EFFECTS OF POLYDISPERSITY, BRANCHING AND CHAIN STIFFNESS ON QUASIELASTIC LIGHT SCATTERING

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Abstract - Aspects of polarized coherent quasi-elastic scattering by dilute macromolecular solutions are discussed. Effects of polydispersity, branching and chain stiffness are considered, particularly in respect to the observable first cumulant of the dynamic structure factor and its dependence on the scattering angle. A combination of integrated and time-resolved scattering data yields the maximum information.

INTRODUCTION

During the past decade, thanks to both experimental and theoretical advances, dynamic light scattering has become an important technique of polymer characterization. A very useful review of the theoretical situation for solutions of macromolecules was published last year by Akcasu, Benmouna and Han (1) and our purpose here is to supplement that article. Older standard references (2-4) may also be read with profit.

As our major interest here is in applications to the characterization of individual macromolecules, and particularly in those features mentioned in the title, discussion is confined to dilute solutions, thus perforce with neglect of some very interesting phenomena encountered with semidilute solutions or gels. For similar reasons, we restrict ourselves to polarized scattering and leave untouched both depolarized scattering and incoherent scattering.

In the earlier history of the field, most measurements were made interferometrically and the line width and line shape were reported. With the development of photon correlation methods, the common technique is now in the time domain, and leads to the determination of the dynamic structure factor $S(q,t)$ as a function of time and of scattering vector magnitude, $q = 4\pi\lambda^{-1}\sin(\bar{\theta}/2)$. Effectively, the time autocorrelation function of the scattered electric field strength is the quantity obtainable from these experiments.

TRANSLATIONAL DIFFUSION

For a dilute solution of identical structureless solute particles, the correlation function has the simple exponential form

$$S(q,t)/S(q,0) = \exp(-q^2Dt), \qquad (1)$$

where $\underline{D}$ is the translational diffusion coefficient. At sufficiently small values of q, the same relation holds strictly for arbitrary solutes only if there is no coupling between translational and rotational or deformational motions. If, as is usually true (see below), the effects of this coupling cannot be seen experimentally, then observations of $S(q,t)$ for polydisperse solutions offer information about the distribution of $\underline{D}$. Chu and coworkers (5,6) and Provencher and coworkers (7,8) have implemented practical methods for inverting such data, closely related to similar tasks long confronting students of the ultracentrifuge.

The study of migration in external fields by light scattering is well developed in the case of electrophoresis (Ref. 9), and this has even found application to medical diagnosis (Ref. 10). Less well known is the ingenious experiment of Wada, Nishio and Soda (11), who showed that the scattering from a solution confined in a sinusoidally vibrating cell affords a determination of the sedimentation coefficient. The initial experimental results are of

moderate precision, but are fully adequate to establish the correctness of the analysis. Thus the ratio of sedimentation to diffusion coefficients, which leads to the molecular weight via the Svedberg equation, can be determined by dynamic scattering methods at low angles without the need of angular-dependence information.

We return now to the problem of coupling between translation and internal motion. The initial time-dependence of the time correlation function always corresponds to an unbiased sampling of all conformations and orientations of the solute molecule, as given by an equilibrium ensemble average. However, as time proceeds, the coupling (if it exists) favors certain internal states over others and eventually produces a steady-state value of D which differs from the instantaneous initial value. As a result, even at low q, a plot of $\log S(q,t)$ against time will become linear only after a certain time interval, of the order of magnitude of the effective orientational correlation time of the molecule. Specific model calculations dealing with this phenomenon are available for rigid dumbbells (Ref. 12), rigid rods (Refs. 13-15), hinged rods (Ref. 16) and Gaussian chains with pre-averaged hydrodynamic interaction (Refs. 17-20) (the Zimm model). In the case of Gaussian ring molecules with pre-averaged hydrodynamic interaction, no coupling exists, the "center of resistance" coinciding with the center of mass; this is in contrast to the open chain, where the average hydrodynamic shielding is less for terminal atoms than for those in the middle of the chain contour.

For the Zimm chains the initial value of D is given by the well-known equation of Kirkwood (21,22)

$$D(0) = 4k_BT/9\pi^{3/2}\eta_o<S^2>_o^{1/2},\qquad(2)$$

where η_o is solvent viscosity and $<S^2>_o$ the unperturbed mean square radius of gyration. In the final steady state the value $D(\infty)$ is only 1.7 percent lower than $D(0)$. The time required for the transition from initial to steady-state behavior is of the order of the longest internal normal-mode relaxation time. The complete expression actually involves all the even modes; it was first given explicitly by Dubois-Violette and deGennes (18) in the Appendix of their paper but not further pursued. More recent numerical estimates (Refs. 19,20) indicate that the effect would be too small to measure for Zimm chains of any molecular weight under present experimental capabilities.

A survey of the considerably body of data on polystyrene under unperturbed theta conditions (Ref. 23) reveals that in fact the measured diffusion coefficients are no less than 15% lower than the Kirkwood value; and even lower results have been recorded for poly(methylmethacrylate) (Ref. 24). Zimm (25) has recently reported Monte Carlo studies of unperturbed Gaussian chains in which pre-averaging of the hydrodynamic interactions has been avoided, and has found rather good agreement with the experimental data, but his method contains one approximation that needs further exploration (Ref. 26). In any case, since the time scale of the coupling effect cannot be greatly altered by the pre-averaging approximation, it may be concluded that even a 15% drop in D would occur over such short times as to elude definite experimental detection.

The behavior of D for flexible chains in good solvents has continued to generate interest as an aspect of the excluded volume effect. If we define an effective Stokes-Einstein hydrodynamic radius by $R_h = k_BT/6\pi D\eta_o$, we may expect, for very high molecular weights M in sufficiently good solvents, the power laws

$$<S^2> \sim M^{2\nu}\qquad;\qquad R_h \sim M^{\nu'},\qquad(3)$$

and intuitively we would set $\nu' = \nu$. However, in view of the analogy between these limiting exponents and those for certain model magnetic critical phenomena (cf. Ref. 27), a possibility remains that the equality is not exact, no matter how tempting on ordinary physical grounds. Earlier data on polystyrene in benzene (Ref. 28) were best correlated with an exponent $\nu' = 0.55$; but when the molecular weight range (in toluene) was extended to some 40 million by Appelt and Meyerhoff (29), the value $\nu' = 0.58$ was obtained, which within experimental uncertainty matches the best values of $\nu = 0.59$ to 0.60.

At lower molecular weights, no really reliable theories of $\underline{D}$ have been worked out for chains with excluded volume. The so-called "blob" model has been used in its most primitive form (Refs. 1,30) and a cluster-series first coefficient was long ago computed (Ref. 31). All these efforts started from the general Kirkwood (21) equation which, as has been seen, is not exact except at $t = 0$. Further theoretical efforts in this area would be useful.

Translational diffusion alone is thus probably the most important aspect of dynamic light scattering for polymer characterization, as theories are fairly well developed (cf. Ref. 22) for linear and branched flexible macromolecules as well as for stiff-chain models (Refs. 32-34). Dimensionless ratios, such as $h \equiv R_h(\text{branched})/R_h(\text{linear})$ at the same M_w and $\rho \equiv <S^2>_z^{\frac{1}{2}}<R_h^1>_z$ at the same M_w, show considerable dependence on both polydispersity or on branching, and results are available for quite a few models (cf. Ref. 35).

OBSERVABLE QUANTITIES

In principle the photon correlation method yields the complete normalized correlation function $S(q,t)/S(q,0)$ at all times and over a range of $\underline{q}$ values. In practice, the $\underline{q}$ range is of course rather restricted and the values of $S(q,t)$ at long times are too small to distinguish from the noise level. As with many other similarly limited measurable properties, we then have two more or less alternative ways of proceeding (cf. Ref. 1): (a) Develop theoretical models predicting complete function $\underline{S}(q,t)$ and obtain the molecular parameters of the model by matching experimental and theoretical curves. (b) Distinguish certain features of the correlation function which can be evaluated more or less unambiguously from the experimental data, independently of any particular model, and then consider the applications of various models to these results.

Method (a) is rather restricted because few models have been worked through in sufficient detail. The second method was greatly enhanced in value a few years ago when Akcasu and Gurol (36), hereafter AG, derived a very general theoretical formula for the initial time derivative $[-d\ln S(q,t)/dt]_0$ or so-called first cumulant of the correlation function (cf. Refs. 37,38). A frequently used symbol for this quantity is Γ, or more explicitly $\underline{\Gamma}(q)$, but Akcasu and his coworkers (cf. Ref. 1) prefer the symbol $\underline{\Omega}(q)$.

At very low $\underline{q}$, the first cumulant is equal to $q^2\underline{D}$, as seen in eq. 1 for a single solute species. In a polydisperse sample, a z-average value is obtained, since the scattering power of a molecule in a homogous series varies as the square of its molecular weight:

$$D_z = \Sigma_j w_j M_j D_j / \Sigma_j w_j M_j \qquad (4)$$

As $\underline{q}$ is increased, contributions from the internal molecular motions begin to contribute to Γ. The leading term is proportional to q^4 and is an increasing function of molecular size. It is useful to express this behavior in the form

$$\Gamma = q^2 D_z (1 + Cq^2 <S^2>_z + ...) \qquad (5)$$

where $<S^2>_z$ is the z-average mean square radius of gyration obtainable by conventional ("integrated") light scattering and $\underline{C}$ is a dimensionless number that in general depends on chain structure, polydispersity and solvent power. It is given special attention in the next section.

At higher $\underline{q}$, flexible macromolecules reach a domain in which Γ is due mainly to rather short-scale motions and varies as q^3. In this region (cf. Ref. 1) no information about molecular weights, dimensions, or topology is obtainable, and we do not consider it further. Nor can we pass to still higher $\underline{q}$, where Γ begins to display oscillatory behavior due to local chain structure. This has been seen in neutron scattering experiments and discussed theoretically by Akcasu and Higgins (39) for one model.

THE C-COEFFICIENT; RESULTS FOR FLEXIBLE MACROMOLECULES

Calculations of the coefficient C for a number of Gaussian models, linear and branched, are available (Refs. 1,35,36,40). In all of these, the general theoretical equation of Akcasu and Gurol (36) was used together with the familiar Kirkwood-Riseman form (cf. Refs. 21,22) of the polymer diffusion tensor. It is not necessary to repeat the general equations here. The effects of pre-averaging the hydrodynamic interactions are interesting: for linear chains, $C = 13/75 = 0.1733$ without pre-averaging, but this drops to $C = 2/15 = 0.13333$ if the pre-averaging manoeuvre is used. For linear polydisperse systems with a Flory "most probable" distribution, the corresponding values rise to 1/5 and 1/6, respectively. On the other hand, branching lowers the value of C; for example, a regular star with four rays has $C = 0.1482$ without pre-averaging and $C = 0.1020$ with pre-averaging.

In addition to the quantity C and the ratios h and ρ mentioned earlier, of course we also have the classical ratio g of mean square radii for branched and linear molecules of the same molecular weight. If all four of these quantities have been measured, it is often possible to narrow considerably the choice of molecular models consistent with the data (cf. Ref. 35).

Two questions remain about the above-described calculations. One is the possible effect of excluded volume on the coefficient C. The first term in the cluster expansion has been evaluated by Tanaka (41), with the interesting result that the effect of excluded volume on C is rather small, though dependent on whether or not pre-averaging is invoked. It is probably too small to measure with present accuracy. For larger excluded volumes, Benmouna and Akcasu (42) have made extensive calculations with the "blob" model, and some of their results are discussed by Akcasu, Benmouna and Han (1).

The other question concerns the possibility that the true initial value of C predicted by the AG equation may not always be the measured one. We have seen earlier that the translational diffusion coefficient itself has a time dependence in the scattering experiment, albeit a small one. The terms in q^4
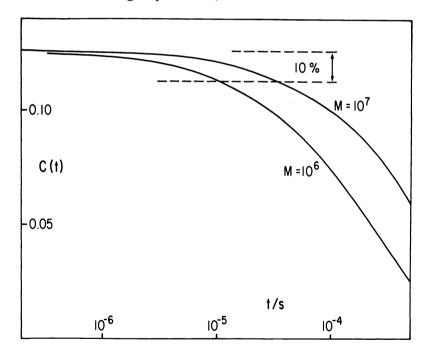

Fig. 1. Time dependence of the coefficient C of q^4 in the first cumulant. The examples are for monodisperse polystyrene in cyclohexane at the theta temperature, for the two molecular weights indicated.

and beyond, however, being due to internal motions, are bound to decay
steadily and to vanish at long times. It is an experimentally related ques-
tion as to whether these terms vary appreciably during the early times of the
correlation measurements. To probe this question, we present here some re-
sults for Zimm chains (i.e., Gaussian chains without excluded volume and with
pre-averaged strong hydrodynamic interaction). These were obtained by ex-
panding the Pecora (17) complete solution for S(q,t) in the form

$$\ln S(q,0) - \ln S(q,t) = q^2 tD(t)[1 + q^2 <S^2>C(t) + ...] \qquad (6)$$

For the present purpose, it was adequate to use the zeroth-order (free drain-
ing) eigenfunctions. This fails to give the aforementioned small time depen-
dence of $\underline{D}$ and misses the initial value $\underline{C}(0)$ by a few percent, yielding $\underline{C}(0) =$
0.126 instead of the theoretically correct $\underline{C}(0) = 2/15 = 0.13333$ for pre-
averaged Gaussian chains. Taking the numerical parameters appropriate to
polystyrene in cyclohexane at the theta temperature (cf. Ref. 23), we then
find the curves shown in Fig. 1 above for two different molecular weights.

If the shortest experimental time of observation is somewhere around 1 μs, it
is seen that there is a possibility of finding somewhat too small a value of
$\underline{C}(0)$.

SEMI-FLEXIBLE CHAINS

Many macromolecules of interest show conformational behavior intermediate to
that of rigid rods and random coils, and so it would be extremely useful to
have a reliable theory of the dynamic scattering function, particularly the
first cumulant, for such systems. The pursuit of this goal turns out to be
hampered by a difficult problem related to the fact that the internal relaxa-
tion times grow shorter and shorter as the rigidity of the molecule increases.
If some of these times become sufficiently short, the corresponding contribu-
tions to the first cumulant fall below the full initial value, as we saw
earlier even for Gaussian chains, and in extreme cases may be entirely in-
visible on the experimental time scale. Uninformed application of the AG
expression for the first cumulant can therefore be dangerous.

It is easy to work out the specific example of the almost-rigid free-draining
dumbbell. In this case (Ref. 43), the scattering function contains contribu-
tions not only from translational and rotational motions, but also a term
proportional to $a^2 exp(-4Dt/a^2)$, where $\underline{D}$ is the translational diffusion coef-
ficient and $\underline{a^2}$ is the equilibrium mean square amplitude of the bond stretch-
ing motion. For fairly stiff dumbbells, the stretching relaxation time $\underline{a^2/4D}$
will be shorter than those for rotation and translation. A numerical example,
showing the slope of the structure factor as a function of time at a fixed
angle, is given in Fig. 2. It is seen that if the stretching relaxation is
rapid enough it may escape detection if the smallest time observable in the
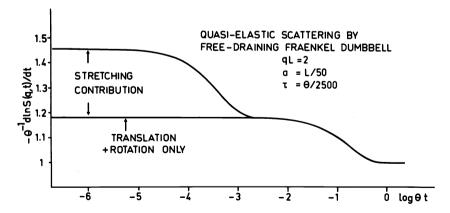experiment is much greater than $\underline{a^2/4D}$.

Fig. 2. Computed decay of the scattering function for a rather
stiff dumbbell, according to Ref. 43. The rotatory diffusion
coefficient is Θ; for other symbols, see text. Observe that for
$\Theta t > 10^{-3}$ the stretching contribution is negligible.

As we pass to the limit of a perfectly rigid dumbbell, an interesting double limit problem arises. As _a_ is allowed to decrease toward zero, the scattering contribution of the stretching motion vanishes. However, as seen from the expression given above, if the time derivative is first taken and _t_ is set equal to zero before passing to the rigid limit, then a non-zero contribution to the first cumulant from the stretching motion is retained, whatever the value of _a_. Thus, an AG evaluation of the first cumulant which embraces all six degrees of freedom of the dumbbell will include the stretching contribution; but if the diffusion equation appropriate to a completely rigid dumbbell is taken as the starting point then the AG recipe necessarily produces a completely consistent result.

Analogous behavior is seen for a rigid rod (cf. Ref. 1); if this consists of _n_ scattering elements, the AG formula applied to the space of all 3n coordinates gives (in the free-draining case) the value $C = 1/3$, while if rigidity is invoked at the start there are only 5 degrees of freedom in the problem and one obtains $C = 2/15$. We thus see that the AG formalism gives physically correct results in limiting cases, provided the appropriate conditions are recognized _a priori_. For chains of limited but non-vanishing flexibility, however, these conditions appear not to be readily available, and consideration of the diffusion problem seems mandatory. Also, of course, the actual experimental time scale has to be explicitly brought into the problem. At this writing only rather rudimentary results are offered.

It is reasonable to assume that for small departures from Gaussian flexibility it should be adequate to retain the full-coordinate-space version of the AG formula, and we shall do so. A frequently employed model for semi-flexible macromolecules is the Kratky-Porod wormlike chain (cf. Ref. 22) for which reliable calculations of the translational diffusion coefficient exist (Ref. 32). To evaluate the _C_ coefficient by means of the AG formula, we use an approximation to the wormlike chain statistics due to Koyama (44) which gives correct second and fourth moments of end-to-end separation for all degrees of stiffness and makes only modest errors for the higher moments. The results are shown in Fig. 3 in both the pre-averaged (curve AGK$_p$) and non-pre-averaged (curve AGK$_n$) treatments of the hydrodynamic interactions. In this figure, the abscissa is the contour length _L_ (on a log scale) of the chain measured in units of the Kuhn length $1/\lambda$, which is kept constant along each curve.
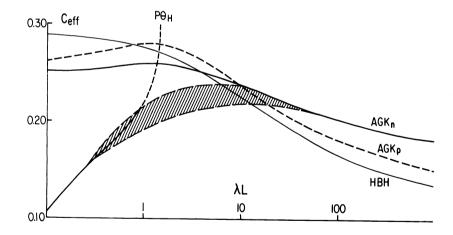

Fig. 3. Effective values of the coefficient _C_ in the first cumulant for various approximate models of semiflexible chains. Curves AGK are for wormlike chains, based on the Akcasu-Gurol (36) formula and the approximate statistics of Koyama (44). Curve HBH uses the dynamical model of Hearst, Beals and Harris (51). Curve PΘ_H modifies Pecora's rigid-rod solution (45) by use of a rotatory diffusion coefficient for slightly bent wormlike chains due to Hearst (52). The shaded area represents the authors' estimate of the correct curve. Abscissa is chain contour length in units of the Kuhn length λ^{-1}. Recall that the persistence length is half the Kuhn length.

(The symbol λ is unfortunate but common; of course it should not be confused with the wavelength of the applied radiation.) We see in Fig. 3 that both the AGK curves ascend monotonically to the left as the chains get shorter and their relative stiffness increases. The correct non-draining rodlike limit, obtainable from the Pecora (45) treatment but without taking account of the small effect of rotation-translation coupling, is $\underline{C}$ = 1/10. Manifestly the small-scale motions of the macromolecule are gradually getting too rapid to contribute to the observable scattering behavior, but AGK curves themselves give no guidance as to how far they may be trusted.

An ingenious approximate treatment of semi-flexible chains, the "sliding rod" model, has been presented by Benmouna, Akcasu and Daoud (46), based on the full-space AG formula. It thus does not yield a proper rigid-rod limit, just like our AGK calculations, nor can this be remedied by simply tinkering with the "rodlike" parts of the model. We do not discuss this model further.

There is one stiff-chain model, unfortunately not completely realistic, which offers a normal-coordinate separation and therefore allows a full treatment of the dynamical light-scattering problem. This is the Harris-Hearst (44) model, which has been useful in illuminating viscoelastic behavior (Ref. 48). The original model used free-draining hydrodynamics, and in this version it has been applied to the light-scattering case by Fujime (49,50). We have made calculations with the corresponding pre-averaged non-draining model of Hearst, Beals and Harris (51), with results for the $\underline{C}$ coefficient also shown in Fig. 3 as curve HBH. It is seen that the results for this model also become untrustworthy as the chain gets stiffer. In the HBH case it is in fact true that for rigid chains the relaxation times of the internal modes become very short, as they should, but unfortunately the large-scale normal modes of the model are then so far from resembling rigid-chain motions (for example, they remain separable in the three Cartesian spatial directions) that they give highly erroneous amplitudes to the computed scattering function.

In a crude attempt to estimate the initial departures from the rigid rod limit at the left side of Fig. 3, we suppose that the most important $\underline{initial}$ effect of introducing some flexibility into a rod is to shorten the end-to-end distance and increase the rotatory diffusion coefficient $\underline{\Theta}$ above its stiff-rod limit. Ignoring the third rotational degree of freedom which then appears, neglecting bending motions, and using the formula of Hearst (52) for Θ of slightly bendable rods, we modify Pecora's (45) rigid rod formula and obtain the curve $P\Theta_H$ of Fig. 3, which ascends rapidly upward to the right and must at best have a very limited range of applicability. Nonetheless, we now boldly sketch out a range (shaded area) within which we estimate the effective observable value of $\underline{C}$ should lie as a function of $\underline{\lambda L}$. Only further detailed calculations will be able to check on the correctness of this crude estimate.

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