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Notes

Light Scattering from Coils in Isorefractive Ternary Solutions

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Introduction

Recently, Cantor and Pecora[1] presented some very interesting results on the presence of a fast diffusive relaxation mode in isorefractive ternary solutions besides the usual translation diffusion mode of the probe molecule. Their system consisted of nearly monodisperse polystyrene (PS) probe molecules of molecular weight 390 000 present in dilute amounts in a solution of semirigid poly(n-hexyl isocyanate) (PHIC) of varying molecular weight and with concentration varying from dilute to semidilute. The solvents were either tetrachloroethane (TCE), which is completely isorefractive with PHIC at 75.0 °C, or toluene, which is nearly isorefractive with PHIC. Dynamic light scattering (DLS) measurements were performed from 25 to 75 °C, and the results were not influenced by small mismatches between the refractive indices of the matrix polymer and the solvent. The measurements revealed the presence of a fast diffusive relaxation mode whose appearance seemed to coincide with the onset of the semidilute regime of the matrix PHIC polymer. Cantor and Pecora did a thorough analysis and discussion of various possible explanations for the physical source of this relaxation mode only to eliminate them in favor of a descriptive model in which "on a short time scale the PS chain is constrained or "caged" by neighboring PHIC chains".[1]

The purpose of this note is to point out that the dynamics of a simplified physical model incorporating some of the features of Cantor and Pecora's descriptive "cage" hypothesis has been worked out by Bird and DeAguiar[2] in terms of an encapsulated Hookean dumbbell. The implications of that model to the dynamic scattering spectrum were presented by Wei and Cohen.[3] This model does indeed lead to the prediction of a fast diffusive mode at short times besides the usual translational mode of the probe molecule observed at long times. We review the results of this model here and use it to compare its predictions with Cantor and Pecora's experimental results.

Summary of Relevant Experimental Results

We shall first summarize some of the features of the fast relaxational mode observed by Cantor and Pecora. The relaxation frequency of this mode exhibited a clear linear dependence on the square of the wavevector q and is therefore characteristic of a diffusive mode. The intensity (amplitude) of this mode remained always much smaller than the intensity of the PS translational diffusion mode and accounted for only 5% of the total intensity at the highest matrix (PHIC) concentration used. At the lowest concentrations of PHIC used, corresponding to the dilute regime, the fast relaxation mode was absent. The amplitude of the fast mode increased with increasing PHIC concentration, and these results were extrapolated to lower concentrations to determine the lowest value of PHIC concentration for which the first appearance of the fast mode is expected. This value was observed to coincide reasonably well with the onset of the semidilute regime of the PHIC solution. The amplitude of the fast mode showed a weak dependence on q^2 although there is a fair amount of scatter in the data and the errors must be large since the amplitudes are quite small. Nonetheless, at large q values, the amplitude of the fast mode was clearly larger than at lower q values. The time scale of the fast relaxation mode was approximately 10 times faster than the translational diffusion mode of the PS probe in TCE and about 4 times faster in toluene. Finally, as the temperature was increased, the amplitude of the fast mode tended to increase.

Several groups[4–7] have reported earlier observations of bimodal diffusive relaxation modes in the dynamic light scattering spectrum from ternary solutions (two polymers and a solvent). These results appear to be the direct consequence of the coupling of the dynamics of concentration fluctuations of the two different polymers in the solution and theories based on this realization[8,9] provide a good interpretation of these experimental results. These two modes will still be present in an isorefractive ternary system (as defined here) only if the probe concentration is not very dilute, otherwise only the probe diffusion will be observed.[9] The features of the fast diffusion relaxation mode observed by Cantor and Pecora are markedly different from those of these earlier experimental results on ternary solutions, as their system was isorefractive with a dilute probe concentration and the time scale of their additional relaxation is faster than either polymer translational diffusion mode. Furthermore, the amplitude of this fast mode increases as the matrix concentration increases (i.e. as the relative probe concentration decreases). Many of these features could be physically explained in terms of a caging effect around the PS probe chain by the surrounding PHIC chains.[1]

The Encapsulated Dumbbell Model

In an attempt at capturing some of the features of the dynamics of flexible or semiflexible macromolecules in semidilute and concentrated solutions, Bird and DeAguiar[2] proposed the tractable model of the encapsulated dumbbell. Due to the presence of neighboring macromolecules in a nondilute polymer solution (or for the case at hand, a probe molecule surrounded by matrix molecules), one expects anisotropic hydrodynamic forces on the segments of the surrounded molecule. In the encapsulated dumbbell model, this translates into an anisotropic drag force on the beads of the dumbbell given by

$$\mathbf{F}^{\mathrm{h}} = -\zeta\dot{\mathbf{r}}(\mathbf{uu} + \sigma^{-1}(\mathbf{ss} + \mathbf{tt})) \qquad (1)$$

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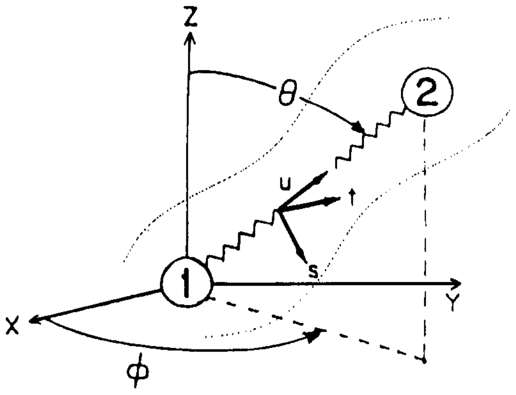

Figure 1. Encapsulated elastic dumbbell showing the triad of mutually orthogonal unit vectors, **s**, **t**, and **u**. The vector from bead 1 to bead 2 is $\mathbf{R} = R\mathbf{u}$.

where $\mathbf{F}^h$ is the hydrodynamic force on a bead, ζ is a friction coefficient, $\dot{\mathbf{r}}$ represents the velocity of the bead averaged with respect to the velocity distribution function in momentum space, and σ reflects the anisotropy in the hydrodynamic drag force law. The unit vectors **s**, **t**, and **u** (Figure 1) represent an orthogonal set of vectors with **u** pointing in the direction from bead 1 to bead 2 of the dumbbell and **s** and **t** pointing in the θ and ϕ directions, respectively. The original model also contained an additional anisotropy in the Brownian motion of the beads that we shall ignore here to simplify the presentation but also because the presence of such a Brownian anisotropy has been questioned.[10] Equation 1 reduces to the classical Stokes' drag law when $\sigma = 1$. When $\sigma < 1$, the dumbbell beads encounter a greater resistance as they move in the θ and ϕ directions compared to the **u** direction and this corresponds to the dumbbell being restricted to move more freely along **u**, mimicking the effect of a cage or an encapsulation by the surrounding molecules. The equation of the balance of forces acting on a bead is

$$\mathbf{F}^{h} + \mathbf{F}^{b} + \mathbf{F}^{el} = 0 \qquad (2)$$

where the two other forces $\mathbf{F}^b$ and $\mathbf{F}^{el}$ are the Brownian and elastic forces, respectively, given by well-established expressions.[11] Use of eq 2 with the appropriate expressions for the forces and the equation of continuity for the probability distribution function $\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$ of the bead positions of the dumbbell lead to the governing equation on Ψ which can then be used to determine the scattering spectrum.[12] Assuming that the dynamics of the center of resistance and of the conformation change occur on a different time scale and are decoupled, $\Psi(\mathbf{r}_1,\mathbf{r}_2,t)$ may be written as the product of two distributions, $\psi_c(\mathbf{r}_c,t)\ \psi(\mathbf{R},t)$, where $\mathbf{r}_c$ is the position of the center of resistance and $\mathbf{R}$ is the vector between the two beads of the dumbbell. The resulting governing equation is given by

$$\psi\frac{\partial\psi_c}{\partial t} + \psi_c\frac{\partial\psi}{\partial t} = \psi\frac{\partial}{\partial\mathbf{r}_c}\mathbf{D}_{tr}\frac{\partial\psi_c}{\partial\mathbf{r}_c} - \psi_c\frac{\partial}{\partial\mathbf{R}}\dot{\mathbf{R}}\psi \qquad (3)$$

where

$$\mathbf{D}_{tr} = \frac{kT}{2\zeta}\left(\frac{1+2\sigma}{3}\boldsymbol{\delta} + (1-\sigma)\left(\mathbf{uu} - \frac{1}{3}\boldsymbol{\delta}\right)\right) \qquad (4)$$

and $\dot{\mathbf{R}}$ is given by eq 63 of ref 3.

The translation diffusion tensor $\mathbf{D}_{tr}$ depends on the orientation **u** of the dumbbell and in fact couples ψ and ψ_c in eq 3 except for two limiting cases in which eq 3 can be decoupled. These two cases are as follows:

(i) Short time scale when the translational displacement $\mathbf{r}_{c,u}$ of the center of resistance of the dumbbell $\mathbf{r}_c$ along **u** occurs on a time scale shorter than the time scale for the variation of **u**. The time scale of variation of **u** in this Hookean dumbbell model, λ_H, corresponds to the longest internal relaxation mode of a more sophisticated kinetic model representation of the macromolecule. The component of $\mathbf{D}_{tr}$ along **u**, D_u, can be obtained by rewriting eq 4 as

$$\mathbf{D}_{tr} = \frac{kT}{2\zeta}(\mathbf{uu} + \sigma(\boldsymbol{\delta} - \mathbf{uu})) \qquad (5)$$

from which

$$D_u = \frac{kT}{2\zeta} \qquad (6)$$

In this short time scale ($t < \lambda_H$), eq 3 can then be decoupled into

$$\frac{\partial\psi_c}{\partial t} = D_u\left(\frac{\partial}{\partial\mathbf{r}_{c,u}}\frac{\partial\psi_c}{\partial\mathbf{r}_{c,u}}\right) \qquad (7)$$

and

$$\frac{\partial\psi}{\partial t} = -\frac{\partial}{\partial\mathbf{R}}\dot{\mathbf{R}}\psi \qquad (8)$$

(ii) Long time scale compared to the orientation time scale of **u** (or internal relaxation of a more complex model) such that the term $\mathbf{uu} - {}^1/_3\boldsymbol{\delta}$ in eq 4 averages out to zero, leaving only the long time "isotropic" translation diffusion coefficient of the encapsulated dumbbell given by

$$D_{tr}^{*} = \frac{kT}{2\zeta}\left(\frac{1+2\sigma}{3}\right) \qquad (9)$$

In this limit the governing equation for ψ_c is given by

$$\frac{\partial\psi_c}{\partial t} = D_{tr}^{*}\frac{\partial}{\partial\mathbf{r}_c}\frac{\partial\psi_c}{\partial\mathbf{r}_c} \qquad (10)$$

Dynamic Scattering Spectrum

The dynamic scattering spectrum of the encapsulated dumbbell model was calculated by Wei and Cohen using a method of directly calculating the averages representing the correlation function expression of the scattering spectrum and bypassing the need to solve for the distribution function in eq 8.[3] For short times, $t < \lambda_H$ where λ_H corresponds to the internal relaxation time of the dumbbell, the spectrum consists of an initial fast decay corresponding to the segmental diffusion of a more complex model and which we shall ignore here as it would be too fast to observe by light scattering for a real molecule and another decay which for $t < \lambda_H$ is given by

$$S(q,t_s) = \left(P_2 + \frac{1}{2}P_0 e^{-4A}\right)e^{-D_u q^2 t} \qquad (11)$$

where

$$P_2 = (1-\sigma)\sigma^{-1}(2q^2 D_u\lambda_H - 1 - \sigma^{-1}) \qquad (12)$$

$$P_0 = \sigma^{-2} \quad \text{and} \quad A = \sigma D_u q^2 \lambda_H \qquad (13)$$

For long times, $t > \lambda_H$, the spectrum reveals the isotropic tracer diffusion of the particle (or the diffusion of a probe molecule) and is given by

$$S(q,t_L) = (P_2 + P_0 e^{-2A}) e^{-D_{tr}^* q^2 t} \tag{14}$$

In eqs 11–14 we have assumed an isotropic Brownian diffusion of the beads such that the parameters α and β of the original model are equal to unity and an anisotropic drag force with $\sigma < 1$. We note that P_2 vanishes as σ approaches unity, that is as the anisotropy of the hydrodynamic drag coefficient (or the caging effect) disappears such that P_2 must be the dominant contribution to the fast mode. We can also argue this on the basis that as $\sigma \rightarrow 1$, the translation diffusion in eq 4 becomes isotropic, the decoupling of eq 3 occurs at all times, and we are only left with what we defined as the long time spectrum.

We can now see that the results of this rather crude and simple model of the dynamics of a constrained macromolecule lead to a spectrum with features similar to the experimental observations reported by Cantor and Pecora. The fast mode is clearly diffusive in nature and shows a q^2 dependence. In semidilute solution, just past the dilute region, the anisotropy in the drag is not expected to be very large and σ will not be too much smaller than unity. The amplitude factor P_2, which is proportional to $(1 - \sigma)\sigma^{-1}$, remains fairly small. As the matrix concentration increases, the constraints on the probe molecule increase, the anisotropy in the drag will increase, and σ will decrease, leading to an increase in P_2. Furthermore, the amplitude P_2 of the fast mode depends on q^2 in a rather weak way since a constant is subtracted from the q^2-dependent term in the bracket of eq 12. The model predicts a larger magnitude of the fast mode at higher q values for the same value of σ (which translates into the same matrix concentration). This is clearly observed in the experimental results of Cantor and Pecora[1] reported in their Figure 10.

The encapsulated dumbbell model is too crude to make predictions that can be quantitatively compared to experimental results. For example, the relaxation times of the two diffusion modes in this model, although separate, remain however fairly close with a factor of only 2 difference when $\sigma = 0.25$. A small improvement can be made by introducing the anisotropic Brownian diffusion parameters α and β. An analysis of a more complex model such as an encapsulated Rouse chain may lead to relaxation ratios closer to the experimentally observed value. In general, however, we have demonstrated that the simple encapsulated dumbbell model shows that a model which contains the essence of the physical description proposed by Cantor and Pecora to explain the features of their fast relaxation results in an isorefractive ternary system does indeed show very good promise for the interpretation of these results.

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