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Microemulsions under steady shear flow

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Abstract Dynamic response of microemulsions to shear deformation on the basis of two-order-parameter time dependent Ginzburg–Landau model is investigated by means of cell dynamical system approach. Time evolution of anisotropic factor and excess shear stress under steady shear flow is studied by changing shear rate and total amount of surfactant. As the surfactant concentration is increased,

overshoot peak height of the anisotropic factor increases whereas that of the excess shear stress is almost unchanged.

Key words Microemulsions – rheology – shear flow – Ginzburg–Landau model

Microemulsions being mixture of oil, water and surfactant are known to exhibit various interesting mesoscopic structures depending on the temperature or the composition [1]. For relatively low concentration of surfactant and if the volumes of oil and water are not very different, microemulsions form a bicontinuous structure where a multiply connected randomly oriented monolayer of surfactants separate oil-rich and water-rich subvolumes with a mesoscopic length scale (10 ~ 100 nm).

When one applies an external flow to the microemulsion system, its mechanical response is deeply affected by its internal structure. Using a single-order-parameter time-dependent Ginzburg–Landau (TDGL) model, Mundy et al. have investigated rheological properties of microemulsions theoretically [2]. In their model, the order parameter represents the concentration difference between oil and water, and the presence of surfactants is taken into account through the surface tension parameter. Their work has been extended by Pätzold and Dawson, and it was shown that the microemulsions behave in an essentially non-Newtonian manner [3].

In this proceeding, we investigate the rheological properties of microemulsions using a two-order-parameter TDGL model. The two-order-parameter Ginzburg–Landau free energy for microemulsions has already been proposed by Laradji and his coworkers to study their microphase separation dynamics [4]. However, the proposed free energy is not applicable to the rheological study, since the pattern does not deform even in the presence of a flow [5]. This is related to the fact that their free energy is unbounded from below for the configurations with large surfactant concentration at the oil/water interfaces [1]. Thus, we use a different free energy which has been proposed in our previous paper as an improved model [5].

Let $\psi(\mathbf{r})$ describe the local concentration difference between oil and water, and $\rho(\mathbf{r})$ the local surfactant concentration. What we have assumed in our model is that (i) the profiles of ψ and ρ at oil/water interfaces do not depend on the average values of ψ and ρ (denoted hereafter as $\bar{\psi}$ and $\bar{\rho}$, respectively) and that (ii) the coarse-graining dynamics of ψ based on the free energy becomes slow when the amplitude of ρ at the interface takes a certain

saturated value. One of the minimum models which reproduce the properties of microemulsions is [5]

$$F = \int d\mathbf{r} [w(\nabla^2\psi)^2 + d(\nabla\psi)^2 - a\psi^2 + u\psi^4 + e\rho^2(\rho - \rho_s)^2 - s\rho(\nabla\psi)^2], \quad (1)$$

where w, d, a, u, e, ρ_s and s are positive constants. The first term $w(\nabla^2\psi)^2$ with positive w prevents the model from becoming unbounded, whereas the double-minimum potential $e\rho^2(\rho - \rho_s)^2$ guarantees that ρ locally takes either 0 or ρ_s . The last term $-s\rho(\nabla\psi)^2$ favors the surfactants to sit at the oil/water interfaces [4].

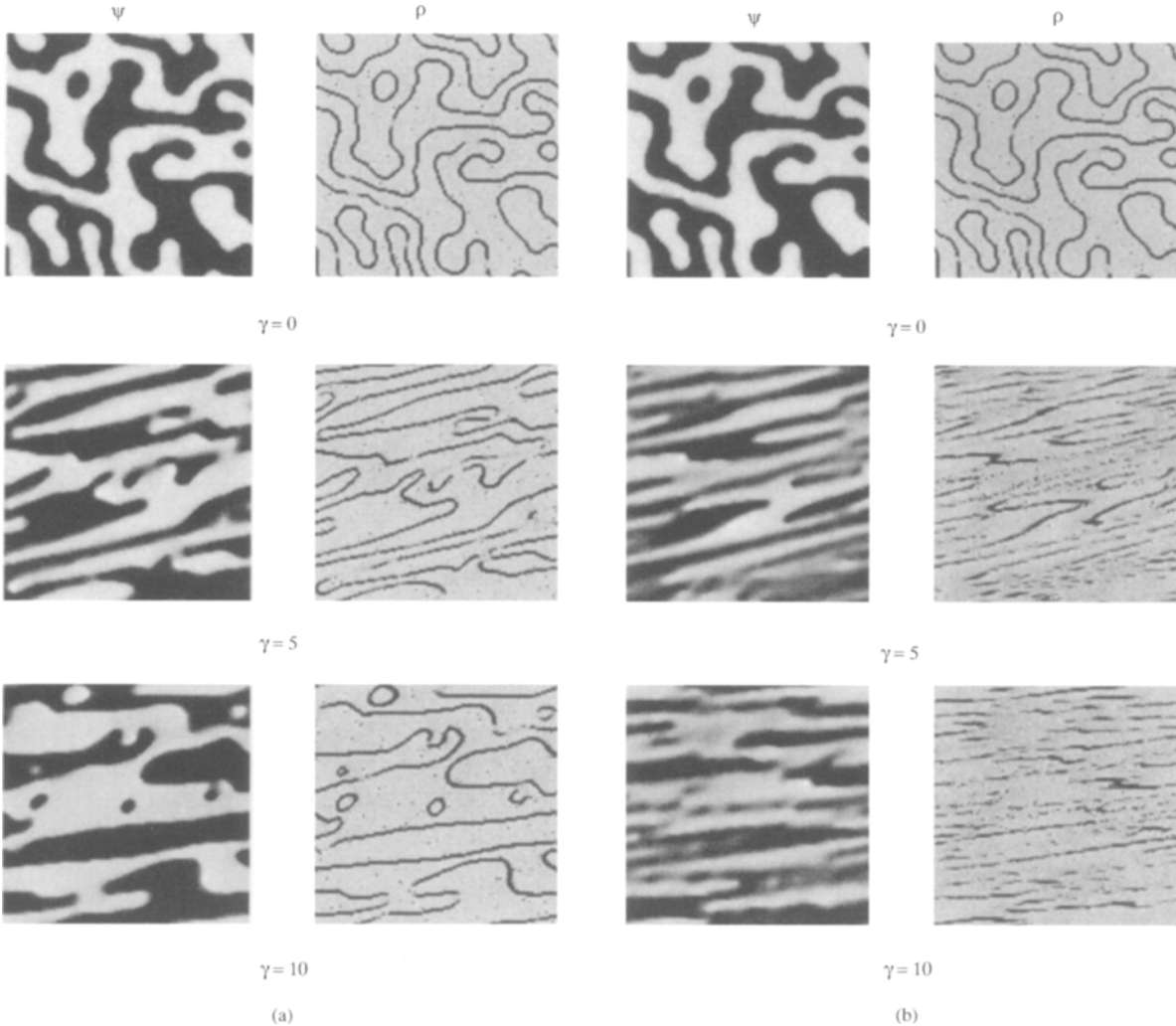
For the evolution of $\psi(\mathbf{r}, t)$ and $\rho(\mathbf{r}, t)$, we assume the standard TDGL equations with a macroscopic flow \mathbf{v} . Since both ψ and ρ are conserved quantities, TDGL

equations are given by

$$\begin{aligned} \frac{\partial\psi}{\partial t} + \nabla \cdot (\mathbf{v}\psi) &= M_\psi \nabla^2 \frac{\delta F}{\delta\psi} + \eta_\psi(\mathbf{r}, t), \\ \frac{\partial\rho}{\partial t} + \nabla \cdot (\mathbf{v}\rho) &= M_\rho \nabla^2 \frac{\delta F}{\delta\rho} + \eta_\rho(\mathbf{r}, t). \end{aligned} \quad (2)$$

Here M_ψ and M_ρ are transport coefficients, η_ψ and η_ρ represent the thermal noise which satisfy the fluctuation-dissipation theorem $\langle \eta_{\psi(\rho)}(\mathbf{r}, t) \eta_{\psi(\rho)}(\mathbf{r}', t') \rangle = -2k_B T M_{\psi(\rho)} \times \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t')$, where k_B is the Boltzmann constant and T the temperature. As regards the macroscopic flow in Eq. (2), we consider a simple shear flow $v_x(\mathbf{r}) = \dot{\gamma}y$, $v_y = v_z = 0$, where the shear rate $\dot{\gamma}$ is the time derivative of the strain γ . In our work, we have entirely ignored the

Fig. 1 Time evolution of ψ (left) and ρ (right) for (a) $\bar{\rho} = 0.1$, $\dot{\gamma} = 2 \times 10^{-4}$ ($\dot{\gamma}\tau_0 = 0.1$) and (b) $\bar{\rho} = 0.1$, $\dot{\gamma} = 2 \times 10^{-3}$ ($\dot{\gamma}\tau_0 = 1$)



hydrodynamic interactions which might play an important role in microemulsions.

We solved the above time-evolution equations numerically by using the “cell dynamical system” approach proposed by Oono et al. [6]. The details of the numerical method have been mentioned in our previous paper [5]. The simulation conducted here is essentially equivalent to solving Eq. (2) with the parameter values fixed as $w = 0.1$, $d = 0.25$, $a = 0.3$, $u = 0.18$, $e = 0.125$, $\rho_s = 1$, $s = 0.25$ and $M_\psi = M_\rho = 0.05$. The noise terms are treated as a random noise with an amplitude 0.02. We fixed $\bar{\psi}$ as $\bar{\psi} = 0$, whereas $\bar{\rho}$ has been changed as $\bar{\rho} = 0.1, 0.2, 0.3$ and 0.4 . Here, we restricted ourselves to a two-dimensional system. The system size is chosen as 128×128 , and the sheared-periodic boundary condition is imposed both for ψ and ρ . We first started from random uniform distributions of ψ and ρ in the range $[\bar{\psi} - 0.01, \bar{\psi} + 0.01]$ and $[\bar{\rho} - 0.01, \bar{\rho} + 0.01]$, respectively. We relaxed them according to Eq. (2) without any shear flow up to $t = 5 \times 10^5$, and then applied the shear flow with a constant shear rate $\dot{\gamma} = 2 \times 10^{-4}$, 5×10^{-4} , 1×10^{-3} and 2×10^{-3} . Since we have not included any hydrodynamic interactions, our model lacks a bare viscous time scale against which we can compare these shear rates. Nevertheless, we can choose the model intrinsic time scale τ_0 as the inverse of the initial growth rate of the most unstable mode, which is estimated as $\tau_0 \approx 5.0 \times 10^2$ for the above parameter values. The investigated shear ranges from weak to medium shear ($\dot{\gamma}\tau_0 = 0.1 \sim 1$).

Typical time evolutions of ψ and ρ are shown in Fig. 1 for (a) $\bar{\rho} = 0.1$, $\dot{\gamma} = 2 \times 10^{-4}$ ($\dot{\gamma}\tau_0 = 0.1$) and (b) $\bar{\rho} = 0.1$, $\dot{\gamma} = 2 \times 10^{-3}$ ($\dot{\gamma}\tau_0 = 1$). By changing $\bar{\rho}$ and $\dot{\gamma}$, we found the following general behaviors. When the shear rate is small (Fig. 1a), surfactants move under the flow keeping themselves attached to the oil/water interfaces. The total amount of the interface does not seem to change appreciably during the deformation. On the other hand, when the shear rate is large (Fig. 1b), some surfactants are blown off the interfaces by the shear. The coagulation and break-up processes take place as has been observed in the spinoidal decomposition under steady shear flow [7], and the total amount of the interface increases.

Given the evolving patterns, we have evaluated the anisotropic factor defined by [2, 3]

$$Q_{xy} = -2d \left\langle \frac{\partial\psi}{\partial x} \frac{\partial\psi}{\partial y} \right\rangle - 4w \left\langle \frac{\partial^2\psi}{\partial x\partial y} \nabla^2\psi \right\rangle, \quad (3)$$

where $\langle \dots \rangle$ denotes the average over the total volume. Although this quantity essentially represents the xy -component of the macroscopic excess stress tensor in the case of one-order-parameter model, this is not the case in the present model since there should be a contribution to the

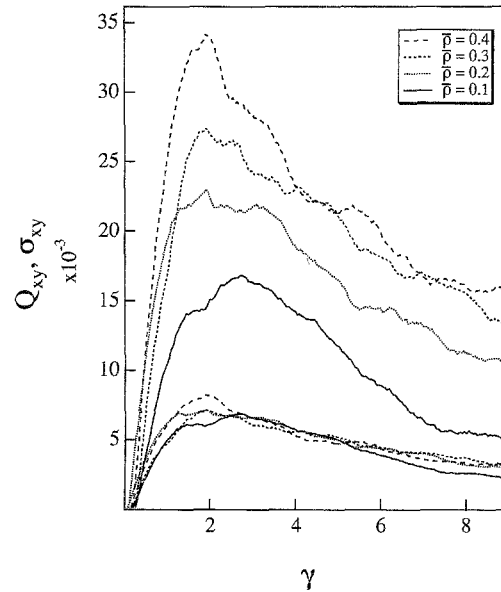


Fig. 2 The anisotropic factor Q_{xy} (upper 4 curves, see Eq. (3)) and the shear stress σ_{xy} (lower 4 curves, see Eq. (4)) as a function of the shear strain $\gamma = \dot{\gamma}t$ for fixed $\dot{\gamma} = 2 \times 10^{-4}$ ($\dot{\gamma}\tau_0 = 0.1$) and $\bar{\rho} = 0.1, 0.2, 0.3, 0.4$

stress due to the non-local coupling term in Eq. (1). Nevertheless, the problem of stress division between ψ and ρ is theoretically not yet clear. Instead, we propose here the following quantity:

$$\sigma_{xy} = -2 \left\langle (d - s\rho) \frac{\partial\psi}{\partial x} \frac{\partial\psi}{\partial y} \right\rangle - 4w \left\langle \frac{\partial^2\psi}{\partial x\partial y} \nabla^2\psi \right\rangle, \quad (4)$$

which is assumed to express the excess shear stress. Figure 2 shows the plots of Q_{xy} and σ_{xy} as a function of the shear strain γ for several values of $\bar{\rho}$. Here the shear rate is fixed as $\dot{\gamma} = 2 \times 10^{-4}$ ($\dot{\gamma}\tau_0 = 0.1$). In the time region where Q_{xy} and σ_{xy} increase the domains are elongated, whereas these quantities start to decrease once the burst and the recombination take place. We observed that the strain giving the peak position of Q_{xy} and σ_{xy} is almost constant throughout the present simulation ($\gamma \approx 2$). On the other hand, the peak height of Q_{xy} is larger than that of σ_{xy} as a whole. $\bar{\rho}$ dependencies of the peak height of Q_{xy} and σ_{xy} are also different; the peak height of Q_{xy} increases linearly with $\bar{\rho}$, while that of σ_{xy} is almost independent of $\bar{\rho}$. However, a clear shear rate dependence of the peak height of σ_{xy} could be observed as in ref. [7].

Details of the present work have been published elsewhere [8].

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