Macromolecules **1992,** *25,* 6897–6903

Dynamic Light Scattering by Permanent Gels: Heterodyne and Nonergodic Medium Methods of Data Evaluation

Liqi Fang* and Wyn Brown

Department of Physical Chemistry, University of Uppsala, Box 532, 751 21 Uppsala, Sweden

Received May 1, 1992; Revised Manuscript Received September 9, 1992

ABSTRACT: Four relationships between the intensity and field correlation functions are used in the analysis of measured intensity correlation functions in dynamic light scattering with data obtained for four different polymer gel samples. The evaluation of diffusion coefficients has been performed using inverse Laplace transformation (ILT) and the cumulants method, respectively. Diffusion coefficients derived from the nonergodic medium method are almost the same as those from the heterodyne method when ILT is used. ILT gives similar results by all four procedures even when large baselines exist, whereas the cumulants method leads to incorrect diffusion coefficients from the correlation function derived using the nonergodic medium method. The approach used in our previous work, which implicitly incorporates correction for partial heterodyning through a fitting parameter β', gives somewhat lower diffusion coefficients than the heterodyne method. The partial heterodyne method using ILT also gives satisfactory results. An estimation of the degree of heterodyning can be made from the initial amplitude of the intensity correlation function. When the initial amplitude of the intensity correlation function is smaller than 0.01, the scattering should be treated as fully heterodyned.

Introduction

It is a common observation that the intensity in dynamic light scattering measurements from permanent polymer gels usually contains a nonfluctuating component. Wun et al.[1] proposed a model with a harmonically bound particle to interpret it. This approach leads to a non-single-exponential correlation function for polymer gels. Geissler et al.[2] attributed the origin of the static scattering to microscopic heterogeneities formed during cross-linking. The polymer concentration close to the cross-links is higher than the average since cross-links restrict the motions of the chains, giving permanent departures from uniformity. These authors treated the intensity correlation function as the heterodyne mode[3] because the static scattering from the sample is much larger than the dynamic scattering and the former then serves as a reference intensity. A reference sample[4] of known longitudinal modulus was used to calibrate instrumental parameters. Munch et al.[5] also made dynamic light scattering measurements in the heterodyne mode for gels. On the other hand, Pusey and van Megen[6] explained the existence of nonfluctuating components by regarding polymer gels as non-ergodic media since the constraints of the cross-links inhibit polymer chains from taking all spatial configurations within the time of the Brownian motion. Joosten and Pusey[7,8] provide a theoretical framework which describes the main features of dynamic light scattering by gels and used experimental data to test their theory.

Although it was found in our previous work[9] that the amplitude of the intensity correlation function for aqueous polyacrylamide (PAA) gels is smaller than that for the corresponding solutions, the dynamic light scattering from gels was treated as a so-called "homodyne" mode. The present work aims to reanalyze some of our earlier data using the several methods described in the literature. This is desirable since the plurality of methods referred to has led to some confusion. In particular, we would like to elucidate which approaches yield similar diffusion coefficients and which give divergent results.

Method I is Joosten and Pusey's nonergodic medium method.

Method II is a partial heterodyne method without the β correction.

Method III is a partial heterodyne method with the β-correction. β is an instrumental parameter which takes into account partial spatial coherence effects. Ideally, β equals unity.

Method IV is a homodyne method incorporating a correction for heterodyning.

These approaches yield different relationships between the intensity and field correlation functions from which the diffusion coefficients are obtained. It is the purpose of this communication to compare and contrast these approaches. The diffusion coefficient is evaluated from the field correlation function using the ILT routine REPES[10] and the cumulants method, respectively. Four polymer gels were chosen for the comparison: a polyacrylamide gel in water (PAA–W), a polyacrylamide gel in a mixture of water and glycerol (PAA–WG), a poly(methyl methacrylate) gel in butyl acetate (PMMA–BA), and a poly(vinyl alcohol) (PVA–W) gel in water.

Theoretical Background

Method I (the nonergodic medium method). The intensity correlation function in dynamic light scattering is defined as

$$g^{(2)}(q,t) = \langle I(q,0)\, I(q,t)\rangle / \langle I(q,0)\rangle^2 \qquad (1)$$

The angular brackets denote an ensemble average, but in most practical situations, an autocorrelator takes a time-average. According to Birkhoff's ergodic theorem,[11] which states that two correlation functions will be identical if the mechanical system studied is ergodic, the ensemble average correlation function is replaced by the time-average in dynamic light scattering experiments. However a gel is to be regarded as a nonergodic medium since the time-average measurement is not generally equivalent to the ensemble-average measurement.

The time-average intensity correlation function obtained from the correlator is written here as $g_T^{(2)}(t) - 1$, while the ensemble average intensity correlation function is written $g_E^{(2)}(t) - 1$. Ideally the ensemble average intensity correlation function is the average of all the time-average intensity correlation functions at the different speckles of a sample. Similarly, the ensemble-average intensity will

0024-9297/92/2225-6897$03.00/0

be the average of all the time average intensities at different speckles of a sample. The time and ensemble average intensities are expressed as $\langle I(q)\rangle_T$ and $\langle I(q)\rangle_E$, respectively.

In a gel the polymer segments restricted by the cross-links to particular regions of the sample are able to perform limited Brownian motion about a fixed average position. Therefore the scattered field will contain both a fluctuating component and a time-independent component

$$E(q,t) = E_F(q,t) + E_C(q) \qquad (2)$$

where subscripts F and C denote fluctuating and time-independent properties, respectively.

The normalized field correlation function of a nonergodic medium is related to the fluctuating component of the scattered field as follows:[6]

$$\langle E_F(q,0)E_F(q,t)\rangle_T = \langle E_F(q,0)E_F(q,t)\rangle_E = \langle I(q)\rangle_E[g_{NE}{}^{(1)}(q,t) - g_{NE}{}^{(1)}(q,\infty)] \qquad (3)$$

where $g_{NE}{}^{(1)}(t)$ is the normalized ensemble-average field correlation function obtained from the time average intensity correlation function through (see ref 8 eq 9)

$$g_T{}^{(2)}(q,t) - 1 = Y^2[g_{NE}{}^{(1)}(q,t)]^2 + 2Y(1 - Y)g_{NE}{}^{(1)}(q,t) \qquad (4)$$

where the mean-square intensity fluctuation is

$$\sigma_I{}^2 = \langle I^2(q)\rangle_T/\langle I(q)\rangle_T{}^2 = g_T{}^{(2)}(0) - 1 \qquad (5)$$

The ratio of the ensemble average intensity to the time average intensity is

$$Y = \langle I(q)\rangle_E/\langle I(q)\rangle_T \qquad (6)$$

For an ergodic medium $\sigma_I{}^2 = 1$ and $Y = 1$.

Method II (the partial heterodyne method without β correction). If the scattered light from a gel is partially heterodyned because the heterogeneities provide a source of static scattering, the relationship between the measured intensity correlation function and the normalized field correlation function can be described by (see ref 8 eq 20)

$$g_T{}^{(2)}(q,t) - 1 = X^2[g_{HT}{}^{(1)}(q,t)]^2 + 2X(1 - X)g_{HT}{}^{(1)}(q,t) \qquad (7)$$

where X represents the ratio of the fluctuating component to the total scattered intensity. X is given by

$$X = \langle I_F(q)\rangle_T/\langle I(q)\rangle_T = 1 - (1 - \sigma_I{}^2)^{1/2} \qquad (8)$$

The relationship between the normalized field correlation functions from the nonergodic and heterodyne methods is

$$g_{NE}{}^{(1)}(q,t) = [1 - g_{NE}{}^{(1)}(q,\infty)]g_{HT}{}^{(1)}(q,t) + g_{NE}{}^{(1)}(q,\infty) \qquad (9)$$

Method III (the partial heterodyne method with β correction). Geissler et al.[12] also assumed that the scattered field from a polymer gel contains two parts, of which the static part derives from the heterogeneities. The total detected field is

$$E = E_f + E_r \qquad (10)$$

The detected intensity is then

$$\langle I\rangle = \langle(E_f + E_r)^2\rangle \qquad (11)$$

where E_r is the static field and E_f is the fluctuating field.

The normalized intensity correlation function is

$$g^{(2)}(t) = \langle(E_f(t) + E_r(t))^2({}_{Ef}(0) + E_r(0))^2\rangle/\langle I\rangle^2 \qquad (12)$$

Expansion of eq 12 yields 10 terms, some of which are zero. The relationship between the heterodyned intensity correlation function and the field correlation function is thus given by[14]

$$g^{(2)}(t) - 1 = \beta(\langle I_f\rangle^2/\langle I\rangle^2)[g_{HTB}{}^{(1)}(t)]^2 + 2\beta(\langle I_f\rangle\langle I_r\rangle/\langle I\rangle^2)g_{HTB}{}^{(1)}(t) \qquad (13)$$

where β is an instrumental parameter of the order unity and which depends on the scattering geometry. Here it is assumed that the partial spatial effect and the incomplete mixing efficiency have the same coefficients for the second and the third terms in the formula. The field correlation function is

$$g_{HTB}{}^{(1)}(t) = \langle E_f(0)\, E_f(t)\rangle/\langle E_f{}^2(0)\rangle = \langle E_f(0)\, E_f(t)\rangle/\langle I_f\rangle \qquad (14)$$

If the ratio of the fluctuating intensity to the total intensity is defined as

$$R = \langle I_f\rangle/\langle I\rangle \qquad (15)$$

then the normalized intensity correlation function can be rewritten

$$g^{(2)}(t) - 1 = \beta R^2[g_{HTB}{}^{(1)}(q,t)]^2 + 2\beta R(1 - R)g_{HTB}{}^{(1)}(t) \qquad (16)$$

The ratio of the fluctuating intensity to the total intensity can be estimated from the initial amplitude of the normalized intensity correlation function.[15] Ideally, if this is unity, i.e. $g_{HTB}{}^{(1)}(0) = 1$, then

$$\sigma_I{}^2 = g^{(2)}(0) - 1 = \beta R^2 + 2\beta R(1 - R) \qquad (17)$$

Solving the following equation

$$\sigma_I{}^2 + \beta R^2 - 2\beta R = 0 \qquad (18)$$

leads to

$$R = 1 - (1 - \sigma_I{}^2/\beta)^{1/2} \qquad (19)$$

The apparent diffusion coefficient obtained from the measured intensity correlation function, assumed to correspond to the homodyne mode, is

$$D_A = -(1/2q^2) \lim_{t\to 0} \partial \ln [g^{(2)}(t) - 1]/\partial t \qquad (20)$$

In the heterodyne mode the diffusion coefficient can be obtained from the (heterodyne) intensity correlation function using

$$D_A = -(1/2q^2) \lim_{t\to 0} \partial \ln [\beta R^2 \exp(-2Dq^2t) + 2\beta R(1 - R) \exp(-Dq^2t)]/\partial t \qquad (21)$$

Expanding the exponential functions

$$D_A = -(1/2q^2) \lim_{t\to 0} \partial \ln [\beta R^2(1 - 2Dq^2t) + 2\beta R(1 - R)(1 - Dq^2t)]/\partial t \qquad (22)$$

Therefore

$$D_A = D/(2 - R) \qquad (23)$$

From this relationship, when $R = 1$, i.e. when the fluctuating field is the total field and there is no static field, the $D = D_A$ and the operation is fully homodyned. On the other hand, when $R = 0$, i.e. the total field is static and $D = 2D_A$, the operation is fully heterodyned.

Method IV. The intensity correlation function defined in our previous work[9] was fitted to the following form and was termed the "homodyne" mode due to the use of the squared field correlation function, but which additionally incorporates corrections for heterodyning

$$g^{(2)}(t) - 1 = \beta'[g^{(1)}(t) + B]^2 \qquad (24)$$

It should be emphasized that β' constitutes a fitting parameter in method IV which takes a particular value for a given data set. It will equal β used above if there is no static scattering. When heterodyning occurs from local oscillators, $\beta' < \beta$.

B is sometimes inappropriately termed the baseline, but this leads to confusion with the correctly-defined baseline ($\langle I\rangle^2$) used in dynamic light scattering.

With a finite value for the parameter B, the relationship between the diffusion coefficient obtained using this method and the apparent diffusion coefficient derived from the measured intensity correlation function may be written

$$D_A = D/(1 + B) \qquad (25)$$

With eq 25, correction is made for quasi-static scattering since the factor ($1 + B$) takes into account partial heterodyning from very slow motions which lie outside the time window of the autocorrelator.

Experimental Section

Dynamic light scattering measurements were made by the apparatus and technique described earlier.[16] The laser was a 35-mW He–Ne (633 mm) Spectra Physics model. The autocorrelator was a multi-τ and multibit ALV-3000 model from ALV-Langen, FRG, allowing 23 simultaneous sampling times and thus a monitoring of very widely space decays (up to 9 decades in time) in the same experiment. Inverse Laplace transformation, to obtain the distribution of relaxation times, was made by using REPES, which directly minimizes the sum of the squared differences between the experimental and calculated intensity correlation function $g^{(2)}(t) - 1$ using nonlinear programming.

The direct measurable quantities are the time-average intensity and the corresponding intensity correlation function, the ensemble-average intensity, and its corresponding intensity correlation function. When a gel is measured in one position at one angle, the time-averaged intensity and intensity correlation function at one speckle are obtained. By rotating the sample in the holder at the same scattering angle, different time-averaged intensities and the corresponding intensity correlation functions are obtained for various speckles of the sample. After these and correlation functions have been accumulated in the correlator, the ensemble-average intensity and intensity correlation function at that scattering angle may be obtained according to method I (the nonergodic medium method). The normalized field correlation functions have then been calculated using methods I–IV, respectively. The corresponding diffusion coefficients were subsequently obtained using the ILT routine REPES and the cumulants method.

The ALV-autocorrelator gives the time average intensity as

$$\langle I\rangle_T = \text{MONB}/(\text{SAMP*STC}) \qquad (26)$$

where SAMP is the number of samples processed, STC is sample time in μs, and MONB is the sum of samples processed. The instrumental parameter $\beta = 0.7$–0.8, the value of which has been determined by calibration using a control sample (in the present case a dilute suspension of stearic acid coated silica spheres; hydrodynamic radius 1600 Å[17]). Four polymer samples have been used in the measurements: a PAA gel in water[8] ($C = 2.5\%$; $C_{\text{cross}} = 2.5\%$); a PVA gel in water[18] ($C = 4\%$; $C_{\text{cross}} = 1\%$); a PAA gel in mixture of water and glycerol[19] ($C = 5\%$; $C_{\text{cross}} = 2.5\%$ water/glycerol = 1:1 (v/v)); a PMMA gel in butyl acetate[20] ($C = 10\%$; $C_{\text{cross}} = 3.5\%$).

Results and Discussion

Examples of time-average and ensemble-average intensity correlation functions for four polymer gels are shown in Figure 1. Plots on the left-hand side are the time-average intensity correlation functions, those on the right-hand side are the ensemble-average ones. The initial amplitudes of the ensemble-average correlation function are always larger than that for the time average; however the former also contain a large baseline and therefore the initial amplitudes of the decaying part are not so different for the averaged intensity correlation functions. The initial amplitude of the decaying part is calculated from

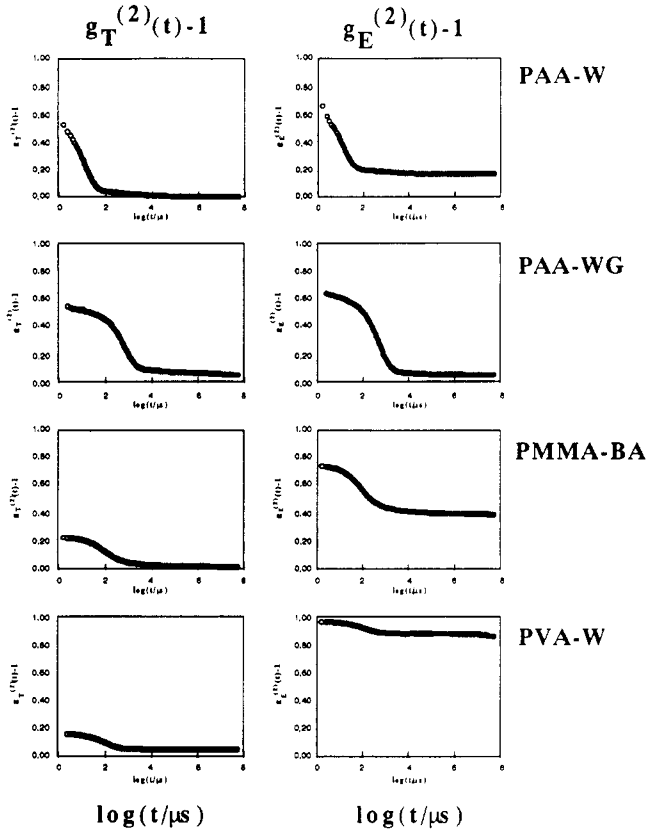

Figure 1. Time-average $g_T^{(2)}(t) - 1$ and ensemble-average $g_E^{(2)}(t) - 1$ intensity correlation functions for the four polymer gels: PAA gel in water ($C = 2.5\%$, $C_{\text{cross}} = 2.5\%$), PVA gel in water ($C = 4\%$, $C_{\text{cross}} = 1\%$), PAA gel in mixture of water and glycerol ($C = 5\%$, $C_{\text{cross}} = 2.5\%$ water/glycerol = 1:1 (v/v)), PMMA gel in butyl acetate ($C = 10\%$, $C_{\text{cross}} = 3.5\%$).

$$\Delta\sigma_I^2 = \sigma_I^2 - g^{(2)}(\infty) \qquad (27)$$

These values are shown in Table I for the time- and ensemble-average correlation functions.

The baseline arises from nonergodicity since the initial amplitude for an ergodic medium should ideally equal unity; i.e. there should be no baseline according to Goosten and Pusey's nonergodic medium method. It is seen that the PAA-WG gel has insignificant nonergodicity while the PVA-W gel is substantially more nonergodic. With the PAA-WG gel only a small baseline is observed for the ensemble-average correlation function whereas for the PVA-W gel there is a large baseline. This shows that polymer gels are not invariably nonergodic media, or, at least, they display strongly varying degrees of nonergodicity.

The distribution of the time-average intensity at different speckles and the probabilities of the time-average intensity are shown in Figure 2. The probability of the time-average intensity is similar to the illustration of Joosten and Pusey used in ref 8 exhibiting an approximately exponential decay after the intensity maximum. However the cutoff at low intensity is not so sharp as in their case. The types of probabilities are almost the same for the four gels.

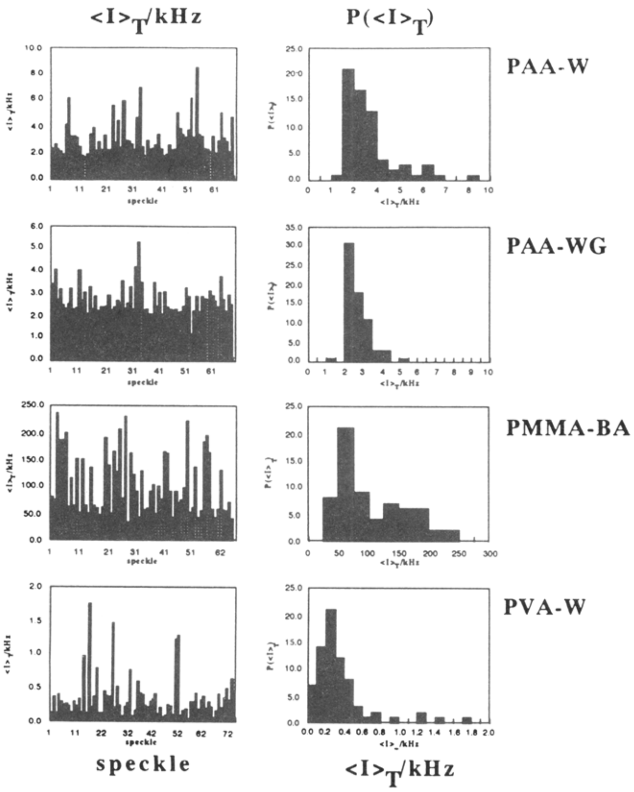

Figure 2. Distributions of the time-average intensity at different speckles and the probabilities of the time-average intensity for the four polymer gels (as in Figure 1).

Table I
Initial Amplitude of the Decaying Part of the Time- and Ensemble-Average Intensity Correlation Functions[a]

gel	$\Delta\sigma_I^2(T)$	$\Delta\sigma_I^2(E)$
PAA-W	0.526	0.490
PAA-WG	0.555	0.660
PMMA-BA	0.211	0.350
PVA-W	0.113	0.104

[a] $\Delta\sigma_I^2(T)$ and $\Delta\sigma_I^2(E)$ represent the initial amplitudes of the decaying part of the time and ensemble average intensity correlation functions, respectively, see eq 27 in the text.

The square of the field correlation function obtained by using methods I–III is plotted in Figure 3 for the four polymer gels. The experimental parameters used in these methods are listed in Table II.

The initial amplitudes of the curves from methods I and II are unity. The field correlation functions obtained from method I all have large baselines. From eq 9 one can see that the field correlation function from method I will have a larger baseline compared to that obtained by method II. The initial amplitudes of the decaying part of the field correlation functions from method I for the different gels are coincident with those of the intensity correlation functions. The field correlation functions from method III have smaller initial amplitudes compared with those from methods I and II.

Diffusion coefficients obtained by the four methods using ILT are listed in Table III and shown in Figure 4. The field correlation functions are first obtained from the experimental intensity correlation functions according to methods I–IV. The diffusion coefficients were then evaluated from these field functions by ILT. Table IV lists diffusion coefficients derived from the field correlation functions using methods I–III and those from the square roots of the time-average and ensemble-average intensity correlation functions using the cumulants method. Here the time-average and ensemble-average intensity correlation functions are treated as in the homodyne mode. (The values for the PAA-W gel are much higher than those measured previously because the structure of the gel changes irreversibly with time. However this is irrelevent to the present discussion.)

The diffusion coefficients for each gel obtained using ILT with the different methods are approximately coincident. The initial amplitude and baseline have little influence on the diffusion coefficient when ILT is used since the different modes are weighted prior to calculation. The values from method IV are the lowest for each gel, however. While those deduced with method IV applied to the ensemble-average intensity correlation functions are slightly higher than those from the time-average, the values from methods I, II, and III are very close to each other. In general, the value from method I is largest while the value from method III smallest. From this point of view, the results from all methods are similar in magnitude when ILT is used to evaluate diffusion coefficients.

The cumulants method gives different results from ILT. Diffusion coefficients were also evaluated using the cumulants method applied only to the decaying part of the correlation function. The last point at which the correlation function is cut off to be fitted was chosen at the beginning of the flat baseline in each case. Here it should be mentioned that this baseline is an "internal" baseline, i.e. the baseline existing after the subtraction of baseline $\langle E\rangle^2$ (see Figure 3 the first column). It is shown that the diffusion coefficients from method I are quite different from those from methods II and III even if the baseline has been cut off. Cutoff of the baseline when using the cumulants method cannot significantly improve the value of the diffusion coefficient since the first moment inevitably includes the baseline. The field correlation functions from methods I and IV for the ensemble-average intensity correlation function contain large baselines and therefore the cumulants method will give a large error. Only for the data for the PAA-W and PAA-WG gels which do not exhibit large baselines will the results from the cumulants method not deviate substantially from the others.

For the PMMA-BA and PVA-W gels there are large baselines in the curves using the nonergodic medium approach so that the values of D obtained by cumulants from these two methods deviate by almost 1 order of magnitude from the D values of other methods. If the time-average intensity correlation function is treated as in the homodyne mode (see Table IV, D_{HMB} column), the diffusion coefficients are approximately half the values of those from the partial heterodyne method. This result shows that the time-average intensity correlation function can be treated as in the heterodyne mode if the cumulants method is used. If the ensemble-average intensity correlation function is treated as in the homodyne mode (see Table IV, D_{E} column), the diffusion coefficient for PAA-W gel is approximately half that from the partial heterodyne method. The diffusion coefficients for the PMMA-BA and PVA-W gels are quite different from those obtained by using the partial heterodyne method. This result shows that the ensemble-average intensity correlation function should be treated differently if the cumulants method is used.[7] The cumulants method is unsuitable for treating the correlation function by the nonergodic medium method and for analysis of the ensemble-average intensity correlation function. Furthermore, it is shown that methods I–III have the same form in the relationships between the

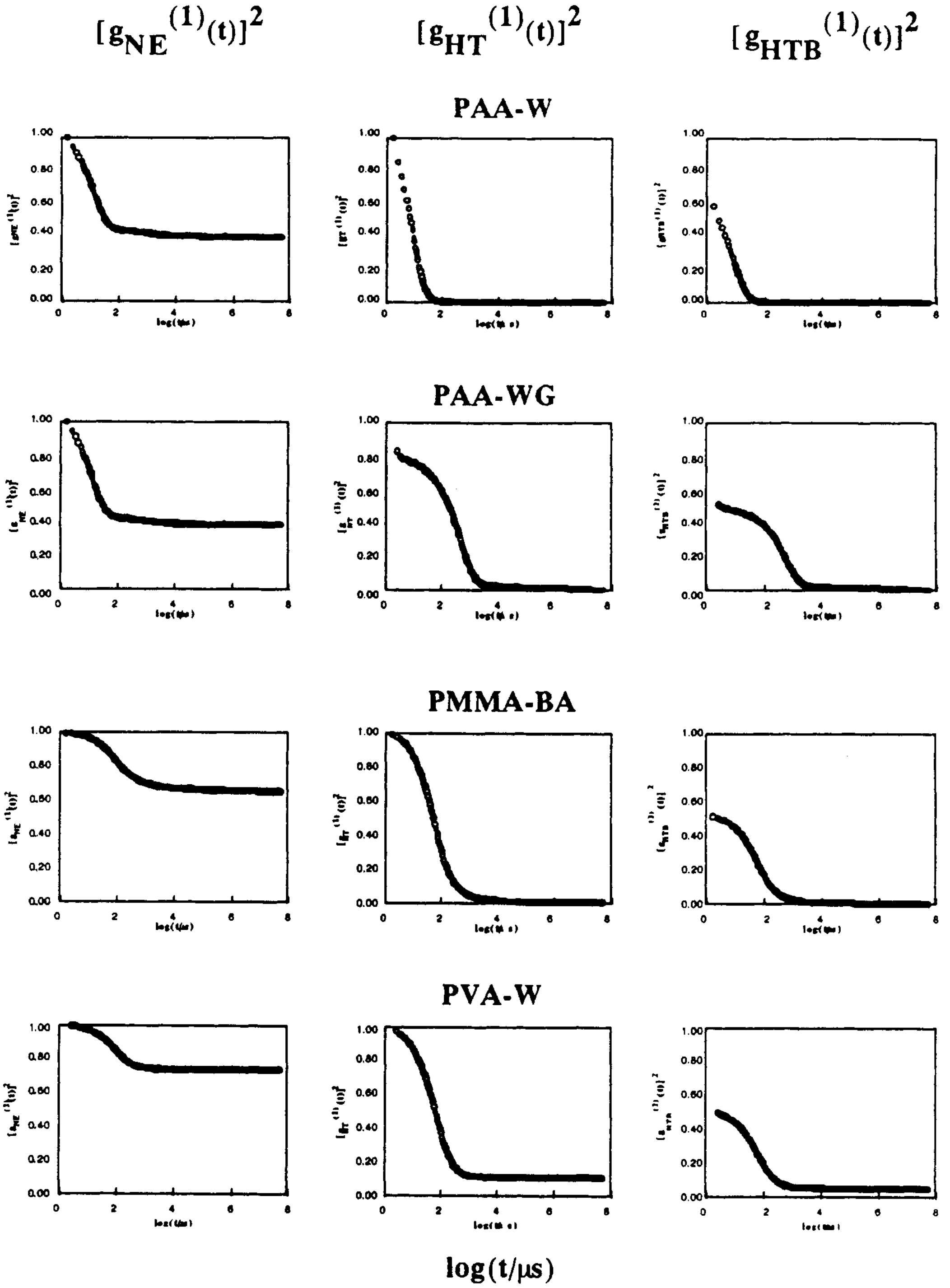

Figure 3. Square of the field correlation function $[g^{(1)}(t)]^2$ obtained from methods I, II, and III for the four polymer gels (as in Figure 1).

Table II
Experimental Parameters *Y*, *X*, *R*, *β'*, and *B* for the Four Polymer Gels

gel	Y	X	R	β'^{a}	B
PAA-W	0.8244	0.5260	0.7510	0.6042	0.05
PAA-WG	0.8242	0.6043	0.8633	0.5506	0.30
PMMA-BA	0.5835	0.2267	0.3289	0.2342	0.26
PVA-W	0.4101	0.1641	0.2344	0.1681	0.52

[a] β' is the fitting parameter in method IV; see eq 24.

intensity correlation function and the field correlation function, i.e. the difference between methods I–III only lies in that Y (eq 6), X (eq 8), and R (eq 19) are used, respectively. Y has the same physical implication as X and R; i.e. these parameters all represent the ratio of the fluctuating field to the total field but different approaches are used. The diffusion coefficients obtained from Methods I–IV are in the proportions (see eqs 23 and 25)

$$D_{NE}:D_{HT}:D_{HTB}:D_{HTB} = (2-Y):(2-X):(2-R):(1+B) \tag{28}$$

However the diffusion coefficients evaluated either by using ILT or by the cumulants method do not maintain this proportion quantitatively. The values from method II are somewhat larger than those from method III since R is always greater than X after making the β correction (see eqs 8 and 19). This fact only qualitatively proves the above proportion. This result is not unexpected because the latter is given by the initial slope of the correlation function. The factors in this proportion are between 1 and 2 and are listed in Table V. Generally the diffusion coefficients obtained using ILT are close to this proportion. The diffusion coefficients from method I and from the ensemble-average correlation function using the cumulants

Table III
Diffusion Coefficients ($D \times 10^{11}$/m^2 s^{-1}) Evaluated by Different Methods and Using the Inverse Laplace Transformation Routine REPES for the Four Polymer Gels[a]

gel	D_{NE}	D_{HT}	D_{HTB}	D_{HMB}	D_E
PAA-W	20.01	19.14	18.09	14.54	17.70
PAA-WG	0.3529	0.3519	0.3229	0.2847	0.3333
PMMA-BA	2.920	2.918	2.902	2.300	2.886
PVA-W	2.624	2.708	2.702	2.205	2.25

[a] D_{NE} is the diffusion coefficient obtained from method I (the nonergodic medium method). D_{HT} is the diffusion coefficient obtained from method II (the partial heterodyne fit without β correction). D_{HTB} is the diffusion coefficient obtained from method III (the partial heterodyne fit with β correction). D_{HMB} is the diffusion coefficient obtained from method IV. D_E is the diffusion coefficient obtained from method IV applied to the ensemble-average intensity correlation function.

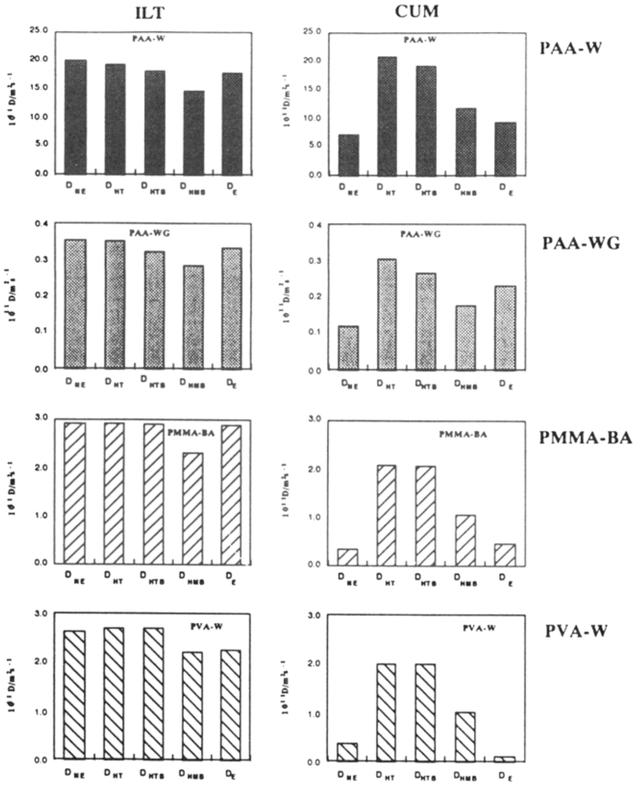

Figure 4. Diffusion coefficients obtained from the four methods and using the ILT routine REPES and the cumulants method for the four polymer gels (as in Figure 1). Columns from the left to the right in each plot are, respectively, D_{NE}, D_{HT}, D_{HTB}, D_{HMB}, and D_E.

method lie far from this proportion. These factors in the proportionality can be also considered as a measure of the degree of heterodyning in dynamic light scattering, since they are the ratios of the diffusion coefficients from methods I–IV to the apparent diffusion coefficients assumed to be in the full homodyne mode. From Table V it can be seen that the factors for the PAA-W gel take the lowest values and the factors for the PVA-W gel have the highest values. Furthermore the trends in the factors for the different gels are almost the same except that the value (1 + B) = 1.30 for the PAA-WG gel is unusually high. This also shows that these factors have essentially the same physical content.

However, Joosten and Pusey[8] obtained different relationships between the apparent diffusion coefficients and the diffusion coefficients from the nonergodic medium method and those from the heterodyne method compared to those from Method IV. The ratio of the diffusion coefficients from method I to that from method II is D_{NE}:D_{HT} = X:Y according to ref 8, eqs 14 and 21. It is shown in Table V that the diffusion coefficients do not coincide with this ratio.

Table IV
Diffusion Coefficients ($D \times 10^{11}$/m^2 s^{-1}) Evaluated from Different Methods and Using the Cumulants Method for the Four Polymer Gels[a]

gel	D_{NE}	D_{HT}	D_{HTB}	D_{HMB}	D_E
PAA-W	7.079	20.79	19.08	11.62	9.258
PAA-WG	0.118	0.3048	0.2647	0.1746	0.2310
PMMA-BA	0.341	2.077	2.062	1.055	0.4590
PVA-W	0.360	2.002	1.995	1.008	0.0945

[a] D_{NE} is the diffusion coefficient obtained from method I (nonergodic medium method). D_{HT} is the diffusion coefficient obtained from method II (heterodyne fit without β correction). D_{HTB} is the diffusion coefficient obtained from method III (the heterodyne fit with β correction). D_{HMB} is the diffusion coefficient obtained from the square root of the time-average intensity correlation function. D_E is the diffusion coefficient obtained from the square root of the ensemble-average intensity correlation function.

Table V
Proportionality between the Diffusion Coefficients Obtained from Methods I–IV(Equation 28)

gel	$2-Y$	$2-X$	$2-R$	$1+B$
PAA-W	1.176	1.474	1.249	1.05
PAA-WG	1.178	1.400	1.137	1.30
PMMA-BA	1.417	1.773	1.676	1.26
PVA-W	1.590	1.836	1.766	1.52

Table VI
Degree of Heterodyning Estimated from the Initial Amplitude of the Intensity Correlation Functions Assuming β = 0.7

gel	σ_I^2	R	D/D_A
PAA-W	0.60	0.62	1.38
PAA-WG	0.20	0.15	1.85
PMMA-BA	0.10	0.074	1.93
PVA-W	0.01	0.0072	1.99

It is obvious from a comparison of eqs 16 and 25 that β' in method IV involves a combination of β and R. This means that at least partial correction for the local heterodyne scattering is included in the fitting parameter β'. When $R = 1$ then $\beta' = \beta$. Calibration of the instrument with a control sample is performed under this condition. The difference between methods III and IV thus lies in the different ways the corrections are made.

The relationship between the intensity correlation function and the field correlation function for the heterodyne mode can be written in a more complete form if further conditions are included[14]

$$g^{(2)}(t) - 1 = (\langle I_f\rangle^2/\langle I\rangle^2)[g^{(1)}(t)]^2 + 2(\langle I_f\rangle\langle I_r\rangle/\langle I\rangle^2)g^{(1)}(t) + (\langle I_r\rangle^2/\langle I\rangle^2)X \tag{29}$$

where $\langle I_f\rangle$ is the fluctuating part of scattering, $\langle I_r\rangle$ is the intensity of reference light, X is defined by

$$X + 1 = \langle I_r^2\rangle/\langle I_r\rangle^2 \tag{30}$$

I_r = constant if the reference field is stationary and X = 0; if the reference field is a Gaussian variable, then X = 1.

Method IV treats the static part in dynamic scattering as "Gaussian dust"[21] (Gaussian static scattering) instead of "constant dust", i.e. if a large number of dust particles is present in the scattering volume at all times. Therefore the last term still remains in eq 29, and it can be rewritten as

$$g^{(2)}(t) - 1 = [(\langle I_f\rangle/\langle I\rangle)g^{(1)}(t) + (\langle I_r\rangle/\langle I\rangle)]^2 \tag{31}$$

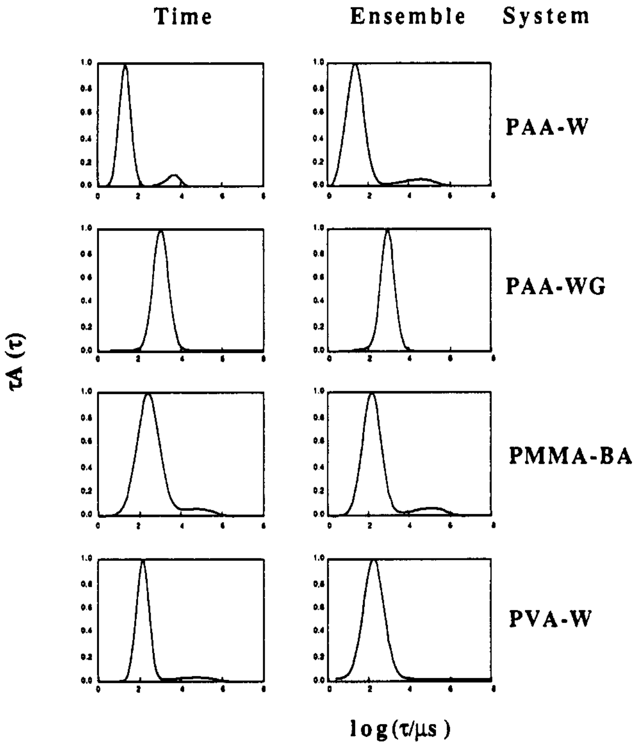

Figure 5. Relaxation time distributions obtained using a GEX fit (17) corresponding to the time-average and ensemble-average intensity correlation functions for the four polymer gels (as in Figure 1). Plots on the left-hand side are obtained from the time-average; plots on the right are from the ensemble-average.

This is the relationship used in method IV.

The diffusion coefficients obtained from method IV using ILT gives somewhat lower values compared to the heterodyne methods I and II. The cumulants method yields approximately half the value given by ILT of the square root of the time-average intensity correlation functions (see D_{HTB} in Tables IV and V) whereas the cumulants method takes the square root of the experimental time-average intensity correlation function and then expands it. This result also shows that method IV is not a true homodyne method.

An estimate can be made of the degree of heterodyning in dynamic light scattering and may be represented by the ratio of the diffusion coefficients from the partial heterodyne method (methods II or III) to the apparent diffusion coefficients D_{A} given by the homodyne method. If $D = D_{\mathrm{A}}$, the operation is fully homodyned, while if $D = 2D_{\mathrm{A}}$, the operation is fully heterodyned. From the initial amplitude of the intensity correlation function σ_{I}^2, the ratio R is obtained by eq 19. The ratio of the diffusion coefficient in the heterodyne mode to that in the homodyne mode is given by eq 23. Some calculated results are shown in Table VI with $\beta = 0.7$. Thus if the initial amplitude of the intensity correlation function is 0.60, then $D_{\mathrm{HTB}} = 1.38D_{\mathrm{A}}$, i.e. the operation is partially heterodyned. If the initial amplitude of the intensity correlation function is 0.01, then $D_{\mathrm{HTB}} = 1.99D_{\mathrm{A}}$, i.e. the operation is almost fully heterodyned. Thus if the initial amplitude of the intensity correlation function is smaller than 0.01, the diffusion coefficient cannot be treated by the homodyne method. The value R may be used in the evaluation of the osmotic longitudinal modulus obtained from static scattering.

Conclusions

Inverse Laplace inversion methods give more reliable diffusion coefficients from measured intensity correlation functions regardless of which relationship is used between the intensity and field correlation functions (methods I–IV). The cumulants method will not give a physically reasonable diffusion coefficient using method I or from the ensemble-average intensity correlation function.

Method I (the nonergodic medium method) may constitute an alternative to the heterodyne methods but will lead to incorrect diffusion coefficients if the cumulants method is applied since the baseline strongly influences the evaluation of the diffusion coefficient.

The procedure (method IV) used in our previous work takes into account partial heterodyning through a fitting parameter β' and, in combination with use of ILT, yields a diffusion coefficient somewhat lower than that given by the heterodyne method and inverse Laplace transformation. While method IV is not a completely satistfactory approach for dealing with a heterodyne system for which method III should be used, it provides a robust and practical means of obtaining diffusion coefficients in such complex systems. Measurement of the ensemble-average correlation function for systems containing local oscillators is a tedious and time-consuming experiment. Use of a cumulants analysis together with such data does not yield the correct diffusion coefficient. On the other hand, use of inverse Laplace transformation for analysis of both the ensemble-average and time-average correlation functions gives satisfactory results.

Acknowledgment. This work has been supported by the Swedish National Board for Technical Development (NUTEK) and the Bo Rydin Fund (SCA, Sundsvall Sweden). Dr. Erik Geissler is thanked for instructive discussions during the course of this work.

References and Notes

(1) Wun, K. L.; Carlson, F. D. *Macromolecules* **1975**, *8*, 190.
(2) Geissler, E.; Horkay, F.; Hecht, A. M. *Macromolecules* **1991**, *24*, 6006.
(3) Geissler, E.; Hecht, M. A. *J. Chem. Phys.* **1976**, *65*, 103.
(4) Scholte, T. G. *J. Polym. Sci., Part A2* **1970**, *8*, 841.
(5) Munch, J. P.; Lemarechal, P.; Candau, S.; Herz, J. *J. Phys. (Paris)* 1977, *38*, 1499.
(6) Pusey, P. N.; van Megen, W. *Physica A* **1990**, *157*, 705.
(7) Joosten, J. G. H.; Gelade, E.; Pusey, P. N. *Phys. Rev. A* **1990**, *42*, 2161.
(8) Joosten, J. G. H.; McCarthy, J. L.; Pusey, P. N. *Macromolecules* **1991**, *24*, 6690.
(9) Fang, L.; Brown, W.; Konak, C. *Polymer* **1990**, *31*, 1960.
(10) Jakes, J. *Czech. J. Phys. B* **1988**, *38*, 1305.
(11) Berne, R. J.; Pecora, R. *Dynamic Light Scattering with Applications to Chemistry, Biology & Physics*; Wiley: New York, 1976.
(12) Geissler, E. In *Dynamic Light Scattering, the Method and Some Applications*; Brown, W., Ed.; Oxford University Press, in press.
(13) Horkay, F.; Geissler, E.; Hecht, A. M.; Zrinyi, M. *Macromolecules* **1988**, *21*, 2594.
(14) Jakeman, E. I. In *Photon Correlation Spectroscopy and Velocimetry*; Cummins, Z. H., Pike, E. R., Ed.; Plenum: New York, 1974.
(15) Geissler, E. Private communication.
(16) Brown, W.; Rymdén, R. *Macromolecules* **1988**, *21*, 840.
(17) Nicolai, T.; Brown, W.; Johnsen, R. M.; Stepanek, P. *Macromolecules* **1990**, *23*, 1165.
(18) Fang, L.; Brown, W. *Macromolecules* **1990**, *23*, 3284.
(19) Fang, L.; Brown, W.; Hvidt, S. *Macromolecules*, to be submitted for publication.
(20) Fang, L.; Brown, W.; Konak, C. *Macromolecules* **1991**, *24*, 6839.
(21) Cummins, H. Z.; Pusey, P. N. In *Photon Correlation Spectroscopy and Velocimetry*; Cummins, Z. H., Pike, E. R., Ed.; Plenum, New York, 1976.

Registry No. (PAA)($NH_2COCH{=}CHCH_2CH{=}CHCONH_2$) (copolymer), 25034-58-6; ($H_2C{=}CHOH$)($OHC(CH_2)_3CHO$) (copolymer), 32630-65-2; (PMMA)($CH_2{=}C(CH_3)CO_2(CH_2)_2CO_2C(CH_3){=}CH_2$) (copolymer), 25777-71-3.