Scattering . 2 **Basics:Light**

Colloidal precipitation

One nice example of Rayleigh scattering is to make a sulphur colloid, by precipitation. As $I \sim v^4 a^6$ the scattering is strongly affected by the growth of the particles. As growth occurs more blue light is scattered and hence the transmitted light becomes more red.

Rayleigh ratio

Recalling the Rayleigh equation and rewriting for a solution where n_1 is the refractive index of the solution and n_0 is that of the solvent medium.

 $\frac{I_{\theta}}{I_0} = \frac{9\pi^2 (n_1^2 - n_o^2)^2}{2r^2 \lambda^4 (n_1^2 + 2n_o^2)^2} V_p^2 N_p (1 + \cos^2(\theta)) \quad [1.13] \text{ we can combine some of the constants as } R_{\theta} = \frac{I_{\theta} r^2}{I_o} \quad [2.1] \text{ and instead of the Lorentz-Lorentz equation [1.9] we}$

can use a simplified form $\alpha = \varepsilon_o \frac{(n_1^2 - n_o^2)}{N_o}$ [2.2] by noticing that $n_1 \approx n_o \approx 1$ [2.3]

a condition for Rayleigh scattering. Then $R_{\theta} = \frac{\pi^2}{2\lambda^2 N_-} (n_1^2 - n_0^2)^2 (1 + \cos^2(\theta))$ [2.4]

If we fix the angle to 90° then we can write $R_{\theta} = R_{90}(1 + \cos^2(\theta))$ [2.5]

We can use this equation to determine if we have a Rayleigh scatterer. To measure molecular mass we need two more approximations valid in dilute solutions:

 $(n_1^2 - n_o^2)^2 = (n_1 - n_o)(n_1 + n_o) \approx 2n_0(n_1 - n_o)$ [2.6] and the difference in refractive index of the solution and the medium is proportional to concentrations c: $(n_1 - n_o) \propto c$ [2.7], c is defined as $c = \frac{N_\rho M}{L}$ then $R_{90} = kcM$ [2.8]

Hence if we know all the optical constants then we can find M the molar mass. There are many equations (surprised?) for relating the total scattered intensity to particle concentration one useful one for the turbidity \Im (which is defined differently

to equation [1.1]) as $\Im = \frac{16\pi}{3}R_{\theta} = -\ln(\frac{l_{\tau}}{l_{\tau}})/\ell$ [2.9] (cf equation 1.2) and

 $\Im = 24\pi^3 \phi \left(\frac{n_1^2 - n_o^2}{n_1^2 + 2n_0^2} \right) \frac{V_p}{\lambda^4}$ [2.10] Using this equation is a route to measure the

particle volume V_{ρ} .

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Rayleigh-Gans-Debye theory

The stuff so far is limited to very small particles and we would like to know not only the volume of a particle but also its shape. In order to do this we need to probe inside the particle and this means that the wavelength must be more comparable to the particle size i.e. $d < \lambda$.



The figure above shows that dependent on the ratio of d /λ , internal interference may or may not occur. The formalism for calculating these effects requires summing all the scattering centres in the particle. Debye simplified this for light by introducing the formula:

$$P(Q) = \sum_{l} \sum_{J} \left\langle \frac{\sin(Qr_{lJ})}{Qr_{lJ}} \right\rangle_{\text{orientations}}$$
[2.11]

The following figure shows how the scattering from the various shapes looks like. The formulae are obtained by using equation 2.11 with the appropriate limits for the vector r_{IJ} which defines the shape of the object.

In many instances polydispersity can blur out the distinction between shapes. The method however is very useful if you have an a-priori knowledge of the shape. We shall discuss this aspect of scattering in more detail when we discuss neutrons and X-rays.

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The formulae for the different shapes shown in the figure given above are quite complex and not much fun to derive. However the form for a sphere and a guassian polymer random coil aren't too bad!.

for a sphere
$$P(Q) = 9\left[\frac{\sin(Qa) + Qa\cos(Qa)}{(Qa)^3}\right]^2$$
[2.12]

for a random coil where R_{G} is the radius of gyration

$$P(Q) = \frac{2}{(QR_G)^4} \left[\exp(-Q^2R_G^2) + (QR_G)^2 - 1 \right] [2.13]$$

here $Q = \frac{4\pi n_o}{\lambda} \sin(\theta/2)$ [2.14] NB we added the refractive index of the solvent.

The Guinier and Zimm approximations

A useful approximation to these forms can be made if scattering at very small values of Q can be obtained [LALLS low-angle light scattering] For example the expansion of both the above forms gives: $P(Q) = 1 - (Q^2 R_G^2/3) + O()^5 \dots [2.15]$ which for $QR_G < 1$ [2.16] only the leading term is required. Equation [2.15] is often written in a logarithmic form as [2.15] is the first term in a logarithmic expansion: $P(Q) = \exp(-Q^2 R_G^2/3)$ [2.17] and so a plot of ln(P(Q)) vs Q^2 is a straight line with slope $-R_G^2/3$. This form is quite general for arbitrary shaped objects fulfilling the condition of equation [2.16]. Another form that can be used is the Zimm expression: $1/P(Q) = 1 + (Q^2 R_G^2/3)$ [2.18]

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Debye model: fluctuations

Well Rayleigh was correct for very small objects and for materials that were solid as above however for polymers in solution there is another and very important factor: the concentration of polymer segments inside a polymer coil varies

randomly: there are 'fluctuations in the structure' and that means there are fluctuations in the local refractive index and hence in the polarisability α .



Using the Rayleigh equation per particle BUT replace α by $\delta \alpha$. [Equations 2.19]

$$I_{\theta} = I_0 \frac{8\pi^4}{r^2 \lambda^4} (1 + \cos^2 \theta) V_p^2 m^2 \left(\frac{\partial m}{\partial c}\right)^2 (\delta c)^2$$

Now we must somehow eliminate $(\delta c)^2$ and the way to do this is to use the Boltzmann equation but this is truly grim. The basic equation is just an way to find the average value of a property based on probabilities:

$$<\delta c^2 >= \int (\delta c)^2 \exp(-\delta G/kT) d(\delta c) / \int \exp(-\delta G/kT) d(\delta c)$$
 [2.22]

The exp() bit is the probability or weighting factor that a certain fluctuation occurs. Note we have to use $\langle \delta c^2 \rangle$ as $\langle \delta c \rangle$ is 0!.

The result of this averaging process is $\langle \delta c^2 \rangle = kTc/Vd\Pi/dc$ [2.23] where Π is the osmotic pressure of the solution. OP is really the driving force for the fluctuations. as the concentrations will try to equalise by solvent flowing from high concentration to low. This gives:

$$I_{\theta} = I_0 \frac{2\pi^2}{r^2 \lambda^4} (1 + \cos^2 \theta) V_{\rho} m^2 \left(\frac{\partial m}{\partial c}\right)^2 ckT / d\Pi / dc \quad [2.24]$$

Oh dear- well for a polymer solution we can use the Flory Huggins theory a mean field lattice theory developed form the simple Bragg Williams model for an ideal solution:

$$\Pi = RTc\left[\frac{1}{M} + Bc\right] \text{ hence } \frac{d\Pi}{dc} = RT(1/M + 2Bc) \text{ [2.25]} \text{ Hence } \frac{Kc}{R_{\theta}} = \frac{1}{M} + 2Bc \text{ [2.27]}$$

Simplify using $R_{\theta} = I_{\theta}r^2/I_0(1 + \cos^2\theta)$ [2.26]

Well the final equation is not too bad and it is really useful B is the Flory parameter. It's a bit like the second virial coefficient for a gas which tells us how strong the polymer/solvent interaction is. The analysis allows us to get values of both M and B.