

## Rheological behavior of microemulsions

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We study the stationary and transient behaviors of a microemulsion phase subjected to a shear flow. The system is described by a diffusion-convective equation that generalizes the usual Cahn-Hilliard equation. Nonlinear terms are treated in a self-consistent approximation. Shear, first and second normal stresses are calculated as momenta of the structure factor. Shear thinning is observed in stationary conditions. After a Newtonian regime at small values of the shear rate, the excess viscosity decreases when the shear rate becomes of the order of the inverse of the relaxation time of the system without flow. In transient regimes, when the flow is applied starting from a quiescent state, we find that the shear stress reaches a maximum before decreasing to a constant value.

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### I. INTRODUCTION

The rheological behavior of complex fluids such as polymer solutions, polymer melts, emulsions is of considerable interest both in technology and in basic research [1]. While the behavior of the stress response to applied flows is of fundamental importance in many applications, it also reflects the existence of mesoscopic structures in the fluid and is intimately related to its constitution. For example, when a shear flow is applied to a polymer solution, the stress first reaches a maximum and then relaxes to a constant value [2]. This phenomenon, at small strain, is related to the entanglement of the polymer network which is distorted by the flow with a resulting increase of the stress. At larger values of the strain, however, the disentanglement of the system is favored and the stress is observed to decrease. In general, non monotonic relaxational properties of the stress are typical of complex fluids which are also characterized, in stationary conditions, by non-Newtonian behavior. The effective viscosity depends on the applied shear flow, and different behaviors can be observed [1].

In this paper we consider the rheological behavior of the microemulsion phase in both stationary and transient conditions. In ternary self-assembling systems, the surfactant forms interfaces between oil-like and waterlike domains. These interfaces, in the microemulsion phase, constitute an intertwined bicontinuous structure disordered on large scales but with mesoscopic order on distances of the order of 500 Å [3]. The observed structure factor is given by

$$I(q) \sim \frac{1}{a + gq^2 + cq^4} \quad (1)$$

which, for  $g < 0$ , has a maximum at  $q = \sqrt{|g|/2c}$  [4–6]. In real space, this corresponds to the two-point correlation function

$$G(r) = \frac{d}{2\pi r} e^{-r/\xi} \sin\left(\frac{2\pi r}{d}\right), \quad (2)$$

where  $\xi$  plays the role of the usual correlation length in disordered phases,  $d$  is related to the size of coherent regions of oil or water domains, and typical values of the ratio  $d/\xi$  are in the interval 2–4.

The behavior of the stress in the microemulsion phase was first considered in Ref. [7] and then in Ref. [8] where also the two-time correlation functions were studied. Here we complete the analysis of the steady state of Ref. [8] and consider also the transient behavior. Our approach is based on the use of a continuum free-energy functional and is similar to that of Onuki and Kawasaki [9], applied also to evaluate the effects of a shear flow on copolymer melts [10–12], on the disorder-lamellar transition [13,14], and on the phase separation of binary mixtures [15].

We consider a Cahn-Hilliard equation generalized by the presence of a convective term. Hydrodynamical effects are neglected; moreover, the surfactant is assumed to relax faster than the other components of the mixture so that its degrees of freedom are not explicitly considered. Nonlinear terms, which become relevant close to transition lines, will be treated self-consistently. A renormalization procedure is introduced and the system is studied in terms of the physical variables  $\xi, d$  of the case without flow.

Our main result for the stationary regime is the behavior of the constitutive curve. Shear thinning, which is the decrease of the effective viscosity when the shear rate is increased, is observed in two different ranges of the shear rate. It first occurs at a value of the shear rate of the order of the inverse of the relaxation time of microemulsions without shear. The morphological changes occurring, when the shear rate is increased, can be deduced by the patterns exhibited by the structure factor. In the transient behavior after the application of the flow, at sufficiently high shear rates, we observe a maximum in the shear stress followed by a relaxation to a constant value, analogous to what is observed in other systems. We have also studied the behavior of the stress tensor when, starting from a stationary state with shear, the flow is switched off.

The paper is arranged as follows. In Sec. II we specify the model and solve formally the dynamical equation for the

structure factor. Results for the stationary regime and for the transients are, respectively, described in Secs. III and IV. Sec. V contains some conclusions.

## II. THE MODEL

Our study of rheological properties of microemulsions is based on a functional Landau-Ginzburg approach with one scalar order parameter  $\phi(\vec{x})$  representing the concentration difference between oil and water. We consider the Hamiltonian

$$\mathcal{H}[\phi] = \int d^3x \left\{ \frac{1}{2} [a_2 \phi^2 + (g_0 + g_2 \phi^2)(\vec{\nabla} \phi)^2 + c(\nabla^2 \phi)^2] + \frac{\lambda}{4} \phi^4 \right\} \quad (3)$$

that has been largely demonstrated to well describe equilibrium properties of ternary mixtures [3]. Here we briefly discuss the properties of this Hamiltonian relevant for the microemulsion phase. The expression (3) differs in the gradient terms from the usual Landau-Ginzburg Hamiltonian used to study binary mixtures. A negative value of the function  $g(\phi) = g_0 + g_2 \phi^2$  ( $g_2 > 0$ ) favors the appearing of interfaces. In particular, the value of  $g_0$  can be related to the amount of surfactant present in the system. The term proportional to  $c > 0$  assures stability at large momenta and weights the curvature of interfaces.

The presence of the quartic terms  $\phi^4$  and  $\phi^2(\vec{\nabla} \phi)^2$ , which also in a disordered phase could have a role in the proximity of a transition line, makes impossible an exact determination of the two point correlation functions. However, following Ref. [7], it is possible to use a renormalization procedure based on a self-consistent approximation to find an expression for the equilibrium scattering function and for the two-point correlation function in real space. For the first, defined as  $\phi(\vec{k})$  the Fourier transform of  $\phi(\vec{x})$ , it is found that

$$S(k) \equiv \langle \phi(\vec{k}) \phi(-\vec{k}) \rangle = \frac{T}{a_r + g_r k^2 + c k^4}, \quad (4)$$

where  $k \equiv |\vec{k}|$ , the renormalized parameters are given by

$$a_r = a_2 + \lambda \mathcal{S}_0 + g_2 \mathcal{S}_2, \quad (5)$$

$$g_r = g_0 + g_2 \mathcal{S}_0, \quad (6)$$

and the loop integrals are defined as

$$\mathcal{S}_p = \int_{|\vec{k}| < \Lambda} \frac{d^3 \vec{k}}{(2\pi)^3} k^p S(k) \quad (7)$$

( $p=0,2$ ) with  $\Lambda$  being a high momentum phenomenological cutoff. The region  $g_r < 0$  and  $4a_r c - g_r^2 > 0$ , as discussed in the Introduction, can be identified with the microemulsion phase with the function  $S(k)$  having a peak at  $k \equiv k_M$

$= \sqrt{|g_r|/2c}$ . Moreover, the characteristic lengths  $\xi$  and  $d$  appearing in the real space two-point correlation function (2) are given by

$$\xi = \left[ \frac{1}{2} \left( \frac{a_r}{c} \right)^{1/2} + \frac{1}{4} \left( \frac{g_r}{c} \right) \right]^{1/2}, \quad (8)$$

$$d = 2\pi \left[ \frac{1}{2} \left( \frac{a_r}{c} \right)^{1/2} - \frac{1}{4} \left( \frac{g_r}{c} \right) \right]^{1/2}. \quad (9)$$

Therefore, equilibrium properties can be expressed in terms of renormalized parameters and, by Eqs. (8) and (9), through the physical lengths  $\xi$  and  $d$  (once the parameters  $\lambda$ ,  $c$ ,  $g_2$ , and the cutoff  $\Lambda$  are given).

The dynamics of the order parameter in the presence of convective motion [16] is described by the equation

$$\frac{\partial \phi}{\partial t} + \vec{v} \cdot \vec{\nabla} \phi = \Gamma \nabla^2 \left( \frac{\delta \mathcal{H}}{\delta \phi} \right) + \eta_\phi, \quad (10)$$

where  $\mathcal{H}$  is the Hamiltonian of Eq. (3). The velocity field  $\vec{v}$  is a planar Couette shear flow

$$\vec{v} = \gamma y \vec{e}_x, \quad (11)$$

where  $\gamma$  is the shear rate and  $\vec{e}_x$  is the unit vector in the flow direction;  $\eta_\phi$  is a white Gaussian noise representing thermal fluctuations with momenta given by

$$\langle \eta_\phi(\vec{x}, t) \rangle = 0, \quad (12)$$

$$\langle \eta_\phi(\vec{x}, t) \eta_\phi(\vec{x}', t') \rangle = -2T\Gamma \nabla^2 \delta^3(\vec{x} - \vec{x}') \delta(t - t') \quad (13)$$

( $\langle \dots \rangle$  means the ensemble average) as required by the fluctuation-dissipation theorem that holds in the absence of flow. The functional derivative  $\delta \mathcal{H} / \delta \phi$  represents the difference in chemical potentials between oil and water;  $\Gamma$  is a mobility coefficient, and  $T$  is the temperature of the heat bath. By assuming Eq. (10) as the evolution equation for  $\phi$ , we are neglecting hydrodynamic fluctuations as well as the motion of the surfactant.

We will study the evolution equation for the dynamical structure factor

$$S(\vec{k}, t) \equiv \langle \phi(\vec{k}, t) \phi(-\vec{k}, t) \rangle \quad (14)$$

in the same self-consistent approximation used in equilibrium to write Eqs. (5) and (6). The convection-diffusion equation can be formally linearized as [17]

$$\frac{\partial \phi}{\partial t} + \vec{v} \cdot \vec{\nabla} \phi = \Gamma \nabla^2 \{ [a_2 + \lambda \mathcal{S}_0(t) + g_2 \mathcal{S}_2(t)] \phi - [g_0 + g_2 \mathcal{S}_0(t)] \nabla^2 \phi + c \Delta^2 \phi \} + \eta_\phi, \quad (15)$$

where the quantities  $\mathcal{S}_p(t)$  are given by expressions analogous to those of Eq. (7) but now with  $S(\vec{k}, t)$  of Eq. (14)

self-consistently calculated with Eq. (15). A standard procedure gives from Eq. (15) the dynamical equation for  $S(\vec{k}, t)$ ,

$$\left\{ \frac{\partial}{\partial t} - \gamma k_x \frac{\partial}{\partial k_y} + 2\Gamma k^2 K_R(k) \right\} S(\vec{k}, t) = 2T\Gamma k^2, \quad (16)$$

where  $K_R(k) \equiv a_r + g_r k^2 + c k^4$  is the renormalized vertex function and the parameters  $a_r$  and  $g_r$  can be obtained as in Eqs. (5) and (6) using  $S_p(t)$ .

A formal solution of Eq. (16) may be obtained by the method of characteristics,

$$S(\vec{k}, t) = \Delta_0[\vec{K}(t)] \mathcal{I}_1(t) + 2T\Gamma \mathcal{I}_2(t), \quad (17)$$

where we have defined the functions

$$\mathcal{I}_1(t) = \exp \left\{ -2\Gamma \int_0^t ds \mathcal{K}^2(s) [a_r + g_r \mathcal{K}^2(s) + c \mathcal{K}^4(s)] \right\}, \quad (18)$$

$$\mathcal{I}_2(t) = \int_0^t du \mathcal{K}^2(u) \mathcal{I}_1(u), \quad (19)$$

and  $\vec{K}(u) \equiv \vec{k} + \gamma k_x u \vec{e}_y$ ;  $\Delta_0(\vec{k})$  is the structure factor at the initial time  $t=0$ . Since the quantities  $a_r$  and  $g_r$  contain the momenta of  $S(\vec{k}, t)$ , Eq. (17) is actually a nonlinear integral equation for  $S(\vec{k}, t)$ . This equation can be solved numerically for all times by iterative methods.

Our results will first concern steady state properties. The stationary solution can be readily obtained from the  $t \rightarrow +\infty$  limit of Eq. (17), observing that in this limit the first term of the solution tends to zero (except for the  $\vec{k}=0$  mode). Therefore we write the stationary structure factor as

$$S(\vec{k}; \gamma)_\infty = 2T\Gamma \mathcal{I}_2(\infty), \quad (20)$$

where

$$\mathcal{I}_2(\infty) = \int_0^\infty dz \mathcal{K}^2(z) \exp \left\{ -2\Gamma \int_0^z ds \mathcal{K}^2(s) [a_r + g_r \mathcal{K}^2(s) + c \mathcal{K}^4(s)] \right\}.$$

We will also study transient behaviors with the fluid evolving from a quiescent state towards the stationary state with shear, or with the system relaxing, after interruption of the flow, from the sheared stationary state into the quiescent state. For the latter case we use the solution of Eq. (16) with  $\gamma=0$ ,

$$S(\vec{k}; \gamma; t)_{relax} = S(\vec{k}; \gamma)_\infty e^{-2\Gamma k^2 K_R(k)} + \frac{T}{K_R(k)} \left( 1 - \exp \left[ -\frac{t}{2\Gamma k^2 K_R(k)} \right] \right). \quad (21)$$

Finally, once the structure factor is known, we may evaluate the stresses that can be obtained as momenta of the structure factor [7]. The shear, first, and second normal stresses are, respectively, given by

$$\sigma_{xy}(t) = - \int_{|\vec{k}| < \Lambda} \frac{d^3 \vec{k}}{(2\pi)^3} k_x k_y (g_r + 2c k^2) S(\vec{k}, t), \quad (22)$$

$$N_1(t) = - \int_{|\vec{k}| < \Lambda} \frac{d^3 \vec{k}}{(2\pi)^3} (k_x^2 - k_y^2) (g_r + 2c k^2) S(\vec{k}, t), \quad (23)$$

$$N_2(t) = - \int_{|\vec{k}| < \Lambda} \frac{d^3 \vec{k}}{(2\pi)^3} (k_y^2 - k_z^2) (g_r + 2c k^2) S(\vec{k}, t). \quad (24)$$

In addition, the excess viscosity is defined as

$$\Delta \eta(t) = \frac{\sigma_{xy}}{\gamma}, \quad (25)$$

which represents the contribution of interfaces to the full viscosity of the fluid (that is, evaluating the viscosity of the fluid by means of Eq. (25) we are neglecting the hydrodynamical contribution to the viscosity itself).

### III. STATIONARY REGIME

In this section we present results for the steady states reached under the action of the shear flow with the structure factor given by Eq. (20). We have studied this expression numerically for several values of  $\xi$ ,  $d$ , and  $\gamma$ . The other parameters have been fixed as  $g_2=1, c=1, \lambda=0.5, \Lambda=3$ .

The effects of the flow on the structure factor can be seen in Fig. 1 where the projections on the planes  $k_y=0$  and  $k_z=0$  are shown for different  $\gamma$  and  $\xi=2, d=6$ . Similar results have been obtained for other choices of  $\xi$  and  $d$  [8]. [At  $k_x=0$ , the shape of the structure factor is the same as that of the case without flow, see Eq. (16).] At  $\gamma=0.5$  the structure factor remains almost isotropic and its pattern for each Cartesian plane is close to that of a circular volcano. The patterns are progressively distorted when the shear rate is increased. On the plane  $k_z=0$ , at  $\gamma=2$ , the edge of the volcano has assumed an elliptical shape and four peaks are visible. These peaks initially appear on the coordinate axes; then, when  $\gamma$  is increased, the ones located at  $k_x \approx 0$  become comparatively more important while the two others rotate clockwise and decrease their amplitude linearly with  $\gamma$  until they disappear. Indeed, in the limit  $\gamma \rightarrow \infty$ , since terms proportional to powers of  $\gamma k_x$  damp the exponential term on the right-hand side of Eq. (20), only the maxima of  $C(\vec{k})$  with  $k_x=0$  and  $k_y = \pm k_M$  survive. On the other plane  $k_y=0$ , two peaks at  $k_x=0, k_z = \pm k_M$  are also observed to become sharper and sharper as  $\gamma$  is increased.

The above results can be related to the orientation of the interfaces in the mixture, as also observed in Ref. [8]. A peak of  $C(k)$  defines a characteristic length proportional to the inverse of its position and, since the system is not isotropic,

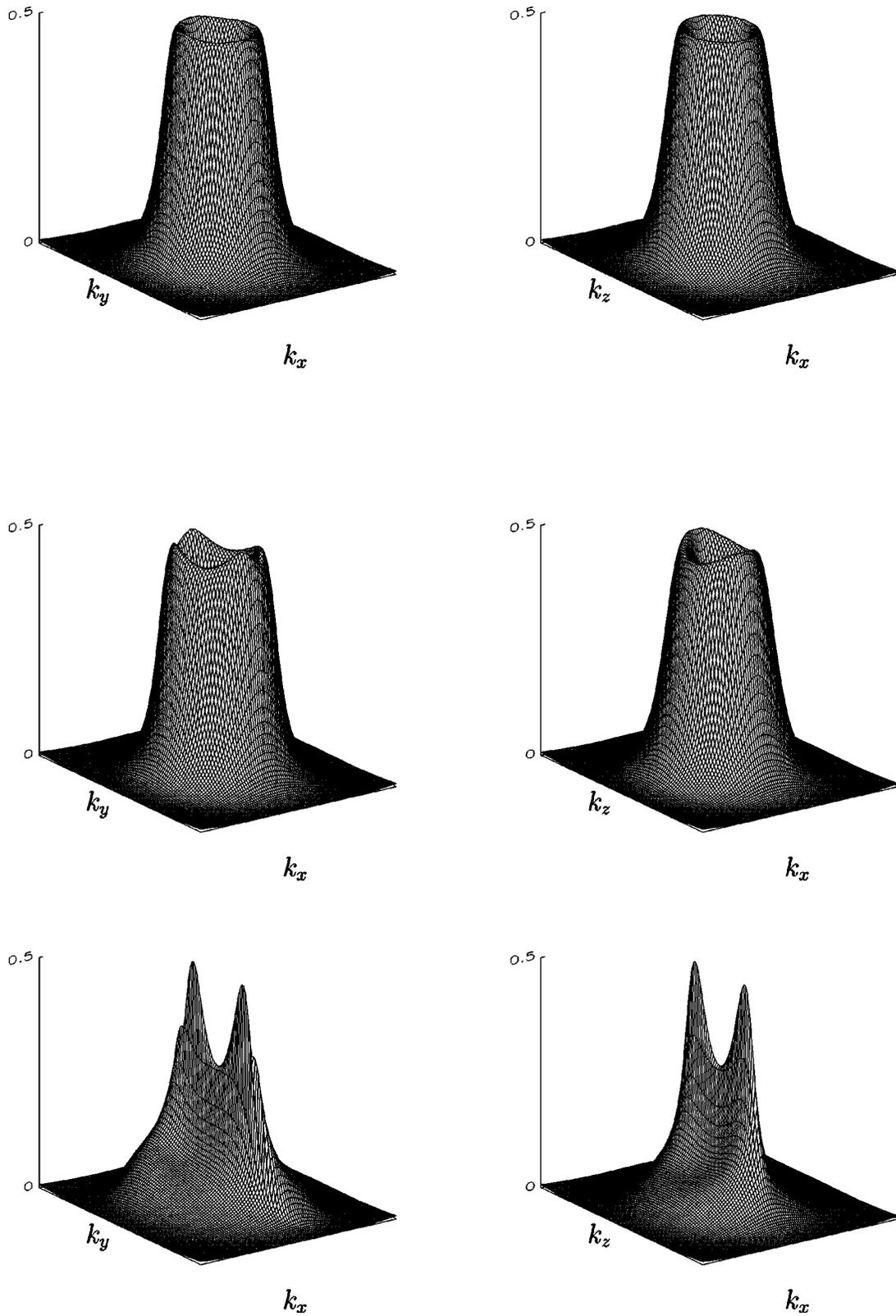


FIG. 1. Projections of the structure factor in the stationary state on the planes  $k_y=0$  (right column) and  $k_z=0$  (left column) for  $\xi=2$ ,  $d=6$ . The shear rate is, from the top to the bottom,  $\gamma=0.5$ ,  $\gamma=2$ , and  $\gamma=100$ ;  $k_x, k_y, k_z$  vary between  $-3$  and  $3$  in adimensional units.

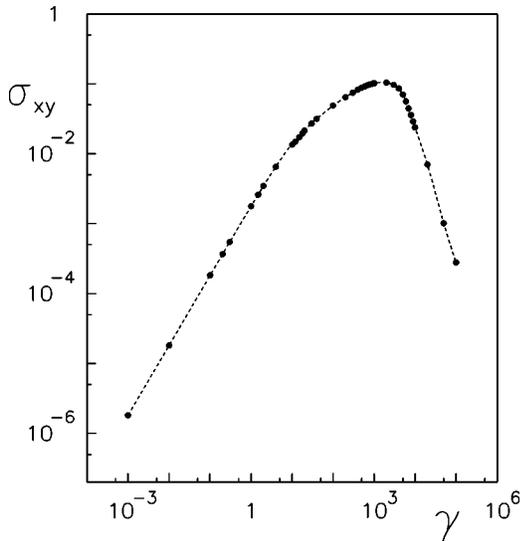


FIG. 2. The stationary shear stress  $\sigma_{xy}$  versus the shear rate  $\gamma$  for  $\xi=2$  and  $d=6$ .

to each maximum one associates three lengths, one for each space direction. Due to the symmetry  $\vec{k} \rightarrow -\vec{k}$ , only the peaks not related by reflection around the origin can be considered. At very large shear rate the existence of a single couple of maxima at  $k_x=0$  signals that interfaces are preferentially aligned along the flow with symmetry recovered in the transverse directions and the characteristic lengths being the same as without shear. For intermediate values of  $\gamma$  the additional peaks at  $(\tilde{k}_x, \tilde{k}_y, \tilde{k}_z)$  reveal the presence of interfaces oriented with an angle  $\alpha = \arctan(-\tilde{k}_x/\tilde{k}_y)$  with respect to the flow, besides those aligned along the  $x$  direction. These additional peaks are better seen in a region of parameters closer to the microemulsion-lamellar transition line corresponding to a larger value of  $\xi$  [8]. As  $\gamma$  is increased, the tilt angle  $\alpha$  and the relative abundance of lamellas oriented at this angle diminish as suggested by the behavior of the maxima with  $k_x \neq 0$  previously discussed.

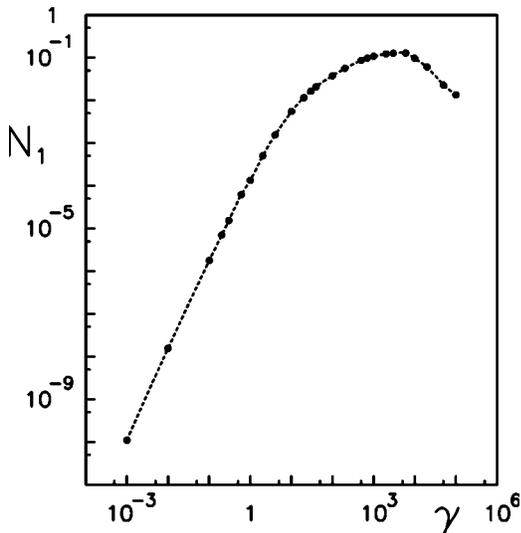


FIG. 3. The first normal stress  $N_1$  for  $\xi=2$  and  $d=6$ .

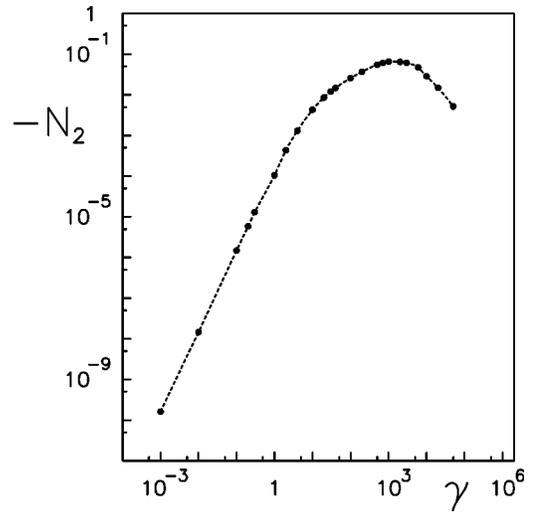


FIG. 4. Absolute value of the second normal stress  $N_2$  for  $\xi=2$  and  $d=6$ .

The behavior of the stress tensor as a function of the shear rate is reported in Figs. 2–4. At small values of  $\gamma$  the shear stress is a linear function of  $\gamma$  so that the viscosity is constant and the fluid is Newtonian. Shear thinning occurs for  $\gamma$  between 1 and 2, when the slope of the curve of the stress changes significantly. At this point the original volcano shape of the structure factor has also appreciably changed. In terms

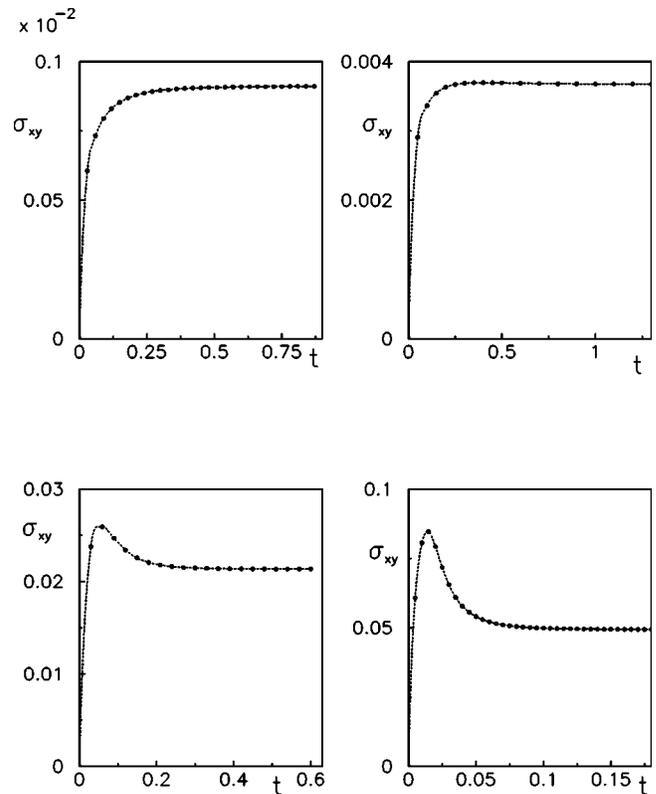


FIG. 5. Time evolution of the stress  $\sigma_{xy}$  for various values of the shear rate  $\gamma$  with  $\xi=2$  and  $d=6$ . Results are shown for  $\gamma=0.5$  (top left),  $\gamma=2$  (top right),  $\gamma=20$  (bottom left), and  $\gamma=100$  (bottom right).

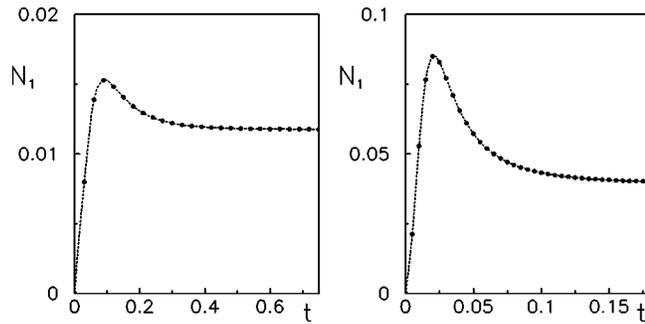
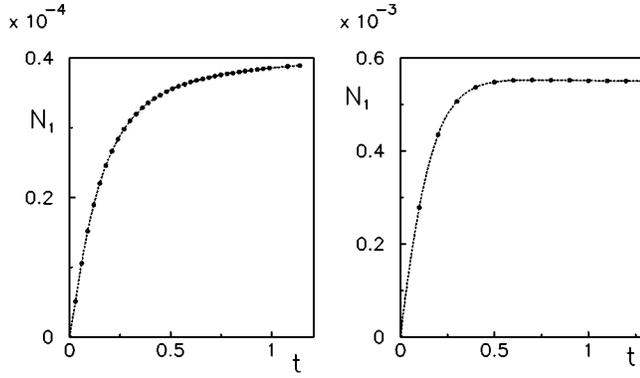


FIG. 6. Time evolution of the first normal stress  $N_1$ ; the parameters are the same as in Fig. 5.

of interfaces we expect that, when shear thinning is observed, the bicontinuous network of interfaces, which is only distorted in the Newtonian regime, is affected by many ruptures with a significant decrease of connectivity. We can say that a strong shear regime is entered. Indeed, we can compare the shear temporal scale  $\gamma^{-1}$  with the relaxation time  $\tau_M$  of microemulsions in equilibrium. The relaxation time of a mode with wave vector  $k$  is given by

$$\tau(\vec{k}) = \frac{1}{\Gamma k^2 (a_r + g_r k^2 + c k^4)}. \quad (26)$$

Following Ref. [7], we choose  $k = k_M$  corresponding to the peak of microemulsions, so that

$$\tau_M = \frac{1}{8\Gamma c} \frac{\xi^2 d^2}{4\pi^2 [(2\pi^2/d)^2 - 1/\xi^2]}. \quad (27)$$

The corresponding Deborah number is given by

$$\text{De} = \frac{\tau_M}{\tau_S}, \quad (28)$$

where  $\tau_S = 1/\gamma$ . If we take  $\gamma = 2$  we get  $\text{De} \sim 1.9$  for the case of Fig. 2. This indicates that shear thinning becomes evident when the shear rate is of the order of the inverse of typical structural times of the system without shear. We checked for other values of  $\xi, d$  that the Deborah number at shear thinning is always of order 1.

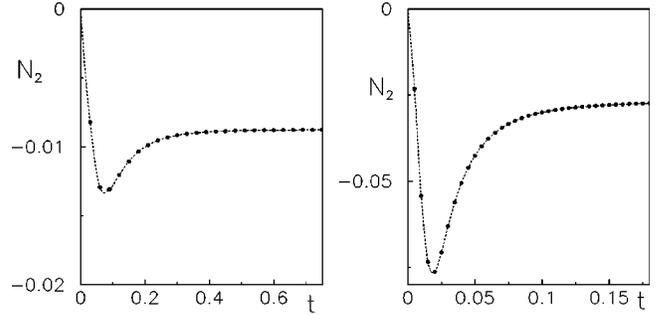
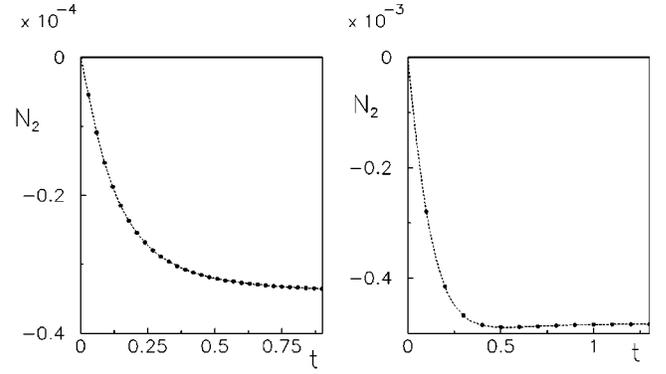


FIG. 7. Time evolution of the second normal stress  $N_2$  with parameters as in Fig. 5.

Shear thinning is observed again at  $\gamma \sim 10^3$  when, as we have seen, peaks with  $k_x = 0$  largely prevail. We expect that at these values of the shear rate the original bicontinuous interface network has changed significantly its topology, becoming more similar to a stack of lamellae. At very large  $\gamma$ , the excess viscosity is found to decrease as  $\gamma^{-s}$  with  $s = 1.87$ , which is close to the analytical limit  $s = 2$  [7]. In this final stress regime the lamellae are expected to become more and more aligned with the flow with fluctuations very inhibited. We observe that the shear stress corresponding to a completely ordered lamellar phase is zero.

The other stress components  $N_1, N_2$  behave similarly. At small  $\gamma$ ,  $N_1, N_2 \sim \gamma^2$  while they decrease as  $\gamma^{-1}$  when  $\gamma \rightarrow \infty$  (see Figs. 3 and 4).

#### IV. TRANSIENTS

We have studied the evolution of the system under the action of the shear flow from the initial equilibrium configuration of Eq. (4) towards the steady state of the preceding section, as described by Eq. (17). The behavior of the stress components for different values of  $\gamma$  is shown in Figs. 5–7. When  $\gamma$  is large enough that  $\text{De} \geq 1$ , a nonmonotonic behavior of the stress is observed with  $\sigma_{xy}, N_1, |N_2|$  exhibiting a maximum before relaxing to a constant value. A similar behavior has been measured in polymer solutions [2]. In our case we can think that at initial times the surfactant interfaces are stretched by the flow with a consequent increase of the stress. When the maximum stress is reached, the interface

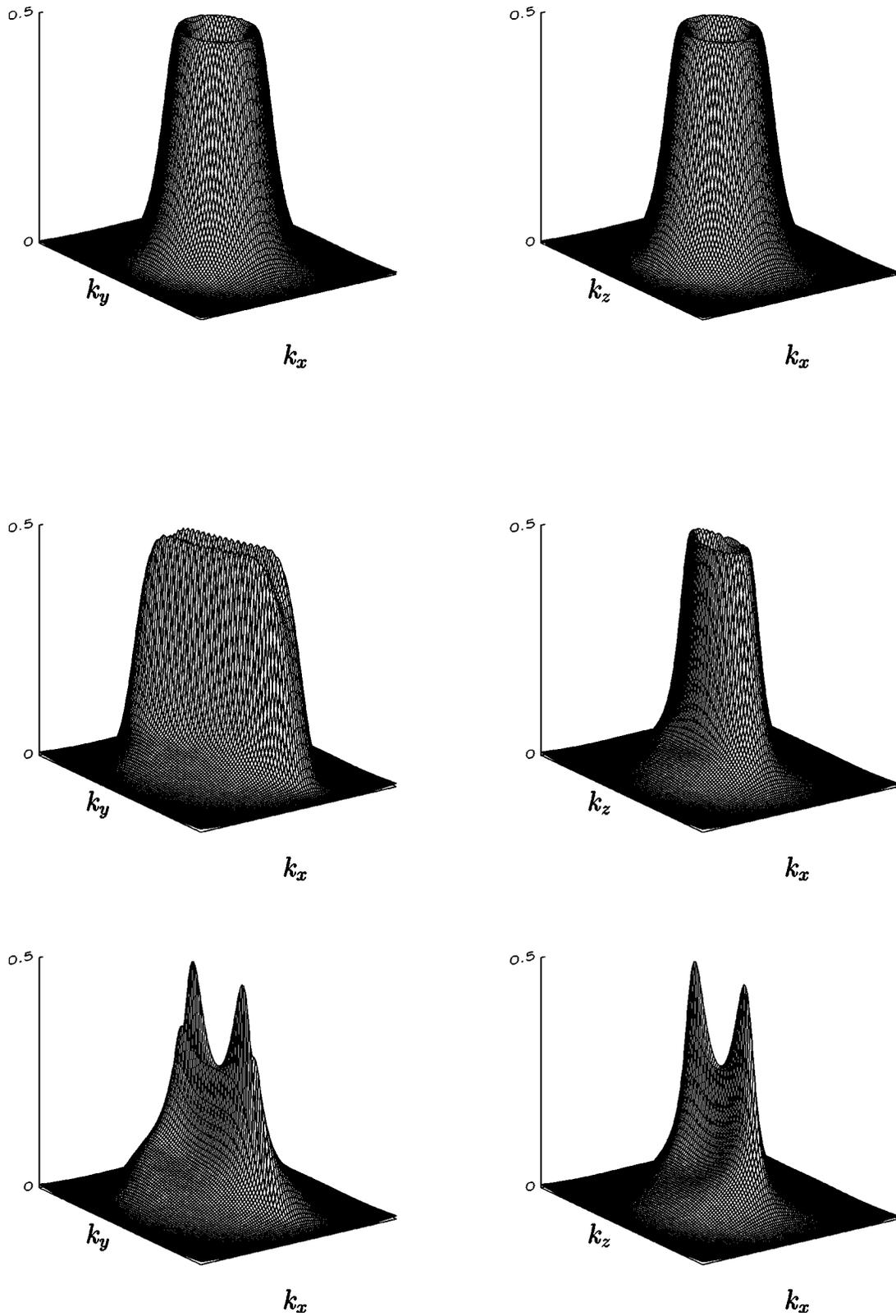


FIG. 8. Time evolution of the structure factor for  $\xi=2$ ,  $d=6$ , and  $\gamma=100$ . The projections on the planes  $k_z=0$  (left column) and  $k_y=0$  (right column) are shown, respectively, for  $t=0$  (top),  $t=2.5 \times 10^{-2}$  (middle), when the maximum of  $\sigma_{xy}$  is reached, and  $t=2.0 \times 10^{-1}$  (bottom).

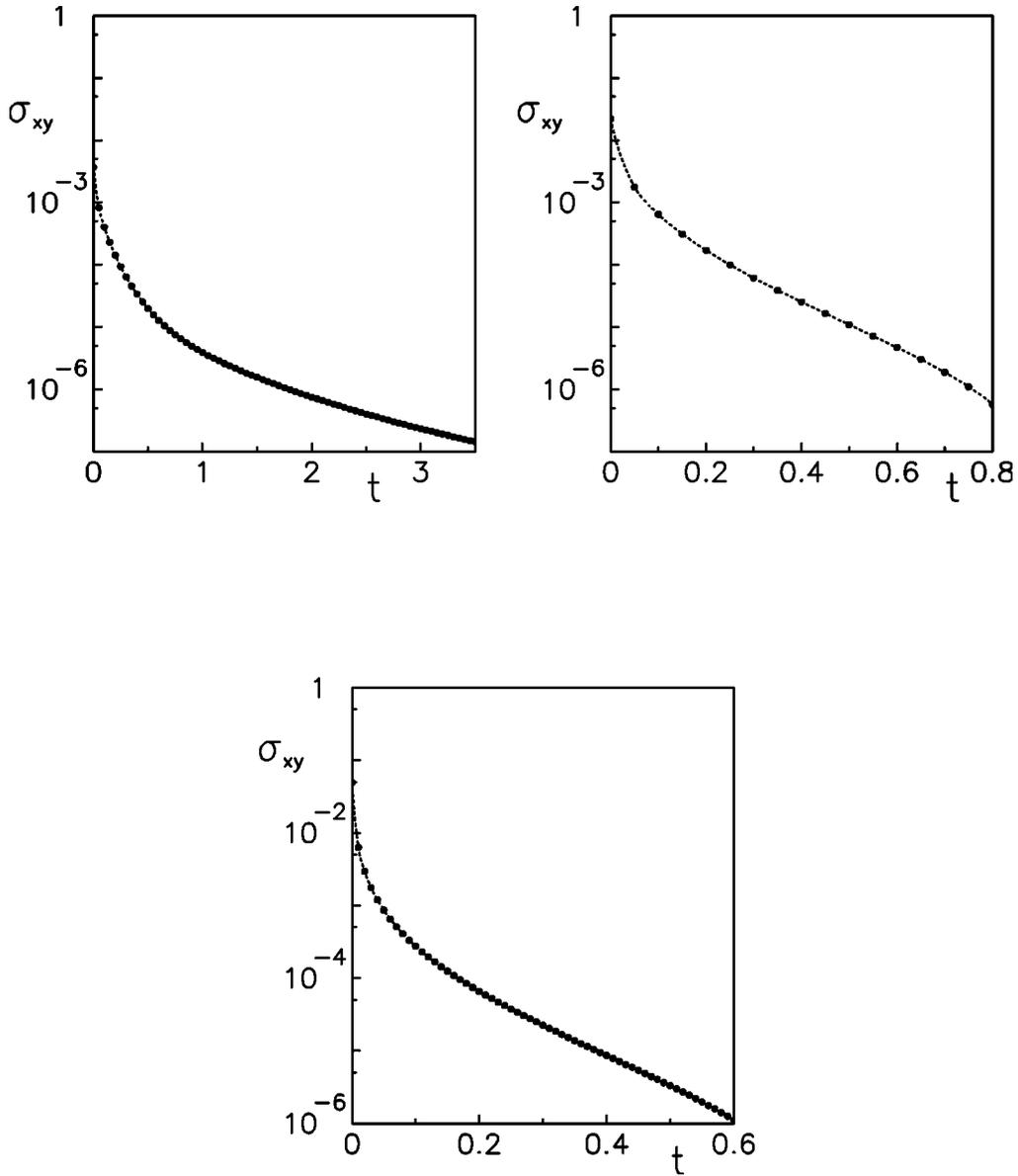


FIG. 9. Relaxation of the stress  $\sigma_{xy}$  for  $\xi=2$ ,  $d=6$ ,  $\gamma=2$  (top left),  $\gamma=20$  (top right), and  $\gamma=100$  (bottom).

structure starts to break and the stress relaxes to a lower value. The temporal evolution of the structure factor for  $\gamma=100$  is shown in Fig. 8. The largest distortion observed corresponds to the maximum stress. In the case  $\gamma=2$ , when the relaxation of the stress is monotonic, a prolate pattern like that in the middle of Fig. 8 at  $k_z=0$  is not observed.

We have also considered the opposite situation with the system, initially in a stationary state with shear, evolving without flow as described by Eq. (21). In this case the behavior is exponentially monotonic after an initial faster decay, as can be seen in Fig. 9. The time constant  $\tau$  of the exponential part of the relaxation decreases with  $\gamma$ , as shown in Fig. 10.

V. CONCLUSIONS

We have used a generalized Cahn-Hilliard equation with a convective term to study the rheological behavior of the

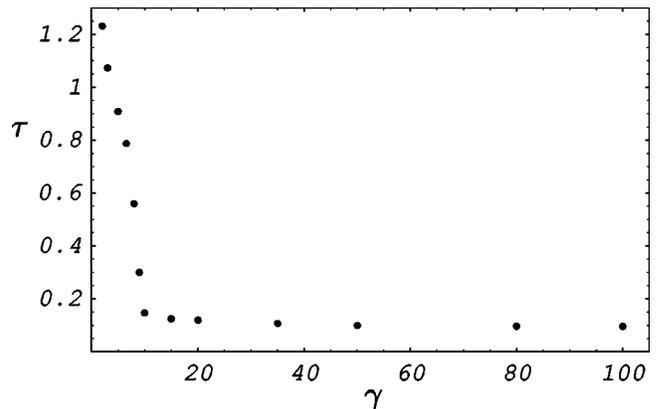


FIG. 10. Relaxation time  $\tau$  as a function of the shear rate  $\gamma$ .

microemulsion phase. The steady state constitutive curve shows shear thinning, first occurring at a shear rate of the order of the inverse of the equilibrium relaxation time. We have also obtained analytical expressions for the temporal behavior of the structure factor. From this we derive a non-monotonic evolution of the stress. This is similar to what is observed in other systems that relax into the steady state with a shear flow. We believe that these predictions are useful for future experiments. From the theoretical point of view, this analysis can be completed by studying how the equilibrium

phase diagram, including the disorder and the Lifshitz lines [3–6], is changed by the presence of the flow. Moreover, hydrodynamic fluctuations should be taken into account for a full description of the system.

#### ACKNOWLEDGMENTS

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