

# Measurement of the intramolecular fluctuations of random coil polymers by photon correlation spectroscopy

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The correlation function of light scattered from dilute solutions of large molecular weight polystyrene has been measured using a photon-counting digital autocorrelator. By determining the effective spectral broadening and the change in the spectral profile due to intramolecular fluctuations, the range of validity of the Zimm–Rouse model of intramolecular dynamics has been examined.

## INTRODUCTION

Precise information on the intramolecular dynamics of macromolecules in dilute solutions has recently been sought using the method of photon correlation of quasi-elastically scattered laser light<sup>1–9</sup>. In 1964 Pecora<sup>10–12</sup> pointed out the feasibility of obtaining such information from measurements of the correlation function (or the spectrum) of scattered light. Assuming a Zimm–Rouse model<sup>13,14</sup> for the polymer dynamics, he showed that the correlation function can be expanded as a sum of exponential functions the first of which corresponds to the translational motion of the polymer's centres of mass and subsequent terms correspond to translational motion plus contributions from the internal fluctuation normal modes. The number of internal modes which contribute to the correlation function is determined by the parameter  $x = (1/6)q^2\langle l^2 \rangle$ , where  $\langle l^2 \rangle$  is the mean square end-to-end distance of the polymer and  $q$  is the scattering vector determined by the scattering geometry and the laser wavelength  $\lambda$ . For small  $x$  (small  $\langle l^2 \rangle/\lambda^2$ ), the intramolecular motion does not contribute to the measured correlation function. As  $x$  increases, the first (slowest) internal mode shows up and with further increase in  $x$  more and more modes are manifested.

A number of theoretical investigations<sup>15–19</sup> have examined Pecora's expression more closely and provided a more thorough analysis by including finer effects such as the effect of sample polydispersity. Moreover, other theoretical models for the polymer dynamics have also been considered<sup>20–22</sup>.

On the experimental side, published results<sup>1–9</sup> are limited to measurements in the small range of  $x$  where only one internal mode contributes and whose relaxation time and amplitude can be determined by fitting procedures.

Kramer and Frederick<sup>2</sup> reported measurements of the effective spectral width for a wider range of the parameter  $x$  but they compared it to the theoretical values only in the range where one or two internal modes contribute.

In a previous paper<sup>23</sup>, we have suggested abandoning the idea of expanding the correlation function in terms of exponentials, to study the profile of the correlation function as it is. We have computed graphs of the correlation func-

tion normalized in such a way as to show the effect of internal fluctuations and have also calculated the effective spectral broadening due to internal motion for a wide range of values of the parameter  $x$ .

In this paper, we report the result of some measurements on solutions of large molecular weight polystyrene samples in toluene and in cyclohexane with the objective of determining the range of validity of the Zimm–Rouse model in the free draining limit. The correlation function profile has been measured at several values of  $x$  (several scattering angles) and compared to the Zimm–Rouse model profiles; deviations are noted. Each profile has also been fitted to an exponential function and an effective internal motion spectral broadening ratio determined. By fitting the measured function to two exponential functions, the collective internal motion relaxation time has been determined and compared to predictions of the Zimm–Rouse model.

## ANALYSIS

The Zimm–Rouse model describes a flexible-coil macromolecular chain by a set of  $Z + 1$  identical and optically isotropic beads connected by  $Z$  segments. The beads provide the friction with which the chain interacts with the surrounding viscous fluid and the segments which have complete flexibility at the beads provide Hookean restoring forces. Each polymer molecule undergoes random motion of its centre of mass as well as large scale configurational changes as part of its Brownian motion. The dynamics of this model correspond to a solution of random diffusion equations in the multidimensional configuration space of the chain. This can be represented by a set of uncorrelated fluctuating normal modes through a proper linear transformation. The motion of the centre of mass of the molecule is an independent Brownian motion. In the absence of hydrodynamic interaction between the beads (the free-draining case), the internal motion modes have relaxation times given by<sup>13,14</sup>:

$$\tau_n \approx \frac{\langle l^2 \rangle}{3\pi^2 n^2 D_T} \quad n = 1, 2, \dots \quad (1)$$

and variances:

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$$\langle \mu_n^2 \rangle = \frac{Z \langle l^2 \rangle}{\pi^2 n^2} \quad n = 1, 2, \dots \quad (2)$$

where  $\langle l^2 \rangle$  is the mean square end-to-end distance of the molecule and  $D_T$  is the coefficient of translational diffusion of its centre. Hence in this model, the dynamics of the system are completely described by two parameters,  $D_T$  and  $\langle l^2 \rangle$ , which of course depend on the physical parameters of the solution.

The method used in the present study of probing the fluctuations in the solution is the measurement of the correlation function of scattered light. This function can be obtained by averaging over the Brownian fluctuations of the normal modes and is given by<sup>10-12</sup>:

$$G(t) \sim \exp(-D_T q^2 t) \frac{1}{Z^2} \sum_{j=0}^Z \sum_{l=0}^Z \exp \left\{ - \sum_{n=1}^Z \frac{q^2}{3Z} \langle \mu_n^2 \rangle \right. \\ \left. \times [R_{jn}^2 + R_{ln}^2 - 2R_{jn}R_{ln} \exp(-t/\tau_n)] \right\} \quad (3)$$

where

$$R_{nj} = \begin{cases} \sin \\ \cos \end{cases} n\pi \left( \frac{j}{Z} - \frac{1}{2} \right), \quad \begin{cases} n \text{ odd} \\ n \text{ even} \end{cases} \quad (4)$$

Using equations (1) and (2), equation (3) can be written in the form:

$$G(t) \sim \exp(-t/T) \frac{1}{Z^2} \sum_{j=0}^Z \sum_{l=0}^Z \exp \left\{ - \sum_{n=1}^Z \frac{2x}{\pi^2 n^2} \times \right. \\ \left. \left[ R_{jn}^2 + R_{ln}^2 - 2R_{jn}R_{ln} \exp \left( - \frac{\pi^2 n^2}{2x} \frac{t}{T} \right) \right] \right\} \quad (5)$$

where  $T = (q^2 D_T)^{-1}$  is the relaxation time due to translational motion and:

$$x = \frac{1}{6} q^2 \langle l^2 \rangle = \frac{8}{3} \pi^2 \frac{\langle l^2 \rangle}{\lambda^2} \sin^2(\theta/2) \quad (6)$$

where  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of the laser light in the medium. Thus the correlation function as a function of  $t/T$  depends on  $x$  and  $Z$ . In a previous paper<sup>23</sup>, we obtained graphs for this function for several values of  $x$  and showed that it is insensitive to the actual value of  $Z$  provided  $Z$  is large. Since it is possible to determine  $T$  from measurements of the correlation function at small values of  $x$  (small scattering angle) and to determine  $x$  from knowledge of  $\langle l^2 \rangle$  based on other experimental techniques or empirical laws, we are in a position to compare the measured correlation functions with the corresponding functions based on the Zimm-Rouse model and determine the range of validity of the model. This will be carried out in a later section of this paper.

## EXPERIMENT

In this experiment TSK standard polystyrene samples prepared by anionic polymerization were used. These samples

were obtained from the Toyo Soda Mfg Co. Ltd, Japan. Three high molecular weight samples (F225, F510 and F870) were used, and their characteristics are summarized in *Table 1*. We also used two samples with smaller molecular weight ( $2 \times 10^5$  and  $8.6 \times 10^5$ ). These samples were obtained from the Mann Research Laboratories, USA. To eliminate dust particles, the solutions were centrifuged.

As a light source, a Spectra Physics model 165 Argon laser carefully adjusted in the TEM<sub>00</sub> mode was used. A single temporal mode was selected by inserting a quartz etalon in the cavity and the stability of the system was monitored during the course of the experiment by a Fabry-Perot interferometer. These precautions are necessary since the correlation function can be distorted due to multimodes.

A 40-channel clipped digital correlator developed in our laboratory<sup>25</sup> was used to measure the correlation function. This correlator is a modified version of the conventional correlator<sup>26</sup>.

The correlator was interfaced to a PDP11/20 computer and the measured correlation function normalized every 10 sec. A dust filter was obtained by rejecting after the 10 sec periods and showed exceptionally high counting rates. Distortions due to dust particles were thus reduced considerably. The average number of clipped counts was recorded in each experiment and compared to its theoretical value.

The data have been fitted to sums of exponential functions using a modified version of the method of moments<sup>27</sup>.

## RESULTS AND DISCUSSIONS

The clipped photon-counting autocorrelation function of light scattered from dilute solutions of the above mentioned polystyrene samples in toluene was measured at several scattering angles and for different concentrations. The results are analysed in several ways.

(a) By force fitting each of these functions to a single exponential function plus a constant term, we obtain an estimate for the effective spectral width which should be proportional to  $\sin^2(\theta/2)$  for small molecules or for small scattering angles (small  $x$ ). *Figure 1* shows how this linear relationship no longer holds for larger values of  $x$  because of the contributions from intramolecular fluctuations.

(b) By estimating the coefficient of translational diffusion from small angle measurements (the slope of the bandwidth *versus*  $\sin^2(\theta/2)$  relation, at small  $\theta$ ), we can determine the spectral broadening ratio which is the ratio between the effective bandwidth and the bandwidth due to translational motion alone. This is plotted in *Figure 2* together with theoretical curves which we have previously computed<sup>23</sup> from the Zimm-Rouse model. The mean square end-to-end distance of polystyrene in toluene at

*Table 1* Characteristics of the polystyrene samples used

Sample	Light scattering $\bar{M}_w \times 10^{-6}$	G.p.c.		
		$\bar{M}_w \times 10^{-6}$	$\bar{M}_n \times 10^{-6}$	$\bar{M}_w/\bar{M}_n$
F225	2.42	2.35	2.25	1.04
F510	5.53	5.33	5.09	1.04
F870	9.5	8.78	8.5	1.03

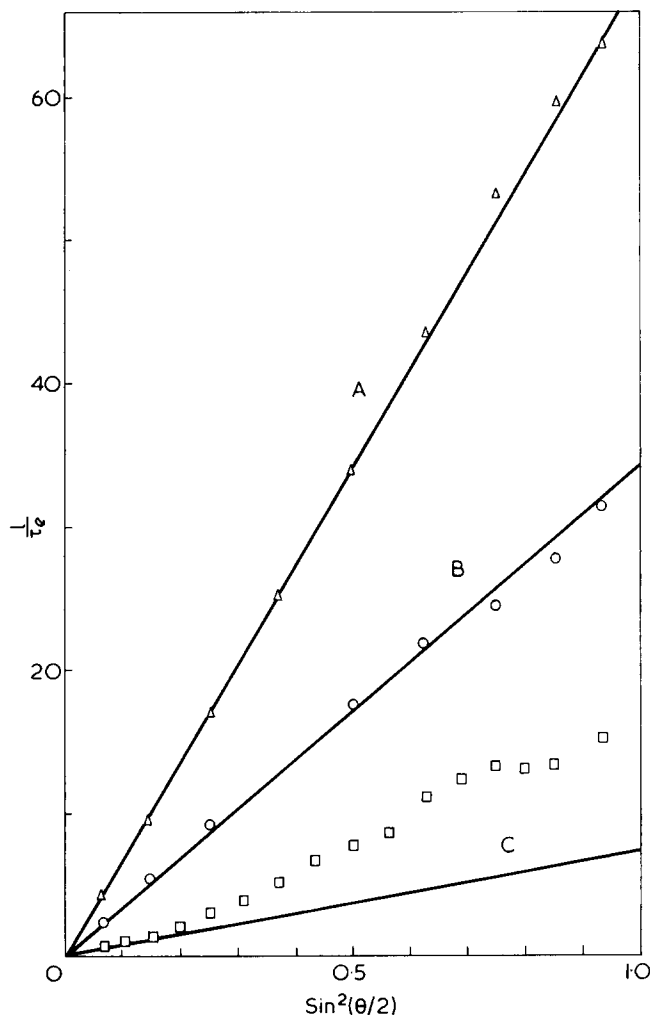


Figure 1 The effective bandwidth ( $1/\tau_e$ ) as a function of  $\sin^2(\theta/2)$  for samples having the indicated molecular weights: A,  $0.2 \times 10^6$ ; B,  $0.86 \times 10^6$ ; C,  $9.5 \times 10^6$

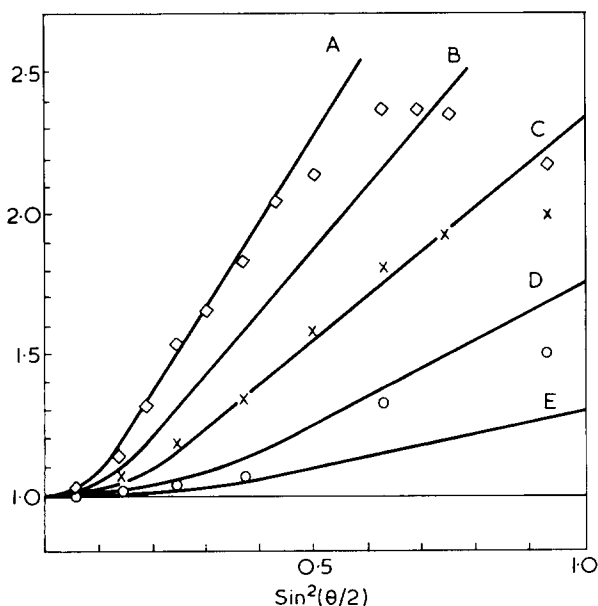


Figure 2 The spectral broadening ratio  $r = 1/(q^2 D T \tau_e)$  as a function of  $\sin^2(\theta/2)$ . Curves A–D represent theoretical curves based on the Zimm–Rouse model and calculated for the root mean square end-to-end distances: A, 3500 Å; B, 3000 Å; C, 2500 Å; D, 2000 Å; E, 1500 Å. The points represent the measured values for the indicated samples in toluene at concentration 0.1 mg/ml:  $\diamond$ , F870, 3521 Å; X, F510, 2570 Å;  $\circ$ , F225, 1594 Å. The indicated mean square end-to-end distances are calculated from ref 7

40°C is calculated from the relation<sup>24</sup>:

$$\begin{aligned} \langle l^2 \rangle &= \alpha^2 \langle l_0^2 \rangle \\ \langle l_0^2 \rangle^{1/2} &= 0.675 M^{1/2} A^0 \\ \alpha^5 - \alpha^3 &= 0.002933 M^{1/2} \end{aligned} \quad (7)$$

where,  $M$  is the molecular weight. From this we can determine the value of  $x$  at different angles.

Approximate agreement between theory and experiment is observed for small values of  $x$ . The spectral broadening ratio increases almost linearly with  $\sin^2(\theta/2)$  and then flattens at larger angles. Such a deviation has also been observed by Kramer and Frederick<sup>2</sup>.

It should be noted however that when a non-exponential function is force fitted to an exponential function, the resultant relaxation time is sensitive to the covered time range. This introduces some ambiguity in the interpretation of the results. Although we have attempted to fit the experimental results in a time interval approximately equal to that used in obtaining the theoretical curves, the equality was not always exact. The errors introduced because of such ambiguities are not, however, sufficiently large to account for the discrepancy between experiment and theory.

(c) The spectral broadening ratio is also plotted in Figure 3 for sample F870 for different concentrations. It is noted that at higher concentrations the spectral broadening ratio decreases, presumably owing to intermolecular effects. The dynamics of internal fluctuations at high concentrations is not understood and we have not made any attempt to interpret these measurements quantitatively.

(d) Figure 4 is obtained by fitting the measured correlation function to a sum of two exponential functions one of them with a known relaxation time (the translational diffusion relaxation time). From the fitted value of the relaxation time of the second exponential, we can obtain the collective internal motion relaxation time. This is also compared to its corresponding theoretical value calculated from the Zimm–Rouse model<sup>23</sup>. The measured results follow qualitatively the theoretical pattern of increasing

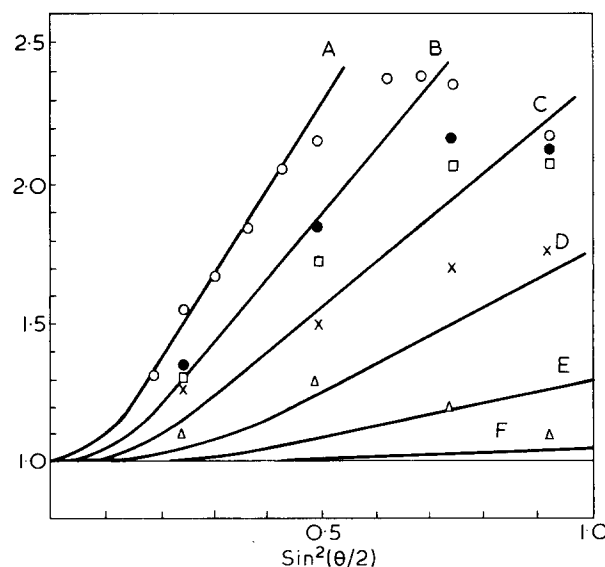


Figure 3 The spectral broadening ratio as in Figure 2 for sample F870 at different concentrations:  $\circ$ , 0.1;  $\bullet$ , 0.2;  $\square$ , 0.5; X, 1.0;  $\triangle$ , 2.5 mg/ml. Root mean square end-to-end distances: A, 3500 Å; B, 3000 Å; C, 2500 Å; D, 2000 Å; E, 1500 Å; F, 1000 Å

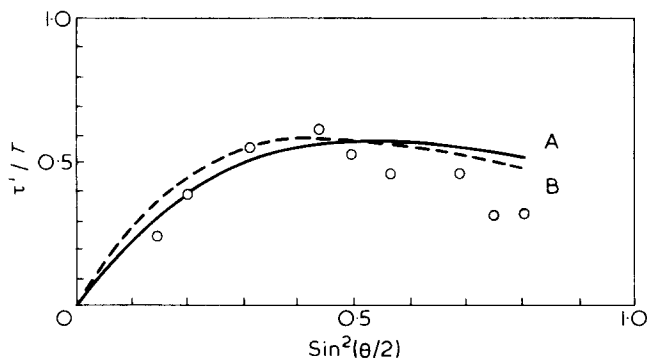


Figure 4 The ratio between the collective internal motion and the translational diffusion relaxation times as a function of  $\sin^2(\theta/2)$ . The solid and broken lines are calculated from the Zimm-Rouse theory. The experimental points are calculated from measurements on sample F870 in toluene at concentration 0.1 mg/ml. Root mean square end-to-end distances: A, 3000 Å; B, 3500 Å

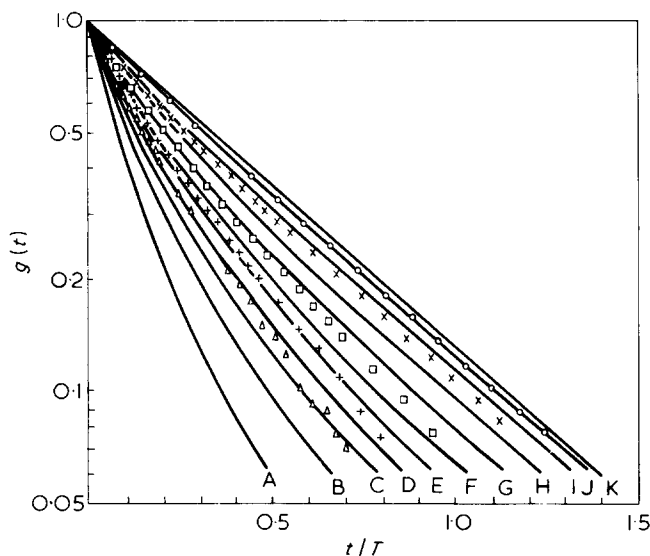


Figure 5 The normalized correlation function. Curves A-K are calculated from the theory for values of  $x$ : A, 15; B, 10; C, 8; D, 7; E, 5; F, 4; G, 3; H, 2; I, 1; J, 0. The points are measurements taken on sample F510 in toluene at the indicated scattering angles. The corresponding values of  $x$  are calculated from ref. 7.  $\circ$ ,  $\theta = 30^\circ$ ,  $x = 1.1$ ;  $\times$ ,  $\theta = 45^\circ$ ,  $x = 2.4$ ;  $\square$ ,  $\theta = 75^\circ$ ,  $x = 6.0$ ;  $+$ ,  $\theta = 90^\circ$ ,  $x = 8.2$ ;  $\triangle$ ,  $\theta = 120^\circ$ ,  $x = 12.2$

linearly then flattening and decreasing with increase in  $\sin^2(\theta/2)$ .

Huang and Frederick<sup>4</sup> have obtained similar behaviour in some of their measurements although they incorrectly take the average value of the collective internal motion relaxation times at different angles instead of the value at small angles as a measure of the relaxation time of the first internal mode. King *et al.*<sup>5</sup> have also reported a collective internal motion relaxation time which is a factor of 0.4 smaller than that of the Zimm-Rouse model first internal mode. This can easily be understood by examining Figure 4.

(e) In Figure 5 the profiles of the measured correlation functions are compared to the profiles obtained from the Zimm-Rouse model<sup>23</sup>. These functions are normalized such that the relaxation time owing to translational diffusion is equal to one and that their values at zero time delay are also equal to one. Since we do not measure the zero time delay correlation function, we extrapolate it to perform the normalization. As Figure 5 shows, reasonable agreement between the experimental results and the model

is obtained for small values of the parameter  $x$ . This has also been found by other authors<sup>2-9</sup>. For  $x$  exceeding a value of  $\sim 5$  we observe that the relaxation of the measured correlation function is generally slower than the theoretical function. Moreover the profile itself is different.

This discrepancy could possibly be accounted for by the effect of hydrodynamic interactions which are neglected in the free draining model. As the measurements were performed in toluene, a good solvent, these effects are likely to modify the expressions of the relaxation times<sup>14</sup>. The measurements were therefore repeated in cyclohexane at  $35.5^\circ\text{C}$  where the free draining assumption is more likely to hold. In this case, however, the mean end-to-end distance, which is now given by:

$$\langle l^2 \rangle = \langle l^2 \rangle_0$$

is considerably smaller (2080 Å in cyclohexane instead of 3521 Å in toluene). Therefore, the range of values of the parameter  $x$  covered by the measurement is smaller. Results are displayed in Figures 6 and 7 for the largest sample F870. The discrepancy remains. The effective broadening ratio

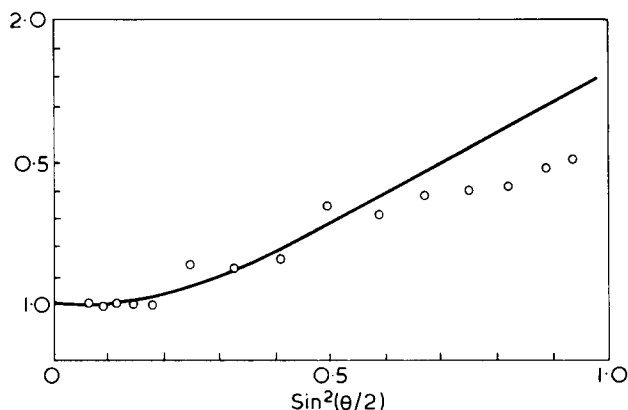


Figure 6 The spectral broadening ratio as in Figure 2 for sample F870 in cyclohexane at  $35.5^\circ\text{C}$ . The parameter  $x \approx 10.27$   $\sin^2(\theta/2)$

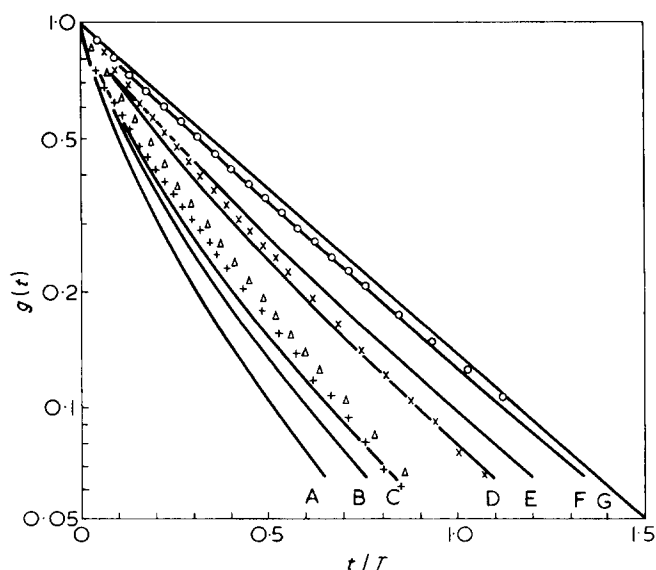


Figure 7 As in Figure 5 for sample F870 in cyclohexane at  $35.5^\circ\text{C}$ . Values of  $x$ : A, 10; B, 8; C, 7; D, 4; E, 3; F, 1; G, 0.  $\circ$ ,  $\theta = 35^\circ$ ,  $x = 0.93$ ;  $\times$ ,  $\theta = 70^\circ$ ,  $x = 3.4$ ;  $\triangle$ ,  $\theta = 120^\circ$ ,  $x = 7.7$ ;  $+$ ,  $\theta = 150^\circ$ ,  $x = 9.6$

as a function of  $x$  flattens at higher values of  $x$  and the profiles of the correlation function are less steep than those predicted by the theoretical model.

This result is actually not very surprising because the Zimm-Rouse model is expected to be a reasonable approximation only for the long wavelength (slow relaxation time) modes where the hydrodynamic model is applicable.

The high degree of precision in the photon correlation technique which revealed this large discrepancy between experiment and the Zimm-Rouse model encourages a turn to more sophisticated models of intramolecular dynamics. It is of great importance that this should be considered next.

#### ACKNOWLEDGEMENT

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