ISC 5228
Markov Chain Monte Carlo

Light Scattering and Monte Carlo Integration

1 Introduction

Light scattering is a fairly common characterization technique used to infer the size, shape, and arrangement of particles.

In a typical setup an experimenter:

(i) prepares a dilute solution of the particles
(ii) shines light using a laser
(iii) collects the "scattered" light using a detector (see figure 1),
(iv) plots the average intensity of the scattered light as a function of the angle $I(\theta)$.
(v) compares the observed pattern with known patterns to figure out the size and shape of the particles.

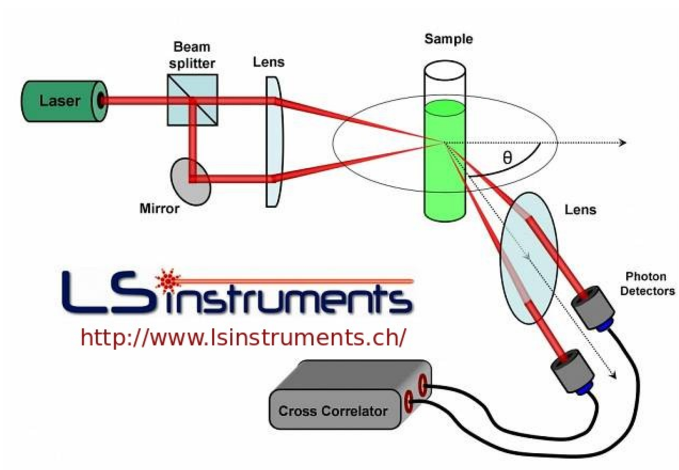

Figure 1: Typical light scattering set up

Notes:

- In the literature, it is common to use something called the wave-vector $\mathbf{q}$ instead of the angle θ. The relationship between the two will be made explicit shortly.
- The particle could be colloid, a polymer, a protein, etc. (generally in the μm range).
- If you want to watch a cool video of how to measure the width of your hair using a laser pointer and principles of light scattering/diffraction see this or something similar.

1.1 Form Factor

In this lab we shall consider the simple case of dilute and isotropic systems.

Essentially, by *dilute*, we stipulate the concentration of the scatterers is small enough that light bounces off directly from a particle to the detector.[1] By *isotropic*, we stipulate that all spatial orientations are equally likely, and the signal detected reflects a rotationally averaged measurement.

Under these restrictions, we can use

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

instead of the angle θ. Here n is the refractive index, and λ is the wave length of light. Recall, from figure 1 that θ is the angle between the incident and scattered beam of light.[2]

The form factor is then defined as the ratio,

$$P(q) = \frac{I(q)}{I(0)} \tag{1}$$

and depends on the shape and size of the particle.

The form factor for standard shapes like spheres, ellipsoids, cylinders, polymers etc. are well established.

1.1.1 Mathematical Model: Debye Formula

The form factor can be *measured* using light scattering equipment to tell us something about the geometry of an unknown sample via eqn. 1. Inversely, if we know the shape and size of the particle, then we can predict the $P(q)$ using the so-called **Debye formula**.

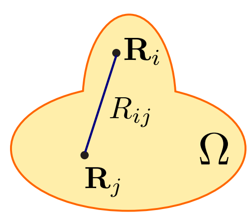

Figure 2: Schematic of a general object

Consider figure 2. Let the domain Ω represent the particle. Let $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ represent the distance between two points $\mathbf{R}_i$ and $\mathbf{R}_j$ ($\mathbf{R}_i \neq \mathbf{R}_j$) in the domain Ω.

[1] At high concentrations, it maybe tossed around between particles, before escaping to the detector. This requires a more complex analysis.

[2] The units of q are 1/length.

Then the Debye formula for the form factor for dilute and isotropic systems is given by:[3]

$$P(q) = \frac{\int_\Omega \frac{\sin qR_{ij}}{qR_{ij}} d\mathbf{R}_i d\mathbf{R}_j}{\int_\Omega d\mathbf{R}_i d\mathbf{R}_j}. \tag{2}$$

2 Setup

If we select N points randomly *inside the domain* Ω, then we can estimate $P(q)$ by the Debye formula:

$$P(q) \approx \frac{1}{N(N-1)} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{\sin qR_{ij}}{qR_{ij}}. \tag{3}$$

Plot $P(q)$ versus q on a log-log scale.
We can cut the number of terms in the summation in half by using symmetry, $R_{ij} = R_{ji}$. Thus,

$$P(q) \approx \frac{2}{N(N-1)} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\sin qR_{ij}}{qR_{ij}}. \tag{4}$$

2.1 Sphere

Now consider a sphere of radius $R = 1$ μm, centered at (0,0,0). Analytically the $P(q)$ for a sphere is found to be:

$$P_{\text{exact}}(q) = \left[\frac{3}{(qR)^3} \left(\sin(qR) - qR\cos(qR) \right) \right]^2. \tag{5}$$

3 Exercises

(i) Find the $P(q)$ using eqn. 4. Choose 100 logarithmically equispaced values of q between 0.1 and 30μm^{-1}, and at least 10^3 MC samples at each q. Estimate the error in your estimate.

(ii) Plot $P(q)$ versus q on a log-log scale with error-bars. Compare it with the analytical solution (eqn. 5).

(iii) Modify the code to find the form factor of a **hemi-sphere** of radius 1 μm. Repeat (i) and plot $P(q)$ versus q on a log-log scale. Compare it with $P(q)$ for a sphere.

(iv) Discuss relative advantages and disadvantages of using MC integration to evaluate the Debye formula.

[3]Note that $P(q)$ is simply the average value $\langle (\sin qR)/qR \rangle$.