

Dynamic relaxation of rodlike micelles

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We study theoretically the angular relaxation and translational diffusion of stiff rodlike micelles that can undergo reversible scission reactions, in both the dilute and the entangled regime. The very strong dependence of the angular diffusion constant on rod length leads to an anomalous superdiffusive behavior of the typical angular deflection of a subunit at short times. Despite this, angular correlation functions such as $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ (also the linear birefringence and entropic stress response) decay exponentially with a relaxation time that is a power law combination of the time scales for reversible scission and for angular rotation of a (hypothetical) unbreakable rod. This relaxation time corresponds to the waiting time for a subunit to find itself on a rod that is short enough to rotate through an angle of order π before recombining with another rod. The translational diffusion of rodlike micelles shows no anomaly in contrast to the angular case. However, the collective diffusion and self-diffusion constants differ by a factor of 2 at all concentration ranges for which rod micelles exist. The diffusion equation for collective motion is nonlinear (even below the overlap threshold) since the mobility of the rods depends on their local concentration. The dynamic structure factor $S(q,t)$ is calculated to order q^4 , the quartic terms providing, in principle, a probe of the micellar scission time.

I. INTRODUCTION

In recent years, there has been intense experimental and theoretical interest in the dynamics of elongated surfactant micelles.¹ Most work has focused on the case of “wormlike” micelles, whose contour lengths greatly exceed the persistence length of the locally cylindrical aggregate,²⁻⁴ although there is also interest in very stiff, rodlike structures.⁵⁻⁷ In aqueous surfactant solutions the latter tend to arise at low concentration, when mass action effects cause the micelles to be relatively short, and/or at low salinity, when polyelectrolyte effects cause an increase in stiffness. The idealized limit of very long, stiff micelles may soon be realized even in systems with short-range forces, for example, by synthesizing lyotropic analogs to the columnar discotic liquid crystal compounds.⁸ We therefore assume the absence of long range interactions, in which case the law of mass action requires that the size distribution of rods is exponential, the number density of rods of length L obeying (in suitable units)

$$C(L) = \exp[-E/k_B T] \exp[-L/\bar{L}], \quad (1)$$

$$\bar{L} = \phi^{1/2} \exp[E/2k_B T]. \quad (2)$$

Here ϕ is the volume fraction of solute, and E the energy required to create a pair of end caps in the middle of an infinite cylindrical rod. These results should apply throughout the dilute and semidilute regimes; only at relatively high concentrations (near the Onsager threshold) should excluded-volume forces between rods come into play.⁹

We consider in what follows the angular relaxation (Secs. II-VI) and translational diffusion (Secs. VII-X) of stiff self-assembled rods that can undergo scission and re-

combination reactions. We summarize our conclusions in Sec. XI. For simplicity we assume that micellar reactions obey the random scission scheme used in previous studies.¹⁰⁻¹³ This assigns a uniform probability for the scission of a micelle at any point along its length. In this case, there is a well-defined characteristic time τ_b for the micellar kinetics. This may be defined as the mean lifetime of a rod of the average length before it breaks; it is also (to within order unity factors) the lifetime of the end of a micelle before a recombination event occurs.^{10,13} In the usual mean-field approach, such recombination is presumed to involve a random member of the population of rods (subject to the constraint that fusing rods are collinear) rather than the partner from the preceding dissociation step.

Other reaction schemes are possible, for example, scission can be induced by the end of another micelle (the so-called end-interchange process). In this case we expect results that differ only in numerical factors from those presented below. In some cases, the exchange of material between rods may occur mainly by sequential release and adoption of individual subunits¹⁴ rather than random scission and recombination; this case is qualitatively different and we do not treat it here.

II. FORMAL STATEMENT OF THE ROTATIONAL DIFFUSION PROBLEM

It is straightforward formally to express the problem of computing the response of our system of “living” rods to perturbations in the angular distribution function.¹² At the level of linear response theory, we obtain for perturbations

$c(L, \mathbf{u})$ in the number density of rods of length L with director \mathbf{u} , the following equation:

$$\begin{aligned} \dot{c}(L, \mathbf{u}) = & -k(L + 2\bar{L})c(L, \mathbf{u}) \\ & + 2k \int_0^L c(L', \mathbf{u}) \exp[-(L - L')/\bar{L}] dL' \\ & + 2k \int_L^\infty c(L', \mathbf{u}) dL' - 2k \exp[-L/\bar{L}] \\ & \times \int_0^\infty c(L', \mathbf{u}) dL' + D(L) \mathbf{R} \cdot [\mathbf{R}c(L, \mathbf{u})], \quad (3) \end{aligned}$$

where $\mathbf{R} = \mathbf{u} \times (\partial/\partial \mathbf{u})$ and $D(L)$ is the angular diffusion constant of a rod of length L . The last term on the right-hand side arises from the angular diffusion of rods and the remaining terms are the linearized chemical rate equations for the scission-recombination scheme described above. (The recombination rate has been eliminated in favor of k using the principle of detailed balance.)

We do not attempt a complete analysis of this equation in the present paper, but focus on certain limiting cases of physical interest. Parts of our analysis are closely related to that of Lequeux¹⁵ who has presented a general formalism for treating first order relaxation processes in systems undergoing reversible scission.

In what follows we allow the following general form for the angular diffusion constant:

$$D(L) = D(\bar{L}) \times (L/\bar{L})^{-\kappa}. \quad (4)$$

The value $\kappa = 3$ corresponds to dilute rods so long as a weak logarithmic factor is neglected; in this case $D(\bar{L}) = D_0/\bar{L}^3$ with D_0 a constant. (The logarithmic factor is easily restored in principle.) Another case of interest is for entangled stiff rods, where according to the tube model of Doi and Edwards,⁹ one has Eq. (4) with

$$D(\bar{L}) = \frac{D_0}{\phi^2 \bar{L}^7}, \quad (5)$$

$$\kappa = 7. \quad (6)$$

Equations (5) and (6) can be adopted for use in Eq. (3) so long as the motion of a (hypothetical) unbreakable rod, at time scales of order τ_b , can in fact be represented as a simple angular diffusion process. In the tube model, the angular motion of an entangled rod is complicated at short times but crosses over to simple angular diffusion at time scales $\tau_{\text{rep}} \sim D_0 L^3$.⁹ This is the time taken for a rod to escape its tube by sliding along its own tangent; during one such escape, the rod undergoes only a small angular deflection [$\theta \sim (\phi L^2)^{-1}$] because its rotation is hindered by the constraints of the other rods. Adopting this as the elementary diffusive step, we see that the angular motion of an unbreakable rod for times $t \gg \tau_{\text{rep}}$ is indeed a pure diffusion with $D(L)$ obeying Eqs. (5) and (6). To exploit this simplification we below assume $\tau_b \gg \tau_{\text{rep}}$ throughout our discussion of the entangled case.¹⁶

III. ANGULAR CORRELATION FUNCTIONS

We focus now on the angular correlation function defined as $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ where the average is over all subunits

(monomers). For a diffusing unbreakable rod of length L , this obeys⁹

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle_L = \exp[-2D(L)t]. \quad (7)$$

This single-exponential behavior of the one-rod relaxation turns out to be a crucial simplification in what follows.¹⁵ Note that higher moments of the angular distribution function also decay exponentially:

$$\langle P_n[\mathbf{u}(t) \cdot \mathbf{u}(0)] \rangle_L = \exp[-D(L)n(n+1)t], \quad (8)$$

as do correlators of tensors such as $\langle \mathbf{u}\mathbf{u} \rangle$ which are probed experimentally using linear birefringence and entropic stress response.⁹ Since all these decay exponentially without breakage, they should all behave alike when scission effects are included,¹⁵ and therefore we take $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ as the canonical example.

It is, of course, easy to calculate $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ in the limit where scission processes are negligibly slow. (In doing this for the entangled case, we ignore any corrections to the simplest tube model that might arise from the polydispersity.) The limit we consider is formally $\tau_b \rightarrow \infty$, although qualitatively the results should apply whenever $\tau_b \gg \tau_{\text{rot}}$, where

$$\tau_{\text{rot}} \simeq D(\bar{L})^{-1} \quad (9)$$

is a characteristic time scale for angular relaxation of an unbreakable rod of the mean length.

Clearly in this limit the angular correlation function is the weight average

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \int P(L) \exp[-D(L)t] dL \quad (10)$$

$$P(L) = \frac{L}{\bar{L}^2} \exp[-L/\bar{L}], \quad (11)$$

where $P(L)$ is the probability that a subunit is on a rod of length L . For long times, a saddle point approximation can be applied with the result

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \sim \exp[-(t/\tau_{\text{rot}})^\alpha] \quad (12)$$

$$\alpha = \frac{1}{\kappa + 1}, \quad (13)$$

where the "stretched exponent" α is 1/4 for dilute rods and 1/8 in the entangled regime. These equations were previously given by Bellini *et al.* who confirmed the prediction $\alpha = 1/4$ for dilute micellar rods in a birefringence experiment.¹⁷

At short times, Eq. (10) must be treated differently. The leading behavior is found by recognizing that at time t , rods with $D(L)t \gg 1$ have essentially relaxed their orientations whereas the remainder have not. This yields the short time behavior

$$\langle \theta(t)^2 \rangle = 2[\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle - 1] = \left(\frac{t}{\tau_{\text{rot}}} \right)^{2/\kappa} \quad (14)$$

which does not coincide with the Taylor expansion of Eq. (12) for small t .

IV. FAST BREAKING CASE

It is notable from the data of Bellini *et al.* that the exponent α measured in birefringence becomes larger rather than smaller as the concentration is raised above the overlap

threshold for micelles.¹⁷ The tube model predicts a very low $\alpha = 1/8$; the observation of the opposite trend suggests that in this regime (for the particular system studied in Ref. 17) the micellar breaking time may cease to be very much longer than the rotational time of a typical rod. (This is not conclusive, however; an increase in micellar flexibility could also increase α .) This is what happens in the case of *flexible* elongated micelles, for which both theory and experiment suggest that the relaxation becomes narrowed to a pure single exponential decay, in the regime where scission occurs rapidly on the time scale of orientational relaxation.^{1-4,10}

To analyze the relaxation of stiff micelles in the regime $\tau_b \ll \tau_{\text{rot}}$ we can exploit the Markov property of the angular correlation function. The history of a given subunit or monomer, between time zero and time t may be divided into intervals t_i on which it is on a rod of diffusivity $D_i = D(L_i)$, where $\sum_i t_i = t$. Since the angular correlation function during any of these intervals decays exponentially (though with a relaxation rate that depends on the current rod length), the angular correlator for subunits may be broken down as

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \left\langle \exp \left[-2 \sum_{i=1}^n D_i t_i \right] \right\rangle, \quad (15)$$

where the angle brackets $\langle \rangle_r$ denote an average over the stochastic scission and recombination events that determine D_i , t_i , and n .

The behavior of averages like Eq. (15) in systems with reversible scission has been studied recently by Lequeux.¹⁵ Here we give a simpler treatment based on the following approximations: (i) we assume that the L_i are uncorrelated samples from the population $c(L)$; (ii) we assume that all the t_i are the same and equal to τ_b . (Hence $n = t/\tau_b$.) For the scission and recombination processes described by Eq. (3), neither approximation is quite correct. First, successive L values are correlated, but the correlation decays rapidly on times of order τ_b ; only a few reversible scission events are needed before a subunit loses all memory of its earlier rod-length history.¹³ Second, the t_i are in reality random variables, having Poisson statistics with mean $t_i(L) = \tau_b/(2 + L/\bar{L})$.¹⁵ However, it can be checked by performing more elaborate calculations that these approximations do not alter our results except at the level of numerical factors.

With these simplifications we have for times large compared to τ_b the obvious formula $n(t) = t/\tau_b$, and Eq. (15) reduces to the following form:

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \left\{ \int_0^\infty \exp[-2D(L)\tau_b] P(L) dL \right\}^{t/\tau_b}. \quad (16)$$

Since we are assuming $\tau_b \ll \tau_{\text{rot}}$ (recall that the latter is the angular rotation time of a hypothetical unbreakable rod of length \bar{L}), we may use the approximation in Eq. (14) to write this as

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle \simeq \left[1 - \left(\frac{\tau_b}{\tau_{\text{rot}}} \right)^{2/\kappa} \right]^{t/\tau_b}, \quad (17)$$

which for $\tau_b \ll \tau_{\text{rot}}$ approaches the single exponential form

$$\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \exp[-t/\tau], \quad (18)$$

$$\tau = \tau_b^1 - 2/\kappa \tau_{\text{rot}}^{2/\kappa}. \quad (19)$$

The second formula is as found by Lequeux.¹⁵ The physical content of these results is as follows. At each time step τ_b , all monomers are redistributed at random among the rods, which continuously relax by angular diffusion. Only those monomers which are on rods of length $L \leq L^*$ such that $D(L^*)\tau_b \simeq 1$ can relax orientation before the next redistribution of rod lengths takes place; the fraction of such monomers is of order $(\tau_b/\tau_{\text{rot}})^{2/\kappa}$. The relaxation thus proceeds by a sequence of independent steps in which this proportion of the remaining orientational bias is eliminated at each step. The characteristic relaxation time τ for angular relaxation is the waiting time for a monomer to find itself on a rod of length $L \leq L^*$ whose orientation can relax significantly between one scission event and the next. The single exponential relaxation arises because the final relaxation time τ is much larger than the time scale τ_b at which each subunit loses memory of what length rod it is on. Hence all subunits receive equal treatment and relax at the same rate, an effect similar to that found previously for flexible rather than stiff micelles.¹⁻⁴

It is interesting to translate Eqs. (18) and (19) into predictions for the concentration dependence of the relaxation time τ . Using the results of Secs. I and II for $\bar{L}(\phi)$ and thus $\tau_{\text{rot}}(\phi)$, and assuming a scission rate k [Eqs. (1) and (2)] that is independent of volume fraction, we obtain $\tau \sim \phi^\beta$, with $\beta = 5/6$ (17/14) for dilute (entangled) rods in the rapid breaking regime, compared to $\beta = 3/2$ (11/2) in the opposite limit of slow breaking. The much reduced values for the concentration exponent β , allied to the prediction of single exponential relaxation, should make it easy to identify experimentally the regime of fast breaking in stiff micellar rods, especially in the entangled case.

V. THE STRESS-OPTICAL LAW

The linear response calculations given above for $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$ generalize to any probe of the angular distribution of subunits that decays exponentially for a single rod. This includes both entropic shear stress and birefringence. For rods these are proportional to the off-diagonal parts of the tensors $\int c(L, \mathbf{u}) \mathbf{u} \mathbf{u} dL$ and $\int L c(L, \mathbf{u}) \mathbf{u} \mathbf{u} dL$, respectively; the stress-optical law is said to hold when these two quantities are linearly related to one another. Clearly, the stress-optical law is obeyed for monodisperse rods; in contrast it is not obeyed in the case of polydisperse unbreakable rods, since the alignment of a rod under external perturbation is dependent in general on its length. According to the above description of the fast breaking regime, however, each subunit gets randomized over the rod-size distribution with the time scale τ_b . According to Eqs. (18) and (19), τ , the angular relaxation time for subunits, greatly exceeds τ_b , which implies that there can be almost no correlation between the orientation of a given subunit and the length of the rod it is on. Hence the stress-optical law must be recovered in the fast breaking regime. This agrees with observations on several systems that are argued to contain rather stiff micelles.⁵⁻⁷ This could be a useful diagnostic: if an experimental system of micellar rods obeys the stress-optical

law it seems reasonable to conclude that the fast breaking limit applies in that system.¹⁸

VI. ANOMALOUS DIFFUSION: AN ANGULAR LÉVY FLIGHT

Above we considered the time dependence of $\langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle$, which is typical of that expected for any correlation function whose dependence is exponential for unbreakable rods of a given length. Let us now consider instead the probability distribution for angular displacements $\theta(t)$ as a function of time. For small times on a rod of length L this is Gaussian distributed with variance

$$\sigma(t) = \langle \theta^2(t) \rangle = 4D(L)t. \quad (20)$$

The motion in the θ variable is essentially the same as a diffusion process for a particle with diffusion constant $D(L)$ in real space; this analogy holds for times short enough that there is negligible probability of θ values of order π being reached. Likewise, in the fast breaking regime one has, for any given sequence of reactions, a conditional probability for θ which is Gaussian distributed with variance

$$\sigma(t) = 4 \sum_{i=1}^n D_i t_i. \quad (21)$$

The problem is now to combine this with the probability distributions for D_i , t_i , and n .

Let us temporarily ignore the fact that θ is really an angle. The probability distribution $P(\theta)$ may then be calculated by standard methods from the asymptotic statistics of the sum in Eq. (21).^{19,20} (This is done most easily if we adopt the same approximations as used in Sec. IV.) We find that for $\kappa > 2$, the stochastic process this represents is an anomalous one corresponding to superdiffusive behavior.^{19,21} The result

$$P[\theta(t)] \propto L_\mu[\theta/\bar{\theta}(t)], \quad (22)$$

$$\mu = 4/\kappa \quad (23)$$

is a symmetric Lévy stable distribution,^{19,20} with a characteristic angular displacement

$$\bar{\theta}(t) \sim \left(\frac{t}{\tau}\right)^{\kappa/4}. \quad (24)$$

At large values of its argument, $L_\mu(x)$ decays slowly as $|x|^{-1-\mu}$, which means that moments $\langle x^k \rangle$ with $k \geq \mu$ do not exist.

The reason for an anomalous diffusion $\bar{\theta}(t) \sim t^{\kappa/4}$ (which applies for all $\kappa > 2$) is that the motion of a subunit is controlled by those time intervals t_i during which it is on a rod that is much shorter than the mean length. Indeed, the sum in Eq. (21) is dominated by its largest term, and hence the effective angular mobility of a subunit increases with time. The typical angular deflection $\bar{\theta}(t)$ obeys $\bar{\theta} \approx D(L_{\min})\tau_b$, where $L_{\min}(t)$ is the expected length of the shortest rod visited between times zero and t ; since in this interval $n \sim t/\tau_b$ different rods are sampled, we have

$$\int_0^{L_{\min}} P(L)dL = 1/n = \tau_b/t \quad (25)$$

which leads directly to Eq. (24) for $\bar{\theta}(t)$.

We must now take account of the fact that θ is not a

spatial coordinate but an angular one, and cannot exceed π . The above analysis applies to the probability distribution for angles θ that are very small compared to π . This remains the case for the main part of the probability distribution until such time that $\bar{\theta}(t) \sim \pi$; the crossover time is easily checked to be τ [Eq. (19)], which we recall is the time a subunit has to wait until it is on a rod short enough to undergo an order-unity angular deflection before recombining. Hence we confirm that the anomalous angular diffusion regime arises for time scales $\tau_b \ll t \ll \tau$, between the characteristic time for reactions, and that of angular relaxation. This regime can be very large in the fast breaking limit when $\tau \gg \tau_b$.

Note that, despite this anomalous diffusion, averages such as $\langle \theta(t)^2 \rangle$ now remain finite; since these would otherwise diverge, they are immediately sensitive to the fact that angular and not spatial motion is involved. In principle, we may also study a winding number $\theta(t)$, now defined as the total angle traversed by a subunit and hence not subject to periodic boundary conditions. This is simple to define for motion on a circle (angles in two dimensions) where the preceding Lévy analysis (without restraint on θ) describes the diffusion in winding number space. It is notable in that case that all circular harmonics $\int_{-\infty}^{\infty} d\theta L_\mu(\theta/t^{1/\mu})e^{im\theta}$ decay monoexponentially in time (this follows directly from the definition of L_μ ¹⁹). In three dimensions the situation is more complicated, since we must consider two angle variables; winding around a particular axis is dominated by singular contributions that arise when the rod lies nearly parallel to that direction, and we do not pursue this issue here. Nonetheless, we do know from the results of Secs. III and IV that all spherical harmonics of $P(\mathbf{u})$ decay exponentially in the fast breaking regime.

Obviously it would be very interesting to think of experiments that could probe the anomalous motion described in Eqs. (22)–(24). In the analogous problem of spatial diffusion in flexible micelles, fluorescence recovery after photobleaching has been used to demonstrate a similar Lévy flight behavior.²¹ Unfortunately, our results indicate that, to see any anomalous *angular* diffusion, the experimental quantity probed must be of sufficient complexity that it cannot be written as a simple sum of angular correlation functions (all of which decay exponentially, as described above). This rules out many of the standard methods,²² and so a rather original experiment may be needed to see this effect.

VII. TRANSLATIONAL MOTION

We now turn from the problem of angular relaxation to that of translational diffusion and mass transport. The translational diffusion constant $D_t(L)$ for rods is much less sensitive to micellar length than is the rotational diffusion constant $D(L)$. It is also rather insensitive to entanglements; according to Doi and Edwards⁹ we have

$$D_t(L) \sim D_0 \log(L)/L \quad \text{dilute} \quad (26)$$

$$D_t(L) \sim D_0/L \quad \text{entangled}, \quad (27)$$

where the logarithmic factor arises through hydrodynamic self-interactions that are screened in the semidilute regime. For simplicity we ignore the logarithmic factor below, whenever we need a definite form for $D_t(L)$. The entanglements

present in the semidilute regime are very effective at impeding the translational motion but reduce translational mobility by only an order unity factor.

The problem of translational *self*-diffusion can be dealt with immediately. This concerns the asymptotic dependence of the spatial displacement $r^2(t)$ for a monomer as a function of time t . Over a long time interval the monomer will spend a fraction of the time $P(L)$ [Eq. (11)] on rods of length L . The asymptotic self-diffusion constant is therefore

$$D_s = \int_0^\infty P(L) D_i(L) dL, \quad (28)$$

which implies $D_s = D_0/\bar{L}$, for $D_i(L)$ obeying Eq. (27). In contrast to the angular diffusion case, the average in Eq. (28) exists and there is no anomalous behavior. (This also contrasts with the translational behavior of *flexible* entangled micelles.²¹) The probability distribution for monomer displacements \mathbf{r} approaches a Gaussian for times $t \gg \tau_b$, whereas at short times (when the rod length distribution is effectively quenched) it obeys instead

$$P(\mathbf{r}) \propto \frac{(D_s t)^2}{(2D_s t + r^2)^{7/2}}. \quad (29)$$

This formula is found simply by averaging the Gaussian distributions corresponding to chains of different lengths.

VIII. COLLECTIVE DIFFUSION

Our next task is to find the collective translational diffusion behavior. We start from the linearized equation of motion, which is the direct analog of Eq. (3) for the rotational case. The equation reads

$$\begin{aligned} \dot{c}(L, \mathbf{r}) = & -k(L + 2\bar{L})c(L, \mathbf{r}) \\ & + 2k \int_0^L c(L', \mathbf{r}) \exp[-(L - L')/\bar{L}] dL' \\ & + 2k \int_L^\infty c(L', \mathbf{r}) dL' - 2k \exp[-L/\bar{L}] \\ & \times \int_0^\infty c(L', \mathbf{r}) dL' + D_i(L) \nabla \cdot [\nabla c(L, \mathbf{r})]. \quad (30) \end{aligned}$$

We consider the limit of large length scales, such that $D_s q^2 \tau_b \ll 1$, where q is a wave vector of interest. In this case, the collective motions involve only the local concentration $\phi(\mathbf{r})$, which is the first moment of $c(L, \mathbf{r})$:

$$\phi(\mathbf{r}) = \int_0^\infty L c(L, \mathbf{r}) dL. \quad (31)$$

At large length scales the chemical relaxation processes are fast compared to diffusion and we may in this limit assume there is always full *local* equilibration of the micelle size distribution. [This will depend, through Eqs. (1) and (2), on the local density $\phi(\mathbf{r})$.] The first moment of Eq. (30) then reads

$$\delta \dot{\phi}(\mathbf{r}, t) = 0 + \int_0^\infty L dL D_i(L) \nabla^2 c(L, \mathbf{r}), \quad (32)$$

where $\delta \phi(\mathbf{r}) = \phi(\mathbf{r}) - \bar{\phi}$ (subtracting the global average) and the contribution to $\delta \dot{\phi}$ arising directly from the reaction terms has been set to zero.¹² This is because reactions are

local processes and cannot, in themselves, redistribute matter from one region of the system to another.

Under conditions of local equilibrium, $c(L, \mathbf{r})$ in Eq. (32) is related to $\phi(\mathbf{r})$ by thermodynamic considerations. In the linear response regime, we may deduce this from Eqs. (1) and (2) by performing a small change $\phi \rightarrow \phi + \delta \phi$ and find the corresponding shift in $C(L)$, using

$$c(L, \mathbf{r}) = \frac{\partial C(L)}{\partial \bar{L}} \frac{\partial \bar{L}}{\partial \phi} \delta \phi(\mathbf{r}). \quad (33)$$

The result is as follows:

$$c(L, \mathbf{r}) = \frac{LC(L)\delta\phi(\mathbf{r})}{2\phi\bar{L}}, \quad (34)$$

where $C(L)$ and ϕ refer to the globally averaged size distribution and concentration. Substituting in Eq. (30) we find the collective diffusion equation

$$\dot{\phi}(\mathbf{r}) = \bar{D}_i \nabla^2 \phi(\mathbf{r}) \quad (35)$$

$$\bar{D}_i = (2\bar{L})^{-1} \int_0^\infty dL P(L) L D_i(L). \quad (36)$$

This \bar{D}_i is the "mass-squared average" diffusion constant, and it governs collective diffusion whenever the correlation between local concentrations and the total density obey Eq. (34).²³ For $D_i(L)$ obeying Eq. (27), the result is simply

$$\bar{D}_i = D_s/2, \quad (37)$$

so that the collective diffusion constant is half the self-diffusion constant. Note that this holds even far below the overlap threshold for micelles: the micelles "interact" even in this regime since their size distribution is coupled to the local density by mass-action effects.

IX. NONLINEAR DIFFUSION EQUATION

It is notable that hardly any change is needed to the preceding discussion, in order to write down a *nonlinear* collective diffusion equation describing the response of the system to large concentration gradients. Under conditions of local equilibrium, we may apply Eqs. (1) and (2) locally (without linearization); moreover, the argument leading to Eq. (32) can equally well be applied directly to the full density $\phi(\mathbf{r})$ rather than the small fluctuation $\delta \phi(\mathbf{r})$. [The reaction contributions to $\dot{\phi}(\mathbf{r})$ vanish whether or not they are linearized as was assumed in Eq. (30); the argument that reactions cannot move material from one place to another still applies.]

In the case of most interest, where $D_i(L) = D_0/L$ [Eq. (27)] we obtain

$$\dot{\phi}(\mathbf{r}) = \bar{D}_i \bar{\phi}^{1/2} \nabla^2 [\phi(\mathbf{r})^{1/2}], \quad (38)$$

where, to avoid confusion, the global average density is now denoted $\bar{\phi}$. It may easily be checked that Eqs. (35) and (36) are recovered in the linear response regime. The factor of half between \bar{D}_i and D_s can be viewed as arising from the linearization of the square root in Eq. (38).

Related nonlinear diffusion equations should arise whenever the diffusivity is coupled locally to the concentration, a generic effect in self-assembling systems where the complexation of the particles is a function of density, even at low enough concentrations that the aggregates do not "inter-

act" by conventional interaggregate forces. Experiments on this aspect of collective diffusion would be of great interest; in their absence, we defer to future work the detailed analysis of Eq. (38).

X. DYNAMIC STRUCTURE FACTOR

The collective relaxation of concentration fluctuations is generally studied by measuring the dynamic structure factor²²

$$S(q,t) = \left\langle \sum_n \sum_m \sum_j^{L_n} \sum_k^{L_m} \exp\{iq \cdot [r_j^n(t) - r_k^m(0)]\} \right\rangle, \quad (39)$$

where j and k are monomer indices and the n and m indices run over all the rods of sizes L_n and L_m present, respectively, at time t and at time 0 in the scattering volume. The weighting probabilities for the average $\langle \rangle$ describe not only the configurational space for position and orientation of the rods but also for the distribution of sizes L . In this sense the dynamical structure factor of "living" rod micelles is fundamentally different from the structure factor of a quenched polydisperse set of rodlike particles.

The behavior of $S(q,t)$ in different wave vector regimes will probe different aspects of the micellar dynamics. At high wave vector, the angular processes discussed in Secs. II–VI will play an important role. We focus here on the low wave vector expansion, for which we may write

$$S(q,t) = \langle \phi_q(t) \phi_q^*(0) \rangle \quad (40)$$

so long as $q\bar{L} \ll 1$. The leading behavior is then

$$S(q,t) = \exp[-\bar{D}_t q^2 t], \quad (41)$$

which follows directly from the collective diffusion equation found in Sec. VIII. This is totally independent of the micellar kinetics, and it is interesting to see whether a more informative behavior can be found by keeping terms of the next order in the low q expansion. We may expect the next corrections to be important, not just at very high q where the internal structure of the rods starts to matter (i.e., $q\bar{L} \approx 1$), but at wave vectors in the range $\bar{D}_t q^2 \tau_b \approx 1$. This corresponds to distances of order that moved by an average rod during its lifetime before scission, and if chemical relaxation is slow this can be far larger than the mean micellar size. If this is the case, which we assume from now on, the q^4 terms can yield information on the micellar kinetics.

To calculate $S(q,t)$ to order q^4 we consider the Laplace transform (on L)¹³ and Fourier transform (on \mathbf{r}) of Eq. (30) which then takes the form

$$\begin{aligned} \frac{1}{k} \dot{c}_q(t,s) = & \frac{d}{ds} c_q(t,s) + 2 \left[\frac{\bar{L}}{s\bar{L} + 1} - \frac{1}{s} \right] \\ & \times [c_q(t,s) - c_q(t,0)] - 2\bar{L}c_q(t,s) \\ & - q^2 \frac{D_0}{k} \int_s^\infty c_q(t,s') ds', \end{aligned} \quad (42)$$

where $c_q(t,s)$ is the Laplace transform of $c_q(t,L)$; we have divided through by the scission rate constant k . The last term in the right-hand side of Eq. (42) is the contribution of spatial diffusion of rods, the other terms arising from the usual

scission–recombination scheme. We have assumed Eq. (27) for simplicity.

Note that in Laplace space, $c_q(t,0)$ is the total number of rods and $dc_q(t,s)/ds|_{s=0} = -\phi_q(t)$ is the total monomer density. Taking the limit of $s \rightarrow 0$ in Eq. (42) and in its derivative one gets the following coupled equations for the density and chain number:

$$\begin{aligned} \frac{1}{k} \dot{c}_q(t,0) = & \phi_q(t) - 2\bar{L}c_q(t,0) - q^2 \frac{D_0}{k} \int_0^\infty c_q(t,s') ds', \\ \phi_q(t) = & -q^2 D_0 c_q(t,0). \end{aligned} \quad (43)$$

By solving these with suitable initial conditions, we can find the memory kernel for ϕ_q fluctuations [which is the same thing as $S(q,t)$, by Eq. (40)]. The correct initial condition is provided by Eq. (34) which determines the response of $c_q(L)$ conditional on a given density fluctuation ϕ_q . [The result may readily be checked by considering the correlation matrix for $c_q(L)$ and ϕ_q which can be calculated directly by assuming Poisson statistics for each species of rod.]

The initial decay rate of the scattering function $S(q,t)$ can immediately be obtained by combining Eqs. (43) and (34):

$$\dot{S}(q,t)|_{t=0} = -q^2 \bar{D}_t. \quad (44)$$

In contrast, the general (arbitrary q) solution for $S(q,t)$ cannot be extracted easily from the equations because they are not closed. For a full solution one must therefore deal directly with Eq. (42) rather than attempting to find an autonomous equation for the density ϕ_q . It is, however, possible to find the leading (q^4) corrections to the simple diffusive behavior [Eq. (41)], by treating perturbatively the diffusive contribution (the last term on the right) in Eq. (42). At first sight there is a danger that this term could be divergent, but in fact it remains finite for all s , as may be shown from studying the behavior of the size distribution of short chains $c_q(t,L) \leq c_q(0,L) \sim L$. [In other words, although the diffusion constant diverges for short chains, these are, according to Eq. (34), only rather weakly coupled to the local density and do not dominate the relaxation of that quantity.]

This allows us to set in Eq. (43)

$$\int_0^\infty c_q(t,s') ds' = A_q(t) \bar{L} c_q(t,0), \quad (45)$$

where $A_q(t)$ is an unknown, but well-behaved function of q and t . Combining with Eq. (43), it is now possible to obtain an autonomous expression for the time evolution of the concentration fluctuation

$$\ddot{\phi}_q(t) + \left[\frac{1}{\tau_b} + 2A_q(t) q^2 \bar{D}_t \right] \dot{\phi}_q(t) + \frac{q^2 \bar{D}_t}{\tau_b} \phi_q(t) = 0. \quad (46)$$

In order to proceed, we first solve Eq. (42) for $q = 0$, choosing a normalized concentration fluctuation $\phi_0(0) = 1$. This allows us to determine the zero order term of the unknown function $A_q(t)$; in this manner we obtain the result

$$A_q(t) = 1 + O(\bar{D}_t q^2 \tau_b). \quad (47)$$

This can be substituted back in Eq. (46) to obtain an equation that determines the scattering function to the fourth order in q . Note that this relies on the fact that $\dot{\phi}_q$ is itself of

order q^2 ; one can confirm that, if one carries through the term of order $\bar{D}_i q^2 \tau_b$ in Eq. (47), the result given below for $S(q, t)$ does not depend on the coefficient of this term, to the required order. By the procedure just described, we have avoided expanding to order q^4 in the full coupled equations for $c_q(s, t)$ —a complicated step which would otherwise have been necessary.

We may now solve Eq. (46) for an arbitrary initial disturbance $\phi_q(t=0)$. There are two eigenmodes whose decay rates obey a quadratic equation. Working to order q^4 in both the amplitudes and the decay rates, we obtain the following result for the dynamic structure factor $S(q, t) = \langle \phi_q(t) \phi_q^*(0) \rangle$:

$$S(q, t) = \exp[-q^2 \bar{D}_i t + q^4 \bar{D}_i^2 t \tau] - q^4 \bar{D}_i^2 \tau_b^2 \times \exp\left[-q^2 \bar{D}_i t - \frac{t}{2\tau_b}\right] \sinh\left[q^4 \bar{D}_i^2 \tau_b t + \frac{t}{2\tau_b}\right]. \quad (48)$$

Of course, this reduces to the standard form of Eq. (41) for $\bar{D}_i q^2 t \ll 1$; the leading departures, calculated here, could, in principle, be used to extract from $S(q, t)$ data a quantitative estimate of the chemical relaxation time τ_b . This might pose experimental problems, in practice, since the corrections are always small in the limit where our perturbative approach is valid. It would therefore be desirable to obtain a closed-form approximation to $S(q, t)$ over the entire q range, but we have not yet found a simple way to do this.

Another limiting case can be solved easily, however: that of $(\bar{D}_i \tau_b)^{-1/2} \ll q \ll \bar{L}^{-1}$. This corresponds to disturbances which relax much too quickly to allow local equilibration of the size distribution, but which are nonetheless on a large length scale compared to the size of a typical micellar rod. In this case, one can again write $S(q, t) = \langle \phi_q(t) \phi_q^*(0) \rangle$, but this time calculate the latter by propagating an initial disturbance ϕ_q using the dynamics for an effectively quenched system of rods. The initial conditions for $c_q(L)$ are found, as before, from Eq. (34) in which case the result for $S(q, t)$ follows immediately:

$$S(q, t) = (2\bar{L})^{-1} \int_0^\infty dL P(L) L e^{-D_i(L) q^2 t}, \quad (49)$$

which at long times approaches a stretched exponential relaxation

$$S(q, t) \sim \exp[-2(D_i q^2 t)^{1/2}]. \quad (50)$$

[At short times, on the other hand, one recovers Eq. (44).]

This result of course resembles those found in Sec. III for rotational relaxation in the slow breaking regime.

XI. DISCUSSION AND CONCLUSIONS

We have presented a theoretical analysis of angular relaxation and translational diffusion in stiff micellar rods undergoing reversible scission processes. We summarize our results in Table I.

A. Angular relaxation

In the limit of slow scission reactions, we recover a stretched exponential behavior, with exponent $\alpha = 1/4$ for dilute rods (as seen in birefringence by Bellini *et al.*¹⁷) whereas $\alpha = 1/8$ for the entangled case. In contrast, for the limit of fast breaking we obtained single exponential relaxation for angular correlation functions, with a relaxation time $\tau \sim \tau_b^{1/3} \tau_{rot}^{2/3}$ (dilute) and $\tau \sim \tau_b^{5/7} \tau_{rot}^{2/7}$ (entangled). These results agree with the analysis by Lequeux¹⁵ of first order relaxation processes in living systems, of which the angular correlation functions for stiff rods provide a concrete, and experimentally interesting example. However, the simple exponential relaxation of the correlation functions disguises the fact that the angular diffusion of a subunit or monomer is highly anomalous: in effect an “angular Lévy flight” with typical angular deflection $\bar{\theta} \sim t^{3/4}$ for dilute rods and $\bar{\theta} \sim t^{7/4}$ in the entangled regime.

B. Translational diffusion

There is no anomaly in the translational diffusion of rod micelles, and we recover earlier results²³ equating the self-diffusion constant D_s to the mass average diffusivity and the collective diffusion constant \bar{D} , to the mass-squared average diffusivity for the aggregated species. For rodlike micelles, we found $D_s = 2\bar{D}$, a result that applies even far below the overlap threshold. This discrepancy arises from the local coupling between the mean micellar size and the concentration, which also results in a nonlinear diffusion equation $\dot{\phi} \sim \nabla^2(\phi^{1/2})$ when concentration perturbations are large. We calculated the dynamic structure factor $S(q, t)$ to order q^4 , the q^2 terms arising simply from the collective diffusion constant but with q^4 corrections that are sensitive to the micellar kinetics. An intermediate q regime can arise $((\bar{D}_i \tau_b)^{-1/2} \ll q \ll \bar{L}^{-1})$ in which $S(q, t)$ should show a stretched exponential time dependence (with stretched ex-

TABLE I. Summary of a theoretical analysis of angular relaxation and translational diffusion in stiff micellar rods undergoing reversible scission processes.

Rotation		$\tau_b \gg \tau_{rot}$	$\tau_b \ll \tau_{rot}$
$\langle u(t) u(0) \rangle$	Dilute	$\text{Exp}\{-[t/\tau_{rot}]^{1/4}\}$	$\text{Exp}\{-t/(\tau_b^{1/3} \tau_{rot}^{2/3})\}$
	Entangled	$\text{Exp}\{-[t/\tau_{rot}]^{1/8}\}$	$\text{Exp}\{-t/(\tau_b^{5/7} \tau_{rot}^{2/7})\}$
Diffusion		$\tau_b \gg \tau_D$	$\tau_b \ll \tau_D$
$\langle \phi(t) \phi(0) \rangle$		$\text{Exp}\{-2[2t/\tau_D]^{1/2}\}$	$\text{Exp}\{-t/\tau_D\}$
$\tau_b = 1/(2k\bar{L})$		$\tau_{rot} = 1/D_{rot}(\bar{L})$	$\tau_D = q^2 D_0 / (2\bar{L})$

ponent $\alpha = 1/2$) arising from an effectively quenched polydispersity.

All of our new predictions await experimental test, and this will require work on materials that form very stiff long micelles at low volume fractions; to avoid complications brought about by Coulomb forces,²⁴ it would help to find aggregates that are inherently very stiff. In addition to normal surfactant materials it may be interesting to seek candidates of somewhat different architecture, for example, among disk-shaped molecules which might in some cases form a relatively rigid precolumnar aggregate even at low concentrations. Although in the absence of detailed experiments some of our calculations may appear premature, we hope that in fact the theoretical predictions made in this paper will stimulate renewed experimental interest in stiff micellar systems.

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