DYNAMIC LIGHT SCATTERING STUDIES OF RODLIKE PARTICLES

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Abstract - Dynamic light scattering (DLS) is a major method for studying
the dynamics of rodlike particles in solution and suspension. The recent
development by Provencher of a smoothed inverse Laplace transform technique
for analyzing DLS time correlation functions allows an objective determina-
tion of the distribution of relaxation times in the system to be made. An
example of the use of this technique for determining whether or not a
micellar system is rodlike is given. Other important developments include
detailed theoretical treatments of the effect of rotational-translational
coupling in rigid rod systems on DLS time correlation functions, and some
advances in the theory of DLS from semi-rigid rods.

INTRODUCTION

The dynamic light scattering (DLS) technique has, since its inception in the early 1960's,
been applied to a wide variety of problems in polymer science (Ref. 1-3). The most wide-
spread of these applications involves measurement of macromolecular translational diffusion
coefficients for molecules in dilute solution. These diffusion coefficients are often used
to deduce information about molecular size and shape and molecular interactions. In addi-
tion, in these dilute solutions, information about size and molecular weight distributions
for polydisperse solutions is frequently obtained. For large, flexible polymers in dilute
solution, the longest relaxation times for intramolecular motions strongly affect the time
autocorrelation functions measured in DLS experiments and DLS has proven to be a rich source
of information about intrachain dynamics. DLS is also a valuable method for studying polymer
dynamics in semi-dilute and concentrated solutions.

Although they are of considerable scientific biological and commercial importance, the use of
DLS to study solutions of long, rigid and semirigid rodlike structures has been limited.
The reasons for this, apart from the practical difficulties of obtaining and preparing
samples suitable for DLS, include the current lack of theories of the dynamics of rigid and
semirigid rods in both dilute and semi-dilute solutions as well as the lack of universally
accepted methods of data analysis. Thus, although studies of rod translational diffusion may
be performed by polarized DLS at low scattering vector lengths, at higher values of the
scattering vector length, modes which represent rotational internal flexing and rotational-
translational coupling motions become important in the measured time autocorrelation
function. Often, however, the functional form of the results is unknown, so that it is not
known how to fit the data. Currently, then there is a need for adequate theories of DLS
time correlation functions for systems of rodlike structures as well as methods of data
analysis suitable for the functional forms predicted or, more importantly, data analysis
techniques which may be used in the absence of a particular theoretical form.

In this article, some trends and recent progress in DLS studies of rodlike structures are
reviewed citing as examples some work being performed in my laboratory.

RIGID RODS

The theory of DLS from long rigid rods in dilute solution was first presented by Pecora (Ref.
4) in 1964. This theory used the Rayleigh-Gans-Debye approximation for the electromagnetic
part of the theory. It, furthermore, makes the important hydrodynamic approximation that
rotational and translational motions are independent of each other.

The first order (heterodyne) correlation function for polarized DLS from dilute rod systems
then may be shown to be proportional to

$$S(q,t) = S_0(qL)e^{-q^2Dt} + S_2(qL)e^{-(q^2D + 6\,\Theta)t} + \ldots \tag{1}$$

where L is the rod length, q is the scattering vector length which is related to the wavelength of light in the medium, λ, and the scattering angle, θ,

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right).$$

In Eq. (1) the decay constant of the first exponential depends on the translational diffusion coefficient D, while that in the second one depends on both D and the rotational diffusion coefficient, Θ. The functions S_0 and S_2 are known as dynamic structure factors. When $qL \to 0$, S_2 and the coefficients of higher terms not written in Eq. (1), go to zero so that at small L (and/or small q), the correlation function becomes one exponential which decays with decay constant

$$\Gamma = q^2D$$

that is, the decay of the correlation function is determined solely by the translational diffusive motion. At about $qL \approx 5$ the second term in the series begins to become important. The correlation function then becomes a double exponential. At still higher qL, more exponential terms become important in the series in Eq. (1). Equation (1) has been applied by several groups to the study of rodlike structures with lengths about 3000 Å (Ref. 1, 5-7). For these systems a one exponential form of the correlation function is obtained at low angles allowing extraction of the translational diffusion coefficient. At larger angles an "extra" exponential appears from which the value of the rotational diffusion coefficient may be extracted.

DATA ANALYSIS

Practical applications of these formulas to DLS data on rodlike macromolecules in solution presents several difficulties. One difficulty is that often the systems studied are not monodisperse so that two exponential fits to the data may not be stable. There is, in this case, often a continuous distribution of relaxation times in the data. In other cases, it may not be known with certainty whether or not the system is rodlike so that forcing the data to fit two exponentials may lead to serious misinterpretation of the entire experiment. In fact, this last problem occurs very frequently in DLS experiments. Many experiments have as their whole purpose the detection of the presence of relaxation modes other than the purely translational diffusive mode of a given species. Examples of such "extra" modes include, rotational diffusion (cf. Eq. (1)), intramolecular flexing, and dimer or aggregate translational diffusion. Thus, since one is trying to decide whether or not these modes are present, data analysis methods are required which do not force the data to be fit to a form which assumes that they are present. An objective technique taking into account the noise in the data should be used to determine how many relaxation modes are present. A promising new technique for this purpose was first applied to DLS data analysis by Provencher (8,9). Bott (10,11) has recently extended Provencher's method and compared it with other data analysis methods.

Basically, for systems exhibiting a distribution of relaxation times, the normalized first order DLS time correlation function may be written as

$$g^{(1)}(t) = \int_0^\infty x(\Gamma)\exp(-\Gamma t)d\Gamma \tag{2}$$

where Γ is the decay constant and $x(\Gamma)$ represents the relative intensity of light scattered with decay constant Γ.

Equation (2) is the Laplace transform of $x(\Gamma)$ with respect to Γ. The $g^{(1)}(t)$ are obtained by experiment and the data analysis task is to perform a numerical inverse Laplace transform (ILT) on the $g^{(1)}(t)$ to obtain the distribution of decay constants, $x(\Gamma)$. Until recently it was thought that this numerical ILT required DLS data of unattainable accuracy to give meaningful $x(\Gamma)$. Provencher (8,9) and later Bott (10,11) have, however, shown that an inversion technique which favors smooth $x(\Gamma)$ over those with higher frequency oscillations can give reliable $x(\Gamma)$ with data that is currently attainable in DLS experiments. In this method, a computer search is made for the smoothest, nonnegative $x(\Gamma)$ that is consistent

with the data (including the noise). The degree of smoothing is chosen by a criterion using the Fisher test.

APPLICATIONS

The smoothed ILT method briefly described above has been applied in my laboratory to study several liquid dispersions containing or suspected to contain long rodlike structures. These include a micellar system, a series of plasmid DNA molecules, and the collagen molecule.

The case of the micellar system (Ref. 12 & 13) provides a good example of the use of the smoothed ILT method and of how it may be used to obtain information from the data that would be difficult to obtain using other data analysis techniques.

Aqueous solutions of the surfactant molecule, dodecyldimethylammonium chloride (DDAC) have been studied by Ikeda and co-workers (14) using surface tension, viscosity, static light scattering and C-13 NMR measurements. Molecular weights, radii of gyration and other evidence obtained from these experiments indicates that as the ionic strength is increased by adding increasing amounts of NaCl, the originally small, "spherical" micelles (radius ≈ 25 Å) appear to undergo a transition to an elongated, flexible, rodlike form. For DDAC molecules above the critical micelle concentration, this transition appears to take place at NaCl concentrations of about 2 M. At NaCl concentrations of 4 M, Ikeda et al. (14) estimate the length of the rodlike micelles to be about 3000 Å. For micelles of this length observed at high scattering angles, the term in Eq. (1) dependent on the rotational diffusion coefficient of the micelle should be observable in a polarized DLS experiment. Thus, if the micelles were monodisperse, at low angles only one exponential dependent on micellar translational diffusion would contribute to the DLS time correlation function. At higher angles the "extra" exponential would appear.

DLS experiments were performed in our laboratory on DDAC in 4 M NaCl. At low angles the DLS data fit well to single exponentials, while at high angles, one exponential fits were very poor. Attempts to fit the high angle data to two exponentials usually gave good fits but the fits were not stable. The decay times and weights of the exponentials in the correlation function varied greatly from run to run. These inconsistent results were probably related to the polydispersity of the sample. In any case when data on these samples were analyzed using the smoothed ILT technique, the high angle data clearly showed a peak in the $x(\Gamma)$ at fast times. At lower scattering angles, this fast peak disappears, as it should for a nonspherical structure, leaving only the translational peak. This technique, as remarked above, does not prejudice the data analysis by forcing the data to fit two peaks in $x(\Gamma)$ at high angles. The computer program implementing the technique chooses the smoothest $x(\Gamma)$ consistent with the data including the noise in it. The criterion for choosing two peaks over one is an objective one.

Thus, for the case of this micellar system, the DLS experiments using the smoothed ILT method of data analysis have clearly shown that DDAC micelles grow to form elongated structures at high NaCl concentrations. The precise size and geometry of this structure and its degree of flexibility are, however, not yet entirely clear.

TRANSLATIONAL ROTATIONAL COUPLING IN SYSTEMS OF LONG RIGID RODS

Long, thin, rigid rods should exhibit a coupling between the rotational and translational motions arising from the anisotropy of the translational motion. Long thin rods have different translational diffusion coefficients parallel ($D_\parallel$) and perpendicular ($D_\perp$) to their long axes. Thus, the degree of translational motion in a given direction depends upon the molecular orientation. Theories of this rotational-translational coupling and its effect on DLS time correlation functions have been given by many authors (Ref. 15-25).

A major result of these theories is that when a rigid rod in dilute solution is long enough to exhibit terms dependent on the rotational diffusion coefficient in the polarized DLS time correlation function, it is also long enough to exhibit significant translation-rotation coupling effects. Until very recently (Ref. 23 & 24) attempts to detect this effect in solutions of long thin viruses (mainly tobacco mosaic virus) failed. This failure has usually been attributed to low signal to noise ratios in the early experiments. Wilcoxon and Schurr (23) have detected rotational-translational coupling effects in dilute tobacco mosaic virus solutions by measuring first cumulants of the polarized DLS time correlation function as a function of q. In the limit of very high q, a simple formula for the first cumulant was derived. High values of q were experimentally obtained by using ultraviolet radiation. Kubota et al. (24) have used both first cumulant analysis and two-exponential fits to the data for tobacco mosaic virus to observe the effects of the translational-rotational coupling. The results of these experiments are, however, not in quantitative agreement with each other or with the predictions of hydrodynamics. More DLS work performed on a variety of rigid rod particles (perhaps using smoothed ILT data analysis techniques)

would be very valuable in elucidating this basic problem.

It is worthwhile to mention at this point that translational-rotation coupling for rod shaped particles can also occur for relatively short rods due to solution crowding effects. Thus, $D_\perp$ for a rod could become very small because of hindrances provided by neighboring rods. This effect is expected to occur in "semi-dilute" solutions (Ref. 20,22,25-30).

SEMI-RIGID MOLECULES

Many macromolecules and biological structures are semirigid so that the theories described in the previous sections cannot be applied to them. Of course, for semirigid macromolecules in dilute solution, the DLS time correlation function at low q directly gives the translational diffusion coefficient of the molecule. The diffusion coefficient may then be related to the chain persistence length through approximate, but well-known theories (Ref. 31-33). The more complex case in which the scattering vector length is large enough to directly give contributions of rotational and intramolecular relaxation time to the DLS time correlation functions is currently attracting the attention of several research groups. A related problem is the contribution of the rotational and intramolecular modes to the depolarized DLS forward angle time correlation function.

There is as yet no consistent theory for the dynamics of semirigid chains. The most widely used approximate formulation is that of Harris, Hearst and Beals (34,35). This theory has been applied by Fujime and co-workers (36-38) to the calculation of polarized DLS time correlation functions for semirigid chains and by Moro and Pecora (39) to the depolarized DLS correlation functions. The Harris-Hearst-Beals theory includes a longitudinal stretching term in the equation of motion of the chain elements. Since the chain should, strictly speaking, have a constant contour length, this stretching term introduces artificial fluctuations in the chain contour length. Harris, Hearst and Beals have pointed out this inconsistency (Ref. 35) and have shown how it leads to an incorrect total intensity light scattering structure factor. Aragon and Pecora (40) have recently proposed that inconsistencies in this theory may be removed by setting the stretching term in the equation of motion equal to zero and then imposing an initial condition on the solution which requires that the chain contour length be constant. This theory has been used to calculate the form of depolarized DLS correlation function, but has not yet been used to calculate the polarized correlation function.

The very interesting work in this area by Schmidt and Stockmayer (41) should be mentioned. These authors have computed the first cumulant of the polarized DLS correlation function for several models of stiff chains (including the Harris-Hearst-Beals theory) and, recognizing the uncertainty in the applicability of these formulas to semirigid chains, have proposed an interpolation curve to determine the DLS first cumulant in the stiffness regime between the rigid rod and the flexible coil.

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