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Quasi-Elastic Light Scattering Study of Linear Flexible Macromolecule Dynamics

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ABSTRACT: There are two approaches to the quasi-elastic light scattering study of polymer intrinsic dynamics. The first one includes cumulant analysis of the scattered light spectrum. Its main advantage consists of the possibility of the unambiguous and precise determination of the first cumulant both in theory and in experiment. The second approach is founded on the solution of the inverse spectral problem by means of various regularization methods, which permit one to decompose the spectrum observed into the sum of the contributions of pure diffusional and several lower relaxational modes. Such an approach is much more informative, but the interpretation of results obtained is somewhat ambiguous and in addition quantitative theoretical predictions seem to be irrelevant. We discuss here some previously published and also new results concerning polymer coil intrinsic dynamics both in Θ-conditions and in good solvent. Significant attention is paid to the asymptote $\bar{\Gamma}(q) \sim q^3$ observed at $qR_g \gg 1$ and to its small but distinct deviation from theoretical prediction and also to the universality of the polymer dynamical behavior. It is shown that relaxation times of the lowest modes are proportional to R^3 but with coefficients approximately twice as large as predicted, and the reasons for this discrepancy are discussed. It is shown also that for the explanation of relaxation times, the angle-dependent hydrodynamical interaction should not be preaverge. In conclusion we discuss further possibilities of the polymer intrinsic dynamics study by means of scattered light correlation spectroscopy.

I. Introduction

Potentialities of quasi-elastic light scattering of macromolecule intrinsic dynamics are now generally known. Light correlation spectroscopy provides a unique possibility of direct investigation of the relatively slow, large scale macromolecule dynamics in the region of times practically unaccessible to such methods as NPR, EPR, and fluorescence depolarization. The intrinsic dynamics affects the scattered light spectrum through modulation of the form factor and diffusion coefficient. Both these effects are small when the fluctuation extent is small as compared to light wavelength. Besides, the spectral broadening due to diffusion of the scatterers makes it complex to distinguish the contribution of the intrinsic dynamics. This explains why the favorite objects for such investigations are polymer or biopolymer coils. The main reasons are (1) dimensions of the polymer coil could be sufficiently large, (2) the relative magnitude of the coil size fluctuations is of the order of unity, and (3) the theoretical description of the polymer coil dynamics is rather elaborate.

Progress in the light scattering study of the polymer dynamics was connected with perfection of experimental data analysis. By means of a single-exponent analysis the significant deviation of the effective decay time angular dependence from one expected for pure diffusion has been ascertain.[1–5] But in general the correlation function of light scattered by polymer coil is not single exponential.[6] Moreover, as we shall see the quantitative evaluation of this function for a real polymer chain is practically impossible. Nevertheless, there is the possibility suggested by Ackasu and co-workers[7–9] of a quantitative approach based on the cumulant method. The first cumulant $\bar{\Gamma}$ can be reliably determined in experiment and predicted theoretically. Since $\bar{\Gamma}$ is the initial derivation of the scattered light correlation function, one does not have to solve dynamical equations, describing the time evolution of the polymer chain. It is sufficient to know the equations. So, this approach permits one to check the correspondence of the dynamical model to reality.

In other papers[8,10–12] $\bar{\Gamma}$ was calculated for linear, ring, and branched chains, taking into account hydrodynamical interaction and in free-draining limit, both in Θ-condition and in a good solvent. In all cases $\bar{\Gamma}(q) = Dq^2$, where D has the sense of short-time diffusion coefficient. This behavior holds until $qR_g \lesssim 1$, where R_g is the mean-squared radius of gyration. In the region $qR_g \gg 1$ but $qL \ll 1$, where L is the statistical segment length, for non-free-draining models the power law $\bar{\Gamma}(q) = Bq^3$ is fulfilled. Constant B depends on whether the hydrodynamical interaction has been preaveraged or not and also on solvent quality. When $qL \gtrsim 1$, $\bar{\Gamma}(q)$ is determined by local motion of chain segments and depends on polymer structure. Usually $qL \ll 1$ ($q \sim 10^4$–10^5 cm^{-1}), but in over half of the coil dynamics investigations various DNAs have been used, since due to DNA's stiffness its space extent is often of the order of λ. For DNA, the parameter qL approaches unity at large scattering angles which results in the nonuniversal behavior analyzed in details by Schurr.[13,14] Comparing the correlation function in the plateau region $qL \gtrsim 1$ with the predictions of the Rouse–Zimm theory, one can determine the length and mobility of the model chain segments.[15,16]

In recent years quite a lot of measurements of $\bar{\Gamma}$(q) have been made for different polymers.[17–24] As a whole, the results of these works are in a fairly good agreement with theoretical predictions. However, a small but distinct descrepancy is also observed. We feel that it is now the time to revise these results systematically in comparison with each other and with the theory.

Though the cumulant method is simple and practical, its possibilities are limited. In fact, the average reciprocial relaxation time of all coil modes, weighted in a complex way, is determined. But fundamental characteristics of the system dynamical behavior are the relaxation times of these modes by themselves, the most interesting being the first, slowest large-scale modes. Today, clear qualitative understanding of the quasi-elastic light scattering by random coils is achieved.[21] Both the relaxation times of the slowest modes and their contribution to the light scattering are determined analytically in the free-draining limit and numerically, with a preaveraged hydrodynamical interaction,[25] and also approximately when the exact hy-

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Table I

sample	[η]	$M_w \times 10^{-6}$	$D \times 10^8$	$M_w(D) \times 10^{-6}$
1. LPA-51	7.4	3.5	3.3 ± 0.1	3.6 ± 0.2
2. LPA-267	16.5	9.8	1.7 ± 0.1	10.9 ± 1.1
3. LPA-31	20.0	12.6	1.55 ± 0.05	13.2 ± 0.8
4. LPA-36	26.0	18.0	1.30 ± 0.05	18.0 ± 1.1

drodynamical interaction is taken into account.[26] However, in all these calculations such an important circumstance as the impossibility of the chain self-crossing is ignored. As the influence of this circumstance on the coil internal relaxation is unknown, the experimental study of the problem is very interesting.

Such experimental possibilities appeared recently, in connection with development of regular methods of the scattered light spectrum (correlation function) analysis.[27-29] These methods permit one to distinguish the contributions of the relaxation processes with different decay times without any a priori information involved. Of course, the "resolution" of the regularization procedure is restricted by statistical errors of the experiment. With typical accuracy of about one percent, only the pure diffusion mode and what seems to be a summary contribution of several slowest intrinsic modes hereafter called the "lowest mode" can be resolved.

In this work we revise our and other author's previous quasi-elastic light scattering studies of random coil intrinsic dynamics. We compare experimental dependences of $\bar{\Gamma}(q)$ for the collection of different polymers and analyze the origin of small but systematic deviations from the theoretical predictions which have been already noted.[18] We present also the new results concerning four polyacrylamides of various molecular weights both in Θ-conditions and in a good solvent and discuss the dependence of the lowest mode decay time on polymer coil dimensions and solvent quality.

II. Materials and Methods

Linear polyacrylamide was obtained by radical polymerization on acidic catalysts.[30] The acrylamide used was twice recrystalized from benzene. The polymer solution obtained was dialyzed from residual monomers and catalyst, concentrated at 30 °C, and precipitated by a 20-fold amount of ethanol. The precipitated polymer was washed by ethanol and sublimated. The solutions were prepared without intensive stirring. Bidistilled water filtered by 0.17-m millipore with or without addition of a known amount of acetone was used as a solvent. Table I contains the molecular weights of polymers used, which were calculated by means of the relations $[\eta] = 7.9 \times 10^{-5} M_w^{0.76}$ and $D = 2.1 \times 10^{-4} M_w^{-0.58}$ hold for polyacrylamide in water.[31] (Viscosity measurements were performed with an Ubbelohde viscosimeter.)

Optical measurements were made in heterodyne scheme at scattering angles from 25° to 90°. Photocurrent processing was performed by a 200-channel spectrometer described elsewhere.[32] All experiments were made at room temperature. The mathematical analysis of the spectra obtained included a regularization procedure.[27] The algorithm we had used earlier was slightly modified. In the present work the quasi-solution of inverse spectral problem A(Γ) is sought on a nonuniform grating. Besides, shot noise is introduced in the algorithm as an adjustable parameter F. So the minimization of the function

$$\sum_{i=1}^{200} (I(\omega_i) - \sum_j A(\Gamma_j)\Gamma_j/(\omega_i^2 + \Gamma_j^2) - F)^2 \sigma_i^2$$

where σ_i are the experimental errors of spectral intensities, is performed simultaneously both in relation to quasi-solution and to F, taking into account their nonnegativity. The first cumulant was calculated according to reconstructed distribution function $A(\Gamma)$:

$$\bar{\Gamma} = \sum_j \Gamma_j A(\Gamma_j) / \sum_j A(\Gamma_j)$$

III. First Cumulant Approach

Time evolution of the polymer chain is described by a generalized diffusion equation

$$P = \frac{\partial}{\partial x_i} D_{ij} \left(\frac{\partial}{\partial x_j} P + \frac{\partial U}{\partial x_j} \frac{1}{kT} P \right) \qquad (1)$$

Here $P(\{x\})$ is the probability of finding the chain in the configuration $\{x\}$, $U(\{x\})$ is the potential energy of this configuration, and $D_{ik}(\{x\})$ is the diffusion tensor. It is convenient to define the function $g = P/P_0$, where $P_0 = e^{-U/kT}$ is the equilibrium distribution function, which obviously is a stationary solution of eq 1. Then,

$$\dot{g} = \hat{L} g \qquad (2)$$

where $\hat{L}$ is the self-ajoint operator with weight function P_0

$$\hat{L} = 1/P_0 \frac{\partial}{\partial x_i} P_0 D_{ik} \frac{\partial}{\partial x_k} \qquad (3)$$

Operator $\hat{L}$ posseses a set of eigenfunctions g_n (modes) with respective eigenvalues λ_n (reciprocal relaxation times),

$$\hat{L} g_n = -\lambda_n g_n \qquad (4)$$

which one has to know for full description of the system dynamical behavior.

The quantity measured in the dynamic light scattering experiment is the correlator $G(\tau)$ of the scattered light fields $E(\{x(t)\})$,

$$G(\tau) = \langle E(\{x(0)\}) E^*(\{x(\tau)\}) \rangle \qquad (5)$$

or the Fourier transform of this correlator—the scattered light spectrum. The angular brackets mean the averaging over equilibrium distribution function P_0. Optically isotropic chain being the case,

$$E(\{x\}) \sim \sum_\alpha e^{i\bar{q}\bar{r}^\alpha(t)} \qquad (6)$$

where $\bar{r}^\alpha$ is the radius vector of the α-th chain segment. According to (2)

$$G(r) = \langle E(\{r\}) e^{-\tau \hat{L}(\{r\})} E(\{r\}) \rangle \qquad (7)$$

From this it is easy to obtain the expression for the first cumulant

$$\bar{\Gamma} \equiv \frac{1}{G(0)} \frac{\partial G(\tau)}{\partial \tau} \bigg|_{\tau=0} = \langle E(\{r\}) \hat{L}(\{r\}) E^*(\{r\}) \rangle \qquad (8)$$

Expanding in (7) and (8) $E(\{x\})$ in terms of the eigenfunctions g_n, we could see that $\bar{\Gamma}$ is averaged over the contributions of all the modes reciprocal relaxation time. But we need not to solve the equation (2) to find $\bar{\Gamma}$. According to (8) one has only to know an explicit from of $\hat{L}$.

The diffusion tensor $D_{ik}(\{x\})$ has the following form

$$D_{ik}{}^{\alpha\beta} = \frac{kT}{\xi} \delta_{ik} \delta^{\alpha\beta} + (1 - \delta^{\alpha\beta}) \frac{kT}{8\pi\eta} \frac{r_i{}^{\alpha\beta} r_k{}^{\alpha\beta} + \delta_{ik} |r^{\alpha\beta}|^2}{|r^{\alpha\beta}|^3} \qquad (9)$$

where η is the solvent viscosity, $\bar{r}^{\alpha\beta} = \bar{r}^\alpha - \bar{r}^\beta$, and ξ is the mobility of a single segment. The second term in this expression, which is in essence the Oseen tensor, describes the hydrodynamical interaction of the chain segments, that is the solvent flow in the vicinity of the α-th segment due to the force acting on the β-th segment. The simplified models are often considered, when the term responsible for hydrodynamical interaction is omitted or replaced by a preaveraged one. However, such approximations neither have physical grounds nor are they necesasary for the $\bar{\Gamma}(g)$ calculation, and we shall not discuss them.

To calculate $\bar{\Gamma}$ one has also to know the equilibrium pair distribution function $P_2(r^{\alpha\beta})$. In Θ-conditions this function is

$$P_2(r^{\alpha\beta}) \sim \frac{1}{|\alpha - \beta|^{3/2}} e^{-|r^{\alpha\beta}|^2/|\alpha-\beta|L^2} \qquad (10)$$

It appears that the hydrodynamical interaction gives the main contribution and

$$\bar{\Gamma}(q) = Dq^2 \quad \text{when} \quad qR_g \ll 1 \qquad (11a)$$

$$\bar{\Gamma}(q) = kT/6\pi\eta Bq^3 \quad \text{when} \quad qR_g \gg 1, qL \ll 1 \qquad (11b)$$

where $B = 1.18$ and

$$D = \frac{kT}{6\pi\eta R_g} \frac{8}{\pi^{1/2}3} \qquad (12)$$

In intermediate region $qR_g \sim 1$, $\bar{\Gamma}(q)$ can be calculated numerically.

Let us discuss the physical sense of asymptotic behavior (11). The correlation function decays after the displacement of the chain segments became of the order $1/q$. When $qR_g \ll 1$ this could be only due to the diffusion of the coil as a whole in a distance larger than its dimension. When $qR_q \gg 1$, the diffusion of the chain fragment with space extent of the order $1/q$ in a distance of the same order is decisive. According to eq 12 the diffusion coefficient of such a fragment is proportional to q and the characteristic time appears to be proportional to q^3. This consideration does not exploit the explicit form of pair distribution function (10), hence, the asymptotic expressions (11) should be valid also for a polymer in a good solvent as has been pointed out by de Gennes.[33]

In a good solvent the pair distribution function is not known exactly. To calculate $\bar{\Gamma}(q)$ in this case, Ackasu et al. used the "blob" concept:

$$P_2(r^{\alpha\beta}) = \frac{1}{|\alpha - \beta|^{3\nu} L_1} e^{-|r^{\alpha\beta}|^2/|\alpha-\beta|^{2\nu}L_1^2} \qquad (13)$$

where $\nu = 0.5$, $L_1 = L$, when $|\alpha - \beta| \leq N_\tau$ and $\nu \approx 0.6$, $L_1 = LN_\tau^{(1/2)-\nu}$, when $|\alpha - \beta| \geq N_\tau$. N_τ is a solvent quality dependent cutoff, separating Gaussian and excluded-volume regimes. $LN_\tau^{1/2}$ is the so-called "screening length" L_τ. However, the constant B in the asymptotic (11b) could be calculated without knowledge of the explicit form of $P_2(r^{\alpha\beta})$. It is sufficient that this function satisfies the scaling law; that is, $P_2(r^{\alpha\beta})$ depends on $r^{\alpha\beta}$ only through combination $r^{\alpha\beta}|\alpha - \beta|^\nu$. Indeed, substituting eq 3 and 9 into eq 8 we get

$$\bar{\Gamma} = \frac{kT}{8\pi\eta} \frac{\sum_{\alpha,\beta} \int e^{i\bar{q}\bar{r}} \frac{(\bar{q}\bar{r})^2 + q^2r^2}{r^3} P_2(r,\alpha-\beta)\, d^3r}{\sum_{\alpha,\beta} \int e^{i\bar{q}\bar{r}} P_2(r,\alpha-\beta)\, d^3r} \qquad (14)$$

When $qR_g \gg 1$, the summation could be replaced by integration up to infinity and taking into consideration that due to scaling property P_2: $\int d(\alpha-\beta)\, P_2(r,\alpha-\beta) \sim r^{(1/\nu)-3}$ we find

$$\bar{\Gamma} = \frac{kT}{8\pi\eta} q^3 \frac{\int_{-1}^{1} dx \int e^{i\bar{x}r}(x^2 + 1) r^{(1/\nu)-2}\, dr}{\int_{-1}^{1} dx \int e^{i\bar{x}r} r^{(1/\gamma)-1}\, dr} \qquad (15)$$

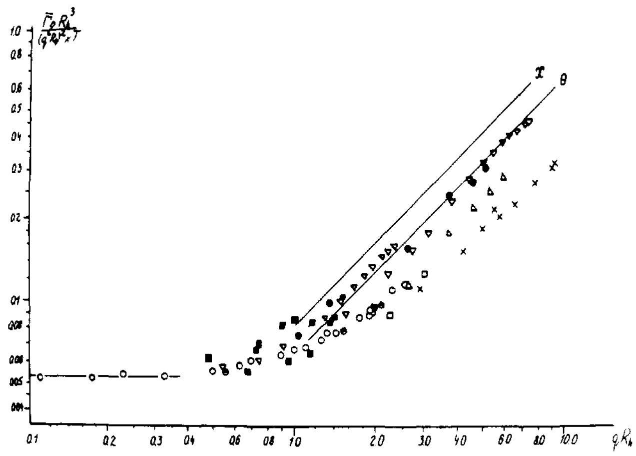

Figure 1. Plot of $\bar{\Gamma}\eta^0 R_h^3/(qR_h)^2 kT$ versus qR_h. The theoretical curve is calculated without preaveraging the Oseen tensor. Θ-solvent: (□) polyacrylamide; (◓) polystyrene;[46] (○) polystyrene;[21] (△) DNA;[1] (▽) DNA.[24] Good solvent: (■) polyacrylamide; (●) polystyrene;[22] (×) polystyrene.[17]

When $0.5 < \nu < 1$, the integrals in eq 15 are convergent and

$$B = \frac{3}{2} \frac{1 + \beta}{2 + \beta} \frac{1}{\beta} tg \frac{\pi\beta}{2}, \qquad \beta = 2 - \frac{1}{\nu} \qquad (16)$$

which coincide of course with the result obtained in another form by Askasu et al.[8] with the help of eq 13. Thus, in Θ-conditions and in a good solvent when $qL_\tau \gg 1$, $\nu = 0.5$ and $B = 1.18$. When $qL_\tau \ll 1$ (but $qR_g \gg 1$) taking $\nu = 0.58$ we get $B = 1.49$.

Up to this time there have been performed the number of experimental measurements of the first cumulant angular dependence for a random coil of various polymers.[17-24] The $\bar{\Gamma}(q)$ should be an universal function of the single variable qR_g; therefore, it is interesting to compare these data with both each other and all of them as a whole with theoretical predictions. In such a comparison it is natural to use the dimensionless variables $\bar{\Gamma}_\eta R_g^3/kT(qR_g)^2$ and qR_g. Then each polymer is characterized by a single parameter R_g (taking apart the solvent quality). Unfortunately, very different methods have been used to determine this parameter. Some authors have used the total scattering intensity data, others the small-angle dynamic light scattering and theoretical or empirical relations between diffusion coefficient and R_g, still others characteristic viscosity, and so on. This leads to small but unpleasant scatter of the data due to errors of the R_g determination. To avoid this, we, when possible, use R_g recalculated according to formula 12 from the angular dependence of $\bar{\Gamma}$ in the region of small qR_g. Such a procedure leads to an automatic coincidence of all experimental data with the theoretical curve when $qR_g \ll 1$ and is equivalent to choosing the hydrodynamical radius of the polymer coil $R_h = kT/(6\pi D)$ as its single characteristic.

Figure 1 presents several results of the $\bar{\Gamma}(q)$ measurements modified in the described manner. The solid lines are the predictions for the Gaussian chain and also for the coil with excluded-volume interactions in a suggestion that $\nu = 0.58$. One can see that these data are in fairly good agreement both with each other and with theory even for such different macromolecules as polystyrene and DNA. This fact supports strongly the universality of the coil dynamical behavior.

As described, the coincidence of the theory and experiment when $qR_h \ll 1$ is exact as a consequence of the definition of R_h. But in the region $qR_h \gg 1$ one can see a small but systematic discrepancy which already has been

Table II

sample	$M_w \times 10^{-6}$	solvent	$B \times 10^2/6\pi$	qR_h	method of anal.
		Θ Solvents			
1.[18] polystyrene	4.1	cyclohexane, 35 °C		1.38	cumulant anal.
	5.05		5.0 ± 0.5	1.53	
	7.5			1.87	
	13.4			2.49	
	44.0			4.52	
2.[23] polystyrene	9.7	*trans*-decalin, 20.4 °C	4.8	2.56	
	9.7		4.5	2.56	regularization
3.[21]	0.78			0.72	
	2.42		5.7	1.23	
	6.53		4.7	1.93	
	9.7		4.5	2.56	
4. polyacrylamide	18.1	water + acetone	5.2	2.34	
5.[45] DNA	24.7		5.4	4.75	
6.[47]	3.5		8.5	2.43	cumulant anal.
	3.5		7.4	2.43	
7.[4] DNA	4.3	water–salt buffer	4.8	4.15	single-exp. fit
8.[1]	3.75		5.4	2.10	
9.[48]	10.3		15.0	2.80	
10.[24]	4.37		6.1	2.46	
	32.5		6.1	7.37	
theory			6.25		
		Good Solvents			
1.[18] polystyrene	4.1	toluene			
	5.05		6.5 ± 1.5		
	7.5				
	13.4				
	44.0			10	
2.[20] polystyrene	44.0	THF, 23.0 °C	6.5		cumulant anal.
	44.0	cyclohexane, 45.0 °C	5.0	7.8	
	44.0	cyclohexane, 55.2 °C	5.0	8.8	
3.[17]	24.0		3.4	7.8	
4.[22]	0.78			1.03	regularization
	2.42		5.4 ± 0.2	1.95	
	5.53	benzene		2.83	
	9.7			4.12	
	13.4			5.10	
5. polyacrylamide	3.6		6.0	1.22	
	10.9		4.7	2.06	
	13.3	water	4.3	2.34	
	18.1		4.4	2.80	
theory			7.9		

pointed out by different authors.[18,20-23] This discrepancy, though small (about 15–20%) is far above the typical errors of $\bar{\Gamma}$ measurements, which are usually about 1%. The scatter of the data of different authors also exceeds this value. It seems, however, that the points corresponding to a good solvent (shaded) lie systematically above ones corresponding to Θ-conditions (hollow) in correlation with the presented values of constant B. The pointed out features are still better illustrated by Table II, where available data $\bar{\Gamma}$ behavior at $qR_h \gg 1$ are systematized.

Coefficient B should be a rather well-defined value both in theory and in experiment. From the theoretical point of view the scaling property of the pair distribution function is of no question, the correction due to finiteness of the segment length is as small as $1/qR_h$. Individual mobility of segments, their nonzero dimensions, and corresponding corrections to the Oseen tensor give the contribution as small as qL. On the other hand, it is clear that polydispersity could have no influence on the correlation properties of the scattered light when $qR_h \gg 1$. Possible parasite contribution from any dust is in proportion to q^2 and could not change the asymptote of q^3 type. Therefore we conclude that discrepancy in question is of fundamental nature.

We suggest that when light scattered by a random coil is analyzed in a limited spectral band (with a finite resolution time), the principal underestimation of $\bar{\Gamma}$ takes place. Such a possibility has been already mentioned.[20,34] Let us estimate the error of the $\bar{\Gamma}$ connected with the finiteness of the time resolution interval $\Delta\tau$. For simplicity we determine $\bar{\Gamma}_{\exp}$ as a slope of the correlation function at the time $\Delta\tau$. (The real procedure of the $\bar{\Gamma}$ determination is of no importance for our qualitative conclusions.) Let the correlation function by a sum of exponents with decay times Γ_n^{-1} and magnitudes A_n. Then,

$$\bar{\Gamma}_{\exp} = \sum_n A_n \Gamma_n e^{-\Gamma_n \Delta\tau} \Big/ \sum_n A_n e^{-\Gamma_n \Delta\tau} \tag{17}$$

and if $\Gamma_n \Delta\tau \ll 1$ we have

$$\bar{\Gamma}_{\exp} = \bar{\Gamma}\left(1 + \frac{\overline{\Gamma^2} - \bar{\Gamma}^2}{\bar{\Gamma}^2}(\bar{\Gamma}\Delta\tau)\right) \tag{18}$$

Usually, when polydispersity of the system is under investigation, $\Delta\Gamma^2 = \overline{\Gamma^2} - \bar{\Gamma}^2 \lesssim \bar{\Gamma}^2$. And optimal $\bar{\Gamma}\Delta\tau$ is recommended to be $(5{:}10)/M$, where M is the number of correlator channels. So with M being of the order of several hundreds, the systematic underestimation of $\bar{\Gamma}$ constitutes several percent of the distribution relative width, which as a rule meets our demands of experimental accuracy.

The situation changes for a light scattering on polymer coils. Indeed, estimating $\overline{\Gamma^2}$ for correlation function (7),

$$\overline{\Gamma^2} \equiv \frac{1}{G(0)} \left.\frac{\partial^2 G(\tau)}{\partial \tau^2}\right|_{\tau=0} \tag{19}$$

we get in a region $qR_h \gg 1 \gg qL$

$$\overline{\Gamma^2} \sim (kT/\eta)^2 q^4/L^2 \sim \bar{\Gamma}^2/(qL)^2 \gg \bar{\Gamma}^2 \tag{20}$$

and formula 19 gives if $L \to 0$ the infinite error of $\bar{\Gamma}$. This happens of course due to the existence of relaxation modes with decay times less than $\Delta\tau$ and therefore relation 18 is invalid.

To evaluate the underestimation of the $\bar{\Gamma}$ in this case let us set the contribution of the modes with relaxation times less than $\Delta\tau$ at zero. This seems to correspond to a real procedure of experimental data analysis by the histogram method[28] or by the regularization method used in our works.[27] Then,

$$\bar{\Gamma} - \bar{\Gamma}_{\exp} = \int_{1/\Delta\tau}^{\infty} \Gamma A(\Gamma)\, d\Gamma \tag{21}$$

where $A(\Gamma)$ is a normalized distribution of the contributions of the modes with different decay times. Since the fastest relaxation process is the orientational motion of the single segment, independence of the $\bar{\Gamma}$ on L in the scaling region $qL \ll 1$ indicates that $A(\Gamma)$ decreases more rapidly then Γ^{-2} when $\Gamma \gg \bar{\Gamma}$. Vice versa, the dependence of the $\overline{\Gamma^2}$ on L means that $A(\Gamma)$ decreases more slowly than Γ^{-3}. So, it seems reasonable to suggest that if $\Gamma \gg \bar{\Gamma}$,

$$A(\Gamma) \sim 1/\Gamma(\bar{\Gamma}/\Gamma)^{\mu-1} \tag{22}$$

where $2 < \mu < 3$ and the factor $(\bar{\Gamma})^{\mu-1}$ is introduced to provide the right dimension of $A(\Gamma)$. Substituting eq 22 into eq 21 we obtain

$$\bar{\Gamma} - \bar{\Gamma}_{\exp} \sim \bar{\Gamma}(\Delta\tau\bar{\Gamma})^{\mu-2} \tag{23}$$

We see that the underestimation of $\bar{\Gamma}$ in the case of the random coil is proportional to the number of channels M in the power less than unity, which lays harder claims on the analyzer band width than in the usual situation.

The exponent μ presumably could be determined from the following qualitative consideration. $\int_x^\infty A(\Gamma)\, d\Gamma$ is the total contribution of the intrinsic dynamics with relaxation times less than $1/x$ or, similarly, with space extent a less than $(\eta/kTx)^{1/3}$. If $x \gg \bar{\Gamma}$, $qa \ll 1$ and this contribution is of the order of $(qa)^4$. Thus, $\int_x^\infty A(\Gamma)\, d\Gamma \sim q^4(\eta/kTx)^{4/3}$ and $\mu = {}^7/_3$. The asymptote $A(\Gamma) \sim q^4(\eta/kT)^{4/3}\Gamma^{-7/3}$ is supported by the correctness of the $\bar{\Gamma}$ and $\overline{\Gamma^2}$ values it gives.

So, according to eq 23, relative systematic underestimation of the $\bar{\Gamma}$ is proportional to $(\bar{\Gamma}\Delta\tau)^{1/3}$ with the coefficient which is generally of the order of unity but depends on the way the experimental data are treated. Such a dependence has been observed.[23] We see that with no precautions the precise determination of $\bar{\Gamma}$ is impossible. For example, one has to have an analyzer with a band of resolution ratio 10^6 to obtain 1% accuracy. This systematic error could be diminished if the explicit asymptotic behavior of $A(\Gamma)$ would be known. We shall consider this question in more detail later.

IV. The Lowest Mode

It is more difficult to reconstruct the contribution of different modes to the scattered light spectrum than to determine the first cumulant. Until recently there has been no reliable approach to this problem. Several attempts have been made to fit the homodyne correlation function by the squared sum of two exponents.[3,4,35–38] The results thus obtained seem to be sensible; however, one could not accept them with confidence since the bimodal form of the correlation function has been suggested a priori. The correct method is to solve the inverse spectral problem by means of any regularization procedure.[27–29] Such a method requires no ad hoc information to reconstruct the modal composition of the spectrum or correlation function. Resolution of this method is connected with measurement accuracy and unfortunately is not too precise. With accuracy of about 1% it appears possible to distinguish unambiguously only the contributions of the lowest mode and the pure diffusion mode, and that only when $qR_h \sim 1$. At lesser q the scattering is mainly due to pure diffusion, and at greater q too many intrinsic modes give a similar contribution.

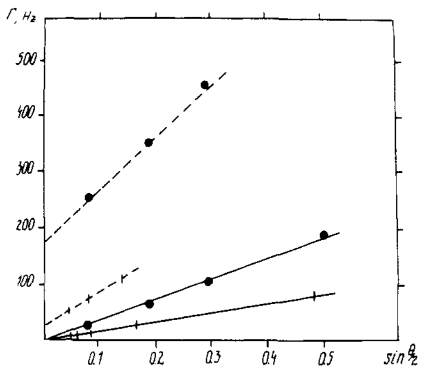

Figure 2. Plots of Γ_0 and Γ_1 versus $\sin^2 \theta/2$ for polyacrylamide LPA-51 and LPA-267.

The angular dependence of the pure diffusion (Γ_0) and lowest intrinsic (Γ_1) modes determined by the regularization method is shown in Figure 2. The decay time of the lowest mode can be found by the extrapolation of the $\Gamma_1^{-1}(q)$ to $q = 0$. Figure 3a presents τ_1 as a function of hydrodynamical radius R_h for several polymers in Θ-conditions together with a prediction for the preaveraged Zimm model.[25] (As has been shown,[26] preaveraging leads only to few percent change of τ_1.) Again the universality of the coil dynamical behavior draws attention. It seems that the law

$$\tau^{-1} = K\frac{kT}{\eta R_h^3} \tag{24}$$

is fulfilled, but with a constant K about one-half of the predicted value. Analogous results in a good solvent reveal for the coil of the same R_h approximately 2.5 times greater values of τ_1 than in Θ-conditions. (Since R_h is dependent on solvent quality, the different coils are thus compared.) We would like the emphasize that the difference between decay times of Gaussian and expanded coils greatly exceeds one between the first cumulants which is only about 20%. This shows once more the low informativity of $\bar{\Gamma}$—an integral characteristic which levels the differences in dynamical behavior.

Unfortunately, up to this time there is no theory able to predict quantitatively the slowest relaxation times of polymer chains not only in a good solvent but also in Θ-conditions. The reason is that the existing theories ignore the impossibility of chain self-crossing, which affects the coil dynamics even in absence of the excluded-volume effects. It seems that the ban on self-crossing should at least numerically change the spectrum of operator $\hat{L}$.

At a qualitative level two items are to be stressed. First, in Θ-conditions there is universal dependence.[24] Similar dependence holds in a good solvent. This fact seems natural from the dimensional consideration. Second, the slope of $\Gamma_1(q^2)$ at small qR_g, which is the "diffusion coefficient" D_1 of the coil in the state, described by the lowest mode, differs from the slope of $\Gamma_0(q^2)$ which is the

Table III

sample	$M_w \times 10^{-6}$	solvent	$K \times 10^2$	D_1/D_0	method of anal.
		Θ-Condition			
1. polyacrylamide	13.3 ± 0.7	water + acetone	19.2		regularization
2.[45] DNA	24.7 ± 1.5	water–salt buffer	21.6	2.7	
3.[46] polystyrene	5.5	*trans*-decalin, 20.4 °C	19.6	1.57	
4.[21] polystyrene	2.42	*trans*-decalin, 20.4 °C	18.5		
	5.53		19.9		
	9.70		21.8	2.42	
5.[35]	27.3	cyclohexane, 35.5 °C	8.6–13.3		bimodal fit
6.[37] DNA	31.6	water–salt buffer	18.6	3.0	
7.[14]	3.75 ± 0.15		11.2		
8.[47]	3.5		4.36		
theory			64		
		Good Solvent			
9. polyacrylamide	3.6 ± 0.2	water	8.4	2.2	regularization
	10.9 ± 1.1		8.6	2.3	
	12.6 ± 1.2		10.1	2.4	
	18.1 ± 1.2		7.7	2.67	

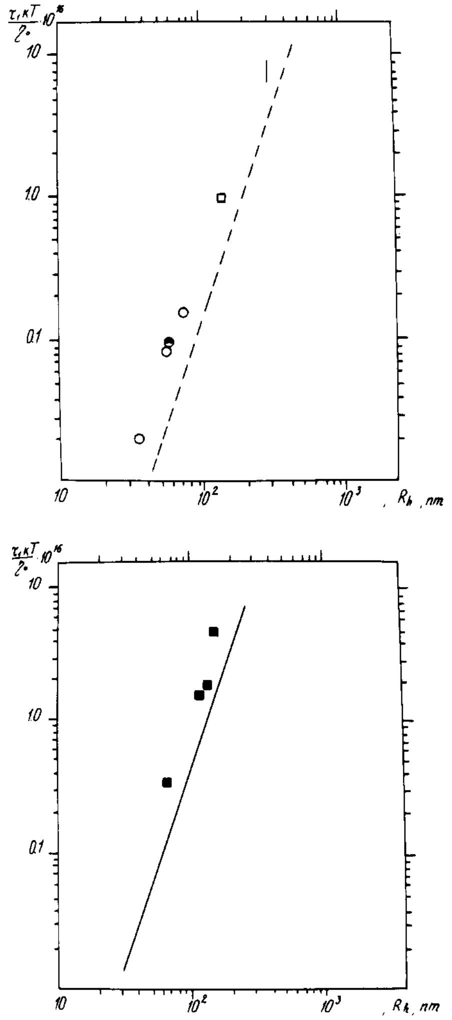

Figure 3. (Top, a) Plot of τ_1 (the decay time of the lowest mode) as a function of R_h in the Θ-condition. The theoretical curve corresponds to the prediction for the preaveraged Zimm model: (□) polyacrylamide; (|) DNA;[45] (○) polystyrene;[21] (◓) polystyrene.[46] (Bottom, b) Plot of τ_1 versus R_h for polymers in Table I (good solvent); curve corresponds to experimental results at the Θ-conditions: (□) polyacrylamide; (●) polystyrene;[22] (◓) polystyrene.[46]

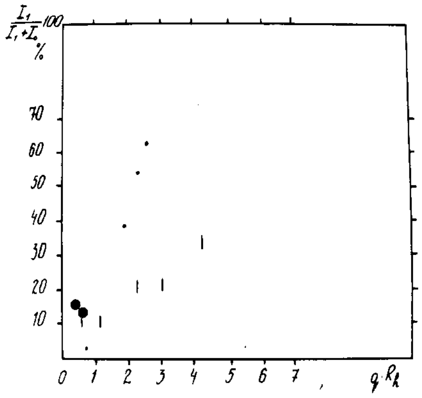

Figure 4. Angular dependence of the lowest mode relative contribution into the light scattering: (|) DNA;[45] (•) polystyrene;[21] (●) polyacrylamide.

true diffusion coefficient D_0 (Figure 2). Proceeding from the idea about the universality of the polymer chain dynamics, one might expect that the ratio D_1/D_0 is independent of any characteristic of the system except solvent quality. Unfortunately, both D_1 and D_0 are to be determined in the region $qR_g \ll 1$, where observation of the lowest mode is a difficult problem. Therefore, the accuracy of D_1 is very low and the universality of the ratio D_1/D_0 as well as the variation of this ratio with solvent quality remains a question. We gather available information concerning dimensionless parameters D_1/D_0 and K in Table III.

The angular dependence of the relative contribution of the lowest mode to light scattering (Figure 4) does not contradict the theoretical predictions. However, on account of defects of the theory noted above and low experimental accuracy, the quantitative comparison is senseless. The general consideration shows that when $qR_g \ll 1$ this relative contribution should be proportional to $(qR_g)^4$ if the scattering center coincides with the center of diffusion (as it is in the free-draining model). If this is not the case and R is a mean-squared distance between scattering and diffusion centers, the term of the order of $(qR)^2$ should be added to the mentioned one.

V. Discussion

Two approaches discussed in previous sections differ significantly both in the level of theoretical and experimental complexity and in the character of the information obtained. The interpretation of the first cumulant measurements presents no problems. If the diffusion operator $\hat{L}$ is known explicity, $\bar{\Gamma}$ can be calculated exactly. The ban on the self-crossing which mathematically appears as some boundary conditions, does not influence on $\bar{\Gamma}$, since the $\bar{\Gamma}$ is a time derivative of the correlation function at infinitely short time, during which no collision in the chain of typical configuration could occur. Experimental measurements of $\bar{\Gamma}(q)$ permit one to check the correctness of the diffusion tensor and the equilibrium pair distribution function. The later is known in Θ-conditions. As for the diffusion tensor D_{ij}, it, as could be seen from section III, is sufficiently accurate in its main features. In this the study of the Gaussian coil dynamics by the cumulant method is in essence complete. Moreover, in an asymptotic region $qR_g \gg 1$, this method cannot yield any information except that about the quality of the experiment.

But in a good solvent $\bar{\Gamma}(q)$ could provide useful information about the pair distribution of the expanded coil. Indeed, in the region $qR_g \gg 1$, $\bar{\Gamma}(q)$ is proportional to constant B given by eq 16 with $\nu = 0.5$ when $qL_\tau \gg 1$ and with $\nu \approx 0.6$ in the opposite case. So, it became possible to study the screening length L_τ as a function of solvent quality. It seems also that the cumulant method provides a very interesting opportunity to determine with high precision the exponent ν of the expanded coil. According to eq 16 1% variation of ν leads to approximately 2% change of the constant B, which could be in principle measured with about 0.1% accuracy. Such an approach is not useful for several specimens with well-known molecular weights. Moreover, in contrast with the direct determination of the coil mean-squared radius as a function of the molecular weight, no hard conditions are laid upon the monodispersity and purity of the specimen.

To fulfill this program we have first of all to learn how to avoid the underestimation of $\bar{\Gamma}$ considered in section III. There are two ways to overcome this difficulty. The first one consists in taking into account the real behavior of the correlation function at short time. As follows directly from the above consideration, the correlation function at a time less than $\bar{\Gamma}^{-1}$ (but larger than orientational time of single segment) should behave as $G(\tau) \sim \epsilon^{-(\bar{\Gamma}\tau + \gamma\tau^{3/2})}$. In connection with this, the paper of Soda and Wada[24] is of interest. They replaced several initial points of the correlation function by extrapolation of all subsequent points according to the low $G(\tau) = Ae^{-(\bar{\Gamma}\tau + \gamma\tau^2)}$ and then fit the data obtained by one exponent. By this rather arbitrary procedure the initial slope of the correlation function was artificially increased and $\bar{\Gamma}$ in very good agreement with theoretical prediction obtained. Of course, only when the true short time asymptotic of the $G(\tau)$ is used, the objective determination of $\bar{\Gamma}$ is possible. Since our qualitative reasoning could not be surely relied on, especially in the presence of the excluded-volume effects, we consider this question as needing experimental examination. The measurement of $\bar{\Gamma}$ as a function of the observation band width would provide us with information both about the initial asymptote of $G(\tau)$ and about the true value of $\bar{\Gamma}$. Sufficiently large variation of the effective band width could be achieved by proper conjunction of the data from several subsequent bands of the analyzing apparatus. However, such research is not yet fulfilled.

The approach founded on the regularization procedure yields significantly more information about intrinsic dynamics in comparison with the cumulant method, but unfortunately, this information is somewhat ambiguous. Moreover, the theoretical predictions available are not too trustworthy. Indeed, to calculate the decay times of the intrinsic modes, their dependence on q, and their contribution in the scattering, one has to solve eq 2. This can be done numerically for a Gaussian coil with preaveraged and even with real hydrodynamical interactions, but only provided the ban on chain self-crossing is ignored. The necessity of taking into account excluded-volume effects in a good solvent creates the further great difficulties. We have to conclude that our knowledge of the polymer coil intrinsic dynamics remains essentially on the qualitative level. Further experimental research in this field should prove interesting.

Nevertheless several conclusions can be already made. The characteristic relaxation time of the coil as determined by quasi-elastic light scattering is proportional to R_g^3 whereas the diffusion coefficient is proportional to R_g^{-1}. These results conform to the nondraining model. As for the quantitative agreement, we have no reasons for it. The results available cannot be considered as a proof of the absence of a very slow relaxation connected with chain entanglement. Let us imagine, for example, the ring chain which can cross itself with very low probability. The ring chain forms knots of different topology,[39,40] each with its set of relaxation modes. Let the time T of the chain topology relaxation be large as compared to the usual intrinsic relaxation time of a typical low $\tau \sim R_g^3/kT$. At $T = \infty$, we have many pure diffusion modes and a rich set of intrinsic modes. If T would be finite but large then only one pure diffusion mode would remain with ensemble-averaged diffusion coefficient $\bar{D}$. Other diffusion modes would gain finite decay times of the order of T at $q = 0$. The intrinsic relaxation times would be changed slightly: instead of τ^{-1} we would have $\tau^{-1} + T^{-1}$. There are few chances that the regularization procedure resolves diffusion modes of various knots where $T = \infty$, since their diffusion coefficients are of the same order. With T finite, the pure diffusion mode differs significantly from the "quasi-diffusion" modes, when $Dq^2 \leqslant T^{-1}$, but in this region of q the contribution of anything except pure diffusion in light scattering is negligible. Whether T is infinite or not, or even of the order of τ, we would see essentially the same picture: the "pure" diffusion mode and the "lowest" mode with characteristic time τ. Though the chain topology is not a determinable conception, a linear polymer being the case, the disentanglement of the chain could be very slow and the above picture adequate. We conclude that the results presented in section IV are in agreement with the non-free-draining model but do not elucidate the entanglement problem.

Another distinct fact is an approximately twofold difference between the initial slope of the $\Gamma_1(q^2)$ and true diffusion coefficient. The existing theory does not allow calculation of the ratio D_1/D if the diffusion tensor depends on the configuration. In the opposite case (in the free-draining limit or when the diffusion tensor is preaveraged) whether the ban on self-crossing is taken into account or not D_1/D is equal to unity. Since Table III gives $D_1/D = 2.2$, the exact consideration of the hydrodynamic interaction is important for an adequate description of the angular behavior observed.

The universality of the parameters K and D_1/D is also an interesting problem. If self-crossing is permitted, this universality should take place, since large-scale dynamics is determined mainly by hydrodynamic interactions and the pair distribution function of distant segments and consequently is independent of the polymer chemical structure. On the other hand, the ban on self-crossing means the existence of boundary conditions on the hypersurface, representing in the polymer configurational space all conformations with at least one self-crossing. Namely, the flow of the probability density P through this hypersurface should be equal to zero. As this hypersurface has $3N - 1$ dimensions, it is not unique for a polymer with given R_g but depends on the number of segments. Therefore, the question about universality of the large-scale chain dynamics remains open. Experimental results, however, seem to support the indea of universality but not too certainly because of their low accuracy and the variety of data treatment.

VI. Conclusion

In conclusion we would like to discuss the nearest perspective of the polymer dynamic study by means of quasi-elastic light scattering. It is an inherent property of the ill-conditioned mathematical problems that the resolution of the regularization procedure increases very slowly with data accuracy. So, further progress cannot be readily achieved by simple perfection of the experiment. There are, however, several methodical alternatives. First this is a cross-correlation technique,[42-44] which consists of a measurement of the cross-correlation between the intensity fluctuations of light scattered in two different directions. It appears that the cross-correlation function is not sensitive to the scatterers translational motion; hence the diffusion mode does not contribute at all and there is no angular dependence of other modes decay times. This simplifies significantly the analysis of intrinsic dynamics. Additionaly there is a remarkable opportunity to control the ratio and sign of the contributions of the modes with different rotational symmetry by the positioning of the photodetectors. (Due to isotropy of the polymer coil, each mode transforms according to some representation of the rotational group.) The pay for these advantages is low accuracy of the cross-correlation measurements as compared to those of autocorrelation. Moreover, if the photodetectors are not near each other, the condition of nonnegativity is absent, which decreases the regularization procedure resolution. As a result, in the first cross-correlation study of polymer dynamics[42] only a rough estimation of the slowest relaxation time was obtained.

An interesting opportunity is connected with nonuniform polymers. Since the scattering and diffusion centers of the uniform polymers are not far from each other, in the region $qR_g \ll 1$ where the unambiguous separation of the diffusion and intrinsic modes is possible, the relative contribution of the latter is very small. But when the scattering is mainly due to only part of a polymer, the scattering center coincides with the center of this part and is removed from that of diffusion at a distance of the order R_g. In this situation the relative contribution of the lowest modes is of the order of $(qR_g)^2 \sim \Gamma_0/\Gamma_1$. This means that the lowest mode could be observed in principle even if $qR_g \ll 1$. Moreover, when the mean refractive index of the polymer matches that of solvent, the pure diffusion does not contribute at all at q tending to zero. Such a situation could be created also by bounding a small but strongly scattering particle to the polymer. The large-scale dynamics of such a system is essentially the same as that of the free polymer, but the contribution of the intrinsic motion should change drastically depending on the relations between refractive indices of the particle, polymer, and solvent.

Registry No. Polyacrylamide, 9003-05-8.

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