A study of long time behavior of aqueous solution of polyethylene oxide (Peo) and aqueous salt (potassium sulfate) solution of Peo using dynamic light scattering

Ziyi Hu
University of Nevada, Las Vegas
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A study of long time behavior of aqueous solution of polyethylene oxide (PEO) and aqueous salt (K\textsubscript{2}SO\textsubscript{4}) solution of PEO using dynamic light scattering

Hu, Ziyi, M.S.

University of Nevada, Las Vegas, 1991
A Study of Long Time Behavior of Aqueous Solution of Polyethylene Oxide (PEO) and Aqueous Salt ($K_2SO_4$) Solution of PEO using Dynamic Light Scattering

by

Ziyi Hu

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The thesis of Ziyi Hu for the degree of Master of Science in Physics is approved.

Chairperson, J. C. Selser Ph.D.

Examining Committee Member, L. D. Spight Ph. D.

Examining Committee Member, J. W. Farley Ph. D.

Graduate Faculty Representative, D. W. Emerson Ph. D.

Graduate Dean, R. W. Smith Ph.D.

University of Nevada, Las Vegas

July 1991
Abstract

This work involves the study of the long time behavior of dilute aqueous solutions of polyethylene oxide (PEO) and the properties of dilute aqueous salt (K\textsubscript{2}SO\textsubscript{4}) solutions of PEO by using the dynamic light scattering technique.

The aqueous solutions of PEO were prepared with a PEO sample obtained from Pressure Chemical Co., with a molecular weight of 838,000, and ultrapure water with a nominal resistivity of 12M\(\Omega\)-cm-16M\(\Omega\)-cm. The solutions with concentrations of 0.45mg/ml and 1.0mg/ml were filtered into the sample cell through a 0.2\(\mu\)m filter for a dynamic light scattering measurement. The dynamic measurements were carried out at a scattering angle of 45° and the temperature of samples was kept at 30°C. The long time study measurement results indicated that the values of the polydispersity factor and the mutual diffusion coefficient of the PEO particles of the solutions changed very slowly. The analysis of the measured data implied that the aggregation of PEO in a dilute aqueous solution might not be an inherent property of the solution, and the aggregation was probably caused by the impurities in the solution.

A series groups of aqueous salt (K\textsubscript{2}SO\textsubscript{4}) solutions of PEO with the K\textsubscript{2}SO\textsubscript{4} concentrations of 0.5M,1.0M,2.0M,3.0M and 0.4M, were investigated using the dynamic light scattering technique. The results indicated that the \(K_d\) values decreased with increasing the concentration of K\textsubscript{2}SO\textsubscript{4}. The solvent of the salt solutions became poorer with addition of salt K\textsubscript{2}SO\textsubscript{4} into the solutions.
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Chapter 1 Some Concepts of Polymer Solutions

1.1 Introduction

Polymers are molecules of very high molecular weight. For this reason, polymers are frequently called macromolecules. Macromolecules can be divided into biological and nonbiological macromolecules. Biological macromolecules such as proteins and DNA form the very foundation of life. Nonbiological macromolecules, which include many synthetic polymers and a few natural polymers, are indispensable to modern society\(^{(1,2)}\).

A polymer is built up by the repetition of small, chemically simple units called monomers\(^{(2)}\). For example, the polymer polyethylene oxide(PEO) is built up by repetition of the monomer \(-\text{O-CH}_2\text{-CH}_2\text{-}\), and the chemical structure of PEO is represented as \([-\text{O-CH}_2\text{-CH}_2\text{-}]_n\). The number of repetitive unit \(n\) is called the degree of polymerization. In some cases, the repetitions is linear, as a chain is built up from its links (Fig.1.1a). In other cases, the chains are branched (Fig. 1.1b) or interconnected to form three-dimensional networks (Fig.1.1c).
The length of a polymer chain is specified by the number of the repeated units in the chain. The molecular weight of a polymer is the product of the molecular weight of the repeat unit (monomer) and the number of the units. Unlike low-molecular weight molecules, which have a fixed molecular weight, all polymer (except for some biological macromolecules) have a distribution of chain lengths and molecular weights. Because of this distribution, the experimental measurements of molecular weight can only give an average value\(^ {1-3}\). Two types of average molecular weight used to describe the average value, are the number-averaged and the weight-averaged molecular weight. The number-average molecular weight \(\bar{M}_n\) is defined as

\[
\bar{M}_n = \frac{\sum_i M_i N_i}{\sum_i N_i}.
\] (1.1)

Here, \(N_i\) is the number of molecules with molecular weight \(M_i\), and \(\sum_i N_i\) is the total number of the polymer molecules.

The weight-average molecular weight \(\bar{M}_w\) is defined as

\[
\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}.
\] (1.2)

As \(\frac{N_i M_i}{\sum_i N_i M_i} = w_i\), which is weight fraction of the molecules with molecular weight \(M_i\),

\[
\bar{M}_w = \sum_i w_i M_i.
\] (1.3)
There is generally no simple relationship between $\bar{M}_n$ and $\bar{M}_w$ except for the "Hypothetical Monodispersed Polymer" whose $\bar{M}_n$ is equal to $\bar{M}_w$. Because heavier molecules contribute more to $\bar{M}_w$ than light ones, $\bar{M}_w$ is always larger than $\bar{M}_n$, except for a hypothetical monodisperse polymer. The quantity $\bar{M}_w/\bar{M}_n$ is a useful measure of the width of the molecular-weight distribution, and this parameter is most frequently used to describe that feature of the distribution\(^{(2,3)}\).

1.2 The Configuration of the Linear Polymer Chain

The materials in this section were mainly drawn from reference 1.

1.2.1 Random Coil

The configuration of a linear polymer chain with large number of the repetive units (or monomers), is a long flexible chain which looks like a three-dimensional random coil in space coordinates\(^{(1)}\), as illustrated in figure 1.2

![Figure 1.2](image)

In a linear polymer chain, the length of the monomer (bond) as well as the
angle (bond angle) between two successive monomers is fixed. A monomer may rotate along its neighbor to some extent. Because of the large number of monomers in a polymer, it is impossible to give the configuration information of each individual polymer chain in detail. A statistical method has been used to describe the configuration of the polymer chain. The statistical method is based on a "freely jointed chain" model which is a hypothetical chain consisting of linkages of fixed bond length joined in linear sequence without any restrictions of angle between two successive bonds\(^1\). The "freely jointed chain", exhibiting Gaussian statistics, is often called the ideal chain.

Despite the fact that the real polymer chain has fixed bond angles and a restricted rotation angle to some extent, it can be shown that the statistical properties of a real chain with a large number of monomers is equivalent to a freely jointed chain\(^1\). In a real chain, the direction of a given bond is strongly influenced or correlated by the direction of its predecessor in the chain. The influence of the nearby bonds (second, third, and perhaps the fourth neighbor) should also be considered. The influence between a pair of bonds decreases with the increasing the number of interval bonds. When the number of interval bonds between the pair of bonds become large enough, these two bonds are no longer correlated. If the resultant of a sequence of \(m\) bonds is chosen as a statistical subunit, instead of taking the individual bond in the real chain, when \(m\) is large enough, these subunits are uncorrelated with each other. Therefore, the statistical result of this configuration is equivalent to that of the freely jointed chain.

The size of a polymer chain may be calculated based on the freely jointed chain model. The result is an average value. Typically, the distance from one end of the chain to the other end is used to represent the size of the polymer. For a freely jointed chain, the end-to-end vector is the sum of \(N\) "randomly joined vectors"\(^4\).
\[ \mathbf{r} = \mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3 + \cdots + \mathbf{a}_n = \sum_{i=1}^{n} \mathbf{a}_i, \tag{1.4} \]

where \( \mathbf{a}_i \) is the vector for the \( i \)th bond. The mean value of the square of the end-to-end distance is

\[ <r^2> = \sum_{i}^{n} \sum_{j}^{n} <a_i \cdot a_j>. \tag{1.5} \]

For the freely jointed model, because all the bonds are uncorrelated with each other, so that

\[ <a_i \cdot a_j> = a_i^2 \delta_{ij}, \text{ thus} \]

\[ <r^2> = \sum_{i=1}^{N} <a_i^2> = N a^2. \tag{1.6} \]

The root mean square of \( r \) is

\[ r_{\text{rms}} = N^{0.5} a. \tag{1.7} \]

The distribution of end-to-end distances of the ideal chain is given by the Gaussian distribution function.

Because the molecular weight of a polymer chain is proportional to \( N \), the root mean square of end-to-end \( r_{\text{rms}} \) can also be expressed as

\[ r_{\text{rms}} = C M^{0.5}. \tag{1.8} \]

Here, \( M \) is the molecular weight and \( C \) is a constant.

Neutron scattering and light scattering experimental results have verified that the polymer chains in the molten state and in the Flory \( \theta \)-solvent (which will be described in section 1.3) are ideal chains. The mean sizes of these polymer chains are proportional to \( M^{0.5} \).

Another important parameter used to describe the effective size of a polymer chain, is the root-mean-square distance of the elements of the chain from the center of gravity of the polymer. This quantity is called the radius of gyration of the polymer chain. For an ideal chain, the relation between radius of gyration \( R_g \) and mean distance
of end-to-end is \( R_g = r_{rms}/6^{0.5} \) \( (1.9) \)

1.2.2 The Configuration of the Polymer Chain in Dilute Solution

The configuration of polymer chains in a dilute solution is different from that of the ideal chain, except for the chains in Flory \( \theta \)-solvents (which will be described in section 1.3). In a solution, no two portions of a given polymer can overlap in space which is referred to as the effect of volume exclusion \( (1) \). Because this condition is not required for the ideal chain, the mean size of a long polymer chain in solution tends to be larger than that of the corresponding ideal chain. This will be discussed below.

The environment of a polymer chain also influences the configuration of the chain. When the interaction energy between a polymer element and a solvent molecule adjacent to it exceeds the mean energy of the interactions between the polymer-polymer and the solvent-solvent, the polymer molecule will tend to expand in order to reduce the contacts between pairs of polymer element. The solvent is then called a good solvent. When the interaction energy between polymer and solvent is smaller than the mean energy of polymer-polymer and solvent-solvent, the polymer molecule will tend to contract, the polymer-polymer contacts will occur more frequently. The solvent of this kind is then defined as a poor solvent.

A given polymer chain dissolved in a good solvent is swollen due to the osmotic action of the surrounding solvent molecules. As the chain expands to a larger configuration, a elastic force is developed along the chain. At equilibrium, the elastic force is in balance with the osmotic force. Flory derived a relation between the mean end-to-end distance and the molecular weight of the polymer in a good solvent, i.e.

\[ r_{rms} = C M^{0.6}. \] \( (1.10) \)
The eqn. 1.10, to a good approximation, is in agreement with many experimental results.

For a polymer chain in a poor solvent, the influence of interactions is against the effect of volume exclusion. The poorer the solvent is, the less the polymer molecules repel one another. When the solvent become poor enough that the effect of interactions exactly conceal the effect of volume exclusion, the net interaction between polymer molecules is zero. Then, the polymer chain in the solvent become an ideal chain, and this solvent is defined as a Flory θ-solvent. For a given polymer in a given solvent, the state of Flory θ-solvent may be reached at a unique temperature which is defined as the Flory θ-temperature.

The mean size of a polymer chain in dilute solution can be determined by various standard experimental methods. Three of them are listed below:\(^{(4)}\)

(i) The dynamic light scattering measurement gives the diffusion coefficient \(D_0\) for a single chain. From this coefficient, the hydrodynamics radius \(R_h\), defined by the Stokes relation for a sphere, may be obtained. The Stokes relation is:

\[
D_0 = \frac{kT}{6\pi\eta R_h},
\]

where \(\eta\) is the solvent viscosity.

(ii) The static light scattering measurement gives the radius of gyration \(R_g\).

(iii) The viscosity measurement gives a effective radius \(R_\eta\).

According to many literatures, for a polymer chain in good solvent, the static scattering measurements give a radius \(R_g\) proportional to \(N^{0.6}\), while dynamic light
scattering and viscosity measurements give a $R$ proportional to $N^{0.55} - N^{0.57}$ (4).

1.3 Thermodynamics of Polymer Solutions

The materials in this section was mainly drawn from reference 1.

1.3.1 General thermodynamic properties of polymer solutions

For a dilute solution of simple molecules, solute and solvent molecules have roughly the same size. The theoretical treatment of this kind of solution is based on the ideal solution law or the Raoult's law. In an ideal solution, it is assumed that the solute and solvent molecules are interchangeable. This means that replacement of solute molecules by solvent molecules does not cause any change in the net molecular interaction energy. The ideal solution law is

\[
\begin{align*}
\Delta H_{\text{mix}} &= 0, \quad (1.12) \\
\Delta S_{\text{mix}} &= -k(n_1 \ln v_1 + n_2 \ln v_2), \quad (1.13) \\
\Delta G_{\text{mix}} &= \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} = kT(n_1 \ln v_1 + n_2 \ln v_2), \quad (1.14)
\end{align*}
\]

where $\Delta H_{\text{mix}}$, $\Delta S_{\text{mix}}$ and $\Delta G_{\text{mix}}$ are heat of mixing, entropy of mixing and total free energy of mixing, respectively. $n_1$ and $n_2$ are the numbers of solvent and solute molecules, and, $v_1$ and $v_2$ are their mole fractions, respectively.

In a polymer solution, however, because the solute molecules are much larger than the solvent molecules, the thermodynamics of polymer solutions deviate greatly from the ideal solution law.

The entropy of mixing of polymer solutions
Flory developed an expression for the entropy of mixing for polymer solutions based on the liquid lattice theory\(^{(1)}\). According to this theory, a given polymer chain in a polymer solution consists of \(x\) chain segments and these segments have roughly the same size as a solvent molecule. These segments and solvent molecules are assumed interchangeable. Each individual segment or solvent molecules occupies a lattice site in an imaginary lattice. If a segment of the polymer chain is treated as a solute element instead of the polymer molecule itself, the polymer solution is analogous to a simple molecule solution. The difference is that the \(x\) segments of a polymer chain must be linearly connected. The total number of the lattice sites \(N_0\) is \(N_0 = N_1 + xN_2\), where \(N_1\) and \(N_2\) are the number of solvent and polymer molecules, respectively.

The entropy of mixing of a polymer solution, from the lattice model and equation (1.13), may be expressed as

\[
\Delta S_{\text{mix}} = -k(N_1 \ln \nu_1 + N_2 \ln \nu_2),
\]

(1.15)

where \(\nu_1\) and \(\nu_2\) are the volume fractions of solvent and solute, i.e.

\[
\nu_1 = \frac{N_1}{N_1 + xN_2},
\]

\[
\nu_2 = \frac{xN_2}{N_1 + xN_2}.
\]

(1.16)

Heat of mixing and and free energy of mixing of a polymer solution

When a polymer solute is dissolved in a solvent, there is a total interaction energy change because solvent-solvent and solute-solute interactions are replaced by solute-solvent interactions. This interaction energy change is referred to as the heat of
mixing. From the lattice theory, these interactions can be represented by the contacts of the nearest neighbor in the lattice. There are three type of these contacts, \([1,1]\), \([2,2]\) and \([1,2]\), 1 and 2 represent solvent and solute, respectively. The dissolving process may be represented as:

\[
\frac{1}{2}[1,1] + \frac{1}{2}[2,2] \longrightarrow [1,2].
\] (1.17)

The interaction energy change associated with the formation of a solvent-solute contact may be expressed as

\[
\Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22}).
\] (1.18)

Let \(P_{12}\) represent the average number of the total solvent-solute contacts in the solution, the heat of mixing is given as:

\[
\Delta H_{\text{mix}} = \Delta w_{12} P_{12}.
\] (1.19)

There are \(xN_2\) polymer segments in the solution, and each of them occupies a lattice site. A lattice site has \(z\) nearest neighbors. The probability that a given lattice site adjacent to a polymer segment is occupied by a solvent molecule is approximately equal to the solvent volume fraction \(v_1\), which is given in eqn. 1.16. Thus, \(P_{12}\) may be expressed as

\[
P_{12} = xN_2 \cdot zv_1 = zN_1 v_2,
\] (1.20)

and therefore, the heat of mixing is

\[
\Delta H_{\text{mix}} = zN_1 v_2 \cdot \Delta w_{12}.
\] (1.21)

Let

\[
z \Delta w_{12} = \chi_1 kT,
\]

the eqn. 1.21 is manipulated as:

\[
\Delta H_{\text{mix}} = \chi_1 kT \cdot N_1 v_2.
\] (1.22)

\(\chi_1\) is an interaction energy change(in unit of \(kT\)) of a solvent molecule removed from the pure solvent and immersed in the pure polymer.
From equations 1.15 and 1.22, the free energy of mixing is

\[ \Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} = kT(N_1 \ln v_1 + N_2 \ln v_2 + \chi_1 N_1 v_2). \]  

(1.23)

The chemical potential of a solvent in a solution relative to the pure solvent is

\[ \mu_1 - \mu_1^0 = (-\frac{\partial [G_{\text{so}}]}{\partial N_1})_{T,P,N_2} = (-\frac{\partial \Delta G_{\text{mix}}}{\partial N_1})_{T,P,N_2}. \]  

(1.24)

From eqn. 1.23 and eqn. 1.16, eqn. 1.24 may be manipulated as:

\[ \mu_1 - \mu_1^0 = RT \ln (1 - v_2) + (1 - \frac{1}{x})v_2 + \chi_1 v_2^2. \]  

(1.25)

The osmotic pressure \( \pi \) of a polymer solution is defined as

\[ \pi = \frac{(\mu_1 - \mu_1^0)}{v_1} = \frac{RT}{v_1} [\ln (1 - v_2) + (1 - \frac{1}{x})v_2 + \chi_1 v_2^2], \]  

(1.26)

where \( v_1 \) is the molar volume of the solvent. For a dilute polymer solution, \( v_2 \) is much less than one, thus, the eqn. 1.26 may be manipulated as

\[ \pi = \frac{RT}{v_1} \left[ \frac{v_2}{x} + (\frac{1}{2} - \chi_1)v_2^2 + \frac{1}{3} v_2^3 + \cdots \right]. \]  

(1.27)

\( v_2 \) may be expressed as \( v_2 = cv \), \( c \) is the polymer concentration in the unit of g/ml and \( v \) is the specific volume of the polymer. Since \( x \) is the ratio of the molar volumes of polymer and solvent, we get \( v_2/xv_1 = cv/xv_1 = c/M \). Therefore

\[ \frac{\pi}{c} = RT \left[ \frac{1}{M} + (\frac{v^2}{v_1})(-\frac{1}{2} - \chi_1)c + (\frac{v^3}{v_1})c^2 + \cdots \right]. \]  

(1.28)
1.3.2 Thermodynamics of Very Dilute Polymer Solutions

The configuration of a very dilute polymer solution is discontinuous, as illustrated in figure 1.3. The structure of the solution consists of a dispersion of clusters (or coils) of polymer chain segments and the region of polymer-free solvent between those clusters with no overlapping from different clusters. The shape of these clusters is approximately spheric, and the mean density of the segments in a coils decreases with the distance from the mass center of the polymer chain. The overall mean density of the polymer segment within the domain of the polymer coils is very low\(^{(1)}\).

![Figure 1.3](image)

**Figure 1.3**

a. Thermodynamic properties in a domain of uniform segment concentration

A volume element in the domain of the polymer coils, volume \(\delta v\) occupies only a small portion of a polymer coil. Since \(\delta v\) is small, the segment density in \(\delta v\) may be assumed to be uniform. The entropy of mixing and heat of mixing in the element volume \(\delta v\) may be deduced from equations 1.15 and 1.22 and can be represented as:

\[
\delta(\Delta S_{\text{mix}}) = -k\delta n_1 \ln \nu_1,
\]
where $\delta n_1$ and $\nu_1$ are the number and volume fraction of the solvent molecules in the volume element $\delta v$, respectively. $\nu_2$ here represents the volume fraction of polymer segment in the volume element $\delta v$ instead of in the whole solution.

The free energy of mixing in $\delta v$ is

$$\delta(\Delta G_{\text{mix}}) = kT \left[ \delta n_1 \ln(1-\nu_2) + \chi_1 \delta n_1 \nu_2 \right]. \quad (1.30)$$

The chemical potential of the solvent in the volume element $\delta v$ may be deduced from eqn. 1.30, i.e.

$$\langle \mu_r - \mu_r^0 \rangle_e = RT \left[ \ln(1-\nu_2) + \nu_2 + \frac{1}{2} \nu_2^2 \right] + R T \left[ \left( \frac{4}{3} - \frac{1}{2} \chi_1 \right) \nu_2^2 \right]. \quad (1.31)$$

The chemical potential here is different from that in eqn. 1.25 which is the chemical potential for the whole solution.

When the concentration of the polymer segment in the volume element $\delta v$ is very low, the higher term in equation (1.31) can be neglected. Thus

$$\langle \mu_r - \mu_r^0 \rangle_e = RT \left[ \left( \frac{1}{2} - \chi_1 \right) \nu_2^2 \right] = \Delta H_1 - \Delta S_1, \quad (1.32)$$

where $\Delta H_1$ and $\Delta S_1$ are the partial molar heat of mixing and the entropy of mixing in the volume element, respectively. $\Delta H_1$ and $\Delta S_1$ may be expressed as

$$\Delta H_1 = RT \chi_1 \nu_2^2,$$

$$\Delta S_1 = R \psi_1 \nu_2^2. \quad (1.33)$$

Also
By comparing equations 1.32 and 1.34, we have
\[ \kappa_1 - \psi_1 = \chi_1^{-1/2}. \quad (1.35) \]

The Flory temperature is defined as
\[ \theta = \kappa_1 T / \psi_1 \quad (1.36) \]

And,
\[ \psi_1 - \kappa_1 = \psi_1 (1 - \theta / T) \quad (1.37) \]

The chemical potential of solvent in the volume element is
\[ (\mu_1 - \mu_1^0)_e = -RT \psi_1 (1 - \theta / T) \quad (1.38) \]

At temperature \( T = \theta \), the free energy of interaction within the volume element is zero.

b. The excluded volume and osmotic pressure in very dilute polymer solution

A polymer molecule in a dilute solution will tend to exclude other polymer molecules from the volume it occupies. If the solvent is a good solvent, the excluded volume is defined as the volume from which a given polymer molecule effectively excludes all others. Flory calculated the excluded volume \( u \) based on the lattice model, i.e.
\[ u = 2JM^2 \mathcal{J}(J \xi), \quad (1.39) \]
and \( J \) is
\[ J = \psi_1 (1 - \theta / T) - \frac{\bar{v}^2}{v_1} \quad (1.40) \]

where \( M \) is the molecular weight of the polymer, \( v \) is the specific volume of the polymer and \( v_1 \) is the volume of one solvent molecule. \( \xi \) is
\[ \xi = \frac{3M^3}{r_{\text{rms}}^2} \left( \frac{1}{2\pi \xi} \right) \]
where $r_{rms}$ is the mean value of the end-to-end distance of the polymer chain. The function $F(X)$ is defined as

$$F(X) = (4\pi^{0.5}X^{-1}\int_0^\infty (1-\exp(-X\cdot\exp(-y^2)))y^2dy, \tag{1.41}$$

where $X = J\xi$ and $y$ the integration variable.

The excluded volume $u$ is depends strongly on $J$. When the solvent is made poorer, the quantity $\psi_1(1-\theta/T)$ become smaller, the excluded volume $u$ decreases, and at $T=\theta$, $u$ is zero. At this point, the polymer chains will not repel or attract each other, and the chains are equivalent to the ideal chains. At the temperature below $\theta$, the excluded volume $u$ is negative, the polymer chains attract each other, and at some temperature lower than $\theta$, precipitation occurs.

By considering the effect of the excluded volume, the osmotic pressure $\pi$ is

$$\frac{\pi}{c} = RT\left(-\frac{1}{M} + \frac{N_a u}{2M^2}c\right), \tag{1.42}$$

where $N_a$ is the Avogadro constant and $c$ is the mass concentration of the polymer in solution.

A more general expression of the quantity $\frac{\pi}{c}$ is

$$\frac{\pi}{c} = RT[A_1 + A_2c + A_3c^2 + \cdots \cdots], \tag{1.43}$$

a virial expansion of $\pi/c$. Here,

$$A_1 = \frac{1}{M}.$$
In the application of osmotic data, the equation 1.43 is frequently represented as

\[ f - \left( - \frac{f}{c} \right)_o \left[ 1 + \Gamma_2 c + \Gamma_3 c^2 + \cdots \right] \]  

(1.45)

where \( (-\frac{f}{c})_0 = \frac{RT}{M} \). When \( u = 0 \), the equations 1.43 and 1.45 reduce to

\[ \frac{\pi}{c} = \frac{RT}{M} \]  

(1.46)

which is similar to the ideal gas law.

1.4 Hydrodynamics of Dilute Polymer Solutions

The materials in this section was mainly drawn from reference 1 and 5-8.

1.4.1 The viscosity of dilute polymer solutions

It was observed that adding polymer solute to a solvent, even at very low concentration, would significantly increase the viscosity of the solution relative to that of the solvent. The increase in viscosity occurs because of the unusual configuration of polymer chains in solutions\(^{(1,5-7)}\). As described in previous sections, a given polymer chain in a solution is a three-dimensional coil which "holds" a large number of solvent molecules within it. The coil and the solvent held in it form a single "particle" which is more massive than the polymer itself. Thus, a small amount of polymer solute might form a relatively large number of those large, more massive "particles", and these particles might significantly increase the viscosity in the solution. The coils filled with
solvent molecules are sometimes called molecular colloids. In general, the viscosity of dilute polymer solutions can be expressed as

\[ \eta = \eta_0 [1 + H_1 c + H_2 c^2 + H_3 c^3 + \cdots] \]

(1.47)

Here \( \eta_0 \) is the viscosity of the solvent. This equation may be manipulated as

\[ \frac{\eta - \eta_0}{\eta_0 c} \approx \eta_{sp} = [\eta] + k_1 [\eta]^2 c + k_2 [\eta]^3 c^2 + \cdots \]

(1.48)

Here \( k_1, k_2, k_3 \) etc. are dimensionless parameters, \( \eta_{sp} \) is the specific viscosity, and \( \eta_{sp}/c \) sometimes is called the reduced specific viscosity. \([\eta]\) is the intrinsic viscosity which is defined as

\[ [\eta] = \lim_{c \to 0} \left( \frac{\eta_{sp}}{c} \right) \]

(1.49)

Here \( k_h = k_1 \), the Huggins coefficient\(^{(8)}\).

1.4.2 The friction coefficient and diffusion coefficient of polymer molecule in dilute polymer solutions

In polymer solutions, if a force \( F \) is exerted on the center of mass of a polymer molecule and the molecule is accelerated to its terminal velocity \( u \), the friction coefficient \( f \) is given as

\[ F = fu. \]

(1.51)

Usually, the friction coefficient \( f \) depends on the concentration of the solution, and \( f \) may be expressed as\(^{(6)}\).
Here, $f_0$ is the friction coefficient at infinite dilute and $k_s$ is the second virial coefficient of the friction coefficient.

The mutual diffusion coefficient of a polymer molecule in a dilute solution may be expressed as:

$$D = D_0 (1 + k_s c + \cdots \cdots),$$

where $D_0$ is the diffusion coefficient at infinite dilution or the self diffusion coefficient of an isolated polymer, and $k_d$ is the second virial coefficient of the diffusion coefficient.

By considering the relation between the thermodynamics and the hydrodynamics of polymer solutions, the diffusion coefficient may also be represented as:

$$D = \frac{M}{N_a f} (1 - \bar{v} c) \frac{\partial \pi}{\partial c} .$$

The quantity $\frac{\partial \pi}{\partial c}$ may be deduced from eqn. 1.43, and eqn. 1.54 can be rewritten as:

$$D = \frac{kT}{f} (1 - \bar{v} c) (1 + 2A_2 M c + \cdots \cdots).$$

The relation between $D_0$ and $f_0$ is given by the Stokes-Einstein relation:

$$D_0 = \frac{kT}{f_0} .$$
By comparing equations 1.52, 1.53, 1.55 and 1.56, a relation between the
dynamics parameters $k_d$ and $k_s$, and the thermodynamic parameters $A_2$ and $v$ is
obtained, the relation may be represented as:

$$k_s + k_D^c = 2A_2Mv.$$  \[(1.57)\]

References for Chapter 1

   York, 1953.


   1971.


Chapter 2 Some Basic Concepts of Dynamic Light Scattering

2.1 Introduction

The materials in this section was mainly drawn from references 1-3.

In the view of classical electrodynamics theory, light scattering is due to the acceleration of electric charges in a medium under the influence of the field of an incident light wave, resulting in the emission of scattered light which is illustrated in Figure 2.1.

![Diagram of light scattering](image)

Figure 2.1

The microscopic mechanics of light scattering must be investigated by quantum theory. In terms of the quantum theory of light, the scattering process involves the absorption of a photon of energy $\hbar \omega$ from the incident light and then emission of a photon of energy of $\hbar \omega_s$ of scattered light. The spectrum of the scattered light generally contains an elastic component in which the scattered frequency $\omega_s$ equals the incident light frequency, and inelastic components for which the scattered frequencies differ from the incident frequency.

Two types of light scattering of interest can be distinguished, depending on the change of frequency of the light. One type is Raman scattering, where $\omega_s$ differs from
the incident frequency \( \omega \). Another type is Rayleigh scattering, where the scattered frequency \( \omega_s \) is essentially unchanged.

Raman scattering results from a change in the incident light due to the rotational, vibrational or electronic states of the scattering molecule. Rayleigh scattering, on the other hand, does not involve a change in the internal state of the molecule. In the later sections of this chapter, the discussion will be focused on Rayleigh scattering.

The macroscopic mechanics of light scattering, however, is not necessarily studied in terms of quantum theory. Light scattering processes can also be explained on the basis of classical electrodynamics, where all physical quantities must be regarded as average values. In most cases, and those cases treated here, the results of classical theory are the same as the results of quantum theory. In this chapter, the scattering process will therefore be described in terms of classical theory.

In the view of classical theory, the light scattering process is: the incident light field exerts a force on the loosely bond electrons in the scattering medium, and these accelerated charges then radiate scattered light.

In the macroscopic theory of light scattering, the scattering volume of the scattering medium is considered to be composed of many subregions. The size of each of these subregions is small in comparison with the wavelength of the incident light, thus the scattering medium inside the subregion experiences essentially the same incident light field. The amplitude of the scattered field depends on the polarizability of the scattering medium. The scattered field from the scattering volume is the superposition of the scattered field from each of these subregions.

Einstein gave a description of the light scattered from a scattering medium: scattered light observed in the direction other than the forward direction is a result of fluctuations in the polarizability of the scattering medium.
As mentioned above, the scattered field from the scattering volume is the sum of scattered fields from a large number of subregions. If each subregion has the same polarizability, since the scattered fields from each subregion are identical except for a phase factor which depends on the relative position of the subregions. The superposition of the scattered fields is zero except in the forward direction. This is because, in the scattering volume, each subregion can always be paired with another subregion whose scattered field is identical in amplitude but opposite in phase, and these will cancel each other, leaving no net scattered field in other than the forward direction. However, if the subregions have different polarizabilities, then the amplitude of the light scattered from different subregions are no longer identical. Therefore, complete cancellation will no longer take place, and there will be net scattered light in other than the forward direction. In a liquid or gas state, molecules are constantly translating and rotating, so that the instantaneous polarizability of a given subregion fluctuates constantly, and thus gives rise to light scattering.

2.2 Light Scattering and Correlation Functions

The materials in this section was mainly drawn from references 1 and 5-7.

Light scattering results from fluctuations in the instantaneous polarizability of the scattering medium. The fluctuations of polarizability are due to perpetually translating, rotating and vibrating molecules in the scattering volume. The fluctuations contain important structural and dynamical information about the positions and orientations of the scattering molecules. Because of fluctuations in the polarizability of the scattering medium, the total scattered field at the detector will fluctuate. The purpose of light scattering measurements is to obtain the structural and dynamical information about the scattering medium from the detected scattered fields.
2.2.1 The Scattered Light Field From The Scattering Volume

In classical electrodynamic theory, the light scattering process can be described as follows: the incident fields induce electric and magnetic multipoles which oscillate in definite relationship with the incident wave, and these radiate light in all directions. The angular distribution of the radiated energy depends on the superposition of the light emitted by the multipoles induced by the incident field, and on the state of polarization of the incident light. If the dimensions of the scatterer are small in comparison with the wavelength of the incident light, only lower multipoles radiation, usually electric and magnetic dipole radiation, are important. The scattered fields radiated from the induced electric dipole and magnetic dipoles are:

\[
E_{s,e} = -\frac{1}{4\pi\epsilon_0}((k_s \times p_i) \times k_s) \frac{\exp(ik_s \cdot r)}{r} + \frac{1}{4\pi\epsilon_0} \frac{3k_s(k_s \cdot r)}{|k_s|^2} \cdot p_i \left(1 - \frac{\exp(ik_s \cdot r)}{r^2}\right),
\]

(2.1)

where \(E_{s,e}\) is the scattered electric dipole field, \(p_i\) is the induced dipole that is located at the scattering point, \(k_s\) is the scattered wave vector and \(r\) is the position of the observer relative to \(p_i\).

\[
E_{s,m} = -\frac{k_s^2}{4\pi\epsilon_0} (k_s \times m_i) \frac{\exp(ik_s \cdot r)}{r} \left(1 - \frac{1}{ik_s r}\right),
\]

(2.2)

where \(E_{s,m}\) is the scattered magnetic dipole field and \(m_i\) is the induced magnetic dipole.

When a monochromatic plane wave impinges on a nonmagnetic, nonconducting and nonabsorbing medium, the incident electric field is

\[
E_i = n_i E_0 \exp(ik_i \cdot x - i\omega t),
\]

(2.3)
where \( n_i \) is the incident polarization vector, \( k_i \) is the incident light wave vector and \( \omega_i \) is incident frequency.

If in light scattering experiments, the detectors are far away from the scatterers, the scattered electric field, from eq. (2.1) and eq. (2.2), is

\[
E_s = E_{s,e} + E_{s,m} = \frac{\exp(ik_s \cdot r)}{4\pi\varepsilon_0 r} \left[ (k_s \times p_i) \times k_s - k_s(k_s \times m_i) \right].
\]  

(2.4)

For a nonmagnetic medium, the scattered field from magnetic dipole can be neglected. Therefore, the scattered field \( E_s \) is simply

\[
E_s = \frac{\exp(ik_s \cdot r)}{4\pi\varepsilon_0 r} [k_s \times p_i] \times k_s.
\]  

(2.5)

In light scattering experiments, the incidents light fields are usually sufficiently weak that the scattering systems can be assumed to respond linearly to them, i.e.

\[
P = \alpha \cdot E_i,
\]

(2.6)

where \( P \) is the polarization of the scattering medium, \( \alpha \) is the polarizability tensor and \( E_i \) is the incident electric field.
A light scattering system illustrated in Figure 2.2, the scattered electric field from subregion $d^3r$ is

$$dE_s = \frac{\exp\left[ ik_s \cdot (R - r) \right]}{4\pi\varepsilon_0 |R - r|} \left[ (k_s \times dp) \times k_s \right].$$ \hspace{1cm} (2.7)

The dipole moment $dp$ can be expressed as:

$$dp(r,t) = \alpha(r,t) \cdot E_i \; d^3r = \alpha(r,t) \cdot n_i E_o \exp(ik_i \cdot r - i\omega t) d^3r$$ \hspace{1cm} (2.8)

And as $r \ll R$, the total scattered field from the scattering volume is

$$E_s = \int dE_s = \int_{V_s} d^3r \frac{\exp\left[ ik_s \cdot (R - r) \right]}{4\pi\varepsilon_0 R} \left\{ \left[ (k_s \times (\alpha(r,t) \cdot n_i E_o \exp(ik_i \cdot r - i\omega t))) \right] \times k_s \right\}$$

$$= \frac{E_o \exp(ik_s \cdot R - i\omega t)}{4\pi\varepsilon_0 R} \int_{V_s} d^3r \exp[i\mathbf{r} \cdot (k_i - k_s)] \left[ k_s \times (\alpha(r,t) \cdot n_i) \right] \times k_s$$ \hspace{1cm} (2.9)

For Rayleigh scattering, $|k_i| \equiv |k_s|$, and the scattering wave vector $q$ is defined as:

$$q = k_s - k_i, \quad \text{and} \quad |q| = 2k_i \sin(\theta/2),$$

as illustrated in Figure 2.3.

Thus,

$$E_s = \frac{E_o \exp\left( ik_s \cdot R - i\omega t \right)}{4\pi\varepsilon_0 R} - k_s \times \left\{ \int_{V_s} d^3r \exp(-iq \cdot r) \alpha(r,t) \cdot n_i \right\} \times k_s$$ \hspace{1cm} (2.10)

The polarizability tensor can be represented as:
\[ \alpha(r,t) = \langle \alpha \rangle + \delta \alpha(r,t), \] (2.11)

where, \( \langle \alpha \rangle \) is the average value of \( \alpha(r,t) \), and \( \delta \alpha(r,t) \) is the deviation of \( \alpha(r,t) \) from its mean value that is usually referred as a "fluctuation". \[ \int_V \exp(-i\mathbf{q} \cdot \mathbf{r}) \alpha(r,t)d^3r \] is the Fourier transformation of \( \alpha(r,t) \). Therefore

\[ \alpha(q,t) = \int_V \exp(-i\mathbf{q} \cdot \mathbf{r}) \alpha(r,t)d^3r = \int_V \exp(-i\mathbf{q} \cdot \mathbf{r})[\langle \alpha \rangle + \delta \alpha(r,t)]d^3r \]

\[ = \langle \alpha \rangle \delta(q) + \delta \alpha(q,t). \] (2.12)

Equation (2.12) indicates that if the fluctuation of the polarizability is zero, no scattered field can be detected other than forward direction. So, \( E_s \) in other than the forward direction, is

\[ E_s = \frac{E_0 \exp(ik_s \cdot R - i\omega t)}{4\pi\varepsilon_0 R} k_s \times [\delta \alpha(q,t) \cdot n_i] \times k_s. \] (2.13)

And as,

\[ E_s = n_s \cdot E_s = \frac{k_s^2}{4\pi\varepsilon_0 R} E_0 \exp(ik_s \cdot R - i\omega t) n_s \cdot \delta \alpha(q,t) \cdot n_i \]

So \( E_s(R,t) = \frac{k_s^2}{4\pi\varepsilon_0 R} E_0 \exp(ik_s \cdot R - i\omega t) \delta \alpha_{is}(q,t) \) (2.14)

where \( \delta \alpha_{is}(q,t) = n_s \cdot \delta \alpha(q,t) \cdot n_i \) which is the component of the dielectric constant fluctuation tensor along the initial and final polarization direction. The relationship between the scattered field and the fluctuation of polarizability has been established.

2.2.2 Time Correlation Functions

Fluctuations of the scattered field reflect the fluctuations of the instantaneous polarizability of the scattering medium, which contains structural and dynamic information about the molecules in the scattering volume. This information can be extracted by means of time correlation functions of dynamical variables (1, 3, 5-7).

Correlation analysis provides a measurement of the similarity between two quantities, and the temporal correlation function \( G(\tau) \) is used to express the degree to
which two signals are correlated over a characteristic period of time $\tau_c$.

The temporal correlation function between two quantities $H(t)$ and $K(t)$ is defined as:

$$G(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} H(t)K(t+\tau)dt,$$

$$(2.15)$$

where $T$ is integration time, $t_0$ is initial time and $\tau$ is a shift in time. $H(t)$ and $K(t)$ are the instantaneous amplitudes of two quantities.

If $H(t)$ and $K(t)$ are the same function, $G(\tau)$ is called the autocorrelation function. If $H(t)$ and $K(t)$ represent different functions, $G(\tau)$ is called the cross correlation function. As the correlation function is calculated by a statistical average over all values at time $t$ and $t+\tau$, the result does not depend on the absolute time $t$. The correlation is a function only of the time delay $\tau$ between two quantities.

Let $H(t)$ represent a dynamic quantity which fluctuates with time. $H(t)$ can be regarded as a "random" signal which is illustrated in Figure 2.4.

![Figure 2.4](image)

From Figure 2.4, it is seen that substantial change in $H$ can occur over a time span $\tau_o$. However, when a $\tau$ is small compared to time span $\tau_o$, $H(t)$ and $H(t+\tau)$ are close to
each other. Thus, it is said that $H(t+\tau)$ is correlated with $H(t)$ when $\tau$ is small. As $\tau$ increases, the correlation between $H(t)$ and $H(t+\tau)$ is gradually lost, and when $\tau$ is large compared with $\tau_0$, the correlation is completely lost. The auto correlation function of $H(t)$ is:

$$G(\tau) = \langle H(t)H(t+\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T H(t)H(t+\tau)dt.$$  \hspace{1cm} (2.17)

When $\tau = 0$, $G(0) = \langle H^2(t) \rangle = \langle H^2(0) \rangle$. \hspace{1cm} (2.18)

From Figure 2.4, it is seen, in some regions, $H(t)H(t+\tau)$ is negative; but for $G(0)$, in all regions, $H^2(T)$ is positive. Therefore, $G(0) \geq G(\tau)$.

When $\tau \to \infty$, $H(t)$ and $H(t+\tau)$ are no longer correlated,

$$G(\infty) = \lim_{T \to \infty} \langle H(0)H(\tau) \rangle = \langle H(0) \rangle \langle H(\tau) \rangle = \langle H \rangle^2$$ \hspace{1cm} (2.19)

For nonperiodic stochastic stationary signal $H(t)$, the autocorrelation function $G(\tau)$ decays from $\langle H(0)^2 \rangle$ to $\langle H \rangle^2$ with increasing $\tau$ which is illustrated in Figure 2.5.

![Figure 2.5](image-url)

In many cases, the autocorrelation function of $H(t)$ decay exponentially, and $G(\tau)$ can be expressed as:
\[ G(t) = \langle H \rangle^2 + [\langle H^2 \rangle - \langle H \rangle^2] \exp(-t/\tau_c), \]  
where \( \tau_c \) is the "relaxation time" that represents the characteristic decay time.

Let \( H(t) = \langle H \rangle + \delta H(t) \), since \( \langle \delta H(t) \rangle = \langle \delta H(t + \tau) \rangle = 0 \),

\[ G_T(t) = \langle H(t)H(t+T) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T [\langle H \rangle + \delta H(t)][\langle H \rangle + \delta H(t+\tau)]dt \]
\[ = \langle H \rangle^2 + \langle \delta H(t)\delta H(t+\tau) \rangle. \]  

Combining eqn. 2.20 and eqn. 2.21, the autocorrelation function of the fluctuation of \( H(t) \) is:

\[ G'(T) = \langle \delta H(t)\delta H(t+\tau) \rangle = [\langle H^2 \rangle - \langle H \rangle^2] \exp(-T/\tau_c) \]
\[ = G(T) - \langle H \rangle^2. \]  

The normalized first-order autocorrelation function of fluctuation of \( H(t) \) is defined as:

\[ g_1(\tau) = \frac{\langle \delta H(t)\delta H(t+\tau) \rangle}{\langle \delta H(0)\delta H(0) \rangle} = \frac{\langle \delta H(t)\delta H(t+\tau) \rangle}{\langle \delta H \rangle^2}, \]  
and \( 0 \leq g_1(\tau) \leq 1 \).

This quantity is called the degree of first-order temporal coherence of \( H(t) \).

2.2.3 The Time-Autocorrelation Function of The Scattered Electric Field and Light Intensity

From Eq. (2.14), the time-autocorrelation function of the scattered electric field can be evaluated as:
\[ G(q,\tau) = \langle E^*_s(R,0)E_s(R,\tau) \rangle = \frac{k_4^4 E_0^2}{(4\pi\varepsilon_0)^2R^2} \langle \delta\alpha_{1s}(q,0)\delta\alpha_{1s}(q,\tau) \rangle \exp(-i\omega_\tau \tau). \quad (2.24) \]

Because the autocorrelation function only depends on time shift \( \tau \) but not time \( t \), \( t \) is chosen zero here.

The normalized first order autocorrelation function of the scattered field is:

\[ g_1(\tau) = \frac{\langle E^*_s(R,0)E_s(R,\tau) \rangle}{\langle E^*_s(R,0)E_s(R,0) \rangle}. \quad (2.25) \]

Eq. (2.24) indicates that the correlation function of the fluctuation of the polarizability can be determined by measuring the correlation function of the scattered field. From the correlation function of the fluctuation of polarizability, we can extract structural and dynamic information about molecules in the scattering volume.

The Fourier transformation of the time-correlation function of the scattered field is the spectral density of scattered light at the scattering wave vector \( q \).

\[ I_h(q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle E^*(0)E(\tau) \rangle \exp(-i\omega\tau) d\tau = \frac{E_0^2 k_4^4}{16\pi^2 R^2 \varepsilon_0^2} \int_{-\infty}^{+\infty} \exp[i(\omega_\tau - \omega_\omega)\tau] d\tau = C \delta\alpha_{1s}(q,\omega) \delta\alpha_{1s}(q,\tau) \exp[i(\omega_\tau - \omega_\omega)\tau]. \]

\[ I_h(q,\omega) = C L_{1s}(q,\omega). \quad (2.27) \]

Here \( \omega = \omega_\tau - \omega_\omega \), \( \omega \) and \( \tau \) are the conjugate transform variables, \( C = \frac{E_0^2 k_4^4}{16\pi^2 R^2 \varepsilon_0^2} \) and

\[ I_{1s}(q,\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \delta\alpha_{1s}(q,0)\delta\alpha_{1s}(q,\tau) \rangle \exp(-i\omega\tau) \quad (2.28). \]
$I_{is}(q,\omega)$ is the spectral density of the polarizability fluctuations.

The Fourier transformation of $I_{is}(q,\omega)$ is

$$I_{is}(q,t) = \int_{-\infty}^{+\infty} I_{is}(q,\omega) \exp(i\omega t) d\omega = \langle \delta \alpha_{is}(q,0) \delta \alpha_{is}(q,t) \rangle.$$  \hfill (2.29)

This is the time-correlation function of the fluctuation of the polarizability which can be determined by measuring $I_{is}(q,\omega)$. In light scattering experiments, $I_{is}(q,\omega)$ can be measured in the frequency domain by using filter techniques which will be described in the next section.

We have described the fluctuation of the scattered field and the autocorrelation function of the scattered field. Another important topic concerns the intensity fluctuations of the scattered light. Many dynamic light scattering efforts concern the measurement of the time-autocorrelation function of the intensity of scattered light. In many cases of intensity fluctuation measurements, the fluctuations in the cycle-average intensity are too rapid for direct observation, and what is measured, instead of the true instantaneous intensity, is some average of the fluctuation over the detector response time.

The normalized auto-correlation function of the intensity of scattered light is defined as:

$$g_2(\tau) = \frac{<I(t)I(t+\tau)>}{I^2} = \frac{<E^*(t)E^*(t+\tau)E(t+\tau)E(t)>}{<E(t)E(t)>'^2}.$$ \hfill (2.30)

where $\bar{I}(t)$ is the average intensity over the detector response time, and $\bar{I}$ is the long-time average intensity. $g_2(\tau)$ is called the normalized second-order time correlation function of scattered field.

As $I^2 = <I(t)>^2 \leq <I^2(t)>$, and $I(t) \geq 0$, so $g_2(0) \geq 1.$
The scattered field from the scattering volume is assumed to be a superposition of scattered fields from subregions that can be represented as:

\[ E = \sum_i E_i \]

\( E_i \) is the scattered field from the ith subregion. The second order electric-field correlation is thus:

\[
< E^*(t)E^*(t+\tau)E(t+\tau)E(t) > = \sum_i < E_i^*(t)E_i^*(t+\tau)E_i(t+\tau)E_i(t) > \\
+ \sum_{i \neq j} < E_i^*(t)E_j^*(t+\tau)E_j(t+\tau)E_i(t) > + < E_j^*(t)E_i^*(t+\tau)E_i(t+\tau)E_j(t) > , \quad (2.31)
\]

where only those terms are retained in which the field of each subregion is multiplied by its complex conjugate. All other terms vanish because of the random relative phases of the waves originating from different subregion. As each subregions, statistically, should be identical, therefore

\[
< E^*(t)E^*(t+\tau)E(t+\tau)E(t) > = N < E_i^*(t)E_i^*(t+\tau)E_i(t+\tau)E_i(t) > \\
+ N(N-1) \{ < E_i(t)E_i^*(t) >^2 + | E_i^*(t)E_i(t+\tau) |^2 \} , \quad (2.32)
\]

where \( N \) is the number of subregions in the scattering volume. For \( N \gg 1 \), that is usually true in dynamic light scattering measurements, to a very good approximation

\[
< E^*(t)E^*(t+\tau)E(t+\tau)E(t) > = N^2 \{ < E_i^*(t)E_i(t) >^2 + | E_i^*(t)E_i(t+\tau) |^2 \} . \quad (2.33)
\]

Thus, by comparison with the first-order electric-field correlation function given in eqn.(2.25), the second-order electric field correlation function can be expressed as:
\[
g_2(\tau) = \frac{N^2 \{ <E_i^*(t)E_i(t)^2> + |<E_i^*(t)E_i(t+\tau)>|^2 \}}{N^2 <E_i^*(t)E_i(t)^2>} = 1 + |g_1(\tau)|^2. \tag{2.34}
\]

This important relationship, called the Siegert relation, holds for that scattered field which is a Gaussian stochastic variable. The Gaussian assumption is true for most cases, but it is not valid for all cases.

2.3 Some Experimental Methods of Dynamic Light Scattering

The materials in this section were mainly drawn from references 1 and 8.

In previous sections, we have described autocorrelation functions of the scattered light field and intensity, and discussed the relation between the correlation function of the scattered field and that of fluctuations of polarizability of the scattering medium. The purpose of this section is to give a brief description of some of the main experimental methods employed to measure autocorrelation functions.

In a light scattering experiment, an incident light beam is focused onto a region of the scattering medium and is scattered into a detector. Polarizers and analyzers are used to define the polarizations of the incident and scattered light, respectively. There are mainly two kinds of techniques used to analyze these fluctuation signals. One is the filter method which is employed to analyze relatively rapid molecular dynamic processes, the other one is a beating technique or photon correlation spectroscopy which is usually used to analyze relatively slow processes.

2.3.1 Selected Geometries of Light Scattering

Before discussing filter and beating techniques, this section will give a brief description of scattering geometries. Scattering geometries give the relationships of the polarizations of the incident light (defined by the polarizer) and the scattered light (defined by the analyzer), and define which component of the polarizability tensor is measured.
The plane defined by the incident and scattered wave vectors of light is called the scattering plane, which is illustrated in Figure 2.6.

Four different scattering geometries are given in Figure 2.7.

In Figure 2.7, \( n_i \) and \( n_s \) are unit vectors in the directions of the incident electric field and the scattered electric field, respectively. \( V \) and \( H \) correspond to the directions that are vertical and horizontal with respect to scattering plane.
2.3.2 The Filter Technique

According to eqn. 2.29, the time-correlation function of fluctuations of the polarizability is

\[ I_{1s}(q,t) = \alpha^{*}_{1s}(q,0) \alpha_{1s}(q,t) = \int_{-\infty}^{+\infty} I_{ls}(q,\omega) \exp(i\omega t) d\omega \quad (2.29) \]

The time-correlation function of fluctuations of the polarizability can be determined by measuring the scattered light spectral density \( I_{ls}(q,\omega) \).

In the filter method, a filter (diffraction grating or Fabry-Perot interferometer) is inserted between the scatterers and the photomultiplier. The output of the filter, that is a scattered light with a very narrow band of frequencies, is incident upon a photomultiplier tube whose average output is proportional to the spectral density of the scattered light at the filter frequencies. The spectral density and the time correlation function of the scattered light is a Fourier transformation pair.

2.3.3 The Photon Beating Technique

In photon beating techniques, the scattered light impinges on the photomultiplier tube. Two methods can be employed. In the homodyne method (or self-beat), only scattered light impinges on the photomultiplier tube. In the heterodyne method, however, a small portion of the unscattered light beam is mixed with the scattered light on the PMT (photomultiplier tube).

Since the phototube is a square-law detector, its instantaneous current output is proportional to the square of the incident electric field, \( i(t) = c|E(t)|^2 \) (where \( c \) is independent of \( E(t) \)). And, \( |E(t)|^2 \) is proportional to the intensity of the light incident
upon the phototube. In experiments, the PMT output is passed into an autocorrelator which calculates its time-autocorrelation function, and that is

$$<i(0)i(t)> = B <|E(0)|^2|E(t)|^2>$$, \hspace{1cm} (2.35)

where B is a proportionality constant which contains the efficiency of the PM tube. In our study, the scattered photons are proportional to the current i in eqn. 2.35.

2.3.3.1 The Homodyne Method

In the case of a scattering volume containing a large number of statistically independent subregions, from section (2.2.3), we know that

$$B<|E(0)|^2|E(t)|^2> \equiv B N^2 \{ |<E_i(0)E_i^*(0)>|^2 + |<E_i^*(0)E_i(t)>|^2 \}$$, \hspace{1cm} (2.36)

where N is the number of subregions inside the scattering volume and $E_i$ is the scattered electric field from the $i$th subregion.

The normalized PMT output (photon number) autocorrelation function is

$$g_2(t) = \frac{<i(t)i(0)>}{<i(0)i(0)>} = \frac{B <|E(0)|^2|E(t)|^2>}{B<|E(0)|^2|E(0)|^2>} = 1 + \lg_1(t)^2$$, \hspace{1cm} (2.37)

where $g_1(t) = \frac{<E^*(0)E(t)>}{<E^*(0)E(0)>}$, is the normalized first-order autocorrelation function of the scattered electric field from the scattering volume. According to Eq.(2.14), $E_i$ is proportional to $\delta \alpha_{ia}(q,t)$, so that

$$g_1(t) = \frac{<\delta \alpha_{ia}^*(q,0)\delta \alpha_{ia}(q,t)>}{<\delta \alpha_{ia}^*(q,0)\delta \alpha_{ia}(q,0)>}$$, \hspace{1cm} (2.38)

This is the normalized first-order autocorrelation function of fluctuations of the polarizability of the scattering medium. Therefore, through measuring $<i(0)i(t)>$, we
can obtain the autocorrelation function of the fluctuations of the polarizability of the scattering volume from which we can extract dynamic information about molecular motions.

2.3.3.2 Heterodyne Method

Eqn. 2.37 holds for the situations for which the Gaussian approximation can be applied. However, for situations in which the Gaussian approximation is not satisfied, the homodyne method may not be useful. We may then use the heterodyne method instead. In this method, a small portion of the unscattered light beam (local oscillator) is mixed with the scattered light upon the face of the phototube.

Let $E_u$ represent the unscattered light beam, the total electric field on the phototube is:

$$E_t = E_u(t) + E_s(t),$$

and the autocorrelation function of the PMT output can be expressed as:

$$\langle \psi(0)\psi(t) \rangle = B\langle |E_t(0)|^2 |E(t)|^2 \rangle = B\langle |E_u(0) + E_s(0)|^2 |E_u(t) + E_s(t)|^2 \rangle$$

By choosing proper experimental conditions, the amplitude of $E_u$ can be made much greater than that of $E_s$, $|E_u(t)| >> |E_s(t)|$. And assuming the fluctuations of the unscattered light beam are negligible, so that the unscattered field and scattered field are statistically independent. Eq.(2.39) can be simplified to:

$$\langle \psi(0)\psi(t) \rangle \approx B[I_u^2 + 2I_uI_s(t)],$$

where $I_u = \langle |E_u|^2 \rangle$ and $I_s(t) = \langle E_s(0)E_s(t) \rangle$

This is the first-order autocorrelation function of the scattered field which is proportional to the first-order autocorrelation function of the fluctuation of the polarizability of scattering medium. By using the heterodyne method, we can directly measure the first-order autocorrelation function of scattered field without having to
satisfy the Gaussian approximation.

2.4 Dynamic Light Scattering From Dilute Polymer Solution

The materials in this section from this section was mainly drawn from reference 1,7 and 9.

In the previous sections of this chapter, the relationship between the correlation function of the scattered field (or scattered light intensity) and the autocorrelation function of fluctuations of polarizability of the scattering medium was described, and experimental methods of measuring correlation functions were also discussed. The purpose of this section is to study the relationship between dynamic properties of polymer molecules in solution with the time-correlation function of fluctuations of polarizability of the polymer molecules, and how to extract the information of the dynamic properties of polymer molecules in solution from time-correlation functions of the fluctuations of polarizability of polymer molecules in solution. In order to extract information from correlation functions, models must be employed that, inevitably, involve some degree of approximation.

In polymer solutions, the polarizability of polymer molecules is usually much higher than that of solvent molecules, and polymer molecules move much slowly than solvent molecules do. The much higher polarizability of polymer molecules means that the polymer molecules are much more efficient scatterers, and the slow motion of polymer molecules implies that these polymer molecules contribute a slowly fluctuating field on the detector compared to that of the solvent. Therefore, in dynamic light scattering measurements, scattered light from polymer molecules can be distinguished from the scattered light from solvent molecules.

In a light scattering experiment, an incident laser beam impinges on a molecule
with a polarizability tensor $\alpha$ and induces a dipole moment $u(t) = \alpha \cdot E(t)$. The induced time-varying dipole emits electromagnetic radiation. According to eqn. 2.14, the electric field radiated from the dipole is

$$E_s(q, R, t) = \frac{k_s^2}{4\pi \varepsilon_0 R} E_0 \exp \left( i k_s R - i \omega t \right) \delta \alpha_{is}(q, t), \quad (2.41)$$

with $\delta \alpha_{is}(q, t) = n_s \cdot \delta \alpha(q, t) \cdot n_i$.

For a single molecule, $\delta \alpha_{is}(q, t)$ can be expressed as $\delta \alpha_{is}(q, t) = \alpha'_{is}(t) \exp(iq \cdot \mathbf{r}(t))$

$\alpha'_{is}(t)$ varies in time because the molecule rotates and vibrates, while the phase factor $\exp(iq \cdot \mathbf{r}(t))$ varies in time because the molecule translates.

In a molecular system, if the molecules are weakly coupled, that is if the electronic states of the molecules are not perturbed very much by their neighbors, it is reasonable to assume that the light field scattered from the molecules in the scattering volume is a superposition of the scattered fields from each of the molecules. Thus

$$E^s = \sum_i E^s_i = K \sum_i \delta \alpha^i_{is}(q, t) = K \sum_i \alpha'^i_{is}(t) \exp(iq \cdot \mathbf{r}(t)), \quad (2.42)$$

where $E^s_i$ is the scattered field from the scattering volume, $E^s$ is the scattered field from the ith molecule in the scattering volume, $K$ is

$$K = \frac{k_s^2}{4\pi \varepsilon_0 R} E_0 \exp \left( i k_s R - i \omega t \right),$$

and $\delta \alpha^i_{is}(q, t) = \sum_j \alpha'^i_{is}(t) \exp(iq \cdot \mathbf{r}(j)(t)). \quad (2.43)$

The above treatment is obviously an approximation because the effects of interactions between molecules are ignored. In the case of light scattering from very
dilute polymer solution, this approximation is adequate.

2.4.1 Light Scattering from Spherical Molecules System

The polarizability tensor of a spherical molecule is $\alpha = \alpha I$, where $I$ is the unit matrix. The induced dipole moment is parallel to the incident field. Then

$$u(t) = \alpha E(t)$$

and

$$\alpha_{is} = n_s \cdot \alpha \cdot n_i = (n_s \cdot n_i) \alpha.$$  \hspace{1cm} (2.45)

From eqn. 2.45 and eqn. 2.43,

$$\delta \alpha_{is}(q,t) = (n_s \cdot n_i) \sum_j \alpha^{ij}(t) \exp(iq.r_j(t)).$$ \hspace{1cm} (2.46)

The sum is only over the molecules which are in the scattering volume. $\alpha^{ij}(t)$ can be expressed as:

$$\alpha^{ij}(t) = \langle \alpha^{ij}(t) \rangle + \delta \alpha^{ij}(t) = \alpha' + \delta \alpha^{ij}(t)$$

Since $\alpha(t)$ varies in time due to the molecule rotating and vibrating, $\alpha(t)$ varies much more rapidly than the term $\exp(iq.r(t))$. So, it is reasonable to ignore the term $\delta \alpha(t)$, and $\delta \alpha_{is}(q,t)$ is

$$\delta \alpha_{is}(q,t) = (n_s \cdot n_i) \alpha \sum_j \exp(iq.r_j(t)).$$

For spherical molecules, the first-order normalized time-autocorrelation function of the scattered field is

$$g_1(q,t) = \frac{\langle E_s^*(q,0)E_s(q,t) \rangle}{\langle E_s^*(q,0)E_s(q,0) \rangle} = \frac{\langle \delta \alpha_{is}^*(q,0)\delta \alpha_{is}(q,t) \rangle}{\langle \delta \alpha_{is}^*(q,0)\delta \alpha_{is}(q,0) \rangle} = \frac{\langle \alpha'(q,0)\alpha(q,t) \rangle}{\langle \alpha'(q,0)\alpha(q,0) \rangle}.$$ \hspace{1cm} (2.47)
where \( \alpha(q,t) = \alpha \sum_j \exp(iq.r_j(t)) \).

(2.48)

\( \alpha(q,t) \) can also be expressed as:

\[
\alpha(q,t) = \alpha \sum_j \delta(r - r_j(t)) \exp(iq.r) d^3r = \alpha \int \sum_j \delta(r - r_j(t)) \exp(iq.r) d^3r
\]

(2.49)

The sum \( \sum_j \delta(r - r_j(t)) \) is the instantaneous number density \( \rho(r,t) \) at position \( r \) and at time \( t \). \( \rho(r,t) \) can be expressed as

\[
\rho(r,t) = \rho_0 + \delta\rho(r,t)
\]

(2.50)

\[
\alpha(q,t) = \alpha \int \rho_0 \delta(q) + \delta\rho(q,t)
\]

(2.51)

The instantaneous number of molecules in the scattering volume can also be expressed as

\[
N(t) = \sum_j b_j(t), \text{ where } b_j(t) = \begin{cases} 1, & j \in V_i \\ 0, & j \notin V_i \end{cases}
\]

(2.52)

The sum is now over the molecules in the whole sample cell, and \( \alpha(q,t) \) is

\[
\alpha(q,t) = \alpha \sum_j b_j(t) \exp(iq.r_j(t))
\]

(2.53)

and the first-order autocorrelation function of \( \alpha(q,t) \) is

\[
G_1(q,t) = \langle \alpha^*(q,0) \alpha(q,t) \rangle = \sum_j \sum_k b_j(t) b_k(0) \exp[iq(r_j(t) - r_k(0))]
\]

(2.54)

For the light scattering from dilute solutions of spherical macromolecules, the macromolecules can be assumed to be statistically independent of each other. Scattered fields from different macromolecules are not correlated. Only the scattered field from the same macromolecules are correlated. Therefore eqn. (2.54) can be simplified to

\[
G_1(q,t) = \langle \sum_j b_j(0) b_j(t) \exp[iq(r_j(t) - r_j(0))] \rangle.
\]

(2.55)

The term \( b_j(0)b_j(t) \) either equals 1 or 0, and the characteristic time scale for changing \( b_j(0)b_j(t) \) is simply the time it takes a macromolecule to translate across the scattering volume. It is easy to show that the term \( b_j(0)b_j(t) \) varies in time much more slowly than that of term \( \exp[iq(r_j(t) - r_j(0))] \). Thus, it can be assumed
\(b_j(0)b_j(t) = b_j(0)\).

And, as the macromolecules are statistically independent, \(G_1(q,t)\) can be expressed as:

\[
G_1(q,t) = \langle \sum_j b_j(0) \exp[iq(r_j(t) - r_j(0))] \rangle \\
= \sum_j \langle b_j(0) \rangle \langle \exp[iq(r_j(t) - r_j(0))] \rangle \\
= \langle \sum_j b_j(0) \rangle \langle \exp[iq(r_j(t) - r_j(0))] \rangle >. \tag{2.56}
\]

The term \(\sum_j b_j(0)\) is the average number of macromolecules inside the scattering volume. Thus

\[
G_1(q,t) = \langle N \rangle \langle \exp[iq(r_j(t) - r_j(0))] \rangle = \langle N \rangle G_1^s(q,t) \\ 
\]

(2.57)

with \(G_1^s(q,t) = \langle \exp[iq(r_j(t) - r_j(0))] \rangle\). \tag{2.58}

\(G_1^s(q,t)\) is called self-intermediate scattering function, and obviously, \(G_1(q,t)\) is the normalized first-order autocorrelation function of \(G_1(q,t)\). The Fourier transformation of \(G_1^s\) is

\[
\int_{-\infty}^{+\infty} G_1^s(q,t) \exp(iq \cdot r) dq = \int_{-\infty}^{+\infty} \langle \exp[iq(r_j(t) - r_j(0))] \rangle \exp(iq \cdot r) dq \\
= \langle \int_{-\infty}^{+\infty} \exp[iq(r_j(t) - r_j(0))] \exp(iq \cdot r) dq \rangle \\
= \langle \delta[r - (r_j(t) - r_j(0))] \rangle = G_s(r,t) \\ 
\]

(2.59)

\(G_s(r,t)\) is called the Van-Hove self space-time correlation function which represents the probability distribution for molecules to suffer a displacement \(r\) in the time \(t\). As time progresses, the probability that a macromolecule diffuses from the original point \((r=0, t=0)\) to the point \(r\) at time \(t\) is \(G_s(r,t) d^3r\). According to random walk theory, the diffusion equation describes this probability. Thus, to a very good
approximation, \( G_s(r,t) \) can be regarded as a solution to the diffusion equation

\[
\frac{\partial}{\partial t} G_s(r,t) = D V^2 G_s(r,t).
\]  \hspace{1cm} (2.60)

where \( D \) is the diffusion coefficient of isotropically diffusing macromolecules in solution. The Fourier transform of eqn. 2.60 is

\[
\frac{\partial}{\partial t} G_f(q,t) = -q^2 D G_f(q,t).
\]  \hspace{1cm} (2.61)

The solution of this equation with boundary conditions \( G_f(q,0) = 1 \) and \( G_f(q,\infty) = 0 \) is

\[
G_f(q,t) = \exp(-q^2Dt).
\]  \hspace{1cm} (2.62)

For situations in which the Gaussian approximation is satisfied, from Eqn. 2.37, the second-order autocorrelation function of the scattered field is

\[
g_2(q,t) = 1 + |g_1(q,t)|^2 = 1 + |G_f(q,t)|^2
= 1 + \exp(-2q^2Dt).
\]  \hspace{1cm} (2.63)

In dynamic light scattering experiments, the parameter \( \Gamma = q^2 D \) is extracted from fits of measured \( g_2(q,t) \) to eqn. 2.63.

As \( |q| = |k_s-k_l| = 2k \cdot \sin(\theta/2) = \frac{4\pi n}{\lambda_0} \sin(\theta/2) \) with \( n \) the refractive index and \( \lambda_0 \) the wave length of incident light in vacuum, the diffusion coefficient \( D \) is:

\[
D = \frac{\Gamma}{q^2}
\]

According to the Stokes-Einstein relation, the self-diffusion coefficient is
\[ D = \frac{kT}{6\pi\eta a} \]  

(2.64)

where \( \eta \) is the solvent viscosity and \( a \) is the hydrodynamics radius of the spherical macromolecule. Thus, the hydrodynamic radius \( a \) can be determined by measuring the diffusion coefficient \( D \).

In practical situations, the polymer solution, although dilute, still has a certain range of concentration \( c \), and the diffusion coefficient \( D \) is a function of concentration \( c \). In the range of very low concentration, \( D(c) \) can be expressed as

\[ D(c) = D_0(1 + k \frac{c}{D_0} \cdot c). \]  

(2.65)

In practical light scattering measurements, \( D(c) \) for different values of \( c \) are measured, and then, \( D_0(=D(0)) \) is determined by extrapolating \( D(c) \) to \( c=0 \):

\[ D_0 = \lim_{c \to 0} D(c) \]

2.4.2 Light Scattering From Very Large, Optically Isotropic, Macromolecules

When the macromolecules are very large, with sizes of the order of \( \lambda \) for example, the effects of intramolecular interference are no longer negligible. For light scattering from very large macromolecules, a large number of the identical "segments" rather than the whole macromolecule are regarded as the basic scattering elements, as illustrated in Figure 2.8

![Figure 2.8](image-url)
The segment is chosen so that its size is small compared with \( q^{-1} \), so that \( q/l \ll 1 \), with \( l \) the characteristic length of a segment and each segment can thus be regarded as a point scatterer.

For a scattering volume containing \( N \) macromolecules and each macromolecule containing \( n \) segments, the total number of segments in the scattering volume is \( nN \) and

\[
\langle \delta \alpha_{ls}(q,t) \rangle = \langle n_1 \cdot n_s \rangle \sum_i \sum_j \alpha \exp(iq \cdot r_{ij}) = \alpha \langle n_1 \cdot n_s \rangle \sum_i \exp(iq \cdot r_{ij})
\]

(2.66)

where \( i \) is the \( i \)th molecule and \( j \) is the \( j \)th segment on the \( i \)th molecule. As the macromolecules are optically isotropic, \( \alpha = \alpha l, \) and \( \alpha \) is a scalar. The normalized first-order autocorrelation function of \( \delta \alpha_{ls}(q,t) \) is

\[
g_1(q,t) = \frac{\langle \delta \alpha_{ls}^*(q,0) \delta \alpha_{ls}(q,t) \rangle}{\langle \delta \alpha_{ls}^*(q,0) \delta \alpha_{ls}(q,0) \rangle} = \frac{\sum_{i,j} \sum_{m,l} \exp[iq(r_{ij}(t) - r_{im}(0))] >}{\langle \sum_{i,j} \sum_{m,l} \exp[iq(r_{ij}(0) - r_{im}(0))] \rangle}
\]

(2.67)

where \( r_{ij} \) is the position of the \( j \)th segment on the \( i \)th molecules, and \( r_{im} \) is the position of the \( l \)th segment on the \( m \)th molecule.

Let

\[
F_1(q,t) = \langle \sum_{i,j} \sum_{m,l} \exp[iq(r_{ij}(t) - r_{im}(0))] \rangle.
\]

(2.68)

If the macromolecular solution is sufficiently dilute, segments on different macromolecules are not correlated. Only the segments on the same macromolecules are correlated. The macromolecules in solution are therefore statistically independent with
each other. Thus, eqn. 2.68 can be simplified to

\[ F_I(q,t) = < \sum_i \sum_m \exp[iq(r_i(t)-r_m^i(t))]> \]

\[ = <N>< \sum_j \exp[iq(r_j(t)-r_m(0))]> , \tag{2.69} \]

where \( r_j \) and \( r_m \) are the positions of the jth and mth segments on the same macromolecule respectively.

Let

\[ F_I(q,t) = < \sum_j \exp[iq(r_j(t)-r_m(0))]> . \tag{2.70} \]

As \( r(t) \) can be expressed as

\[ r_i(t)=R(t) + d_i(t), \]

\( R(t) \) is the position of mass center of macromolecule, and \( d_i(t) \) is the ith segment position relative to the mass center. Thus

\[ F_I(q,t) = <\exp[iq(R(t)-R(0))]> < \sum_j \exp[iq(d_j(t)-d_m(0))]> . \tag{2.71} \]

It is seen from Eqn.2.71, the autocorrelation function \( F_I(q,t) \) not only contains the information about the translation of the macromolecule center of mass (in the factor \( <\exp[iq(R(t)-R(0))]> \)), but also contains information about the "internal" motion or vibration (factor \( \sum_j \exp[iq(d_j(t)-d_m(0))]> \) of the macromolecule in solution.

If intramolecular interference is negligible,

\[ F_I(q,t)=<\exp[iq(R(t)-R(0))]> , \tag{2.72} \]

and if macromolecules in effect only move by the translational diffusion process, from section (2.4.1), \( F_I(q,t) \) is

\[ F_I(q,t)= \exp(-q^2Dt). \tag{2.73} \]

The "center of mass" translational diffusion coefficient of macromolecules in
solution may be determined from the autocorrelation function $F(q,t)$, with $F(q,t)$ obtained from dynamic light scattering measurements.

### 2.4.3 Method of Cumulants

The materials in this section was mainly drawn from reference 10.

In sections (2.4.1) and (2.4.2), we have dealt with dilute, monodisperse macromolecular solutions. In practice, all synthetic macromolecules are more or less polydisperse. Therefore, the effects of polydispersity must be considered in dynamic light scattering measurements. This problem has been studied extensively\(^1\),\(^5\),\(^10\). For example, Koppel developed the method of cumulants which is now widely used for the analysis of macromolecular polydispersity in dynamic light scattering measurements of polymer solutions.

For a monodisperse macromolecule solution, according to eqn. 2.62, $G_f(q,t)$ is:

$$G_f(q,t) = \exp(-q^2Dt)$$

For a polydisperse macromolecule solution, the CM translational diffusion coefficient depends on the size and thus on the molecular weight of the macromolecules. Therefore, $G_f(q,t)$ must be generalized to a distribution of exponentials:

$$G_f(q,t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) d\Gamma,$$

where $\Gamma = q^2D$, $G(\Gamma)$ is the normalized distribution function of the decay rates, and

$$\int_0^\infty G(\Gamma) d\Gamma = 1$$

Take the logarithm on both side of above eqn.2.75 and expand the right hand side in a power series in $t$. This gives

$$\ln(G_f(q,t)) = 1 - K_1t + \frac{1}{2}K_2t^2 - \frac{1}{3!}K_3t^3 + \cdots$$

where
\[ K_n = [(-1)^n \frac{d^n}{dn} \ln(G_f(q,t))]. \tag{2.78} \]

Since \( G_f(q,t) \) may also be expressed as \( G_f(q,t) = \langle \exp(-q^2Dt) \rangle \), the explicit forms of the first two cumulants are

\[ K_1 = \langle \Gamma \rangle = \langle q^2D \rangle = q^2\langle D \rangle \]
\[ K_2 = \langle (\Gamma-\Gamma)^2 \rangle = \langle (q^2D - q^2\langle D \rangle)^2 \rangle. \]

\( K_1 \) contains information of mean value about the diffusion coefficient and \( K_2 \) (or \( \mu_2 \)) contains information about the width of the distribution of molecular weight or the "polydispersity" of these macromolecules.

In dynamic light scattering experiments, for \( I_{\nu \nu} \) geometry, the parameters

\[ \bar{\Gamma} = q^2\langle D \rangle_z \]
and

\[ \frac{\mu_2}{\bar{\Gamma}^2} = \frac{\langle (D_z - \bar{D}_z)^2 \rangle}{D_z^2} = \frac{\bar{D}_z^2 - D_z^2}{D_z^2} \]
are usually determined. Thus \( \bar{\Gamma} \) is a measure of the mean diffusion coefficient of the molecules being studied while \( \mu_2/\bar{\Gamma}^2 \), which is called the polydispersity factor, is a measure of the width of the molecular weight distribution.

### 2.5 Static Light Scattering from Macromolecular Solutions

The materials in this section were mainly drawn from reference 1,11.

In section (2.4), we have described how to obtain the CM translational diffusion coefficient of macromolecules in solution, as well as the polydispersity of macromolecules from dynamic light scattering measurements. In this section we will discuss static or integrated light scattering. From static light scattering measurements, information about macromolecular weight, the radius of gyration and the second virial coefficient of osmotic pressure \( A_2 \) in polymer solutions can be obtained.
2.5.1 Structure Factor

From eqn. 2.27, eqn. 2.29 and eqn. 2.66, the first-order autocorrelation function of scattered field is

\[ G^q(t) = B \delta \alpha_0^* \delta \alpha_0(q,t) \]

\[ = B \sum \sum \alpha_j \alpha_m \exp[iq(r_j(t) - r_m(0))] > \] (2.79)

where \( B = \frac{k^2 E_0^2}{4 \pi \epsilon_0} (n_1 \cdot n_2)^2 \), and the macromolecules are assumed to be optically isotropic and \( \alpha_j \) is the polarizability of the jth segment on the ith molecule. For very dilute macromolecular solutions, according section (2.4.2), eqn. 2.79 can be simplified to

\[ G^q(t) = B <N> \alpha_w^2 \frac{1}{n^2} \sum \exp[iq(r_j(t) - r_j(0))] > \] (2.80)

where \( <N> \) is the average number of macromolecules in the scattering volume, \( n \) is the segment number of each macromolecule and \( \alpha_w = n \alpha_j \) is the polarizability of the whole macromolecule.

The structure factor is defined as:

\[ S(q,0) = \frac{1}{n^2} \sum \exp[iq(r_j - r_j)] > \] (2.81)

The quantity of \( S(q) \) depends on the shape of the macromolecule. For a Gaussian coil, \( S(q) \) is:

\[ S(q) = \frac{2}{y^2} [\exp(-y)-1+y] \] 2.82

where \( y = q^2 R_g^2 \), \( R_g \) is the gyration radius which is defined as:
\[ R_g^2 = \frac{\sum_{i} m_i (r_i - R)^2}{\sum_{i} m_i} . \]  

(2.83)

\( R \) is the center of mass of macromolecule, and \( r_i \) is the vector of location of \( i \)th segment with mass \( m_i \).

For a macromolecule with arbitrary shape, with \( q^2 R_g^2 \) at low value, \( S(q) \) can be expanded to

\[ S(q) = 1 - \frac{q^2 R_g^2}{3} + \cdots \cdots . \]  

(2.84)

And

\[ \frac{1}{S(q)} = 1 + \frac{q^2 R_g^2}{3} + \cdots \cdots . \]  

(2.85)

2.5.2 Macromolecular Weight Determination—The Zimm Plot

From Eq. (2.80), at \( t=0 \),

\[ G_1(q,0) = B <N> \alpha_w^2 S(q) \]  

(2.86)

For the scattered light from a unit volume

\[ G_1'(q,0) = B c \alpha_w^2 S(q) \]  

(2.87)

where \( c \) is the number of macromolecules in a unit volume.

Let, \( \alpha_w' = \frac{\alpha_w N_a}{M} \), \( \alpha_w' \) is the polarizability per unit mass, \( M \) the macromolecule weight and \( N_a \) is the Avogadro constant.

Define \( c' = \frac{M}{N_0} c \), \( c' \) is the mass concentration of macromolecular solutions.

So eqn. 2.87 becomes

\[ G_1'(q,0) = \frac{B}{N_0} \alpha_w^2 c' M S(q). \]  

(2.88)

From eqn. 2.88
At small $q^2R_g^2$ value, eqn. 2.89 becomes

$$\frac{Bc'\alpha^2}{N_o G_1(q,0)} = \frac{1}{MS(q)} \cdot$$ \hspace{1cm} (2.89)

Plot $\frac{Bc'\alpha^2}{N_o G_1(q,0)}$ against $q^2$. The $q^2 = 0$ intercept is then the reciprocal of molecular weight.

Eqn. 2.90 works for infinitely dilute, monodisperse solution. In real situations, however, solutions have a certain range of concentration and macromolecule sample have some degree of polydispersity. When these effects become important, eqn. 2.90 is no longer valid. Zimm developed a method to treat these problems and that method is illustrated in the "Zimm" plot (11).

As the measurements are made at finite concentration and finite $q$, the basic idea of the Zimm plot is to plot $\frac{Bc'\alpha^2}{N_o G_1(q,0)}$ against $q^2$ and $c'$, and then extrapolate both $q^2$ and $c'$ to zero simultaneously.

If the macromolecular sample has some degree of polydispersity, eqn. (2.88) becomes

$$G_1(q,0) = \frac{B_o \alpha^2}{N_o} \sum_i M_i c_i' S_i(q) \cdot$$ \hspace{1cm} (2.91)

where $M_i$, $c_i'$ and $S_i(q)$ refer to the $i$th species of molecular weight, mass concentration and structure factor, respectively.

At low values of $q$ and with

$$<M> = \frac{\sum_i c_i'M_i}{\sum_i c_i'}$$

the "weight-average" molecular weight, and $c' = \sum_i c_i'$. eqn. 2.91 can be simplified as:
The Zimm-plot is a plot of $\frac{B\alpha_w^2 c'}{N_0 G_1(q,0)}$ as the ordinate against $q^2 + kc'$ where $k$ is an adjustable fit constant. In experiments, $\frac{B\alpha_w^2 c'}{N_0 G_1(q,0)}$ is determined with different values of $q$. Then, the procedure is repeated for a series of concentrations $c'$. A typical plot is illustrated in Figure 2.9.

**Figure 2.9**

Double extrapolation is made to zero for $q$ and $c'$. The intercept is the reciprocal of the weight-average molecular weight.

For the $c'=0$ line (that implies only one macromolecule in the solution), from eqn. 2.90 (as $c'\to0$, it works), \( \frac{R^2}{3\xi} \) is obtained.

For $q = 0$, 

\[
G_1(q,0) = \frac{B\alpha_w^2}{N_0} <M>c'.
\] (2.92)
\[ \frac{Bc' \alpha_2^s}{N_a G_1(q, 0)} = \frac{1}{<m^s>} + 2A_2c' + \cdots \cdots \cdot \] (2.93)

\(A_2\) is the solution second osmotic virial coefficient. So, from the \(q=0\) line, \(A_2\) is also obtained.

Therefore, the weight-average molecular weight, the radius of gyration and the second osmotic virial coefficient can be determined from the Zimm-Plot.
References for Chapter 2

Chapter 3 Experimental Apparatus And Data Analysis Methods

3.1 Introduction

In chapter 2, some aspects of the basic dynamic light scattering theory have been discussed. This chapter will describe the main apparatus of the light scattering experiment, and the methods of data analysis.

The experimental set up of our experiments is illustrated in Figure 3.1. The light scattering experimental system, in general terms, contains four major components, as illustrated schematically in Figure 3.2. They are the light source (usually a laser), the spectrometer system which contains a sample cell assembly system and an optical system to define the scattering angle, the detector system which is composed of a main detector optics and a photomultiplier, a signal analyzer which may be either a correlator or a spectrum analyzer, and a computer is usually connected to the whole system to extract the information from the correlation functions and to operate the system. Before describing the four major components, the effects of unwanted scattered light will be discussed first.

3.2 The Effects of Unwanted Scattered Light

The main effects due to unwanted scattered light include:

a. fluctuations in laser intensity,

b. unwanted laser light due to reflections or flare that has not been scattered from the sample but acts as a local oscillator,

c. convection current in the scattering cell,

d. dust, air bubbles, glass particles, bacteria and other foreign particles in the sample
Figure 3.1 Laser Light Scattering System.
Figure 3.2 Four Major Components of the Light Scattering System.
solutions,
e. improper or inadequate sample preparation,
f. light scattered by the solvent.

All the above effects, more or less, affect the quality of light scattering measurement results. For example, if a small amount of light compared to the real scattered light is detected by the detector system, according to section 2.3.3, the autocorrelation function will contain two exponentials, one with a decay rate of $2Dq^2$ and another one with the decay rate of $Dq^2$ proportional in amplitude to the intensity of the "local oscillator". While designing a light scattering experiment, it is very important to minimize the unwanted scattered light.

3.3 The Light Source

In our light scattering measurements, the light sources are a Coherent Innova—100/20 Ar–ion laser using the 514.5nm emission and Coherent CR-500K Kr-ion laser using the 647.1.nm emission.\(^{(5-6)}\)

Two factors of the light source might affect the results of the light scattering measurement\(^{(1)}\). One is fluctuations in the power of the laser, the other one is the laser modes. In our work, the laser was warmed up for about two hours to reach a stable state before conducting any light scattering measurements. Fluctuations remaining in the power output did not have observable effects on the results of the light scattering measurements because their time scale was much longer than the time scale of autocorrelation functions of light scattered from macromolecular solutions. The laser modes used in light scattering study should be TEM\(_{00}\) mode which is circularly symmetric. Off–axis modes, such as TEM\(_{01}\), can cause undesired contributions to the analyzed signal and therefore should be eliminated. The Coherent Innova—100/20
Ar-ion laser used in our study has an intracavity iris that can be adjusted to eliminate the off-axis modes, and the mode of the Kr-ion laser was checked periodically.

The performance parameters of the Coherent Innova—100/20 Ar-ion laser at the 514.5nm emission, according to manufacturer manual\(^5\), are

- **Beam Diameter:** 2.0 mm
- **Beam Divergence:** 0.39 mrad
- **Long Term Power Stability:**
  - Current Regulation: ±3.0%
  - Light Regulation: ±0.5%
- **Optical noise:**
  - In Current Regulation: 0.5% RMS
  - In Light Regulation: 0.3%

The performance parameter of CR-500K Kr-Ion Laser at the 671.1nm emission are:\(^6\)

- **Beam Diameter:** 1.5 mm
- **Beam Divergence:** 0.8 mrad
- **Long Term Power Stability:** 0.5%
- **Optical Noise:** 1%

### 3.4 The Spectrometer System

The spectrometer system used in our study uses a Brookhaven BI—200SM goniometer system. A polarizer and polarization rotator were used to define the polarization of the incident beam. The spectrometer system is composed of beam focus & steering assembly, a sample cell assembly and the goniometer.

#### 3.4.1 Beam Focus & Steering
The polarized incident laser beam was focused by a front focusing or entrance lens. The lens used in our study is an achromatic lens with focal length of 30mm for the wavelengths employed. Several apertures were placed in the path of the incident beam. The apertures were needed for the alignment procedure and reducing the stray light from the back reflections from the various surfaces. Two neutral density filters were used to adjust the intensity of the incident light beam.

3.4.2 The Sample Cell Assembly

The sample cell assembly includes a modified sample cell, a vat used to contain index matching liquid, a temperature controller, a filtration and circulation system used to clean the index matching liquid and an insulated, black anodized metal pot\(^{(2,4)}\).

The modified sample cell was designed to fulfill specific needs in our work\(^{(4)}\). Two teflon stopper were placed at the upper and bottom part of a glass cylindrical cell with inner diameter of 10mm and length of 100mm. The actual sample volume that is the volume between two stopper was about 0.4ml. The small sample volume and its shape are helpful in reducing convective flows in the cell. The teflon stopper were machined precisely to match the cylindrical cell inner wall and several viton O–rings were used to seal the gaps between the stoppers and the inner wall of the cell. There are two channels in the upper stopper which allow the solutions to be filtered into and pumped out of the sample volume. The sample cell could be to keep the solution clean over a period of more than a month.

The index matching liquid used in our study is Toluene whose refractive index is close to the index of the glass and can thus reduce the reflections of light at outer wall of the cell. The vat with diameter 85mm used to contain index matching liquid has
a optical flat and antireflection coated entrance window. The index matching liquid can be cleaned with a filtration and circulation system which has a combination of two membrane filters with pore-sizes of 2μm and 0.5μm, respectively.

The temperature of the sample solutions as well as the index matching liquid was controlled by a temperature controller with temperature range from -20°C to 100°C and stability of ± 0.02°C.

3.4.3 The Goniometer

The goniometer is composed of a rigid rotating arm for mounting the detector system, a precisely machined base with mounting holes and a X–Y centering table with micrometer adjustments and locking screw. The rigid arm was driven by a stepping motor with 0.01° steps and the motor was controlled by a PC–AT..

3.5 The Detector System

The detector system includes the Main Detector Optics (MDO), a photomultiplier and a pulse amplifier–discriminator. The MDO is composed of an adjustable iris (1 to 18mm), a built in analyzer, a transfer lens system with focal length of 200mm, a filter wheel with 632.8nm, 514.5nm and 488.0nm narrow–band (about 8nm width) optical filters, a pinhole turret with 50μm, 100μm, 200μm, 400μm, 800μm, 1mm, 2mm and 3mm pinholes which could be used for selecting the number of coherence areas and adjusting the intensity of incoming light, and a 200μm slit with X–Y adjustment and a viewing eyepiece for alignment.

In light scattering measurements, the scattered light is collected and focused by the transfer lens system. The focused light passes through the 514.5nm band optical filter, and the pinhole turret with an 800μm pinhole which corresponds to one
coherence area. The light beam then enters the photomultiplier tube which is mounted directly behind the MDO on the goniometer arm.

The photomultiplier tube (PMT) used in our study is an FMI 9863 PMT. The PMT, in general terms, includes a cathode usually made of one or more alkali metals which will absorb a photon and immediately emit an electron. The electron is accelerated by an electric field and then collides with a sheet of metal (a dynode) ejecting out several electrons. The group of electrons is again accelerated with a second dynode, and so forth, until the single electron has been "multiplied" into $10^5$ to $10^7$ or more electrons$^{(1)}$. This group of electrons originating from the capture of a single photon forms the output of the photomultiplier.

Usually, the single photon events are processed by a digital correlator$^{(1)}$. The first step is to convert the relatively small single–photon signal into a pulse of proper amplitude and duration for employment by the correlator. At the same time, very small photomultiplier pulses are rejected as most likely arising from sources other than the detection of a photon. These two functions are normally combined in a single unit called a pulse amplifier-discriminator (PAD). The output of the PAD is then fed to the signal analyzer.

3.6 The Signal Analyzer

The signal analyzer used in our study is a Bi–2030AT digital correlator. From section 2.2.2, the correlation function between signals $A(t)$ and $B(t)$ is defined as:

$$G(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{t_0}^{t_0+T} A(t)B(t+\tau)dt.$$

(3.1)
For stationary signals (signals independent of initial time), the correlation function can be expressed as:

\[
G(\tau) = A(0)B(\tau) = \lim_{T \to \infty} \frac{1}{T} \int_{0}^{T} A(t')B(t'+\tau)dt.
\] (3.2)

The integral can be approximately considered as a sum of n products obtained by sampling the signals in discrete interval of of equal duration \(\Delta\tau\)(sample time), that is

\[
G(j\Delta\tau) = \lim_{N \to \infty} \frac{1}{n} \sum_{i=1}^{N} A_{i} B_{i+j}.
\] (3.3)

For digital signals, the pulse rate \(n(t)\) which is proportional to the signal amplitudes replace \(A(t)\) and \(B(t)\). The correlation function, therefore, can be expressed as:

\[
G(j\Delta\tau) = \lim_{n \to \infty} \frac{1}{n} \sum_{i=1}^{n-1} n_{i} n_{i+j}.
\] (3.4)

For \(j = 1\), that is the first channel accumulation of the correlator,

\[
G(\Delta\tau) = \frac{1}{n} \left(n_{0}n_{1} + n_{1}n_{2} + n_{2}n_{3} + \cdots \right)
= \frac{1}{n} \sum_{i=0}^{n-1} n_{i} n_{i+1}.
\] (3.5)

For \(j = k\), that is the k channel accumulation of the correlator,

\[
G(k\Delta\tau) = \frac{1}{n} \left(n_{0}n_{k} + n_{1}n_{1+k} + n_{2}n_{2+k} + \cdots \right)
= \frac{1}{n} \sum_{i=0}^{n-1} n_{i} n_{i+k}.
\] (3.6)
In order to understand the operating principle of the correlator, a simplified block diagram of part of the Bi-2030AT circuit is shown in Figure 3.3(3). For the Bi-2030AT, during every sample time, several processes take place that include:(3)

1. Deadtime and derandomization circuitry are used to separate and to synchronize these pulses with the sample time clock. The number of pulses, \( n_i \), is prescaled if necessary.
2. The derandomized pulses are fed into a 4-bit counter.
3. The value in the 4-bit counter is entered into the first stage of a 4-bit shift register. Values already in the shift register are shifted up by one stage. Thus, after \( i \) sample periods, the \( j \)th stage contains the value \( n_{i+j} \), representing the history of the signal.
4. During every sample period the number of pulses, \( n_i \), applied to the input are separated, prescaled if necessary, derandomized, and routed through the B input circuitry. If these pulses came from the A input, then the final result is a autocorrelation function; if these pulses came from the B input, then the final result is a cross correlation.
5. During every sample period the instantaneous \( n_i \) is multiplied by the values in each of the multiplier shift registers, each one of these corresponding to a real-time, hardware channel.
6. During each sample time the product from each of the multipliers is counted into a 36-bit store corresponding to a real-time data channel. Later, this information is transferred to memory for display and further analysis.

After \( n \) samples, the contents of the \( j \)th correlator channel will be:
\[
G(j\Delta \tau) = \sum_{i=1}^{B} n_i n_{i+j}, \quad (3.7)
\]
where during each sample, the current number of pulses \(n_i\) has been multiplied by the contents of the jth shift register \(n_{i+j}\) and added into the jth channel store.

3.7 Data Analysis Methods

Through the correlator, a correlation function of the signal is obtained. The next step is to analyze this correlation function and to extract the dynamic information about the macromolecular solution.

For a dilute, monodisperse macromolecular solution, the first order correlation function, as described in section 2.4, is:

\[
G(\tau) = \exp(-q^2D\tau) = \exp(-\gamma\tau). \quad (3.9)
\]
This correlation function contain only one decay constant (the intramolecular interference effects are ignored here). However, for macromolecular solutions with polydispersity, the correlation functions contain multiple decay constants and the correlation functions can be expressed as:

\[
G(M_i,\tau) = \sum_{i=1}^{K} A_i(M_i) \exp[-\gamma(M_i)\tau] \quad (3.10)
\]
where \(A_i(M_i)\) is the relative amplitude of the ith decay with a decay rate of \(\gamma(M_i)\) and \(M_i\) is the molecular weight of the ith species molecules. For homodyne measurements used in our study, the general form of correlation function is assumed to be:

\[
G_2(M_i,\tau) = \left[\sum_{i=1}^{K} A_i(M_i) \exp(-\gamma(M_i)\tau)\right]^2 + B, \quad (3.11)
\]
where \(B\) is a constant baseline.

To analyze the multiple decay problem, one of the most widely used method is the cumulants analysis method \((^8)\) which is employed by BI-2030AT system. The cumulants method, as described in section 2.4.3, is used to obtain the average decay
rate or the average diffusion coefficients of the macromolecular solutions, and the polydispersity factors.

Besides using the cumulants analysis method, the DISCRETE method (9) is also employed in our study. In the case of multicomponent system, like aggregation macromolecular solutions, the cumulants method usually can only give the average decay rate of the multiple decay rate system along with an indication of polydispersity. However, DISCRETE might give the information about each decay function that corresponds to the individual component of the multicomponent system. DISCRETE is a Fortran program which interprets $G(M_i,t)$ in terms of a sum of discrete delta functions. The "discrete" decay constants $\gamma_i(M_i)$ and corresponding amplitudes $A_i(M_i)$ can be obtained using the DISCRETE to analyze the correlation function.
Figure 3.3 Simplified block diagram of part of Bi-2030AT circuit.
Reference for Chapter 3

5. Instruction Manual for Coherent Innova-100/20 Ar-ion Laser, Coherent, Palo Alto, CA
9. DISCRETE Users manual, Provencher, S. W., Max–Planck Institut fuer Bio-Physikalische Chemie, Postfach 2842, D-3400 Goettingen, Germany.
Chapter 4  Dynamic Light Scattering Measurements on Aqueous Solutions of Polyethylene Oxide (PEO) and Aqueous Salt (K$_2$SO$_4$) Solutions of PEO

4.1 Introduction

Water-soluble polymers constitute an important group of polymers which includes natural polymers (e.g. many biopolymers) and synthetic polymers. Since the synthetic water-soluble polymers have much simpler chain structure than most natural polymers, the aqueous solutions of synthetic polymers are good models for studying and testing theories of aqueous solutions of polymers$^{(1)}$. For example, much helpful information about aqueous solutions of protein might be obtained from the study of aqueous solution of the synthetic homopolypeptides$^{(2)}$. In spite of the differences between biopolymers and synthetic polymers, the study of aqueous solutions of synthetic polymers may provide useful information about interactions among polymer component groups and water molecules, and this information in turn might be helpful in understanding the behavior of the more structurally complex biopolymers.

Among all these water-soluble polymers, polyethylene oxide (PEO) has perhaps the simplest structure. This synthetic polymer is not only soluble in water but also soluble in many organic solvents, and the polymer has numerous applications$^{(3)}$. For these reasons, PEO has been the most extensively and intensively studied water-soluble polymer.

A popular application of PEO is use in turbulent water flows because of its drag-reduction property.$^{(4-7)}$ The efficiency in drag-reduction was believed to be enhanced by the propensity of PEO to form aggregates in aqueous solutions, even at very low PEO concentration.$^{(8-9)}$ The efficiency in drag-reduction decreases with
aging, and this change is considered as a result of the disentanglement of aggregates in stead of a chemical degradation of the chain.\textsuperscript{(10-13)}

The aggregates of PEO in aqueous solutions have been detected both by the light scattering studies\textsuperscript{(14-15)} and electron microscopy studies\textsuperscript{(16-17)} It had been believed by some that PEO in aqueous solutions invariably aggregated. However, in a recent light scattering study carried out in this lab on this system\textsuperscript{(18)}, aggregate-free aqueous solutions of PEO were obtained. This work demonstrated that aggregation has not necessary an inherent property of aqueous solutions of PEO.

The aqueous solutions of PEO exhibit both upper and lower critical solution temperatures(UCST and LCST)\textsuperscript{(15,19-22)} The lower and upper critical solution temperatures are estimated to be about -10°C and 103°C,\textsuperscript{(15,22)} respectively. For high polymer solutions, the critical solution temperature is very close to Flory-\(\theta\) temperature. In the temperature range between LCST and UCST, aqueous solutions of PEO exhibit marginal-good solvent properties.\textsuperscript{(22-23)} The critical solution temperature, as well as the \(\theta\) temperature, is strongly dependent on the competition between interactions among polymer segments and solvent molecules. Adding inorganic salt might affect the strength of these interactions and thus change the critical solution temperature of the solution. About the properties of the aqueous salt solutions of PEO, several investigations, mainly on viscosity properties were carried out.\textsuperscript{(22,24-27)} It was shown that the Flory \(\theta\) temperature in aqueous salt solution of PEO was independent of molecular weight of PEO. In aqueous salt (K\textsubscript{2}SO\textsubscript{4}) solutions of PEO of 0.45M K\textsubscript{2}SO\textsubscript{4} concentration, the \(\theta\) temperature was 35°C. The solution with 0.39M MgSO\textsubscript{4} had a \(\theta\) temperature of 43°C.\textsuperscript{(22,24)}

In this study, the dynamic light scattering technique was used to study the aggregation phenomenon of aqueous solutions of PEO, and the behavior of aqueous salt (K\textsubscript{2}SO\textsubscript{4}) solutions of PEO. The aggregation studies were carried out by observing
the long-time behavior of aqueous solutions of PEO. Properties of aqueous salt (K_2SO_4) solutions of PEO with various K_2SO_4 concentrations were investigated by measuring the mutual diffusion coefficients D(c) and their second virial coefficient k^c_D

4.2 Experimental

4.2.1 Solution Preparation

The PEO sample used in this study was obtained from the Pressure Chemical Company, Pittsburgh, Pennsylvania. The molecular weight of the PEO sample which was determined by light scattering measurement (23), is 838,000, and the polydispersity, M_w/M_n, is 1.2(23). The PEO sample was kept in a freezer whose temperature was maintained between -15°C and -20°C.

It was observed in our study that aggregation behavior in aqueous solutions of PEO and aqueous salt(K_2SO_4) solutions of PEO were extremely sensitive to the impurities in the solution: any contamination of the solutions might result in the aggregation of PEO in the solution. As water is a highly polar solvent, it is very easily contaminated. Therefore, solution preparation was a particularly crucial step in our study.

The water used in preparation of the solutions was first purified through a reverse osmosis/deionization/filtration system. Then, the water was fed into a Lab 5 Ultrapure Water System (Technic Control Systems). Here, the water was further purified through a filter and a mixed charcoal/deionizing resin bed. The output "ultrapure" water had a nominal resitivity of 12-16MΩ.cm. Before preparing the solutions, the ultrapure water was mildly heated to remove gases in the water. Then the water was slowly cooled down to room temperature.

The cleaning procedure of the sample cell and the glassware (flask and beaker) included several steps. First, the cell and the glassware were washed in warm soap
water, then rinsed with clean water. After drying, the cell and glassware were put into a sulfuric acid tank with Nochromix added for removing all organic impurities. The glassware were kept in the acid tank for about a day, and the cell was kept only for an hour to avoid pitting. Finally, the cell and the glassware were rinsed with house purified water then ultrapure water.

Other parts, such as teflon stoppers and syringes which were of contact with the solutions were sonicated thoroughly and rinsed with ultrapure water.

The PEO sample was weighed using an analytical balance with an accuracy of 10µg. The weighed sample was then put into a 25ml or 50ml clean flask, and the ultrapure water added into the flask. One drop of chloroform was added to the solution to prevent the bacterial growth. It was shown earlier (18) that a drop of chloroform added to the solution did not affect the dynamic light scattering measurement result. In addition, the air above the solution in the flask was replaced by freon to prevent oxidation. In order to let the PEO completely dissolve, the solutions were kept in an oven for about three days at 30°C. During this period, the solution were mildly stirred occasionally. Finally, the solutions were ready for measurement. The stock solution, if necessary, was diluted to provide lower concentration solutions.

The K$_2$SO$_4$ salt used in this study was reagent grade with a nominal purity of 99.1%. A K$_2$SO$_4$ salt solution with ultronic grade K$_2$SO$_4$ having a purity of 99.999% , was also measured using dynamic light scattering. By comparing the measurement results of the reagent grade K$_2$SO$_4$ and the ultronic grade K$_2$SO$_4$ solutions, no difference was observed. The method used of preparing the aqueous salt solution involved two steps: (i) A higher concentration K$_2$SO$_4$/water solution was prepared with ultrapure water and the salt. The salt solution was mildly heated to remove gases. (ii) The salt solution was then mixed with the PEO/water solution and ultrapure water to obtained aqueous salt solutions with desired PEO and K$_2$SO$_4$ concentrations,
respectively. After mixing, the PEO aqueous salt solutions were kept in the oven at 30°C for about 12 hours.

The final solutions were filtered directly into the sample cell with a special cleaned syringe. The filter used in our study were the 0.2µm Schleicher and Schiell Nylon 66 (hydrophobic) disposable filters.

4.2.2. Dynamic Measurements

The Dynamic light scattering measurement, as described in Chapter 2, is a noninvasive technique which can both accurately measure the mutual diffusion coefficient D(c) of polymer in the dilute solution, and sensitively detect the aggregates in the solutions. Even a very small amount of the aggregates shows up using this technique.

In the dynamic measurements, the scattering angle was fixed at 45°. The solution temperature was maintained at 30°C by the temperature control system described in Chapter 3. The light sources used were the Ar-ion laser with the 514.5nm emission and the Kr-ion laser with the 647.1nm emission. The Kr-ion laser was only used for the measurement of the long time behavior of the PEO/water solution with concentration of 1.00mg/ml. Before each set of measurement, the alignment of the instrument was checked using "Isinθ" measurement\(^{(28,29)}\). The Isinθ measurement is based on the fact that the product of the scattered light intensity I and sinθ (θ the scattering angle), to a good approximation, should be a constant. In the Isinθ measurement, the intensities of scattered light with various scattering angles were measured. The instrument was adjusted until the products Isinθ of different scattering angles became very close to each other. The accuracy of the scattering angle could be adjusted within ± 0.1°.
The measured data were analyzed using the method of cumulants on-board the BI-2030AT digital correlator system described in Chapter 3. The first cumulant (mean value of the decay constant) $\Gamma_1 = \bar{D}(c)q^2$, and the polydispersity factor $\mu_2/\Gamma_1^2$ were obtained. The value of the polydispersity factor $\mu_2/\Gamma_1^2$ reflects the width of the distribution of particle (polymer coil) sizes in solutions.

The $z$-averaged mutual diffusion coefficient $\bar{D}(c)$ is determined from the first cumulant $\Gamma_1$. For a dilute polymer solution,

$$D(c) = D_0 (1+k_D^c c).$$

(4.1)

The self diffusion coefficient $D_0$ of an isolated polymer and the diffusion coefficient second virial coefficient $k_D^c$ can be determined from the mutual diffusion coefficients $D(c)$ measured at various concentrations. From $D_0$, the hydrodynamic radius of the polymer coil can be obtained from the eqn. (1.11). The information of the thermodynamic parameter $A_2$ may be obtained from $k_D^c$ through eqn. (1.57). (31)

Some of the measured long time study data were fed to the DISCRETE analysis program for obtaining information about discrete decay constants in PEO solutions.

4.3 Experimental Results and Discussion

4.3.1. The diffusion coefficients and the polydispersity factors of dilute aqueous solutions of PEO

The mutual diffusion coefficients $D(c)$ and the polydispersity factors $\mu_2/\Gamma_1^2$ of a series of dilute aqueous PEO solutions with various concentrations were measured using dynamic light scattering. The measurements were carried out shortly after the solutions were filtered into the sample cell (about 10 minutes). The concentrations of
the solutions and the measurement results are listed in Table 4.1. The dependence of mutual diffusion coefficient $D(c)$ on PEO concentration $c$, from the data in Table 4.1, is illustrated in Figure 4.1. These results are in excellent agreement with earlier work carried out in this lab by Devanand and Selser (22).

It is shown in the Table 4.1 that the values of the polydispersity factors of the solutions are pretty low. Devanand's work and this result indicate that the solutions are essentially aggregate free. It was noticed in this work that when a solution was prepared inadequately or contaminated, the measurement result of this solution would showed that the polydispersity factor of the solution was quite high, about 0.2-0.4, and the mutual diffusion coefficient was considerably lower than that of aggregate-free solution with the same concentration, even through the 0.2µm filter was used. This indicated that the PEO aggregate was formed in the "contaminated" solution. This kind of the "contaminated" solution was frequently encountered in our study.

The results listed in Table 4.1 reflect single chain behavior in the solutions. eqn.4.1 represents the relationship among $D_0$, $k^c_D$ and $D(c)$. The $D_0$ and $k^c_D$ of the aqueous solution of PEO are obtained from Figure 4.1

$$D_0=7.98 \times 10^{-8} \text{(cm}^2/\text{s}), \quad \text{and}$$

$$k^c_D=249 \text{ (ml/g)}.$$

The mutual diffusion coefficient $D(c)$ of the solution may be represented as

$$D(c)=7.98 \times 10^{-8}(1 + 249 \cdot c) \text{ (cm}^2/\text{s})$$  \hspace{1cm} (4.2)

where $c$ is in the units of g/ml.

The hydrodynamic radius $R_h$ can be determined from the Stokes-Einstein relation $D_0=-\frac{kT}{6\pi\eta R_h}$, using the water viscosity $\eta$ measured in this lab. As $\eta=0.798\text{cp}$, the $R_h$ is 349 Å.
4.3.2 The Long Time Behavior of Aqueous PEO Solution

In the long time studies of aqueous PEO solutions, the solutions with concentrations of 0.45 mg/ml and 1.0 mg/ml were measured for observing the evolution of the mutual diffusion coefficient of the polymer $D(c)$ and the polydispersity factor $\mu_2\bar{r}_2$ in the solutions with time.

The solution with concentration 0.45mg/ml was observed for a period of 0-140 hours, and the long-time measurements of this solution were carried out twice; The second set of measurements began a week after the first set. The results of the first and the second set of measurements are listed in Table 4.2 and Table 4.3, respectively. The evolutions of the polydispersity factor and the diffusion coefficient of the solution with time are illustrated in Figures 4.2 and Figure 4.3, respectively. The dashed line in Figure 4.3 is the value of the diffusion coefficient calculated from Eqn. 4.2 which serves as a reference. The solution with concentration 1.0mg/ml has been observed through a period of 0-4 weeks. The measurement results are listed in Table 4.4; The evolution of the polydispersity and the diffusion coefficient are illustrated in Figure 4.4 and Figure 4.5, respectively.

The above results show that the solutions were almost aggregate-free for the initial period of 0-10 hours; The diffusion coefficients are very close to the reference values. Then, the diffusion coefficient decreased gradually with time, and the polydispersity factor increased gradually. After about 70 hours, the diffusion coefficients from the first and the second set of measurements of the solution with concentration 0.45mg/ml decreased 18% and 8.8% comparing with their initial values, respectively; The diffusion coefficient of the solution with concentration 1.0mg/ml decreased 3%. These changes indicate that PEO aggregates formed gradually in these solutions.
It was observed in our study that when some well prepared solutions were filtered into the sample cell which was not clean enough or was not sealed well, the solutions were found aggregate-free just after being filtered into the cell. However, after 20-30 minutes, the aggregates of PEO in the solutions were clearly present. The PEO aggregation-process in these cases was quite rapid.

From the results of these long time study, it is reasonable to suggest that the aggregation of PEO in the solutions was caused by impurities. Because, if the aggregation were the inherent property of PEO in aqueous solution, the aggregating-process in higher concentration solution should be more rapid than that in lower concentration solution. However, our results show that the aggregating-process in the 1.0mg/ml solution was actually slower than that in the 0.45mg/ml solution during the period of 0-70 hours. Therefore, the aggregation in the solutions was apparent not caused by the polymer itself but, more probably, by some external impurities. It is known in particular that silica particles readily cause aggregation of PEO in aqueous solutions\textsuperscript{(33)}.

For aqueous solutions of PEO, there are always some impurities, more or less, existing in the solution. When the number of these impurities is large, a large number of PEO aggregates will be formed in the solution due to the impurities. Because of the large number of the aggregates, even when the size of the aggregates is small, the aggregates may still show up in dynamic light scattering measurements. In this situation, the PEO aggregation-process looks quite rapid; and because of the small size of the aggregates, the aggregates might not be filtered out by the 0.2\textmu m filter, just like the situation of the "contaminated" solutions mentioned in section 4.3.1.

If the number of impurities in aqueous solutions of PEO is very small, as in a well prepared solution, the PEO aggregates caused by the impurities might not show up until these aggregates have grown up to considerably large sizes because of the small
number of the aggregates. While the aggregates are growing, the PEO molecules in these aggregates might dissolve into the water again. It might take a relatively long time for a PEO aggregate to grow to become a large one. Our long-time measurement results clearly indicate that the aggregation-process of a well prepared solution was quite slow.

Some of the measured data of the first set measurement of the 0.45mg/ml solution were fed to the program DISCRETE to obtain information about discrete decay constants \( \Gamma_i(i=1,2, \ldots \ldots) \). The analysis results are listed in Table 4.5. In the initial period, only one mode of decay constant is observed which apparently corresponds to the single chain system in the solution. In the period of 40-140 hours, two modes are observed. One of the modes is quite stable. The diffusion coefficients calculated from this mode, illustrated in Figure 4.6, are quite close to the reference value; the other one is "jumping around", and the diffusion coefficients calculated from the unstable mode are much smaller than that of the stable mode. Apparently, the unstable mode reflects the aggregates in the solution and the stable one reflects the single chain system. In any event, accurate determination of the slower mode was not possible.

As the value of the diffusion coefficient varies inversely as the diameter of particle, the size of the aggregates related to the unstable mode must be much bigger than that of the single chain. It is also seen in Table 4.5 that the amplitude of the unstable mode is considerably smaller than that of the stable mode although the aggregates are much bigger than the single molecules. This result suggests that the number of the aggregates in the solution must have been quite small.

4.3.3 The property of the PEO in aqueous salt\((K_2SO_4)\) solution
Dynamic measurements were made on five groups of aqueous salt (K$_2$SO$_4$) solutions with K$_2$SO$_4$ concentration of 0.05M, 0.1M, 0.2M, 0.3M and 0.4M. The results of each set of measurements are listed in Table 4.6 (0.05M K$_2$SO$_4$), Table 4.7 (0.1M), Table 4.8 (0.2M), Table 4.9 (0.3M) and Table 4.10 (0.4M). The mutual diffusion coefficient D(c) vs PEO concentration plots of each group of the solution are illustrated in Figures 4.7 (0.05M K$_2$SO$_4$), 4.8 (0.1M K$_2$SO$_4$), 4.9 (0.2M K$_2$SO$_4$), 4.10 (0.3M K$_2$SO$_4$) and 4.11 (0.4M K$_2$SO$_4$), respectively. All of the plots are linear. The diffusion coefficient second virial coefficient $k^c_D$ and the intercept $D_0$ are determined from D(c) using linear least squares fits. The hydrodynamic radius $R_h$ is determined from $D_0$ via the Stokes-Einstein relation. The values of $k^c_D$, $D_0$ and $R_h$ of the PEO/water solution and the aqueous K$_2$SO$_4$ solutions with different K$_2$SO$_4$ concentrations are listed in Table 4.11. The dependencies of $k^c_D$ and $R_h$ on K$_2$SO$_4$ concentrations are illustrated in Figures 4.12 and 4.13, respectively. For aqueous K$_2$SO$_4$ solutions, the refractive index $n$ and the shear viscosity $\eta$, which are used for determining D(c) and $R_h$, on the salt concentration. The dependence of $n$ and $\eta$ on K$_2$SO$_4$ concentration at 30°C may be represented as:

$$n = 1.3329 + 0.0223c - 0.0044c^2$$

$$\eta = 0.7960 + 0.1420C - 0.0033c^2$$

The typical value of polydispersity factors of the aqueous salt (K$_2$SO$_4$) solutions of PEO, which are listed in Table 4.6–4.10, are quite small, even for the solutions with high K$_2$SO$_4$ concentration (e.g. 0.4M K$_2$SO$_4$). This implies that the salt K$_2$SO$_4$ or K$^+$ and SO$_4^{2-}$ ions do not necessarily cause aggregation of PEO in the solutions.

In spite of experimental error, it is clear in Table 4.11 and Figures 4.12, 4.13 that $k^c_D$ and $R_h$ decrease with increasing K$_2$SO$_4$ concentration. The reduction of $R_h$ which is consistent with earlier viscometry result indicates the "water-K$_2$SO$_4$" solvent became poorer with the addition of salt K$_2$SO$_4$. 
Recent work carried out in this lab by Devanand and Selser\textsuperscript{(23)} indicated that PEO in water at 30°C exhibited asymptotic good solvent behavior and the size of PEO coils in water was unusually larger compared with those found for typical polymer coils in organic solvents. This behavior was attributed to the unusual ability of water molecules to "pack" into the PEO coils. The unusually large size of the PEO coil in water implies that the PEO chain segment-solvent interaction is unusually strong with the segments within a PEO coil strongly repelling each other.

From Table 4.10, it is found that the hydrodynamic radius $R_h$ of PEO coil in 0.4M $K_2SO_4$ aqueous $K_2SO_4$ solution is about 20% smaller than that in pure water. This considerable reduction reveals that the salt $K_2SO_4$ has the ability to "unpack" water molecules from PEO coils.

4.4 Conclusions

The observation of the aging aqueous solution of PEO indicates that PEO gradually aggregates in well prepared aqueous solutions. The aggregation of PEO is probably caused by the impurities in the solutions.

In well prepared aqueous salt ($K_2SO_4$) solutions of PEO, the salt $K_2SO_4$ does not necessarily cause the aggregation of PEO. When the concentration of $K_2SO_4$ in the solutions increases the hydrodynamic radius of PEO coil and the diffusion coefficient second virial coefficient decrease, which indicates that the solutions become poorer with addition of $K_2SO_4$ salt.
Table 4.1: The Dynamic Measurement Reference Results For PEO/Water Solutions.

$\theta=45^\circ$, $\lambda_0=514.5$nm

<table>
<thead>
<tr>
<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $\Gamma$ (1/s) ($\pm 0.8%$)</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ ($\pm 30%$)</th>
<th>Diffusion Coefficient $D(c) \times 10^8$ cm$^2$/s ($\pm 0.8%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
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<td>0.09</td>
<td>8.09</td>
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<tr>
<td>0.10</td>
<td>1270</td>
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<td>8.17</td>
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<tr>
<td>0.20</td>
<td>1300</td>
<td>0.08</td>
<td>8.36</td>
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<tr>
<td>0.30</td>
<td>1340</td>
<td>0.12</td>
<td>8.62</td>
</tr>
<tr>
<td>0.51</td>
<td>1400</td>
<td>0.14</td>
<td>9.00</td>
</tr>
<tr>
<td>0.61</td>
<td>1426</td>
<td>0.12</td>
<td>9.17</td>
</tr>
</tbody>
</table>
Figure 4.1 The Mutual Diffusion Coefficient $D(c)$ vs PEO Concentration $c$ for the PEO/Water Solutions.
Table 4.2: Long Time Observation Results for the 0.45mg/ml PEO/Water Solution. (1st set)

<table>
<thead>
<tr>
<th>Age (hour)</th>
<th>Polydispersity Factor $\mu_2/\bar{I}^2$ (±30%)</th>
<th>Decay Constant $\bar{I}$ (1/s) (±4%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8}$ cm$^2$/s (±4%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1376</td>
<td>8.84</td>
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<td>1310</td>
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</tr>
<tr>
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<td>0.13</td>
<td>1320</td>
<td>8.49</td>
</tr>
<tr>
<td>25</td>
<td>0.14</td>
<td>1250</td>
<td>8.04</td>
</tr>
<tr>
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<td>1280</td>
<td>8.23</td>
</tr>
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<td>46</td>
<td>0.20</td>
<td>1240</td>
<td>7.97</td>
</tr>
<tr>
<td>48</td>
<td>0.22</td>
<td>1240</td>
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<td>0.25</td>
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Table 4.3: The Long Time Observation Results for the 0.45mg/ml PEO/Water Solution. (2nd set)

<table>
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<tr>
<th>Age (hour)</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ (±30%)</th>
<th>Decay Constant $\Gamma^t$ (1/s) (±3%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8}$ cm$^2$/s (±3%)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
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<td>0.19</td>
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<tr>
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<tr>
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</table>
Figure 4.2: Polydispersity Factor vs. Time for the 0.45mg/ml PEO/water Solution.
Figure 4.3: The Diffusion Coefficient vs Time for the 0.45mg/ml PEO/Water Solution. The dashed line indicates the value calculated from eqn. 4.2 with concentration 0.45mg/ml.
Table 4.4: Long Time Observation Results for the 1.00mg/ml PEO/Water Solution.

$\theta=45^\circ \quad \lambda_0=647.1\text{nm}$

<table>
<thead>
<tr>
<th>Age (hour)</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ (±30%)</th>
<th>Decay Constant $\Gamma$ (1/s) (±2%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8} \text{ cm}^2/\text{s}$ (±2%)</th>
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</tr>
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<tr>
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<td>915</td>
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</tr>
<tr>
<td>Age (hour)</td>
<td>Polydispersity Factor $\mu_2/T^2$ (±30)</td>
<td>Decay Constant $\Gamma$ (1/s) (±2%)</td>
<td>Diffusion Coefficient $D(c) \times 10^{-8}$ cm$^2$/s (±2%)</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------</td>
<td>------------------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
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</tr>
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<td>893</td>
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Figure 4.4: Polydispersity Factor vs Time for the 1.00mg/ml PEO/Water Solution.
Figure 4.5: The diffusion coefficient vs Time for the 1.00mg/ml PEO/water solution.
Table 4.5: DISCRETE Analysis Results

<table>
<thead>
<tr>
<th>Age (hour)</th>
<th>Mode 1</th>
<th>Mode 2</th>
<th>(A_1/A_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Gamma (1/s)) (±13%)</td>
<td>Amplitude (A_1)</td>
<td>(D \times 10^{-8} \text{cm}^2/\text{s}) (±13%)</td>
</tr>
<tr>
<td>0</td>
<td>1230</td>
<td>—</td>
<td>7.9</td>
</tr>
<tr>
<td>20</td>
<td>1210</td>
<td>—</td>
<td>7.8</td>
</tr>
<tr>
<td>46</td>
<td>1500</td>
<td>450</td>
<td>9.6</td>
</tr>
<tr>
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</tr>
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<td>490</td>
<td>9.9</td>
</tr>
<tr>
<td>79</td>
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<td>520</td>
<td>8.7</td>
</tr>
<tr>
<td>137</td>
<td>1400</td>
<td>490</td>
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Table 4.5: DISCRETE Analysis Results.
Figure 4.6: DISCRETE Analysis Results for Stable Mode

D(c) Determined From the Stable Modes
Table 4.6: The Measurement Results for the K$_2$SO$_4$ PEO/Water Solutions with 0.05M K$_2$SO$_4$

<table>
<thead>
<tr>
<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $\Gamma$ (1/s) (+1%)</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ (+20%)</th>
<th>Diffusion Coefficient D(c) x 10$^{-8}$ cm$^2$/s (+1%)</th>
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<td>8.86</td>
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<td>0.12</td>
<td>10.72</td>
</tr>
<tr>
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<td>1770</td>
<td>0.18</td>
<td>11.36</td>
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<tr>
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Table 4.7: The Measurement Results for the K$_2$SO$_4$ PEO/Water Solutions with 0.1M K$_2$SO$_4$

<table>
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<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $\Gamma$ (1/s) (+0.7%)</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ (+20%)</th>
<th>Diffusion Coefficient D(c) x 10$^{-8}$ cm$^2$/s (+0.7%)</th>
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</thead>
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<tr>
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<td>11.3</td>
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</table>
Table 4.8: The Measurement Results for the K$_2$SO$_4$ PEO/Water Solutions with 0.2M K$_2$SO$_4$

$\theta=45^\circ$, $\lambda_0=514.5$nm.

<table>
<thead>
<tr>
<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $\bar{\Gamma}$ (1/s) (±0.8%)</th>
<th>Polydispersity Factor $\mu_2/\bar{\Gamma}^2$ (±30%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8}$cm$^2$/s (±0.8%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>1300</td>
<td>0.08</td>
<td>8.30</td>
</tr>
<tr>
<td>0.81</td>
<td>1390</td>
<td>0.08</td>
<td>8.87</td>
</tr>
<tr>
<td>1.01</td>
<td>1430</td>
<td>0.08</td>
<td>9.13</td>
</tr>
<tr>
<td>1.22</td>
<td>1440</td>
<td>0.13</td>
<td>9.20</td>
</tr>
<tr>
<td>2.03</td>
<td>1590</td>
<td>0.14</td>
<td>10.15</td>
</tr>
</tbody>
</table>

Table 4.9: The Measurement Results for the K$_2$SO$_4$ PEO/Water Solutions with 0.3M K$_2$SO$_4$

$\theta=45^\circ$, $\lambda_0=514.5$nm.

<table>
<thead>
<tr>
<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $\bar{\Gamma}$ (1/s) (±1%)</th>
<th>Polydispersity Factor $\mu_2/\bar{\Gamma}^2$ (±20%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8}$cm$^2$/s (±1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1300</td>
<td>0.11</td>
<td>8.28</td>
</tr>
<tr>
<td>0.40</td>
<td>1328</td>
<td>0.08</td>
<td>8.45</td>
</tr>
<tr>
<td>0.60</td>
<td>1330</td>
<td>0.12</td>
<td>8.47</td>
</tr>
<tr>
<td>0.80</td>
<td>1384</td>
<td>0.10</td>
<td>8.81</td>
</tr>
<tr>
<td>1.20</td>
<td>1470</td>
<td>0.10</td>
<td>9.35</td>
</tr>
<tr>
<td>1.60</td>
<td>1500</td>
<td>0.14</td>
<td>9.55</td>
</tr>
</tbody>
</table>
### Table 4.10: The Measurement Results for the K$_2$SO$_4$ PEO/Water Solutions with 0.4M K$_2$SO$_4$

$\theta=45^\circ$, $\lambda_0=514.5$nm.

<table>
<thead>
<tr>
<th>PEO Concentration (mg/ml)</th>
<th>Decay Constant $T$ (1/s (±0.9%))</th>
<th>Polydispersity Factor $\mu_2/\Gamma^2$ (±30%)</th>
<th>Diffusion Coefficient $D(c) \times 10^{-8}$cm$^2$/s (±0.9%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>1430</td>
<td>0.08</td>
<td>9.07</td>
</tr>
<tr>
<td>0.41</td>
<td>1420</td>
<td>0.08</td>
<td>9.01</td>
</tr>
<tr>
<td>0.51</td>
<td>1380</td>
<td>0.12</td>
<td>8.76</td>
</tr>
<tr>
<td>0.61</td>
<td>1390</td>
<td>0.13</td>
<td>8.82</td>
</tr>
<tr>
<td>0.71</td>
<td>1330</td>
<td>0.15</td>
<td>8.44</td>
</tr>
<tr>
<td>0.82</td>
<td>1350</td>
<td>0.14</td>
<td>8.56</td>
</tr>
</tbody>
</table>

### Table 4.11: The $R_h$ and $K_d$ of Various K$_2$SO$_4$ Concentrations.

<table>
<thead>
<tr>
<th>K$_2$SO$_4$ Concentration</th>
<th>$D_0 \times 10^{-6}$cm$^2$/s (± 1.4%)</th>
<th>$k_D$(ml/g) (± 12%)</th>
<th>$R_h$(Å) (± 1.4%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.98</td>
<td>249</td>
<td>349</td>
</tr>
<tr>
<td>0.05M</td>
<td>8.00</td>
<td>274</td>
<td>346</td>
</tr>
<tr>
<td>0.1M</td>
<td>8.15</td>
<td>199</td>
<td>336</td>
</tr>
<tr>
<td>0.2M</td>
<td>7.92</td>
<td>142</td>
<td>340</td>
</tr>
<tr>
<td>0.3M</td>
<td>8.03</td>
<td>123</td>
<td>330</td>
</tr>
<tr>
<td>0.4M</td>
<td>9.32</td>
<td>-101</td>
<td>279</td>
</tr>
</tbody>
</table>
Figure 4.7: $D(c)$ vs PEO Concentration for the Aqueous Salt($\text{K}_2\text{SO}_4$) solutions of PEO with 0.05M $\text{K}_2\text{SO}_4$. 
Figure 4.8: $D(c) \times 10^{-8} (\text{cm}^2/\text{s})$ vs PEO Concentration for the Aqueous Salt($K_2SO_4$) Solutions of PEO with 0.10M $K_2SO_4$. 
Figure 4.9: $D(c)$ vs PEO Concentration for the Aqueous Salt($K_2SO_4$)
Solutions of PEO with 0.20M $K_2SO_4$.
Figure 4.10: $D(c) \times 10^{-8}$ (cm$^2$/s)

$D(c) \times 10^{-8}$ (cm$^2$/s) vs. $c$ (mg/ml)

The graph shows a linear relationship between $D(c)$ and $c$ for PEO concentrations in aqueous salt solutions of PEO with 0.30M $K_2SO_4$. Solutions of PEO with 0.30M $K_2SO_4$. 

$D(c)$ represents the diffusion coefficient, which is a measure of the rate at which a substance diffuses through a medium.
Figure 4.11: $D(c)$ vs PEO Concentration for the Aqueous Salt ($K_2SO_4$) Solutions of PEO with 0.40M $K_2SO_4$. 
Figure 12: $k_p$ vs $K_2SO_4$ concentration.
Figure 13: $R_h$ vs $K_2SO_4$ concentration.
References for Chapter 4


32. DISCRETE Users Manual, Provencher, S. W., Max-Planck Institute fer Bio-Physikalische Chemie, Postfach 2842, D-3400 Goettingen, Germany.

33. Merrill, E. D., private communication.