

Steady state of microemulsions in shear flow

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Steady-state properties of microemulsions in shear flow are studied in the context of a Ginzburg-Landau free-energy approach. Explicit expressions are given for the structure factor and the time correlation function at the one-loop level of approximation. Our results predict a four-peak pattern for the structure factor, implying the simultaneous presence of interfaces aligned with two different orientations. Due to the peculiar interface structure a nonmonotonous relaxation of the time correlator is also found.

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Self-assembling amphiphilic systems are binary or ternary mixtures with a surfactant forming interfaces between the other fluid components. These systems show a very rich phase behavior with ordered and structured disordered phases at different temperatures and relative concentrations [1]. Particularly interesting for the applications is the microemulsion phase where coherent domains of oil and water on scales between 100 and 1000 Å form disordered isotropic intertwined structures on larger scales [2].

While a satisfactory comprehension of the equilibrium behavior of amphiphilic systems is now available [1] the dynamical features are far less understood. In particular, in microemulsions, the existence of correlated mesoscopic structures makes the effects of imposed flows very different than in simple fluids. Interfaces between oil and water are elongated in the flow direction and an excess stress appears in the system. This can give a peculiar dynamics with unusual relaxation properties and a non-Newtonian rheological behavior [3]. Moreover, from a statistical mechanics point of view, complex fluids in external flow [4] are an interesting example of an out of equilibrium driven system [5].

In this Rapid Communication we study the behavior of microemulsions in shear flow with a continuum free-energy approach similar to that used by Fredrickson and Larson [6] for the study of rheology of block copolymers and by Onuki and Kawasaki [7], Cates and Milner [8], and Nakatani *et al.* [9] for the critical properties. This approach is justified when the molecular relaxation times of the constituents are much less than the time scales imposed by the flow field. Pätzold and Dawson first considered a Ginzburg-Landau model for describing the rheological behavior of ternary mixtures [10]. However, the results of [10] are based on an evaluation of the structure factor obtained numerically or analytically only in the limit of vanishing shear rate γ . Here we solve in the self-consistent one-loop approximation the model for any value of γ showing that in an intermediate shear range the structure factor is characterized by four pronounced peaks in the plane of the shear and flow directions. This phenomenon can be interpreted in terms of a complex spatial pattern where interfaces with two different orientations coexist; their

relative abundance is tuned by γ . Shear thinning is observed at a characteristic shear rate of the order of the inverse of typical microemulsion relaxation times. We also consider the behavior of the two-time correlator. Due to the coupling between the flow and the interface structure, this function has a remarkable nonmonotonic behavior characterized by the presence of maxima preceding a fast asymptotic decay.

The Ginzburg-Landau free-energy generally used to describe the equilibrium properties of ternary mixtures is [11]

$$\mathcal{F}\{\varphi\} = \int d^3x \left\{ \frac{a}{2} \varphi^2 + \frac{b}{4!} \varphi^4 + \frac{1}{2} (g_0 + g_2 \varphi^2) |\nabla \varphi|^2 + \frac{c}{2} (\nabla^2 \varphi)^2 \right\} \quad (1)$$

where the scalar field φ represents the concentration difference between oil and water components. The amount of surfactant present in the system is related to the value of g_0 which can be negative, favoring the appearing of interfaces. The term proportional to c makes stable the free-energy at large momenta and weights the curvature of interfaces. The quadratic part of the free-energy in the disordered phase with $a > 0$ and $g_0^2 < 4ac$ gives a suitable description of the microemulsion phase; in particular the space correlation function

$$G(r) \sim \frac{e^{-r/\xi}}{r} \sin \frac{2\pi r}{d} \quad (2)$$

well fits the experimental data [12–15]. The characteristic length $d = 2\pi(1/2\sqrt{a/c} - g_0/4c)^{-1/2}$ represents the size of coherent oil or water regions which are correlated up to a distance $\xi = (1/2\sqrt{a/c} + g_0/4c)^{-1/2}$. At negative g_0 , the structure factor obtained by Fourier transforming Eq. (2) has a peak at a finite momentum $k_M = \sqrt{|g_0|/2c}$. Finally, the non-harmonic terms in Eq. (1) describe the possible effects due to mode coupling and become more important in approaching the phase boundary.

The kinetic behavior of the mixture, neglecting hydrodynamical effects [16], is described by the convection-diffusion equation [17]

$$\frac{\partial \varphi}{\partial t} + \vec{\nabla} \cdot (\varphi \vec{v}) = \Gamma \nabla^2 \frac{\delta \mathcal{F}}{\delta \varphi} + \eta, \quad (3)$$

where the velocity field is given by $\vec{v} = \gamma \gamma \vec{e}_x$, γ being the shear rate and \vec{e}_x the unit vector in the flow direction. The stochastic term η is a Gaussian white noise, representing thermal fluctuations, with zero mean and correlation $\langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle = -2T\Gamma \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t')$, as required by the fluctuation-dissipation theorem, where $\langle \dots \rangle$ means the ensemble average. Here Γ is a mobility coefficient and T the temperature of the heat bath.

The cubic terms in the functional derivative of Eq. (3) will be treated in the one-loop approximation, which describes appropriately disordered phases. The resulting equation for the Fourier components $\varphi(\vec{k}, t)$ is given by

$$\begin{aligned} \frac{\partial \varphi(\vec{k}, t)}{\partial t} - \gamma k_x \frac{\partial \varphi(\vec{k}, t)}{\partial k_y} = & -\Gamma k^2 \left[X(k) + g_2 k^2 S_0(t) \right. \\ & \left. + \left(\frac{b}{2} S_0(t) + g_2 S_2(t) \right) \right] \varphi(\vec{k}, t) \\ & + \eta(\vec{k}, t), \end{aligned} \quad (4)$$

where $X(k) = ck^4 + g_0 k^2 + a$, $S_p(t)$ (with $p=0,2$) are defined self-consistently by the relations

$$S_p(t) = \int_{|\vec{k}| < \Lambda} \frac{d\vec{k}}{(2\pi)^D} k^p C(\vec{k}, t), \quad (5)$$

where $C(\vec{k}, t)$ is the structure factor defined as $\langle \varphi(\vec{k}, t) \varphi(-\vec{k}, t) \rangle$ and Λ is a phenomenological ultraviolet cut-off. Starting from Eq. (4) a straightforward calculation [10,18] give the dynamical equations for the various correlation functions [19]. We first focus on the properties of the structure factor. Using the method of characteristics the $t \rightarrow \infty$ expression of the structure factor $C(\vec{k})$ can be calculated as

$$\begin{aligned} C(\vec{k}) = \int_0^\infty dz 2\Gamma T \vec{K}^2(z) \exp \left\{ - \int_0^z ds 2\Gamma \vec{K}^2(s) [a^R \right. \\ \left. + g^R \vec{K}^2(s) + c \vec{K}^4(s)] \right\}, \end{aligned} \quad (6)$$

where $\vec{K}(s) = (k_x, k_y + \gamma k_x s, k_z)$, $\vec{K}^4 \equiv (\vec{K}^2)^2$, $a^R = a + b/2S_0^\infty + g_2 S_2^\infty$, $g^R = g_0 + g_2 S_0^\infty$, and S_0^∞ and S_2^∞ are the limit for $t \rightarrow \infty$ of $S_0(t)$ and $S_2(t)$.

Since ξ and d are the physical quantities to be compared with experimental data, the model parameters are tuned [10] with the following procedure: We first calculate the one-loop renormalization of the bare coefficients a and g without shear and express the correlation lengths ξ and d in terms of the

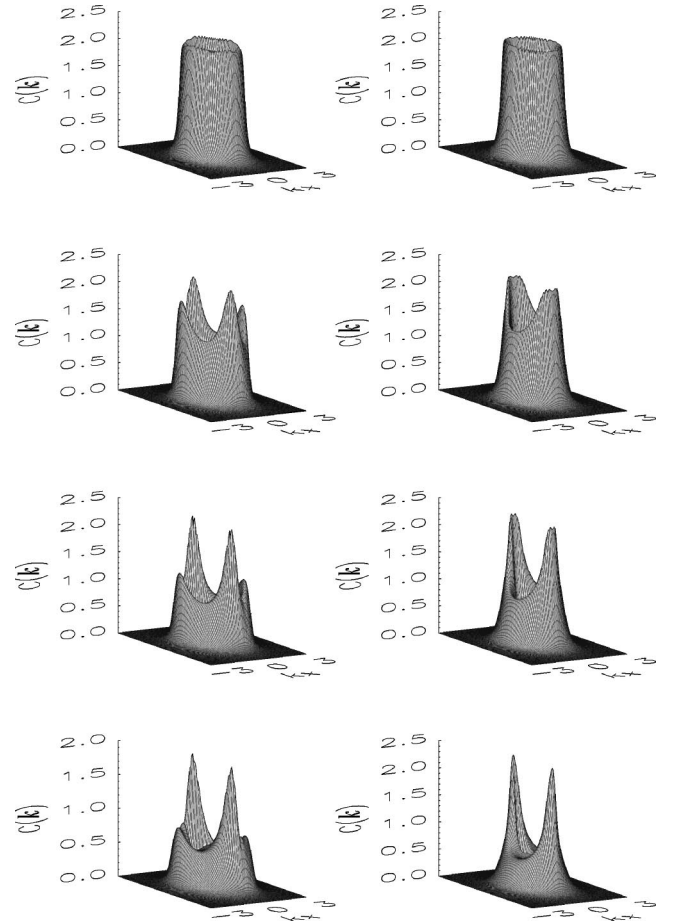


FIG. 1. Projections of the structure factor on the planes $k_z=0$ (left column) and $k_y=0$ (right column) at shear rates $\gamma = 0.25, 2, 4, 8$ (from top to bottom). The axis without label is k_y in the left column and k_z in the right column ($-3 \leq k_y, k_z \leq 3$). The edge of the circular volcano at $\gamma=0.25$ is at about $k_M = 1.26$.

renormalized parameters. Then, for a given choice of ξ and d , we invert the above mentioned relations and compute the values of a, g_0 to be used in the case with shear. In the following we show results for the case $\xi = 7, d = 5$. The other parameters are set to the values $c = 2, b = g_2 = T = 1$. Similar results have been obtained for different choices of parameters with d/ξ in the range between 0.5 and 2.5.

The effects of the flow on $C(\vec{k})$ are shown in Fig. 1, where the projections of the three-dimensional structure factor on the planes $k_y=0$ and $k_z=0$ are plotted at different γ . At $\gamma=0$ the structure factor is isotropic and its shape on each Cartesian plane is that of a circular volcano with radius k_M . When shear is applied, the projection on the $k_x=0$ plane gives the same results of the $\gamma=0$ case because the velocity field is along the x direction. On the $k_z=0$ plane, instead, this pattern is progressively distorted as the shear rate is increased. For small γ (see the case $\gamma=0.25$ in the left column of Fig. 1) the edge of the volcano becomes elliptical and slightly depressed along the $k_x = -k_y$ direction. As γ is increased four peaks are clearly observable, as shown in Fig. 1 at $\gamma=2$ and $\gamma=4$. By increasing the shear rate, the maxima located at $k_x \approx 0$ become comparatively more important

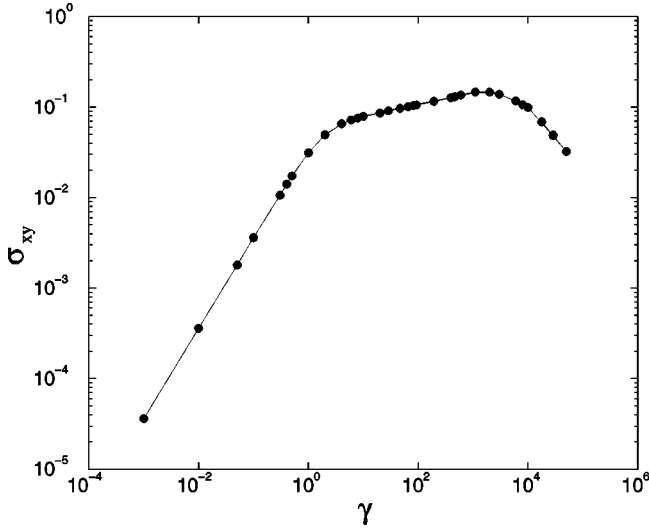


FIG. 2. Stress tensor as a function of the shear rate γ .

while the other peaks rotate clockwise and decrease their amplitude linearly in γ until they disappear. Indeed, in the limit $\gamma \rightarrow \infty$, since terms proportional to powers of γk_x damp the exponential term on the r.h.s. of Eq. (6), only the maxima of $C(\vec{k})$ with $k_x=0$ survive. Figure 1 shows that this is already observable for $\gamma=8$. Then, by letting $k_x=0$ in Eq. (6) we find the peaks located at $k_y = \pm k_M$. The description is completed with the projection of the structure factors on the plane $k_y=0$ shown in the right column of Fig. 1. Here two peaks at $k_x=0, k_z = \pm k_M$, are observed to become sharper and sharper as the shear is increased.

A peak of $C(k)$ is generally interpreted as the signature of a characteristic length in the system which is proportional to the inverse of its position. In this case, since the system is not isotropic, 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. For large shear the existence of a single couple of maxima at $k_x=0$ signals that interfaces are aligned along the flow. In the transverse directions the characteristic lengths are the same as without shear. For intermediate values of γ the additional peaks at $(\vec{k}_x, \vec{k}_y, \vec{k}_z)$ reveal the presence of interfaces oriented with an angle $\alpha = \arctan(-\vec{k}_x/\vec{k}_y)$ with respect to the flow, besides those aligned along the x direction. As γ is increased these features are progressively tilted in the direction of the flow while their relative abundance diminishes, as suggested by the behavior of the maxima with $k_x \neq 0$ previously discussed. The existence of a fourfold peaked structure factor has been also reported in scattering experiments on segregating mixtures [20,21].

Stretching of domains requires work against surface tension and results in an increase $\Delta\eta$ of the viscosity [22]. The excess viscosity is generally defined as $\Delta\eta = \sigma_{xy}/\gamma$ with the shear stress given by $\sigma_{xy} = -\int [d\vec{k}/(2\pi)^D] k_x k_y (g^R + 2ck^2)C(\vec{k})$ [10]. In Fig. 2 σ_{xy} is plotted as a function of γ . For small γ , σ_{xy} grows linearly with γ , as is also found in Ref. [10]. This behavior is observed in correspondence of a structure factor similar to that shown in Fig. 1 at $\gamma=0.25$.

When $C(\vec{k})$ develops four maxima at $k_z=0$ shear thinning or decreasing of $\Delta\eta$ is first observed: σ_{xy} keeps increasing with a much smaller effective exponent consistent with the value 0.13. The characteristic value γ_1 where σ_{xy} changes its behavior can be related to the internal structure of a microemulsion in equilibrium. Indeed, relating the typical time scale of the system to the relaxation time τ_M of the mode corresponding to the peak of the structure factor [10], it is straightforward to calculate that $\tau_M = (1/8\Gamma c) \{ \xi^2 d^2 / 4\pi^2 [(2\pi^2/d)^2 - 1/\xi^2] \}$. For the choice of parameters in Fig. 2, $\tau_M = 1.37$ close to the inverse of γ_1 , which is of the order 1. We have found a similar relation also for other choices of parameters. For very large γ , when the peaks at $k_x=0$ alone survive, σ_{xy} decreases to zero because the excess stress vanishes when the interfaces are aligned with the flow. A similar behavior is shown by the first normal stress $N_1 = \int [d\vec{k}/(2\pi)^D] (k_y^2 - k_x^2)(g^R + 2ck^2)C(\vec{k})$ [23].

Next we consider the dynamical properties of the microemulsion phase. In the steady state the two-time correlation function $D(\vec{k}, \vec{k}', t) = \langle \varphi(\vec{k}, t) \varphi(\vec{k}', 0) \rangle = D(\vec{k}, t) \delta(\vec{K}(t) + \vec{k}')$ [24] can be computed through

$$D(\vec{k}, t) = C(\vec{K}(t)) \exp \left\{ - \int_0^t \Gamma \vec{K}^2(s) [a^R + g^R \vec{K}^2(s) + c \vec{K}^4(s)] ds \right\}. \quad (7)$$

D is the product of two terms: the structure factor evaluated at the translated momentum $\vec{K}(t)$ and an exponential term. For a given $\vec{k} = \vec{K}(0)$, $\vec{K}(t)$ moves along the k_y direc-

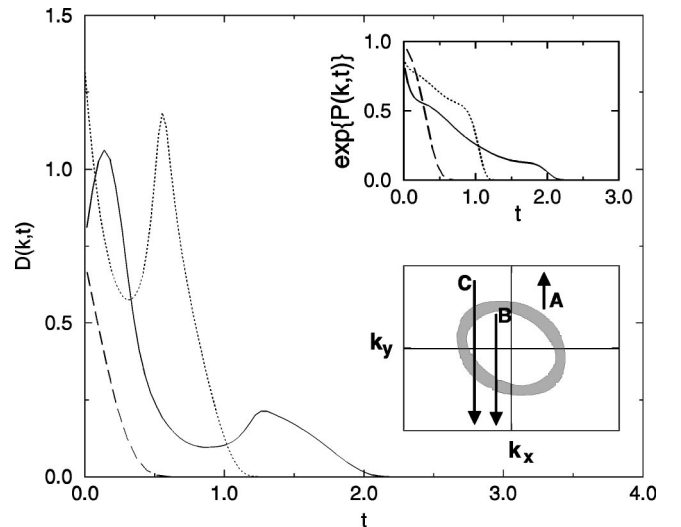


FIG. 3. Behavior of the time correlation function (7) is shown for the three values of the wavevector corresponding to the positions A, B, and C in the lower inset of the figure. The elliptical shape in this inset represents schematically the contour plot of the structure factor in the plane $k_z=0$. Solid, dotted, and dashed lines correspond respectively to the cases C, B, and A. In the upper inset the exponential factor in the right-hand side of Eq. (7) is plotted for the same three values of \vec{k} .

tion upward or downward depending on the sign of k_x , as represented schematically in the lower inset of Fig. 3. Therefore, when $\vec{K}(t)$ crosses the edge of the structure factor, $C(\vec{K}(t))$ shows a pronounced maximum. This feature is peculiar to microemulsions, where the presence of interfaces gives the patterns of structure factor discussed above and cannot be observed in simple fluids. The exponential term in Eq. (7) contains a polynomial of t and behaves as $\exp(-\Gamma\gamma^6 k_x^6 c t^7 / 7)$ for long times. However, due to the presence of negative coefficients, the decay can be much slower at earlier times, as can be observed in the upper inset of Fig. 3. In particular, one can show that an inflection point is developed at $\tan\theta = k_x/k_y = -\gamma t$ in the sectors with $k_x k_y < 0$. Other inflection points come out, even in the other sectors, due to the negative value of g^R . Such a slow decay can preserve the observation of the maximum of $C(\vec{K}(t))$ in the full time correlator (7). In Fig. 3 the behavior of D is shown for three typical values of \vec{k} . In case A, $\vec{K}(t)$ does not intersect the volcano of the structure factor so that D decays monotonously. When the edge of $C(\vec{k})$ is crossed once or

twice, as in cases B and C respectively, D is characterized by a corresponding number of peaks. This rich behavior has never been described before to our knowledge and could be searched for in experiments [25].

In conclusion, we have presented explicit expressions for the steady-state structure factor and the time correlation function of a Ginzburg-Landau model describing mixtures of oil, water, and surfactant in the microemulsion phase under the action of a shear flow. The structure factor exhibits a four peak pattern which implies a nonuniform orientation of interfaces with two preferred directions. The time correlator, reminiscent of the interface structure, shows maxima superimposed on a global decay. All these predictions can be tested experimentally and show that together with the equilibrium behavior also the dynamics of complex fluid is characterized by a very rich phenomenology.

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