{0\rm AB}}{S_{0\rm AA}S_{0\rm BB}-S_{0\rm AB}^2}-\frac{2\chi v_0}{V}\right)\right).$$

From this, we can read off the correlation function

$$S\left(\mathbf{q}\right) = \left\langle\tilde{\rho}\left(\mathbf{q}\right)\tilde{\rho}\left(-\mathbf{q}\right)\right\rangle = \left(\frac{S_{0\rm AA}+S_{0\rm BB}+2S_{0\rm AB}}{S_{0\rm AA}S_{0\rm BB}-S_{0\rm AB}^2}-\frac{2\chi v_0}{V}\right)^{-1} \tag{12}$$

and we note that, due to incompressibility,

$$\begin{aligned} s_{\rm AA} &= \left\langle\rho_{\rm A}\left(\mathbf{q}\right)\rho_{\rm A}\left(-\mathbf{q}\right)\right\rangle = S\left(\mathbf{q}\right) \\ s_{\rm AB} &= \left\langle\rho_{\rm A}\left(\mathbf{q}\right)\rho_{\rm B}\left(-\mathbf{q}\right)\right\rangle = -S\left(\mathbf{q}\right) \\ s_{\rm BB} &= \left\langle\rho_{\rm B}\left(\mathbf{q}\right)\rho_{\rm B}\left(-\mathbf{q}\right)\right\rangle = S\left(\mathbf{q}\right). \end{aligned}$$

In general, we can see that as χ increases, $S\left(\mathbf{q}\right)$ will grow. When χ reaches the critical value of

$$\chi_{\rm c} = \frac{V}{2v_0}\min\frac{S_{0\rm AA}+S_{0\rm BB}+2S_{0\rm AB}}{S_{0\rm AA}S_{0\rm BB}-S_{0\rm AB}^2}$$

then the predicted scattering diverges at some wavevector $\mathbf{q}$. This signals the onset of instability towards phase separation.

8.1 Example: diblock copolymer

As an example, let's consider a melt of diblock copolymers. Suppose each copolymer consists of N beads, a fraction f of which are of type A. If there are n copolymer molecules in total, then the total number of beads is

$$\frac{V}{v_0} = nN.$$

In order to calculate the scattering, we need to compute the correlation functions $S_{0\mathrm{AA}}$ etc. This proceeds in a similar manner to the calculation of the Debye function in section 3.2 above. Summing over chains a, β and beads m, l:

$$S_{0\mathrm{AA}} = \sum_{\alpha,\beta} \sum_{m,l \in \mathrm{A}} \left\langle \exp\left(i\mathbf{q}\cdot\left(\mathbf{r}_{\alpha,m} - \mathbf{r}_{\beta,l}\right)\right)\right\rangle_0 .$$

As before, since these are calculated in the limit of no interactions, there is no contribution from different chains $a \neq \beta$. We restrict the variables m and l to the section of chain containing A beads, and we replace the sum by an integral, so that

$$\begin{aligned} S_{0\mathrm{AA}} &= \sum_{\alpha} \int_0^{fN} dl \int_0^{fN} dm \exp\left(-\frac{1}{6}q^2b^2\left|l-m\right|\right) \\ &= nf^2N^2 j\left(fQ^2\right) \\ &= \frac{V}{v_0} N s_{0\mathrm{AA}} \\ s_{0\mathrm{AA}} &= f^2 j\left(fQ^2\right) \end{aligned}$$

where $Q^2 = q^2Nb^2/6$ and the function $j\left(x\right)$ is just the Debye function

$$j\left(x\right) = \frac{2}{x^2}\left(\exp\left(-x\right) - 1 + x\right).$$

Similarly, since the B beads occupy a fraction $(1-f)$ of the chain:

$$\begin{aligned} S_{0\mathrm{BB}} &= \frac{V}{v_0} N \left(1-f\right)^2 j\left(\left(1-f\right)Q^2\right) \\ &= \frac{V}{v_0} N s_{0\mathrm{AA}} \\ s_{0\mathrm{AA}} &= \left(1-f\right)^2 j\left(\left(1-f\right)Q^2\right) \end{aligned}$$

To calculate the correlation function $S_{0\mathrm{AB}}$, we restrict one monomer variable to the A beads, and the other to the B beads:

$$S_{0\mathrm{AB}} = \sum_{\alpha} \int_0^{fN} dl \int_{fN}^{N} dm \exp\left(-\frac{1}{6}q^2b^2\left(m-l\right)\right).$$

There are various ways though this calculation; my favourite is to use a change of variables to $l' = fN - l$ and $m' = m - fN$ (so that both l' and m' are zero at the A-B link of the

copolymer and count away from it). Then

$$\begin{aligned} S_{0\mathrm{AB}} &= n\int_0^{fN} dl' \exp\left(-\frac{1}{6}q^2b^2l'\right)\int_0^{(1-f)N} dm' \exp\left(-\frac{1}{6}q^2b^2m'\right) \\ &= nN^2 f\left(1-f\right)h\left(fQ^2\right)h\left(\left(1-f\right)Q^2\right) \\ &= \frac{V}{v_0}Ns_{0\mathrm{AB}} \\ s_{0\mathrm{AB}} &= f\left(1-f\right)h\left(fQ^2\right)h\left(\left(1-f\right)Q^2\right). \end{aligned}$$

where the function $h\left(x\right)$ is

$$h\left(x\right) = \frac{1}{x}\left(1-\exp\left(-x\right)\right).$$

You will notice that all the correlation functions contain a common factor $\frac{V}{v_0}N$ which can be factored out of equation 12, giving:

$$S\left(\mathbf{q}\right) = \left\langle \rho_{\mathrm{A}}\left(\mathbf{q}\right)\rho_{\mathrm{A}}\left(-\mathbf{q}\right)\right\rangle = \frac{V}{v_0}N\left(\frac{s_{0\mathrm{AA}}+s_{0\mathrm{BB}}+2s_{0\mathrm{AB}}}{s_{0\mathrm{AA}}s_{0\mathrm{BB}}-s_{0\mathrm{AB}}^2}-2\chi N\right)^{-1}$$

and hence, using (11), the absoluted scattering is

$$I_{abs} = \frac{\left(\tilde{b}_{\mathrm{A}}-\tilde{b}_{\mathrm{B}}\right)^2 N}{v_0}\left(\frac{s_{0\mathrm{AA}}+s_{0\mathrm{BB}}+2s_{0\mathrm{AB}}}{s_{0\mathrm{AA}}s_{0\mathrm{BB}}-s_{0\mathrm{AB}}^2}-2\chi N\right)^{-1}.$$

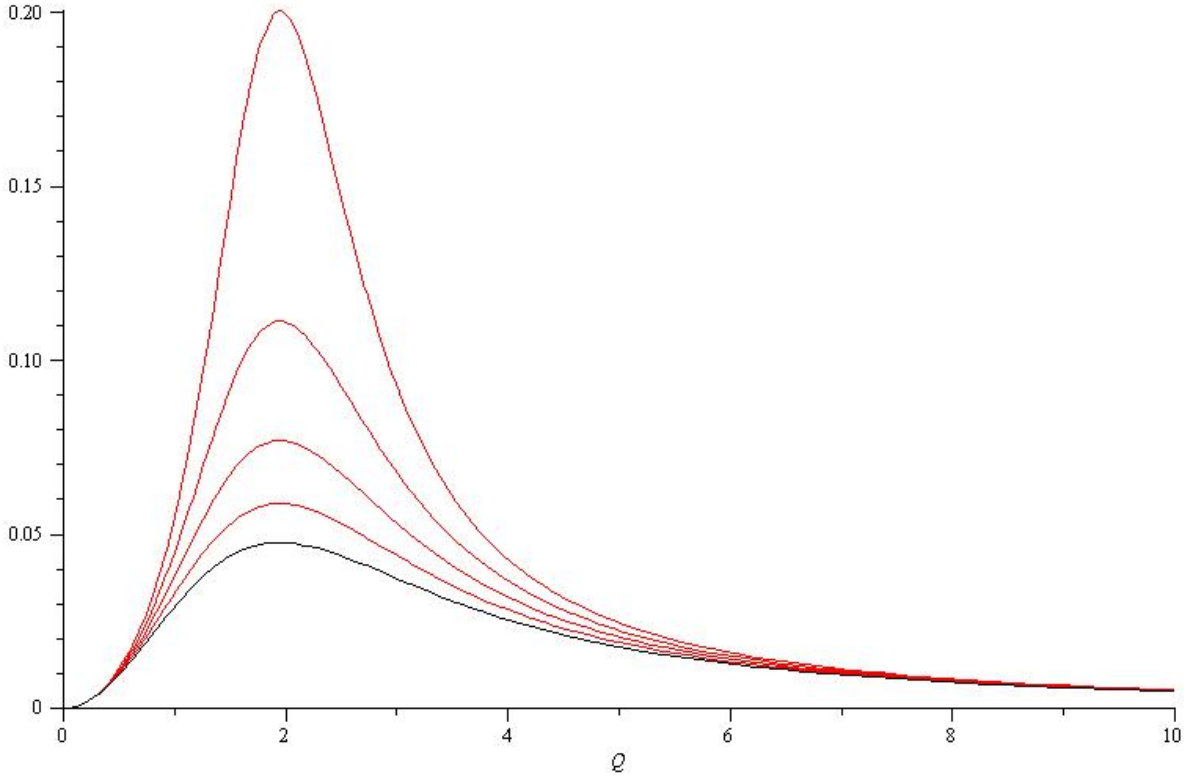
Notice that the combination χN, together with structural information encoded within the scattering functions $s_{0\mathrm{AA}}$, that determines the limit of phase separation.

The figure above plots

$$\left(\frac{s_{0\mathrm{AA}}+s_{0\mathrm{BB}}+2s_{0\mathrm{AB}}}{s_{0\mathrm{AA}}s_{0\mathrm{BB}}-s_{0\mathrm{AB}}^2}-2\chi N\right)^{-1}$$

as a function of Q for $f = 0.5$ and $\chi N = 0$ (black line) and $\chi N = 2, 4, 6, 8$. You can observe the following features:

- There is no scattering in the limit of zero Q. This is due to incompressibility and the fact that we assumed all copolymers contain the same fraction f of A beads. As a result, there can be no composition variations at large lengthscales.
- There is a scattering peak at non-zero Q (actually at $Q \approx 1.95$). This is called the "correlation hole" peak, indicating that there are fluctuations in composition at the lengthscale of a polymer.
- As χN is increased, the peak grows, indicating that composition variations are enhanced. The predicted peak diverges at $\chi N \approx 10.5$ indicating that there is an instability towards phase separation. Since the instability occurs at non-zero Q this instability is towards *microphase* separation - the diblocks will form small domains rich in one bead or the other.



8.2 Calculations for arbitrary architecture

The paper D.J. Read *Macromolecules* **1998**, *31*, 899 gives a general method for RPA calculations for polymers of arbitrary architecture (for H -polymers, combs, Cayley trees, multiblocks, etc.)