

Observation of a Topological Relaxation Mode in Microemulsions

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We report the observation of two diffusive relaxation modes in a very swollen microemulsion, measured by quasielastic light scattering experiments. In addition to a short-time diffusion process, we observe a long-time diffusive relaxation mode with unusual scaling behavior: the diffusion constant D is an exponential function of the characteristic length scale ξ , $D \propto \exp(-\xi)$. This observation provides experimental evidence for thermally activated topological relaxation of random fluid phases, as predicted by Milner *et al.* [J. Phys. (Paris) **51**, 2629 (1990)]. We describe the activation energy of such a process by some simple microscopic model for the surfactant layer and give an estimation of the membrane elastic and Gaussian moduli κ and $\bar{\kappa}$, and its spontaneous curvature.

Microemulsions are thermodynamically stable, fluid oil/water/surfactant mixtures. Their structure can be described as a surfactant monolayer, dividing space into regions of water and oil, which are either globular or bicontinuous random assemblies. A lot of interest has been focused on these systems in the last few years because of their enormous potential for practical applications as well as their interesting physical properties [1].

The structure of microemulsions has been extensively studied using electrical conductivity, field gradient NMR, neutron and x-ray scattering, and electron microscopy [1]. These experiments show that microemulsions can be described as a phase of separated droplets in the dilute regime, percolating in most cases to a bicontinuous structure when water and oil concentration become comparable [1]. Theoretical approaches describe the phase stability in terms of a competition between curvature energy and entropy [1]. The dynamical behavior of droplet phases in the diluted regime has been studied using both light and spin echo neutron scattering. The hydrodynamic size as well as the hydrodynamic interactions of the droplets was obtained using light scattering [2]. The shape fluctuations of spherical droplets were studied by their neutron spin echo and compared to theoretical models [3]. Comparatively, much less effort has been done to study experimentally the dynamical behavior of concentrated microemulsions and of the bicontinuous phase. Two theoretical works have been proposed to account for the dynamics of bicontinuous microemulsions by Milner *et al.* [4] and Gompper and Hennes [5].

In this Letter, we report on quasielastic light scattering experiments on the fluctuation spectrum of a microemulsion, as found while concentrating a dilute droplet oil-in-water microemulsion. While in the dilute droplet regime one relaxation mode is observed and corresponds to the droplet diffusion, in the more concentrated region we observe an additional diffusive relaxation mode, which we interpret as a topological relaxation mode resulting from membrane fusion.

Recently, we reported on a microemulsion phase, remarkable in view of its swelling capacity, the characteristic size varying from 35 Å to more than 2000 Å upon adding oil [6]. This phase was found in a pseudoquaternary system composed of sodium dodecylsulfate (SDS), octanol, octane, and brine solution (NaCl, 9 g/l). The ratio of brine to SDS is fixed to 18 by weight. The phase diagram is shown in Fig. 1. It is rich and complex, and only the well-established phases are presented here. Some precision of the phase diagram has been made since our first paper and will be presented in detail elsewhere [7]. Phase I is a direct microemulsion (L_1): upon adding oil, the system goes continuously from small micelles (35 Å diameter at 0 wt% oil content) to a microemulsion of a characteristic length of around 2000 Å for samples containing

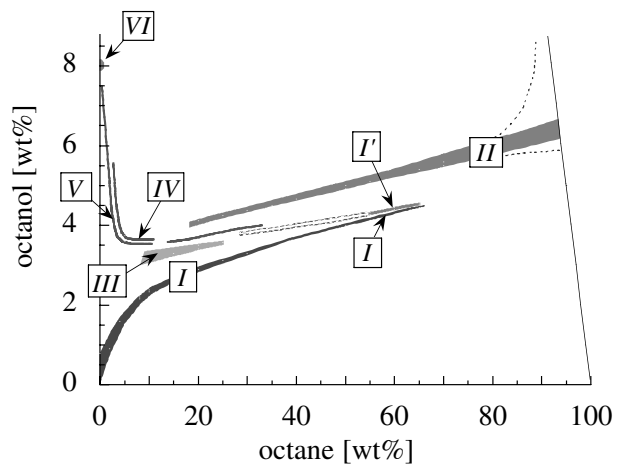


FIG. 1. Representative drawing of a cut of the pseudoquaternary phase diagram of SDS, octanol, octane, and brine solution (NaCl, 9 g/l) at $T = 24.5^\circ\text{C}$. The ratio of brine solution and SDS is fixed to 18 (by wt). At very low (surfactant + cosurfactant) concentration, a very rich phase behavior is found. Phase I is the microemulsion phase studied in this Letter. The other phases are described in the text. Shaded regions in the phase diagram represent monophasic samples; nonshaded regions are multiphase equilibria.

60 wt % oil, as observed in high resolution x-ray scattering [6,7]. At oil concentrations above 55 wt %, we observe a first order phase transition from the liquid microemulsion towards a mesophase region I' while adding alcohol. This region of extremely diluted mesophases will be presented in detail elsewhere [7]. Phase II is an inverse microemulsion (L_2), phase III consists probably of swollen wormlike micelles, phases IV and V are, respectively, a hexagonal and a lamellar phase, and phase VI is a sponge phase. Here, we present only experimental results obtained by quasielastic light scattering in the direct microemulsion phase denoted I.

The experiments were performed using a coherent IK-90 krypton ion laser light source operating at 647.1 nm and linearly polarized. The scattered light is collected with a photon-counting photomultiplier tube (Hamamatsu) for scattering angles between 20° and 155° . The time autocorrelation function of the scattered intensity $\langle I(q, t)I(q, 0) \rangle$ was accumulated in homodyne detection using either a 72-channel multi-sample-time autocorrelator (BI-2030AT) or a BI-9000AT correlator (maximum 522 channels), both from Brookhaven Instruments.

The time autocorrelation function of the scattered intensity can be related to the autocorrelation function of the electric field (concentration) fluctuations $g_1(q, t)$ through $\langle I(q, t)I(q, 0) \rangle = \langle I(q, 0) \rangle^2 [1 + \beta |g_1(q, t)|^2]$. β is the coherence factor of the experiment and ideally should be 1. A loss of coherence can be due to the experimental setup, as well as the presence of some multiple scattering. Upon adding oil, our samples become optically turbid, so that we cannot exclude some multiple scattering. Typically, the coherence factor obtained in our experiments was 0.88 for samples at 10 wt % oil concentration, and 0.8 for samples at 50 wt % oil concentration, while the coherence factor of the setup was proven to be better than 0.9. We consequently used cylindrical scattering cells of different diameters to control the contribution of multiple scattering. For comparison, the represented correlation functions are normalized to the scattered intensity $\langle I(q, 0) \rangle$ and the coherence factor β .

Figure 2 shows four normalized time autocorrelation functions as observed with the BI-9000AT correlator in samples at 10, 30, 40, and 50 wt % oil concentration at an observation angle of 90° . While at oil concentrations below 10 wt % a single exponential decay of the autocorrelation function is observed, with increasing oil concentration a second relaxation mode appears. Both characteristic relaxation times increase with increasing oil concentration and, consequently, increase with the characteristic length of the structure [8]. While the fastest mode remains of the order of a few tenths of milliseconds, the slowest mode can reach time scales as large as 1 s.

We fitted $|g_1(q, t)|^2$ with a single exponential $\exp(-2\omega t)$ at oil concentrations below 10 wt %, and at oil concentrations above this value as a two-exponential function $[A_f \exp(-\omega_f t) + (1 - A_f) \exp(-\omega_s t)]^2$, where

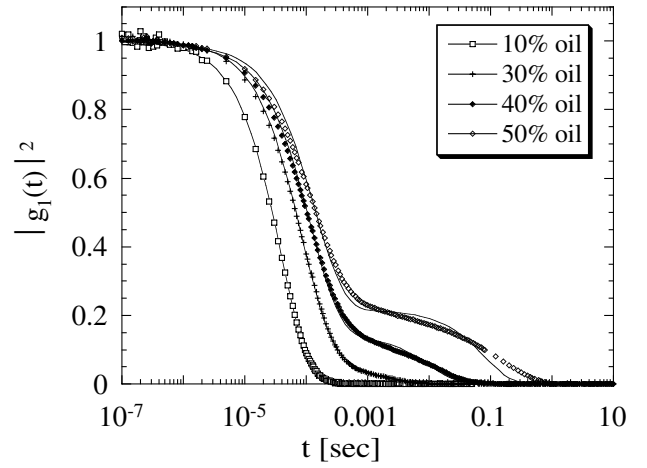


FIG. 2. Normalized time autocorrelation function of the scattered intensity $|g_1(q, t)|^2$, as observed in samples at 10, 30, 40, and 50 wt % oil concentration at a scattering angle of 90° . While increasing the oil concentration, two relaxation modes are observed. The full lines represent the fits described in the text.

A_i are the amplitudes and ω_i are the characteristic relaxation frequencies of a mode i . In the following, the indexes f and s will stand for “fast” and “slow,” respectively. The corresponding fits are also shown in Fig. 2 (full lines). This type of fit function gives very satisfying fit results for oil concentrations up to 35 wt %. Above this concentration, systematic deviations of the two-exponential fit function from the experimental data exist and should be due to some polydispersity. Alternatively, the data can be analyzed using the inverse Laplace transform program CONTIN [9], that better accounts for a dispersion in the relaxation rates. In all cases, the dispersion relation seems to be diffusive; i.e., the characteristic relaxation frequency varies to a good agreement with the square of the wave vector,

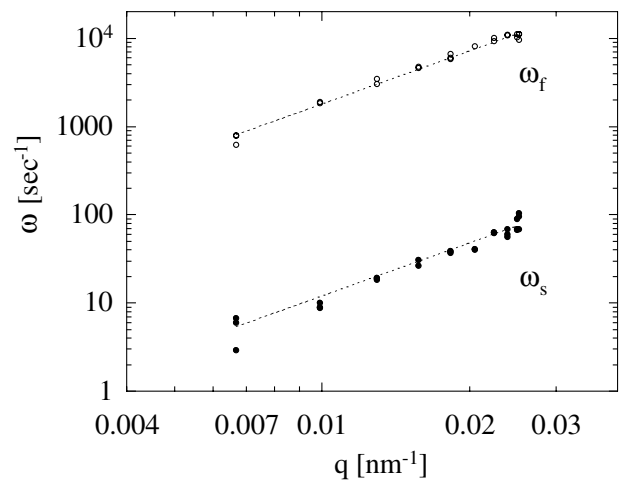


FIG. 3. Wave vector dependence of the characteristic relaxation frequencies ω_f and ω_s observed in a sample at 40 wt % oil concentration. Both frequencies vary to a good agreement with the square of the wave vector (fitted dashed line), indicating diffusive processes.

indicating a hydrodynamic origin of the modes. This is representatively shown in Fig. 3 for a sample at 40 wt% oil concentration. The dashed lines represent a fit of $\omega_i = D_i q^2$ to the relaxation frequencies.

In Fig. 4, the diffusion constants D_f and D_s of the two relaxation processes are plotted versus the oil concentration: at oil concentrations below ≈ 10 wt%, only one relaxation mode is observed. Above oil concentrations of 20 wt%, two diffusive modes can clearly be seen. While the fastest mode diffusion constant remains of the same order of magnitude, the slow mode diffusion constant varies strongly with the oil concentration. For comparison, the diffusion constant extracted from the Stokes-Einstein relation, $D = k_B T / 6\pi\eta r$, is also plotted in Fig. 4, where the viscosity η is fixed to the water viscosity, and the hydrodynamic radius r is taken as half the characteristic length ξ measured with x-ray scattering [6,7]. The fast mode diffusion constant is of the order of magnitude of the Stokes-Einstein diffusion constant. This is especially true in the dilute limit of small oil micelles in water. However, at higher oil concentrations, there is an expected deviation from this dilute limit description, as in the concentrated system both thermodynamic and hydrodynamic interactions have to be taken into account.

More interesting is the variation of the slow relaxation mode as a function of the characteristic length [8]: the slow mode diffusion constant follows an exponential decay, instead of a power law as expected from the Stokes-Einstein relation. A possible origin of such an exponential function could be an energy-activated process. Such an activated process was proposed some years ago by Milner *et al.* [4]. The authors suggested a topological relaxation mode in microemulsions by membrane fusion, allowing oil to flow from one region of space to the other, involving fusion of domains. Such a topological rearrangement by creation or

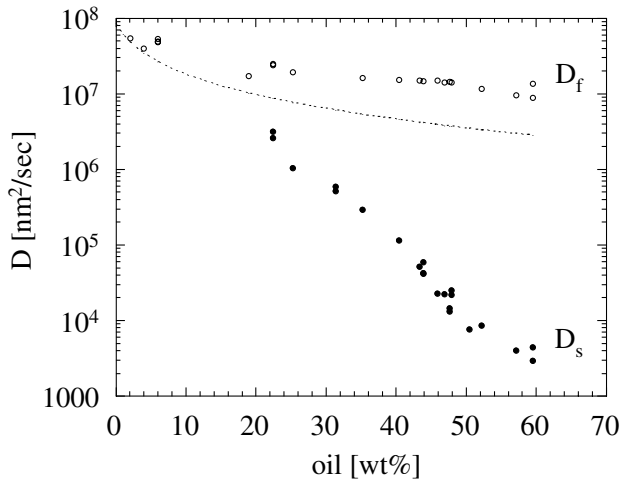


FIG. 4. Diffusion constants of the two diffusive relaxation processes observed as a function of the oil concentration of the sample. The dashed line represents the diffusion constant extracted from the Stokes-Einstein relation (see text).

destruction of necks is illustrated in Fig. 5(a). This process is supposed to be activated, as the intermediate state of membrane rupture will exhibit an energy barrier. Thus, the diffusion constant can be described as

$$D = D_0 \exp(-\Delta E/k_B T), \quad (1)$$

where the attempt diffusion described by the diffusion constant D_0 should be a diffusion process such as the Stokes-Einstein one, i.e., the short-time diffusion constant D_f observed. The authors estimate for this process relaxation times from 0.01 to 0.1 s for a structure of characteristic lengths of around 1000 Å and an energy barrier for handle creation of around $5k_B T$. These time scales are confirmed in our experiments, where the relaxation time varies from 0.01 to 0.1 s for characteristic lengths varying from 1000 to 1300 Å.

Our results eventually allow us to determine the energy barrier of such a process from a more microscopic model for the fusion process, illustrated in Fig. 5(b). We consider an infinite membrane, getting connected by a handle. The energy change as a result of a handle creation can be evaluated by the elastic energy difference between the initial (two separated membranes) and the final state (membranes connected by a handle), which are described by the Helfrich Hamiltonian [10]

$$H_{el} = \oint dS \left[\frac{\kappa}{2} (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right], \quad (2)$$

where c_i are the principal curvatures of the membrane, and c_0 is its spontaneous curvature. Thus, the elastic energy difference between the initial and the final state is entirely given by the bending elastic energy of the handle, including the change in topology. The last term is independent of the exact form of the handle but is a topological invariant. The first term depends on the exact handle

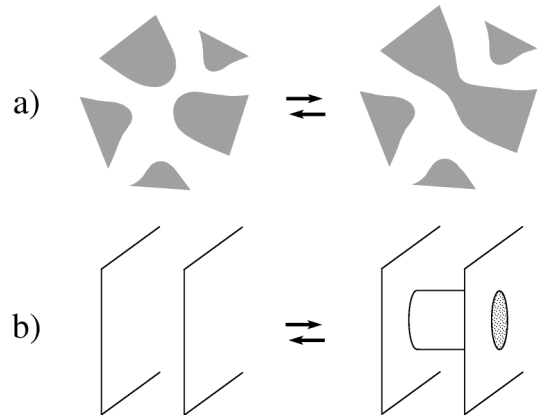


FIG. 5. (a) Topological relaxation process by membrane fusion as described by Milner *et al.* [4]. This topology change by creation and destruction of necks permits a diffusion of water and oil on the characteristic length scale ξ (illustration taken from [4]). (b) Microscopic model for the relaxation process described in (a) (see text).

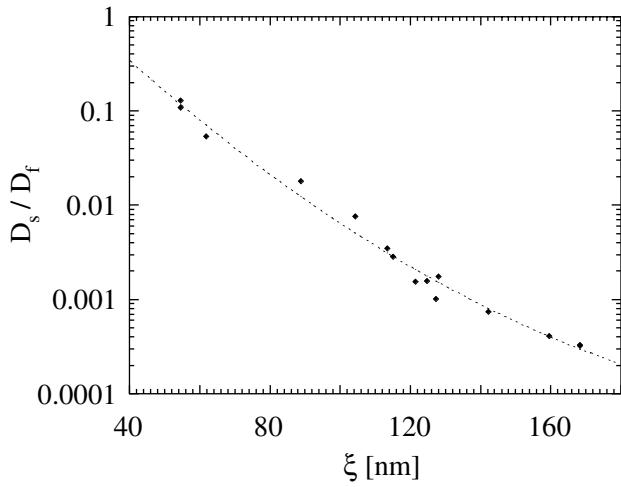


FIG. 6. Fit of the microscopic model proposed for a topological relaxation mode by energy activated membrane fusion [Eq. (4)] to the experimental data (see text).

shape and area. This expression is scale invariant for zero spontaneous curvature, and we can already note here that the requisite scale dependence of the energy barrier results from a nonzero spontaneous curvature. For convenience, we choose a cylindrical handle form to evaluate Eq. (2) and take for both the cylinder length and diameter the characteristic length ξ . Consequently, the requisite energy for the handle creation, i.e., the elastic energy difference between the initial and the final state, is written as

$$\Delta H_{el} = \pi \kappa (2 - 4c_0\xi + 2c_0^2\xi^2) - 4\pi \bar{\kappa}. \quad (3)$$

Introducing this relation for the activation energy in Eq. (1) leads to the observed size dependence of the diffusion constant as an exponential function of the characteristic length

$$D = D_f \exp\left(\frac{4\pi \bar{\kappa} - 2\pi \kappa}{k_B T}\right) \exp\left(\frac{2\pi \kappa (2c_0\xi - c_0^2\xi^2)}{k_B T}\right). \quad (4)$$

Quantifying the value of the attempt diffusion constant D_0 with the experimental short-time diffusion constant D_f leads to three free parameters, which are the elastic modulus κ and $\bar{\kappa}$ of the membrane, and its spontaneous curvature c_0 . Figure 6 presents the fit of this model to the ratio of the experimental long-time diffusion constant D_s and the short-time diffusion constant D_f , as a function of the characteristic length of the structure (determined by

x-ray scattering [6,7]). We can extract from this fit the bending elastic modulus ($\kappa = 1.9k_B T$), the spontaneous curvature ($c_0 = 1/270 \text{ nm}^{-1}$) and the Gaussian modulus ($\bar{\kappa} = 1.2k_B T$). While the values for the bending elastic modulus and the spontaneous curvature, which define the specific shape of the decay as a function of ξ , are rather insensitive to the choice of the attempt diffusion constant D_0 , the Gaussian modulus is more sensitive. However, these values seem reasonable taking into account the crudeness of the model.

In summary, we have shown the existence of two diffusive relaxation modes present in microemulsions, as predicted by Milner and co-workers. Because of the unusual variation of the slow relaxation mode as an exponential function of the characteristic length, we are able to identify this process as an energetically activated process, probably due to topological relaxation by membrane fusion.

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