# Growth of Dynamic Polymers (Micelles) in Shear Flow

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ABSTRACT: A nonequilibrium statistical mechanical theory for dilute micellized surfactant solutions undergoing shear flow is presented based on the wide separation of time scales of hydrodynamics and self-assembly "reaction". In two dimensions, a simple shear flow is found to promote cylindrical micelles to grow so that they can be better aligned in the flow direction. When the rodlike micelles acquire sufficient rotational kinetic energy in the shear, they break. Introduction of a micellar size cutoff due to this breakage smooths this shear-induced micellar growth. The phenomenon predicted here appears to be different from the experimental observations made by the Bayreuth group.

## I. Introduction

One of major problems in nonequilibrium statistical thermodynamics is how to describe a given thermodynamic solution undergoing a simple shear flow. No general theoretical principles have been found that can be employed to extend equilibrium statistical mechanics in the presence of shear. For other flows such as a potential flow, often one can arguably make a generic treatment of the flow effect on statistical thermodynamics by combining the Kramers' idea[1] with an equilibrium free energy formulation. There are many examples where a flow field affects molecular structures of polymer solutions. A uniaxial extensional flow has been shown[2-6] to drive the weak first-order Onsager phase transition in rodlike polymers to a critical point where polymers go from a less oriented to a more oriented state in a narrow concentration range via a second-order phase transition. Upon further increase in flow rate beyond a critical value, the transition becomes supercritical. Shear flow has been found to shift the point of phase separation in polymer solutions.[7] Flows should also affect the dynamic equilibrium of associating polymers (including self-assembling micellar systems). Here we study the coupling between the self-assembly thermodynamics of micelles and simple shear flow.

In recent experimental endeavors to explore flow phenomena of micellized surfactant solutions, a sudden increase in flow birefringence and a remarkable buildup of steady-state shear viscosity were observed at a "critical" shear rate.[8,9] This phenomenon is believed to be associated with the formation of a shear-induced supermolecular structure (SIS), i.e., the occurrence of a gellike phase. We have shown previously that a dilute rodlike micellar solution does not exhibit such a phase change in a unaxial extensional flow.[10] The goal of this paper is to develop further theoretical understanding of peculiar flow phenomena in a dilute solution of rodlike micelles. We study the effect of shear flow on the orientation of rodlike micelles which will affect the nonequilibrium self-reorganized aggregation of surfactant molecules. Our motivation for pursuing this research comes from the lack of consistent theories on viscoelasticity of micellar solutions. Very often experimental data on viscosity are interpreted according to a standard dynamic theory for polymer solutions without account for the change of micellar sizes due to flow.[11-14] Even polydispersity of micellar size distribution is frequently ignored for the sake of simplicity. Our present approach, incorporating equilibrium free energy formulation of micelles,[15,16] will provide a systematic theoretical treatment of flow properties of dilute rodlike micellar solutions.

For a dilute solution of cylindrical micelles, it is a good starting point to hypothesize that each micelle maintains its integrity during its hydrodynamic motion. Therefore the effect of shear flow on orientation of each individual micellar particle can be described by setting up its rotational diffusion equation (RDE). The solution of the RDE, once combined with equilibrium theories, will provide information not only on its alignment by flow but also on the relative preference for the constituent surfactants to be in that micelle. The nonequilibrium steady-state self-assembly is ultimately determined by the balance between all the species (micelles of various sizes) through the mass conservation, i.e., conservation of the total number of surfactant molecules. More discussion is provided in the beginning of section III.

For technical simplicity, we restrict ourselves to the case where all the micelles are confined to move in the plane of the *shear* flow defined by the flow direction $X$ and the direction $Y$ of the velocity gradient. This simplification allows us to fully explore the problem since the diffusion equation is exactly solvable in two dimensions.[17] In section II, an equilibrium thermodynamic theory of rodlike micelles is briefly described. Then we model a rodlike micelle as an anisotropic elastic particle in order to incorporate the viscous forces on it. Finally, a Smoluchowski (diffusion) equation is introduced to describe its rotational motion in a flow field. In section III, we show that the micellar sizes increase under the influence of the shear flow for a given total mole fraction (concentration) $\chi$ of surfactant molecules. A cutoff for the micellar size is introduced in section IV and its effect on the shear-induced micellar growth of surfactant solutions is discussed. The inflection point in the plot of averaged micellar size versus shear rate seems to suggest that the dilute micellar solution can only be driven to a supercritical state by the simple shear flow.

## II. The Model

**(i) Equilibrium Free Energy Formulation.** Before proceeding to discuss the mechanical model for our micelle-flow problem, let us first briefly review the free energy approach to equilibrium micelles. Consider the excess Helmholtz free energy $A$ of a cylindrical micellar solution

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given by[18]

$$\beta A/N = \sum_{n \geq n_{\min}}^{\infty} f_{\mathrm{eq}}(n)\{\beta\mu_n{}^0 + \ln [f_{\mathrm{eq}}(n)] - 1\} \quad (2.1)$$

where $\beta = 1/k_B T$, with $k_B$ the Boltzmann constant and $T$ the temperature, and $n_{\min}$ is the minimum aggregation number (corresponding to a spherical micelle). $f_{\mathrm{eq}}(n)$ is the mole fraction of micelles of size $n$, and $\mu_n{}^0$ is the standard chemical potential of an $n$ micelle. Then the mole fraction $\chi_n$ of surfactants forming $n$ micelles is simply $\chi_n = nf_{\mathrm{eq}}(n)$. In terms of $\chi_n$, the total mole fraction of surfactant molecules is given by

$$\chi = \chi_1 + \sum_{n \geq n_{\min}}^{\infty} \chi_n \quad (2.2)$$

where $\chi_1$ is the mole fraction of *free* surfactant molecules.

The distribution function $f_{\mathrm{eq}}(n)$ is obtained by minimizing the free energy (2.1) with the constraint (2.2). It is found that

$$f_{\mathrm{eq}}(n) = nf_{\mathrm{eq}}(n) = \chi_1{}^n \exp[\beta(n\mu_1{}^0 - \mu_n{}^0)] \quad (2.3)$$

where $\mu_1{}^0$ is the chemical potential of a free surfactant. The micellar chemical potential $\mu_n{}^0$ can be written in terms of the chemical potentials $\bar{\mu}_b$ and $\bar{\mu}_c$ for a surfactant in the bulk portion of a micelle and in the ends (i.e., "caps"), respectively

$$\mu_n{}^0 = (n - n_{\min})\bar{\mu}_b + n_{\min}\bar{\mu}_c = n\bar{\mu}_b + n_{\min}(\bar{\mu}_c - \bar{\mu}_b) \quad (2.4)$$

where $n_{\min}$ is the aggregation number of a spherical micelle. With use of (2.4) the equilibrium mole fraction $\chi_n$ is given by

$$\chi_n = n \exp(-\beta\delta)[\chi_1 \exp(\beta\Delta)]^n \quad (2.5)$$

Here the quantity $\delta = n_{\min}(\bar{\mu}_c - \bar{\mu}_b) > 0$ is the energy cost for $n_{\min}$ surfactants to form two caps, i.e., one spherical micelle, rather than to go into the micellar body. Therefore, $\delta$ precisely corresponds to the amount of energy needed to break up one micelle into two, producing two additional end caps. The magnitude of $\delta$ dictates the equilibrium micellar size since it directly evaluates the energy cost to have more shorter micelles (i.e., more end caps) as opposed to fewer longer ones. The energy $\Delta = \mu_1{}^0 - \bar{\mu}_b$ is the standard chemical potential difference between a free surfactant and one in the micellar body, and it measures the degree of tendency for surfactant molecules to aggregate in solution. It is stressed that the distribution is only for a dilute equilibrium solution of rodlike micelles.

**(ii) Diffusion Equation Model.** Our model consists of a rodlike micelle with a large aspect ratio in the plane of a simple shear flow, where the micelle can be regarded as an elastic rod represented by a string of $\omega_n$ beads interacting through harmonic springs along a straight line. A short description of the present model has been reported elsewhere.[19] Here we highlight the essential parts of our formulation. By considering the tension within the micelle due to viscous forces, we can write down the total deformation energy due to flow stretching[19]

$$U(\Gamma,n,\theta) = (\omega_n{}^5/240H)(\zeta_0\Gamma b \sin\theta \cos\theta)^2 \quad (2.6a)$$

where the "Hookean" constant $H$ is determined by $Hb^2 = 2\delta$, with $\delta$ defined below (2.5). Using the Stokes law $\zeta_0 = 3\pi\eta_s b$, we rewrite (2.6a) as

$$\begin{aligned}\beta U(\Gamma,n,\theta) &= \Gamma^2(3\pi\eta_s b^3/2k_B T)^2(1/480\beta\delta)\omega_n{}^5 \sin^2(2\theta) \\ &= 8.44 \times 10^{-28}(1/\beta\delta)n^5 \sin^2(2\theta)\Gamma^2 \quad (2.6b)\end{aligned}$$

In evaluating (2.6b) we have chosen the solvent viscosity $\eta_s$ as that of water $\eta_s = 10^{-2}$ poise, $b = 10$ Å, $n_{\min} = 20$, and $T = 300$ K. We note that the magnitude of this deformation energy depends upon how strongly the surfactants are associated with one another in the micelle, i.e., on the value of $\beta\delta$.

Cylindrical micelles in dilute surfactant solutions can be viewed as rods of different "fixed" lengths when their hydrodynamic movement is considered. The self-reassembly of surfactant molecules in response to the shear flow takes place on the time scale much larger than the characteristic hydrodynamic times such as the inverse rotational diffusivity and the inverse shear rate. Therefore it is acceptable to set up a Smoluchowski equation for orientational distribution of each micelle. The flow alignment of an $n$ micelle in the $X-Y$ plane of the shear flow $\mathbf{v}_0 = \Gamma y\mathbf{e}_x$ is described by the following Smoluchowski-type equation in two dimensions[19]

$$\frac{\partial\psi(n,\theta,t)}{\partial t} + \frac{\partial}{\partial\theta}J(\psi) = 0 \quad (2.7)$$

where $J(\psi)$ is the angular flux of the rodlike micelle defined by

$$J(\psi) = -D_r(n)\left[\left(\frac{\partial}{\partial\theta}\ln\psi + \beta\frac{\partial U}{\partial\theta}\right) + \left(\frac{\Gamma}{D_r}\right)\sin^2\theta\right]\psi \quad (2.8)$$

with $\theta$ being the angle between the micellar axis and the flow direction $X$ and $D_r$ the rotational diffusion constant for a micellar rod of length $\omega_n b$.[20] The steady-state solution of (2.7) can be readily obtained

$$\psi(\Gamma,n,\theta) = \exp[-E(\Gamma,n,\theta)]\,[C(\Gamma,n)\int_0^\theta \mathrm{d}\alpha \exp[E(\Gamma,n,\alpha)] + C'(\Gamma,n)] \quad (2.9)$$

where $C$ and $C'$ are integration constants. The function $E(\Gamma,n,\theta)$ is given by

$$E(\Gamma,n,\theta) = \beta U(\Gamma,n,\theta) + G(\Gamma,n)[\theta - ({}^1/{}_2)\sin(2\theta)] \quad (2.10)$$

with $G = \Gamma/2D_r$. Because of the indistinguishability of the two micellar ends, we can limit the range of $\theta$ to $(0,\pi)$ and apply the boundary condition $\psi(\Gamma,n,\theta = 0) = \psi(\Gamma,n,\theta = \pi)$, which provides a relationship between the two integration functions $C(\Gamma,n)$ and $C'(\Gamma,n)$:

$$C(\Gamma,n) = C'(\Gamma,n)\{(e^{\pi G} - 1)/\int_0^\pi \mathrm{d}\beta \exp[E(\Gamma,n,\beta)]\} \quad (2.11)$$

Equation 2.11, together with (2.10) and (2.9), specifies $\psi(\Gamma,n,\theta)$ up to the function $C'(\Gamma,n)$.

## III. Nonequilibrium Self-Assembly

The driving force for self-assembly of surfactant molecules essentially arises from the hydrophobic nature of amphiphilic particles. Energetically, surfactants prefer to aggregate in aqueous solution and form clusters so that their hydrocarbon "tails" can be shielded from water. Entropically, the molecules like to be free in the solution so that their translational and conformational entropies are maximized. There is also an energy penalty to be in the curved part (two ending caps in cylindrical micelles) of certain aggregates. The balance between these competing factors results in a size distribution for micelles that depends on the surfactant concentration and temperature. In the absence of a macroscopic (systematic) flow field, the thermodynamics of such an *equilibrium* self-assembly was formulated previously.[15,16] It is even possible to consider a straightforward extension of the free energy formulation[10] or reaction kinetics approach[21] for cylindrical micelles in an extensional (potential) flow. But it is not clear at all how to incorporate the effect of shear flow on the micellar self-assembling organization since the shear flow has a rotational component. The purpose of this paper is to shed some light on this issue by simplifying the problem to a two-dimensional analog. It should be emphasized that the same principle presented here is applicable in three dimensions without any additional conceptual difficulty.

Similar to the equilibrium case, formation of surfactant aggregates in flow depends upon (a) what gain there is for a surfactant to be in a micelle and what gain to be free in the solution, and upon (b) how the flow affects the probability for surfactants to go into micellar aggregates of various sizes. The first part (a) of the question can be dealt with on the basis of previous work.[15,16] For an extensional flow, the second part (b) is also not difficult[10] within the free energy consideration:[15,16] an increase in the free energy due to the potential flow can be determined according to the original idea of Kramers.[1] For nonpotential flows such as shear flow, it is nontrivial to treat the two factors (a) and (b) in a unified scheme. Here it is important to realize that, because of the wide separation of self-assembly reaction and flow-hydrodynamic time scales, the micellar integrity is maintained during hydrodynamic movement.

Let us proceed by introducing the distribution function $\chi_n(\Gamma,\theta)$, i.e., the mole fraction of surfactants forming micelles of aggregation number $n$ with orientational angle $\theta$ (with respect to the flow direction). Namely, $\chi_n(\Gamma,\theta) = N(\Gamma,n,\theta)/(N+N_w)$, where $N(\Gamma,n,\theta)$ is the number of such amphiphilic molecules, $N$ and $N_w$ are, respectively, the total number of amphiphiles and water molecules in the system. The mole fraction $\chi_n(\Gamma)$ of surfactants forming $n$ micelles is given by the angular integration of $\chi_n(\Gamma,\theta)$. This means surfactant molecules undergo self-assembling aggregation every time the flow condition is altered, i.e., for every value of $\Gamma$. Our first goal is to obtain $\chi_n(\Gamma)$ for different shear rates. In the decoupling approximation valid for dilute surfactant solutions, angular dependence of the size-orientation mole fraction is completely described by the orientation distribution $\psi(\Gamma,n,\theta)$. Therefore, we have

$$\chi_n(\Gamma,\theta) = \chi^0{}_n(\Gamma)\psi(\Gamma,n,\theta) \tag{3.1}$$

where the proportionality constant $\chi^0{}_n(\Gamma)$ is actually the mole fraction of surfactants forming $n$ micelles in the absence of any viscous forces (see (2.5))

$$\chi^0{}_n(\Gamma) = n\exp(-\beta\delta)[\exp(\beta\Delta)\chi_1(\Gamma)]^n \tag{3.2}$$

Here $\chi_1(\Gamma)$ is the mole fraction of free surfactants in the shear-flowing solution, and other parameters have previously been defined in section II (i). Thus we have the following full description of the mole fraction $\chi_n$ in presence of the shear flow[19]

$$\begin{aligned}\chi_n(\Gamma,\theta) = (1/\pi)n\exp(-\beta\delta)[\exp(\beta\Delta)\chi_1(\Gamma)]^n \times \\ \exp[-E(\Gamma,n,\theta)] \times \{[(e^{\pi G}-1)/\int_0^\pi \mathrm{d}\beta \times \\ \exp[E(\Gamma,n,\beta)]]\int_0^\theta \mathrm{d}\alpha\exp[E(\Gamma,n,\alpha)] + 1\}\end{aligned} \tag{3.3}$$

where the constant function $C'(\Gamma,n)$ in (2.9) and (2.11) is determined[19] by the fact that the effect of shear flow is zero in the flow direction $X$ and therefore $\chi_n(\Gamma,\theta=0,\pi) \propto \chi^0{}_n(\Gamma)$. It describes reorganization of surfactant molecules into a new collection of micellar aggregates as a result of the applied shear flow.

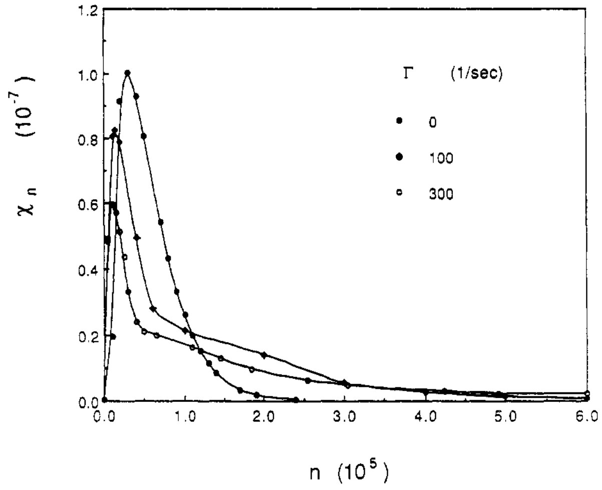

**Figure 1.** Micellar size distribution at concentration $\chi = 7.5 \times 10^{-3}$ for shear rates $\Gamma = 0$, 100, and 300 s$^{-1}$.

The *nonequilibrium* self-assembly occurs through the global balance between micelles of all sizes (all "species"). The corresponding mathematical statement is simply the mass conservation law that mole fractions of different "species" add up to the total mole fraction of surfactants

$$\chi = \chi_1 + \sum_{n \geq n_{\min}}^{\infty} \int_0^\pi \mathrm{d}\theta\, \chi_n(\Gamma,\theta) \tag{3.4}$$

Equations 3.3 and 3.4 provide the analytical foundation for discussing the shear flow effects on micellar self-assembly and are an extension of the equilibrium expressions 2.2 and 2.5. It is important to remark that the present formulation of nonequilibrium self-assembly of cylindrical micelles in dilute solution can be immediately adopted to treat the extensional flow case. Therefore our Smoluchowski diffusion-dynamics approach provides the highly sought after basis upon which the previous free energy theory[10] for extensional flows can be rigorously justified. In fact, this advancement in our theoretical understanding of nonequilibrium thermodynamics of surfactant aggregates will lead to a series of investigations into rheological properties of micelles.[22] There are at least two major difficulties in rheological studies of micelles, which are essentially related. One is how to deal with the large micellar polydispersity; the other is what the flow does to the averaged micellar sizes, i.e., how the polydispersity distribution depends on the flow. The flow-dependent orientation and size distribution $\chi_n(\Gamma,n,\theta)$ derived above is the answer to both questions.

For a quiescent solution, the equilibrium micellar sizes are determined by the magnitude of $\beta\delta$ and the degree of micellization is controlled by $\beta\Delta$ in (2.5). In our calculation, we take $e^{-\beta\delta} = 10^{-11}$ and $e^{\beta\Delta} = 10^5$. This corresponds to taking $\beta\delta = 25.3$ and $\beta\Delta = 11.51$. We choose the monomer mole fraction $\chi_1{}^{\mathrm{eq}}$ such that $e^{\beta\Delta}\chi_1{}^{\mathrm{eq}}$ equals 0.999 963 5. The total surfactant mole fraction is found to be $\chi^{\mathrm{eq}} = 7.5 \times 10^{-3}$, according to (2.2) and (2.5). For these values, the equilibrium (i.e., $\Gamma = 0$) size distribution $\chi_n{}^{\mathrm{eq}}$ is plotted as a function of aggregation number $n$ in Figure 1. The same micellar solution, when subject to a shear flow, can be studied by use of our theory developed above. We examine the effects of shear flow on self-assembly by calculating the modified micellar size distribution and the micellar orientational order parameter for different shear rates.

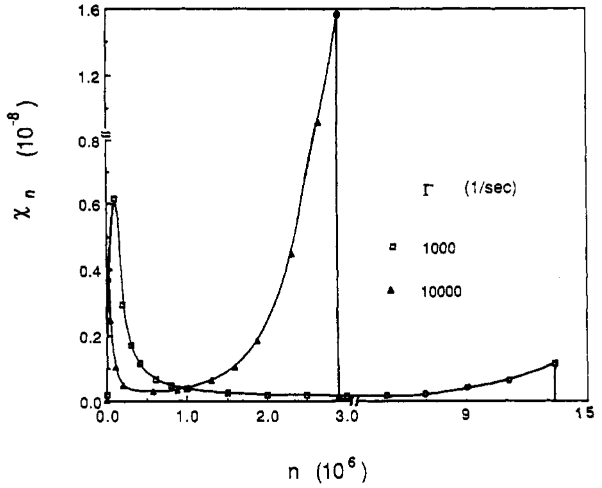

**Figure 2.** Micellar size distribution at concentration $\chi = 7.5 \times 10^{-3}$ for shear rates $\Gamma = 10^3$ and $10^4$ s$^{-1}$.

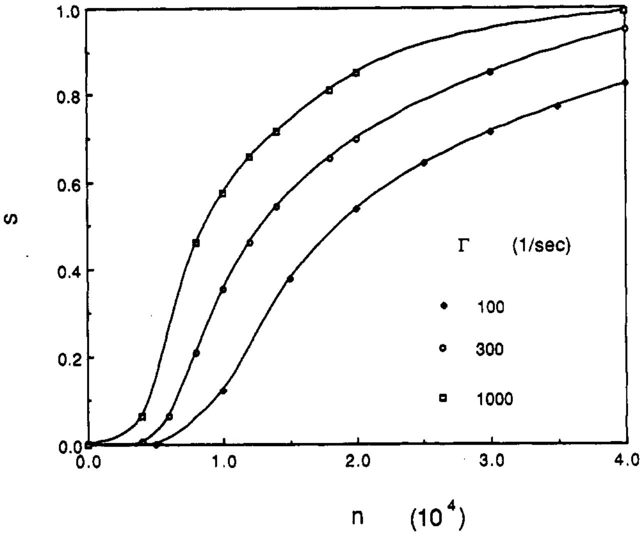

**Figure 3.** Orientational order parameter $S$ for different micellar sizes and three shear rates, $\Gamma = 100$, 300, and 1000 s$^{-1}$.

Consider shearing a dilute micellar solution of total mole fraction $\chi = 7.5 \times 10^{-3}$. For a moderately strong flow, we take the shear rate $\Gamma = 100$ s$^{-1}$. Now the mole fraction distribution $\chi_n(\Gamma,\theta)$ is completely specified by (3.3), with the function $E$ given by (2.10). The monomer mole fraction $\chi_1$ in (3.3) is adjusted so that eq 3.4 gives the same concentration $\chi = \chi^{\mathrm{eq}} = 7.5 \times 10^{-3}$ after summation over the aggregation number. We find, after a trial and error procedure, that a value of $\chi_1 e^{\beta\Delta}$ equal to 0.999 996 0 produces the same surfactant concentration as in the equilibrium (the quiescent solution) case. Now we plot the size distribution $\chi_n(\Gamma)$ for $\Gamma = 100$ s$^{-1}$ in Figure 1 as well. The application of such a shear flow results in a remarkable change in the micellar size distribution. In order to explain the trend let us introduce and discuss the degree of micellar-rod orientation as a function of micellar size and shear strength.

The orientational order parameter $S_n$ for micelles of size $n$ is defined as

$$S_n(\Gamma) = \int_0^\pi \mathrm{d}\theta\,(2\cos^2\theta - 1)\chi_n(\Gamma,\theta) \Big/ \int_0^\pi \mathrm{d}\theta\,\chi_n(\Gamma,\theta) \tag{3.5}$$

where $\chi_n(\Gamma,\theta)$ has been given in (3.4). We plot $S_n(\Gamma)$ versus $n$ for three values of $\Gamma$ in Figure 3. For $\Gamma = 100$ s$^{-1}$, micelles with aggregation number smaller than $10^4$ still assume random orientation and the strong alignment starts at $3 \times 10^4$. For higher shear rate of $\Gamma = 300$ or 1000 s$^{-1}$, the micelles are aligned at smaller aggregation numbers. For example, when $\Gamma = 1000$ s$^{-1}$, micelles with $n = 10^4$ are already strongly aligned. Now we are in position to discuss the influence of shear flow on micellar size distribution. Compare the curve $\Gamma = 0$ with that of $\Gamma = 100$ in Figure 1: When the shear flow with $\Gamma = 100$ is turned on, the population of small micelles remains essentially unchanged, but the micelles of sizes between $5 \times 10^4$ and $10^5$ (which exist in large numbers before the shear is on) start to combine to form few yet much longer (with $n > 10^5$) ones. The population of those long ones starts to buildup roughly at the aggregation number $n = 10^5$ at the expense of the shorter micelles. According to Figure 3, micelles with $n \geq 10^5$ are virtually completely aligned. These long ones with almost perfect alignment in the flow direction assume the most probable state. For $\Gamma = 100$ s$^{-1}$, a large number of micelles with intermediate aggregation numbers would pay more energy in the shear flow than the entropic gain that they would receive by retaining their relatively small sizes. Therefore the distribution $\chi_n(\Gamma)$ shifts to a larger population of *long* micelles than in equilibrium.

## IV. Shear-Induced Micellar Growth

From the above discussion, we see clearly that the longer the micelle, the better it is aligned by the shear flow. Likewise, the stronger the flow field, the more aligned the micelles are. When a micelle is almost completely aligned ($\theta \sim 0$), the deformational potential given by (2.6a) is vanishing. Therefore, we anticipate that perhaps there is a critical value $\Gamma_c$ for the shear rate beyond which infinitely *long* micelles start to form so that perfect alignment can be achieved to minimize the energy cost. If this indeed happens, then above the critical shear rate $\Gamma_c$ the free surfactants will coexist with the infinitely long micelles. In this case, the chemical potential of a *free* surfactant ("monomer") equals $\bar{\mu}_b$, that of a surfactant in an infinite micelle. The mathematical expression of this statement is simply $\chi_1 e^{\beta\Delta} = 1$, or taking the logarithmic, $\ln \chi_1 + \mu_1{}^0 = \bar{\mu}_b$, where $\mu_1{}^0$ is the standard chemical potential of a free monomer. The search for the critical shear rate $\Gamma_c$ proceeds by setting $\chi_1 e^{\beta\Delta} = 1$ in (3.4) and selecting a particular value for $\Gamma_c$ so that the summation leads to $\chi = 7.5 \times 10^{-3}$. We find $\Gamma_c = 300$ s$^{-1}$ for this concentration of surfactant solution. Conversely, for any value of $\Gamma$ there is a critical concentration $\chi_c$ determined from (3.4) by setting $\chi_1 e^{\beta\Delta} = 1$. Upon approaching this critical shear rate $\Gamma_c = 300$ s$^{-1}$, the size distribution starts to develop a long tail at large micellar sizes, as illustrated in Figure 1.

For clarity of presentation, we have left out an important piece of detail in the preceding discussion. In section II (ii), we set up a condition $(^1/_2)Hb^2 = \delta$ for the breakage of a micelle; that is, it will break if its neighboring constituent surfactants exceed a separation of the molecular distance $b$ due to flow stretching. Since the shear flow has a rotational component, it is not effective for tearing micelles apart. So far we have not included any mechanism for micellar breakage. Such a physical consideration will introduce a shear-rate dependent cutoff for the micellar size. The last curve (the critical one) in Figure 1 has been plotted by using a cutoff $n^*(\Gamma_c)$. We proceed to derive the functional form of $n^*(\Gamma)$ before discussing what happens when $\Gamma > \Gamma_c = 300$ s$^{-1}$.

An $n$ micelle rotates freely in the shear flow with angular velocity $\Gamma/2$, and its kinetic rotational energy, on the average, is of the order

$$K(n) = (^1/_{24})M(n)(\omega_n b)^2(\Gamma/2)^2 \tag{4.1}$$

where $M(n)$ is the mass of the micelle, proportional to the aggregation number $n$ and $\omega_n b = (n/n_{\min})b$ is its length. The relationship between $M(n)$ and $n$ is $M(n) = nm_s$ where $m_s$ is the mass of a surfactant, typically on the order of a few hundreds in atomic units. Therefore, the micellar kinetic energy $K$ scales as $n^3$ and reduces to $K/4$ when the $n$ micelle breaks (in the middle, say) into two. If $\Delta K = -3K/4$ is large, it can provide enough energy needed to break the $n$ micelle, which is around $\delta$. This argument allows us to set up a cutoff $n^*(\Gamma)$ for the maximum micellar size for a given value $\Gamma$ of the shear rate:

$$n^* \sim [\delta(96/m_s)(n_{\min}/b)^2]^{1/3}\Gamma^{-2/3} = 1.34 \times 10^9\Gamma^{-2/3} \quad (4.2)$$

where $\delta$ has previously been chosen as $25.3k_BT$ with $T$ = 300 K, $m_s$ is taken as large as $10^3$, and $\Gamma$, as usual, is given in the units of inverse second. Below $\Gamma_c$, even the largest micelles is still much smaller than an $n^*$ micelle (e.g., see the $\Gamma = 100\ \text{s}^{-1}$ curve in Figure 1 where, according to (4.2), $n^* = 6.2 \times 10^7$), and consequently the micelles do not break.

For $\Gamma \geq \Gamma_c$, the infinite micelles would form if no cutoff $n^*(\Gamma)$ was implemented. From now on, we introduce the cutoff $n^*(\Gamma)$ of (4.2) to replace the infinity in the summation (3.4). It is crucial to remark here that once such a cutoff is put in, the "critical point" defined by $\Gamma_c$ no longer assumes the ordinary meaning of a second-order phase transition. But we will continue to use the $\Gamma_c = 300\ \text{s}^{-1}$ notation for convenience. At $\Gamma_c$, $n^*(\Gamma_c)$ is much larger than $6 \times 10^5$ and the total range of the micellar size distribution at $\Gamma_c$ is only partially covered in Figure 1. If its complete curve is plotted, the area under it would have the same value (the total concentration $\chi$) as that under the other two curves.

After the cutoff $n^*(\Gamma)$ for micellar size is introduced, setting $\chi_1 e^{\beta\Delta} > 1$ becomes permissible so that our discussion can go beyond into the $\Gamma > \Gamma_c$ regime. In Figure 2, the size distributions for $\Gamma = 10^3\ \text{s}^{-1}$ and $\Gamma = 10^4\ \text{s}^{-1}$ are plotted. Of course, one can be more sophisticated about the introduction of a cutoff $n_c$. For example, the distribution for $\Gamma = 10^4\ \text{s}^{-1}$ should fall off continuously. One can take the Boltzmann distribution $f(n_c) = A \exp[-\beta[K(n_c) - K(n^*)]]$ as the appropriate form for the distribution of $n_c$ where the constant $A$ is determined by the normalization condition $\int_{n^*}^{\infty} \mathrm{d}n_c f(n_c) = 1$. Since the $K$'s in $f(n_c)$ are on the order of $\delta$ and $\beta\delta \gg 1$, the distribution $f(n_c)$ very quickly drops to zero and therefore it is a good approximation to simply cut the micellar sizes at $n^*$.

Finally, we calculate the mean micellar size $\bar{n}(\Gamma)$ as a function of the shear rate $\Gamma$. For the polydisperse micellar size distribution, the correct definition for the mean size should be the number *average*, not weight average. Therefore it follows that

$$\bar{n}(\Gamma) = \sum_{n \geq n_{\min}}^{n^*(\Gamma)} \int_0^{\pi} \mathrm{d}\theta\, \chi_n(\Gamma,\theta) \left[ \sum_{n \geq n_{\min}}^{n^*(\Gamma)} \mathrm{d}\theta (1/n)\chi_n(\Gamma,\theta)\right]^{-1} \quad (4.3)$$

where the mole fraction $\chi_n(\Gamma,\theta)$ of surfactants is given by eq 3.4 and $n^*(\Gamma)$ is defined by (4.2). We calculate $n^*(\Gamma)$ for six different values of $\Gamma$ and plot $n^*(\Gamma)$ versus $\Gamma$ in Figure 4. The inflection point in this curve $\bar{n}(\Gamma)$ clearly suggests a supercritical micellar growth in shear flow since we expect a similar trend for the averaged orientation order parameter $\bar{S}$.[22] The supercriticality actually arises directly from the existence of a cutoff for the micellar size. If the cutoff was many times bigger than it is, there might be a critical point and a second-order phase transition. But there can be no first-order transition unless no size cutoff exists. Physically such a cutoff $n^*(\Gamma)$ should appear as we have argued in (4.2). Thus, the dilute surfactant solution is supercritical and the micellar breakage due to the fluid rotation in the shear flow acts as an external field. In the liquid–vapor phase diagram (taking a van der Waals gas for instance), the system undergoes a crossover from the first-order phase transition (vapor condensation) through the critical point (second order) to the supercritical regime, driven by the "external field", temperature. A similar situation occurs when an Onsager nematic fluid is brought into a uniaxial extensional flow, where the flow, being the external field, takes the weakly first order Onsager transition to the second order at some critical flow rate $\gamma$, and upon further increasing in $\gamma$, the system become supercritical.[2-6] Other examples can be found in studies of the substrate effect and of the effect of broken symmetry on nematic ordering of liquid crystals and grafted rods, where the substrate and impenetrable surface play the role of external field in these two respective cases.[23,24]

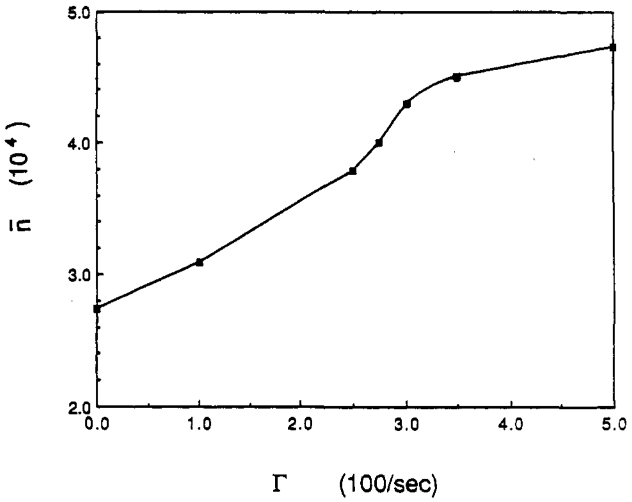

**Figure 4.** Number-averaged micellar sizes at different shear rates. The inflection point occurs at $\Gamma_c$ = 300.

## V. Conclusion

Theoretical analyses of dilute rodlike micellar solutions in shear flow presented in this paper are the first attempt to formulate a first principles hydrodynamic theory of such micelle-flow systems.[25] It predicts supercritical micellar growth in dilute surfactant solutions subject to shear flow. The theoretical results, obtained here based on the two-dimensional model, cannot be expected to be quantitatively reliable although they are believed to be qualitatively correct. There is no fundamental difficulty in generalizing our treatment to three dimensions.[22]

According to Hoffmann et al.,[9] the SIS has been observed only in ionic surfactant solutions where the micelles contain charges. Depending on salt concentration and temperature, Debye screening length varies and the electrostatic intermicellar interaction may become very strong. Therefore the charges on micelles could play an indispensable role in the occurrence of the shear-induced supramolecular structure. Furthermore, since the SIS occurs at a shear rate much lower than[9] the rotational relaxation rate of micelles, the mechanism for SIS may be very different from that presented here. The supercritical increase of micellar sizes with shear rate is predicted here to occur only at relatively high shear rates and consequently is perhaps more relevant to the understanding of turbulent drag reduction by micelles and to the molecular structure formation in turbulent surfactant solutions.[26,27]

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