Chapter 7

Light Scattering

7.1 Introduction

Figure 7.1 shows light scattering off a particle in solution or in vacuum. The incident light scatters in all different directions. The intensity of the scattered light depends on the polarizability (to be defined later) and the polarizability depends on the molecular weight. This property of light scattering makes it a valuable tool for measuring molecular weight.

Because the intensity of scattered light depends on molecular weight of the particle, light scattering will depend on weight average molecular weight. This result contrasts to colligative properties, such as osmotic pressure, which only depended on number of particles and therefore gave the number average molecular weight. Besides molecular weight dependence, light scattering also has a direct dependence on particle size. For polymer solutions, this dependence on size can be used to measure the radius of gyration of the polymer molecule. As with osmotic pressure, we expect all light scattering experiments to be done in non-ideal solutions. Nonideality complicates the data analysis, but, like osmotic pressure, allows you to determining a virial coefficient, A_2. In summary, light scattering experiments can be used to measure three things: weight average molecular weight ($\overline{M_W}$), mean-squared radius of gyration ($\langle s^2\rangle$), and the second virial coefficient (A_2 or Γ_2).

To interpret light scattering experiments, we begin with a discussion of light scattering theories. Classical light scattering theory was derived by Lord Rayleigh and is now called Rayleigh theory. Rayleigh theory applies to small particles. By small particles, we mean particles whose size is much less than λ or the wavelength of the light that is being scattered. By "much less" we mean

$$\sqrt{\langle s^2\rangle} < \lambda/20 \tag{7.1}$$

Because visible light has λ between 4000Å and 8000Å, we need the root mean squared radius of gyration $\sqrt{\langle s^2\rangle} < 200$ to 400Å. Many polymers will violate this criterion and the light scattering results will have to be corrected for large particle size effects.

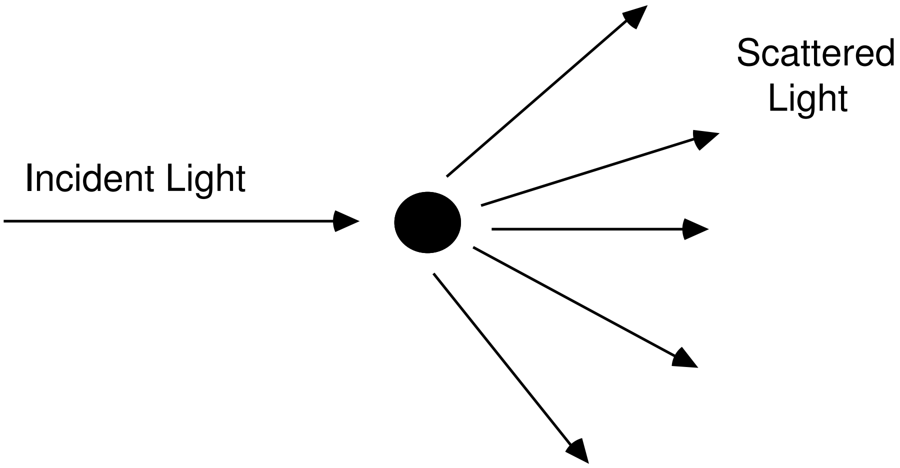

Figure 7.1: Scattering of incident light off a particle in solution or in vacuum.

A light scattering theory known as the Rayleigh-Gans theory was developed to extend Rayleigh theory to particles that are not optically small. The correction method involves extrapolation techniques that extrapolate light scattering intensity to zero scattering angle. This correction technique is important for analyzing results on polymer solutions.

Analysis of osmotic pressure experiments requires extrapolation techniques to account for non-ideal solutions. In light scattering there are two non-ideal effect — nonideal solutions and large particle size effects. Thus, analysis or deconvolution of light scattering data requires two extrapolations. One is an extrapolation to small particle size to remove the large particle size effect. The other is an extrapolation to zero concentration to remove the effect of non-ideal solutions. The slope of the first extrapolation gives the mean squared radius of gyration ($\langle s^2 \rangle$). The slope of the second extrapolation gives the second virial coefficient (A_2). The intercept of the two extrapolations gives the weight average molecular weight ($\overline{M_W}$).

7.2 Rayleigh Theory

We begin by describing the theory for light scattering off a small particle in an ideal solution. Light is an electromagnetic field. At the origin the field is time dependent and described by:

$$E_z = E_0 \cos\left(\frac{2\pi\overline{c}t}{\lambda}\right) \tag{7.2}$$

where E_0 is the amplitude of the electric field, $\overline{c}$ is the speed of light, and λ is the wavelength of light. The subscript z on E means we are considering plane polarized light with the light polarized along the z axis. An incident beam of light polarized in the z direction is shown in Fig. 7.2.

If the particle at the origin in Fig. 7.2 is polarizable, the incident electric field will induce a dipole moment in that particle. The magnitude of the dipole moment is proportional to the field.

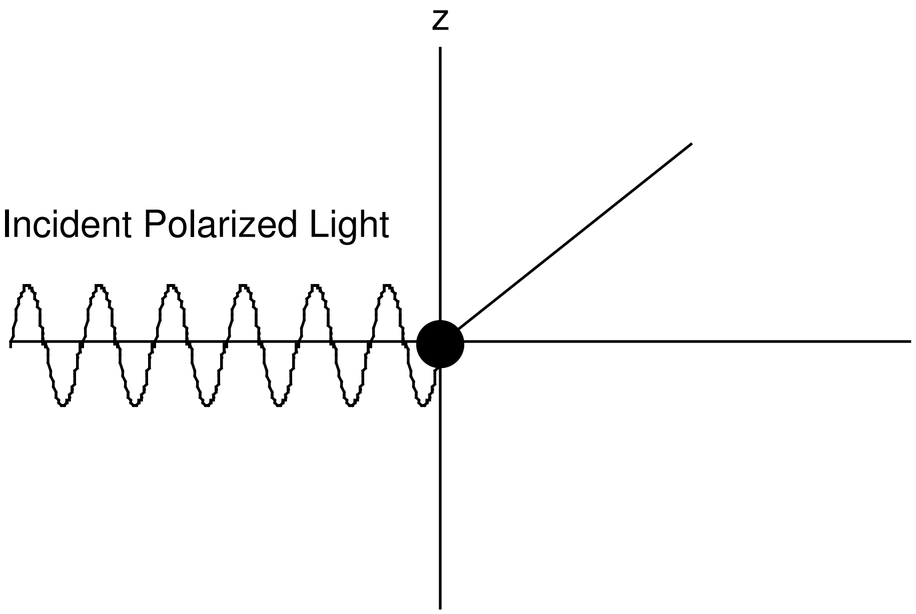

Figure 7.2: Plane polarized light polarized in the z direction and incident on a small particle.

The proportionality constant is called the polarizability — α_p. The higher a particle's polarizability the higher will be the magnitude of the dipole moment induced by a given electromagnetic field. The dipole moment is

$$p = \alpha_p E_0 \cos\left(\frac{2\pi \bar{c} t}{\lambda}\right) \tag{7.3}$$

The induced dipole moment will radiate light in all directions. We consider observing the radiated or scattered light at a distance r from the origin along a line that makes an angle θ_z with the z axis (see Fig. 7.3). The scattered light field will be proportional to $(1/\bar{c}^2)(d^2p/dt^2)$. The second derivative of p is the acceleration of the charge on the dipole moment. To include spatial effects, the scattered light is also proportional to $1/r$ (electromagnetic fields die off as $1/r$) and to $\sin\theta_z$ (the projection of the dipole moment on the observation direction). Combining all these effects, the electric field for light scattered in the θ_z direction is

$$E_s = \frac{1}{r}\frac{1}{\bar{c}^2}\frac{d^2p}{dt^2} = -\frac{1}{\bar{c}^2}\alpha_p E_0 \frac{4\pi^2\bar{c}^2}{r\lambda^2}\sin\theta_z \cos\left(\frac{2\pi\bar{c}t}{\lambda}\right) \tag{7.4}$$

Equipment that measures scattered light is typically only sensitive to the intensity of light. The intensity of light is equal to the amplitude of the electromagnetic field squared. Thus, squaring the amplitude of E_s gives the scattered light intensity at r and θ_z:

$$I_s = \alpha_p^2 I_{0z}\frac{16\pi^4}{r^2\lambda^4}\sin^2\theta_z \tag{7.5}$$

where I_{0z} is the intensity of the z polarized incident light.

$$I_{0z} = E_0^2 \tag{7.6}$$

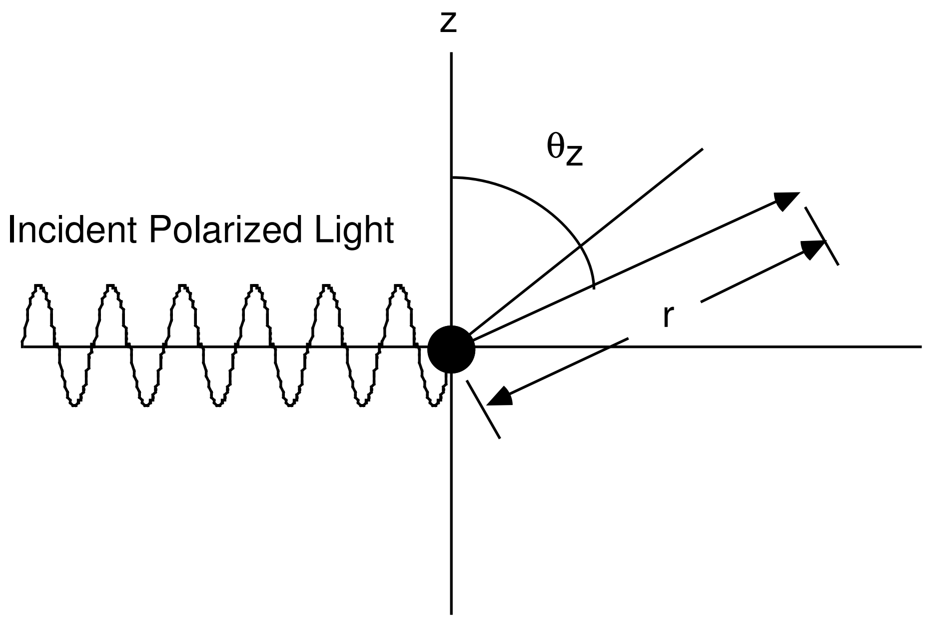

Figure 7.3: Observation direction for light scattered off a particle at the origin in a direction that makes an angle θ_z with respect to the z axis. The observation distance is r.

The above results are for incident light polarized in the z direction. Experiments, however, are usually done with unpolarized light. We can account for unpolarized incident light by summing the intensity of equal parts of incident light polarized in both the z direction and the y direction. The incident intensity becomes

$$I_0 = \frac{1}{2}I_{0z} + \frac{1}{2}I_{0y} \tag{7.7}$$

and the intensity of scattered light becomes

$$I_s = \frac{1}{2}I_{sz} + \frac{1}{2}I_{sy} = I_0\frac{8\pi^4\alpha_p^2}{r^2\lambda^4}\left(\sin^2\theta_z + \sin^2\theta_y\right) \tag{7.8}$$

where θ_y is the angle the observation direction makes with the y axis. Scattering of unpolarized light is illustrated in Fig. 7.4.

By geometry the θ_z and θ_y terms can be related to the angle θ_x that the observation direction makes with the x axis (see Fig. 7.4). This angle will simply be referred to as θ. Because the sum of the direction cosines is 1:

$$\cos^2\theta_x + \cos^2\theta_y + \cos^2\theta_z = 1 \tag{7.9}$$

the geometric result is easily derived to be

$$\sin^2\theta_z + \sin^2\theta_y = 1 + \cos^2\theta \tag{7.10}$$

We now have the scattered light intensity for scattering off a single particle. For scattering off n moles of particles or nL particles (L is Avagadro's number) in a dilute solution of volume V, the

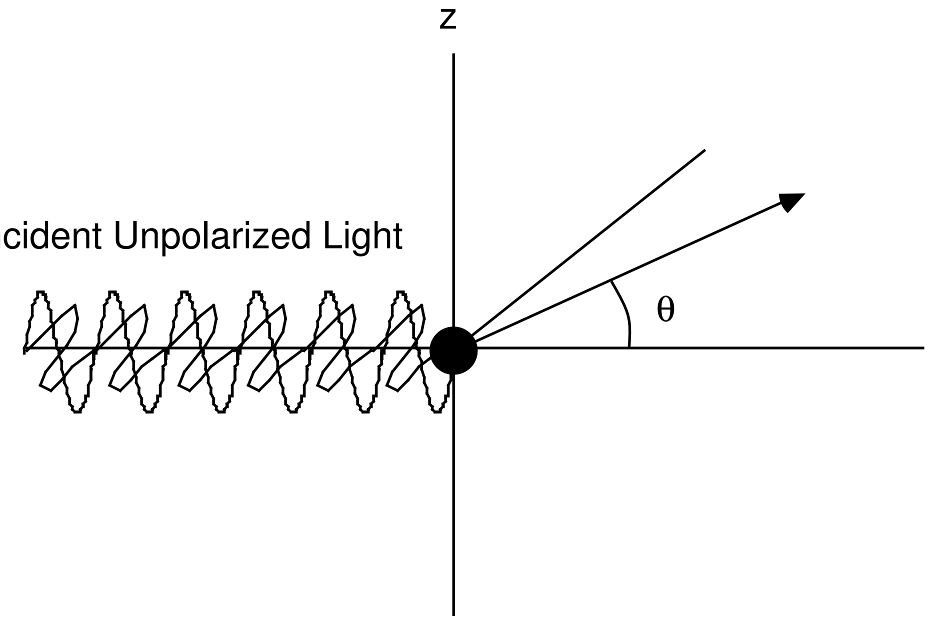

Figure 7.4: Scattering of unpolarized light is analyzed by considering scattering of incident light polarized in both the z and y directions.

scattered intensity at θ is:

$$i_\theta^0 = \frac{I_0 n L}{V} \frac{8\pi^4 \alpha_p^2}{r^2 \lambda^4} \left(1 + \cos^2\theta\right) \tag{7.11}$$

The superscript 0 on the i indicates that this is scattering due to small molecules.

The light scattering intensity depends on scattering angle. The shape of the diagram is determined by the $(1 + \cos^2\theta)$ term. A plot of this term is given in Fig. 7.5. The maximum scattering intensity is at $\theta = 0$. The minimum scattering intensity is at $\theta = 90$. The scattering intensity for forward scattering is equal to the intensity for back scattering at the corresponding angle. In other words, the scattering intensity at angle θ is equal to the scattering intensity at angle $180 - \theta$.

As a function of λ, the scattered intensity is proportional $1/\lambda^4$. This strong wavelength dependence makes short wavelength light scatter more than long wavelength light. This effect explains why the sky is blue. Short wavelength or blue light scatters the most. Normally we do not look at the sun and θ is not zero. When θ is not zero you see the scattered light or the blue light. At sunset you normally do look in the direction of the sun and θ is zero or near zero. Because blue light is scattered away, you are left with the red light and sunsets appear red.

7.3 Ideal Polymer Solutions with Small Particles

For practical results, we need to make a connection between the scattering intensity derived in the previous section and molecular weight of the polymer particles in solution. The connection arises because polarizability depends on molecular weight. First, the polarizability can be thought of as

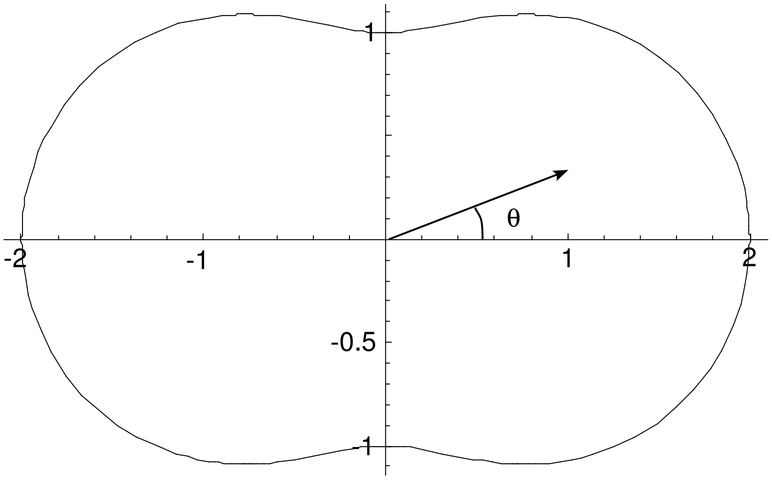

Figure 7.5: Shape of the scattering intensity as a function of scattering angle for scattering off a small particle.

a difference in the index of refraction between the polymer and the solvent. In other words light scattering only occurs in mediums that have an inhomogeneous index of refraction. Specifically, the polarizability of particles at concentration c is

$$\alpha_p = \frac{n_0 c V}{2\pi n L}\frac{dn_0}{dc} \tag{7.12}$$

where n_0 is the index of refraction of the solution and dn_0/dc is the concentration dependence of the index of refraction. Note that if the index of refraction of the solvent and of the polymer are the same then dn_0/dc will be zero and there would be no polarizability and therefore no scattered light. Writing c as nM/V (in units of g/ml) yields

$$\alpha_p = \frac{n_0 M}{2\pi L}\frac{dn_0}{dc} \tag{7.13}$$

and substituting into the scattered light intensity gives (where we also replace n/V by c/M):

$$\frac{i_\theta^0}{I_0} = \frac{2\pi^2}{r^2\lambda^4}\frac{n_0^2}{L}\left(\frac{dn_0}{dc}\right)^2 Mc\left(1+\cos^2\theta\right) \tag{7.14}$$

In a given scattering experiment, I_0 and r will be fixed and we will measure i_θ^0. These measured quantities can be combined into one quantity called the Rayleigh ratio — R_θ^0:

$$R_\theta^0 = \frac{r^2 i_\theta^0}{I_0} \tag{7.15}$$

The advantage of the Rayleigh ratio is that it is independent of the incident light intensity and the distance to the scattered light detector (*i.e.*, independent of I_0 and r). From the scattering equation, the Rayleigh ratio can be written as:

$$R_\theta^0 = KMc \tag{7.16}$$

where

$$K=\frac{2\pi^2n_0^2}{\lambda^4L}\left(\frac{dn_0}{dc}\right)^2\left(1+\cos^2\theta\right) \tag{7.17}$$

The constant K depends only on the solvent properties, on λ, and on θ. K is therefore a system constant that is independent of the concentration of the solution and the molecular weight of the polymer.

For a dilute, polydisperse polymer solution, the total Rayleigh ratio can be written as a sum of the Rayleigh ratios for scattering of polymers of each possible molecular weight:

$$R_\theta^0=K\sum_i c_iM_i \tag{7.18}$$

or

$$\frac{Kc}{R_\theta^0}=\frac{\sum_i c_i}{\sum_i c_iM_i}=\frac{\sum_i N_iM_i}{\sum_i N_iM_i^2}=\frac{1}{\overline{M_W}} \tag{7.19}$$

The Rayleigh ratio for an ideal polymer solution with small particles is thus directly related to the weight average molecular weight ($\overline{M_W}$).

7.4 Non-Ideal Polymer Solutions

As done with osmotic pressure, the possibility of non-ideal solutions is handled by adding virial coefficients and concentration terms to the ideal result. Thus expanding Kc/R_θ^0 gives

$$\frac{Kc}{R_\theta^0}=\frac{1}{\overline{M_W}}+2A_2c+3A_3c^2+\cdots \tag{7.20}$$

The virial coefficients A_2 and A_3 are the same as the virial coefficients we discussed in osmotic pressure theory. The factors of 2, 3, *etc.*, come from the thermodynamic theory of fluctuations which can be used to show that

$$\frac{Kc}{R_\theta^0}=\frac{1}{RT}\frac{\partial\pi}{\partial c} \tag{7.21}$$

where π is osmotic pressure. In a virial expansion

$$\pi=\frac{RT}{\overline{M_N}}c+RTA_2c^2+RTA_3c^3+\cdots \tag{7.22}$$

To convert to the light scattering experiment, the $\overline{M_N}$ in the π expression must be changed to $\overline{M_W}$. The only difference between the A_2 in osmotic pressure and the A_2 in light scattering is that the light scattering A_2 is formally a weight-average virial coefficient. Besides that difference, the light scattering A_2 gives similar information, notably information about the quality of the solvent.

Typically, we will ignore terms beyond the second virial coefficient. Then Kc/R_θ^0 is predicted to be linear in c. From experiments we can plot Kc/R_θ^0 as a function of c. The slope will give the second virial coefficient (slope $=2A_2$) and the intercept will give the molecular weight (intercept $=1/\overline{M_W}$). This extrapolation, however, ignores any possible large particle size effects The extrapolated $\overline{M_W}$ will therefore be in error. The next section considers how to correct for large particle size.

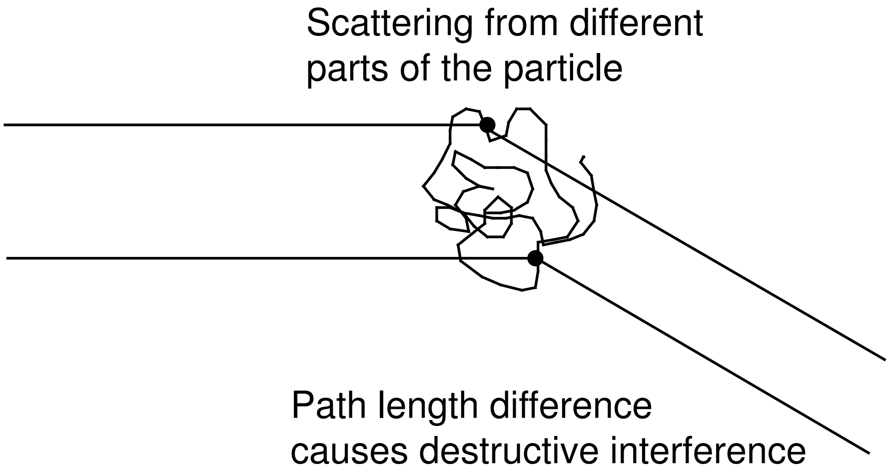

Figure 7.6: Scattering of light of two different parts of a large polymer molecule.

7.5 Large particles

If a particle is not small compared to the wavelength of light, the light can scatter from different parts of the particle. Fig. 7.6 shows a large polymer that is scattering light. Light scattering from different parts of the particle will reach the detector by traveling different path lengths. The difference in path lengths can lead to destructive interference that reduces the intensity of the scattered light. The net effect is that the scattering diagram for large particles is reduced in intensity from the scattering diagram for small particles (see Fig. 7.5).

The amount of intensity reduction or the amount of destructive interference depends on the scattering angle. At θ equal to zero, the path lengths will always be identical. With identical path lengths, there will be no destructive interference. In other words at $\theta = 0$, the intensity of scattered light will be identical to i_θ^0. At θ not equal to zero there will be destructive interference. As θ increases, the interference will increase reaching a maximum and $\theta = 180^\circ$. A comparison of the scattering diagrams for large particles *vs.* small particles is given in Fig. 7.7. The large particle scattering diagram shows the effect of large particles and now shows asymmetry in scattering; *i.e.*, the back scattering intensity is much reduced from the forward scattering intensity.

To correct for large particles, we merely need to do the light scattering experiments at zero scattering angle ($\theta = 0$). Unfortunately, these experiments cannot be done. At $\theta = 0$ most light will be transmitted light that is not scattered. The transmitted light will swamp the scattered light preventing its measurement. Because scattered light and transmitted light have the same wavelength, there is no way to distinguish between them. Instead, we must do experiments at $\theta > 0$ and extrapolate to $\theta = 0$. We thus do a second extrapolation, an extrapolation to zero scattering angle.

To develop an extrapolation method, we define a new function, $P(\theta)$, that describes the large

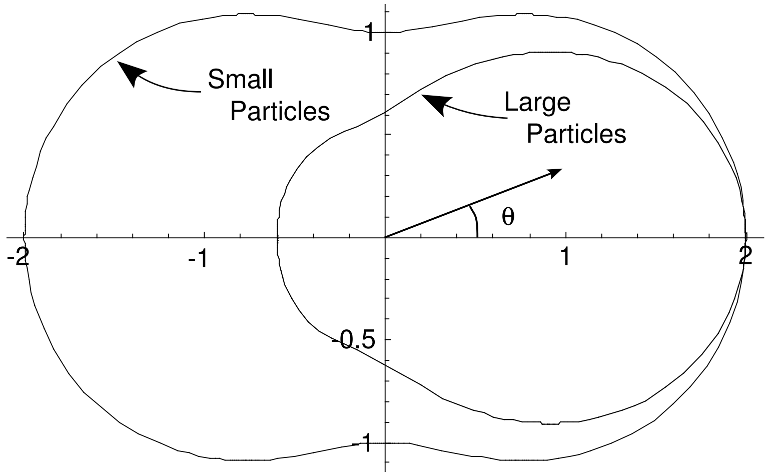

Figure 7.7: Scattering diagrams for both small particles and large particles.

particle size effect. $P(\theta)$ is the ratio between the actual scattering (i_θ) and the scattering that would occur off small particles (i_θ^0)

$$P(\theta) = \frac{i_\theta}{i_\theta^0} = \frac{R_\theta}{R_\theta^0} \tag{7.23}$$

From the above discussions we know that $P(0) = 1$ (there is no effect at zero scattering angle) and $P(\theta) < 1$ for all other θ (destructive interference can only cause a reduction in intensity). The larger effect on back scattering than on forward scatter means that $P(\theta < 90) > P(180 - \theta)$.

First consider an ideal solution. The measured Rayleigh ratio, written as R_θ, includes the large particle size effect. Using $P(\theta)$ we can write $R_\theta = P(\theta)R_\theta^0$. The key measured quantity becomes

$$\frac{Kc}{R_\theta} = \frac{Kc}{P(\theta)R_\theta^0} = \frac{1}{\overline{M_W}P(\theta)} \tag{7.24}$$

The second equality follows from the previously derived ideal solution result with small particles. To use this equation, we need some information about $P(\theta)$. That information can sometimes be derived by theoretical analysis of large-particle scattering. Fortunately, some theoretical results are available for scattering off a large random coil. The results are accurate as long as the particle size is not too large. Instead of requiring $\sqrt{\langle s^2\rangle} < \lambda/20$ as done before for small particles, we can use the theoretical result to handle particles with $\sqrt{\langle s^2\rangle} < \lambda/2$. For scattering with visible light we now can use $\sqrt{\langle s^2\rangle} < 2000\mathring{A}$ to $4000\mathring{A}$. Most polymers fall within or below this range and thus we can derive effective extrapolation methods for scattering off polymer molecules.

The theoretical result for $P(\theta)$ is

$$\frac{1}{P(\theta)} = 1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle \sin^2\frac{\theta}{2} + \cdots \tag{7.25}$$

The "$\cdots$" means that there are higher order terms in $\sin(\theta/2)$. Those terms are normally assumed to be negligible. For a polydisperse polymer, the scattering intensity as a function of scattering angle becomes

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M_W}}\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \sin^2\frac{\theta}{2}\right) \tag{7.26}$$

Note we have changed $\langle s^2\rangle$ to $\langle s^2\rangle_w$, the weight average radius of gyration squared. In terms of the various polymer weights, the relevant radius of gyration squared is

$$\langle s^2\rangle_w = \frac{\sum_i N_i M_i \langle s^2\rangle_i}{\sum_i N_i M_i} = \sum_i w_i \langle s^2\rangle_i \tag{7.27}$$

where $\langle s^2\rangle_i$ is the average squared radius of gyration for polymers with molecular weight M_i

To find weight-average molecular weight ($\overline{M_W}$) in ideal solutions, we truncate $1/P(\theta)$ after the $\sin^2(\theta/2)$ term and plot Kc/R_θ as a function of $\sin^2(\theta/2)$. That plot should be linear. The intercept will give the molecular weight:

$$\text{intercept} = \frac{1}{\overline{M_W}} \tag{7.28}$$

The slope divided by the intercept will give the radius of gyration

$$\text{slope/intercept} = \frac{16\pi^2\langle s^2\rangle_w}{3\lambda^2} \tag{7.29}$$

7.6 Light Scattering Data Reduction

To handle both non-ideal solutions and large particle effects, we need to do two extrapolations. First, we introduce non-ideal solution effects into the large particle analysis in the previous section. Instead of using $P(\theta)$ to correct the ideal solution result, we use it to correct the non-ideal solution result. Thus the actually measured Kc/R_θ is

$$\frac{Kc}{R_\theta} = \frac{Kc}{P(\theta)R_\theta^0} = \left(\frac{1}{\overline{M_W}} + 2A_2c\right)\frac{1}{P(\theta)} \tag{7.30}$$

where we have truncated the non-ideal solution result to a single virial coefficient. Inserting the theoretical result for $P(\theta)$ truncated after the $\sin^2(\theta/2)$ term gives

$$\frac{Kc}{R_\theta} = \left(\frac{1}{\overline{M_W}} + 2A_2c\right)\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \sin^2\frac{\theta}{2}\right) \tag{7.31}$$

A set of light scattering experiments consists of measure Kc/R_θ for various concentrations and at various scattering angles. To get $\overline{M_W}$, we do two extrapolations. First, plotting Kc/R_θ as a function of $\sin^2(\theta/2)$ at constant c gives a straight line with the following slope and intercept:

$$\text{slope} = \left(\frac{1}{\overline{M_W}} + 2A_2c\right)\frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \tag{7.32}$$

$$\text{intercept} = \left(\frac{1}{\overline{M_W}} + 2A_2c\right) \tag{7.33}$$

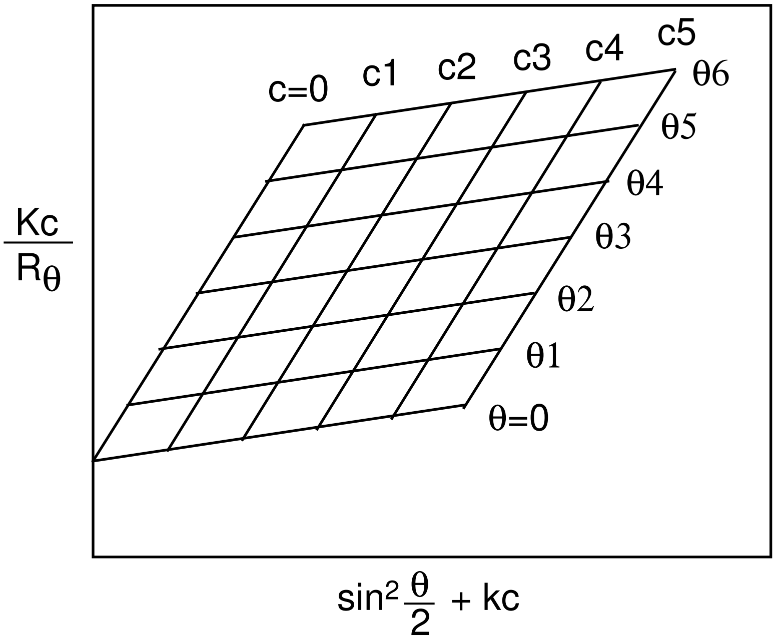

Figure 7.8: Typical Zimm plot. The experimental data points are at the grid intersection points except along the $\theta = 0$ and $c = 0$ lines.

Next we plot the intercepts of the first plots as a function of concentration. The resulting plot should be a straight line with

$$\text{slope} = 2A_2 \tag{7.34}$$

$$\text{intercept} = \frac{1}{\overline{M_W}} \tag{7.35}$$

The slope and intercept of the second line gives us $\overline{M_W}$ and A_2. Substituting these results into the slope of the first line allows us to find $\langle s^2\rangle_w$. We could achieve similar results by first plotting as a function of concentration and then plotting the intercept of those plots as a function of $\sin^2(\theta/2)$.

The above analysis assumes that all c's are low enough such that the concentration dependence is linear in concentration and only requires the second virial coefficient. It also assumes all scattering angles are low enough that terms higher than the $\sin^2(\theta/2)$ can be neglected. Both these conditions are easy to satisfy for light scattering with polymer solutions.

The analysis method described above is easy to do in a personal computer. When light scattering techniques were first developed, however, computers were not available and the numerous linear fits were tedious. To avoid the tedium the Zimm plot was developed. In the Zimm plot technique, you plot Kc/R_θ versus $\sin^2(\theta/2) + kc$ where k is a constant. k is chosen to spread out the plot and give equal weights to each variable. For example $\sin^2(\theta/2)$ is always less than 1 or has a maximum of 1. The range in kc should also go from 0 to 1 or $kc_{max} = 1$ which means a good k might be $1/c_{max}$ where c_{max} is the maximum concentration used. A typical Zimm plot is given in Fig. 7.8.

Plotting all Kc/R_θ points on a Zimm plot should result in a grid such as the one shown in

Fig. 7.8. There will be experimental points at all grid points except along the lower line (the $\theta = 0$ line) and the left-most line (the $c = 0$) line. Connecting all the grid lines and extrapolating to the lower-left corner, the intercept point gives the molecular weight (intercept $= 1/\overline{M_W}$). Incorporating the k constant, the Zimm plot is plotting

$$\frac{Kc}{R_\theta} = \left(\frac{1}{\overline{M_W}} + \frac{2A_2}{k}kc\right)\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \sin^2\frac{\theta}{2}\right) \tag{7.36}$$

The slopes of the two directions in the parallelogram have physical meaning. The lines labeled θ_1, θ_2, *etc.*, are lines at constant θ. Inspection of the Zimm equation shows that the slopes of these lines are:

$$\text{slope of the contant } \theta \text{ lines} = \frac{2A_2}{k}\left(1 + \frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \sin^2\frac{\theta}{2}\right) \tag{7.37}$$

Notice that these slopes are a function of θ. Thus the slope of the $\theta = 0$ line and the θ_5 (or any θ_i line) are different. In other words the Zimm plot is not actually a parallelogram. The lines labeled c_1, c_2, *etc.*, are lines at constant concentration. Inspection of the Zimm equation shows that the slopes of these lines are:

$$\text{slope of the constant } c \text{ lines} = \left(\frac{1}{\overline{M_W}} + 2A_2c\right)\frac{16\pi^2}{3\lambda^2}\langle s^2\rangle_w \tag{7.38}$$

Notice that these slopes are a function of c. Thus the slope of the $c = 0$ line and the c_5 (or any c_i line) are different. In other words the Zimm plot is not actually a parallelogram. The slopes of constant θ and constant c lines both depend on A_2 and on $\langle s^2\rangle_w$. The slopes of the constant θ lines are mostly sensitive to A_2. The slopes of the constant c lines are mostly sensitive to $\langle s^2\rangle_w$. Because A_2 and $\langle s^2\rangle_w$ are independent physical quantities, it is possible to get Zimm plots that are inverted from the plot in Fig. 7.8. If A_2 increases and/or $\langle s^2\rangle_w$ decreases, it is possible for the steeper lines to be the constant θ lines and for the shallower lines to be the constant c lines.