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# Short-Time Behavior of the Dynamic Structure Factor for Flexible-Chain Molecules

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ABSTRACT: The short-time behavior of the dynamic structure factor $S(q,t)$ for flexible Gaussian chains is discussed with the familiar Zimm model. Although the drift from initial to steady-state translational diffusion coefficient may not be observable, the angle-dependent term proportional to the fourth power of the scattering vector decays at a rate that may influence the evaluation of the first cumulant from photon correlation measurements.

In recent years, much valuable information on the dynamical behavior of dissolved flexible macromolecules has been obtained from measurements of quasi-elastic light scattering.[1,2] Attention has often been concentrated on the first cumulant $\Gamma$ (initial time derivative) of the dynamic structure factor $S(q,t)$, both because it appears to be readily obtainable from experiment and because it can theoretically be expressed in terms of equilibrium averages over the macromolecular conformations. The latter circumstance was recognized by Akcasu and Gurol (hereafter AG)[3] and has been extensively utilized in the theoretical study of different molecular models.[3-11] The theoretical expression is sufficiently tractable so that premature averaging of the hydrodynamic interactions among the various parts of the dissolved macromolecule can often be avoided.

A possible difficulty in the evaluation of the true first cumulant from experiment is that the structure factor at short times contains contributions from all the chain coordinates, including some that decay very rapidly. Thus, because the time resolution of any photon-correlation apparatus is limited, there is a danger that the apparent first cumulant found experimentally will differ from the true initial value. In the limiting case of rigid molecules, most of the internal molecular modes become infinitely fast, and the problem just described becomes acute.[12]

At low scattering angles the first cumulant can be written as

$$\Gamma = q^2 D[1 + Cq^2\langle S^2\rangle + ...] \qquad (1)$$

where $D$ is the translational diffusion coefficient, $\langle S^2\rangle$ is the mean square radius of gyration, and the magnitude of the scattering vector is $q = (4\pi/\lambda)\sin(\theta/2)$. For polydisperse samples, both $D$ and $\langle S^2\rangle$ are $z$-average values. The dimensionless coefficient $C$ depends on chain structure (e.g., presence of branches[10] or rings[11]), on polydispersity,[10] and on chain stiffness,[13] but it is only slightly affected by excluded volume.[14] Perhaps more interestingly, its theoretical value depends[3,9] on whether the intrachain hydrodynamic interactions, as expressed in the customary Oseen–Kirkwood–Riseman formulation,[15,16] have been preaveraged or allowed their full range of fluctuating values. For the latter reason alone, a careful evaluation and full understanding of $C$ is worth pursuing, and this pursuit is the principal goal of the present work.

## Translational Diffusion

Because of coupling between translational and internal motions, the aforementioned short-time problem is already seen in the limiting low-angle term $q^2D$. The initial value necessarily corresponds to an unbiased equilibrium distribution of chain conformations and orientations (and to a corresponding theoretical equation for $D$ originally derived by Kirkwood[17]), but eventually a steady-state value of $D$ is reached in which the differing translational resistances of the various conformations are weighted accordingly.[18-20] For flexible chains the effect is most easily seen for the Zimm model,[21] where the hydrodynamic interactions are preaveraged and an analytical solution is possible. In this case the dynamic structure factor at low scattering vectors[22,23] can be expressed in the form

$$\ln [S(q,t)/S(q,0)] = -q^2tD(t) + \mathcal{O}(q^4) \qquad (2)$$

with

$$[D(t) - D(\infty)]/D(\infty) = \sum_{k=1} J_k{}^2\nu_k f(u_k)/J_0{}^2\nu_0 \qquad (3)$$

where $D(\infty)$ is the final steady-state diffusion coefficient, the $\nu_k$ are the eigenvalues of Zimm's hydrodynamic $\mathbf{N}$ matrix, and

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$$f(u_k) \equiv u_k^{-1}[1 - \exp(-u_k)]; \qquad u_k \equiv t/\tau_k' \tag{4}$$

$\tau_k'$ being the relaxation time associated with the $k$th normal tensile mode.[21] Finally, the coefficients $J_k$ are given by

$$J_k = \sum_j Q_{jk} \tag{5}$$

where the $Q_{jk}$ are the elements of the $k$th eigenvector of the normal coordinate transformation matrix $\mathbf{Q}$. The sum $J_k$ is proportional to the projection of the $k$th eigenvector onto the zeroth one and thus measures the contribution of this mode to overall translation of the macromolecule. When the modes are orthogonal (e.g., rings or any free-draining model), $D(t) = D(0) = D(\infty)$ and the Kirkwood equation[17] is exact. For symmetric open chains, $J_k$ vanishes for all odd $k$, since only even modes contribute to the net translational motion. It can be shown that eq 3 yields the Kirkwood value for $D(0)$, as it should. Numerically, the Zimm model makes $D(0)$ and $D(\infty)$ differ by only 1.7%. However, published observable diffusion coefficients by the QELS method are lower than the Kirkwood $D(0)$ by about 15% for polystyrene[24] and 23% for poly(methyl methacrylate).[25] This rather large discrepancy may possibly be due to the effects of premature averaging of the hydrodynamic interactions,[19,26] but it may reflect more fundamental shortcomings of the Kirkwood–Oseen formalism. If we suppose that the time dependence of $D(t)$ is at least approximately given by eq 3, but with an augmented amplitude forcing $D(\infty)$ to agree with the observed diffusion coefficients, we should still conclude[23] that the change in $D$ with time is probably not observable. This conclusion is not, however, valid for the term of $\mathcal{O}(q^4)$, as will now be seen.

## Time Dependence of the $q^4$ Term

Extending eq 2 one term further and in imitation of eq 1, we write

$$\ln [S(q,t)/S(q,0)] = -q^2 t D(t)[1 + q^2\langle S^2\rangle C(t) + ...] \tag{6}$$

An alternative formulation is

$$-\mathrm{d} \ln S(q,t)/\mathrm{d}t = q^2 D'(t)[1 + q^2\langle S^2\rangle C'(t) + ...] \tag{7}$$

For the translational term, this latter formulation with the Zimm model leads to the analogue of eq 3 with each $f(u_k)$ replaced by $\exp(-u_k)$.

To obtain the time dependence of the $C$ term, we start with Pecora's solution[27] for the Zimm model, which may be written

$$S(q,t) = \exp(-q^2 Dt)\sum_j^N \sum_l^N \exp(-q^2 b^2 R_{jl}/6) \tag{8}$$

where

$$R_{jl} \equiv \sum_{k=1}^{N} \mu_k^{-1}[Q_{jk}^2 + Q_{lk}^2 - 2Q_{jk}Q_{lk} \exp(-u_k)] \tag{9}$$

In these relations, the symbol $D$ is the steady-state $D(\infty)$ of the Zimm model, $b$ is the root-mean-square length of each of the $N$ Gaussian submolecules, so that $\langle S^2\rangle = Nb^2/6$, and the $\mu_k$ are the eigenvalues of Zimm's[21] coordinate matrix $\mathbf{M}$.

To effect economy in the computations and display the behavior of $C(t)$ most simply, we now resort to a familiar approximation: the true Zimm eigenvectors are replaced by their free-draining values

$$Q_{jk} = (2/N)^{1/2} \cos (\pi jk/N) \qquad (k \geq 1) \tag{10}$$

and also

$$\mu_k = \pi^2 k^2/N^2 \tag{11}$$

This trick, which was observed to afford a good approximation at any degree of hydrodynamic interaction by Zimm, Roe, and Epstein[28] and later successfully exploited by Hearst[29] and others,[30] has the immediate consequence (since the eigenvectors are now orthogonal) of eliminating the previously discussed time dependence of the translational diffusion coefficient. However, the time dependence of $C(t)$ is necessarily much greater and, we believe, not much altered by this approximation.

We now replace the sums over $j$ and $l$ by integrals and then find

$$\ln [S(q,0)/S(q,t)] = q^2 Dt + (q^4 b^4 N^2/18\pi^4)\sum_{k\geq 1} k^{-4}(1 - e^{-2u_k}) + \mathcal{O}(q^6) \tag{12}$$

Comparison to eq 6 and 7 then gives

$$C(t) = (2\langle S^2\rangle/\pi^4 D)\sum_{k\geq 1} k^{-4}\tau_k^{-1} f(\upsilon_k); \qquad \upsilon_k \equiv 2u_k \tag{13}$$

$$C'(t) = (2\langle S^2\rangle/\pi^4 D)\sum_{k=1} k^{-4}\tau_k^{-1} \exp(-\upsilon_k) \tag{14}$$

Finally, we simplify the final result by appropriate substitution of the Zimm expressions[16,21] for $D$ and $\tau_k$, and eventually we find

$$C'(t) = [2^{3/2}\pi^{-5/2}\Gamma(3/4)/\Gamma(5/4)]\sum_{k=1} k^{-4}\lambda_k' \exp(-\upsilon_k) \tag{15}$$

with a corresponding expression for $C(t)$. The reduced times also can be expressed as

$$\upsilon_k = 2t/\tau_k' = t/\tau_k = (\lambda_k'/\lambda_1')(t/\tau_1) \tag{16}$$

where

$$\tau_1 = 0.416 M[\eta]\eta_0/RT \tag{17}$$

in terms of the molecular weight $M$, the steady-flow intrinsic viscosity $[\eta]$, and the solvent viscosity $\eta_0$. In eq 14 and 15, the $\lambda_k'$ are the dimensionless Zimm eigenvalues for the nondraining limit, appropriately taken as those of Hearst,[29] which are consistent with the eigenfunction approximation of eq 9; for numerical values, see Yamakawa, *loc. cit.*,[16] Table VI.2, p 288.

From eq 15 the initial value $C'(0)$ is calculated to be 0.126, which is 5% lower than the correct value of $^2/_{15}$ for the nondraining Zimm chain.[9] The error is surely due to the use of the approximate eigenfunctions of eq 1 and the attendant disappearance of some small terms.

From eq 14 we calculate the dimensionless ratio $C'(t)/C(0)$ as a function of the reduced time $t/\tau_1$, with the result displayed in Figure 1. If we specialize to the numerical case of polystyrene in cyclohexane at the Θ temperature, this curve predicts that $C'(t)$ drops to 90% of its initial value after about 10 μs for a molecular weight of 10,$^6$ and after about 40 μs for a molecular weight of 10.$^7$ These figures, which have already been reported elsewhere[13] along with a preliminary account of the present results, suggest that evaluation of $C(0)$ from experiment may often require consideration of the time dependence to avoid reporting too small a value. This is confirmed by some recent experimental results on polystyrene[31] that show the apparent value of $C$ to be a decreasing function of the sampling time of the correlator and for which extrapolation to zero sampling time yields a value of $C$, in good accord with the theory[9] for a nondraining nonpreaveraged chain.

The time dependence of the apparent first cumulant at still higher scattering vectors ($q^3$ region) is a less trivial

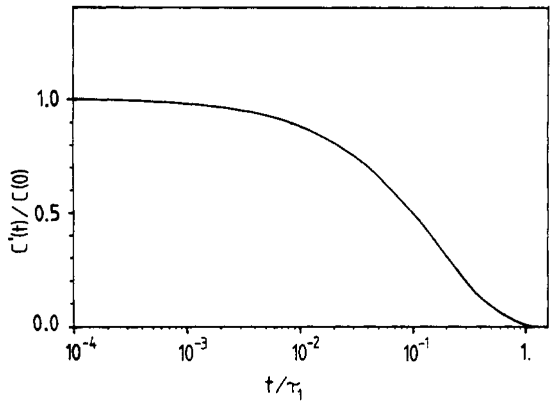

**Figure 1.** Reduced values $C'(t)/C(0)$ of the $q^4$ term as a function of reduced time $t/\tau_1$, where $\tau_1$ is the terminal nondraining Zimm viscoelastic relaxation time.

problem that will be discussed elsewhere.

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# Neutron Quasi-Elastic Scattering by Small-Ring Polymers

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ABSTRACT: The quasi-elastic incoherent neutron scattering spectrum for ring polymers in the Rouse regime is computed on the basis of a next-neighbor diffusion model. The evolution equation involves an orientation correlation due to fixed bond angles and a particular distance scaling due to next-neighbor bond correlations. In the case of a small-ring polymer, an exact mode analysis is possible and gives rise to an expression for the quasi-elastic line shape appropriate for any model leading to an evolution equation of the diffusion type (in one dimension). The translational autocorrelation function, the half-width at half-height, and the quasi-elastic line shape for different ring sizes and static correlations as predicted by the freely jointed chain and the next-neighbor diffusion models are presented and discussed.

## Introduction

Quasi-elastic scattering by polymers in the melt and in solution has interested theoreticians for a long time. In 1967, de Gennes[1] predicted for an infinite Rouse chain a $q^4$ dependence of both incoherent and coherent spectra half-width, $\Delta\omega(q)$, in the low-$q$, long-time limit. This work was extended[2] by Dubois-Violette and de Gennes to include hydrodynamic interactions, thus predicting a $q^3$ dependence of $\Delta\omega(q)$. These predictions have been successfully checked by experiments.[3,4] Moreover, the validity of these unusual $q$ dependences seemed to extend to unexpectedly high $q$ values: $q\sigma \sim 1$, where $\sigma$ is the bond length of the chain. At low $q$ values the de Gennes regime is limited by the overall diffusion of the molecule (which has a finite size) and there should appear a crossover to a classical $q^2$ dependence. At high $q$ values, neutron scattering is only sensitive to local motions, and the following question arises: Does the spectrum behave as predicted by a local conformation jump model or not (see, for example, ref 5 and 6)?

In a series of papers[7-9] Akcasu et al. applied the Zwanzig–Mori formalism to polymer solutions in order to investigate the crossover between these different regimes. These authors used the bead–spring and freely jointed