Measurement of the first internal mode of polystyrene in cyclohexane and toluene through dynamic light scattering

Albert Raymond Ellis
University of Nevada, Las Vegas

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Measurement of the first internal mode of polystyrene in cyclohexane and toluene through dynamic light scattering

Ellis, Albert Raymond, M.S.
University of Nevada, Las Vegas, 1989
Measurement Of The First Internal Mode
Of Polystyrene In Cyclohexane And
Toluene Through Dynamic Light Scattering

By
Albert Raymond Ellis

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science
In
Physics

Department of Physics
University of Nevada, Las Vegas
June 9, 1989
The thesis of Albert Raymond Ellis for the degree of Master of Science in Physics is approved.

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University of Nevada
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July 12, 1989
Abstract

A study of the longest internal relaxation time $\tau_i$ of $8.42 \times 10^6 \text{ M}_w$ macromolecular polystyrene dissolved in both toluene and cyclohexane was done through the use of photon correlation spectroscopy from scattered laser light. The data obtained (autocorrelation functions) were then analyzed by means of a multi-exponential fitting programme (Discrete) on the Cyber 830 computer and by a non-linear least squares program (NLLSQ) on an Apple IIe computer. The exponential decay constants derived from these fits were further used to obtain a value of $\tau_i$ in each solvent and also to find the power relation between these decay constants and $q$, the magnitude of the scattering wave vector. The relaxation time $\tau_i$, together with the $q$ dependence of the decay constant, was then compared to the predicted results from the Rouse-Zimm bead-and-spring model of polymers as well as other models and other researchers' published results.

For polystyrene in cyclohexane, $q^{1.96 \pm 0.02}$ was obtained with $\tau_i = 343 \mu s$. The $\tau_i$ result in cyclohexane agrees well with the Zimm non-free draining model but the predicted $q^3$ dependence was not observed. In toluene, $q^{2.86 \pm 0.24}$ is obtained with $\tau_i = 215 \mu s$. The
predicted $q^4$ dependence agrees well with our result but the expected value for $\tau_1$ from theory of 1256 $\mu$s. was not observed.

These results indicate that more work should be done with shorter wavelengths to increase $q$ and thereby probe more extensively the intermediate scattering region.

In addition, subsequent work by Mr. Johannes K. Schaller and Dr. James C. Selser indicates that there is a concentration dependence of $\tau_1$ for toluene. It is therefore suggested to continue research on the concentration dependence of $\tau_1$ as well.
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Last, but not least, thanks are in order to Judy Earl for her help in the printing of this work.

Thank God I'm done!
Introduction

The study of the basic properties of the dynamic behavior of polymers in solution is very important with respect to our understanding of macromolecules as a whole. In view of the explosive development of the various uses of polymers for commercial products, the economics of producing better products cheaper is immediately obvious. In addition, since the basic components of life itself (protein, DNA etc.) are composed of polymers, basic understanding of their motions in solution would again be beneficial.

The study of very large, linear molecules in solution (such as the molecule used in this research, polystyrene as in Figure 1) provides a unique opportunity to study a constrained many-body problem. If one represents a dissolved linear chain molecule in solution by a ball of entwined threads, then one can form a conceptual picture as in Figure 2. The polymer chain in this figure tends to be randomly coiled into the form of a ball.

This enwrapped molecule, since it is in solution, can physically react to the random collisions of the
The macromolecule is referred to as atactic when the benzene ring occurs randomly on either side of the backbone of the polymer (lack of stereoregularity).

Figure 1. Atactic Polystyrene
Figure 2. Polystyrene in Solution
solvent molecules. The overall motion generated by the forces due to these random collisions on the polymer is most commonly known as Brownian motion.

If one considers each segment (statistical length) of the polymer chain as being composed of a ball and spring (such as in the inset in Figure 2) then the motions of this polymer in solution about its equilibrium configuration may be considered as being that of a many-body model.

This model is most commonly known as the Rouse-Zimm bead-and-spring model\(^1\)\(^2\) and is the model by which the polymer in solution will be represented. Since the internal forces for the polymer will be considered primarily as Hookean, an analysis of the equation of motion for this model should yield a set of expressions for the normal modes. The topic of this research was to primarily determine experimentally the longest wavelength or first internal mode of oscillation (relaxation time \(\tau_1\)).

The experimental method by which this mode was studied was through photon correlation spectroscopy. Through an analysis of the changes in scattered light intensities at various angles with time, one may obtain information about the motions of the polymer in solution.\(^3\) These motions include the center-of-mass translational motion as well as internal motions.
From the scattered light intensities one may extract the required polymer motion information through the use of an autocorrelator. This device, when properly set, is designed to detect similarities in the scattered light signal intensity through the use of an autocorrelation function.

A more specific description of the autocorrelation function as well as a derivation of the Rouse model will follow in the theory section. A description of the experimental procedure and set-up, as well as the numerical analysis of the data, will also follow in other specified sections. A comparison of our final results to other groups' and existing theories will be found in the concluding section.
Endnotes


3 Benjamin Chu, *ibid.*, 226
Theory

A linear, flexible, random coil macromolecule in solution may be considered as a constrained many-body problem in that the molecule may be viewed as being composed of a series of beads and springs. The beads ("bodies") represent the portion of the polymer atoms that account for the scattering (statistical length or unit) and the springs the segments that constrain the bodies tending to restore the configuration of the polymer coil to equilibrium.

One way of detecting the motions of polymers in solution is through Rayleigh (quasi-elastic) light scattering. Highly coherent and monochromatic (laser) light incident with a wave-vector $\mathbf{K}_i$ upon a polymer solution will be scattered through an angle $\theta$ with a final wave-vector $\mathbf{K}_f$. If a scattering wave-vector is defined as $\mathbf{q} = \mathbf{K}_f - \mathbf{K}_i$ (see Figure 3) and $\mathbf{K}_i \sim K_r$ (quasi-elastic light scattering), then

$$q = 2K_i \sin(\theta/2) = \frac{4\pi n}{\lambda_0} \sin(\theta/2) \quad (1)$$

where $n$ is the index of refraction of the solution solvent, $\lambda_0$ is the wavelength in vacuum and $\theta$ is the
Scattering Region of the Polymer in Solution

Figure 3. Scattering Vector $\vec{q}$
scattering angle. The magnitude of this scattering vector is very important in the light scattering analysis of the motion of macromolecules. For small angles \( \theta \), only the center-of-mass Brownian motion of the polymer coil is detectable.\(^8\)

Since changes in the scattered light are directly attributable to polymer concentration fluctuations,\(^7\) the translational diffusion equation may be used to determine the time development of these fluctuations. For isotropic center-of-mass diffusion (D a scalar),\(^8\)

\[
D \nabla^2 C(r,t) = \frac{\partial C(r,t)}{\partial t} \tag{2}
\]

Upon taking the Fourier transform of equation (2) and solving the resulting differential equation,

\[
D \int_0^\infty q^2 C(q,t) e^{i \vec{q} \cdot \vec{r}} dV = \int_0^\infty \frac{\partial C(q,t)}{\partial t} e^{i \vec{q} \cdot \vec{r}} dV \\
- D q^2 \int_0^\infty C(q,t) e^{i \vec{q} \cdot \vec{r}} dV = \frac{\partial}{\partial t} \int_0^\infty C(q,t) e^{i \vec{q} \cdot \vec{r}} dV \\
- D q^2 C(q,t) = \frac{\partial C(q,t)}{\partial t} \\
C_q(q,t) = C_0(q,0) e^{-D q^2 t} \tag{3}
\]

where D is the translational diffusion coefficient, q the magnitude of the scattering vector and \( C(q,t) \) the "q-th" Fourier component of the concentration fluctuations.

The different Fourier components of the scattered
light may then be experimentally determined by scanning different q (i.e. through different scattering angles). Since concentration fluctuations may be directly related to the fluctuations in the scattered light (E) field, the motions of the polymer may be analyzed through the scattered light from these motions by using autocorrelation (ACF) functions. By comparing a signal with itself over a range of successive time shifts or delays, the ACF may be used to extract the repetitive structure, if any, of a given waveform. This may also be viewed as how well the waveform compares or relates to itself over time.

The ACF of a function f(t) is defined as

$$ACF = \lim_{T \to \infty} \frac{1}{T} \int_{t}^{t+T} f(t)f(t+\tau)\,dt$$

where T is the total time of measurement and \( \tau \) is the sample or correlation time. It is important to note that \( \tau \) measures time differences and not absolute time \( t \).

As an example of how to calculate an ACF consider \( f(t) = \sin(\omega t) \),

$$ACF = \lim_{T \to \infty} \frac{1}{T} \int_{t}^{t+T} \left( e^{i\omega t} - e^{-i\omega t} \right) \left( e^{i\omega(t+\tau)} - e^{-i\omega(t+\tau)} \right) \, dt$$

$$ACF = -1/4 \lim_{T \to \infty} \frac{1}{T\omega} \left( [e^{2i\omega t} e^{i\omega \tau} - e^{-2i\omega t} e^{-i\omega \tau}] - \right)$$
\[
- \left[ \left( e^{i\omega T} + e^{-i\omega T} \right) t \right]^{t+T} \]
\[
ACF = -\frac{1}{4} \lim_{T \to \infty} \frac{1}{T} \left( 2i \left[ \sin \omega (2t + \tau) \right] - 2t \cos (\omega t) \right)
\]

The first term goes to zero in the limit of infinitely long time \( T \) yielding the final solution

\[
ACF = \frac{1}{2} \cos (\omega \tau)
\]

thus revealing the repetitive "temporal structure" of \( f(t) = \sin (\omega t) \) through the frequency \( \omega \).

As another example, consider the measurement of pressure on the wall of a container due to a gas.\(^{10} \) The pressure on the wall is proportional to the total force exerted on the wall by the gas molecules. The origin of this force is predominantly the dipole-dipole interaction between the gas molecules and the wall. This is a very short range force. As the number of individual gas molecules interacting with the wall fluctuates, the pressure on the wall will also fluctuate.

Note the following figure to be an example of the time behavior of the pressure on the wall of the container (Figure 4). Over small time intervals \( \tau = t_{j+1} - t_j \) the change in pressure is relatively small \( (P_j - P_{j+1}) \). However, as \( \tau \) is increased the pressures at times \( t_{j+1} \) and \( t_j \) begin to more greatly deviate
Figure 4. Time Behavior of Pressure
from each other until for large $\tau$ the deviation is
great.

One can therefore state that the pressures at $t_j$
and $t_{j+1}$ for small $\tau$ are highly correlated (related to
each other) and for large $\tau$ uncorrelated.

The ACF for pressure may now be defined as the
following,

$$<P(t)P(t + \tau)> = \lim_{T \to \infty} \frac{1}{T} \int_0^T P(t)P(t + \tau)dt$$

If $\tau$ is small enough, then $P(t) \sim P(t + \tau)$ and

$$<P(t)P(t + \tau)> \sim <P(t)^2> = Q_1.$$

For large enough $\tau$, $P(t)$ will be totally inde­
dependent of $P(t + \tau)$ and

$$<P(t)P(t + \tau)> \sim <P(t)> <P(t + \tau)> = Q_2.$$

To see which is the larger, $Q_1$ or $Q_2$, first con­sider the integral as a series of integrals such that

$T = n\tau$ where $n$ is the integral number of intervals that
the total measurement time $T$ is divided into,

$$<P(t)P(t + \tau)> = \lim_{n\tau \to \infty} \frac{1}{n\tau} \sum_{j=1}^{n-1} \int_0^{t+n} P_j(t)P_{j+1}(t + \tau)dt$$

For small enough $\tau$, all $P_j > <P>$ will be paired
with $P_{j+1} > <P>$ and all $P_j$ less than $<P>$ will be paired
with $P_{j+1} < \langle P \rangle$, as can be seen from inspection of Figure 4. The result of this is that all of the integrals in the sum will be positive.

If $\tau$ were large enough, however, then for some $P_J > \langle P \rangle$ there could be paired $P_{j+1} < \langle P \rangle$ and vice-versa. This would result in some of the integrals being negative which would tend to reduce the sum. One can then conclude that for large and small $\tau$,

$$\langle P(t)^2 \rangle > \langle P(t) \rangle \langle P(t + \tau) \rangle$$

which yields a monotonically decreasing curve as in Figure 5.

If one waits for a long enough time the average pressure will remain the same regardless of when the measurement begins. This is an example of a stationary process which is independent of the starting time $t_0$ and would result in the following condition:

$$\langle P(0)^2 \rangle > \langle P(0) \rangle^2$$

for $t_0$ being zero.\textsuperscript{13}

Another example of a stationary process is the light scattered from the motions of random coil polymers in solution due to Brownian motion.\textsuperscript{14} If one looks at the fluctuations in the scattered light (due to concentration fluctuations) at "sufficiently small" angles ($\theta \sim 20^\circ$) then the ACF will be of the form $e^{-Dq^2}$ and will contain information about the center-of-mass translational diffusion coefficient, $D$, of the
Pressure ACF Versus Delay Time $\tau$

Figure 5. Pressure ACF as a Function of $\tau$
polymer. For larger angles, the ACF is no longer approximated well by one decaying exponential, but by two. While the first contains information about the overall translational motion of the polymer, the second exponential contains information pertaining to the slowest internal motion of the polymer (longest wavelength or breathing mode), $\tau_1$.

This breathing mode may be considered as an overall expansion and contraction of the polymer chain about some equilibrium configuration. The source of this behavior is predominantly due to thermal fluctuations in the solvent around and within the polymer coil. Even though these thermal fluctuations are random, being related to Brownian motion, the response of the polymer chain will have a characteristic overall response time $\tau_1$. $\tau_1$ may be found from the longest wavelength mode derived from a model representing the polymer in solution as a series of polymer beads and springs interacting with the surrounding solvent. One of these models is the Rouse bead-and-spring model which will now be presented in the following treatment.

To derive a theoretical expression for $\tau_1$ using the Rouse bead-and-spring model, one begins with the Langevin equation for the stochastic motion of the random coil (x-projection),
\[ m \frac{d^2 \mathbf{x}}{dt^2} = \mathbf{F}_x + \mathbf{F}_x + \mathbf{F}_x \]  

(5)

where \( \mathbf{F}_x \) = the damping force (friction) = \( -\gamma \frac{d\mathbf{x}}{dt} \)

\( \mathbf{F}_x \) = the entropic (restoring) force = \( -\sigma \mathbf{A} \cdot \mathbf{x} \)

\( \mathbf{F}_x \) = the random force due to Brownian motion

\[ \mathbf{A} = \begin{bmatrix} 1 & -1 & 0 & \ldots & 0 \\ -1 & 2 & -1 & 0 & \ldots & 0 \\ 0 & -1 & 2 & -1 & \ldots & \ldots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots \\ 0 & \ldots & \ldots & \ldots & -1 & 1 \end{bmatrix}, \quad \mathbf{x} = \begin{bmatrix} x_0 \\ x_1 \\ \vdots \\ x_{n-1} \end{bmatrix} \]

\[ \sigma = \text{the entropic force constant} = \frac{3 \mathbf{K}_b T}{\langle l^2 \rangle} \]

\[ \langle l^2 \rangle = \text{the mean-squared segment length} \]

\[ \gamma = \text{the damping constant due to the solvent} \]

\( n = \text{the number of beads or statistical segments} \)

\( \mathbf{K}_b = \text{Boltzmann's constant} \)

\( T = \text{temperature in degrees Kelvin} \)

The matrix \( \mathbf{A} \) couples the x-component of neighbouring elements. Similar equations may be formed for the y and z-components.

The entropic force constant \( \sigma \) has the units of a spring constant in that it is proportional to the energy required to deform the polymer from its equilibrium position per mean-squared length.

Since the work done was primarily involved with measuring the longest wavelength mode, the internal
motions of the beads probed are relatively slow and the term involving the second derivative with respect to time may be neglected. The result of this simplification is

$$\gamma \frac{d\ddot{x}}{dt} = \left\{3\right\} \dddot{x} - \sigma \dot{A} \cdot \dot{x}.$$  \hspace{1cm} (6)

From this approximation the Rouse model is expected to hold only for long wavelength modes.

One technique that is often employed to help solve coupled problems is to transform the positions of the beads to a normal set of coordinates.\(^{18}\) This may be done by expanding each position or \(\ddot{x}_i\) in a Fourier series in terms of these normal coordinates

$$\ddot{x}_i = \sum_{k} Q_{i,k} \dddot{x}.$$  \hspace{1cm} (7)

where

$$Q_{i,k} = \begin{cases} \left(2/n\right)^{1/2} \cos k \pi (i/n - 1/2) & \text{for } k = \text{even} \\ \left(2/n\right)^{1/2} \sin k \pi (i/n - 1/2) & \text{for } k = \text{odd} \end{cases}$$

Since similar equations may be derived for \(\ddot{y}_i\) and \(\ddot{z}_i\), the new position vector may be defined as \(\ddot{u}_k = \dddot{x}, \ddot{y}, \dddot{z}\). Upon substitution of equation (7) into (6), Berne and Pecora\(^{19}\) were able to obtain the equation of motion in the transformed coordinate system as

$$\gamma \frac{d\ddot{u}_k}{dt} = \left\{3\right\} \dddot{u}_k(t) - 4 \sigma \sin^2 \left(k \pi / 2n\right) \dddot{u}_k.$$  \hspace{1cm} (8)
Since we are looking at longest wavelength modes (smallest $k$) and $n \gg k$, equation (8) may be simplified by using $\sin^2 \theta = \theta^2$ to

$$\frac{d\tilde{u}_k}{dt} = \frac{1}{\gamma} F_k - \tilde{u}_k / \tau_k,$$

$$\tau_k = \frac{\langle l^2 \rangle \gamma (n/k\pi)^2}{3k_B T}$$

If the temperature is at the so called "theta" temperature where the polymer is just about to precipitate, then the random coil segment distribution is Gaussian in form. By using the Stokes-Einstein equation, $D = k_B T/n\gamma$ and $R_g = n\langle l^2 \rangle /6$ for Gaussian statistics of the random coil distribution, the relaxation time of the $k^{th}$ long wavelength mode becomes

$$\tau_k = \frac{2R_g}{\pi^2 k^2 D} \quad \text{and} \quad \tau_1 = \frac{2R_g}{\pi^2 D}$$

The continuing solution of the new equation of motion becomes rather involved so the interested reader is referred to Berne and Pecora's book. In outline, the equation of motion may be solved by first putting it in the form of a Fokker-Planck equation and then solving the resulting probability distribution function for $\tilde{u}_k$. The predicted electric field ACF function for the light scattered from a polymer coil represented by the bead-and-spring model may then be
determined by applying Green's theorem to the Fokker-Planck equation yielding the following,

\[ |G(t)| = A <\mathbf{I}> \langle \mathbf{E}(t) \mathbf{E}(t + \tau) \rangle \quad (11a) \]

\[ |G(t)| = A <\mathbf{I}> (S_0(x)e + S_2(x)e + \ldots ) \quad (11b) \]

where \( S_0(x) \) and \( S_2(x) \) are time independent coefficients that are functions of the scattering angle (or \( q \)), the polymer molecular weight and the solution concentration. \( A <\mathbf{I}> \) is an instrumental constant including the quantum efficiency of the detector, absorption and reflection losses through the optical system, etc. The square of the product of \( q \) with the radius of gyration \( R_g \) of the polymer, \( x = (qR_g)^2 \), is a measure of the length probed, \( \Lambda = 2\pi/q \), by the light in terms of the size of the polymer. The square of the radius of gyration is defined as

\[ R_g^2 = \frac{\sum m_i r_i^2}{\sum m_i} \]

where \( r_i \) is the magnitude of the displacement vector from the coil center-of-mass to the \( i^{th} \) statistical segment of molecular weight \( m_i \). However, since each \( m_i \) and \( r_i \) pair is difficult to measure, \( R_g \) is usually determined via static light scattering through the use of a Zimm plot. This method is described in Appendix B. Returning to the coefficients \( S_0(x) \) and \( S_2(x) \) from
equation (11), for $x << 1$ and $S_0 (x) \gg S_2 (x)$, $|G^{(1)}(t)|$ is predicted to be a single exponential,

$$|G^{(1)}(t)| = S_0 (x) e^{-Dq^2 t}.$$

For $1 < x < 6$, two exponentials should best represent $|G^{(1)}(t)|$, and for $x > 6$, it is expected that three or more terms may be required.\textsuperscript{23}

Note that in the preceding derivation of the ACF function it was assumed that each macromolecule had exactly the same size ($R_g$) and molecular weight as all the others. For a polydisperse polymer, the weight averaged molecular weight\textsuperscript{24} is defined as

$$\bar{M_w} = \frac{\sum_i^2 M_i n_i}{\sum_i M_i n_i}$$

and the number averaged molecular weight\textsuperscript{25} is defined as

$$\bar{M_n} = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

The ratio of $\bar{M_n}/\bar{M_w}$ is defined as the polydispersity of the sample and is a measure of width of the distribution of molecular weights.\textsuperscript{26} Since in the real world there will always be a finite polydispersity for synthetic polymers, a better treatment should take this into account. Further impetus for this refined treatment is the possibility that values for internal modes
measured by light scattering may be strongly influenced by polydispersity.\textsuperscript{27,28} A modification of the preceding analysis to include polydispersity now follows.\textsuperscript{29} Once again for \( x \ll 1 \), there should be only one decaying exponential or mode in the ACF function. If \( \tilde{\Gamma}_1 \) is defined as the average decay constant for the first mode then

\[
\tilde{\Gamma}_1 = \frac{\langle I_1 \rangle}{\langle I_i \rangle} \Gamma_{i1} = \tilde{D}q^2
\]

\[
\langle I_1 \rangle = \langle I_1 (C, \bar{M}_n, q) \rangle
\]

where \( \langle I_i \rangle \) is the average intensity scattered from the \( i \)th molecular weight polymer from the sample distribution, \( C \) is the polymer concentration in solution, \( \bar{M}_n \) is the polymer number averaged molecular weight and \( q \) is the scattering parameter related to the scattering angle. If the sample were monodisperse then

\[
|G^{(1)}(t)| = A\langle I \rangle \langle E(t) E(0) \rangle = A\langle I \rangle e^{-\Gamma_1 t}
\]

The absolute value was taken since in light scattering experiments a photomultiplier detector is used to measure the scattered light intensity and there is no phase information about the scattered light.

If there is polydispersity then

\[
|G^{(1)}(t)| = A \int_0^\infty f(\Gamma_1) e^{-\Gamma_1 t} d\Gamma_1
\]

\[
|G^{(1)}(t)| = A \sum_i \langle I_i \rangle e^{-\Gamma_1}
\]
where \( f(\Gamma_1) = \sum_i <I_i> \delta(\Gamma_1 - \Gamma_i) \). Note that there now is a separate mode indexed by \( i \) for each molecular weight.

Rewriting equation (16) and expanding the exponential in a Taylor series about \( \bar{\Gamma}_1 \),

\[
|G(t)| = A \exp \left( \bar{\Gamma}_1 t + \sum_i <I_i> \delta(\Gamma_1 - \bar{\Gamma}_1) \left[ 1 - (\Gamma_1 - \bar{\Gamma}_1) t + \frac{(\Gamma_1 - \bar{\Gamma}_1)^2 t^2}{2!} + \ldots \right] d\Gamma_1 \right)
\]

is obtained.

After expanding the expression, the linear term vanishes \((-\sum_i <I_i>(\Gamma_i - \bar{\Gamma}_1) = 0\) leaving the following result for one mode

\[
|G(t)| = A <I> e^{-\bar{\Gamma}_1} \left( 1 + \frac{\mu_2 t^2}{2!} + \ldots \right)
\]

where \( \mu_2 = \sum_i <I_i>(\Gamma_i - \bar{\Gamma}_1)^2 <I> \) is a measure of the polydispersity. Note that if all \( \Gamma_i = \bar{\Gamma}_1 \) (all macro-molecules have the same \( \tilde{D}q^2 \)) then \( \mu_2 = 0 \) and equation (18) reduces to equation (15).

For \( x > 1 \) there should be two modes present. If the sample is monodisperse then

\[
|G(t)| = A <I_1> e^{-\bar{\Gamma}_1} + A <I_2> e^{-\bar{\Gamma}_2}
\]

where \( \bar{\Gamma}_2 = \bar{\Gamma}_1 + \frac{2}{\tau_1} = \tilde{D}q^2 + \frac{2}{\tau_1} \) as previously obtained for the Rouse bead-and-spring model. If once again
there is polydispersity then

\[ |G^{(1)}(t)| = A\sum_i <I_{1i}> e^{-\Gamma_{1i} t} + A\sum_i <I_{2i}> e^{-\Gamma_{2i} t} \] (20)

Now define the following decay averages

\[ \tilde{\Gamma}_1 = \sum_i <I_{1i}> \Gamma_{1i} = \tilde{D}_1 q^2 \quad \text{and} \quad \tilde{\Gamma}_2 = \sum_i <I_{2i}> \Gamma_{2i} = \tilde{D}_2 q^2 + \langle \tau \rangle (21) \]

where \( \tilde{D}_1 = \tilde{D}_2 \) if polydisperse since they are averaged with different weighting. By again expanding through a Taylor series, this time about \( \tilde{\Gamma}_1 \) and \( \tilde{\Gamma}_2 \)

\[ |G^{(1)}(t)| = A <I_1> e^{-\tilde{\Gamma}_1 t} \left( 1 + \frac{\mu_2 t^2}{2!} \right) + \]

\[ + A <I_2> e^{-\tilde{\Gamma}_2 t} \left( 1 + \frac{\mu_2 t^2}{2!} \right) \] (22)

This function looks like Figure 6.

If the proper measurement time \( (t_{\text{max}}) \) is chosen such that \( t_{\text{max}} \sim \tau_1 \) then \( \mu_2 t^2 / 2! \ll 1 \) for all \( t \) and that term may be neglected. This is substantiated through a cumulants analysis of the data (Appendix A) where \( \mu_2 \) has typical values of \( 5 \times 10^4 \) for sample times of \( 1.5 \mu s \) yielding \( \mu_2 t_{\text{max}} / 2! \sim 10^{-4} \). After removing the center-of-mass mode from equation (22) as well as setting the \( \mu_2 \) term equal to zero, one arrives at the following expression:
020587, Theta = 100 Degrees

Figure 6. Electric Field ACF
\[
A\langle I_1 \rangle + A\langle I_2 \rangle - |G^{(1)}(t)| e^{\bar{r}_1 t} = A\langle I_2 \rangle (1 - \\
- e^{(\bar{r}_1 - \bar{r}_2)t} (1 + \frac{\bar{r}_2^2 t^2}{2!}) = H(t)
\]  \hspace{1cm} (23a)

\[
H(t) = |G^{(1)}(0)| - |G^{(1)}(t)| e^{\bar{r}_1 t}
\]  \hspace{1cm} (23b)

Note that since all of the left hand terms in equation (23a) may be experimentally determined, the numerical fit now requires only three fit parameters instead of five as in equation (22). This reduction allowed us to focus on intracoil dynamic behavior and enabled the curve fitting programme to both more efficiently and accurately determine the best numerical fit to the experimental data. Various plots of \(H(t)\) from the experimental data may be found in Appendix C.

From equation (23), \(|G^{(1)}(t)|\) may be obtained from the data (intensity ACF functions) by

\[
|G^{(1)}(t)| = (G^{(2)}(t) - \text{baseline})^{1/2}, \quad \text{with} \quad (24a)
\]

\[
G^{(2)}(t) = \langle I(t) I(0) \rangle, \quad \text{the intensity ACF.} \quad (24b)
\]

Equation (24a) is more commonly known as the Siegert relation.\textsuperscript{30} \(\Gamma_1 = D_1 q^2\) may be obtained from low angle (single mode) measurements. \(A\langle I_1 \rangle + A\langle I_2 \rangle\) may be obtained through fitting the first 10-15 points of \(|G^{(1)}(t)|\) by a non-linear least squares program to a quadratic equation of the form
\[ G^{(1)}(t) = A\langle I_1 \rangle + A\langle I_2 \rangle - (A\langle I_1 \rangle \bar{\tau}_1 + A\langle I_2 \rangle \bar{\tau}_2) t + \]
\[ + \left[ A\langle I_1 \rangle \bar{\tau}_1^2 + A\langle I_2 \rangle \left( \bar{\tau}_2 + \mu^2 \right) \right] t^2 \]

of which the intercept should yield \( A\langle I_1 \rangle + A\langle I_2 \rangle \).
Endnotes


6 Bruce J. Berne and Robert Pecora, *ibid.*, 12

7 Bruce J. Berne and Robert Pecora, *ibid.*, 228

8 Bruce J. Berne and Robert Pecora, *ibid.*, 59

9 Bruce J. Berne and Robert Pecora, *ibid.*, 13

10 Bruce J. Berne and Robert Pecora, *ibid.*, 11

11 Bruce J. Berne and Robert Pecora, *ibid.*, 13

12 Bruce J. Berne and Robert Pecora, *ibid.*, 187

13 Bruce J. Berne and Robert Pecora, *ibid.*, 184

14 Bruce J. Berne and Robert Pecora, *ibid.*, 187

15 Bruce J. Berne and Robert Pecora, *ibid.*, 69

16 Bruce J. Berne and Robert Pecora, *ibid.*, 184

17 Bruce J. Berne and Robert Pecora, *ibid.*, 185

18 Bruce J. Berne and Robert Pecora, *ibid.*, 92


21 Bruce J. Berne and Robert Pecora, *ibid.*, 182

22 Alfred Rudin, *ibid.*, 92

24 Alfred Rudin, ibid., 48

25 Alfred Rudin, ibid., 45

26 Alfred Rudin, ibid., 54


29 As developed by Dr. Selser, U.N.L.V., 1987

Apparatus

Optical System

A schematic of the experimental set-up, including the optical system, may be found in Figure 7. A description of the set-up and the placement of the components now follows.

There were two lasers used in this experiment, a Krypton ion and an Argon ion laser. By employing these two lasers, the range of wavelengths used was from 6471 to 4579 Angstroms.

The output of the Krypton ion laser may be remotely monitored by a Newport Research model 815 Power Meter through the use of a beam splitter placed directly in front of the laser head and stopping aperture. This was not required for the Argon ion laser in that the output was monitored on a remote control unit, with the photodetector located inside the laser head.

Neutral density filters were next used in the optical path. These filters were used to control the intensity of the light going into the sample cell during an experimental run.

Next in line is a polarization rotator that is set so that the incident laser light is vertically polarized. In addition a polarizer is further used to insure that the light is truly vertically polarized.

An aperture stop is now placed in front of the
Figure 7. Laser Light Scattering System
focusing lens in the optical train to prevent back and forth reflections and to help insure that no reflections from the surface of the lens may be reflected back into the laser head. The focusing lens is used to focus the laser light directly onto the sample cell (the thermostatted sample cell will be discussed in detail later).

Another aperture stop is next found in front of the collection lens. This lens is so placed that its focal point is located at the scattering region in the sample cell. In this way, the scattered light detected originates in the center of the scattering volume.

Following this lens is an analyzer to insure that the scattered light detected is also vertically polarized. This VV scattering geometry is chosen so that our results may be directly compared with theory,\textsuperscript{32} and to other groups, most of whom employ VV scattering in their measurements.

Next is found a bandpass filter selected to pass light at the laser line wavelength which further helps to increase the signal to noise ratio of our data.

Following the bandpass filter is a spatial filter which is placed such that only the scattered light coming from the scattering volume in the sample cell will be detected. Since stray scattered light from the other regions is rejected, the result is again an increase in the signal to noise ratio of the data.

Lastly, an adjustable relay lens is placed in the
photomultiplier assembly such that the scattered light is focused onto the photocathode of the photomultiplier tube.

**Sample Cell Assembly**

The sample cell assembly consists of a bakelite insulating cylinder which permits the cylindrical sample cell to be inserted through the top. The cell rests in a glycerin bath which acts as an index matching fluid to reduce any reflections from the outside surface of the cell. These reflections may cause heterodyning with the incoming light, distorting the ACF as well as creating excessive stray light ("flare"), drastically degrading the signal to noise of our data.

The temperature of the flow-through sample cell assembly is controlled by a temperature controlled circulating bath. This device controls the temperature of the sample cell to within about 0.01 C. Monitoring of this temperature at the sample is done by way of inserting a calibrated probe thermistor along the sample cell inside the index matching liquid. From the prior calibration of the resistance of the thermistor, the temperature of the bath is monitored by measuring the thermometer resistance using a digital multimeter.

**Goniometer**

The sample cell assembly forms the center part of the goniometer. A goniometer is a device in which a series of optics may be placed upon a rotatable arm and
rotated very accurately to various angles. In this way the detection optics may be manually placed at any angle in the horizontal plane from 20 to 137 degrees with a nominal accuracy of 0.05 degrees. The scattered light is then detected at various scattering angles and therefore at various q values.

Detector

The scattered light is detected by a photomultiplier tube whose sensitivity reaches into the ultraviolet. The photocathode of this tube has a very small cross-section (14 mill diameter) to help reduce the room temperature dark counts to less than 1 per second. Due to the small photocathode area, the relay lens must be employed to focus the scattered light onto the photocathode. Once a signal is detected, it is sent by a short, well shielded cable to the amplifier/discriminator where it is converted to a logic pulse. A train of robust, noise insensitive logic pulses is then sent to the autocorrelator.

Autocorrelator

The correlator employed is a digital high-speed signal processor which calculates the autocorrelation function of the pulse train signal in real time (during the experiment) and then displays it in graphical form on a monitor. The correlator used was a Brookhaven Instruments model BI-2030 and may also be used to calculate cross-correlation functions or may be used as a
signal averager. The correlator had 136 channels or bins, of which the last 8 are delayed for calculations of the baseline. In addition to baseline calculations, the average decay constant of one exponential and polydispersity of the sample, at low q (θ), are calculated. By monitoring the development of the autocorrelation function on the monitor and the results of the method of cumulants, one can evaluate the quality of the data while the experiment is still in progress.

In principle, the digital autocorrelator works as follows. There are three registers which are chiefly involved in generating an autocorrelation function: a shift register, a parallel register and a buffer. Consider the correlator to be set at a sample time of 1 microsecond and the shift register already filled. After 1 microsecond, the photon counts are placed in the first bin of the shift register and all other previous counts are shifted over one bin (the original counts in the last bin being lost). The photon counts in the first bin are also placed in all the bins of the parallel register. Next, the product is taken of the contents of corresponding bins in the shift and parallel registers and placed in the appropriate bins in the buffer. This forms the first 128 channel correlation function. After the second microsecond, the process is repeated and the buffer update results in a second 128 point correlation function that is averaged with the first.
By waiting for a long enough time, the correlation functions will be "built-up enough" to yield an averaged correlation function with good signal-to-noise in the buffer.
Endnotes

31 The optical system was developed by Dr. Selser, U.N.L.V.

Experimental Method and Analysis

Sample Preparation

The polymer used in these experiments was $8.42 \times 10^6$ molecular weight polystyrene with a polydispersity of 1.17 manufactured by the Toya Soda Company, Inc., Tokyo, Japan. Each sample was weighed on an electronic balance to within 0.01 milligrams. The samples are then added to the solvent, Burdick and Jackson spectrophotometric grade (distilled in glass) cyclohexane or toluene, to a solution volume of 25 or 50 ml. Toluene samples were prepared at 30°C while cyclohexane samples were prepared at 50°C. The sample flasks are then placed in an oven and maintained at 50°C or 30°C, occasionally being slowly swirled to aid in the dissolving of the polymer. If instead the flasks had been vigorously shaken there would have been danger of the polymer chains breaking, resulting in both increased polydispersity and changing molecular weight. The polymer was allowed one week to dissolve. A summary of the sample weights used for various experiments follows on the next page.

Low Angle Measurements

In order to factor out the center-of-mass decay
Table 1. The following is a list of the sample weights used in this study. Uncertainty in these values were typically $\pm 0.02\text{mg}$.

<table>
<thead>
<tr>
<th>Date</th>
<th>Cyclohexane</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nov. 21, 22</td>
<td>31.78 mg.</td>
<td>October 29</td>
</tr>
<tr>
<td>July 16, 17</td>
<td>12.98 mg.</td>
<td>Aug. 17, 18</td>
</tr>
<tr>
<td>February 5</td>
<td>25.76 mg.</td>
<td></td>
</tr>
</tbody>
</table>
mode, one must measure the ACF function at low angle (x<<1). In this regime only the center-of-mass motions will be detectable and the ACF functions will be comprised of only one exponential.

Also, the diffusion coefficient at infinite dilution $D_\infty$ must be determined for the theoretical expression to directly calculate $\tau_1$ and to compare this value of $D_\infty$ for the polystyrene solution with other groups. This is done to verify that the given $M_*$ by the manufacturer was correct. By determining $D(C)$ at a certain concentration from $\bar{\tau}_1$ as obtained from the cumulants analysis from the autocorrelator, a graph of $D(C)$ versus concentration $C$ may be made. The extrapolated intercept at zero concentration yields $D_\infty$.

It is predicted that $D(C)$ should vary linearly with concentration by the form $D(C) = D_\infty (1 + K_d C)$ where $D_\infty$ is the diffusion coefficient at infinite dilution, $K_d$ is the polymer-polymer interaction parameter and $C$ is the polymer concentration in solution. The interaction parameter $K_d$ is a measure of the influence of the solvent and other polymers on the diffusion of any given polymer coil. Measurements of $D(C)$ for 8 different concentrations of polystyrene in cyclohexane were made on November 20 and 21, 1986. These concentrations varied from 0.583 mg./ml. to 0.032 mg./ml. at a temperature of 35°C.
After alignment of the optical system the goniometer was manually set at a scattering angle of 20 degrees. A neutral density filter was employed to prevent the correlator from overflowing.

The correlator was then set at a sample time of 75 microseconds and the 128 ACF data points with the additional 8 baseline ACF points were measured.

The criterion by which it is decided that enough data has been taken to yield a high signal to noise ratio is first done visually by inspecting the ACF functions on the correlator monitor. After the ACF's have decayed by four e-folds (by a factor of \((1/e)^4\)) and are smooth, it is judged that sufficient time has passed collecting data.

A cumulants analysis is then performed on the data and an independently calculated baseline is compared to the measured baseline from the 8 delayed channels. If the difference is less than 0.1\%, the set of data is then accepted. For a discussion of the cumulants analysis see Appendix A. The average decay constant \(\tilde{\tau}_1\) of the first (center-of-mass or CM) decay mode (exponential) in addition to the ratio of its square to the polydispersity per time squared \(\delta_z = \mu_z/\tilde{\tau}_1^2\) is also obtained.\(^{29}\) This is more commonly termed the quality parameter. Typical values of \(\delta_z\) are 0.05 \(\pm\) 0.05. The measurements are repeated 8 times for each of the 8
concentrations.

From the decay mode $I_1 = \tilde{D} \xi^2$ at each concentration, $\tilde{D}(c)$ may be obtained. A plot of $\tilde{D}(C)$ versus $C$ for polystyrene in cyclohexane at $35^\circ C$ may be seen in Figure 8. A linear least squares fit of this straight line yields

$$\tilde{D} = (4.53 \pm 0.02) \times 10^{-8} - (3.74 \pm 0.54) \times 10^{-6} C$$

in units of cm$^2$/sec with a correlation coefficient of $0.943$. The concentration $C$ has units of g/ml.

Note that the correlation coefficient for lines with small slopes is not very accurate since the expression for determining the slope by least squares analysis appears in the numerator of the expression for the correlation coefficient. It is therefore theoretically possible that a perfectly straight line with zero slope would have a correlation coefficient of zero. This is clearly misleading and indicates that caution should be exercised when interpreting this statistic, as is the case for the plot in Figure 8.

Comparison of our $D(c)$ versus $C$ curve for polystyrene in cyclohexane at $35^\circ C$ (theta temperature) compares very favorably with previous literature. Specifically, Jones and Carolline have obtained the relation

...
Figure 8. $D$ vs. $C$ for Toluene and Cyclohexane
\[ D_0 = (1.4 \pm 0.2) \times 10^{-4} \ M_w^{-(0.508 \pm 0.007)} \]

which for our polymer of \( M_w = 8.42 \times 10^6 \) yields a value of \( D_0 = 4.35 \times 10^{-6} \) \( \text{cm}^2/\text{sec} \). Our value of \( 4.53 \times 10^{-6} \) \( \text{cm}^2/\text{sec} \) is only 4% higher than this. King et al\(^3\) obtained a value of \( 4.17 \times 10^{-6} \) \( \text{cm}^2/\text{sec} \) for \( D_0 \) of a polymer of the same size as our sample. This value is 4% lower than ours so it can be seen that our value of \( D_0 \) in cyclohexane agrees well with what has been previously found.

The negative slope as may be seen from Figure 8 indicates a poor solvent (\( K_\theta < 0 \)). By poor solvent it is meant that segments of the macromolecule are more likely to stay near other segments rather than moving towards solvent molecules. The result of this is that the polymer chain tends to contract. However, since cyclohexane is a theta solvent, the attraction of a specific chain segment to the solvent is exactly balanced by its attraction to other chain segments resulting in a Gaussian distributed cross-section of the polymer as a whole.

In the case of a good solvent like toluene at 30°C, the polymer segments tend to move more towards the solvent molecules than other polymer segments. This results in a more swollen macromolecule with larger hydrodynamic radius.
The $K_b D_o$ (slope) as a result should tend to be positive for a good solvent, as can be seen by the other curve in Figure 8. It is expected from theory that the effect of solvent quality on $\tau_i$ for good solvent will differ from that of poor. In view of this it was decided to use both solvents (cyclohexane and toluene) to attempt to measure this difference.

From a linear fit to the rising curve in Figure 8 the diffusion coefficient at zero concentration $D_o$ in toluene at 30°C was $4.13 \times 10^{-8}$ cm$^2$/sec. In comparison with the results found by Appelt and Meyerhof (after corrections for temperature and solvent viscosity differences)

$$D_o = 4.22 \times 10^{-4} M_o^{-0.0577} \text{ cm}^2/\text{sec}$$

which for our molecular weight of $8.42 \times 10^{-6}$ yields a value of $D_o = 4.26 \times 10^{-8}$ cm$^2$/sec. This is only 3% higher than our result, again being in excellent agreement with previous literature.

Since the hydrodynamic radius $R_h$ is inversely proportional to $D$, the lower $D_o$ for toluene indicates a more swollen macromolecule in toluene than in cyclohexane. The exact relation between $R_h$ and $D$ is the Stokes–Einstein relation, $R_h = k_B T/6\pi \eta_o D_o$, where $k_B$ is Boltzmann's constant, $T$ is the temperature of the sol-
vent in degrees Kelvin and $\eta_0$ is the solvent viscosity in Poise.

For cyclohexane with an $\eta_0$ of 0.764 cP and a temperature of 308 Kelvin, one obtains an $R_h$ of 653 Å. This value is 1.7% lower than that found by Schmidt and Burchard. For the polymer in toluene with a solvent viscosity of 0.525 cP and a temperature of 303 Kelvin the $R_h$ is 1024 Å. It can then be seen that the polymer is larger in toluene than in cyclohexane by approximately 40%.

From the agreement between our $\tilde{D}_n$ in both cyclohexane and toluene to the previous research of other groups, we can confidently compare the values of $D(C)$ from the aforementioned curves to that of other low angle measurements at specific concentrations. In this way we can verify whether $\tilde{D}_1$ (from $\tilde{\gamma}_1 = \tilde{D}_1 q^2$) has been accurately determined or not.

A least squares linear fit for the cyclohexane master curve results in

$$\tilde{D}(C) = (4.13 \pm 0.05) \times 10^{-8} - (3.74 \pm 0.54) \times 10^{-9} C$$

and for the toluene master curve

$$\tilde{D}(C) = (4.54 \pm 0.05) \times 10^{-8} + (3.02 \pm 0.41) \times 10^{-8} C.$$

Comparison between the $\tilde{D}(C)$ results from the various dates low angle measurements and the interpolated
master curve values for cyclohexane and toluene results may be found in Table 2 on the next page. From the low percent differences between the low angle measurements of $\tilde{D}(C)$ and the master curve results for both toluene and cyclohexane, it was concluded that the determinations of $\tilde{D}(C)$ were accurate and could be used in the high angle studies with confidence. Upon having determined $\tilde{r}_1$, the next higher mode $\tilde{r}_2$ containing information about the first relaxation mode may now be found through analyzing data taken at a series of higher angles.

**Multi-Angle Measurements**

By "high" angle measurements it is meant that scattering at angles for 40 to 120 degrees ($q = 1.7$ to $3.6 \times 10^3$) will be measured. The higher the scattering angle, the more contributions from the internal modes will be observed relative to the first (center-of-mass) mode in the $\text{ACF}$. For a more complete discussion of this please refer back to equation 11b on page 20.

For both of the cases, for the polymer in toluene or cyclohexane, the correlator was set at a sample time of 1.5 $\mu$s for each of the different measurements at different angles. The nine angles used ranged from 40 to 120 degrees by increments of 10 degrees. The data from each ACF run or trial at a specific angle was sent from the correlator to an Apple IIe computer or sent via
Table 2. A comparison of the experimental values of $D(C)$ to the interpolated values from the calibration curves (master curves) for the polymer in each solvent is presented.

<table>
<thead>
<tr>
<th>Date</th>
<th>Solvent</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>February 5</td>
<td>Cyclohexane</td>
<td>3</td>
</tr>
<tr>
<td>July 16</td>
<td>Cyclohexane</td>
<td>3</td>
</tr>
<tr>
<td>July 17</td>
<td>Cyclohexane</td>
<td>1</td>
</tr>
<tr>
<td>August 17</td>
<td>Toluene</td>
<td>0.4</td>
</tr>
<tr>
<td>August 18</td>
<td>Toluene</td>
<td>1</td>
</tr>
</tbody>
</table>
Hayes micromodem to the UNLV host Cyber 830 computer.

The criterion for "sufficiently" good data during a specific run was determined through two means. First, by a visual inspection of the S/N of the decaying ACF (reduced approximately by a factor of \((1/e)^4\)) and second by comparing the measured baseline (8 delayed correlator channels) to the calculated baseline. If the measured baseline was within 0.1\% of the calculated baseline, then the data was accepted. This criterion was achieved for a vast majority of all measurements. Dust contamination was most likely the source of the occasional discrepancy between the baselines as the integrity of the polymer was well supported by the excellent agreement with the diffusion coefficient \(D_0\) and the master curve interpolated values. In view of this, it can also be concluded that ultra-centrifugation is not required as the technique to remove "dust" while carefully filtering does work well, at least for this polymer.

Each of the nine series of scattering angles for both good and poor solvent solutions were repeated thrice with two different wavelengths; 5145 Å and 4579 Å. Since the scattering vector \(\bar{q}\) is a function of inverse wavelength, we could essentially double our data for the specified range of angles. Also, in going to a shorter wavelength we could extend the range of the \(x\) parameter to \(x^{-32}\), considerably farther than most
researchers to date. This is important in that the effect of higher modes may be observed, although all of our fits were originally designed to only include the longest wavelength mode.

In the next section the numerical analysis of the data obtained at the higher angles to evaluate the $q$ dependence of the ACF decay constant for the internal modes as well as the interpolated value of the relaxation time of the first internal mode will be discussed.
Endnotes


35 Yoshisuke Tsunashima, Norio Nemoto, Michio Kurata, Macro., 16, 584-589 (1983)

36 Bernd Appelt and Gunther Meyerhoff, Macro., 13, 657-662 (1980)

37 Manfred Schmidt and Walter Burchard, Macro., 14, 210-211 (1981)

38 Angelo Perico, Paolo Piaggio, Carla Cuniberti, J. of Chem. Phys., 62(7), 2690-2695 (1973)
Numerical Analysis

In order to reduce the number of fit parameters in equation (23) to extract \( \Gamma_2 - \Gamma_1 \) (which contains information about \( \tau_1 \) and the \( q \) dependence of the ACF) more easily, the amplitudes \( A<\sigma_1> + A<\sigma_2> \) may be determined by fitting the ACF by an equation of the form as in equation (25) in the theory section by a least squares quadratic fit.

By fitting the first ten to fifteen points of \(|G^{(1)}(t)|\) versus time from the data collected from the autocorrelator, the weighted average of the intercepts of the six fits should yield the value of \( A<\sigma_1> + A<\sigma_2> \). The weighting was done with the correlation coefficients for each quadratic fit. Typical values of the average uncertainty in the intercept from the fits is 0.5% and values of the correlation coefficient were consistently at or above 0.99. From this one can see that a quadratic fit for the first ten to fifteen points of the electric field ACF \(|G^{(1)}(t)|\) yields reliable values for the intercept, \( A<\sigma_1> + A<\sigma_2> \).

Upon forming the product of the reciprocal of the first mode \( e^{\Gamma_1 t} \) (from low angle measurements) with \(|G^{(1)}(t)|\) and subtracting from \( A<\sigma_1> + A<\sigma_2> \), one can
fit the following function to yield

\[ H(t) = A < I_1 > + A < I_2 > - \left| \mathcal{G}^{(1)}(t) \right| e^{-\frac{r}{2}} \]

\[ = A < I_2 > \left[ 1 - e^{-\left( r_2 - r_1 \right)^2} \right] \left( 1 + \frac{\mu_2 t^2}{2} \right) \]

By the use of NLLSQ 1.4, a nonlinear least squares program run on the Apple IIe, it was attempted to fit the above function. When this was done, inconsistent and even negative values of \( \mu_2 \) were obtained. Since \( \mu_2 \) is related to the polydispersity of the sample by

\[ \mu_2 = \sum_i < I_i > \left( r_i - \bar{r}_2 \right)^2 / < I >_2 \quad (26) \]

it is clearly impossible for \( \mu_2 \) to be negative.

In view of this, it was assumed that the function \( \mu_2 \sim 0 \) and the simpler function of

\[ H(t) = A < I_2 > \left( 1 - e^{-\left( r_2 - r_1 \right)^2} \right) \quad (27) \]

was attempted. The multi-exponential program Discrete was also employed to fit this function since the program employs a much more sophisticated algorithm to determine convergence to a solution than NLLSQ 1.4. The program Discrete was also run on the Cyber 830, which was much faster than the Apple IIe.

Unfortunately, since Discrete fits only a series of exponentials, equation (27) had to be fit in the form
For the data from cyclohexane for the date of February 5, percent differences between $C_i$ and $-C_z$ were not larger than 5% and were typically lower than this. For the dates July 16, 17 the percent differences were lower than 3%.

For the polymer in toluene, the percent differences between $C_i$ and $-C_z$ were below 2%. Thus it can be seen that from comparing $C_i$ and $-C_z$ in both toluene and cyclohexane that the fitting function is most likely the correct one, at least in terms of the coefficients.

By using the average of $C_i$ and $-C_z$ and $\bar{r}_2 - \bar{r}_1$ from the fit by Discrete, the quality of the fit at various angles may be ascertained graphically from the plots of the data in Appendix C. As can be seen, the different fits to the data worked well throughout the range of data from $40^\circ$ to $120^\circ$ with the exception of an anomalously bad fit at $50^\circ$. The fit for this angle appears to be too low ($A<I_2>$ is too low), decaying more rapidly than the data. At all of the other angles all of the fits fall near the noise level of the data.
Typical standard deviations of the various fits were near 0.2, again indicating good fits.

The above analysis was repeated for both cyclohexane and toluene with NLLSQ 1.4 as a test of the program Discrete. Values of $A\langle I_1 \rangle + A\langle I_2 \rangle$ and $\bar{\tau}_2 - \bar{\tau}_1$ typically agreed to within $\pm 5\%$ between Discrete and NLLSQ 1.4. In addition, both programs were extensively tested with synthetic data including noise $\pm |G(1)\{t\}|^{-0.5}$ added or subtracted depending on the results of a random number generator. Both programs correctly fit the test function, the program Discrete to within 5\% and NLLSQ 1.4 to within 7\%. In view of the greater accuracy of the results from Discrete, these were the values further used in the analysis to determine $\bar{\tau}_1$.

From the decay parameters $\bar{\tau}_2 - \bar{\tau}_1$ from the fits at various angles (or scattering vector amplitudes $q$), the longest internal mode relaxation time may be determined. Recalling that $\bar{\tau}_1 = \bar{D}_1 q^2$ and $\bar{\tau}_2 = \bar{D}_2 q^2 + 2/\bar{\tau}_1$, one can form the difference

$$\bar{\tau}_2 - \bar{\tau}_1 = (\bar{D}_2 - \bar{D}_1) q^2 + 2/\bar{\tau}_1.$$  

This difference will henceforth be termed Delta Gamma. Since these fits were made with the approximation of negligible polydispersity, $\bar{D}_2 \sim \bar{D}_1$ results in $\bar{\tau}_2 - \bar{\tau}_1 = 2/\bar{\tau}_1$. This would be true only if the first two modes
alone were observed at all measured values of $q$ (angle). However, as the scattering angle increases ($q$ increases), higher modes than the first two ($\Gamma_3, \Gamma_4$, etc.) begin to become significant and can no longer be neglected.

Since Discrete was used only to determine the additional decay of the ACF not due to $\Gamma_1$, the experimental values of $\Gamma_2$ are really weighted average decay constants due to all of the decay modes. The weighting is due to the differing amounts of light scattering intensity from each mode. Fortunately, all modes $\Gamma_n$ contain the center-of-mass term $D_n q^2$ which for very low polydispersity results in $D_n \sim D_1$ for all modes.$^{39}$

The light scattering intensities decrease rapidly with each successive mode at a specific angle and $x$.$^{40}$ In view of this $\Gamma_2$ may be rewritten as $\Gamma_2 = D_2 q^2 + 2/\tau_1 + A q^n$ where the last term is a collective term of all higher modes than $\Gamma_2$, having an average $q^n$ dependence and average amplitude $A$.

The effect of modifying $\Gamma_2$ upon Delta Gamma is that there is now $q$ dependence even with zero polydispersity

$$\Gamma_2 - \Gamma_1 = \frac{2}{\tau_1} + A q^n$$

From this equation for Delta Gamma it can be seen that if the proper $q$ dependence ($n$) is chosen, a plot of
Delta Gamma versus \( q^n \) should yield the proper fit. The y-intercept from the fitting curve would also yield \( 2/\tau_1 \).

Several different powers were chosen \( (n = 2, 3, 4) \) to fit the data. For the polymer in cyclohexane it was found that a best fit was obtained for \( q^2 \) dependence (see Figure 9). Ideally, there should be only one curve to represent the data taken on Feb. 5 and July 16, 17. However, since the quality of the data for Feb. 5 is much better than for that of July 16, 17 (as is evidenced by the smaller amount of scatter in the data and smaller error bars), separate curves were plotted for each data set.

The plot for Feb. 5 had the best fitting equation of
\[
\Gamma_2 - \Gamma_1 = (5870 \pm 240) + (621 \pm 43) \times 10^{10} q^2
\]
with a correlation coefficient of 0.99. The y-intercept of this curve yields a value of 341 \( \pm 14 \mu s \) for \( \tau_1 \). The results from the July 16, 17 plot yield a value of 348 \( \pm 29 \mu s \) for \( \tau_1 \) with the equation of the curve being
\[
\Gamma_2 - \Gamma_1 = (5755 \pm 482) + (463 \pm 73) \times 10^{10} q^2
\]
with a correlation coefficient of 0.91. Clearly the fit for the set of data from July 16, 17 are not as good as for Feb. 5. The y-intercepts do, however, agree very
Figure 9. ΔΓ versus $q^2$ in Cyclohexane

ΔΓ versus $q^2$ in Cyclohexane

Figure 9. Delta Gamma vs $q^2$ For Cyclohexane
closely.

The weighted average of τ₁ using the fit uncertainties yields a mean value of 343 μs. The value as predicted by the Zimm model with pre-averaged hydrodynamic interactions (the influence of one coil segment upon another via the solvent) is 228 μs and without is 473μs. These values are 28% lower and 49% higher respectively, fairly well bracketing our result. In addition it is predicted that for a polymer in poor solvent the decay modes of the ACF should exhibit q³ dependence. By a poor, non-free draining solvent it is meant that within the polymer coil the solvent is not free to stream through the polymer chain and as a result moves with the macromolecule throughout the solvent. This is not what we have found; we obtained q² dependence.

For the polymer in toluene from the dates Aug. 17, 18 (see Figure 10), q⁴ dependence has been determined (although q³ dependence is nearly as good a fit in relation to the similar values for the correlation coefficients for each plot). From the plot in Figure 10;

\[ \Gamma_2 - \Gamma_1 = (9298 \pm 134) + (51.9 \pm 2.4) \times 10^2 q^4 \]

with a correlation coefficient of 0.986. The y-intercept from this fit gives a value of 215 μs for τ₁.

The prediction for the Rouse bead-and-spring model
ΔΓ versus q⁴ in Toluene

Figure 10. Delta Gamma vs. q⁴ For Toluene
is for q dependence and a value of 1256 µs for τ₁.
Clearly this is consistent with our q results as would be expected since toluene is a good solvent (free draining) and Rouse's model applies to good solvents. For good solvents with free draining the solvent molecules are able to pass through the polymer coil and are not restricted to move with the polymer through the surrounding solvent molecules as for non-free draining. Our τ₁ value of 215 µs is not consistent with this model, however.

As a check on the q dependence in the two solvents (q² and q⁴), ln-ln plots were made. More specifically, ln(Δτ - 2/τ₁) versus ln(q) plots were made for each set of data using the values of 2/τ₁ as obtained from the fits. The slope of such a graph should yield the q dependence.

For the ln-ln plot for Feb. 5 (see Figure 11), a slope of 1.95 ± 0.11 was obtained from a straight line curve with a correlation coefficient of 0.993. A similar plot for July 16, 17 (see Figure 12) yielded a slope of 1.98 ± 0.3 with a correlation coefficient of 0.918. From these plots a weighted average slope of 1.96 ± 0.02 is obtained.

A similar ln-ln plot was made for the toluene data. Using the 2/τ₁ value from the q curves intercept, a straight line was obtained with a slope of 3.86 ± 0.24
Figure 11. **Ln Plot For Cyclohexane (February 5)**

**Polystyrene in Cyclohexane: Feb. 5**
Figure 12. Ln Plot For Toluene (July 16, 17)
Polystyrene in Toluene: Aug. 17, 18 ($q^4$)

Figure 13. $\ln$ Plot For Toluene (August 17, 18) Using The $q^4$ Plot Value of $\tau_1$
and a correlation coefficient of 0.983 (see Figure 13).

If the value of $2/\tau_1$ was used from the $q^3$ plot, a slope of 2.4 is obtained with a correlation coefficient of 0.956. As can be seen from Figure 14, there is much more scatter in the data for this curve than for that from the $q^4$ plot.

In consideration of the much better straight line fit of the ln-ln plot using the intercept from the $q^4$ curve, the most likely $q$ dependence of the ACF in toluene is $q^{3.88}$ or rounded off to an integer, $q^4$. 
Figure 14. Ln Plot For Toluene (August 17, 18) Using The $q^3$ Plot Value of $T_i$. 

Polystyrene in Toluene: Aug. 17, 18 ($q^3$)
Endnotes


Discussion of Results

In summary our results for $\tau_1$ and the $q$ dependence in toluene and cyclohexane may be found in Table 3.

In comparing our results in cyclohexane and toluene to other groups, one finds a wide variation in published findings for both good and poor solvents.

Most theoretical papers dealing with the $q$ dependence of the ACF modes also have variation, depending upon the conditions set for the specific model used.

P.G. de Gennes and Dubois-Violette\textsuperscript{43} have found that for poor solvents there should be $q^3$ dependence. If the further condition that the solvent molecules cannot occupy the same space as polymer segments is applied (excluded volume) then the dependence becomes $q^{9/3}$.

In perfectly good solvents where there are no hydrodynamic interactions, P.G. de Gennes has found that there should be $q^4$ dependence (Rouse limit).\textsuperscript{44} By hydrodynamic interactions it is meant that:

- a) the motion of a polymer segment relative to the solvent creates a backflow which reacts on other segments,

- b) there is direct friction between segments of the polymer chain.
Table 3. The following is a summary of our experimental results in comparison to various Rouse-Zimm models. The results for cyclohexane are compared to both the non-free-draining model with and without pre-averaged hydrodynamic interactions. The free-draining model without hydrodynamic interactions is compared to the result in toluene.

<table>
<thead>
<tr>
<th></th>
<th>Cyclohexane</th>
<th>Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{1 \text{ RZ}}$ pre-averaged hydr. inter.</td>
<td>228 $\mu$s</td>
<td></td>
</tr>
<tr>
<td>$\tau_{1 \text{ RZ}}$ without pre-av. hydr. inter.</td>
<td>473 $\mu$s</td>
<td></td>
</tr>
<tr>
<td>$\tau_{1 \text{ R}}$ without hydro. inter.</td>
<td>215 $\mu$s</td>
<td></td>
</tr>
<tr>
<td>$q^n$ dependence (experimental)</td>
<td>$q^{1.96}$</td>
<td>$q^{3.86}$</td>
</tr>
</tbody>
</table>
Silbey and Deutch have also analyzed the $q$ dependence in perfectly poor solvents with excluded volume and have determined a $q^{16/5}$ dependence. They further state in their paper that they believe that the difference between $q^3$ and $q^4$ will not be experimentally dramatic. This is in general what we have observed in a good solvent (toluene) in that the differences in the qualities of the two fits, $q^3$ and $q^4$, were slight. Note that $q^3$ and $q^4$ dependences are limiting cases for perfectly non-free-draining and perfectly free-draining. Any dependence between $q^3$ and $q^4$ should therefore be termed "partially" free-draining.

Saleh and Hendrix have numerically tested the bead and spring model with no hydrodynamic interactions and with the inclusion of polydispersity. They have found that there should be $q^4$ dependence for perfectly free-draining and that the effect of polydispersity on the extraction of $\tau_1$ is negligible. In their studies, for $\bar{M}_n/\bar{M}_w = 1.67$ they found a 7% discrepancy between $\tau_1$ from among the polydisperse model and the monodisperse model at an angle such that $x = 30$. For lower angles, the discrepancy was found to be even less.

This further supports our assertion that the approximations of $D_n = D_1^{(1)}$, $\mu_2^{(1)} = 0$ and $\mu_2^{(2)} = 0$ were valid in the numerical analysis of the data.

Jones and Caroline have experimentally studied
polystyrene in cyclohexane at 35°C and have found for
the molecular dependence of $\tau_1$

$$\tau_1 = (7.7 \pm 0.3) \times 10^{-8} \text{ M}^{-1.42 \pm 0.05}$$

For our polymer this turns out to be 525 µs; this is 53% higher than our results.

The range of angles used were only up to $x \leq 3$, a very limited range. This was done to reduce the effect of higher modes than $\Gamma_2$. For this range, they found that Delta Gamma is independent of $q^2$.

The data obtained through these different angles was fit to a four parameter fit of the form

$$g^{(2)}(t) = 1 + e^{-2D\Gamma_{q^2}t} \left( a + b e^{-\Gamma_{\tau_1}t} \right)^2 + \delta$$

where $g^{(2)}(t)$ is the normalized intensity ACF, $a$, $b$ and $\delta$ are constants. $D$ was previously determined from $\Gamma_1$ for $x\ll1$. Furthermore, was arbitrarily adjusted to improve the quality of the fit (a questionable procedure at best). The data collected for this fit was from a 48 channel correlator, with roughly 1/3 the capacity of our correlator.

Another group, Hendrix, Saleh, Gnagig and Maeyer has also looked at polystyrene in cyclohexane at 35°C and in toluene. They have found that $\tau_1$ agrees well with the NFD (non-free-draining) model although the numerical value of $\tau_1$ is not stated in the paper. The
numerical analysis appears to be similar to ours. They do find $q^2$ dependence in the data from a plot of $1/T_1$ vs. $\sin^2 \theta/2$ (where it is assumed that there is only one internal mode present) for small $x$ but their curve flattens out at higher values of $x$. It is not stated what they mean by small $x$, although usually this means that $x<2$.

From the analysis in toluene it was found that $T_1$ was 0.4 times lower than predicted by the FD model and that the $q$ dependence was greater than $q^2$. Our value of $T_1$ by comparison is 0.17 times that predicted by the FD model. The exact value of the $q$ dependence was not stated in the paper, however.

Wu-Nan Huang and J.E. Frederick have looked at a high molecular weight ($27.3 \times 10^6$) polystyrene in both cyclohexane and 2-butanone, a marginal solvent. The intensity ACF's that they obtained through homodyne light scattering were analyzed by a three exponential fit,

$$C(t) = A_2 e^{-2 D q^2 t} + B_2 e^{-\frac{2}{2/T_1} (q^2 D + 2/T_1) t} + 2ABe^{-\left(2 q^2 D + 2/T_1\right) t}$$

where $A$ is the intensity of the translational component and $B$ is the intensity due to the first internal mode.

Upon extracting $T_1$ from the above fit for data from 2-butanone and cyclohexane, they have also found that $T_1$
in 2-butanone is lower than in cyclohexane.

In extracting $\tau_1$ directly from the fit at various angles and averaging the value obtained, no explicit analysis to determine the specific $q$ dependence is mentioned. However, they have observed higher $q$ dependence than $q^2$ for $1 \leq x \leq 6$.

McAdam and King have also looked at the polymer in both cyclohexane (a poor solvent) and 2-butanone (a marginally good solvent). After obtaining the intensity ACF's from homodyne light scattering, the data was analyzed by a similar fit to the function $C(t)$ as by Wu-Nan Huang and Frederick

$$C(t) = A^2 e^{-2Dq^2 t} + 2ABe^{-\left(2q^2 D + 2/\tau_1 \right)t}$$

where the term with the coefficient $B^2$ in the previous analysis has now been considered to be negligible in that $A > B$ for the range of angles McAdam and King had chosen.

For a polymer of the same molecular weight $M_w$ as ours, they have found that in cyclohexane $\tau_1$ is 300 $\mu$s and in 2-butanone $\tau_1$ is 258 $\mu$s. It can be seen that their value of $\tau_1$ is 13% lower than ours in cyclohexane and the trend to lower relaxation times in good solvents than poor is observed. They do not discuss the $q$ dependence of their data, however.

A different method of analysis has been employed by
Nemoto, Makita, Tsunashima and Kurata\textsuperscript{51} in determining the different modes. By employing a histogram method they have been able to identify the two different decay modes (translational and longest wavelength mode) for polystyrene in benzene (a good solvent). For an explanation of the histogram method the interested reader is referred to the paper by the above authors (the source is listed as number 51 in the endnotes). In subsequent analysis using the values of $f_{\gamma_2}$ as obtained from the above analysis they have found that $\tau_1$ conforms well to the NFD model and $q^3$ dependence was observed in the second decay mode. This is typical of poor solvents and is inconsistent with the solvent quality of benzene. Furthermore, there is still some question as to the validity of the histogram method of analysis.

In view of the experimental results of others, our value of $\tau_1$ in cyclohexane agrees reasonably well with other groups in conforming to the predictions of the Rouse-Zimm non-free-draining bead and spring model. However, our $q^{1.96}$ dependence is lower than predicted by the NFD theory ($q^3$) or of that obtained by other groups.

The tendency of $\tau_1$ to be lower in a good solvent than in a poor one is supported by two other groups that I am aware of, McAdam and King\textsuperscript{52} and Huang and Frederick.\textsuperscript{53}

Our results in toluene of the $q^{3.86}$ dependence
agrees well with the FD model in theory. Other groups have obtained mostly $q^3$ dependence in toluene and other good solvents, although there appears to be a general lack of confidence in interpretation of the results from both high angle and high $x$.

Since the results we have obtained in toluene tends to disagree with most other groups using different methods of analysis, it will be important to see if other groups, in using our method of analysis, can obtain results consistent with ours.

As for the results in cyclohexane, I believe that $\tau_1$ has been determined accurately but the $q$ dependence still requires further work (possibly by extending the x range through the use of shorter wavelengths such as ultra-violet). There also appears to be a possibility that $\tau_1$ may be concentration dependent. If $q^2$ dependence holds, then the $q^3$ dependence for NFD will have to be reevaluated.
Endnotes

42 Gwynne Jones and David Caroline, Chem. Phys., 40, 153-156 (1979)


44 P. -G. de Gennes, Phys. 3(1), 37-45 (1967)


48 J. Hendrix, B. Saleh, K. Gnading, L. de Maeyer, Poly., 18, 10-44 (1977)

49 Wu-Nan Huang and J.E. Frederick, Macro., 7(1), 34-38 (1974)


51 Norio Nemoto, Yutaka Makita, Yoshisuki Tsunashima, Michio Kurata, Macro., 17, 425-430 (1984)


53 Wu-Nan Huang and J.E. Frederick, Macro., 7(1), 34-38 (1974)
Appendix A: Method Of Cumulants

To measure the average, width and skewness of a molecular weight distribution (quasi-exponential ACF), the method of cumulants as devised by Koppel et al (1972) may be employed.

If one measures the ACF for low q \((qR_g)^2 < 1\) then the resulting ACF should be well fit by a single exponential. By first normalizing the ACF one obtains

\[ N(q,t) = \sum_i A_i \frac{e^{-Dq^2 t}}{\sum_i A_i} = e^{-Dq^2 t} \quad \text{ (30)} \]

Then by taking the ln of \(N(q,t)\) and expanding in a Taylor series

\[ \ln(N(q,t)) = 1 - K_1 t + \frac{K_2 t^2}{2!} + \ldots \quad \text{ (31)} \]

where \(K_n = \left[ (-1)^n \frac{d^n}{dt^n} \ln(N(q,t)) \right]_{t=0}\) is the \(n^{th}\) cumulant of the normalized ACF, \(K_1 = \langle q^2 D \rangle = \Gamma\) and \(K_2 = \langle (q^2 D - \langle q^2 D \rangle)^2 \rangle\) which is a measure of the variance (width) of the distribution of \(\Gamma\) due to polydispersity.

Another approach, devised by Pusey et al (1972), though less rigorous, is simpler. If one first defines for a polydisperse solution the exponential distribution,
\[ |g^{(1)}(\tau)| = \int_0^\infty g(\Gamma) e^{-\tau\Gamma} \, d\Gamma \quad \text{and} \quad \int_0^\infty g(\Gamma) \, d\Gamma = 1 \quad (32) \]

where \( g(\Gamma) \, d\Gamma \) is the fraction of the total normalized and integrated intensity of scattered light by the portion of molecules which obey \( \Gamma = D_i q^2 \) within the increment \( d\Gamma \). Then factoring \( e^{-\tau\Gamma} \) from the exponential and expanding the remainder by way of a Taylor series about the factored term \( e^{-\tau\Gamma} \)

\[
e^{-\tau\Gamma} = e^{-\tau\Gamma} \left( 1 - (\Gamma - \bar{\Gamma}) + \frac{(\Gamma - \bar{\Gamma})^2}{2!} + \ldots \right)
\]

This results in

\[ |g^{(1)}(\tau)| = e^{-\tau\bar{\Gamma}} \left( 1 + \frac{u_2}{2!} (\Gamma - \bar{\Gamma})^2 + \frac{u_3}{3!} (\Gamma - \bar{\Gamma})^3 + \ldots \right) \quad \text{where} \]

\[
u_2 = \int_0^\infty (\Gamma - \bar{\Gamma})^2 g(\Gamma) \, d\Gamma \quad \text{and} \quad u_3 = \int_0^\infty (\Gamma - \bar{\Gamma})^3 g(\Gamma) \, d\Gamma,
\]

\[ u_2 = 0. \quad (33) \]

Upon taking the \( \ln \) of the right hand side with \( \ln(1 + x) = x - x^2/2! + \ldots \)

\[ \ln[|g^{(1)}(\tau)|] = -\tau\bar{\Gamma} + \frac{u_2}{2!} (\Gamma - \bar{\Gamma})^2 - \frac{u_3}{3!} (\Gamma - \bar{\Gamma})^3. \quad (34) \]

To find \( \bar{\Gamma} \) from the first derivative with respect to \( \tau \), take the limit as \( \tau \) goes to zero,

\[ \lim_{\tau \to 0} \frac{d}{d\tau} \ln[|g^{(1)}(\tau)|] = -\bar{\Gamma}. \quad (35) \]
To derive $u_2$, take the limit of the second derivative,

$$\lim_{\tau \to 0} \frac{\partial^2}{\partial \tau^2} \ln[|g^{(1)}(\tau)|] = u_2 .$$

If a graph is made from the data by plotting the first derivative of the $\ln[|g^{(1)}(\tau)|]$ versus $\tau$ then the $y$-intercept should yield and the slope $u_2$ (please refer to Figure 15).

Another parameter is called the quality parameter

$$\delta_z = \frac{u_2}{\overline{f^2}} = \frac{\langle (D^2)_z \rangle - \langle D_z \rangle^2}{\langle D_z \rangle^2} .$$

$\delta_z$ is the number averaged normalized variance of the diffusion distribution and along with the $\overline{f^2}$ is the information supplied by the correlator through the method of cumulants. If the sample were monodisperse then, $\langle D^2 \rangle_z = \langle D_z \rangle^2$ and $\delta_z = 0$. Hence $\delta_z$ is another relative measure of the polydispersity of the sample.

To obtain $\mu_2$ (the polydispersity due to the distribution in the longest wavelength mode) by the method of cumulants, one would have to go to higher $q$ (multi-exponential ACF). However, the different moments obtained are very sensitive to the fitting function and yielded inconsistent results. The method of $^{(2)}$ cumulants was therefore not used to obtain $\mu_2$. 
Method of Cumulants

\[
\frac{d}{d\tau} \ln \langle |g(1)(\tau)| \rangle
\]

slope = \mu_2

\text{y-intcp.} = -\Gamma_1

\tau \text{ seconds}

Figure 15. Method of Cumulants
Endnotes


55 Bruce J. Berne and Robert Pecora, Dynamic Light Scattering With Applications To Chemistry, Biology And Physics, 1st ed. (John Wiley and Sons, Inc., 1976), 195-196
Appendix B: Zimm Plot

To determine the weight averaged molecular weight \( \bar{M}_w \) and the radius of gyration \( R_g \) of a macromolecule through static or time-averaged light scattering data, a Zimm plot is often employed. Note that we have not in fact done this analysis, since other groups have made these measurements extensively.

The Zimm plot makes use of the function

\[
\lim_{c \to 0} \frac{K_c}{M_w} = \frac{1}{R_0} \left( 1 + \frac{16\pi^2}{3\lambda^2} R_g \sin^2 \theta/2 + \ldots \right)
\]

where \( c \) is the weight concentration and \( R_0 \) is the reduced scattering intensity per unit volume of the scatterer. More specifically

\[
R_0 = \frac{I_0 r^2}{I_\theta}, \quad I_\theta = I_0 \frac{8\pi^5\alpha^2}{\lambda^4 r^2} (1 + \cos^2 \theta)
\]

with \( I_\theta \) being the intensity of scattered light at the angle \( \theta \) and distance \( r \) from a small isotropic scatterer and \( I_0 \) the intensity at zero angle. \( \lambda \) is the wavelength of the laser light in the solvent and \( \alpha \) is the excess polarization of the polymer due to the incident light field over the solute. Even though it is impossible to
directly measure $\alpha$, it may be determined using the theoretical expression $\alpha = n_0 M \Delta n/2L \Delta c$ where $L$ is Avogadro's number, $n_0$ is the solvent index of refraction, $n$ is the solution index of refraction and $M$ is the molecular weight. The fact that at very dilute concentrations $n$ is only a very weak function of concentration is the source of the approximation that $dn/dc \sim \Delta n/\Delta c$.

It so happens that if the macromolecules are small compared to $\lambda$ then $R_\theta$ becomes independent of angle. By measuring $I_\theta$ and $I_\theta$ at ninety degrees, $R$ becomes the Rayleigh ratio $R_\theta = R_\theta = I_{90}/I_\theta$.

The optical constant $K_c$ is comprised of experimentally measurable parameters and is a function of the change in the solution index of refraction with changing polymer concentration. More specifically, $K_c^2$ is related to $n$ by $K_c^2 = 2\pi^2 n_0 (\Delta n/\Delta c)^2 /L\lambda^4$. Upon substitution of $K_c$ into equation (38),

$$\lim_{c \to 0} \frac{2\pi^2 n_0}{c^2 L \lambda^4 \rho^2} \frac{(n-n_0)^2}{(I_\theta/I_{90})^2} \rho = \frac{1}{M_\theta} \left(1 + \frac{16\pi^2 R_\theta \sin^2 \theta/2}{3\lambda^2}\right)$$

If $n,n_0,I_\theta,I_{90},\rho$ are measured for a set of data with various $c$ at set angles and various angles at set concentrations then a plot of $K_c/R_\theta$ versus $\sin^2 \theta/2$ would yield a Zimm plot (see Figure 16). By extrapolating to the zero concentration ($c=0$) and zero angle ($\theta=0$) lines, the resulting $y$-intercept would yield the reciprocal
Figure 16. Zimm Plot
weight averaged molecular weight ($\bar{M}_w$) of the polymer and the slope of the zero concentration line ($16\pi^2 R_g / 3\lambda^2$) would yield the radius of gyration, $R_g$. 
Endnotes

Appendix C: H(t) Versus Time t For Toluene

The following graphs are examples of typical H(t) plots obtained in the solvent toluene for wavelengths of 5145 Å and 4579 Å and for angles ranging from 40 to 120 degrees. This yields a range of x ((qR_e)^2) of from 2.0 to 33.

Note that as the scattering angle increases the H(t) curve appears to "curve over" more rapidly. It is also worth noting that since the scattering volume is a minimum at 90 degrees, the results are noisiest for this data set.
Figure 17. $H(t)$ vs. $t$, theta = 40°
Figure 18. $H(t)$ vs. $t$, Theta = 50°
Figure 19. $H(t)$ vs. $t$, theta = 60°
Figure 20. \( H(t) \) vs. \( t \), \( \theta = 70^\circ \)
Figure 21. $H(t)$ vs. $t$, theta = 80°
Figure 22. \( H(t) \) vs. \( t \), theta = 90°
Figure 23. $H(t)$ vs. $t$, $\theta = 100^\circ$
Figure 24. $H(t)$ vs. $t$, theta = 110°
Figure 25. $H(t)$ vs. $t$, theta = 120°