Flow-induced gelation of living (micellar) polymers

Robijn Bruinsma Department of Physics, University of California, Los Angeles, California 90024

William M. Gelbart Department of Chemistry, University of California, Los Angeles, California 90024

Avinoam Ben-Shaul

Department of Physical Chemistry and the Fritz Haber Molecular Dynamics Center, The Hebrew University, Jerusalem, Israel 91904

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We consider the effect of shear velocity gradients on the size (L) of rodlike micelles in dilute and semidilute solution. A kinetic equation is introduced for the time-dependent concentration of aggregates of length L, consisting of "bimolecular" combination processes L + L' $\rightarrow (L + L')$ and "unimolecular" fragmentations $L \rightarrow L' + (L - L')$. The former are described by a generalization (from spheres to rods) of the Smoluchowski mechanism for shear-induced coalesence of emulsions, and the latter by incorporating the tension-deformation effects due to flow. Steady-state solutions to the kinetic equation are obtained, with the corresponding mean micellar size (\overline{L}) evaluated as a function of the Peclet number P, i.e., the dimensionless ratio of flow rate $\dot{\gamma}$ and rotational diffusion coefficient D_r . For sufficiently dilute solutions, we find only a weak dependence of \overline{L} on P. In the semidilute regime, however, an apparent divergence in \overline{L} at $P \simeq 1$ suggests a flow-induced first-order gelation phenomenon.

I. INTRODUCTION

The structures and phase transitions in self-assembling systems have attracted intensified interest from a broad range of chemists and physicists over the course of the past decade. In particular, the micellization of surfactant molecules in aqueous solution has confronted both experimentalists and theorists with a wide variety of intriguing and challenging problems.¹ The underlying difficulty stems from the fact that-unlike "ordinary" colloidal suspensions in which the number density of interacting particles is fixed by their volume fraction, and the size and shape of particle is essentially constant-self-assembling amphiphiles can aggregate into many different structures. Specifically, these surfactant molecules are capable of organizing into large-scale micelles involving either cylindrical-tubular, bilayer-lamellar, or disordered bicontinuous structures. Furthermore, even in dilute solution, these structures are observed to evolve dramatically from one equilibrium state to another as control parameters such as the temperature or surfactant concentration are varied.

Consider, for example, the much studied case of CTAB/KBr (cetyl trimethyl ammonium bromide/potassium bromide) or CPySal/NaSal (cetyl pyridinium salicylate/sodium salicylate) in water.² These ionic amphiphilecounterion systems exhibit a strong preference for cylindrical micelle formation. That is, above the critical micelle concentration (CMC), they tend overwhelmingly to satisfy the hydrophobic effect by forming tubelike aggregates. These cylinders have an essentially constant radius characterized roughly by the length of the stretched hydrocarbon tail: 10– 20 Å. The *lengths* of the micellar rods, however, are already large—100's of Å's—even just above the CMC. More significantly, they are found to increase dramatically (up to 1000's of Å's) as the surfactant concentration is raised. At volume fractions of the order of 1%, the rods are believed to entangle and to form a gel-like phase. Recently it has been observed by Rehage and Hoffmann³ that concentration is not the only control parameter for self-assembly. They found that shear flow can also induce gelation. As a function of the velocity gradient γ (i.e., the shear rate), they found a dramatic rise in the micellar solution viscosity at a critical flow rate, indicating a sharp increase in the mean rod length. This is a rather surprising result because one expects the delicate, large-scale surfactant structures to be easily destroyed by flow-induced stresses. Previous theoretical studies for *extensional* flow appear to confirm this expectation.⁴

Our basic premise in the present work is that this flowinduced micellar gelation is an important example of a wellknown effect in the hydrodynamics of suspensions: orthokinetic coagulation. Orthokinetic coagulation is the coagulation of colloidal suspensions under shear flow, a phenomenon discovered by Paine⁵ in 1912. It stands in contrast to perikinetic coagulation,⁶ where Brownian motion is the dominant transport mechanism. Orthokinetic coagulation does not require attractive interactions. Dilute dispersions of spheres in shear flow, for example, aggregate due to purely hydrodynamic interactions. In the case of reversible aggregation, the size distribution of the aggregates must, under equilibrium (i.e., no flow) conditions, be given by the Boltzmann distribution, and so this should hold for the perikinetic situation. However, for orthokinetic coagulation, shear flow, in general, prevents the establishment of thermal equilibrium: it will increase the number of particle-particle collisions and thereby shift the steady-state size distribution of aggregates, while at high enough shear rates the flow can actually produce percolationlike patterns in the spatial distribution of particles. The aim of this paper is to apply to the problem of flow-induced micellar gelation the experience gained with colloidal coagulation. Accordingly, we will first review the classical theory of coagulation, considering, in particular, the case of shear-induced coalescence of emulsion drops. Since the interactions between general colloidal particles differ from those between micelles we will concentrate on those aspects of the theory which are independent of the interaction potential.

The first theoretical study of reaction rates during orthokinetic gelation was by von Smoluchowski⁷ in 1916. He assumed that, before colliding, the (spherical) particles move along the flow lines in rectilinear trajectories, i.e., he neglected both hydrodynamic as well as nonhydrodynamic interactions. Furthermore, he assumed that after colliding the two particles would stick together, in other words that the collision cross-section equals the reaction cross section. Under these assumptions, the particle flux J_s on a reference particle (i.e., the reaction rate) is

$$J_s \simeq \dot{\gamma} \phi_R R^3 \tag{1.1}$$

with ϕ_R the particle concentration and R the particle radius. To obtain Eq. (1.1), note that collision rates are proportional to $v\sigma$, with v the impact velocity and σ the scattering cross section, and to the number density ϕ_R . The geometrical cross section of a sphere is proportional to R^2 while typical velocity differences for particles on neighboring stream lines are of order γR .

The underlying assumptions of the Smoluchowski theory are obviously crude. Spheres in close contact feel a very strong hydrodynamic resistance preventing close approach. The result is that instead of true collisions, spheres form "trapped binaries." Moreover, the reaction cross section is, in general, not equal to the collision cross section. The theory has been investigated in further detail along these lines, in particular by Curtis and Hocking⁸ and van de Ven and Mason.9 The result of their work was that the numerical factor of order unity which we have dropped in Eq. (1.1) must be replaced by a constant which depends only weakly on particle radius and other factors: the von Smoluchowski theory is surprisingly good. Mainly because of non-negligible multiparticle hydrodynamic interactions, it is not yet understood how these microscopic mechanisms produce the macroscopic spatial patterns noted earlier. In the following we will restrict ourselves to the "microscopic" level of the Smoluchowski description and not address the question of spatial distribution.

When should we expect orthokinetic gelation to overtake perikinetic gelation? To compare the two processes, we note that the particle flux J_b on a reference particle due to translational Brownian motion is

$$J_b \simeq D_t \phi_R R \tag{1.2}$$

with D_t the translational diffusion constant. Again, Eq. (1.2) may be derived by noting that diffusion currents must be proportional to D_t and collision rates proportional to ϕ_R . Since J_b has dimensions of [1/time], Eq. (1.2) follows immediately from dimensional arguments. Flow-induced colli-

sions will start to dominate when the ratio $P = J_s/J_b$ becomes of order unity. From Eqs. (1.1) and (1.2), we must have

$$P \simeq \gamma / (D_t / R^2). \tag{1.3}$$

This ratio is the well-known *Peclet number*. The Peclet number of a suspended particle determines whether its motion is dominated by hydrodynamic flow or by diffusion. A solution of particles can sustain large concentration gradients if $P \ll 1$, while for $P \gg 1$ the concentration profile is homogenized by the flow. If we applied the preceding arguments to micellar gelation for a solution of rods of length L, then we should expect flow-induced gelation to start when $\dot{\gamma} \simeq \dot{\gamma}_c$ with

$$\gamma_c \simeq D_t / L^2 \tag{1.4}$$

assuming that a tumbling rod of size L approximates a sphere of that size. For rods of length on the order of 1000 Å, this threshold would be of the order of 10^3-10^4 Hertz—a very reasonable number for mechanical stirring. It appears that on the basis of qualitative, but general, arguments we can identify $P \simeq 1$ as the condition for the onset of flow induced gelation.

This naive extension of the von Smoluchowski theory is, in fact, questionable. The first problem is that shear flow can align rods along the flow direction. Flow-induced alignment of rods was investigated by Peterlin and Stuart.¹⁰ They found two regimes. Let D_r be the rotational diffusion constant (dimensions 1/time). If γ/D_r is small compared to one then the rod performs rotational Brownian motion and indeed tumbles. However, for γ/D_r large compared to one, rods are approximately aligned along the flow direction, although every now and then they perform a sweep of about 180° after which they return to their aligned configuration. The borderline between these regimes is defined by the condition that γ/D_r be of order 1. Now, the rotational and translational diffusion constants for rods of length L are approximately related by¹¹

$$D_r \simeq D_t / L^2. \tag{1.5}$$

Comparing with Eq. (1.4) we see that the borderline condition is approximately $\gamma_c \simeq D_r$. Apparently, flow alignment and orthokinetic gelation start at about the same shear rate. Note that flow alignment will reduce the collision cross section, so it becomes unclear whether or not we really should expect gelation to start at γ_c . This problem is addressed in detail in the present work.

The second problem is the shear-flow induced fracture of aggregates noted before. Flow fracture could potentially prevent the onset of orthokinetic gelation. Whereas we arrived at Eq. (1.4) from very general arguments, there appears at first sight to be nothing "universal" about flow fracture. Clearly it depends on the interaction potential between the surfactant molecules which holds the micelles together. The onset of flow fracture was investigated by de Gennes¹² for the case of colloidal coagulation. He concluded that it starts at considerably higher shear rates than P = 1. A similar calculation can be done for micellar aggregation. Remarkably, as we shall see, flow fracture *does* have universal features, and it necessarily occurs at flow rates in large excess of $\dot{\gamma}_c$.

To construct a quantitative theory of flow-induced gelation, we need an explicit model for the combination and breakage reactions which are taking place. (This is not so for zero flow where we have recourse to statistical thermodynamics arguments.) Not much is known about the relevant reaction kinetics. We adopt in Sec. II a generalization to nonzero velocity gradient of the kind of scheme proposed by Cates¹³ for the case of zero flow. In Sec. III we derive expressions for the effect of shear flow on the reaction rate constants. The resulting rate equations are solved in Sec. IV where we construct the "phase diagram" for the gelation of rodlike micelles under shear flow and predict the enhancement of their average size.

Our results are summarized in Fig. 1. We find that rodlike aggregates in shear flow are characterized by the critical velocity gradient $\dot{\gamma}_c$ for which the Peclet number *P* is of order unity, i.e., $\dot{\gamma}_c \simeq D_r$. Using the well-known result¹¹ $D_t \simeq k_B T / \eta L^{(0)}$ we have

$$\frac{\gamma_c}{\gamma_c} \simeq \frac{k_B T}{n L^{(0)^3}}.$$
(1.6)

Here $L^{(0)}$ is the mean rod size for $\gamma = 0$ and η is the solvent viscosity. Since $L^{(0)}$ is proportional to $\phi^{1/2}$ with ϕ the monomer concentration (see Sec. II), γ_c depends on ϕ as $\phi^{-3/2}$. Typically, $\gamma_c \simeq 10^3 \text{ s}^{-1}$. (Note that the aforementioned dependence of D_r and, hence, P on rod length, see Eqs. (1.5)



FIG. 1. Schematic depiction of the weak $(P \leq 1)$ and strong $(P \geq 1)$ flow regimes, in the limit of dilute $(C \leq 1)$ and semidilute $(C \leq 1)$ concentration. V(L) is the effective potential which controls the dynamics of the average micellar length; see Sec. IV.

and (6), obtains only for sufficiently *rigid* rods. When *flexibility* is important, the situation necessarily becomes more complicated, both with regard to $D_r(L^{(0)})$ and the formulation of bimolecular collision cross sections (see Sec. III A 1).

What happens for $\dot{\gamma} \gtrsim \dot{\gamma}_c$ depends on the dimensionless concentration $C \equiv \phi_L L^3$. If $C \ll 1$, L increases linearly with $\dot{\gamma}$ for $\dot{\gamma} \ll \dot{\gamma}_c$; for $\dot{\gamma} > \dot{\gamma}_c$ the mean rod sizes increases more slowly with shear rate, specifically as $P_{L^{(0)}}^{1/3} \sim \dot{\gamma}^{1/3}$, the mean rod size remaining of order $L^{(0)}$. The left-hand side of Fig. 1 shows the schematic "free energy" appropriate to dilute $(C \ll 1)$ solutions as $\dot{\gamma}$ increases through its critical value $(P \simeq 1)$.

If, on the other hand, $C \ge 1$, there are now *two* possible size distributions for $\gamma \le \gamma_c$: A steady-state configuration with a mean rod size of order $L^{(0)}$ and a runaway solution for which the mean rod size diverges. The steady-state configuration can be considered as a *metastable* state. Under a large enough perturbation it degenerates into the runaway solution. For $\gamma \ge \gamma_c$, the steady-state solution is found to disappear in a characteristic time τ of the order of $(\gamma C)^{-1} \ge 10^{-2} - 10^{-3}$ s for $C \ge 1$. It is this rapid runaway of the mean size when $P \ge 1$ which we identify with the flowinduced gelation observed by Rehage and Hoffmann. Of course, the actual gelation process requires a discussion of the formation of an entangled network under shear flow. We only discuss here (see Sec. IV) how shear flow *triggers* the gelation at the microscopic level.

It is useful to compare our results to the work of Cates and Turner¹⁴ who discussed the effect of extensional flow on the rod-size distribution. They allowed only end-to-end reactions and discussed the regime $C \ge 1$. Even though the physics of suspensions in extensional flow is usually very different from that of shear flow, and even though they consider the strongly entangled ($C \ge 1$) regime, they also found a runaway when the Peclet number is of order 1. This suggests that the result for $C \gtrsim 1$, i.e., that flow-induced gelation starts at $P \simeq 1$, is quite robust. Similarly, Wang¹⁵ has treated the case of rodlike micelles in two-dimensional, shear flow, invoking an approximate decoupling of the hydrodynamics and the self-assembly. Again, for high enough concentration, he finds that gelation is triggered at a critical threshold for the velocity gradient. This universal nature of the Peclet number is better understood by writing $P = \gamma \tau$ with $\tau = D_r^{-1}$ the relaxation time. For $P \leq 1$ the system relaxes fast enough to avoid deformation of its microstructure by the flow, whereas for $P \ge 1$ this is no longer possible. The point $P \simeq 1$ also marks the onset of non-Newtonian flow effects.

The onset of flow-induced gelation for $P \gtrsim 1$ as a function of C around $C \approx 1$ is formally similar to a first-order phase transition. One can even identify an effective quasifree-energy V(L)—depending on C and P—which has to be minimized to find the optimal mean rod length (see Fig. 1). Since for $P \leq 1$ we must overcome a barrier, we would expect, on the basis of this analogy, that gelation proceeds via nucleation and growth while for $P \gtrsim 1$ it is likely to proceed via spinodal decomposition. These scenarios are discussed in detail in Sec. IV.

II. REACTION KINETICS

A. Basic mechanism: Slow-reaction regime

In this section we define a reaction kinetic model for the size distribution of rodlike micelles. We are interested in concentration ranges such that in the absence of shear flow we are below the gel point. This limits us to the dilute or semidilute regime where the density of rods is less than—or at most comparable to— $1/L^3$. A crucial distinction is whether we are in the "slow" or "fast" reaction regimes. We will call a reaction slow if, in between collisions, rods have sufficient time for their angular distribution to assume their steady-state angular distribution, i.e., the distribution in the absence of reactions (but in the presence of flow). A reaction is called *fast* if this is not the case.

In the regime of *small* Peclet numbers we are in the slow-reaction regime for sufficiently low concentration. More explicitly, $P \ll 1$ means that the rotational diffusion constant D, exceeds the collision rate J_b of rod collisions due to Brownian motion. Using Eqs. (1.2) and (1.5), we find for the ratio of collision and relaxation rates:

$$J_b/D_r \simeq \phi_L L^3 \tag{2.1}$$

with ϕ_L the concentration (number density) of rods of size L. For small Peclet numbers, then, the ratio J_b/D_r is small, i.e., we are in the slow-reaction limit—if $\phi_L L^3 \ll 1$. In the regime of *large* Peclet numbers, alignment of the rods (in the forward direction) proceeds by rotation of the rods by the shear flow. The characteristic time scale for this rotation is $1/\dot{\gamma}$, and we are in the slow reaction regime if $\dot{\gamma}$ exceeds the flow-induced collision rate J_s . From Eq. (1.1) $(R \to L)$ we find that

$$J_s / \dot{\gamma} \simeq \phi_L L^3 \tag{2.1'}$$

so if $\phi_L L^3 \ll 1$ we are again in the slow-reaction regime. In conclusion, if $\phi_L L^3 \ll 1$ we are in the slow-reaction regime for *all* Peclet numbers, while if $\phi_L L^3 \lesssim 1$ we are in the fast-reaction limit, again for all *P*. This correspondence between dilute (semidilute) concentration and slow (fast) reaction, will be stressed throughout our work and seen to play a crucial part in understanding the shear-induced micellar sizes.

The slow-reaction regime is less dependent on the specific assumptions we have to make concerning the nature of the reaction kinetics. We thus will start by considering the slow-reaction kinetics.

Our first assumption is that we only allow for "bimolecular" reactions of the simplest "combination" type. By this we mean that if two rods of length L_1 and L_2 collide, then they can only form a rod of length $L_1 + L_2$. This assumption forbids "length-redistribution" reactions where the reaction product is two rods of lengths L_3 and $L_1 + L_2 - L_3$. Furthermore, the only "unimolecular" reactions we consider are those in which a rod of length L breaks into a pair of shorter ones with lengths L' and L - L', thereby excluding events where the number of product "fragments" is 3 or greater. Our aim, however, is to get a general understanding of the effects of shear flow on the reaction kinetics, not a rigorous description of all possible microscopic processes (which will differ anyway from one surfactant to another). With that goal in mind we construct in this section a rate equation for the length distribution of the rods.

Let $N(L,\hat{\Omega})dL d\hat{\Omega}$ be the number of rods per unit volume whose length lies in the interval [L,L + dL] and whose orientation lies inside the solid angle $d\hat{\Omega}$ around the unit vector $\hat{\Omega}$. This distribution function is constrained by the requirement that the total surfactant concentration ϕ is fixed. More explicitly, the surfactant concentration is the first moment of the distribution function:

$$\int_0^\infty dL \int d\widehat{\Omega}(L/a) N(L,\widehat{\Omega}) = \phi.$$
(2.2)

Here 1/a is the number of molecules per unit length of rod, characterizing the packing density in each micelle; ϕ is the total number of surfactant molecules, per unit volume, in the overall solution. Note that the dimensionless concentration $C \equiv \phi_L L^3$ can also be written as $\phi a L^2$, since $(L/a)\phi_L = \phi$.

In the slow-reaction regime, a rod "forgets" quickly about the orientation it had immediately following a preceding reaction event. That is, at the next collision, the angular distribution function $f_L(\hat{\Omega})$ of the rod—with a length L will be that of the steady-state angular distribution of an isolated L rod in shear flow. The combined rod distribution function $N(L,\hat{\Omega})$ can, under these conditions, then be decomposed as

$$N(L,\widehat{\Omega}) = N(L)f_L(\widehat{\Omega}).$$
(2.3)

Since a rod and its mirror image are indistinguishable, $f_L(\hat{\Omega}) = f_L(-\hat{\Omega})$. The time-*in*dependent angular distribution function $f_L(\hat{\Omega})$ obeys the normalization condition

$$\int d\widehat{\Omega} f_L(\widehat{\Omega}) = 1.$$
(2.4)

Furthermore, in the absence of shear flow, the angular distribution must be isotropic, so $f_L(\hat{\Omega}) = \frac{1}{4}\pi$.

The next step is the definition of the reaction constants. In a typical *breakage* reaction, a rod of length L and orientation $\hat{\Omega}$ breaks into two parts, with lengths, respectively, L' and L - L' with L' < L. After a time of order D_r^{-1} , the orientational distributions of the two rods become $f'_L(\hat{\Omega})$ and $f'_{L-L}(\hat{\Omega})$, dependent on the ratios $\gamma/D_r(L')$ and $\gamma/D_r(L-L')$, respectively. The ("unimolecular") rate constant is defined to be $k_b(L, \hat{\Omega} | L')$. Now, the new rod L' could have broken off either from the top or bottom of the original rod; by symmetry, then, these two reactions must have the same rate constant, i.e.,

$$k_b(L,\widehat{\Omega}|L-L') = k_b(L,\widehat{\Omega}|L').$$
(2.5)

In a combination reaction, two rods of lengths L and L', orientations $\hat{\Omega}$ and $\hat{\Omega}'$, collide, fuse, and form a new rod of length L + L' whose orientations after a time D_r^{-1} , once more, are distributed according to $f_{L+L'}(\hat{\Omega})$. The associated rate constant is $k_c(L,\hat{\Omega}|L',\hat{\Omega}')$. By symmetry,

$$k_c(L',\widehat{\Omega}'|L,\widehat{\Omega}) = k_c(L,\widehat{\Omega}|L',\widehat{\Omega}').$$
(2.6)

Note that in the presence of shear flow there is no rotational symmetry in the sense that k_c is a separate function of $\hat{\Omega}$ and $\hat{\Omega}'$ and not just of the relative angle $\hat{\Omega} - \hat{\Omega}'$.

We now incorporate the breakage and combination reactions which can contribute to changes in $N(L,\hat{\Omega})$:

$$\frac{\partial}{\partial t}N(L,\widehat{\Omega}) = -\int_{0}^{L} dL'k_{b}(L,\widehat{\Omega}|L')N(L,\widehat{\Omega}) + 2\int_{L}^{\infty} dL'\int d\widehat{\Omega}'k_{b}(L',\widehat{\Omega}'|L)N(L',\widehat{\Omega}')f_{L}(\widehat{\Omega})
-\int_{0}^{\infty} dL'\int d\widehat{\Omega}'k_{c}(L,\widehat{\Omega}|L',\widehat{\Omega}')N(L,\widehat{\Omega})N(L',\widehat{\Omega}')
+\int_{0}^{L/2} dL'\int d\widehat{\Omega}'\int d\widehat{\Omega}''k_{c}(L',\widehat{\Omega}'|L-L',\widehat{\Omega}'')N(L',\widehat{\Omega}')N(L-L',\widehat{\Omega}'')f_{L}(\widehat{\Omega}).$$
(2.7)

The first term in Eq. (2.7) represents the breakage reaction $L \rightarrow L' + (L - L')$, with L' < L. The second term represents the breakage reaction $L' \rightarrow L + (L' - L)$, with $L' \ge L$. The angular distribution $f_L(\hat{\Omega})$ of the product rod L has been included as a factor here, in order to give us the fraction of L products which "end up" with orientation $\hat{\Omega}$. Accordingly, the orientation $\hat{\Omega}'$ of the initial rod L' need not equal $\hat{\Omega}$ since angular redistribution occurs after the breakage. The factor 2 is due to the fact that the rod L may break off from either end of L'. The third term describes the combination reaction $L + (L') \rightarrow (L + L')$ and the fourth term the combination reaction $L' + (L - L') \rightarrow L$, with $L' \le L/2$.

To simplify Eq. (2.7), we perform a weighted angular average over $\hat{\Omega}$ on both sides. Defining $k_b(L|L')$ and $k_c(L|L')$ to be

$$k_{b}(L | L') = \int d\widehat{\Omega} f_{L}(\widehat{\Omega}) k_{b}(L, \widehat{\Omega} | L'), \qquad (2.8a)$$
$$k_{c}(L | L') = \int d\widehat{\Omega} \int d\widehat{\Omega}' f_{L}(\widehat{\Omega}) f'_{L}(\widehat{\Omega}') k_{c}(L, \widehat{\Omega} | L', \widehat{\Omega}'), \qquad (2.8b)$$

and using Eqs. (2.3), (2.4), and (2.8) in the angular average of Eq. (2.7) gives

$$\frac{\partial}{\partial t}N(L) = -N(L)\int_{0}^{L} dL'k_{b}(L|L') + 2\int_{L}^{\infty} dL'N(L')k_{b}(L'|L) - N(L)\int_{0}^{\infty} dL'N(L')k_{c}(L|L') + \int_{0}^{L/2} dL'N(L')N(L-L')k_{c}(L'|L-L').$$
(2.9)

This is the basic kinetic equation which we shall use to describe micellization in the presence of shear flow. First we determine (see Appendixes A-C) the dependence of the rate constants k_b and k_c on rod lengths L and L' and on flow rate γ , and then solve Eq. (2.9) for the steady-state distribution N(L) describing the micellar sizes (Appendixes D-E). We emphasize again here that the derivation of Eq. (2.9) has involved several key assumptions, the most important of which included the following: (1) rotational relaxation (via orientational Brownian diffusion) occurring on a time scale short compared to the time between collisions and (2) the neglect of all micellar combination processes other than the "fusion" reaction $L + L' \rightarrow (L + L')$.

As an example of where we can solve Eq. (2.9), consider the special case where k_c and k_b do not depend on L: $k_b(L | L') \rightarrow k_b^{(0)}$ and $k_c(L' | L - L') \rightarrow k_c^{(0)}$. (2.10) It is then straightforward to show that the exponential distribution

$$N(L) = \frac{1}{4\pi} \left(\frac{\phi a}{L^{(0)^2}}\right) e^{-L/L^{(0)}}$$
(2.11)

satisfies Eq. (2.9) with $(\partial/\partial t)N_L \equiv 0$, if the mean rod size $L^{(0)}$ is given by

$$L^{(0)} = \left(\frac{\phi a k_c^{(0)}}{8\pi k_b^{(0)}}\right)^{1/2}.$$
 (2.12)

If we actually are in thermal equilibrium, i.e., if $\gamma = 0$, then one should of course be able to compute N(L) without having to resort to kinetics arguments. The classic approach is due to Flory and Huggins. Let δ denote the scission energy associated with "capping" a rodlike micelle, ¹⁶ i.e., with reorganizing a single cylindrical aggregate into two. The internal energy density is then given by δ times the number of rods per unit volume. Adding the ideal-solution (low-density) entropy-of-mixing contribution to this scission energy gives

$$f = \int_{0}^{\infty} dL \int d\widehat{\Omega} N(L,\widehat{\Omega}) \left(\delta + k_{B} T \ln \frac{N(L\widehat{\Omega})}{N_{0}/a} \right)$$
(2.13)

for the free-energy density of the micellar solution. Here we have divided $N(L,\hat{\Omega})$ in the argument of the logarithm by

$$\frac{N_0}{a} \equiv \left(\frac{1}{a}\right) \int_0^\infty dL \int d\widehat{\Omega} \ N(L\widehat{\Omega})$$

to make it an appropriately dimensionless quantity. Minimizing f with respect to N, under the mass conservation constraint Eq. (2.2), leads to the exponential distribution Eq. (2.11) with

$$L^{(0)} = a \left(\frac{e}{4\pi}\right)^{1/2} \left(\frac{\phi}{N_0}\right)^{1/2} e^{\delta/2k_B T}.$$
 (2.12')

Again, as in Eq. (2.12), the mean micellar size is seen to increase with the square root of the overall surfactant concentration ϕ . The dependence of $L^{(0)}$ on the capping energy δ is even stronger (exponential). Note that e^{δ/k_BT} in Eq. (2.12') corresponds to the ratio $k_c^{(0)}/k_b^{(0)}$ in Eq. (2.12), consistent with an activation energy (Arrhenius) dependence of $k_b^{(0)}$ on temperature (i.e., $k_b^{(0)} \sim e^{-\delta/k_BT}$).

B. Detailed balance

The rate equation, Eq. (2.9), is, in general, of considerable mathematical complexity. As a guide towards finding appropriate solutions when k_b and k_c do depend on L, we appeal to the principle of detailed balance. In thermal equilibrium, the kinetics of the self-assembling system must obey detailed balance. In the present instance detailed balance requires that

$$N(L')N(L-L')k_{c}(L'|L-L') = 2N(L)k_{b}(L|L'),$$
(2.14)

because the rate at which the combination reaction

$$L' + (L - L') \xrightarrow{\kappa_c} L$$

occurs then equals the rate for the reverse (breaking) process

$$L \xrightarrow{\kappa_0} L' + (L - L').$$

.

Note that the factor of 2 appears in Eq. (2.14) again because the L rod can break at either end to give an L' (and L - L') fragment. Substituting Eq. (2.14) into Eq. (2.9), and using the symmetry property

$$k_{b}(L|L') = k_{b}(L|L-L')$$
(2.5')

which follows from averaging Eq. (2.5) over $f(\hat{\Omega})$, one finds that any solution of Eq. (2.14) is also a steady-state solution of Eq. (2.9), i.e., $(\partial N/\partial t)(L,t) = 0$.

For a nonequilibrium problem such as self-assembly in shear flow, detailed balance may or may not be obeyed. In other words, we are not guaranteed that Eq. (2.14) indeed has (stable) solutions for $\dot{\gamma} \neq 0$. If, however, we assume detailed balance, then according to Eq. (2.14) with L = 2L'the distribution must obey the recursion relation:

$$N(2L) = N^{2}(L)k_{c}(L|L)/2k_{b}(2L|L).$$
(2.15)

Defining $g(L) \equiv k_c (L/L)/2k_b (2L/L)$ and iteratively solving Eq. (2.15) for N(L) in terms of N(1) it is possible to show (see Appendix D) that

$$N(L) \sim \frac{1}{[g(L)]^{1/\ln 2}} e^{-L/\overline{L}}, \qquad (2.16)$$

with

$$\overline{L} = -\left(\ln[N(1)] + \frac{1}{2\ln 2} \int_{1}^{\infty} \frac{dx}{x^{2}} \ln g(x)\right)^{-1}.$$
(2.17)

The proportionality constant in Eq. (2.16) will be determined from the constraint Eq. (2.2), as needed below for each flow rate and concentration regime of interest. Note that the equilibrium distribution Eq. (2.11) is a special case of Eq. (2.16), i.e., with g(L) = const. (independent of L). Later we will use Eq. (2.16) as an "ansatz" for the solution to Eq. (2.9) with \overline{L} as a parameter to be determined selfconsistently [since N(1) remains undetermined].

As an aside, we shall see below that, under shear flow, g(L) is expected to acquire a power-law dependence on L. There is then an interesting mathematical similarity between Eq. (2.16) and the size distribution function in percolation problems. To pursue this analogy we could interpret the undetermined parameter \overline{L} as a "correlation length." The (continuous) percolation transition corresponds to the appearance of infinite clusters and is signaled by the divergence of this correlation length. At the critical point, there should emerge a scale-free power-law distribution. A continuous flow-induced gelation transition in the micellar system would thus correspond to a divergence of \overline{L} at a critical shear rate.

Besides using detailed balance to help with the solution of Eq. (2.9), one may also invoke it to gain insight into the breakage and combination rates on the microscopic level. If, for example, we only allow breakage with the products collinear, then detailed balance requires that we only allow endto-end collinear collisions to be "reactive", i.e., to lead to combination. (Since micellar rods are in reality flexiblethus allowing noncollinear breakage-this is clearly an extreme constraint.) However, the rods lose their "memory" of collinearity after a time of order D_r^{-1} , a time which—in the "slow-reaction" regime-is short compared to the average time between reactive collisions. Accordingly, in writing Eq. (2.9) we are implicitly performing an average over a time of order D_r^{-1} during which the rods undergo rotational reorientation. Thus, even if we do only allow collinear pairs to be reactive (via whatever microscopic mechanism might be operative for the actual combination of micelles), we still must allow for general orientations $\hat{\Omega}$ and $\hat{\Omega}'$ in formulating $k_c (L, \widehat{\Omega} | L', \widehat{\Omega}').$

C. Fast-reaction regime

In the *fast*-reaction limit, the time between collisions becomes *less* than the orientational relaxation time. The micellar rods do not have enough time to undergo rotational Brownian motion or to be reoriented by the flow field before they experience the next collision. An immediate consequence is that the orientational part of the distribution function $N(L,\Omega)$ is no longer governed only by the rotational diffusion coefficient or by the shear rate (velocity gradient). Rather, the angular distribution is expected to depend on the detailed nature of the micellar fission and fusion reactions about which so little is known.

If we assume that the breakage and combination processes control $N(L,\Omega)$ rather than the solvent-induced Brownian and flow reorientation, then we can consider our system as a dense flowing gas of anisotropic particles which can break and combine with one another. The fission and fusion reaction rates must now be interpreted as the microscopic rates rather than as quantities describing an average over a time D_r^{-1} , and the question of whether or not all reactive collisions are collinear becomes relevant. If we indeed enforce strict collinearity, then the different rod orientations become *decoupled*. This scenario, for $C \ge 1$, is discussed in Ref. 14. If, on the other hand, the collinearity constraint is not strict—as we have argued it should not be for flexible rods, for example-then, after a certain number of collisions, the orientation of a rod is expected to be randomized. By analogy with the famous assumption by Boltzmann (the "Stosszahlansatz") for molecular chaos in gases,¹⁷ we thus assume that dynamic correlations between successive reactions are lost because of the high collision rate. This implies that rod orientations are essentially random before any given collision. Under this assumption of "molecular chaos" we choose accordingly:

$$N(L,\hat{\Omega}) \simeq \frac{1}{4\pi} N_L$$
 + higher-order terms. (2.18)

The kinetic equation (2.9) thus remains valid except that everywhere in Eq. (2.8) we must replace $f_L(\hat{\Omega})$ by $1/4\pi$. For $P_L \ge 1$ there is of course always some degree of forward polarization induced by the flow of solvent. In particular, we saw (Sec. II A) that this forward polarization is expected to be of order $\gamma/J_S \simeq 1/\phi_L L^3$. The higher-order terms in Eq. (2.18) will thus be $\vartheta(1/\phi_L L^3)$ and are non-negligible.

The assumption of molecular chaos in rod orientation, on which Eq. (2.18) is based, cannot be derived by *a priori* arguments about relative time scales for rotation and randomization of rod orientations. In fact, neither has the analogous Stosszahlansatz for colliding gas particles been fully justified, even though it is so intuitively reasonable. As in this latter case we must treat our assumption as one whose usefulness has to be determined by comparison with experiment.

III. RATE CONSTANTS IN FLOW

A. Combination in shear flow

1. General cross-section considerations

The collisions between rodlike aggregates leading to micellar combination are, in general, due both to Brownian motion and to flow. For small Peclet numbers, Brownian motion is dominant and—in the spirit of the discussion in Sec. II B—we will approximate $k_c (L | L')$ by the constant value $k_c^{(0)}$. In the regime of very large Peclet numbers, on the other hand, we can equate k_c with an appropriately defined Smoluchowski rate, $k_c^{(S)}(L | L')$, taking into account the shear-induced collisions between rods. To interpolate between these two limiting cases we will assume the simplest form

$$k_{c}(L|L') = k_{c}^{(0)} + k_{c}^{(S)}(L|L'), \qquad (3.1)$$

i.e., we take the Brownian motion and shear flow to be "parallel," noninterfering channels for the collision process. The value of $k_c^{(0)}$ is discussed later [see Eq. (3.19)]. The function $k_c^{(S)}$ can be evaluated by a generalization of Smoluchowski's original idea for spherical emulsion drops. More explicitly, assume we have rods whose center-of-mass (COM) moves along straight-line trajectories under the imposed velocity gradient. We neglect the perturbation of the flow field by the presence of the rods, and compute the rate $J_{S}(L, \hat{\Omega})$ at which a given ("reference") rod undergoes collision with all the other rods. This rate will be of the form $v\sigma\phi_L$, with v the velocity difference between rods on different flow lines (i.e., at different heights in the velocity gradient), σ the collision cross section, and ϕ_L the number density of rods. The actual combination rate for the reference rod is then $\alpha J_{s}(L, \Omega)$, where $\alpha \leq 1$ is the reaction efficiency. Since this rate describes the contribution of combination collisions to the rate of decay of $N(L,\Omega)$, comparing it with the third term in Eq. (2.7) will necessarily provide an expression for k_{c} . It is important to realize that by making α a constant, we are allowing combination reactions between two rods with *arbitrary* angles $\hat{\Omega}$ and $\hat{\Omega}'$ before the reaction. As discussed in Sec. II B, this does *not* imply that, on the *microscopic* level, we allow noncollinear encounters to be reactive. Rather, we are merely asserting that at times D_r^{-1} before a reactive collision two rods can have arbitrary orientations and that *after* a time D_r^{-1} following reaction the products again have arbitrary orientations, constrained only by the steady-state distribution $f_L(\hat{\Omega})$.

We start by defining the shear-flow velocity field

$$\vec{v}(y) = \dot{\gamma} y \hat{z}. \tag{3.2}$$

A reference rod of length L and orientation $\widehat{\Omega} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ is centered at the origin, and a second rod, of length L' and orientation $\widehat{\Omega}' = (\sin \theta' \cos \phi', \sin \theta' \sin \phi', \cos \theta')$, is moving along a flow line at height y. Let [x,y,z(t)] denote its COM coordinates with $z(t) = \dot{\gamma}yt$, according to Eq. (3.2). To describe the collision between the two rods we introduce the differential cross section $d\sigma(L,\widehat{\Omega}|L',\widehat{\Omega}')$. It is the area of a parallelogram strip in the xy plane which is bounded by the interval [y, y + dy] and is such that if x, y is located inside the strip then a collision will indeed take place. It follows that the collision rate of incoming rods with the reference rod is

$$J_{s}(L,\widehat{\Omega}) = \int_{0}^{\infty} dL' \int d\widehat{\Omega}' N(L',\widehat{\Omega}') \int dy \dot{\gamma}|y| \frac{d\sigma}{dy}.$$
(3.3)

Comparing this with the combination rate

$$\alpha J_{S}(L,\widehat{\Omega}) = \int_{0}^{\infty} dL' \int d\widehat{\Omega}' N(L',\widehat{\Omega}') k_{c}(L\widehat{\Omega}|L',\widehat{\Omega}')$$
(3.4)

from Eq. (2.7), we conclude that

$$k_{c}^{(S)}(L,\widehat{\Omega}|L',\widehat{\Omega}') = \alpha \int dy \dot{\gamma}|y| \frac{d\sigma}{dy} (L,\widehat{\Omega}|L',\widehat{\Omega}').$$
(3.5)

The differential cross section $d\sigma/dy$ can be determined straightforwardly from the geometrical considerations outlined in Appendix A. For $y^* > 0$, we find

$$\frac{d\sigma}{dy} = \begin{cases} \left(\frac{d\sigma}{dy}\right)^*, & 0 < y < y^* \\ \left(\frac{d\sigma}{dy}\right)^* \left(1 - \frac{(y - y^*)}{L'\Omega_y'}\right), & y^* < y < y^* + L'\Omega_y' \end{cases}$$
(3.6)

with

$$y^* = \frac{1}{2} (L\Omega_y - L'\Omega_y') \tag{3.7}$$

and

$$\left(\frac{d\sigma}{dy}\right)^* = L'\Omega'_y \frac{\sin|\phi - \phi'|}{\sin\phi\sin\phi'}.$$
(3.8)

For $y^* < 0$, all primed and unprimed quantities in Eqs. (3.6)-(3.8) must be exchanged. (Recall that $\Omega_y = \sin \theta \sin \phi$, etc.) Carrying out the y integration in Eq. (3.5) then gives

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$$k_{c}^{(S)}(L,\widehat{\Omega}|L',\widehat{\Omega}') = \frac{\alpha \dot{\gamma}}{4} \frac{\sin|\phi - \phi'|}{\sin \phi \sin \phi'} (L^{2}L'\Omega_{y}^{2}\Omega_{y}' + \frac{1}{3}L'^{3}\Omega_{y}'^{3})$$

for $L\Omega_{y} > L'\Omega_{y}'.$ (3.9)

(Again, primed and unprimed quantities must be switched in the case $L\Omega_{\nu} < L'\Omega_{\nu}'$.)

It remains only to substitute Eq. (3.9) for $k_{c}(L,\Omega|L',\Omega')$ into the double orientational average, see Eq. (2.8b), which defines the Smoluchowski contribution to $k_{c}(L|L')$. In Secs. III A 2 and III A 3 we evaluate these angular integrations for the cases of small and large Peclet number, respectively. We will see in Appendix E that we need only be concerned with the case L of order L', to which we restrict ourselves henceforth. To evaluate $k_c^{(s)}(L|L)$ we need the angular distribution $f_L(\hat{\Omega})$ for both weak $(P \ll 1)$ and strong $(P \ge 1)$ flow conditions.

2. Small Peclet number (slow-reaction regime)

To obtain the angular distribution $f_L(\widehat{\Omega})$, one must first find the long-time solution to the Smoluchowski equation describing the rotational Brownian motion of isolated (i.e., noninteracting) L rods in the presence of a shear velocity gradient. Boeder¹⁸ has shown that the steady-state orientational distribution for dilute thin rods in weak shear flow can be expanded in powers of the Peclet number according to

$$f_{L}(\widehat{\Omega}) = \frac{1}{4\pi} \left(1 + \frac{P_{L}}{2} \Omega_{y} \Omega_{z} + \frac{P_{L}^{2}}{8} \left[\Omega_{y}^{2} \Omega_{z}^{2} + \frac{1}{3} (\Omega_{z}^{2} - \Omega_{y}^{2}) - \frac{1}{15} \right] + \cdots \right).$$
(3.10)

Here we have subscripted the Peclet number P_L to show explicitly its dependence on rod length L. If η is the solvent viscosity then the rotational diffusion constant can be approximated by

$$D_r \simeq \frac{k_B T}{\eta L^3},\tag{3.11}$$

implying

$$P_L = \frac{\dot{\gamma}\eta L^3}{k_B T}.$$
(3.12)

Note that the lowest-order correction in Eq. (3.10) to the distribution is proportional (through P_L) to the angular factor $\Omega_{p}\Omega_{z}$. This implies that, for small $P_{L}, f_{L}(\hat{\Omega})$ has a maximum along a polar angle (θ) of $\pi/4$ in the yz plane, i.e., $\theta = \pi/4, \varphi = \pi/2$. The next correction, of order (P_I^2) , however, has its maximum at $\Omega_z = 1$, corresponding to alignment in the flow direction ($\theta = 0$). Thus we have the wellknown result that the preferred polar angle is pulled from 45° to 0° as the shear velocity gradient is increased.

Substituting Eq. (3.10) for f_L and Eq. (3.9) for $k_c^{(S)}$ into Eq. (2.8b), we find

$$k_{c}(L | L' = L) = k_{c}^{(0)} + \alpha \gamma L^{3}(c_{0} + c_{2}P_{L}^{2} + \cdots)$$
$$= k_{c}^{(0)}(1 + \alpha c_{0}P_{L} + \alpha c_{2}P_{L}^{3} + \cdots),$$
(3.13)

where c_0 and c_2 are positive numerical constants of order unity (see Appendix B). Note that the term in $k_c^{(S)}$ which is quadratic in P_L vanishes identically by symmetry.

3. Large Peclet number (slow-reaction regime)

The distribution function $f_L(\hat{\Omega})$ is not known in closed form for the limit $P_L \ge 1$ (except in two dimensions). It is possible, however, to solve approximately for steady-state solutions to the kinetic equations describing the second moments

$$S_{\alpha\beta} \equiv \langle \Omega_{\alpha} \Omega_{\beta} \rangle - \frac{1}{3} \delta_{\alpha\beta}. \tag{3.14}$$

Here the angular brackets denote an average over $f_L(\Omega)$ and α and β label the space-fixed x, y, and z directions. Specifically, a decoupling approximation can be introduced which expresses the quartic averages $\langle \Omega_{\alpha} \Omega_{\beta} \Omega_{\gamma} \Omega_{\delta} \rangle$ in terms $S_{\alpha\beta}$, so that a closed set of equations is obtained for the second moments. For $P_L \ge 1$, Doi and Edwards find¹¹ for the steady-state values:

$$\Omega_{\nu}\Omega_{z}\rangle = (2P_{L})^{-1/3}, \qquad (3.15a)$$

$$\langle \Omega_z^2 \rangle = 1 - 2 [(P_L)^2/2]^{-1/3},$$
 (3.15b)

and

(

$$\langle \Omega_y^2 \rangle = \langle \Omega_x^2 \rangle = \left[(P_L)^2 / 2 \right]^{-1/3}.$$
(3.15c)

From Eq. (3.15b) we see that $\langle \sin^2 \theta \rangle = 1 - \langle \Omega_r^2 \rangle$ $\simeq \langle \theta^2 \rangle \simeq 2 [(P_L)^2/2]^{-1/3} \ll 1$ for large Peclet number, i.e., the rods are strongly aligned along the flow direction. In addition, Eq. (3.15c) implies $\langle \cos^2 \phi \rangle \simeq \langle \sin^2 \phi \rangle$ and, hence a broad distribution of rods over azimuthal angles. Finally, it follows from Eq. (3.15a) that $\langle \sin \theta \sin \phi \rangle \approx \langle \theta \rangle \simeq P_L^{-1/3}$, in agreement with $\langle \theta^2 \rangle \simeq P_L^{-2/3}$ from Eq. (3.15b) (ϕ is restricted to $[0,\pi]$). The average $\langle \theta \rangle$ is thus nonzero and $\langle \theta^2 \rangle \simeq \langle \theta \rangle^2$.

Even with $f_L(\Omega)$ peaking sharply at $\widehat{\Omega} = \widehat{z}$, it is still important to determine the behavior of the angular distribution away from its maximum, since we need in Eq. (2.8b) to evaluate the average of $k_c^{(S)}(L,\widehat{\Omega}|L,\widehat{\Omega}')$ over all orientations. To estimate $f_{L_{\lambda}}(\widehat{\Omega})$ for $\widehat{\Omega} \neq \hat{z}$, we note first that strong shear flow stabilizes $\Omega \simeq \hat{z}$ only for $\Omega_v > 0$. Whenever $\Omega_v < 0$, the velocity gradient (through viscous drag) gives rise to a destabilizing torque: The rod rotates ("flips") with angular velocity γ until it has performed a sweep over 180°, after which it is stable again with $\Omega_{\nu} \gtrsim 0$. Let $\tau \simeq 1/\gamma$ denote the duration of such a sweep. For $\Omega_{y} \ge 0$, the rod performs rotational Brownian motion with $\langle \theta^2(t) \rangle \approx D_r t$. For a typical value $\langle \theta^2 \rangle^{1/2} \approx P_L^{-1/3}$, then, we expect that the rod will find itself with $\Omega_{\nu} < 0$ (and hence starting a new sweep) after a time $T \simeq \langle \theta^2 \rangle / D$, or

$$T \simeq 1/(P_L^{2/3}D_r).$$
 (3.16)

It follows that the probability $f_L(\Omega \neq \hat{z})$ of finding a rod away from the flow direction is of order τ/T . Using Eq. (3.12) we find

$$f_L(\hat{\Omega}) \simeq 1/P_L^{1/3},$$
 (3.17a)

so

$$f_L(\widehat{\Omega}) \simeq \left(\frac{k_B T}{\eta \gamma}\right)^{1/3} \frac{1}{L} \quad (P_L \gg 1, \widehat{\Omega} \neq \widehat{z}). \tag{3.17b}$$

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That is, for $P_L \ge 1$, $f_L(\widehat{\Omega})$ is approximately constant for $\widehat{\Omega} \neq \widehat{z}$, while it has a large peak around $\widehat{\Omega} = \widehat{z}$. Indeed, one finds exactly this behavior in the steady-state solution obtained analytically for *two*-dimensional systems of long rods in shear flow.¹⁹

To evaluate the (double) orientational average defining k_c (L | L' = L) in Eq. (2.8b), we break up the angular integrations into their $\hat{\Omega} \approx \hat{z}$ and $\hat{\Omega} \neq \hat{z}$ parts and use Eqs. (3.14c) and (3.17a) to approximate these respective contributions. We find (Appendix B)

$$k_{c}(L | L' = L) = k_{c}^{(0)} + \alpha \dot{\gamma} L^{3} (dP_{L}^{-1} + eP_{L}^{-2/3})$$

$$\approx e \alpha \dot{\gamma} L^{3} P_{L}^{-2/3}, \quad P_{L} \ge 1$$
(3.18)

with d and e both numerical factors of order unity. The first term in parentheses arises from the strong, forward $(\theta \approx 0)$ peak in $f_L(\theta)$ and the second from the nearly constant "wings" $(\theta \neq 0)$ of the distribution. Note that the shear-induced collision (reaction) rate is dominated for large Peclet number by the small fraction of rods which remain unaligned $(\theta \neq 0)$ by the flow, their larger geometric cross section compensating for their lower orientational probability.

We conclude by noting that $k_c^{(0)}$, the collisional rate of "bimolecular" recombination in the absence of flow, can be expressed directly in terms of the rod length L and its rotational diffusion coefficient D_r . More explicitly, recalling our original discussion surrounding Eqs. (1)-(2) and (1.5), we found, in Sec. I,

$$k_c^{(0)} \equiv \alpha J_b / \phi_L \simeq \alpha \frac{k_B T}{\eta}.$$
(3.19)

Using this result in Eqs. (3.12) and (3.18) leads immediately to

$$k_{c}(L) \equiv k_{c}(L | L' = L)$$

$$\simeq \begin{cases} k_{c}^{(0)}(1 + P_{L} + \cdots), & P_{L} \leq 1 \\ k_{c}^{(0)}P_{L}^{1/3}, & P_{L} \ge 1, \end{cases}$$
(3.20)

where numerical factors of order unity have now been dropped altogether.

4. Fast-reaction regime

In the fast-reaction regime, we use Eq. (2.18). The resulting calculation is then identical to the slow-reaction regime with small Peclet number and we can immediately use Eq. (3.13):

$$k_{c}(L|L'=L) = k_{c}^{(0)} + c_{0}\alpha\dot{\gamma}L^{3}$$
(3.13')

with c_0 the same numerical constant as in Eq. (3.13). The second-order term in Eq. (3.13) should not be included as it involves the flow alignment which is suppressed in the fast-reaction regime.

B. Breaking in shear flow

1. Shear-induced fracture mechanism: General

As discussed in Sec. II B, the breaking rate constant in the absence of flow, $k_b^{(0)}$, is expected to be independent of both how long the rod is (L) and just where it breaks at (L'). In the presence of flow, the mechanism whereby viscous

forces contribute to k_b is quite different from that described earlier for k_c . Instead of the velocity gradient resulting in a shear-induced collision rate, it now gives rise to a tension in the rod which enhances the probability of breaking. More explicitly, it is straightforward to show from a bead model for the rod, see Appendix C, that the tension at a distance s from the rod center (-L/2 < s < L/2) is given by

$$t(s) = \frac{\gamma \xi}{2b} \Omega_{y} \Omega_{z} \left[\left(\frac{L}{2} \right)^{2} - s^{2} \right].$$

Here b is the rod diameter and ξ is the friction coefficient associated with each bead (of diameter b) comprising the rod of length L. Let κ be the intrinsic elastic constant characterizing the extension-compression of the rod. Then the deformation at s, due to the shear-induced tension, is $t(s)/\kappa \equiv \delta(s)$ and the local deformation energy at s can be approximated by (Appendix C)

$$E_{\rm def}(L,L') = \frac{\gamma^2 \xi^2}{8\kappa b^2} L'^2 (L'-L)^2 \Omega_y^2 \Omega_z^2, \qquad (3.21)$$

where we have used s = L' - L/2.

Note that E_{def} vanishes at the two ends of the rod, i.e., at L' = 0 and L' = L, and that it has a maximum at the rod center. The maximum deformation energy is

$$E_{\rm max} = E_{\rm def} \left(L, L' = \frac{L}{2} \right) = \frac{\dot{\gamma}^2 \xi^2}{128 \kappa b^2} L^4 \Omega_y^2 \Omega_z^2. \quad (3.22)$$

To estimate the importance of fracture with $L' \neq L/2$, we first specify the connection between the above deformation energy, E_{def} , and the effective breaking rate constant, $k_b(L | L')$, in the presence of flow. Recalling

$$k_{b}^{(0)} \sim e^{-\delta/k_{B}T} \tag{3.23}$$

from Sec. II B, it is natural to write

$$k_b(L,L') \sim e^{-[\delta - E_{def}(L,L')]/k_BT}.$$
(3.24)

However, from Eq. (3.21), i.e., from the parabolic falloff in $E_{def}(L,L')$ from the rod center (L' = L/2), it follows that shear-induced breaking is most likely to occur near the center because, in practice, $k_B T \ll \delta$ or E_{def} , and this maximum must be quite pronounced. Accordingly, we need only estimate E_{def} at its maximum, E_{max} .

2. Small Peclet number

To simplify E_{max} we observe first that the energy κb^2 is essentially the binding, or scission, energy δ of the rodlike micelle. For typical surfactant systems it has been estimated to be on the order of ten's of $k_B T$. Accordingly, we replace κb^2 in the denominator of E_{max} by $\lambda k_B T$, with $\lambda \ge 1$. Then, simple algebraic manipulation allows us to write

$$\frac{E_{\max}}{k_B T} \simeq P_L^2 \left(\frac{b}{L}\right)^2 \Omega_y^2 \Omega_z^2.$$
(3.25)

Here we have used $\xi \simeq 6\pi\eta b$, and dropped the numerical factor $6\pi^2/32\lambda$ of order unity. Since $b/L \ll 1$ and $\langle \Omega_y^2 \Omega_z^2 \rangle \lesssim 1$, it follows immediately that E_{max} is negligible compared to $k_B T$ whenever $P_L < 1$.

3. Large Peclet number

Here the effect of flow on alignment is no longer negligible. We now have

$$\langle \Omega_{\nu}^2 \Omega_{z}^2 \rangle \simeq \langle \theta^2 \rangle \simeq (1/P_L)^{2/3}.$$

From Eq. (3.25), we see that E_{max} becomes of order $k_B T$ only when

$$P_L > \left(\frac{L}{b}\right)^{3/2}.\tag{3.26}$$

With $P_L = \gamma \eta L^3 / k_B T$ and $L / b \simeq 10^{-2}$, this implies that γ must exceed 10⁶ s⁻¹, an unphysically large value. From the aforementioned we conclude that, for all realizable shear flows, the rate constant for breaking is essentially unaffected by imposed velocity gradients:

$$k_b \simeq k_b^{(0)}. \tag{3.27}$$

This result is really a consequence of the one-dimensional nature of our micellar aggregates and the fact that they can "hide" from the shear-induced tension effects by aligning with the flow. For recall [see Eq. (3.21)], the tension in a rod is proportional to the angular factor $\Omega_y \Omega_z$ ($\sim \sin \theta$), which goes to zero when $\langle \theta \rangle \rightarrow 0$ (specifically, as $P^{-1/3}$). For *three*-dimensional colloidal particles (e.g., microemulsion droplets), on the other hand, the shear flow is always able to find (and "grab onto") a "large" dimension. Note also that in *elongational* velocity gradients, the tension-induced deformation effect $[k_b^{(0)} \rightarrow k_b(\dot{\gamma})]$ is important at high flow rates because there the tension is proportional to P_2 ($\cos \theta$), rather than to $\sin \theta$, and is maximized by alignment instead of minimized as in the case of shear flow.

IV. FLOW-INDUCED GELATION

In the preceding sections we constructed a rate-equation [Eq. (2.9)] for the micellar size distribution N_L in the presence of shear flow. To gain insight into the nature of its solutions, and to make the equation generally more tractable, we make certain assumptions about the *form* of the size distribution. Specifically, we insist that it satisfy the detailed balance relation (2.14) and, hence, (see Appendix D) that it have the form of Eq. (2.16), with the length \overline{L} to be determined self-consistently, as described later. Recall that

$$g(L) \equiv \frac{k_c(L/L)}{2k_b(2L/L)}.$$
 (4.1)

Accordingly, for the slow-reaction limit, we have from Eq. (3.20) that (since $k_b \simeq k_b^{(0)}$ for all γ of interest)

$$g(L) = \begin{cases} \text{independent of } L, & P_L \leqslant 1 \\ \sim P_L^{1/3} \sim L, & P_L \geqslant 1 \end{cases}$$

whereas, from Eq. (3.13'),

$$g(L) = \begin{cases} \text{independent of } L, & P_L \ll 1 \\ \sim L^3, & P_L \gg 1 \end{cases}$$

for the fast-reaction case.

Finally, to determine the proportionality constant in Eq. (2.16), we impose the mass-conservation constraint given by Eq. (2.2). It then follows that

$$N_L \simeq \frac{\phi a}{\overline{L}^2} e^{-L/\overline{L}}, \quad \overline{L} \ll \overline{a}$$
 (4.2a)

whereas, for large Peclet number $(\overline{L} \gg \overline{a})$,

$$N_{L} \simeq \begin{cases} \frac{\phi a \overline{L}^{(1/\ln 2) - 2}}{L^{(1/\ln 2)}} e^{-L/\overline{L}} & \text{(slow reaction)} & (4.2b) \\ A = \frac{1}{2} (3/\ln 2) - 2 & \text{(slow reaction)} & (4.2b) \end{cases}$$

$$\frac{\phi a \bar{a}^{(3/\ln 2) - 2}}{L^{(3/\ln 2)}} e^{-L/\bar{L}} \quad \text{(fast reaction)} \quad (4.2c)$$

(see Appendix E). Here \bar{a} is a (shear-rate-dependent) length defined by the condition $P_{L=\bar{a}} = 1$, i.e., $\bar{a} = (kT/\eta\dot{\gamma})^{1/3}$, and enters naturally as a lower limit in the L integrations when we consider large Peclet number $(P_L \ge 1 \leftrightarrow L \ge \bar{a})$. It remains only to substitute for N_L in Eq. (2.9) and to obtain an ordinary differential equation for \overline{L} in each of the aforementioned limits.

A. Slow-reaction regime

Define the first moment of the size distribution by

$$\langle L \rangle \equiv \int_0^\infty dL L N_L \left/ \int_0^\infty dL N_L \right.$$
(4.3)

and consider first the small Peclet number $(\overline{L} \leqslant \overline{a})$ limit. Using Eq. (4.2a) for N_L in the denominator, and recognizing from Eq. (2.2) that the numerator is simply equal to ϕa , it follows immediately that

$$\langle L \rangle = \overline{L} \tag{4.4}$$

and, hence, that

$$\frac{d\langle L\rangle}{dt} = \frac{d\overline{L}}{dt} = -\frac{\overline{L}^2}{\phi a} \int_0^\infty dL \frac{\partial}{\partial t} N_L.$$
(4.5)

Now we evaluate the integral in Eq. (4.5) by substituting for $\partial NL / \partial t$ from Eq. (2.9), using Eq. (4.2a) for N_L , and introducing

$$k_b(L|L') \simeq k_b^{(0)}$$
 (4.6a)

and

$$k_{c}(L|L') \simeq k_{c}^{(0)} \left[1 + \frac{1}{\overline{a}^{3}} \begin{pmatrix} L^{2}L' \\ L'^{2}L \end{pmatrix} \right],$$
 (4.6b)

for the breaking and combination rate constants appropriate to the $P_L < 1$ slow-reaction limit (see Secs. III A 2, III A 3, III B 2, and III B 3). We find (see Appendix E)

$$\frac{d\overline{L}}{dt} \simeq -k_{b}^{(0)}\overline{L}^{2} + \frac{\phi a}{2}k_{c}^{(0)}\left\{1 + \vartheta\left[\left(\frac{\overline{L}}{\overline{a}}\right)^{3}\right]\right\}.$$
 (4.7)

Here, and henceforth, we drop all numerical factors $\vartheta(1)$.

For $L \gg \overline{a}$, on the other hand, we must use Eq. (4.2b) rather than Eq. (4.2a) for N_L , and replace Eq. (4.6b) by

$$k_{c}(L|L') \simeq k_{c}^{(0)^{2/3}} \dot{\gamma}^{1/3} \begin{cases} L\\ L' \end{cases}$$
(4.6b')

[Note that k_b is still given by Eq. (4.6a), i.e., by its shearrate-independent value, even at large Peclet number. Indeed, as argued in Sec. III B 3, k_b deviates from $k_b^{(0)}$ only when γ becomes unphysically large.] Equations (4.4) and (4.5) must now be replaced by

$$\langle L \rangle \simeq \overline{a}^{(1/\ln 2) - 1} \overline{L}^{2 - (1/\ln 2)}$$
(4.4')

and

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$$\frac{d\overline{L}}{dt} \simeq -\frac{(\overline{a}/\overline{L})^{(1/\ln 2) - 1}}{\phi a} \overline{L}^2 \int_0^\infty dL \frac{\partial N_L}{\partial t}.$$
 (4.5')

Substituting Eq. (2.9) for $(\partial / \partial t)N_L$, and using Eq. (4.2b) for N_L and Eq. (4.6b') for $k_c(L | L')$, we find (Appendix E)

$$\frac{d\overline{L}}{dt} \simeq -k_b^{(0)}\overline{L}^2 + k_c^{(0)^{2/3}}\dot{\gamma}^{1/3}\phi a\overline{L}.$$
(4.8)

Recall that we are interested in finding the long-time steady-state solutions for N_L , and, hence, the $t \to \infty$ behavior of Eqs. (4.7) and (4.8) for \overline{L} . To this end it is convenient to rewrite both of these equations in the form

$$\frac{d\overline{L}}{dt} = -\frac{d}{dL} V(\overline{L}).$$
(4.9)

Figure 1 shows (see bottom left) the function $V(\overline{L})$ corresponding to Eq. (4.7), i.e., to the weak-flow $(\overline{L} \leqslant \overline{a})$ slowreaction $(c \leq 1)$ regime and also (upper left) that for Eq. (4.8), i.e., the $\overline{L} \gg \overline{a}$, $c \leq 1$ case. We can think of \overline{L} as the value of a coordinate associated with the overdamped motion of a "particle" in the "potential" $V(\overline{L})$. This latter quantity is the effective potential-the schematic "free energy"-mentioned in the Introduction. Note, however, that V(L) is not an actual potential or free energy-even its dimensions (length²/time) are "wrong"-nevertheless, its \overline{L} dependence determines the various steady-state, metastability, and runaway natures of the long-time solutions to the kinetic equation for micellar length, as discussed later. In particular, $\overline{L}(t \to \infty) \equiv \overline{L}_{\text{steady state}}$ will correspond to the \overline{L} which minimizes $V(\overline{L})$, as follows from the $d\overline{L}/dt = 0$ solution to Eq. (4.9).

For weak flow, we see immediately from Eq. (4.7) that $V(\overline{L})$ has its minimum at

$$\overline{L} \simeq (\phi a k_c^{(0)} / 2 k_b^{(0)})^{1/2} = L^{(0)},$$

the average length in the *absence* of flow [see Eqs. (2.11) and (2.12)]. Furthermore, in this limit, the relaxation time to equilibrium is

$$\tau(\dot{\gamma} \to 0) = (2k_b^{(0)}L^{(0)})^{-1}, \qquad (4.10)$$

as follows from linearization $(\overline{L}^2 \to \overline{L}L^{(0)})$ of Eq. (4.7). For larger γ , but still in the weak-flow $(\overline{L} \leqslant \overline{a})$ limit, the

$$\vartheta\left[\left(\frac{\overline{L}}{\overline{a}}\right)^3\right]$$

terms in Eq. (4.7) have the effect of displacing the minimum in $V(\overline{L})$ towards larger values. More explicitly, we can write

$$L(t \to \infty) \simeq L^{(0)} (1 + \text{const.} P_{L_{(0)}}),$$
 (4.11)

where const. is a numerical factor $\vartheta(1)$ and $P_{L_{(0)}} \equiv \gamma \eta L^{(0)^3}/kT$. Thus, as expected from discussion in the Introduction, the flow-induced micellar size enhancement is controlled completely by the Peclet number. Note, however, that the increase in \overline{L} is modest in the weak-flow regime: $\overline{L}(t \to \infty)$ remains of order $L^{(0)}$ for $P_{L_{(0)}} \leq 1$ (see left solid curve in Fig. 2).

Even for strong-flow conditions, it turns out that the size enhancement is not dramatic. Specifically, for $\overline{L} \gg \overline{a}$, we have from Eqs. (4.8) and (4.9) that the minimum in $V(\overline{L})$ is given by



FIG. 2. Average micellar length as a function of shear rate, for the low and semidilute ranges of concentration.

$$\overline{L}(t \to \infty) \simeq \phi a \dot{\gamma}^{1/3} k_c^{(0)^{2/3}} / k_b^{(0)} \simeq L^{(0)} P_{L_{(0)}}^{1/3}.$$
(4.12)

Thus the steady-state value of \overline{L} rises only slowly with $\dot{\gamma}(\sim \dot{\gamma}^{1/3})$, see the right solid curve in Fig. 2, and we would need to go to very high shear rates to observe a significant increase in \overline{L} .

We conclude that, in the slow-reaction limit, the following occurs.

 \overline{L} is essentially unaffected by flow until the shear rate γ becomes comparable to the rotational diffusion coefficient $D_r = kT/\eta \overline{L}^{(0)^3}$ associated with the zero-flow length $\overline{L}^{(0)}$. In the $P_{L^{(0)}} < 1$ regime, the mean aggregation number \overline{L} increases with flow rate according to a factor $(1 + P_{L^{(0)}})$, with $P_{L^{(0)}}$ proportional to γ and $L^{(0)^3}$ [see Eq. (3.12.)].

In the strong-flow $(P_{L^{(0)}} \ge 1)$ regime, the average length increases even more weakly with velocity gradient, varying as $P_{r^{(0)}}^{1/3} \sim \dot{\gamma}^{1/3}$.

 $\dot{\gamma}_c \simeq D_r \simeq kT/\eta L^{(0)^3}$ is of order 10^3 s^{-1} for the dilute micellar solutions studied experimentally and, hence, $\dot{\gamma} \leq 10\dot{\gamma}_c$ represents an upper bound to the flow rates of physical interest. We conclude that there is no flow-induced gelation in the slow reaction regime.

The origin of the suppression of the "runaway" at large \overline{L} is the reduction by flow alignment of the reaction cross section [see Eq. (3.18)]. We now turn to the *fast*-reaction regime, where we argued earlier that this forward alignment is "spoiled" by repeated collisions and reactions.

B. Fast-reaction regime

In this limit we must use Eq. (4.2c) for N_L when $\overline{L} \gg \overline{a}$. [The $\overline{L} \ll \overline{a}$ regime leads again to Eq. (4.7) for $d\overline{L}/dt$, so we can now confine ourselves to consideration of the $\overline{L} \gg \overline{a}$ case.] Again we want to derive an ordinary differential equation for \overline{L} . However, because of the strong inverse dependence on L of the prefactor $[g(L)]^{-(1/\ln 2)}$ in N_L , we can no longer do so by means of the first moment. In fact, it is straightforward to show (see Appendix E) that Eq. (4.2c) for N_L implies $\langle L^n \rangle \simeq \overline{a}^n$, independent of \overline{L} , for $n \leqslant 3$. For the fourth moment, on the other hand, we find (Appendix E)

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$$\langle L^4 \rangle \equiv \int dL L^4 N_L / \int dL N_L \simeq \overline{a}^{(3/\ln 2) - 1} \overline{L}^{5 - (3/\ln 2)},$$
(4.13)

from which it follows that

$$\frac{d\overline{L}}{dt} \simeq \frac{1}{\phi a} \left(\frac{\overline{a}}{\overline{L}}\right)^{2-(3/\ln 2)} \frac{1}{\overline{L}^{2}} \int dL L^{4} \frac{\partial N_{L}}{\partial t}.$$
 (4.14)

Once more, it remains only to substitute for $\partial N_L/\partial t$ from Eq. (2.9), using there the appropriate (i.e., strong-flow fast-reaction) forms for $k_b (L/L')$ and $k_c (L/L')$, and evaluate the integral on the right-hand-side of Eq. (4.14) as an explicit function of \overline{L} . Thus we use

$$k_b(L/L') \simeq k_b^{(0)}$$

and

$$k_{c}(L/L') \simeq \frac{k_{b}^{(0)}}{\bar{a}^{3}} \begin{cases} L^{2}L'\\ L'^{2}L \end{cases}$$
 (4.15)

and find (Appendix E)

$$\frac{d\overline{L}}{dt} \simeq -k_{b}^{(0)}\overline{L}^{2} + \phi a k_{c}^{(0)} \left(\frac{\overline{L}}{\overline{a}}\right)^{3}.$$
(4.16)

Recalling Eq. (4.9), we have

$$V(\overline{L}) \simeq k_{b}^{(0)}\overline{L}^{3} - \phi a \frac{k_{c}^{(0)}}{\overline{a}^{3}}\overline{L}^{4}.$$

$$(4.17)$$

This effective potential, describing the fast-reaction limit, is shown on the right side of Fig. 1 in both the small $P_{L^{(0)}}$ (bottom) and large $P_{L^{(0)}}$ (top) flow regimes.

 $P_{L^{(0)}} \simeq 1$ corresponds to the "crossover" point in the sense that the metastable (local) minimum and, hence, the *barrier* in $V(\overline{L})$ disappear as γ exceeds $\eta L^{(0)^3}/kT$, i.e., $P_{L^{(0)}} \gtrsim 1$, or equivalently, $L^{(0)} \gtrsim \overline{a}$. For smaller $\gamma(P_L^{(0)})$, there remains a local minimum at $\overline{L} \gtrsim L^{(0)}$ and a maximum at $\overline{L} = L * \simeq k_b^{(0)}/\gamma \phi a$. From our "particle" analog it follows that if at time $t = 0, \overline{L} \leq L^*$ it will relax to $L^{(0)}$, while if $\overline{L} \gtrsim L^*$ it will continue to increase with time. The equation of motion for $\overline{L} > L^*$ can be approximated as

$$\frac{dL}{dt} \simeq \phi a \gamma \overline{L}^{3}, \qquad (4.18)$$

having solution

$$\overline{L}(t) = \frac{\overline{L}(t=0)}{\left[1 - t/\tau(\dot{\gamma})\right]^{1/2}}$$
(4.18')

with

$$\tau(\dot{\gamma}) \simeq (\dot{\gamma}\phi a L^2)^{-1}. \tag{4.18"}$$

The mean length is thus seen to diverge after a time $\tau(\dot{\gamma})$ which depends on the shear rate as discussed in the Introduction, i.e., $\tau \simeq (\dot{\gamma}C)^{-1}$. This divergence of \overline{L} $(t \to \infty)$ at $\dot{\gamma} \simeq \dot{\gamma}_c$ $(P_{L^{(0)}} \simeq 1)$ for $C \gtrsim 1$, i.e., the fast-reaction limit, is shown by the dashed curve in Fig. 2.

If \overline{L} is of order $L^{(0)}$ initially, then we must overcome an energy barrier for the runaway process to start. We thus can think of the state $\overline{L} \cong L^{(0)}$ as *metastable*. In principle, the state $\overline{L} \simeq L^{(0)}$ could thus be destabilized by thermal fluctuations. The free energy $\Delta f(\overline{L})$ (per rod) cost of deviations of \overline{L} from $L^{(0)}$ in the metastable state can be estimated from the Flory-Huggins free energy [see discussion surrounding Eq. (2.13)]

$$\Delta f(\overline{L}) \simeq k_B T \left(\frac{\overline{L} - L^{(0)}}{L^{(0)}} \right)^2.$$

It follows that $\langle (\overline{L} - L^{(0)})^2 \rangle$ is of order $L^{(0)^2}$. Consequently, L^* must be of order of, say, $2L^{(0)}$ before the metastable state can decay via thermal excitations. The condition $L^* \simeq 2L^{(0)}$ once more coincides with $P_{L^{(0)}} \simeq 1$. More explicitly, $L^* \simeq k_b^{(0)}/\phi a \gamma$ from above, while $k_b^{(0)} \simeq \phi a k_c^{(0)}/L^{(0)^2}$ from Eq. (2.12). Accordingly, $L^* \simeq L^{(0)}$ if and only if $k_c^{(0)}/\gamma L^{(0)^3} \simeq 1$. However, from $k_c^{(0)} \simeq kT/\eta$, this latter condition is equivalent to $(kT/\eta L^{(0)^3})/\gamma \simeq 1$ or $D_r \simeq \gamma$. We thus conclude that for $P_{L^{(0)}} \simeq 1$, the metastable state $\overline{L} \simeq L^{(0)}$ will not decay unless exposed to a large perturbation.

Finally, for $P_{L^{(0)}} \gtrsim 1$, $V(\overline{L})$ has no minimum remaining (See the upper right Panel of Fig. 1). For any initial mean length, $\overline{L}(t)$ diverges after a time of order $\tau(\dot{\gamma})$. It is this regime with $C \gtrsim 1$ and $P_{L^{(0)}} \gtrsim 1$ which we identify with gelation. The growth is not activated in this part of the phase diagram.

Recalling our discussion of the analogy between the micellar distribution function and that of the percolation phase translation, it is clear that we are dealing here with a *first*order gelation transition rather than the expected continuous phase change. Moreover, the critical parameter controlling the transition is really the concentration $C \equiv \phi_I L^3$ rather than the shear rate. The first-order transition takes place for any nonzero shear rate at $C \simeq 1$. The shear rate simply controls the energy barrier which must be overcome. At low Peclet numbers the barrier is prohibitively large, thereby preventing gelation even though formally the system is only metastable. The threshold where the Peclet number $P_{I_{c}}(0) \gtrsim 1$ coincides with a vanishing of the energy barrier, i.e., to the approach of a "spinodal point."²⁰ By analogy with spinodal decomposition, we should expect that when we cross the $P_{L^{(0)}} \gtrsim 1$ threshold there will appear homogeneously throughout the sample a periodically modulated structure with alternating gel and solvent. The characteristic length scale of the gel will increase with time until eventually it will extend throughout the whole sample.

Finally, we remark that the critical value of γ is inversely proportional to both concentration ϕ and zero-flow size $L^{(0)}$. Actually, since in turn [see Eq. (2.12)]

$$L^{(0)} \sim \phi^{1/2}$$

we predict that

$$\dot{\gamma}_c \sim \phi^{-3/2}$$

While the micellar growth associated with $\dot{\gamma}$ exceeding $\dot{\gamma}_c$ has been shown to be modest (varying as $\dot{\gamma}^{1/3}$) in the *slow*-reaction limit, measurements^{3,21} of shear stresses and viscosity (η) magnify this effect since η is a strongly nonlinear function of rod length.¹¹ In the *fast*-reaction limit, on the other hand, the semidilute regime for concentration suggests that one should include interaction-induced corrections to

the dependence of D_r (and η) on rod length.¹¹ Clearly, much work remains to be done on the general problem of micellar size distributions in shear flow.

Physically, one can understand as follows the "steadystate" and "runaway" natures predicted for the slow- and fast-reaction limits, respectively. Consider first the "slow" regime where $\phi L^3 \ll 1$. Here—independent of Peclet number $P \equiv \gamma/D_r$ —the time between collisions (and hence between reaction, self-assembly, events) is long compared to the time required for the orientational distribution to take on the form characteristic of the imposed shear gradient. For large P, then, the rods are strongly aligned by the flow; in particular, the alignment becomes increasingly peaked along the flow direction for $P \gg 1$ and the average shear-induced collision rate grows only as $P^{1/3}$ [see Eqs. (3.18b) and (3.20b), with $k_c^{(0)} \simeq (kT/\eta)$]. In the "fast" regime, on the other hand, where collisions occur so fast that a uniform orientational distribution of rods is maintained, the combination rate is able to increase *linearly* with P even for $P \ge 1$. This strong feedback mechanism, i.e., increased rates leading to bigger rods (cross sections) and, hence, to accelerated reaction and bigger rods, etc., then results in the runaway instability predicted for micellar size as $\gamma \rightarrow \gamma_c$ with $\phi L^3 \simeq 1$.

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APPENDIX A: REACTION CROSS SECTION AND ORIENTATION-DEPENDENT RATE CONSTANT

1. Geometric cross section

Consider two rods with lengths L_1 and L_2 and orientations $\hat{\Omega}_1$ and $\hat{\Omega}_2$, respectively. Recall that the flow direction is \hat{z} , so that the projections of the rods onto the xy plane are $L_1 \sin \theta_1 \equiv l_1$ and $L_2 \sin \theta_2 \equiv l_2$, as shown in Fig. 3. The dashed parallelogram shows the region inside which the center of rod 2 must lie in order for the two rods to overlap ("collide", and "react"). Whenever the relative y coordinate is small enough, i.e., $0 < y < y^* (L_1, \hat{\Omega}_1, L_2, \hat{\Omega}_2)$, the differential cross section $d\sigma(L_1, \hat{\Omega}_1 | L_2, \hat{\Omega}_2)$ defined in Sec. III A 1 is given by x^*dy (see Fig. 3). For $y > y^*$, on the other hand, $d\sigma = x(y)dy$ with x(y) a linearly decreasing function of y. In the following we outline the determination of the constants y^* and x^* —for arbitrary L_1 , $\hat{\Omega}_1$, L_2 , and $\hat{\Omega}_2$ —and of the function x(y), thereby specifying completely the differential cross section $d\sigma$. (We note that the geometric con-



FIG. 3. Geometric construction showing the cross section between two rods of lengths L_1 and L_2 and orientations $\theta_1 \varphi_1$ and $\theta_2 \varphi_2$, respectively. $l_1 = L_1 \sin \theta_1$ and $l_2 = L_2 \sin \theta_2$ are the projections of the rods onto the plane (xy) normal to the flow directions (z) (\hat{z} points into the paper).

siderations here are closely related to those entering into the excluded volume calculations for "grafted rods."²²

First, we note by inspection of Fig. 3 that

$$y^* = \frac{l_1 \sin \varphi_1 - l_2 \sin \varphi_2}{2}.$$
 (A1)

For x(y), on the other hand, we need to consult Fig. 4 which shows the triangle *ABC* from Fig. 3. From the similarity of the triangles *ABC* and *A'B'C* we have immediately that $l_2 \sin \varphi_2 / x^* = [l_2 \sin \varphi_2 - (y - y^*)]/x$, a trivial rewriting of which gives

$$x(y) = x^* - \frac{x^*}{l_2 \sin \varphi_2} (y - y^*).$$
 (A2)

It now remains only to determine the constant x^* associated with $y = y^*$. For this purpose we again consult Fig. 4. Specifically, we express the base length $AB = x^*$ as a sum of the projections of the triangle sides AC and CB onto the base AB: $x^* = (l_2 \sin \varphi_2) \cot \varphi_1 + l_2 \cos(\pi - \varphi_2)$, a simple rearrangement of which leads to

$$x^* = l_2 \sin \varphi_2 \frac{\sin(\varphi_2 - \varphi_1)}{\sin \varphi_1 \sin \varphi_2}$$
 (A3)



FIG. 4. Enlargement of triangle *ABC* from Fig. 3, showing the relationship between $x(y > y^*)$ and $x^* \equiv x(y < y^*)$.

Equations (3.6)-(3.8) in the text follow immediately from the identification of x^* with $(d\sigma/dy)^*$ and $l_1 \sin \varphi_1$ and $l_2 \sin \varphi_2$ with $L_1 \sin \theta_1 \sin \varphi_1 = L_1 \hat{\Omega}_{1y} \rightarrow L \hat{\Omega}_y$ and $L_2 \sin \theta_2 \sin \varphi_2 = L_2 \hat{\Omega}_{2y} \rightarrow L' \hat{\Omega}'_y$, etc. Note that the aforementioned discussion pertained to y > 0, an identical development applying to y < 0.

2. Specific bimolecular rate constant

To obtain the orientation-dependent rate constant $k_c^{(s)}$ $(L,\widehat{\Omega}|L',\widehat{\Omega}')$ we need to multiply the differential cross section $d\sigma/dy$ by the relative velocity $\gamma|y|$ and integrate over all y. From the results of Appendix A 1 we have

$$\frac{1}{2}k_{c}^{(s)} = \dot{\gamma} \int_{0}^{y^{*}} dy \, yx^{*} + \dot{\gamma} \int_{y^{*}}^{y^{*} + l_{2} \sin \varphi_{2}} dy \, yx(y). \quad (A4)$$

Note that the factor of $\frac{1}{2}$ on the left-hand side arises from our including only the contributions from y > 0 on the right-hand side. Using Eqs. (A1)-(A3) for y^* , x(y), and x^* , the integrations in Eq. (A4) can be straightforwardly performed and the resulting expressions simplified to give Eq. (3.9).

APPENDIX B: AVERAGED RATE CONSTANTS

1. Small Peclet number

Here we evaluate, for the case of small Peclet number, the orientationally averaged bimolecular rate constant $k_c(L | L')$ defined by Eq. (2.8b). To do this we substitute Eq. (3.11) for $f_L(\hat{\Omega})$, valid in the $P \ll 1$ limit, and the general (all P) result Eq. (3.9) for $k_c^{(s)}(L, \hat{\Omega} | L', \hat{\Omega}')$.

The *P*-independent contributions to $k_c(L|L')$ come from the $1/4\pi$ terms in each of $f_L(\hat{\Omega})$ and $f'_L(\hat{\Omega}')$. Furthermore, since we shall only be concerned with L' = L, we have

$$k_{c}^{(s)}(L|L) = \int \frac{d\widehat{\Omega}}{4\pi} \int \frac{d\widehat{\Omega}'}{4\pi} k_{c}^{(s)}(L,\widehat{\Omega}|L,\widehat{\Omega}') + \vartheta(P)$$
(B1)

or, from Eq. (3.11),

$$k_{c}^{(S)}(L|L) = \alpha \dot{\gamma} L^{3} \int \frac{d\hat{\Omega}}{4\pi} \int \frac{d\hat{\Omega}'}{4\pi} \frac{\sin|\varphi - \varphi'|}{2\sin\varphi\sin\varphi'} \times \left(\Omega_{y}^{2}\Omega_{y}' + \frac{1}{3}\Omega_{y}'^{3}\right) + \vartheta(\dot{\gamma}L^{3}P),$$

$$\Omega_{y} > \Omega_{y}'. \qquad (B2)$$

Here we have used the fact that the averages over the $\Omega_{y} > \Omega'_{y}$ and $\Omega'_{y} > \Omega_{y}$ spaces are equal since one is transformed into the other upon exchanging primed and unprimed quanties in both the integrand and limits. The numerical constant c_{0} in Eq. (3.13) is given by the double integral in Eq. (B2) and is clearly of order unity.

Now, what about the $\vartheta(P)$ contributions to $k_c^{(S)}(L|L)$? Writing Eq. (3.9) as

$$k_{c}^{(S)}(L,\widehat{\Omega}|L,\widehat{\Omega}') = \alpha \gamma L^{3} F(\widehat{\Omega},\widehat{\Omega}')$$
(B3)

they can be expressed as [see. Eq. (3.11)]

$$\alpha \dot{\gamma} L^{3} \frac{P}{2} \int \frac{d\hat{\Omega}}{4\pi} \int \frac{d\hat{\Omega}'}{4\pi} F(\hat{\Omega}, \hat{\Omega}') (\Omega_{y} \Omega_{z} + \Omega_{y}' \Omega_{z}').$$
(B4)

However, from Eq. (3.9) we know that $F(\hat{\Omega}, \hat{\Omega}')$ is an even function with respect to $\theta = \pi/2$ and $\theta' = \pi/2$. The factors in parentheses are odd, however, from which it follows that the integrations in Eq. (B4) give zero identically. Similarly it can be shown that the $\theta(P^2)$ contributions from the cross term $\Omega_y \Omega_z \Omega'_y \Omega'_z$ vanish by symmetry.

It remains only to evaluate the $\vartheta(P^2)$ contributions to $k_c^{(S)}(L|L)$ from the $\vartheta(P^2)$ terms in each of the $f_L(\hat{\Omega})$'s. Again, as with the $\vartheta(P^0)$ terms, these are easily seen to be identical to one another, and we have

$$\frac{d\hat{\Omega}}{d\gamma L} {}^{3}P_{L}^{2} \int \frac{d\hat{\Omega}}{4\pi} \int \frac{d\hat{\Omega}'}{4\pi} \frac{\sin|\varphi - \varphi'|}{16\sin\varphi\sin\varphi'} \left(\Omega_{y}^{2}\Omega_{y}' + \frac{1}{3}\Omega_{y}'^{3}\right) \times \left[\Omega_{y}^{2}\Omega_{z}^{2} + \frac{1}{3}(\Omega_{y}^{2} - \Omega_{z}^{2}) - \frac{1}{15}\right], \quad \Omega_{y} > \Omega_{y}'. \tag{B5}$$

Thus, the numerical constant c_2 in Eq. (3.13) is given by the double integral in Eq. (B5) and is once more of order unity.

2. Large Peclet number

For $P \gg 1$ it is convenient to break up the double integration $\int d\hat{\Omega} \int d\hat{\Omega}'$ in Eq. (2.8b) into two parts according to

$$k_{c}^{(S)}(L|L) = \alpha \dot{\gamma} L^{3} \int d\hat{\Omega} \int d\hat{\Omega}' \{F(\hat{\Omega}, \hat{\Omega}') \\ \times f_{L}(\hat{\Omega}) f_{L}(\hat{\Omega}')\} \quad (\hat{\Omega}, \hat{\Omega}' \text{ near } \hat{z}) \\ + \alpha \dot{\gamma} L^{3} \int d\hat{\Omega} \int d\hat{\Omega}' \{\cdots\} \quad (\hat{\Omega}, \hat{\Omega}' \neq \hat{z}).$$
(B6)

Consider first the $\widehat{\Omega}, \widehat{\Omega}' \approx \hat{z}$ contribution. Since the distributions over φ and φ' are very broad, the averages over these angles are of order unity. It follows that the first term in Eq. (B6) can be written as [see Eq. (3.9)]

$$\alpha \gamma L^{3}(\langle \Omega_{\nu}^{2} \rangle \langle \Omega_{\nu}^{\prime} \rangle + \frac{1}{3} \langle \Omega_{\nu}^{\prime 3} \rangle),$$

where the angular brackets are given by Eq. (3.15c). More explicitly, using $\langle \Omega_y^2 \rangle \simeq P^{-2/3}$, $\langle \Omega_y \rangle \simeq P^{-1/3}$, and $\langle \Omega_y^3 \rangle \simeq P^{-1}$ for $P \ge 1$, the aforementioned expression becomes $\alpha \gamma L^3 (dP^{-1})$ where all numerical factors of order unity have been lumped into the constant "d" appearing in Eq. (3.18).

Now consider the second contribution to Eq. (B6), involving the orientational distributions *away* from the flow direction. Here we use Eq. (3.17a) for $f_L(\hat{\Omega})$ and find immediately that the second term in Eq. (B6) can be written as [see, again Eq. (3.9)]

$$\alpha \dot{\gamma} L^{3} \left(\frac{1}{P_{L}^{1/3}}\right)^{2} \int d\widehat{\Omega} \int d\widehat{\Omega}' \frac{\sin|\varphi - \varphi'|}{2\sin\varphi\sin\varphi'} (\Omega_{y}^{2}\Omega_{y}' + \frac{1}{3}\Omega_{y}'^{3}).$$

The double integral over $\widehat{\Omega}$ and $\widehat{\Omega}'$ is clearly of order unity and corresponds precisely to the constant "e" introduced in Eq. (3.18).

APPENDIX C: SHEAR-INDUCED TENSION AND DEFORMATION ENERGY

In Fig. 5 we show the bead model for a rigid rod of length L and diameter b. Drag (viscous) forces will act at all points were the velocity of the solvent is different from that

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FIG. 5. Bead model for rod of length L and diameter b. $\mathbf{r}_n \equiv nb\hat{u}$ denotes the vector from the rod center of mass to the *n*th bead: $-L/2b \le n \le +L/2b$.

of the rod bead at the same point. Let v denote the relative velocity. Since the center bead (rod center of mass) moves with the solvent (i.e., v = 0 there), we can write

$$\mathbf{v} = \boldsymbol{\gamma} \cdot \mathbf{r} \tag{C1}$$

for the relative velocity at an arbitrary bead. Here r is the bead's position relative to the center of mass, and

$$\dot{\gamma} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \dot{\gamma} & 0 \end{pmatrix}$$
(C2)

is the velocity gradient tensor characterizing the homogeneous shear flow of the solvent. For the drag force on the bead at \mathbf{r} we then have

$$\mathbf{F} = \zeta \mathbf{v},\tag{C3}$$

where ζ is the friction coefficient associated with each bead.

To compute the tension in the rod at an arbitrary position, we need only determine the projection of the drag force there along the rod axis, i.e., $\mathbf{F} \cdot \hat{\mathbf{u}}$. For the *n*th bead, $-L/2b \le n \le +L/2b$,

$$\mathbf{r}_{n} = \begin{pmatrix} nb\sin\theta\cos\varphi\\ nb\sin\theta\sin\varphi\\ nb\cos\theta \end{pmatrix}.$$
 (C4)

It follows from Eqs. (C1)-(C3) that

$$F_{\parallel}(n) = \mathbf{F} \cdot \hat{\mathbf{u}} = \zeta \gamma n b \sin \theta \cos \theta \sin \varphi.$$
(C5)

Integrating this force from the *n*th bead out to the corresponding end of the rod then gives the total force or tension, at the position s = nb of the *n*th bead:

$$t(s) = \int_{n}^{L/2b} dn F_{\parallel}(n) = \frac{\gamma \zeta}{2b} \Omega_{y} \Omega_{z} \left[\left(\frac{L}{2} \right)^{2} - s^{2} \right].$$
(C6)

Here we have replaced $\sin \theta \sin \varphi \cos \theta$ by $\Omega_{\nu} \Omega_{z}$.

Finally, to calculate the local deformation at $L'(0 \le L' \le L)$ in a rod of length L we simply evaluate t(s) at s = L' - (L/2) and write the deformation at s as $\delta(s) = t(s)/\kappa$, where κ is the elastic constant characterizing

the extension-compression of the rod. Then the deformation energy $E_{def}(L,L')$ at s is given by

$$E_{def}(L,L') = \frac{1}{2} \kappa [\delta(s = L' - (L/2))]^2$$

= $\frac{\dot{\gamma}^2 \zeta^2}{8\kappa b^2} L'^2 (L' - L)^2 \Omega_y^2 \Omega_z^2$ (C7)

as in Eq. (3.21).

APPENDIX D: FORM OF SIZE DISTRIBUTION

Iterating Eq. (2.15), starting at $L = 2^{\circ} = 1$ and proceeding through powers of 2 up to $L = 2^{n}$, leads to

$$N(L) = [N(1)]^{L}g\left(\frac{L}{2}\right)g^{2}\left(\frac{L}{4}\right)\cdots g^{L/2}(1)$$
 (D1)

or

$$N(L) = \exp\left\{L\ln[N(1)] + \sum_{p=0}^{n-1} 2^p \ln\left[g\left(\frac{L}{2^{p+1}}\right)\right]\right\}.$$
(D2)

Denote the sum over p by I, and approximate it by an integral over p from 0 to n - 1. With the change of variable $x \equiv L/2^{p+1}$, we have

$$I = \frac{L}{2 \ln 2} \int_{1}^{L/2} dx \, \frac{1}{x^2} \ln g(x).$$

This integral over x can, in turn, be written as

$$\int_{1}^{\infty} dx f(x) - \int_{L/2}^{\infty} dx f(x) \equiv J - K,$$

where $f(x) = \ln g(x)/x^2$. Note that J is independent of L. To evaluate K and, in particular, to determine its L dependence, we integrate by parts and find

$$\int_{L/2}^{\infty} dx \, \frac{\ln g(x)}{x^2} = \frac{2}{L} \left[\ln g\left(\frac{L}{2}\right) + n \right] \simeq \frac{2}{L} \ln g\left(\frac{L}{2}\right).$$

In writing the last steps above we have used the fact that $g(x) \sim x^n$ (with $n \leq 3$) and taken the limit of large L. Substituting into Eq. (D2) leads directly to Eqs. (2.16) and (2.17).

APPENDIX E: KINETIC EQUATIONS FOR \overline{L}

For all of the analysis we shall find it useful to approximate integrals of the form

$$Q_x = \int_{\bar{a}}^{\infty} dL \frac{1}{L^x} e^{-L/\bar{L}}$$

and

$$R_x = \int_{\bar{a}}^{\infty} dL L^x e^{-L/\bar{L}}$$

for x > 0 and specifically for $\overline{L} \gg \overline{a}$.

Starting first with Q_x , we change variable from L to $y \equiv L/\overline{L}$, pull out a factor of \overline{L}^{1-x} , and break up the integral over y into

$$\int_{\epsilon}^{\infty} dy \frac{e^{-y}}{y^{x}} = \int_{\epsilon}^{1} + \int_{1}^{\infty} \equiv J_{1} + J_{2}.$$

Here $\epsilon \equiv \overline{a}/\overline{L} \ll 1$, from which it follows, upon expanding e^{-y} in J, and integrating term by term, that

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$$J_{1} = \left(\frac{1}{1-x} + \frac{1}{x-2} + \frac{1}{2(3-x)}\right) + \frac{1}{x-1}e^{1-x}$$
$$+ \frac{1}{2-x}e^{2-x} + \frac{1}{2(x-3)}e^{3-x} + \cdots$$

As for J_2 , we note from y > 1 and x > 0 that

$$J_2 < \int_1^\infty dy e^{-y} = \frac{1}{e} \, .$$

That is, $J_2 = \vartheta(1)$, just like the $\{\cdots\}$ term in J_1 . We now need only consider two cases; 0 < x < 1 and x > 1.

For 0 < x < 1, all of the powers of ϵ ($\ll 1$) in J_1 are positive and J_1 is thus dominated by the ϵ -independent term, $\{\cdots\}$. This term is, in turn, as we have just noted, comparable in magnitude, $\vartheta(1)$, to J_2 . Thus, recalling that $Q_x = \overline{L}^{1-x}(J_1 + J_2)$, we have

$$\int_{\bar{a}}^{\infty} dL \frac{1}{L^{x}} e^{-L/\bar{L}} \equiv Q_{x} \simeq \bar{L}^{1-x}, \quad 0 < x < 1,$$

where \simeq denotes here and henceforth that we have dropped multiplicative factors of order unity [in this case, (1/(x-1)) + (1/e)].

When x > 1, on the other hand, the dominant term in J_1 is $(1/(x-1))\epsilon^{1-x} \ge 1$, and we have

$$\int_{\bar{a}}^{\infty} dL \frac{1}{L^{x}} e^{-L/\bar{L}} \approx \frac{1}{x-1} \frac{1}{\bar{a}^{x-1}} \approx \frac{1}{\bar{a}^{x-1}}, \quad x > 1.$$

To evaluate the R_x integrals, we consider first the case 0 < x < 1 and integrate by parts. The boundary term gives $\overline{L}\overline{a}^x$, where we have specifically used the fact that $e^{-\overline{a}/\overline{L}} \approx 1$. The " $-\int v du$ " contribution is of the form $x\overline{L}$ times a $Q_{x'}$ integral, with 0 < x' < 1, thereby giving $x\overline{LL}^{1-x'}$. Thus, since x' = 1 - x,

$$\int_{\bar{a}}^{\infty} dL L^{x} e^{-L/L} \approx x \overline{L}^{1+x} \simeq \overline{L}^{1+x}, \quad 0 < x < 1.$$

For 1 < x < 2, we again proceed to evaluate R_x by integrating by parts, again finding $\overline{L}\overline{a}^x$ for the boundary term. Now the " $-\int v du$ " term is $x\overline{L}R_{x-1}$ $\approx x(x-1)\overline{L}^{1+x} \gg \overline{L}\overline{a}^x$. Thus,

$$\int_{\overline{a}}^{\infty} dL L^{x} e^{-L/\overline{L}} \approx x(x-1)\overline{L}^{1+x} \simeq \overline{L}^{1+x}, \quad 1 < x < 2.$$

Similarly, we find

$$\int_{\bar{a}}^{\infty} dLL^{x} e^{-L/\bar{L}}$$

$$\approx x(x-1)(x-2)\overline{L}^{1+x}\overline{L}^{1+x} \simeq \overline{L}^{1+x}, \quad 2 < x < 3$$

and so on.

The next step is to evaluate the constant of proportionality in

$$N_L \sim \frac{1}{g(L)^{1/\ln 2}} e^{-L/L}$$

for the slow- and fast-reaction limits, in the regimes of weak and strong flow. We shall also derive, in each case, the appropriate relationship between \overline{L} and the moments

$$\langle L^n \rangle \equiv \int dL L^n N_L / \int dL N_L$$

and, hence, between dL/dt and the moments of $\partial N_L/\partial t$ — with the latter quantity being determined from the kinetic equation (2.9), as shown later in this Appendix.

In all cases, the constant C in

$$N_L \simeq \frac{C}{g(L)^{1/\ln 2}} e^{-L/\overline{L}},$$

with

$$g(L) \sim \begin{cases} 1 & P \leqslant 1 & \text{slow and fast} \\ L & P \gg 1 & \text{slow} \\ L^3 & P \gg 1 & \text{fast} \end{cases}$$

is determined from the mass conservation condition

$$\frac{C}{a}\int_{\overline{a}}^{\infty}dLL\,\frac{1}{g(L)^{1/\ln 2}}\,e^{-L/\overline{L}}=\phi.$$
(E1)

Consider first the $P \leq 1$ case, where $g(L) \sim 1$. The integral in Eq. (E1) is then simply $R_1 \simeq \overline{L}^2$, implying $C \simeq \phi a/\overline{L}^2$ and, hence, Eq. (4.2a) for N_L . For the $P \geq 1$ slow reaction case, on the other hand, this integral equals Q_x with $x = (1/\ln 2) - 1$ between 0 and 1, i.e., $Q_x \simeq \overline{L}^{2-(1/\ln 2)}$. Thus $C \simeq \phi a \overline{L}^{(1/\ln 2)-2}$ and, hence, Eq. (4.2b) for N_L . Finally, for the $P \geq 1$ fast reaction limit, Eq. (E1) becomes $(C/\overline{a})Q_x$ with $x = (3/\ln 2) - 1$ between 3 and 4. Thus $C \simeq \phi a \overline{a}^{x-1} = \phi a \overline{a}^{(3/\ln 2)-2}$, from which follows Eq. (4.2c) for N_L .

Now we evaluate the first moment of the N_L distribution, defined by

$$\langle L \rangle = \int dL L N_L \left/ \int dL N_L \equiv \frac{NUM}{DEN} \right.$$

Note that $NUM = \phi a$ from the mass conservation condition. For $P \leq 1$, N_L is given by Eq. (4.2a) and, hence, $DEN = \phi a/\overline{L}$, thereby implying, see Eq. (4.4) in the text,

$$\langle L \rangle = \overline{L}$$
 for $P \ll 1$.

In the $P \ge 1$, slow-reaction limit, using Eq. (4.2b) for N_L , we find

$$DEN = \phi a \overline{L} (1/\ln 2) - {}^{2}Q_{1/\ln 2}$$

and, hence, see Eq. (4.4'),

$$\langle L \rangle = \bar{a}^{(1/\ln 2) - 1} \overline{L}^{2 - (1/\ln 2)}, \quad P \gg 1 \text{ (slow)}.$$

Finally, for $P \gg 1$ in the *fast* reaction case, Eq. (4.2c) for N_L leads to

$$DEN = \phi a \overline{a}^{(3/\ln 2) - 2} Q_{3/\ln 2} \simeq \phi a/\overline{a},$$

implying

$$\langle L \rangle \simeq \overline{a}, P \gg 1$$
 (fast)

independent of \overline{L} .

We need to consider, then, the next higher moment in this $(P \gg 1, \text{ fast})$ limit. For

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$$\langle L^2 \rangle = \int dL L^2 N_L \left/ \int dL N_L \right.$$

the *DEN* is still $\phi a/\overline{a}$, but now

$$NUM \simeq \phi a \overline{a}^{(3/\ln 2) - 2} Q_{(3/\ln 2) - 2} \simeq \phi a \overline{a}$$

and, hence,

 $\langle L^2 \rangle = \overline{a}^2$,

still independent of L. Similarly, we find for the next moment that $NUM \simeq \phi a \overline{a}^2$ and

 $\langle L^3 \rangle = \bar{a}^3.$

For the *fourth* moment, however,

 $NUM \simeq \phi a \bar{a}^{(3/\ln 2) - 2} Q_{(3/\ln 2) - 4}$.

Since Q_x here involves 0 < x < 1, it is no longer independent of \overline{L} : $Q_x \simeq \overline{L}^{5-(3/\ln 2)}$ and [see Eq. (4.13)]

$$\langle L^4 \rangle \simeq \overline{a}^{(3/\ln 2) - 1} \overline{L}^{5 - (3/\ln 2)}, \quad P \gg 1 \quad (\text{fast}).$$

It remains only to derive relations for $d\overline{L}/dt$ in terms of $\partial N_L/\partial t$. For the $P \ll 1$ case, where $\langle L \rangle = \overline{L}$, we have directly that

$$\begin{split} \frac{d\overline{L}}{dt} &= \frac{d}{dt} \left(\int dL L N_L \left/ \int dL N_L \right) = \frac{d}{dt} \left(\phi a \left/ \int dL N_L \right) \right) \\ &= - \left[\phi a \left/ \left(\int dL N_L \right)^2 \right] \int dL \frac{\partial}{\partial t} N_L \\ &= - \frac{\overline{L}^2}{\phi a} \int dL \frac{\partial}{\partial t} N_L, \end{split}$$

as in Eq. (4.5). The last equality immediately follows from $\int dL N_L = \phi a / \overline{L}$ in the $P \ll 1$ limit.

For the $P \ge 1$, slow-reaction regime, we consider

$$\langle L \rangle = \phi a \left/ \int dL N_L \simeq \overline{a}^{(1/\ln 2) - 1} \overline{L}^{2 - (1/\ln 2)} \right.$$

or, equivalently,

$$\overline{L}^{(1/\ln 2)-2} \simeq \frac{\overline{a}^{(1/\ln 2)-1}}{\phi a} \int dL N_L.$$

Note that the power of \overline{L} on the left-hand side is *negative* (and of order unity), implying that when we differentiate both sides with respect to t we pick up a minus sign upon dropping all numerical factors $\vartheta(1)$:

$$\frac{d\overline{L}}{dt} \simeq -\frac{(\overline{a}/\overline{L})^{(1/\ln 2) - 1}}{\phi a} \overline{L}^2 \int dL \frac{\partial N_L}{\partial t}$$

as in Eq. (4.5').

Finally, for the $P \ge 1$ fast-reaction limit, we have from

$$\langle L^4 \rangle = \int dL L^4 N_L / \phi a / \overline{a} \simeq \overline{a}^{(3/\ln 2) - 1} \overline{L}^{5 - (3/\ln 2)}$$

that

$$\overline{L}^{5-(3/\ln 2)} \simeq \frac{\overline{a}^{2-(3/\ln 2)}}{\phi a} \int dL L^4 N_L$$

and, hence, that (note that the power of \overline{L} is positive)

$$\frac{d\overline{L}}{dt} \simeq \frac{(\overline{a}/\overline{L})^{2-(3/\ln 2)}}{\phi a} \frac{1}{\overline{L}^{2}} \int dL L^{4} \frac{\partial N_{L}}{\partial t},$$

as in Eq. (4.14).

Finally, we use the expressions derived earlier, relating $d\overline{L}/dt$ and $\partial N_L/\partial t$, along with the kinetic equation (2.9) for $\partial N_L/\partial t$, to derive ordinary differential equations for \overline{L} in each of the flow and concentration regimes of interest.

First, for $P \leq 1$ ($\overline{L} \leq \overline{a}$), we substitute for N_L , $k_b(L/L')$, and $k_c(L/L')$ from Eqs. (4.2a), (4.6a), and (4.6b) and approximate the integral on the right-hand side of Eq. (4.5) by introducing each term in Eq. (2.9) for $\partial N_L/\partial t$. From the first term, for example, we have

$$-\frac{\overline{L}^{2}}{\phi a}\int dL \left(\frac{\partial N_{L}}{\partial t}\right)_{1\text{st}}$$
$$= -\frac{\overline{L}^{2}}{\phi a}\int dL (-N_{L}Lk_{b}^{(0)}) = +k_{b}^{(0)}\overline{L}^{2},$$

where we have used $\int dL N_L L = \phi a$ from the mass conservation condition or, equivalently,

$$\int dL N_L L = \frac{\phi a}{\overline{L}^2} \int dL L e^{-L/\overline{L}} = \frac{\phi a}{\overline{L}^2} R_1 \simeq \phi a.$$

From the second term in $(\partial N_L / \partial t)$ we find the contribution

$$-\frac{\overline{L}^2}{\phi a}\int dL \left[2k_b^{(0)}\int_L^\infty dL' N_{L'}\right] = -2k_b^{(0)}\overline{L}^2,$$

where we have integrated by parts, using the fact that

$$\frac{d}{dL}\int_L^\infty dL' N_{L'} = -N_L.$$

Thus, the first two terms in $(\partial N_L/\partial t)$ give a combined contribution of $-k_b^{(0)}\overline{L}^2$ to $d\overline{L}/dt$. From the third term we have

$$k_{c}^{(0)} \frac{\overline{L}^{2}}{\phi a} \int dL N_{L} \int dL' N_{L'} \left(1 + \frac{1}{\overline{a}^{3}} \begin{cases} L^{2}L' \\ L'^{2}L \end{cases} \right)$$
$$\simeq \phi a k_{c}^{(0)} \left[1 + \left(\frac{\overline{L}}{\overline{a}} \right)^{3} \right],$$

the last line following from $\int dLL^n e^{-L/\overline{L}} \simeq \overline{L}^{n+1}$ for $n \ge 1$. Finally, from the fourth term in $(\partial N_L/\partial t)$ we obtain

$$-k_{c}^{(0)}\frac{\overline{L}^{2}}{\phi a}\int dL \int_{0}^{L/2} dL' N_{L'} N_{L-L'} \left(1 + \frac{1}{\overline{a}^{3}} \begin{pmatrix} L^{2}L' \\ L'^{2}L \end{pmatrix}\right)$$
$$\simeq -\frac{\phi a}{2} k_{c}^{(0)} \left[1 + \left(\frac{\overline{L}}{\overline{a}}\right)^{3}\right].$$

Thus, combining these last two terms with the $-k_b^{(0)}\overline{L}^2$, we find the result for $d\overline{L}/dt$ written in Eq. (4.7).

For the $P \ge 1$ slow-reaction case, evaluation of the four contributions from Eq. (2.9) to $\int dL(\partial N_L/\partial t)$ proceeds largely as shown earlier, except that we need to use the R_x and Q_x approximants with the x nonintegral. Moreover, in the contribution from the fourth term of Eq. (2.9), we now have integrals arising of the form

$$\int_0^{L/2} dL' \frac{1}{L'^{(1/\ln 2)}} \frac{1}{(L-L')^{(1/\ln 2)}}$$

which we approximate by

$$\frac{1}{L^{(1/\ln 2)}} \int_{\bar{a}}^{L/2} dL' \frac{1}{L'^{(1/\ln 2)}} \simeq L'^{1-(1/\ln 2)} |\frac{L'^2}{\bar{a}}/L^{(1/\ln 2)}$$

since (L - L') varies only from L/2 to L over the range $\overline{a} < L' < L/2$, and we drop all numerical factors of order unity. From the first two terms we find

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$$-k_{b}^{(0)}\overline{a}^{2}\left(\frac{\overline{L}}{\overline{a}}\right)^{3-(1/\ln 2)}$$

which we write as $-k_b^{(0)}\overline{L}^2$ in Eq. (4.8), since $3 - (1/\ln 2) \simeq 1.6$. The third and fourth contributions add up to $+k_c^{(0)}\phi a(\overline{L}/\overline{a})$.

Finally, for the $P \ge 1$ fast-reaction case, essentially identical considerations apply and we obtain the kinetic equation for $d\overline{L}/dt$ given by Eq. (4.16). (Here the integral powers of \overline{L} are found without any need to round off irrational ones.)

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