3.1 Zimm Plots





From the previous discussion we can see that fluctuations are the basic source of scattering for polymers in solution and we can derive an expression for the scattering in terms of polymer molecular weight (M), radius of gyration  $R_g$ ) and the second virial coefficient B.

$$\frac{Kc}{R_{\theta}} = \frac{1}{M} + 2Bc \ [2.27]$$

in the Flory Huggins theory *B* is equivalent to  $\frac{1}{2} - \chi$  and is a measure of the strength of the polymer solvent interaction energy as in the figure. If *B* < 0 the polymer expands [good solvent] and if *B* > 0 the coil contracts [poor solvent]. The idea; value is  $\frac{1}{2}$ . Equation [2.27] is good if the coil is small and there is no structure factor present. If we need the *P*(*Q*)term which is the normal case



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For a polymer coil in solution [2.27] becomes

$$\frac{Kc}{R_{\theta}} = \left[\frac{1}{M} + 2Bc\right] \left[1 + \frac{Q^2 R_G^2}{3}\right] \quad [3.1]$$

this equation is very useful as it implies we can also measure the radius of gyration  $(R_g)$  of the polymer at the same time. The way this can be done (conventionally) is to obtain a set of data at different concentrations and over a range of Q values. The data can be plotted then as below

with the ordinate as  $\frac{Kc}{R_{\theta}}$  and the abscissa as  $c + \beta Q^2$  where  $\beta$  is a scaling

constant chosen to make the both terms of similar magnitude. Inspecting [3.1] you can see that by extrapolating to  $Q \Rightarrow 0$  the second term vanishes and extrapolating to  $c \Rightarrow 0$  the first term tends to 1/M.{hence get *M*} at fixed c the slope *vs.*  $Q^2$  is  $R_G^2/3$  and at fixed  $Q^2$  the slope vs *c* is 2*B*. Hence by this quirky 2D plot we get all three parameters. The Zimm analysis can be used very effectively with neutrons and X-rays as well as light.

## Mie Theory

When the particle and wavelength of light are comparable or the scattering becomes very complex and the scattering is strongly biased in the forward direction: The results below [Left Hand] are for a 600nm sphere with  $\lambda = 632.8$  nm and an index of refraction is 1.5. The big difference with this scattering is the extent of forward scattering, which continues to increase as the particle gets bigger; which is not obvious (to me anyway). The Right Hand figure shows the same calculation for a 50nm particle which behaves like a Rayleigh scatter as before. The following web page has a live program for these calculations so you can try these yourselves. Unfortunately the maths required for this is Einsteinean and only works at present for spheres.

http://omlc.ogi.edu/calc/mie\_calc.html



## Structure Factor

So far we have dealt with dilute dispersions such that there is no interparticle interference. However, when the interactions between particles are strong enough or the dispersion is sufficiently concentrated then these affects appear. In this case we must modify our basic scattering equation by adding the structure factor, S(Q).

## I(Q) = A.P(Q).S(Q) [3.2]

S(Q) is directly related to another function called the radial distribution function. g(r) which give us the probability of finding another particle within a distance r. Below is a simulated hard sphere liquid at high density and low density. At the lower density the peaks are slightly further apart.



g(r) is directly related to the number concentration in the system ,  $N_p$  $g(r) = N(r)/N_p$  [3.2]

where N(r) is the number concentration of particles at a distance *r* from a reference particle. We can relate the relative separations of the particles to the potential of mean force that exist between them,  $\Phi(r)$ : (The reversible work theorem)<sup>\*</sup>

$$g(r) = \exp[-\Phi(r)/k_B T)$$
 [3.3]

and  $\Phi(r)$  can be written as a sum of the pair potential between two particles V(r) and a perturbation  $\varphi(r)$  which account for many –body interactions:  $\Phi(r) = V(r) + \varphi(r)$ In the limit where  $N(r) \rightarrow 0$  then  $\varphi(r) \rightarrow 0$ 

One simple model is that of the hard sphere as shown above where the potential becomes infinite when the particles overlap. However in colloidal dispersions results suggest that the 'effective hard sphere radius is larger than the actual geometric radius ( $E_{effective}$ ).

Mathematically we can relate g(r) to S(Q)

<sup>\*</sup> See Chandler Introduction to Modern Statistical Physics OUP 1987 p 201

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$$S(Q) = 1 + \frac{4\pi N_p}{Q} \int_{0}^{\infty} [g(r) - 1]r \sin(Qr) dr \quad [3.4]$$

This looks grim but it is just a Fourier Transform. We shall need this procedure in the next lecture so we shall spend a short time going over it in the next lecture. S(Q) can be complicated function, but typically the form is as given below again for a hard sphere system for 2 different concentrations of 100 nm spheres. The position of the maximum depends inversely on the particle concentration so the more concentrated dispersion has a its first peak at higher Q.

These calculations where performed with the Lekner hard sphere model based on The Perkus Yevick model for liquids (Phys Rev <u>145</u> 83 (1966), where the structure f



factor is given by

$$S(Q) = \frac{1}{[1 - N_{p}C(2QR_{effective})]} [3.5]$$

and the function C is an integral over all values of  $QR_{effective}$  from 0 to 1. We shall look at more structure factors when we look at charged micelles.

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