Flow-induced phase transitions in rod-like micelles

Flow-induced phase transitions in rod-like micelles

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Abstract. We study the dynamics of self-assembling rod-like micelles under both shear and elongational flow. We assume a simple reaction scheme in which two micelles can fuse only if they are collinear. This results in a positive feedback mechanism between micellar alignment and growth. We define τ_{break} as the reaction time for a typical micelle and τ_{rot} as its rotational diffusion time. We consider both the limiting case of $\tau_{break} \ll \tau_{rot}$ and that of $\tau_{break} \gg \tau_{rot}$. By matching these limiting results we are able to make some predictions for the general case. In elongational flow we predict a gelation transition, at some critical flow rate, to a phase of extremely long rods which are fully aligned with the flow axis. It is shown that these rods can be of a length which is very much greater than the mean micellar length in the absence of flow but which is still stable with respect to the tension produced in a flow. We find that the analogous transition in shear flow is absent although the mean micellar size near the flow axis is still expected to increase sharply at high flow rates. We briefly discuss the relevance of our calculations to experiments on shear-induced structures in micellar systems.

1. Introduction

It is known that certain surfactant molecules can, under the correct conditions, self assemble reversibly to form large one- or two-dimensional (2D) structures in solution [1]. The one-dimensional aggregates are polymer-like or rod-like micelles (depending on stiffness) whilst the 2D case represents a bilayer. In either case the structures formed can be extremely large: in the case of polymer-like aggregates linear dimensions of several thousand ångstroms can be obtained. Experimental work on these self-assembling systems has shown that the structures have a highly non-linear response in imposed flow fields which is a consequence of the large size and transient character of the aggregates. In this paper we will restrict our attention to the behaviour of stiff, rod-like micelles which occur in, for example, aqueous TTAS (tetradecyl trimethyl ammonium salicylate). Such micelles are known to be extremely stiff in the absence of added salt where a typical rod length might be 300 Å [2, 3] whereas the electostatic persistence length [4] is of order 3000 Å or more. In the presence of some added salt one can expect the micelles to be semi-flexible although it remains a sensible starting point to treat the rods as completely stiff. Thus we assume a simple reaction scheme in which two micelles can fuse only if they are collinear, this implies, by detailed balance, that the reverse reaction proceeds by a single rod breaking to produce two collinear daughter chains.

Recent experimental work [2, 3] on aqueous TTAS, and other systems close to the overlap threshold of the micelles, has concentrated on measuring the birefringence

and viscosity as a function of shear flow rate. A steep rise in both of these properties is observed near a critical shear rate. The purpose of the present work is to develop a theoretical model of this, and related phenomena, in both elongational and shear flow geometries. For simplicity we ignore any interaction between micelles other than the process of reversible scission and fusion. In practice [5] Coulomb interactions may play an essential role in understanding the flow-induced transition of micellar systems, which often arise at lower flow rates than those predicted by the simple theories outlined later. We hope to address this issue in future work.

A preliminary account of some of our results has appeared in [6]; a simplified treatment based on a 2D model was reported in [7]. Later we give a full account of our new results for 3D flows in the limits of both fast and slow scission reactions. In elongational flow we establish the possibility of a second-order phase transition to a phase of fully aligned extremely long rods. The mechanism for this transition can be explained thus: as the flow is turned on the rods align in the flow and become longer due to the increased amount of material in the preferred direction. The longer rods have a reduced angular mobility (the angular mobility being a strongly decreasing function of the length) and are thus more strongly convected in the flow. At a certain, critical flow rate this feedback mechanism becomes catastrophic and we postulate that 'infinite' rods are formed (see figure 1). In practice the length of these rods is limited by hydrodynamic tensile forces arising from the elongational flow field [8–11]. It would not be suprising in practice if the aligned rod or 'gel' phase in our model developed hexagonal or other long-range order. However this effect cannot be treated without explicitly including steric interactions between rods.
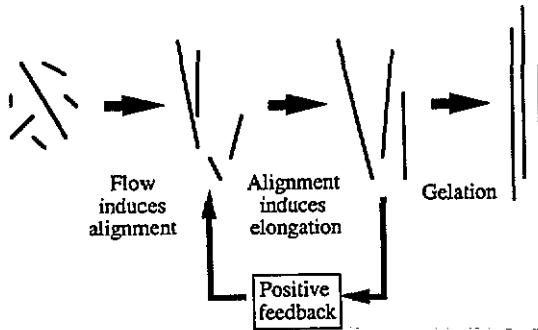

Figure 1. Diagram showing the effect of elongational flow on self-assembled rods.

Our work is based on a set of coupled non-linear integro-differential equations that couple the convection and diffusion of rods to explicit kinetic equations for their scission and recombination. Two basic regimes can be distinguished, that of fast breaking (where scission kinetics are rapid on the timescale of rotation) and the opposite limit of slow breaking.

We shall, in section 2, present in detail a model that should apply for the fast breaking limit. This is solved in section 3 for the case of elongational flow which is analytically tractable [6]. The case of shear flow is, however, more involved and in section 4 we employ a new scaling analysis for the fast reaction limit (which allows a prediction of whether or not there exists a flow-induced phase transition in *any* flow geometry). This method predicts that there is not a true flow-induced phase transition in full 3D shear flow although there is still a strong feedback between

alignment and growth. Mathematically, the 3D shear case is on the margin of the parameter region where a flow-induced transition to aligned long rods can arise. It may be that interaction terms, here ignored, could produce such a transition in practice. This scaling analysis is explained fully in section 4 where it is also applied to the case of elongational flow and is found to agree with the analytic result derived earlier.

In section 5 we study in some detail the opposite limit of slow breaking, focusing on elongational flow, and discover a flow-induced transition that is basically similar in character to the one predicted already for the fast breaking regime. We give our conclusions, and a brief discussion of relevant experimental data in section 6.

As mentioned earlier, in this paper we do not consider any rod–rod interactions which may lead to spatial ordering, such as hexagonal phases. We do include some dynamic effects of steric interactions between rods, but only in a simplified way through the form chosen for the rotational diffusion constant. We expect this treatment of entanglements to give qualitative results in all regimes of concentration, the approximation becoming more reliable in the dilute regime where the exact form of the diffusion constant is known [12]. The rotational diffusive behaviour of entangled micellar rods has been discussed in detail recently [13] but only in the linear response regime whereas the collective non-linear behaviour at strong alignments is of relevance here. This is complicated because the degree of entanglement is a strong function of alignment [12]; we suppress this dependence, for simplicity, in the present work.

Recently Wang and co-workers [8–10] have studied the behaviour of a similar rod-like micellar system in elongational flow by incorporating a Kramers-type hydrodynamic potential [14] into the Gibbs distribution. For shear flows in two dimensions Wang has developed [9] an analogous approximation which involves decoupling the angle-dependent size distribution of rods. This approach is questionable in several respects. It must fail in the fast breaking regime ($\tau_{\text{rot}} \gtrsim \tau_{\text{break}}$), i.e. when the flow effects and reaction kinetics cannot, even approximately, be decoupled. This is the main regime of interest in the present work. We also expect that, close enough to any flow-induced transition, involving extremely long rods, the longest rods present must undergo scission/combination reactions on a time scale fast compared with their rotational relaxation. (This is because the scission time of a rod of length L varies as $1/L$ whereas $\tau_{\text{rot}} \sim L^3$.) Hence the decoupling model of Gelbart *et al* [8–10] is unsuitable to study critical effects.

2. Model for fast reactions regime

2.1. Assumptions

We take as our microscopic reaction scheme a (forward) scission reaction and a (reverse) recombination reaction between collinear rods defined as follows [15]:

(i) Scission reactions occur randomly at any position along the length of the rod with a probability k per unit length per unit time, where k is a rate constant.

(ii) The recombination reaction proceeds with a rate which is proportional to both the product of the concentrations of the reacting species and to a second rate constant k'.

We define τ_{break} to be the reaction time for an average micelle [15],

$$\tau_{\text{break}} = 1/k\lambda_0 \tag{1}$$

where λ_0 is the mean micellar length in the absence of flow. Strictly speaking τ_{break} is the mean time for an average micelle to break once at any point along its length. However this must be of the same order as the average recombination time (by detailed balance). Hence only one time constant is needed to characterize the reaction scheme.

We also define τ_{rot} as the diffusive rotation time of an average micelle, given by the inverse of its angular diffusion constant. It is known that, for dilute slender rods of length L, the angular diffusion constant, $D(L)$ is given by [12],

$$D(L) = \frac{3k_{\text{B}}T\ln(L/b - \gamma)}{\pi\eta_s L^3} \qquad \text{(rigorous form)} \tag{2}$$

with b the diameter of the rod, η_s the solvent viscosity and $\gamma \approx 0.8$ (or very weakly a function of L/b). In contrast, for entangled slender rods at volume fraction ϕ, the behaviour is roughly [12] $D(L) \sim \phi^{-2}L^{-7}$. This is subject to a non-linear correction at strong alignment of the rods which we ignore in the present work. It is also subject to corrections at very short times, $t \lesssim \tau_{\text{entanglement}}$, for which unentangled motion is recovered. In studying the entangled regime we assume $\tau_{\text{break}} \gg \tau_{\text{entanglement}}$ which allows us to ignore this correction [13]. From now on we will, for simplicity, approximate $D(L)$ as an inverse power of L in all concentration regimes:

$$D(L) = D_0/L^\zeta \qquad \text{(approximate form)} \tag{3}$$

where D_0 and ζ are constants. Given that the properties of the system do not depend critically on the precise value of ζ (which, as we shall see later, is the case for $\zeta \geqslant 3$) then we expect any results derived using (3) to remain qualitatively accurate whatever the precise functional form of $D(L)$. To avoid having too many different regimes, we will restrict attention to $\zeta > 2$, which is always justified on physical grounds. We may therefore define

$$\tau_{\text{rot}} = D(\lambda_0)^{-1} = \lambda_0^\zeta/D_0. \tag{4}$$

The regime which we consider here, and throughout sections 3 and 4, is $\tau_{\text{break}} \ll \tau_{\text{rot}}$. This inequality expresses the condition that inter-rod reactions occur many times before a typical rod has had time to significantly rotate. We shall denote this the 'fast reactions' regime. It is clear, however, that the assumption of fast reactions compared with rotation must always fail for short enough rods, $L \lesssim l$, with

$$l = (D_0\tau_{\text{break}})^{1/\zeta}. \tag{5}$$

We expect the 'fast reactions' approximation to be accurate when $l \ll \lambda_0$. Although we do not necessarily expect such an inequality to hold in a very dilute solution of rods it can presumably occur in the entangled case, when inter-rod collisions are frequent, and the angular mobility is greatly reduced [12].

We now make a further assumption that reactions are uncorrelated; this implies that when any rod breaks the two daughter rods are no more likely to recombine

at a later time with each other than with any other rods. Although this mean-field approach will fail for extremely long rods, when there are very few similar rods with which to react, we expect to obtain qualitatively accurate results throughout. As justification for this statement we observe that as the mean-field approximation breaks down a certain proportion of reactions can be described as 'true' reactions (in the sense of our mean-field approach) and the remaining ones are 'null' reactions which effectively do nothing, such as one rod breaking and then recombining with itself. The presence of these 'null' reactions will, in effect, modify the reaction time, τ_{break}, but provided that we still remain in the fast reaction regime, we expect the overall behaviour to be qualitatively similar.

Note finally that we allow only collinear rods to react. This is the only scheme consistent with our requirement of completely stiff rods. It is equivalent to assuming an infinite bending energy for rods which not only implies completely stiff rods but also forbids the transient 'kinks' which would occur in any reaction between non-collinear rods. The dynamics of semi-flexible elongated micelles are more complex because of the coupling that exists between reactions and rotation. Reactions between non-collinear micelles must in some sense redistribute material between angles. However, since we consider the stiff rod limit here, this coupling is absent.

2.2. Equations of motion

We now define $\psi(L, u)$ as the concentration of rods of length L with director parallel to the unit vector u. In any system where the rods are allowed to explore three dimensions the unit vector u will span the surface of a unit hemisphere. (The unit hemisphere is appropriate since rods with directors u and $-u$ are indistinguishable.)

Given the microscopic reaction scheme and the further assumptions set out earlier, it is now possible to write down an evolution equation describing the rate of change of $\psi(L, u)$ per unit time [15] under the influence of reactions alone:

$$\dot{\psi}(L, u) = -kL\psi(L, u) + 2k \int_L^\infty \psi(L', u) \, dL'$$

$$+ \frac{k'}{2} \int_0^L \psi(L', u)\psi(L - L', u) \, dL' - k'\psi(L, u) \int_0^\infty \psi(L', u) \, dL' \tag{6}$$

where the first term corresponds to a rod of length L breaking to form two shorter rods, the second term represents a longer rod breaking to produce a rod of length L (plus another piece), the third term represents two shorter rods combining to form a rod of length L and the fourth term represents a rod of length L combining with another rod to make a longer rod. First we observe that, with E the local free energy cost for breaking a micelle (in units of $k_B T$), the rate constants must obey, by detailed balance, the condition $2k/k' = \exp(-E)$. Hence we obtain, as the general steady state solution ($\dot{\psi}(L, u) = 0$) of (6),

$$\psi(L, u) = \exp(-E)\exp(-L/\lambda(u)). \tag{7}$$

In the absence of a mechanism to redistribute rods between angles the angle-dependent average rod length $\lambda(u)$ is arbitrary. However in the presence of angular diffusion (and without, at the moment, any flow or other external field) we require that $\psi(L, u)$ is isotropic and so $\lambda(u)$ can be replaced with the constant, λ_0.

Parallel micellar rods reach local chemical equilibrium on a timescale τ_{break}. Provided that the condition $\tau_{break} \ll \tau_{rot}$ is satisfied then the micellar length distribution relaxes to the exponential form described in (7) very much faster than rods can diffuse between angles. When we consider the effect of flow on the micellar length distribution, we will continue to assume local equilibrium at each angle provided also that $\tau_{break} \ll \dot{\epsilon}^{-1}$ with $\dot{\epsilon}$ the flow rate. This condition ensures that local equilibrium is reached before the material is convected between angles in the flow. As previously mentioned there is always a low molecular weight 'tail' of short rods (those with $L < l$, see (5)) for which angular rotation is rapid. For these rods, our model based on local equilibrium at each angle fails; we shall need to discuss this population in more detail later on. However, in the fast reaction regime ($\tau_{break} \ll \tau_{rot}$) we can still say that $\psi(L, u)$ is given by (7) for rods of length $L \gg l$.

Defining the arc length density per unit volume, per unit solid angle (of u space), as $\rho(u)$ we have

$$\rho(u) = \int_0^\infty L\psi(L, u)\, dL = \exp(-E)\lambda(u)^2. \tag{8}$$

Hence, after integrating over all u space we obtain an expression for the total arc length density per unit volume. We choose units so that this coincides with the volume fraction, Φ, which is a measure of the mass of micellar material in the system:

$$\Phi = \exp(-E) \int \lambda(u)^2\, d^2u. \tag{9}$$

By considering (9) in the absence of flow we can relate Φ and λ_0 as

$$\Phi = 2\pi \exp(-E)\lambda_0^2. \tag{10}$$

We are now interested in finding the steady-state solution for the system of micellar rods, undergoing reversible scission, in the presence of diffusion and imposed flows. In general $\psi(L, u)$ is made up of two terms,

$$\dot{\psi}(L, u) = F_1[\psi(L, u)] + F_2[\psi(L, u)] \tag{11}$$

where $F_1[\psi(L, u)]$ is a term which arises from the rotational diffusion and convection of the rods and $F_2[\psi(L, u)]$, defined by the right-hand side of (6), arises from the scission and recombination reactions between rods. One important fact about the functional $F_2[\psi(L, u)]$, given our assumption allowing only collinear reactions, is that $F_2[\psi(L, u)]$ cannot redistribute material between angles. By substituting (11) into (8) we therefore obtain,

$$\dot{\rho}(u) = \int_0^\infty L F_1[\psi(L, u)]\, dL \tag{12}$$

where a similar integral, involving $F_2[\psi(L, u)]$, must vanish identically. We will show that, for $\psi(L, u)$ of the form of (7), (12) completely determines the size distribution in steady state.

To find F_1, we introduce a Fokker–Planck equation appropriate to a mixed system of rods of lengths and orientations given by $\psi(L, u)$. We first note that the mean angular drift velocity of the rods $\omega(L, u)$ obeys [12]

$$\omega(L, u) = -D(L)R \ln \psi(L, u) + f(u) \tag{13}$$

where $f(u) \equiv u \times (K \cdot u)$, K is the fluid velocity gradient tensor and R is an angular gradient operator defined as

$$R = u \times \frac{\partial}{\partial u} = e_i \varepsilon_{ijk} u_j \frac{\partial}{\partial u_k} \qquad (14)$$

with e_i the unit vector in the ith direction and u_i the coordinate in this direction. The first term on the right-hand side of (13) can be identified with the angular diffusion of the rods whose average angular velocity is included by way of the 'Brownian potential', $\ln \psi(L, u)$ [12]. The second term represents the convective motion of rods in the flow. For a given $\omega(L, u)$, u changes with velocity $\omega \times u$, and the equation for $F_1[\psi(L, u)]$ becomes,

$$F_1[\psi] = -\frac{\partial}{\partial u}(\omega \times u \psi) = -\left(u \times \frac{\partial}{\partial u}\right)\omega \psi = -R(\omega \psi). \qquad (15)$$

With $\omega(L, u)$ given by (13) this is the standard result for the convection/diffusion of rods of length L in a fluid moving with a velocity gradient described by K.

We now substitute (13) and (15) into (12) and, in order to find the steady-state solution, we set $\dot{\rho} = 0$. This yields the following equation

$$R\left[\int_0^\infty L D(L) R\psi(L, u)\, dL - f(u) \int_0^\infty L\psi(L, u)\, dL\right] = 0. \qquad (16)$$

Now we substitute for $\psi(L, u)$ from (7) and $D(L)$ from (3) to obtain

$$R\left[D_0 \int_0^\infty L^{1-\zeta} R\exp(-L/\lambda(u))\, dL - f(u) \int_0^\infty L\exp(-L/\lambda(u))\, dL\right] = 0 \qquad (17)$$

where the second of the integrals is easily evaluated as $\lambda(u)^2$.

The first of the integrals in (17) is more delicate, and to evaluate this term correctly it is necessary to consider the minority of short rods in the system for which $L \lesssim l$ obeying (5). These short rods have an angular relaxation time less than τ_{break} so our assumption of local equilibrium must fail. However, in the fast reaction regime considered here ($\lambda_0 \gg l$), even flows which strongly align most of the micelles will have little effect on those of size l or less which can be considered as isotropic[†]. Hence we can write in (13)

$$R\ln \psi(L, u) \approx 0 \qquad L < l \qquad (18)$$

using the property that R operates on a constant to yield zero (R being a differential operator). We see that these *isotropic* rods of length l or less impose in effect a short length cutoff for the integrals in (17). In principle we should introduce a smooth crossover function at $L \sim l$ but for simplicity we merely set l as the lower limit of the integrals. The effect of this cutoff is negligible (to leading order in l/λ_0) on the second of the integrals in (17) and also on the first of the integrals in (17), so long

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† The assumption that rods of length l are almost isotropically distributed can be confirmed *a posteriori* for all flow rates of interest in the discussions of flow-induced transitions that follow.

as $\zeta < 3$. However l becomes a relevant parameter for $\zeta \geqslant 3$ since the first of the integrals in (17) is divergent at the lower limit in this case.

We now proceed to evaluate the first of the integrals in (17) for each regime of the parameter ζ (assuming always $\zeta > 2$). We will use the following dimensionless quantities to describe the mean rod length,

$$\Lambda(u) = \lambda(u)/l \tag{19a}$$

$$\Lambda_0 = \lambda_0/l. \tag{19b}$$

On performing the integrals in (17), in the regimes $\zeta < 3, \zeta = 3$ and $\zeta > 3$ respectively (with a short length cutoff at $L = l$ properly incorporated) we obtain [16],

$$R\left[-C_1\Lambda(u)^{1-\zeta}R\Lambda(u) + f(u)\Lambda(u)^2\right] = 0 \qquad \text{for } \zeta < 3 \tag{20a}$$

$$R\left[-\tau_{\text{break}}^{-1}[\ln(\Lambda(u)) - \gamma]\Lambda(u)^{-2}R\Lambda(u) + f(u)\Lambda(u)^2\right] = 0 \qquad \text{for } \zeta = 3 \tag{20b}$$

$$R\left[-C_2\Lambda(u)^{-2}R\Lambda(u) + f(u)\Lambda(u)^2\right] = 0 \qquad \text{for } \zeta > 3. \tag{20c}$$

Here the constants are $C_1 = \tau_{\text{break}}^{-1}\Gamma(3-\zeta)$ and $C_2 = ((\zeta-3)\tau_{\text{break}})^{-1}$; $\Gamma(x)$ is the usual gamma function and $\gamma \approx 0.577$ Euler's constant. The differential equations (20) are much simpler than might have been expected since they involve only the rescaled mean micellar length, $\Lambda(u)$, rather than the full distribution $\psi(L, u)$. This reduction in the effective number of degrees of freedom is the direct result of our fast reaction assumption, whereby the micelle size distribution at a given angle is an equilibrium one, corresponding to a (scaled) angle-dependent mean rod length $\Lambda(u)$.

The equations (20) are derived to leading order in the limit $l/\lambda \rightarrow 0\dagger$. In using (5) for l, we assume that this crossover length exceeds any physical short cutoff of the micellar length distribution, such as the rod diameter, b. If instead $b > l$, it is necessary to set $l = b$ in later equations.

2.3. Potential flows

It is straightforward to solve (20) for $\Lambda(u)$ in the case of a potential flow. Such a flow is defined so as to satisfy the equation

$$RV(u) = -f(u). \tag{21}$$

For some scalar function $V(u)$. In fact elongational flow is a potential flow whilst shear flow is not. This makes the following analysis inappropriate for shear flow. Using (21) we may integrate directly the equations (20) for $\Lambda(u)$. The form of the results differs in the three regimes of ζ defined in (20), and we present them in turn.

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† Taking this limit is the cause of the apparent discontinuity in the functional form of the governing equation near $\zeta = 3$. In a physical system we expect the form of the governing equation to vary smoothly with any control parameter, such as ζ, and, in practice, the contributions from a small but finite l/λ will provide the 'rounding' of any apparent discontinuities. One can quantify this by calculating the size of the regime near $\zeta = 3$ where the functional forms of (20a) and (20c) are unchanged (to leading order). With $\zeta = 3 \pm \delta$ we find that (20a) and (20c) are *not* significantly modified provided that $\Gamma(\delta) \gtrsim (l/\lambda)^{\delta}/\delta$. For the purposes of the calculations we enter into here we will merely need to assume that $l/\lambda \ll 1$ and so the equations (20) hold over the majority of ζ space whilst varying smoothly near $\zeta = 3$.

(i) For $\zeta < 3$ substituting (21) into (20a) and integrating we obtain

$$\Lambda(u) = C_3 V(u)^{-1/\zeta} \tag{22a}$$

with $C_3 = (C_1/\zeta)^{1/\zeta}$.

(ii) For $\zeta = 3$ substituting (21) into (20b) and integrating we obtain

$$\Lambda(u) = C_4 V(u)^{-1/3} \tag{22b}$$

with $C_4 = (\ln(\lambda_0/l)/3\tau_{\text{break}})^{1/3}$, where we have ignored the angle dependence within the logarithmic term using the approximations that $\ln(\Lambda(u)) \approx \ln(\lambda_0/l) \gg \gamma$.

(iii) For $\zeta > 3$ substituting (21) into (20c) and integrating we obtain

$$\Lambda(u) = C_5 V(u)^{-1/3} \tag{22c}$$

with $C_5 = (C_2/3)^{1/3}$.

These results are all derived for the case where the angular diffusion constant $D(L)$ is proportional to an inverse power of the rod length, as given in (3). It is possible to consider other forms for the diffusion constant, such as the rigorous form for dilute rods given in (2). In this case in order to calculate any quantities dependent on the form of $\Lambda(u)$ it is necessary to resort to numerical methods. Where (2) is used (16) becomes

$$\tau_{\text{break}}^{-1} \int_l^\infty \frac{\ln(L/b)e^{-L/\lambda(u)}}{L}\,\mathrm{d}L\,\Lambda(u)^{-4}R\Lambda(u) + RV(u) = 0. \tag{23}$$

The solution of this equation for elongational flow is used for comparison with (22) in section 3.1.

3. Three-dimensional elongational flow: fast reaction regime

We will now consider for the first time a specific flow geometry, elongational flow with axial symmetry [12]. The velocity gradient tensor for uniaxial elongational flow (along the $\hat{z}$ direction), with flow rate $\dot{\epsilon}$, is K, where $K = \dot{\epsilon}/2(3\hat{z}\hat{z} - I)$; hence it is easily shown that $u \times K \cdot u = u \times (3\dot{\epsilon})/2\hat{z}(u \cdot \hat{z})$. Using this expression and (21) we integrate to obtain,

$$V(u) = \tfrac{3}{4}\dot{\epsilon}(v_0 - u_z^2) \tag{24}$$

where the constant of integration v_0, with $v_0 \in [1,\infty)$, is determined by requiring the total amount of micellar material in the system to be equal to Φ. This condition is expressed in (9). Using (24) in (22) we are able to rewrite (9) as

$$\tilde{\Phi} \equiv \frac{\Phi e^E}{l^2} = \int \Lambda(u)^2\,\mathrm{d}^2u = 2\pi\Lambda_0^2$$

$$= \begin{cases} 2\pi C_3^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/\zeta} \int_0^1 (v_0 - u_z^2)^{-2/\zeta}\,\mathrm{d}u_z & \text{for } \zeta < 3 \\[6pt] 2\pi C_4^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/3} \int_0^1 (v_0 - u_z^2)^{-2/3}\,\mathrm{d}u_z & \text{for } \zeta = 3 \\[6pt] 2\pi C_5^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/3} \int_0^1 (v_0 - u_z^2)^{-2/3}\,\mathrm{d}u_z & \text{for } \zeta > 3 \end{cases} \tag{25}$$

where $\tilde{\Phi}$ is a dimensionless measure of the amount of micellar material in the system. Here and later we use the power-law form for the angular diffusion constant, $D(L) = D_0 L^{-\zeta}$ (see (3)), and give results for the three regimes of ζ ($\zeta < 3$, $\zeta = 3$ and $\zeta > 3$) simultaneously. This results in some cumbersome displayed equations, such as (25), but avoids duplicating a large amount of algebra. In fact the physics does not differ much in the three cases.

Using (25) we can determine v_0 for an arbitrary choice of $\tilde{\Phi}$ and $\dot{\epsilon}$ and hence, via (22), obtain the angle-dependent mean micellar length $\Lambda(u)$ for these values. An important feature of (25) is that as either $\tilde{\Phi}$ or $\dot{\epsilon}$ is increased, v_0 decreases until when $v_0 = 1$ each integral in (25) reaches a finite maximum. (This statement applies so long as $\zeta > 2$, which we have already assumed to be the case on physical grounds.) For $\tilde{\Phi}$ constant and $\dot{\epsilon}$ varying we define a critical flow rate $\dot{\epsilon}_c$ at which the constant v_0 first reaches unity. As $\dot{\epsilon} \to \dot{\epsilon}_c^-$, the average length near the z-direction diverges, with a square-integrable singularity at $\dot{\epsilon}_c$. (This conclusion depends on our assumption of flow independent k, k' and is modified slightly later.)

3.1. Gelation transition

The key question that now arises is, 'what happens if, at constant $\tilde{\Phi}$, $\dot{\epsilon}$ is increased above $\dot{\epsilon}_c$?'. For $\dot{\epsilon} > \dot{\epsilon}_c$ the steady-state size distribution calculated in (25) can no longer account for all the material in the system and so we postulate† that the excess material resides in a phase of extremely long rods aligned along the flow axis. Hence we formally write down an expression for $\Lambda(u)^2$ as

$$\Lambda(u)^2 = \frac{\tilde{\Phi}_{gel}}{2\pi}\delta^2(u_z - 1) + \begin{cases} C_3^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/\zeta}(1 - u_z^2)^{-2/\zeta} & \text{for } \zeta < 3 \\ C_4^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/3}(1 - u_z^2)^{-2/3} & \text{for } \zeta = 3 \\ C_5^{\,2}(\tfrac{3}{4}\dot{\epsilon})^{-2/3}(1 - u_z^2)^{-2/3} & \text{for } \zeta > 3 \end{cases} \qquad (26)$$

where $\delta^2(u_z - 1)$ is defined here so that $\int\int \delta^2(u_z - 1)\,d^2u = 1$. For $\dot{\epsilon} > \dot{\epsilon}_c$ we may write $\tilde{\Phi}$ as, $\tilde{\Phi} = \tilde{\Phi}_{normal}(\dot{\epsilon}) + \tilde{\Phi}_{gel}(\dot{\epsilon})$ where $\tilde{\Phi}_{normal}(\dot{\epsilon})$ is the solution ($\tilde{\Phi}$) to (25), for the required value of $\dot{\epsilon}$ and with $v_0 = 1$. This is the mass of 'normal' material in the system, i.e. that residing in rods with finite length. The mass of material in the 'gel' phase of fully aligned long rods, $\tilde{\Phi}_{gel}(\dot{\epsilon})$, accounts for the difference between the total mass $\tilde{\Phi}$ and the 'normal' mass.

From (25) we can see that, at or above the onset of the transition, $\tilde{\Phi}_{normal} \propto \dot{\epsilon}^{-2/3}$ (for $\zeta \geqslant 3$) or $\tilde{\Phi}_{normal} \propto \dot{\epsilon}^{-2/\zeta}$ (for $\zeta < 3$). Imposing the boundary condition $\tilde{\Phi} = \tilde{\Phi}_{normal}$ at $\dot{\epsilon} = \dot{\epsilon}_c$ implies that $\tilde{\Phi}_{normal} = \tilde{\Phi}(\dot{\epsilon}/\dot{\epsilon}_c)^{-2/3}$ and so we obtain an expression for $\tilde{\Phi}_{gel}$, valid for $\dot{\epsilon} \geqslant \dot{\epsilon}_c$.

$$\tilde{\Phi}_{gel} = \begin{cases} \tilde{\Phi}(1 - (\dot{\epsilon}/\dot{\epsilon}_c)^{-2/\zeta}) & \text{for } \zeta < 3 \\ \tilde{\Phi}(1 - (\dot{\epsilon}/\dot{\epsilon}_c)^{-2/3}) & \text{for } \zeta \geqslant 3. \end{cases} \qquad (27)$$

† An alternative way of dealing with the case of $\dot{\epsilon} > \dot{\epsilon}_c$ is to assume that no steady state exists in this regime. This seems improbable on physical grounds (at least in elongational flow). Equation (26) represents an exact solution of the equations of motion for all $u_z < 1$. Whether or not the singularity proposed at $u_z = 1$ is formally a solution of these equations remains open; it is probably a moot point since rod–rod interactions are certain to play a role in the gel phase.

Since we now know the behaviour of the system for all $\dot\epsilon$ we can make predictions for, for example, the birefringence, Δn, as a function of elongational flow rate. We present in figure 2(*a*) a theoretical plot of the birefringence Δn, which obeys [12],

$$\Delta n \propto \int_{L=0}^{\infty} \int L\psi(L, \boldsymbol{u})(u_z^2 - u_x^2)\, \mathrm{d}^2\boldsymbol{u}. \tag{28}$$

This is calculated from (26) and (27) with $\zeta \geqslant 3$. Note from figure 2 that the birefringence varies smoothly near $\dot\epsilon = \dot\epsilon_c$.
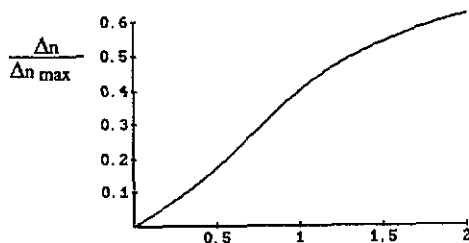

Figure 2. The rescaled birefringence $\Delta n/\Delta n_{\max}$, where Δn is the birefringence and $\Delta n_{\max}$ is the maximum birefringence (all the material contained in rods aligned with the flow axis), plotted against $\dot\epsilon/\dot\epsilon_c$. The plot is obtained numerically from (26) with $\zeta \geqslant 3$.

It is interesting to compare qualitatively this theoretical plot for the birefringence with recent experimental data for rod-like micelles [3]. Experimental data only exist for a *shear*-flow geometry; no data are so far available in the elongational geometry. Nonetheless we note that the predicted theoretical behaviour (for *elongational* flow) is in qualitative agreement with experimental results (for *shear* flow), at least at relatively high salt concentrations. However at low salt concentrations, where we might expect the rods to be more stiff and hence our model to be more appropriate, the birefringence rises steeply from a low initial value at the onset of the gel phase [3], a feature which is not reproduced in the theoretical plot of figure 2. Although we are comparing two very different flows it would be suprising if, in practice, shear flow were to exhibit *more* dramatic flow effects than elongational flow, in which there is a stable flow axis. This observation suggests that rod–rod interactions, here ignored, may be important in practice.

Setting $v_0 = 1$ at the transition in (25) we derive [16] expressions for $\dot\epsilon_c$,

$$\dot\epsilon_c = \begin{cases} C_6 D(\lambda_0) & \text{for } \zeta < 3 \\ C_7 \ln(\lambda_0/l) D(\lambda_0) & \text{for } \zeta = 3 \\ C_8 D(\lambda_0)(\tau_{\text{break}} D(\lambda_0))^{3-\zeta/\zeta} & \text{for } \zeta > 3 \end{cases} \tag{29}$$

where the three constants C_6, C_7 and C_8 are of order unity and have been calculated explicitly [16]†, although they depend somewhat on the mathematical treatment of the crossover to short rods at $L \sim l$, as discussed following (18).

† We find [16]

$$C_6 = \frac{4\Gamma(3-\zeta)}{3\zeta}\left[\frac{\Gamma(\frac{1}{2})\Gamma(1-\frac{2}{\zeta})}{2\Gamma(\frac{3}{2}-\frac{2}{\zeta})}\right]^{\zeta/2} \quad C_7 = \frac{4}{9}\left[\frac{\Gamma(\frac{1}{2})\Gamma(\frac{1}{3})}{2\Gamma(\frac{5}{6})}\right]^{3/2} \quad C_8 = \frac{4}{9(\zeta-3)}\left[\frac{\Gamma(\frac{1}{2})\Gamma(\frac{1}{3})}{2\Gamma(\frac{5}{6})}\right]^{3/2}.$$

Directly from (29) we have $\dot{\epsilon}_c \tau_{rot} \simeq 1$, for $\zeta < 3$, which tells us that the critical flow rate is of the order of the inverse of the rotation time of an average micelle. However for $\zeta > 3$ we find instead that $\dot{\epsilon}_c \tau_{rot} \simeq [\tau_{rot}/\tau_{break}]^{(\zeta-3)/\zeta} \gg 1$. In this regime we have instead that the critical flow rate is very much greater than τ_{rot}^{-1}.

We have shown that the dimensionless quantity $\dot{\epsilon}_c \tau_{rot}$ is very sensitive to whether ζ is above or below 3. This suggests that for dilute rods, which have $\zeta = 3$, the logarithmic correction to the diffusion constant (2) may be important. To study this we can solve (23) numerically and can compare the result with (22) for the case of elongational flow. We see from figure 3 that the logarithmic correction to the diffusion constant does not greatly affect the form of $\Lambda(u)$ which remains close to that obtained using (20b) when $\zeta = 3$. Both of the plots shown in figure 3 represent systems at $\dot{\epsilon} = \dot{\epsilon}_c$ (the flow rate at which the length first diverges at $u_z = 1$) and both plots have the same mean length, $\Lambda = 100$, at $u_z = 0$.
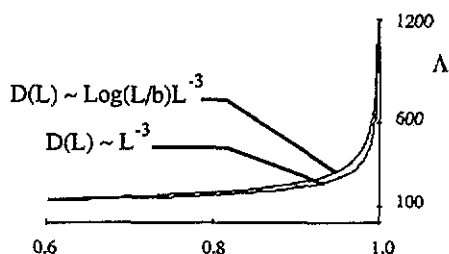

Figure 3. The dimensionless mean micellar length, $\Lambda = \lambda/l$ plotted against u_z for two different forms of $D(L)$ (as shown). In both cases $\dot{\epsilon} = \dot{\epsilon}_c$ and $\Lambda = 100$ at $u_z = 0$ (the two systems have slightly different values of Φ). We can see that the logarithmic correction to the diffusion constant does not greatly affect the form of $\Lambda(u)$ which remains close to that obtained with $D(L) \sim L^{-3}$.

3.2. Discussion

As discussed following (29), our model always predicts $\dot{\epsilon}_c \tau_{rot} \gtrsim 1$ whereas experimentally it has been found that, in several micellar systems [5], flow-induced transitions arise even for $\dot{\epsilon}_c \tau_{rot} \ll 1$. This feature cannot be explained within the present framework and may be due to the presence of strong Coulombic interactions in these systems.

In describing the system for $\dot{\epsilon} > \dot{\epsilon}_c$ as a 'gel' phase we do not imply any form of crosslinking, merely the existence of a population of extremely long rods. However, we do expect our gel to exhibit some physical properties similar to those of a classical gel, e.g. high viscosity and long relaxation times, as found in experiments on flow-induced structures in rod-like micellar systems [2, 3].

We should note, as emphasized elsewhere [8, 9], that due to the effect of longitudinal tension the extremely long rods making up the gel phase cannot, in fact, have infinite length, as assumed mathematically in our treatment. It is known that the tension at the centre of a slender rod of length L in elongational flow, T, is given by [11], $T = \pi \eta_s \dot{\epsilon} L^2 / 2 \ln(L/b)$. In order to obtain an expression for the maximum stable length at a given flow rate, $L_{max}(\dot{\epsilon})$, we need to relate T to the

micelle scission energy, E. We make the assumption that in order to break a micelle the force T must act over a distance of order b (the micellar diameter). Hence the micelle can sustain a maximum tension $T \approx E/b$. This allows us to find expressions for the maximum stable length at transition, $L^* = L_{max}(\dot{\epsilon}_c)$ using (29). We obtain

$$\frac{(L^*/\lambda_0)^2}{\ln(L^*/b)} = \begin{cases} (C_9/C_6)\left(\dfrac{\lambda_0}{b}\right)^{\zeta-2} & \text{for } \zeta < 3 \\[2ex] (C_9/C_7)\dfrac{(\lambda_0/b)}{\ln(\lambda_0/l)} & \text{for } \zeta = 3 \\[2ex] (C_9/C_8)\left(\dfrac{\lambda_0}{l}\right)\left(\dfrac{l}{b}\right)^{\zeta-2} & \text{for } \zeta > 3 \end{cases} \qquad (30)$$

with $C_9 = 2Eb^{\zeta-3}/\pi\eta_s D_0$ a dimensionless constant. With E of order a few $k_B T$ (and ignoring all logarithmic factors) we find that $C_9 \approx 2E/3$ is of order unity and hence (30) implies that $L^*/\lambda_0 \gg 1$ since $\lambda_0/l \gg 1$ and $l/b \geqslant 1$.

Since $L^* \gg \lambda_0$, we expect that our model of the transition to a gel phase consisting of infinite rods will give correct results, to a first approximation, although the tension effect will cause the transition to be slightly rounded, with the nominally infinite rods having a very large but finite length L_{max}. As $\dot{\epsilon}$ increases the length L_{max} will continue to decrease and eventually, when $L_{max} \lesssim \lambda_0$, hydrodynamic tension effects begin to dominate and our description will break down. We do not pursue this here since rod–rod interactions, which we have ignored, are presumably large throughout the gel phase.

4. Scaling analysis

We have already seen in section 3 that for a 3D system in elongational flow there exists a second-order phase transition at finite mass, $\bar{\Phi}$, and flow rate, $\dot{\epsilon}_c$. At or above this transition Λ diverges near the flow axis like an inverse power of the angle θ to the $\hat{z}$-direction. We now employ a scaling analysis, first presented elsewhere [7], which can be used to determine the existence of a gelation transition. In what follows we extend this analysis to 3D elongational flow (section 4.1) and to 3D shear flow (section 4.2) where the governing equations, (20), cannot be solved directly.

4.1. Scaling for elongational flow

We first apply our analysis to 3D elongational flow, so that we may make a comparison with the analytic results of section 3. We convert the equations (20) to spherical polar coordinates. Since we have axial symmetry there is no ϕ dependence. We find,

$$C_{11}\Lambda(\theta)^{1-\zeta}\frac{\mathrm{d}}{\mathrm{d}\theta}\Lambda(\theta) + \sin\theta\cos\theta\Lambda(\theta)^2 = 0 \qquad \text{for } \zeta < 3 \qquad (31a)$$

$$C_{12}\Lambda(\theta)^{-2}\frac{\mathrm{d}}{\mathrm{d}\theta}\Lambda(\theta) + \sin\theta\cos\theta\Lambda(\theta)^2 = 0 \qquad \text{for } \zeta = 3 \qquad (31b)$$

$$C_{13}\Lambda(\theta)^{-2}\frac{\mathrm{d}}{\mathrm{d}\theta}\Lambda(\theta) + \sin\theta\cos\theta\Lambda(\theta)^2 = 0 \qquad \text{for } \zeta > 3 \qquad (31c)$$

with $C_{11}(\dot{\epsilon}) = 2\Gamma(3 - \zeta)/3\dot{\epsilon}\tau_{break}$, $C_{12}(\dot{\epsilon}) = 2\ln(\Lambda_0)/3\dot{\epsilon}\tau_{break}$. (We have assumed $\ln \Lambda(u) \approx \ln \Lambda_0 \gg \gamma$, as used in (22b)) and $C_{13}(\dot{\epsilon}) = 2/3(\zeta - 3)\dot{\epsilon}\tau_{break}$.)

We now assume a scaling (power-law) form for the angle dependence of the scaled mean micelle size $\Lambda(\theta)$:

$$\Lambda(\theta) \sim \theta^{-\mu} \qquad \text{for } \theta \ll 1. \tag{32}$$

Next we impose the condition that powers of θ must balance in (31). Hence,

$$\theta^{(\zeta-1)\mu}\theta^{-\mu-1} \sim \theta^1\theta^{-2\mu} \qquad \text{for } \zeta < 3 \tag{33a}$$

$$\theta^{2\mu}\theta^{-\mu-1} \sim \theta^1\theta^{-2\mu} \qquad \text{for } \zeta \geqslant 3 \tag{33b}$$

which together imply the results $\mu = 2/\zeta$, for $\zeta < 3$, and $\mu = 2/3$, for $\zeta \geqslant 3$. Thus we are able to predict a form for $\Lambda(\theta)$ (near $\theta = 0$) which diverges at $\theta = 0$ in a way which is consistent with (31). Supposing there to be a continuous transition to a gel phase, just such a divergence in the mean micelle size is expected at the critical point. To see if such a transition can indeed takes place, we ask whether this form of $\Lambda(\theta)$ corresponds to a bounded total mass $\tilde{\Phi}$, which is given, according to (9), as $\tilde{\Phi} = \int \Lambda(u)^2 d^2u$. If our choice (32) for Λ corresponds to a bounded mass, then we deduce that at fixed flow rate $\dot{\epsilon}$ the mean length may diverge near the flow axis for some (finite) total mass, and hence a transition to a phase of 'infinite' rods near the flow axis may occur. If, on the other hand, this choice of Λ corresponds to an unbounded total mass then we infer that the transition cannot take place.

The required contribution to the total micellar mass from rods near $\theta = 0$ is governed, in three dimensions, by the following integral:

$$\tilde{\Phi} \sim \int_0 \theta\Lambda(\theta)^2 d\theta. \tag{34}$$

This integral is finite for $\mu < 1$ which implies that a transition point exists in 3D elongational flow (since $\mu < 1$ in this case). The predictions of this scaling analysis, for the form of the divergence near $\theta = 0$ and the existence of a transition, are in complete agreement with the analytic results of section 3.

In a previous communication [7] we applied this scaling analysis to a quasi 2D system, where the rod directors are constrained to lie in a plane. It was found that the gelation transition is absent when an elongational flow is applied to this system. In this case the calculations follow closely the calculations for 3D elongational flow, with the same values of μ obtained from the scaling argument, except that the integral governing the mass in the system is not a surface integral, as in (34), but a line integral over a semicircle (due to the fact that the rods were restricted to motion in a plane) $\int_0 \lambda(\theta)^2 d\theta$. This integral is found to be unbounded when the mean length diverges near $\theta = 0$ and hence a transition cannot arise. The extra power of θ in (34), arising from the fact that (34) is a surface integral, proves to be crucial in determining whether a transition may occur or not. The case of 2D shear flow was also considered [7]. For this case the scaling analysis predicted $\mu = 1$ implying that a gelation transition cannot arise.

4.2. Scaling for 3D shear flow

We now consider the case of rods undergoing full 3D motion in shear flow. As in section 4.1 we use spherical polar coordinates and consider a simple shear flow with the fluid velocity in the $\hat{z}$-direction and its gradient in the $\hat{y}$-direction. The neutral axis is then $\hat{x}$. In spherical polar coordinates about the $\hat{z}$-axis we then have $f(u) = -\dot{\epsilon}\sin^2\theta\sin\phi\hat{\phi}$, where $\dot{\epsilon}$ is the flow rate. We can also rewrite R as

$$R = \hat{\phi}\frac{\partial}{\partial\theta} - \frac{\hat{\theta}}{\sin\theta}\frac{\partial}{\partial\phi}. \tag{35}$$

For simplicity we now consider only the regime $\zeta > 3$, for which the equation of motion is given by (20c). Substituting for $f(u)$ and R (20c) becomes†,

$$\frac{\partial}{\partial\theta}\left[C_2\Lambda^{-2}\frac{\partial}{\partial\theta}\Lambda + \Lambda^2\dot{\epsilon}\sin^2\theta\sin\phi\right]$$
$$+\theta^{-1}\left[C_{10}\Lambda^{-2}\frac{\partial\Lambda}{\partial\theta} + \frac{\partial}{\partial\phi}\left(C_2\Lambda^{-2}\theta^{-1}\frac{\partial}{\partial\phi}\right)\Lambda + \Lambda^2\dot{\epsilon}\sin^2\theta\sin\phi\right] = 0. \tag{36}$$

Once again we will employ a scaling argument to find a form for $\Lambda(\theta, \phi)$, representing a divergence in the mean micellar length, which is consistent with (36). We will then calculate the resultant total mass of micellar material. If a divergence in Λ can occur at finite mass then we deduce that a gelation transition can arise, while if infinite mass is required, we deduce that it cannot.

We must first determine the orientation for which the mean micellar length may diverge. We expect the only stable orientation for rods of infinite length, if indeed they exist at all, to be at $\theta = 0$ on the grounds that at finite θ the rods will experience an infinite torque. This assumption is consistent with the behaviour of non-interacting unbreakable rods. In such systems as $\dot{\epsilon}$ is increased from zero the maximum of $\psi(\theta)$ first occurs at $\theta = 3\pi/4$ and, as $\dot{\epsilon}$ is increased, the position of this maximum tends monotonically towards $\theta = \pi$ (equivalent to $\theta = 0$). This behaviour is reproduced in our numerical results on quasi 2D systems of rod-like micelles [7].

We therefore assume that any divergence in Λ occurs at $\theta = 0$. We first suppress the ϕ-dependence and look for a scaling solution of the form of $\Lambda \sim \theta^{-\mu}$ for $\theta \ll 1$. By substituting this form for Λ into (36) and requiring that powers of θ balance, we obtain

$$\theta^{-1}[\theta^{\mu-1} + \theta^{2-2\mu}] \sim \theta^{-1}[\theta^{\mu-1} + \theta^{\mu-1} + \theta^{2-2\mu}] \tag{37}$$

which implies that $\mu = 1$. This analysis, which neglects the ϕ-dependence, suggests that $\lambda \sim \theta^{-1}$. This naturally leads us to attempt to find a more general solution of the following form:

$$\Lambda(\theta, \phi) = g(\phi)\theta^{-1}. \tag{38}$$

† The corresponding version of (36) for $\zeta = 3$, derived from (20b), is identical up to an exchange of C_2 for the constant C_{10}.

Substituting (38) into (36), with $j(\phi) = g(\phi)^{-1}$, we have

$$\theta^{-1}\left[-C_2\left(\frac{\partial^2 j}{\partial\phi^2}+j\right)+j^{-2}\dot\epsilon\sin\phi\right]+\frac{\theta}{6}\left[-C_2\left(2\frac{\partial^2 j}{\partial\phi^2}+j\right)-j^{-2}\dot\epsilon\sin\phi\right]$$
$$+\theta^3[\ldots]+\cdots = 0. \tag{39}$$

In the limit $\theta \to 0$ we assume that all terms in (39) proportional to θ^ν, with $\nu > 0$, vanish. Thus $g(\phi)$ is defined (in terms of its inverse $j = g^{-1}$) by requiring the first term in (39) to vanish. We write this explicitly as

$$-C_2\left(\frac{\partial^2 j}{\partial\phi^2}+j\right)+j^{-2}\dot\epsilon\sin\phi = 0. \tag{40}$$

Taking the solution of this equation to define $g(\phi) = j(\phi)^{-1}$ we have found, as required, a solution to the equation of motion (20c), which takes the scaling form (38) in the limit of $\theta \to 0$.

We now need to ask how the total mass of material in the system is affected by this form of Λ, diverging near $\theta = 0$. The total mass is finite provided the contribution arising from rods near $\theta = 0$ is finite. This we can write as

$$\tilde\Phi \simeq \int \Lambda(\theta)^2\theta\,\mathrm{d}\theta\,\mathrm{d}\phi \sim \int_{\theta=0}\frac{\mathrm{d}\theta}{\theta}\int_{\phi=0}^{2\pi}g^2(\phi)\mathrm{d}\phi. \tag{41}$$

The factor $\int_{\theta=0}\theta^{-1}\mathrm{d}\theta$ diverges, although only logarithmically, and so we conclude that a divergence in the mean micellar length at $\theta = 0$ cannot arise for finite $\tilde\Phi$ and so a gelation transition cannot arise in 3D shear flow†. However since the existence or otherwise of a transition is marginal ((41) is only logarithmically divergent) we expect that even very weak effects, which have been neglected here, could induce a transition. Inter-rod interactions, either steric or electrostatic in origin, could be just such effects.

5. Slow reaction regime

In section 2 we dealt with rods in the fast reaction limit for which $\tau_{\mathrm{break}} \ll \tau_{\mathrm{rot}}$. In this section we derive a theory describing rods in the opposite, 'slow reaction' regime $\tau_{\mathrm{break}} \gg \tau_{\mathrm{rot}}$ where a typical rod has time to rotate many times before a reaction occurs. The slow reaction assumption must always fail for sufficiently long rods $L \gtrsim l$ whose micellar scission time is less than their rotation time. However, we expect the slow reaction regime to be relevant (at least for the majority of rods) provided $\lambda_0 \ll l$. In order to define l we need to consider the waiting time for a reaction to occur on a rod of length l ($l \gg \lambda_0$), written τ_l. This waiting time is approximately the waiting time for a scission reaction to occur‡. We use the definitions of $\tau_{\mathrm{break}} = 1/k\lambda_0$ (1) and $\Lambda_0 = \lambda_0/l$ (19b) in order to write τ_l as

$$\tau_l \approx \frac{1}{kl} = \frac{1}{k\lambda_0}\left(\frac{\lambda_0}{l}\right) = \tau_{\mathrm{break}}\Lambda_0. \tag{42}$$

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† The only way that this divergence can be avoided is if $g(\phi) = 0$ for all ϕ; from (40) we see that this is not the case.

‡ For long rods (of length $l \gg \lambda_0$), scission reactions occur on a much shorter timescale than combination reactions (a factor of order λ_0/l shorter).

The length l is then defined as the length at which $\tau_l D(l)^{-1} = 1$. Hence we find

$$l = (D_0 \tau_{\text{break}} \Lambda_0)^{1/\varsigma}. \tag{43}$$

In this section we consider only 3D elongational flows. We take $\Lambda_0 \ll 1$ which defines the slow reaction regime. Just as for the fast reaction case considered in sections 2–4, there is always a part of the micelle size distribution for which the assumed separation of time scales is not valid. In the slow reaction limit, the difficulty lies with the small fraction of rods of length $L \gtrsim l$. These rods will always be important near a gelation transition, and to describe adequately any such transition we will need to match in some way the two populations of rods ($L \ll l$ and $L \gg l$) near $L = l$. The matching we employ later introduces errors at the quantitative level but the method should yield qualitatively accurate results.

It is known [12] that for dilute, slender rods in elongational flow the (un-normalized) probability distribution for the orientation of a single rod of length L is

$$\psi_L(u) = \exp 3\dot{\epsilon} u_z^2 / 4 D(L).$$

We now argue that the population of rods with length L relaxes to its equilibrium angular distribution on a much shorter time scale than that characterizing reactions of rods. Hence the distribution of an ensemble of non-interacting rods is given by

$$\psi(L, u) = \frac{\psi(L) e^{\beta u_z^2 / D(L)}}{\int e^{\beta u_z^2 / D(L)} \mathrm{d}^2 u} \tag{44}$$

where β is a rescaled flow rate defined as $\beta = 3\dot{\epsilon}/4$ and $\psi(L) = \int \psi(L, u) \mathrm{d}^2 u$ is the total number density of rods of length L, as yet undetermined.

Even amongst those rods with $L \ll l$, whose rotation is rapid compared with kinetic timescales, there are two well-defined classes of rod lengths. The first consists of rods which are so short that they do not feel the effects of convection and hence are isotropic. These are rods for which $L \ll \tilde{l}$,

$$\tilde{l} = (D_0 / \beta)^{1/\varsigma}. \tag{45}$$

The second class consists of rods which are sufficiently long to feel the effects of the flow, i.e. $\tilde{l} \ll L \ll l$. Using the definitions of $\tilde{l}$ and l we have

$$\tilde{l}/l = (\beta \tau_{\text{break}} \Lambda_0)^{-1/\varsigma}. \tag{46}$$

We now substitute (44) into the equation of motion (6), which describes the effect of the inter-rod reactions, and integrate over all u-space. This gives an equation that determines $\psi(L)$ in the presence of the inter-rod reactions. We find that $\psi(L)$ is given by the steady-state solution ($\dot{\psi}(L) = 0$) to the following equation

$$\dot{\psi}(L) = -kL\psi(L) + 2k \int_L^\infty \psi(L') \, \mathrm{d}L'$$

$$+ k'/2 \int_0^L \psi(L')\psi(L - L')F(L', L - L') \, \mathrm{d}L' - k'\psi(L)$$

$$\times \int_0^\infty \psi(L')F(L, L') \, \mathrm{d}L' \tag{47}$$

where $F(L_x, L_y)$ is an effective reaction kernel for recombination between two rods of length L_x and L_y, and is defined as

$$F(L_x, L_y) = \frac{\int e^{\beta u_z^2/D(L_x)} e^{\beta u_z^2/D(L_y)} \, \mathrm{d}^2 u}{\int e^{\beta u_z^2/D(L_x)} \, \mathrm{d}^2 u \int e^{\beta u_z^2/D(L_y)} \, \mathrm{d}^2 u}. \tag{48}$$

We can evaluate $F(L_x, L_y)$ in the following three asymptotic limits: (i) $L_x, L_y \gg \tilde{l}$; (ii) $L_x \gg \tilde{l} \gg L_y$; and (iii) $L_x, L_y \ll \tilde{l}$. Using the following property,

$$\int e^{\beta u_z^2/D(L_x)} \, \mathrm{d}^2 u \approx \begin{cases} \pi D(L_x) e^{\beta/D(L_x)}/\beta & \text{for } L_x \gg \tilde{l} \\ 2\pi & \text{for } L_x \ll \tilde{l}. \end{cases} \tag{49}$$

We find

$$F(L_x, L_y) \approx \begin{cases} \beta/\pi(D(L_x) + D(L_y)) & \text{for } L_x, L_y \gg \tilde{l} \\ 1/2\pi & \text{for } L_x \gg \tilde{l} \gg L_y \\ 1/2\pi & \text{for } L_x, L_y \ll \tilde{l}. \end{cases} \tag{50}$$

5.1. Strongly convected rods

Rods with lengths $L \gg \tilde{l}$ are strongly convected in the flow field and thus are highly anisotropically distributed. In order to describe the distribution of these rods we first rewrite (47) for $L \gg \tilde{l}$, substituting for F from (50), to obtain†,

$$\dot{\psi}(L) = -kL\psi(L) + 2k \int_L^\infty \psi(L') \, \mathrm{d}L' + (k'/2) \int_{\tilde{l}}^\infty \frac{\beta\psi(L')\psi(L - L') \, \mathrm{d}L'}{\pi(D(L') + D(L - L'))}$$
$$- k'\psi(L) \int_{\tilde{l}}^\infty \frac{\beta\psi(L') \, \mathrm{d}L'}{\pi(D(L) + D(L'))}. \tag{51}$$

We seek a scaling solution of $\dot{\psi}(L) = 0$, from (51). By substitution we confirm that the following is an asymptotic solution to $\dot{\psi}(L) = 0$ in the limit $L \gg \tilde{l}$,

$$\psi(L) \simeq \exp(-E)\beta^{-1} D(L) e^{-\kappa L} \tag{52}$$

provided $\kappa\tilde{l} \gtrsim 1$. Note that in fact (52) is also a solution when $\kappa = 0$ but not for intermediate values of κ. In order to obtain (52) we have used the identity $\exp(-E) = 2k/k'$ (see (7)). We can think of κ as a parameter which determines the mass of material residing in strongly convected rods with $\tilde{l} \ll L \ll l$. For $\kappa \gg \tilde{l}^{-1}$, $\psi(L)$ decreases sharply with increasing L and hence there is little material contained in rods with $L \gg \tilde{l}$. As κ is lowered $\psi(L)$ decreases less sharply (and hence there is more material in these rods) until, at $\kappa \sim \tilde{l}^{-1}$, (52) ceases to be valid and $\psi(L)$ takes on some other, unknown, functional form. However as the mass of rods with $L > \tilde{l}$ is increased (52), with $\kappa = 0$, once again becomes a steady-state solution to (51), corresponding to a certain value of this mass. We identify this ($\kappa = 0$) solution as the maximum of $\psi(L)$, corresponding to a maximum in the mass of material which can be contained in rods with $\tilde{l} \ll L \ll l$.

† The introduction of a short-length cutoff at $L' = \tilde{l}$ for the integrals in (65) is an approximation, and to be exact the integrals should extend down to $L' = 0$ with the correct crossover in F included at $L' = \tilde{l}$. However, in the limit $L \gg \tilde{l}$ considered here, the errors introduced by this approach turn out to be of the order of $(\tilde{l}/L)^2$ and so we retain (47) as stated.

5.2. Gelation transition

We have derived, in (52), an expression for $\psi(L)$ valid in the regime $\tilde{l} \ll L \ll l$. By combining this result with an upper bound for the mass of material made up of isotropic rods with $L \ll \tilde{l}$, we are now able to derive an approximate expression for the maximum mass of micellar material, for a given flow rate β. The dependence on β is not seen explicitly in what follows but is contained implicitly in the definition (45) of $\tilde{l}$.

The total mass of micellar material contained in rods with $L < l$ is denoted $\Phi_{L<l}$. In the absence of flow most of the material will reside in rods with $L < l$ (in this case we can show that $\Phi/\Phi_{L<l} = 1 + O(\Lambda_0^2)$). In this section we are interested in how the *maximum* of $\Phi_{L<l}$, denoted $\Phi_{L<l}^{\max}$, varies with $\tilde{l}(\beta)$. We first define $\Phi_{L<l}$ as

$$\Phi_{L<l} = \int_0^{\tilde{l}} L\psi(L)\,\mathrm{d}L + \int_{\tilde{l}}^l L\psi(L)\,\mathrm{d}L \tag{53}$$

where the first and second terms on the right-hand side are from now on denoted $\Phi_{L<\tilde{l}}$ and $\Phi_{\tilde{l}<L<l}$ respectively. The quantity $\Phi_{L<\tilde{l}}$ represents the mass of micellar material residing in roughly isotropic rods with $L < \tilde{l}$, whilst the quantity $\Phi_{\tilde{l}<L<l}$ represents the mass residing in strongly convected rods with $\tilde{l} < L < l$.

In order to determine $\Phi_{\tilde{l}<L<l}$ we take $\psi(L)$ to be of the form of (52) in the entire region $\tilde{l} < L < l$. Hence we do not attempt to model the precise form of $\psi(L, u)$ near the crossover $L = \tilde{l}$ but we do not expect this approach to alter our results qualitatively. We can predict the maximum value that $\Phi_{\tilde{l}<L<l}$ can take (as a function of β), denoted $\Phi_{\tilde{l}<L<l}^{\max}$, by setting $\kappa = 0$ (as discussed in section 5.1). We find that $\Phi_{\tilde{l}<L<l}^{\max}$ is given by

$$\Phi_{\tilde{l}<L<l}^{\max} \simeq \exp(-E)\tilde{l}^2. \tag{54}$$

This is the maximum mass of material that can be stored in rods of length L obeying $\tilde{l} < L < l$, i.e. those rods sufficiently long to be strongly convected by the flow but not so long that their rotation time exceeds their reaction time.

In order to obtain an approximate value for $\Phi_{L<\tilde{l}}^{\max}$ (the maximum of $\Phi_{L<\tilde{l}}$), we argue† that $\psi(L)$ is roughly flat, and can be approximated by $\psi(L) \simeq \exp(-E)$, for the isotropic population $L < \tilde{l}$. Hence $\Phi_{L<\tilde{l}}^{\max}$ can be approximated as

$$\Phi_{L<\tilde{l}}^{\max} \simeq \exp(-E)\tilde{l}^2 \tag{55}$$

which is of the same order of magnitude as $\Phi_{\tilde{l}<L<l}^{\max}$.

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† We observe that $\psi(0) = \exp(-E)$ (this can be confirmed by substitution into (47), with the appropriate form of F from (50)). We find an approximate value for $\psi(\tilde{l})$ by extrapolating (52) down to $L = \tilde{l}$. We are interested in the maximum mass solution and so we restrict our attention to the $\kappa = 0$ case. We find that, with $\kappa = 0$, $\psi(\tilde{l}) \simeq \exp(-E)$. Hence, assuming that the function $\psi(L)$ is roughly flat for the isotropic rods ($L < \tilde{l}$), and since we now know that $\psi(0) \simeq \psi(\tilde{l}) \simeq \exp(-E)$ we can approximate $\psi(L) \simeq \exp(-E)$ for $L < \tilde{l}$, at least when $\kappa = 0$ (which is the maximum mass solution, of interest here).

We can now write down an approximate value for $\Phi_{L<l}^{\max}$ which we will use to predict the existence of a phase transition. Using (55), (54) and (46) we obtain

$$\Phi_{L<l}^{\max} \simeq \exp(-E) l^2 (\beta \tau_{\text{break}} \Lambda_0)^{-2/\zeta}. \tag{56}$$

We notice from (56) that the maximum mass of material residing in rods with length $L < l$ (for a given flow rate β) is bounded. Similarly, by inversion, there exists a flow rate, denoted $\beta_{\max}$, which is the solution to (56) when all the material *could* just be contained in rods with $L < l$, i.e. $\Phi_{L<l}^{\max} = \Phi$. (In practice there are always some rods with $L > l$ but for $\beta = \beta_{\max}$ these remain a minority.)

Using (56) it can easily be shown that

$$\beta_{\max} \simeq D(\lambda_0) \tag{57}$$

with λ_0 the quiescent mean rod length, as before. We also find that the mass of material which can be contained in rods of length $L < l$ at flow rates above this maximum value is given by

$$\Phi_{L<l}^{\max} = \Phi \left(\frac{\beta}{\beta_{\max}} \right)^{-2/\zeta} \tag{58}$$

where Φ is the total mass in the system.

We can now ask the question 'What happens to any *extra* mass that may be present beyond this maximum value?'. We assume that as β is increased above $\beta_{\max}$ a small number of rods with $L > l$ will be created near the flow axis. These rods are sufficiently long that our slow reaction assumption does not apply; they cannot be described using (16). However, we may discuss their behaviour using the methods developed in sections 2 and 3 for the opposite limit of fast reactions. We will show that a gelation transition to a phase of extremely long, fully aligned rods is predicted, identical in character to the transition described in section 3.

In order to take account of any rods with $L > l$ that may be created we first look at the form of $\psi(L, u)$ for $l > L \gg \tilde{l}$. In this regime $\psi(L) = \int \psi(L, u)\, \mathrm{d}^2 u$ is given by (52) with $\kappa = 0$. We can rewrite $\psi(L, u)$ as $\psi(L, \theta)$, with θ the angle between u and the flow ($\hat{z}$) axis (by symmetry there is no ϕ dependence). Using (52), (44) and (49), and with $\theta \ll 1$, we find

$$\psi(L, \theta) \simeq \exp(-E)\mathrm{e}^{-\beta\theta^2/D(L)} \qquad \text{for } l > L \gg \tilde{l}. \tag{59}$$

We can see that the density of rods with $L \simeq l$ is strongly peaked near $\theta = 0$ with an RMS width obeying

$$\tilde{\theta} = (\beta \tau_{\text{break}} \Lambda_0)^{-1/2}. \tag{60}$$

We now argue† that any mass which, according to (58), cannot be accommodated in rods with $L < l$, goes into rods with $L > l$ and that these extra rods exist mainly in

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† This approximation is sensible provided: (i) rods with $L > l$ are effectively fixed in space, i.e. they break into fragments with $L \lesssim l$ before they have time to rotate significantly; (ii) rods with $L > l$ are only created in the region $|\theta| < \tilde{\theta}$. Assumption (i) is certainly true for rods with $L \gg l$ and it is a sensible starting point to assume that it is true for $L > l$. Assumption (ii) is also plausible since the concentration of rods with $L \sim l$ (59) is highly peaked in the region $|\theta| < \tilde{\theta}$ and a recombination type reaction, necessary to create a rod with length $L > l$, is proportional to the square of the concentration of reactants. These assumptions will introduce errors at the quantitative level but we expect our results to remain qualitatively accurate.

the region $|\theta| < \tilde{\theta}$. We can therefore write down an approximate expression for the mass of material residing in rods with $L > l$,

$$\Phi_{L>l} \simeq \int_{L=l}^{\infty} \int_{\theta=-\tilde{\theta}}^{\tilde{\theta}} L\psi(L,\theta) \,\mathrm{d}L\theta \,\mathrm{d}\theta. \tag{61}$$

We may further approximate the $\psi(L,\theta)$ in (61), describing rods with $L > l$, by the form derived in the fast reaction model of section 3. This is the relevant model for any population of rods with a mean length very much greater than l. We assume that the results of section 3 hold, even though in this case the rods are restricted to a small angular region. This assumption should be valid since, in the fast reaction limit, there is no coupling between rods with different orientations. Given this approximation (61), for the mass contained in long rods, is very similar to (25) (although (61) is an integral over a *small* angular region) and using the results of section 3 and (60) it is straightforward to evaluate the *maximum* value that $\Phi_{L>l}$ can take as a function of flow rate, denoted $\Phi_{L>l}^{\max}$. For brevity we take $\zeta > 3$ (although similar results can be obtained for $2 < \zeta \leqslant 3$). We find that

$$\Phi_{L>l}^{\max} \simeq \exp(-E)l^2(\beta\tau_{\text{break}}\Lambda_0)^{-1}. \tag{62}$$

Since we now know the mass of material that can be contained in either the long ($L > l$) or the short ($L < l$) rod populations, as a function of flow rate, we can finally proceed to calculate the critical flow rate as a function of mass. As discussed in section 3 the critical flow rate, denoted β_c, represents the flow rate for which the maximum mass (including both populations of finite rods, $L < l$ and $L > l$) coincides with the actual mass present in the system:

$$\Phi = \Phi_{L<l}^{\max} + \Phi_{L>l}^{\max} \qquad \text{defines transition} \tag{63}$$

whereas for $\beta > \beta_c$ we presume, as in section 3, that the excess mass resides in a gel phase of fully aligned long rods.

Using (58), (56) and (62) we can solve (63) to find that β_c is only marginally greater than $\beta_{\max}$. In fact†,

$$\frac{\beta_c}{\beta_{\max}} = 1 + \mathrm{O}(\Lambda_0^{\zeta-2}). \tag{64}$$

Hence, for the slow reaction limit, a flow-induced transition is reached almost as soon as there is a significant fraction of material in rods of $L > l$ (material for which the slow reaction approximation has, in fact, broken down).

We can now summarize, for the slow reaction regime, the behaviour of the system as the flow rate is varied (at constant mass). As the flow rate is increased from zero the rods become more aligned until near some flow rate $\beta_{\max}$ the mass *could* just all be contained in rods with $L < l$ (although there will already be some small fraction of rods with $L > l$ at this point). Above this flow rate some extra rods are created

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† We have assumed that (52) is the appropriate description of rods with $L \lesssim l$ at the transition. This is the case *provided* that $\bar{l} \ll l$. We now have an expression for β_c (65) which we can combine with (57) to show that $\beta_c\tau_{\text{break}} \gg 1$ and hence, via (46), we have $\bar{l} \ll l$. This result verifies, *a posteriori*, that (52) provides the appropriate description of rods with $L \lesssim l$.

(near the flow axis) with lengths $L > l$ and a treatment based purely on the slow reactions picture ceases to apply. As the flow rate is increased past β_{max} no dramatic behaviour is expected and the mean rod length near the flow axis increases smoothly. However above some second, critical flow rate, β_c, the material can no longer all be accounted for in rods of finite length and a gelation transition takes place (identical to the phase transition described in section 3). In fact we find (64) that $\beta_{max} \approx \beta_c$ and so the flow rate need only be increased marginally above β_{max} for the transition to occur.

We have thus shown that there exists a critical flow rate in the slow reaction regime above which a gel phase of infinite rods may arise. We may argue that since a phase transition occurs in both the fast reaction ($\Lambda_0 \gg 1$) and the slow reaction ($\Lambda_0 \ll 1$) regimes it is reasonable to assume that a similar transition occurs for all values of Λ_0. We can then use the results of this section and of section 3 to predict $\dot{\epsilon}_c$ for a general value of Λ_0. For $\zeta < 3$ we have $\dot{\epsilon}_c \propto \tau_{rot}^{-1}$ independent of whether $\Lambda_0 \ll 1$ or $\Lambda_0 \gg 1$. This suggests that $\dot{\epsilon}_c \propto \tau_{rot}^{-1}$ for all values of Λ_0. For $\zeta > 3$ we have $\dot{\epsilon}_c \propto (\tau_{rot}/\tau_{break})^{\zeta-3/\zeta} \tau_{rot}^{-1}$ for $\Lambda_0 \gg 1$ and $\dot{\epsilon}_c \propto \tau_{rot}^{-1}$ for $\Lambda_0 \ll 1$. We expect some smooth interpolation between these two forms for $\dot{\epsilon}_c$ to be appropriate in the crossover region $\Lambda_0 \sim 1$.

6. Conclusions

We have developed a theory describing the behaviour of micellar rods in flow. The steric interactions between rods are included only by way of the form of the angular diffusion constant and no long-range forces are included. We find that in elongational flow there exists a critical flow rate above which a gel phase of extremely long rods may arise. This critical flow rate is expected to exist in all regimes of micellar length since the mass of rods of finite length is bounded above by a decreasing function of flow rate. The critical flow rate, $\dot{\epsilon}_c$, is found to scale with the characteristic relaxation times of the quiescent material according to

$$\dot{\epsilon}_c \sim \begin{cases} \tau_{rot}^{-1} & \text{fast reactions, } \zeta < 3 \\ (\tau_{rot}/\tau)^{\zeta-3/\zeta} \tau_{rot}^{-1} & \text{fast reactions, } \zeta > 3 \\ \tau_{rot}^{-1} & \text{slow reactions.} \end{cases}$$

We have found that a similar transition does *not* exist in three-dimensional shear flow, although the problem is marginal. It seems likely that other inter-micelle interactions, even if small, could induce a transition in this case.

Very recent new experimental results on micellar rods in shear flow from the Bayreuth group [5] suggest the creation of a completely aligned phase of rods at extremely low shear rates (much less than the inverse of the characteristic rotation time of an average micelle). This is not consistent with any of the mechanisms considered in this paper. These results strongly suggest that some collective phenomenon (one involving many rods with a long relaxation time) is responsible. A natural candidate is the strong coupling that arises when electrostatic effects are present. Therefore these effects may play an important role in the behaviour of these systems under flow. Indeed, in some systems, they may contribute towards the steep rise in viscosity and birefringence, near some critical flow rate, which is observed experimentally [2, 3, 5]. Our model, as it stands, is inappropriate to describe these effects but should remain

valid, either for reverse systems [17] (surfactant in oil) or for non-ionic systems (neither of which exhibit strong Coulomb effects), as well as providing a starting point for the development of more refined theories. One possible extension, with which one might hope to model the Coulomb forces, is to include a nematic interaction term in the equation of motion. We hope to tackle this in future work.

Acknowledgments

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