

QUASI-ELASTIC LIGHT SCATTERING AS A DIAGNOSTIC OF SINGLE CHAIN DYNAMICS

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Abstract - Aspects of polarized coherent quasi-elastic light scattering by dilute macromolecular solutions are reviewed. Existing theories of translational and conformational diffusion in chain molecules give generally good but not completely quantitative descriptions of the scattering behavior.

INTRODUCTION

In recent years the most challenging problems in the field of light scattering by polymer solutions have been found in semi-dilute and concentrated solutions and molten polymers. Our present knowledge of the dynamical behavior of isolated chain molecules in very dilute solutions, though farther advanced, is still far from complete. As experimental data accumulate and techniques of analysis improve, higher levels of description become necessary. From this point of view we may be at a watershed at the present time. Here we review some selected aspects of recent progress and hope to point out areas where further investigation would be useful.

Experimental techniques or methods are not discussed here. We simply assume that the dynamic structure factor for coherent polarized scattering by isolated macromolecules,

$$S(q,t) = \sum_j^N \sum_k^N \langle \exp i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_k(0)) \rangle \quad (1)$$

can be obtained from the experiments. Here the magnitude of the scattering vector is $q = (4\pi/\lambda)\sin(\theta/2)$, and $\mathbf{r}_j(t)$ is the position of chain element j at time t . An unusual degree of attention has been given to the first cumulant Γ , defined as the initial time derivative,

$$\Gamma = -[d \ln S(q,t)/dt]_0 \quad (2)$$

because it can be related theoretically to an equilibrium average, as first shown in the polymer context by Akcasu and Gurol (1). We shall also focus on Γ in the text to follow, but it should be recognized that in this way a certain part of the experimental material is simply ignored. The reason is not hard to find: only for a very few molecular models (e.g., rigid rods, Gaussian chains with pre-averaged hydrodynamic interaction) has the full expression for $S(q,t)$ been evaluated.

TRANSLATIONAL DIFFUSION

During the past several years there has been ample confirmation (see, for example, refs. 2-4) of the fact that the observed translational diffusion coefficients of flexible chains in theta solvents lie some 15 or 20% below the values predicted by the classical theories of Kirkwood (5) or Zimm (6). Expressed in terms of the ratio ρ of root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$ to Stokes radius, $R_h \equiv k_B T / 6\pi\eta_0 D$, the experiments yield ρ values in the range 1.2 to 1.3, while the classical theories (which differ by only 1.7%) give about 1.5. The effects of polydispersity and of polymer concentration on the analysis of the experiments have been given careful attention, and these clearly cannot account for the discrepancy, so that some improvement of the theory is needed. Several different attempts in this direction have been made recently.

The Kirkwood theory leads (in the long-chain, non-draining limit) to the

identification

$$1/R_h = N^{-2} \sum_{i < j} \langle 1/R_{ij} \rangle \quad (3)$$

where R_{ij} is the distance between chain elements (beads) i and j ; and, if Gaussian statistics are used, a limiting value is reached of $\rho \equiv \langle S^2 \rangle^{1/2} / R_h = 8/3\pi^{1/2} = 1.5045$. It was suggested by Guttman, McCrackin and Han (7) that real chains at the theta temperature, involving both repulsive and attractive interactions among segments, can deviate from this ratio even for very large N , and they offered some Monte Carlo results for self-avoiding lattice chains with nearest-neighbor attractions in support of this idea. More recently Fixman and Mansfield (8) have reconsidered this question, and on the basis of additional simulations, plus a perturbation theory, they do not regard it as the likely explanation. Indeed, they conclude that all physically relevant moments of the chain length distribution must scale at the theta point as they do for Gaussian chains. The rather slow convergence of the sum in eq.(3) to its limit, which has long been known, may account for a small part of the discrepancy, but it seems altogether likely that more fundamental dynamical questions are at hand.

Several years ago Zimm (9) studied by Monte Carlo methods the translation diffusion of an equilibrium assembly of Gaussian chains with the full (not pre-averaged) version of the Oseen hydrodynamic interaction, making the following approximation: each individual chain rigidly retains its conformation, undergoing only rotational and translational motions. This condition, probably originally used by Kramers, is correct for free-draining conditions or for the pre-averaged form of the Oseen interaction, but if the full fluctuating Oseen formula is used it is not exact. Nevertheless, Zimm's results extrapolated to large N are in excellent agreement with the experiments for polystyrene in theta solvents. See also related calculations by Garcia de la Torre and Freire (10) and by Edwards, Kaye and Stepto (11). Fixman (12) investigated the validity of the rigid-body algorithm and found that in fact this offers a lower bound to D , but his own Brownian dynamical simulations (Ref. 13) for even rather long Gaussian chains do not yet approach the Zimm figures.

A surprising turn has been taken very recently with Fixman's (14) discovery that the introduction of a simple form of "internal viscosity", extending no farther than third bonded neighbors, suffices to push the results very close to the Zimm limit. In other words, a local deviation from the standard model seems to produce a sensible effect on a global transport property, with an attendant departure from strict Gaussian scaling! It may be recalled that "internal viscosity" has a long history, and may have several distinct physical bases. For one, there must be some energy transfer among the mechanical degrees of freedom totally within the chain molecule, without solvent participation. It also is generally recognized, however, that departures from a strictly Gaussian chain backbone potential can cause local or semi-local dynamical effects which can be mimicked by introducing an internal-viscosity term into the basic equation for a Gaussian chain (Refs. 15-17). This circumstance is scarcely surprising, but that such an effect should persist in the zero-frequency limit of pure translation is highly disturbing and demanding of further study.

It has been argued by Oono (18) that the Oseen form of the hydrodynamic interaction, or its macroscopic-hydrodynamic extensions, such as that of Rotne and Prager (19), has been pushed too far, and that there is a basic inconsistency in treating the solvent as a hydrodynamic continuum while explicitly considering the full coordinate space of the chain molecule; alternate formulations have been offered by Oono and Freed (20) and by Ng, Kapral and Whittington (21). Oono shows that the Oono-Freed approach, which bears some resemblance to the Onuki-Kawasaki (22) treatment of critical dynamics in binary fluid mixtures, confirms the Oseen-Kirkwood equation when treated by renormalization-group techniques only to first order in the variable $\epsilon = 4-d$, where d is the dimensionality of the system. Unfortunately the higher-order terms are extremely difficult to calculate, which makes a full assessment of Oono's viewpoint rather elusive. However, the first-order (in ϵ) calculation of translational diffusion of Gaussian chains by Oono and Kohmoto (23) gives $\rho = 1.24$, in excellent agreement with the experiments, and in this calculation the full fluctuating (non-preaveraged) Oseen hydrodynamic interaction was used. We need some didactic aid.

Whatever the ultimate hydrodynamic theory may turn out to be, an interesting experimental situation is encountered in the evaluation of QELS from solutions of block copolymers. The first cumulant for both linear and star block copolymers has been discussed by Burchard *et al.* (24). The most interesting situation corresponds to the case where the total refractive index increment of the macromolecule vanishes, one block having a higher index than the solvent and the other block a lower index. In this strange case, the apparent mean square radius of gyration can go to indefinitely large negative values and the apparent translational diffusion coefficient (limit of Γ/q^2 at zero angle) becomes indefinitely large and positive. This latter bizarre behavior is, however, seen only in the initial time derivative (i.e., the defined first cumulant), and after the internal mode relaxation is accomplished the standard translation diffusion coefficient emerges to dictate the time correlation function at low angles. This example may suggest that it is misleading to speak of translational self-diffusion as "center-of-mass" diffusion, as is often done. Although the center of mass is a meaningful quantity in a sedimentation experiment, it plays no special role in QELS or other common methods of observing free translation diffusion: any label or labels on any part of the molecule will suffice to reveal the motion over sufficiently long times or distances, and at shorter times the effects of internal motions have to be explicitly considered and do not require the center of mass to be the center of attention.

GLOBAL INTERNAL MOTIONS

As the scattering angle or scattering vector magnitude is increased, the apparent diffusion coefficient Γ/q^2 increases because of the contributions from internal motions. It has been convenient to discuss the initial increase in terms of a dimensionless parameter \underline{C} defined in the relation

$$D_{app} = \Gamma/q^2 = D(1 + C\langle S^2 \rangle q^2 + \dots) \quad (4)$$

where D is the translational diffusion coefficient. The quantity \underline{C} depends theoretically on chain topology, polydispersity, chain stiffness to a negligible extent on excluded volume, and on whether full or pre-averaged hydrodynamic interactions have been assumed (Refs. 25-27). It can be obtained quite well (Ref. 28) from a graphical procedure analogous to the Zimm plot. Experimental data for polystyrene under theta conditions (Refs. 4, 29) have been interpreted to indicate that the pre-averaged Oseen interaction is superior to the full fluctuating one. However, Bantle, Schmidt and Burchard (30) find that the evaluation of \underline{C} is sensitive to the sampling time of the time-correlator, and suitably extrapolated value leads to the opposite conclusion. It is not hard to show (Ref. 31) from the Pecora (32) solution of the pre-averaged Zimm model that such an effect is indeed to be reckoned with.

The effect of chain stiffness on \underline{C} has been estimated only approximately (Ref. 27), and the very rapid relaxation rates of really stiff coordinates (Ref. 33) render an experimental evaluation of the true first cumulant somewhat arbitrary. As chain stiffness is increased, the apparent value of \underline{C} first rises and eventually decreases again toward the rather low value characteristic of a rigid rod. Thus one cannot really use \underline{C} as a reliable indicator of chain stiffness, and it is much better to work with \underline{D} itself. Schmidt's (28) experimental results, however, are consistent with the theoretical estimate.

INTERMEDIATE-SCALE MOTIONS

At sufficiently high wave vector q , but still corresponding to the condition $qb \ll 1$, where b is a bond length, a regime is reached in which the first cumulant for Gaussian chains becomes proportional to q^3 and independent of molecular weight or branching. For the full Oseen interaction, at the theta point, the theoretical plateau value is given by

$$\Gamma = q^3 k_B T / 16 \eta_0 \quad (5)$$

and for pre-averaged hydrodynamics the constant is lowered from $1/16$ to $1/6\pi$. Again the experimental data (Refs. 24, 34) are in better agreement with the pre-averaged figure, and the observed values of Γ actually lie below both theoretical estimates. Among possible ways of rationalizing this departure we may consider the following:

(1) The contributions of the faster internal modes may relax too rapidly, so that the true first cumulant may be unattainable for this reason. This suggestion may be approximately explored by using the full "shape function" long ago calculated for very long Zimm (pre-averaged) chains by duBois-Violette and deGennes (35), which takes the scaled form $S(q,t) = S(\Gamma t)$ in the q^3 region. The original equations are a bit awkward for numerical use at short times, but Barrett (36) has cast them into handier form. From his results it seems hard to squeeze out more than a 1 or 2% reduction of the effective Γ , and about 15% is needed.

(2) Local deviations from a Gaussian backbone potential, i.e., chain stiffness, may begin to contribute significantly, even for polystyrene. The Kuhn length ℓ for this polymer is about 2 nm, so with an argon ion laser the region of interest corresponds to about $q\ell = 0.06$. To investigate this question, we have extended the work of Schmidt (27) into the higher- q region with both wormlike and "sliding-rod" models for chain stiffness. We find an effect of the desired sign, but again it is difficult to get more than a 2% reduction if realistic parameters are employed.

(3) It is logical to expect that "internal viscosity" would also influence the first cumulant in the q^3 region, although Allegra and Ganazzoli (37) found no effect on Γ in their treatment. Following a perturbation method of incorporating the recent Fixman (14) approximation to an internal viscosity, we do find some reduction of Γ , but no reliable numerical estimate is available. In view of our earlier allegation that internal viscosity is perhaps in large part a manifestation of departures from purely Gaussian conformational statistics, there may be some redundancy between this calculation and the previously described one. A more complete study is needed.

(4) It may be that the basic incompleteness of the Oseen description of hydrodynamic interaction at the molecular level is responsible for the trouble. The apparent superiority of the pre-averaged form of this interaction is not understood. Clearly many challenges remain for the theoretician, even for single chains in theta solvents.

We have not attempted to review QELS in good solvents, although there is a good body of both experimental and approximate theoretical results. And, as said earlier, the most interesting questions concern scattering at higher concentrations, in the semi-dilute region and beyond, but this is not the province of the present discussion.

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