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Photon Correlation Spectroscopy near the Glass Transition

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ABSTRACT: Problems in the collection and analysis of photon correlation data obtained near the glass transition are presented and discussed. The use of the Williams-Watts empirical relaxation function in the analysis of the data is critically examined. A proposed graphical method of analysis is also studied and found to be subject to many limitations. The average relaxation time obtained by photon correlation spectroscopy is related to the half-width at half-height of the corresponding power spectrum and to the frequency of maximum loss of the corresponding susceptibility.

Introduction

Near the glass transition, fluctuations in density and optical anisotropy are slow enough to be observed by photon correlation spectroscopy.[1-4] The relaxation functions which are observed are highly nonexponential. This raises the question of what kind and how much information can be reliably extracted from the data. In the present paper we examine the collection, analysis, and interpretation of photon correlation spectroscopy data near T_g and discuss how such results may be compared with other relaxation techniques.

Data Collection

The basic measured quantity in photon correlation spectroscopy is the correlation function[5]

$$C(t) = \langle I(t)I(0)\rangle / \langle I(0)\rangle^2 \qquad (1)$$

where $I(t)$ is the intensity of scattered light at time t and the brackets denote a time average. In practice this quantity is usually obtained by counting the number of photons n in a fixed time interval T and computing the discrete function

$$C(iT) = \langle n(iT)n(0)\rangle / \langle n\rangle^2 \qquad (2)$$

where i is an integer. The number of discrete values that can be computed at one time depends on the particular digital correlator used for the measurements, which typically has between 24 and 256 channels. The calculations are often further simplified by computing the single-clipped correlation function

$$C_k(iT) = \langle n(iT)n_k(0)\rangle / \langle n\rangle\langle n_k\rangle \qquad (3)$$

where $n_k(iT) = 1$ if $n_k > k$ and 0 otherwise.

The quantity that is actually desired is the relaxation function for the fluctuations which gave rise to the light scattering $\phi(t)$. In the ideal case the relation is

$$C(t) = 1 + \phi^2(t) \qquad (4)$$

In practice the scattered light is observed over a finite coherence area A and for a finite time interval T. The use of clipping also affects the relation between the observed correlation function and the relaxation function. If $\phi(t)$ were a single-exponential decay, these effects could be taken into account by the product of three factors according to[5]

$$C_k(iT) = 1 + \frac{1+k}{1+\langle n\rangle} f(A)g(T)\phi^2(iT) \qquad (5)$$

where $f(A)$ quantifies the loss of correlation due to the finite coherence area and $g(T)$ depends on the ratio of the sample time T to the relaxation time τ of the exponential decay. The above relation also assumes that the fluctuations are a Gaussian random process. This is probably a good assumption for density and anisotropy fluctuations in pure fluids. It has also been assumed that all the scattered light is due to thermal fluctuations in the dielectric tensor and that there are no spurious sources of scattering such as dust. This can be realized for polymers prepared by thermal polymerization from the pure monomer.

The total relaxation function $\phi(t)$ observed by light scattering is never actually a single-exponential decay. There are always fluctuations which lead to light scattering which relax faster than those probed by photon correlation spectroscopy. As a result, even if the three factors which affect the relation between $C_k(iT)$ and $\phi^2(iT)$ are fully taken into account, the calculated value of $\phi^2(iT)$ is always less than 1. If the average total intensity can be separated into fast and slow components, the observed intercept value of $\phi(t)$ can be predicted very accurately.

The effect of finite coherence area can be taken into account experimentally by measuring the intercept of the data under conditions where T is sufficiently short and the relative intensity due to the fluctuations being observed is accurately known. The calculated intercept was always realized for sufficiently small coherence area. Thus, we treat the effect of finite coherence area as a simple multiplicative factor in the analysis of the data. The quantity $g(T)$ depends explicity on the relaxation time τ of the single-exponential decay. If the observed correlation function is nonexponential, then eq 5 is not strictly valid. We discuss this problem more thoroughly below.

If the relaxation function were a single-exponential decay, then only approximately 2 decades in time would be required to characterize $\phi(t)$, and a correlator with 96 channels would be sufficient to determine the relaxation function in a single run with a suitably chosen value of T. Near the glass transition, the range of times necessary to characterize the relaxation function is too large to be measured in a single run. In order to combine data collected with different sample times and coherence areas, it is necessary to obtain absolute values of $\phi^2(t)$ for each run. This is complicated by uncertainty in the function $g(T)$ for nonexponential decays.

For sufficiently short times, the relaxation function should approach a constant value equal to its intercept. In practice, most data are still rising at the shortest measured time. The short-time data is further complicated by the fact that the scattered intensities for pure polymers near T_g are very low. Long times are required to obtain a correlation function under these conditions and the signal-to-noise ratios are only fair. Thus, the true value of the intercept may be uncertain by ±10%, and it may be difficult to splice in the shortest time data.

When the sample time T is longer, there will be distortions in the shape of the observed correlation function. The following argument may lead to some hope of re-

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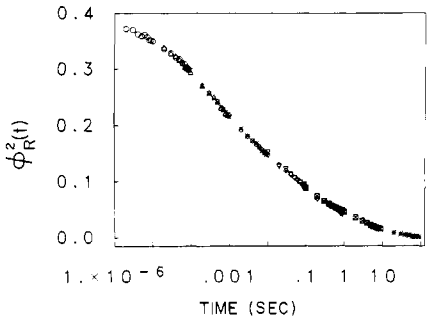

Figure 1. Composite relaxation function $\phi_R^2(t)$ obtained from six 96-point data sets plotted vs. log t for poly(ethyl methacrylate) at 70 °C.

covering the relaxation function from the experimental data. If we represent the relaxation function as a sum of exponential terms, then those terms with times τ comparable to or shorter than T will only contribute to the first few channels of the discrete correlation function. If the first few points of each run are neglected, it may be possible to splice together the remaining data points with only small errors introduced by assuming that there is no residual distortion due to the finite sample time T.

At very long times, the correlation function $C(iT) - 1$ should decay to 0. In practice there are always small discrepancies in the value of the base line due to experimental artifacts. Near T_g it is not always possible to collect data at long enough sample times to ensure that the base line has been reached. However, if the data are collected for times long relative to the longest relaxation times in the system and the sample is fully equilibrated, it may still be possible to characterize $\phi^2(t)$ with the shorter sample time data as long as the relaxation function has fallen to less than its $1/e^2$ point at the longest measured time.

In spite of the reservations about the data at very short or very long times, the relaxation function $\phi^2(t)$ can often be obtained very accurately by splicing together data collected with different sample times. Only small vertical adjustments are required to force the different data sets to overlap smoothly. A typical result is shown in Figure 1. The most illustrative way of plotting this data is $\phi^2(t)$ vs. log t. There is significant change in the relaxation function over many decades in time. Poly(ethyl methacrylate) was chosen to illustrate just how broad the relaxation function can be under some circumstances. In this case the breadth is due to the presence of at least two relaxation processes, but there is no obvious demarcation of them in the data. See ref 9 for a full discussion of this polymer.

Data Analysis

The first major question concerns the type of parameters that can be used to characterize the data. An average relaxation time can be defined as

$$\langle \tau \rangle = \int_0^\infty \phi(t)\,\mathrm{d}t \qquad (6)$$

The average relaxation time depends strongly on the longest time data and numerical integration of the calculated relaxation function would be subject to many errors. Another approach is to fit the data to an arbitrary function whose integral is known. For many materials near T_g, the relaxation function can be described very well by the empirical Williams–Watts[6] relaxation function

$$\phi(t) = \exp(-(t/\tau)^\beta) \qquad (7)$$

where $0 \leq \beta \leq 1$. The average relaxation time is given by

$$\langle \tau \rangle = \frac{\tau}{\beta}\Gamma(1/\beta) \qquad (8)$$

where $\Gamma(x)$ is the gamma function. This method has the advantage that it depends on the best part of the data in the most rapidly varying part of a plot of $\phi^2(t)$ vs. log t. But it does ignore differences between the data and the fitting function at short and long times.

The Williams–Watts function is characterized by only two parameters, τ and β. The value of β is a measure of the width of the underlying distribution of relaxation times implied by the nonexponential character of the relaxation function. The distribution function which corresponds to the Williams–Watts function has now been calculated[7] for values of β characteristic of data near the glass transition (0.2–0.7). This allows the observed values of β to be interpreted at least qualitatively in terms of a known distribution function. Attempts to invert the data directly to obtain the distribution of relaxation times $\rho(\tau)$ are not likely to be meaningful at present, due to the modest quality of the data and the numerical instability of the inversion.

Although a fit of the observed relaxation function to the Williams–Watts form is often satisfactory, only two parameters can be obtained with which to characterize the data. In order to obtain more information, it has been suggested[8] that a graphical method which displays deviations from the form of a single Williams–Watts function would be useful. The Williams–Watts function yields a straight line when it is plotted as log [$-\ln \phi(t)$] vs. log t with slope equal to β and intercept equal to β log τ. The corresponding plot for the calculated data would involve $-{}^1/_2 \ln \phi^2(t)$. However, the application of this graphical method to real data presents several important problems. In order to plot the data in this form, it is necessary to know the true value of the intercept so that the data can be renormalized to a value of 1 at zero time. The shape of the above type of plot at short times is very sensitive to the accuracy with which the data are renormalized. If the value of the intercept is chosen to be greater than the data at the shortest observed time, but still lower than the true intercept, a plot of the above type will be distorted downward at the shortest times. It appears that the results reported by Lee et al.[8] suffer from this type of normalization error. There will also be comparable problems associated with the uncertainty in the base line, but they may be less severe since the base line is usually known much more accurately than the intercept.

If the log ln vs. log plot is not a straight line, then the question arises of how to characterize the deviations. Initial attempts to plot photon correlation data in this form[8] revealed a curve which appeared to be the combination of two straight lines with different slopes. This was interpreted as due to two relaxation processes with values of β given by the respective slopes. This conclusion is not necessarily warranted for the following reasons. If the true relaxation function were the sum of two Williams–Watts functions, the slope at the shortest times on the above type of plot is an average of the two component values of β. The observed slope at short times in the paper noted above was too great to have been due to an average of two components and was more likely strongly influenced by the effect of misnormalization. If the data actually reflected a sum of two functions, the log ln vs. log plot might be a good way of revealing that fact. But the difficulties in preparing the data for such a plot should lead to considerable caution in the interpretation of the results.

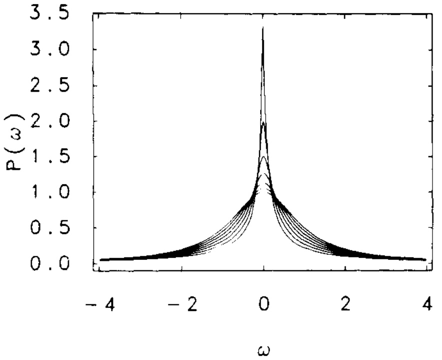

Figure 2. Calculated power spectra $P(\omega) = [S(\omega)\pi]/\tau$ for values of β ranging from 1.0 to 0.4 in increments of 0.1.

Table I
Relative Frequencies

β	$\tau\omega_{\max}$	$\tau/\langle\tau\rangle$	τ(hwhh)
1.0	1.0	1.0	1.0
0.9	0.943	0.950	0.871
0.8	0.886	0.883	0.725
0.7	0.833	0.790	0.563
0.6	0.787	0.665	0.391
0.5	0.743	0.500	0.224
0.4	0.659	0.300	0.088
0.3	0.639	0.108	0.015

There is no fundamental reason that the data should fit perfectly to the Williams–Watts form. It is employed merely as a convenience in the analysis of the data. However, it is remarkable how well the Williams–Watts function does fit the data. Under these conditions, attempts to extract more than two parameters from the data may not be meaningful.

Interpretation of Parameters

In order to compare the average relaxation time obtained by photon correlation spectroscopy to other typical relaxation data, a comparison is made by using the Williams–Watts relaxation function as a model nonexponential decay function. One common measure of relaxation is the half-width at half-height of the power spectrum of the fluctuations. This quantity can be obtained with a spectrum analyzer if the frequency is low enough or with a Fabry–Perot interferometer if the spectrum is broader. The power spectrum is related to the relaxation function by a Fourier transform

$$S(\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-i\omega t}\phi(t)\,\mathrm{d}t \qquad (9)$$

If the relaxation function is a single-exponential decay, the power spectrum is a Lorentzian with half-width at half-height given by $1/\tau$, where τ is the relaxation time of the exponential decay. The value of $S(0)$ is τ/π. If the relaxation function can be expressed as a sum of exponential decays, then the value of $S(0)$ is equal to $\langle\tau\rangle/\pi$. However, the half-width at half-height is not given by $1/\langle\tau\rangle$.

Power spectra corresponding to the Williams–Watts relaxation function were calculated as a function of the parameter β. The results are shown in Figure 2. The spectra fall much faster at low frequencies than would be expected for a Lorentzian line. Calculated half-widths at half-height relative to $1/\tau$ are plotted vs. β in Figure 3. The half-widths at half height are much narrower than would be predicted according to $1/\langle\tau\rangle$. The calculated values are also presented in Table I. The two types of data can now be compared quantitatively if β is known from photon correlation spectroscopy.

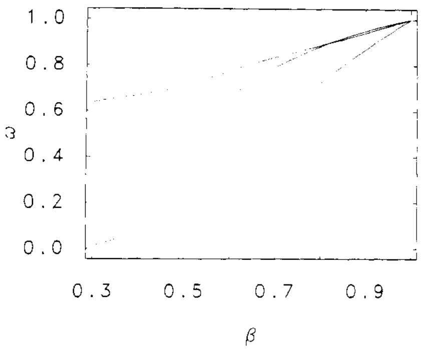

Figure 3. Values of $\tau\omega_{\max}$ (upper curve), $\tau/\langle\tau\rangle$ (middle curve), and τ(hwhh) (lower curve) calculated from the Williams–Watts relaxation function plotted as a function of β.

Depolarized Rayleigh scattering in atactic polystyrene has been studied by photon correlation spectroscopy.[3] Attempts to observe the power spectrum at higher temperatures were unsuccessful. The observed line was always too narrow to be resolved with a Fabry–Perot interferometer with a free spectral range of 8 GHz. Part of the reason for this result is connected with the polymeric nature of the sample. The spectrum is dominated by intramolecular rates of conformation change which may remain slow, even if the local viscosity becomes low. But another important factor is the shape of the power spectrum due to the nonexponential relaxation function. The half-width at half-height remains narrow much longer than would be expected for a Lorentzian line with width given by $1/\langle\tau\rangle$. Attempts to characterize the non-Lorentzian power spectrum in other samples near the glass transition are in progress.

Another common measure of relaxation data is the frequency of maximum mechanical or dielectric loss. The imaginary part of the susceptibility is related to the relaxation function by

$$M''(\omega) = \omega \int_0^{\infty} \cos(\omega t)\phi(t)\,\mathrm{d}t \qquad (10)$$

If the relaxation function is a single-exponential decay, $M''(\omega)$ reaches its maximum value at $\omega = 1/\tau$. For the Williams–Watts function, the frequency of maximum loss relative to $1/\tau$ is plotted as a function of β in Figure 3. The maximum loss occurs at a frequency higher than $1/\langle\tau\rangle$ for values of β typical of polymers near T_g. However, the two frequencies are close enough that an empirical correction can easily be applied to compare photon correlation data and dielectric or mechanical compliance data. The factors are listed in Table I.

Light scattering can be viewed as due to fluctuating strains in the sample. The relaxation function that is measured is equivalent to a compliance. Light scattering can be considered a type of dynamic mechanical spectroscopy where the applied force is due to thermal agitation and the light is used to detect the motion. There are two principal types of motion that are detected by light scattering: (1) density fluctuations and (2) fluctuations in the orientation of the molecular subunits. These orientational motions are coupled to shear strains and probe the local viscosity of the fluid. Depolarized Rayleigh scattering probes the orientation fluctuations, while polarized Rayleigh scattering detects both types of fluctuations. The relaxation functions obtained by photon correlation spectroscopy are expected to be complementary to normal mechanical results, but not necessarily identical. This expectation is borne out in practice for polystyrene[3,4] and for poly(ethyl methacrylate).[9]

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Light Scattering Study of Gelation and Gels Formed during the Thermal Copolymerization of Styrene and Divinylbenzene

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ABSTRACT: The mutual diffusion coefficient D_c is determined by photon correlation spectroscopy during the thermal gelation reaction of styrene and divinylbenzene. The resulting gel is then studied as a function of temperature. The present results do not differ significantly from those obtained for solutions of polystyrene in styrene reported earlier. The quantity D_c is determined by the polymer concentration, the solvent quality, and the temperature T divided by the solvent viscosity η. No information specific to the gel is obtained from the light scattering data.

Introduction

We have recently reported[1] a study of the concentration fluctuations observed by photon correlation spectroscopy during the thermal polymerization of styrene. In the semidilute concentration range it has been suggested[2] that such data can be interpreted in terms of a pseudogel network. We have recently shown[3] that for polystyrene in good solvents, the existence of a pseudogel network should have little or no effect on the observed concentration fluctuations. In the present paper we report a study of the concentration fluctuations observed by photon correlation spectroscopy during the thermal copolymerization of styrene and divinylbenzene. In this way the effect of a solution undergoing gelation is studied. The resulting gel is then studied as a function of temperature.

Theory

The light scattering relaxation function due to concentration fluctuations is given by

$$\phi(t) = \exp(-D_c q^2 t) \tag{1}$$

where D_c is the mutual diffusion coefficient and $q = (4\pi n/\lambda)(\sin(\theta/2))$ is the magnitude of the scattering vector for light of incident wavelength λ traveling in a medium of refractive index n and scattered through an angle θ. The mutual diffusion coefficient for a polymer solution can be expressed as[4]

$$D_c = \frac{M}{N_a f}(1 - \bar{v}c)\frac{\partial \pi}{\partial c} \tag{2}$$

where M is the molecular weight, N_a is Avogadro's number, f is the friction coefficient, $\bar{v}$ is the partial specific volume of the polymer, c is the concentration, and π is the osmotic pressure.

A more general relation for the mutual diffusion coefficient would be[5]

$$D_c = E/\Phi \tag{3}$$

where E is the longitudinal modulus and Φ is the friction per unit volume. For a gel, $E = K + {}^4/_3G$, where K is the modulus of compression and G is the shear modulus. The modulus of compression is given by $c(\partial\pi/\partial c)$, where the osmotic pressure now includes both the effects due to mixing of the polymer and the solvent and the elasticity due to swelling of the network. However, the contribution of elasticity to E is a small fraction of its total value for polystyrene and the observed concentration fluctuations are expected to be insensitive to the presence of the pseudogel or the real gel formed later in the reaction.

Experimental Section

Styrene and divinylbenzene were carefully dried and vacuum distilled into square quartz cells. The divinylbenzene concentration was nominally 8%. The samples were kept in dry ice until use. The thermal polymerizations were carried out at 90 °C as in previous studies.[1,6]

The incident light was as 5145 Å and the scattered light was observed at 90°. The homodyne correlation function $1 + \phi^2(t)$ was obtained with a Malvern correlator operated in the single-clipped mode. Data were collected as a function of elapsed time during the polymerization and as a function of temperature for the gel. The quantity D_c was obtained from a cumulant analysis of the correlation function. The sample time during the initial 5 h of the polymerization was 1 μs. The error in the determination of D_c increased at longer times due to the poorer signal-to-noise ratio obtained with shorter sample times.

Results and Discussion

The thermal copolymerization of styrene and divinylbenzene proceeds faster than that for pure styrene at 90 °C. Another important difference is that the sample undergoes a transformation to an opaque state after approximately 12 h. Examination of the product revealed that the sample was composed of many small clear regions and was a polygel. The reaction was stopped prior to formation of the polygel in order to study a clear gel. Also,

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