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Physics Abstracts

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Hydrodynamic modes and topology in microemulsions and L_3 phases

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Résumé. — Le temps caractéristique de déclin des fluctuations de concentration à petit vecteur d'onde est estimé pour des phases de membranes aléatoires telles qu'on en rencontre dans les microémulsions ou les phases éponges. Nous considérons les effets de deux temps microscopiques (supposés longs) : l'un correspondant à la relaxation de la topologie du film, et l'autre à celle des volumes respectifs des deux régions continues. Ces effets peuvent être observables par des expériences de diffusion dynamique de la lumière, saut de température et biréfringence magnétique. L'ordre de grandeur du temps de relaxation topologique pour des phases éponges de SDS/dodecane/eau/pentanol est estimé être de l'ordre de 0,01 s.

Abstract. — We estimate the decay rates for surfactant and oil/water long-wavelength concentration fluctuations in phases of random fluid films, such as microemulsions and « sponge » L_3 phases. We consider the effects of two (possibly long) microscopic time scales : one for local relaxation of the film topology, and one for relaxation of the relative volumes of the two regions partitioned by the film (when this is not conserved). These effects may be observable in dynamic light scattering, temperature jump and magnetic birefringence studies. For dilute SDS/dodecane/pentanol/ H_2O sponge phases we use experimental data to estimate bounds for the topological relaxation time, and find this to be of order 0.01 s.

1. Introduction.

In certain systems, self-assembly of surfactant molecules leads to the formation of extended random surface structures. In balanced microemulsions, for example, a surfactant monolayer divides regions of oil and water. In the « sponge » (L_3) phase [1-3] of bilayer-forming surfactants, it appears that an extensive bilayer interface divides space into two regions of identical solvent, which may be designated « inside » (I) and « outside » (O) (Fig. 1a). In either of these two systems, we can expect two additional conserved quantities not present in ordinary single-component fluids. In a microemulsion, these may obviously be taken to be the volume fraction ϕ of surfactant, and the fraction ψ of the remaining volume occupied by oil (we loosely refer to ψ as the volume fraction of oil in this paper). The surfactant volume fraction is obviously conserved in an L_3 phase as well. It is less obvious but still true that if

there is no flow of solvent *through* the bilayers, then the partitioning of fluid into I and O regions is maintained dynamically [4]. Hence, the volume fraction ψ of « inside » fluid is a conserved quantity if we assume dynamics in which bilayers fuse and reconnect without tearing, as shown in figure 1b. More physically, if fluid may be slowly transported across the bilayers, the volume fraction ψ of « inside » fluid is not quite a conserved variable, but has some slow non-conservative dynamics associated with the leakage of solvent through the bilayer. Neither of the currents corresponding to the two conserved quantities ψ and ϕ described above is itself conserved, so the related hydrodynamic modes are both diffusive, i.e., the dispersion relation must be of the form $\omega = Dq^2$.

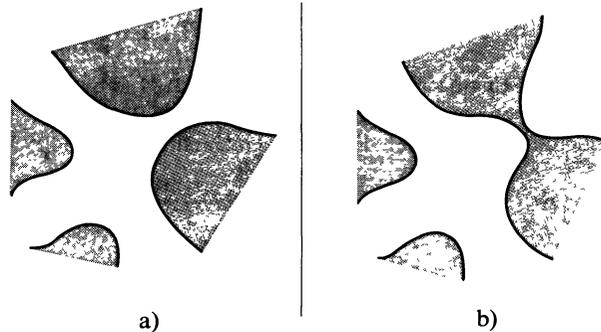


Fig. 1. — (a) The L_3 phase or « sponge » (Ref. [2]). The surfactant forms a bilayer surface without tears, edges or seams. Such a surface, even if it has disconnected components, divides space into two disjoint regions which may be called « inside » and « outside ». (Here, the inside volume (say) has been shaded ; however, the fluids in the inside and outside volumes are *identical* in an L_3 phase.) The free energy is unaltered if the labelling of these regions is interchanged ; this symmetry is not usually present in microemulsions for which e.g., « inside » may be identified with oil and « outside » with water. (b) A change in the topology of a surfactant interface may occur when a narrow « neck » between two fluid regions is created or destroyed.

In this paper, we estimate the values of D and describe the corresponding hydrodynamic modes (eigenvectors of the hydrodynamic matrix), and how they each depend on quantities characterizing the microemulsion or L_3 phase, namely the mean volume fraction of (respectively) oil or « inside » $\langle \psi \rangle$ and surfactant $\langle \phi \rangle$. We shall show that the symmetric state $\langle \psi \rangle = 1/2$ has particularly simple dynamics, with ψ decoupled from ϕ . As the symmetry is broken, the decays of oil and surfactant autocorrelations are mixed.

Also, we consider the effect of a slow microscopic timescale for relaxation of the topology (as depicted in Fig. 1b) of the surfactant (bi)layer on the oil and surfactant autocorrelation functions. This gives rise to a crossover from decay rates corresponding to « quenched » Euler characteristic at high wavenumbers, to decay rates for « annealed » topology at lower wavenumbers. We may expect the microscopic timescale to be slow when the activation energy for the fusion process is large.

In the case of a balanced microemulsion, the symmetry of oil and water is approximate, but can be made almost exact by tuning the salt content etc. so as to obtain a symmetric phase diagram. For the L_3 phase the symmetry is exact in the Hamiltonian ; it is maintained in the symmetric sponge ($\psi = 1/2$) state, but can break spontaneously to make an asymmetric sponge or vesicle state. From now on we use the language of balanced microemulsions (« oil » and « water ») as opposed to « inside » and « outside » ; however, many of our results are actually more pertinent to L_3 systems for which the exact symmetry exists.

2. Relaxation processes and conserved quantities.

2.1 LOCAL SOLVENT FLOW. — We may make an estimate of the diffusion constant for transport of (say) oil in the microemulsion by equating the work done by viscous dissipation and the lowering of the free energy upon the relaxation of a fluctuation, as follows. We imagine that transport of oil occurs by hydrodynamic flow on the characteristic « cell size » or length scale ξ (corresponding to the peak in $S(\mathbf{q})$), which must involve velocity gradients ∇v of the order of $\xi^{-1} v$. Now we consider an initial state in which ψ has the average value ψ_0 , and the value $\phi + \delta\psi$ in some hydrodynamically large ($\gg \xi$) region of size q^{-1} . The corresponding free energy change per unit volume is $\delta F / \delta\psi$.

The microscopic flow velocity is of some characteristic magnitude v , and the corresponding current is

$$j_\psi = \psi_0 v . \tag{1}$$

Viscous dissipation does work per unit volume at a rate

$$\eta (\nabla v)^2 \sim \eta v^2 \xi^{-2} . \tag{2}$$

The corresponding change in the free energy density occurs at a rate

$$\dot{\psi} \frac{\delta F}{\delta\psi} \sim \psi_0 (\nabla \cdot v) \frac{\delta F}{\delta\psi} . \tag{3}$$

Equating these two rates of work done gives the scale of microscopic velocity as

$$v \sim \eta^{-1} \xi^2 \psi_0 q \frac{\delta F}{\delta\psi} . \tag{4}$$

(The factor of q arises from the term $\nabla \cdot v$, since it is only gradients of the macroscopic velocity (coarse-grained on a scale $> \xi$) which have the hydrodynamic length scale q^{-1} , and are effective in relaxing $\delta\psi$ and hence F .)

Now we may substitute the value of v into the continuity equation

$$\dot{\psi} = \nabla \cdot j_\psi \tag{5}$$

to obtain the hydrodynamic equation for relaxation of ψ ,

$$\dot{\psi} \equiv D_\psi q^2 \delta\psi \sim \frac{\xi^2 q^2}{\eta} \psi_0^2 F_{\psi\psi} \delta\psi , \tag{6}$$

where $F_{\psi\psi} \equiv \delta^2 F / \delta\psi^2$, with similar notation to be used throughout the paper. (For the L₃ phase, this equation neglects fluid flow across bilayers, which would lead to nonconservative relaxation of ψ , discussed below.)

We may make an analogy with so-called permeation flow in porous media [5]. There it is argued that a pressure gradient ∇p across a porous rock induces a macroscopic flow velocity v . On dimensional grounds, if we require that $\nabla p / v$ is proportional to viscosity, we find immediately Darcy's law,

$$\nabla p \sim \eta \xi^{-2} v . \tag{7}$$

If we now identify p with osmotic pressure variation $\psi_0 F_{\psi\psi} \delta\psi$, and use the expressions for the current and conservation of ψ , we arrive at the same hydrodynamic equation, equation (6).

2.2 SURFACTANT MOTION. — Now consider the transport of surfactant. In microemulsions and L_3 phases, we may consider two possible modes of transport for surfactant : 1) diffusion across intervening fluid regions, where the surfactant solubility is small but nonvanishing ; and 2) flow which « smooths out wrinkles » in the surfactant (bi)layers separating fluid regions, and sweeps surfactant along the fluid-fluid interface [6].

We examine these in turn. First, the solubility of surfactant in the bulk fluids is quite low, and the resulting macroscopic diffusion constant is proportional to the volume fraction of surfactant in the bulk fluid. We will neglect this process in the present work.

Next, the smoothing out of wrinkles of all length scales ℓ up to $\ell = \xi$ involves microscopic velocity gradients on the scale ℓ . If some excess area is to be added or removed, perhaps forced by some local adjustment of the surfactant chemical potential, the energies of the lowest modes are most affected, and so their amplitudes will be most changed. In other words, the largest wrinkles give the dominant contribution to the change of surfactant density among all undulations. Hence we may say that the viscous dissipation associated with smoothing out undulations occurs primarily on the scale $\ell \sim \xi$. Then the argument given above for the rate of decay of fluctuations of the oil volume fraction ψ may be repeated for the surfactant volume fraction ϕ , and an Onsager coefficient corresponding to a pore size ξ is again obtained [6], $D_\phi \sim \xi^2 \eta^{-1} \phi_0^2 F_{\phi\phi}$.

This result for D_ϕ , and equation (6) for D_ψ , involve the thermodynamic derivatives $F_{\phi\phi}$ and $F_{\psi\psi}$, whose scaling will be discussed in more detail in section 3.2. As shown there, the basic scaling expected for both D_ϕ and D_ψ is (to within logarithmic corrections) $D \sim kT/(\eta\xi)$. This behavior is similar to that in semidilute polymer solutions and other systems with thermal energies and a well-defined correlation length. With a viscosity of 1 cP and a cell size ξ in the range 100-1 000 Å, we have $D \sim 10^{-6}$ - 10^{-7} .

2.3 « LEAKAGE ». — In the L_3 phase, we expect the inside volume fraction ψ to be nonconserved, on a timescale governed by an activated « leakage » process ; namely, the « inside » and « outside » fluid in the L_3 phase may exchange by opening small holes in the bilayer. These holes are expected to be very rare so that their effects are negligible for static properties ; however, their dynamical effects may be significant. If these holes are molecular in size, we are really describing diffusion of solvent molecules directly through the bilayer, a process which is known in thermotropic smectics as permeation [7]. Larger holes (of size $\leq \xi$) would lead to actual hydrodynamic flow of fluid through the bilayer. In any case, the effect of « leakage » across the bilayer is to add a term $\tau_4^{-1} \psi$ to the right-hand side of the relaxation equation (6) for ψ . Note that $\tau_\psi = \infty$ for microemulsions ; such a term is absent for microemulsions since oil and water are not locally interchangeable.

2.4 TOPOLOGICAL RELAXATION. — In addition to this long microscopic timescale, there is another important activated local process to consider in the dynamics of microemulsions and L_3 phases. This process is fission or coalescence of fluid regions which changes the topology of the surfactant layer (Fig. 1b). We may imagine a process in which a « neck » in the surfactant layer is 1) created by the collision of two nearby layers and the opening of a neck between them ; or 2) destroyed, by pinching off a neck and retracting the separated pieces. (Physically, we expect such topological changes to be activated because the intermediate state of the interface undergoing such a change is energetically unfavorable, containing sharp bends and/or bilayers in close contact).

If we forbid such changes in the topology of the surfactant layer, then it is clear that a different state is reached if some control parameter is changed. For example, consider the effect of reducing the surfactant chemical potential with and without topological relaxation. With full equilibration of the layer, including topological relaxation, we expect states of

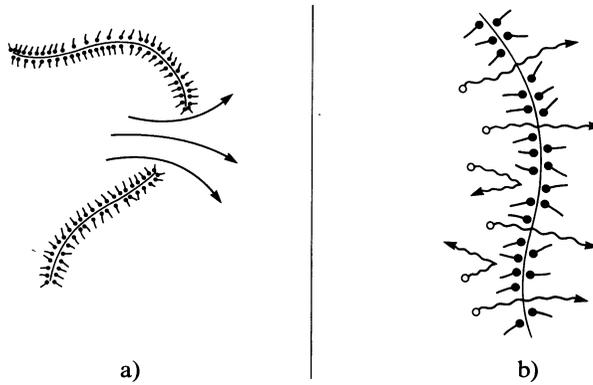


Fig. 2. — In the L₃ phase, in which the fluids on either side of the bilayer are identical, transport across the bilayer may occur either through the opening of large holes in the bilayer through which fluid can flow (2a), or by diffusion of fluid molecules across the bilayer (2b).

different ϕ to be related by a dilation [1, 8] (this is true up to logarithmic corrections, at least in the symmetric state), and the number of handles per unit volume, for example, would scale with ξ^{-3} . Without topological relaxation, the Euler characteristic for the surfactant film is fixed; we might expect this state to contain more surfactant (to form the extra handles) than the totally relaxed state at the same chemical potential.

If no topological changes could occur in the surfactant layer, we would have a new conserved variable in the system, which might be taken to be the Gaussian curvature [9], or equivalently the Euler number per unit volume; we shall define h to be the negative of this quantity and refer to it loosely as the « handle density ». Since we expect the kinetics of local processes involving the formation and removal of handles in the surfactant layer to be activated, the relaxation of the handle density h should be non-conserved, but may be rather slow if the activation energy is large. We characterize this by a time scale τ_h . In general this timescale will be rather different from τ_ψ , as different activation barriers are involved for changing topology and leaking solvent across bilayers. It is possible in an L₃ phase to have $\tau_h \ll \tau_\psi$ if leakage of solvent across the bilayer is slow.

3. Thermodynamic couplings.

We now turn to the issue of the thermodynamic and kinetic couplings between the variables ψ , ϕ , and h , and how these couplings change when the oil-water or « inside-outside » symmetry ($\langle \psi \rangle = 1/2$) is broken.

3.1 HYDRODYNAMICS IN THE SYMMETRIC STATE. — First we consider the thermodynamic couplings, i.e., the entries in a matrix

$$\chi_{\alpha\beta}^{-1} \equiv \frac{\delta^2 F}{\delta \alpha \delta \beta} \equiv F_{\alpha\beta}, \quad (8)$$

where α, β are one of $\{\psi, \phi, h\}$. These entries may be estimated from some « microscopic » model of microemulsions, for which we shall use the model of Safran *et al.* [10, 2]. The model Hamiltonian has (in the absence of spontaneous curvature) the symmetry $\psi \rightarrow (1 - \psi)$, which means that all off-diagonal terms in χ^{-1} involving ψ vanish in the symmetric state. (This symmetry of the Hamiltonian is expected to be an exact one for an L₃ phase.) Physically, we

may say that in the symmetric state, a small change in μ_ϕ or μ_h cannot produce a linear change in $\langle\psi\rangle$ because the sign of the supposed change reverses under the symmetry operation.

In contrast, there should be linear couplings between ϕ and h even in the symmetric state, as we argued above that a state with more handles must have more surfactant, all other things being equal. We may guess the size of this coupling to be such that a doubling of the number of handles gives rise to a similar increase in the amount of surfactant present. In other words,

$$\chi_{\phi h}^{-1} \sim -\chi_{\phi\phi}^{-1} \phi_0 h_0^{-1}. \quad (9)$$

Here ϕ_0 and h_0 are the mean volume fraction of surfactant and handle density respectively. From the model of Safran *et al.* it can be shown that $h_0 \sim \text{const.} \times \xi^{-3}$ in the symmetric state.

We may make similar arguments for the vanishing of the off-diagonal couplings involving ψ in the matrix of Onsager coefficients. Namely, the direction of a current of oil volume fraction j_ψ in response to a gradient in either μ_ϕ or μ_h reverses under the symmetry operation of relabeling oil as water ($\psi \rightarrow (1 - \psi)$), so such a current cannot exist in the symmetric state.

We could in principle have off-diagonal couplings in the Onsager matrix between ϕ and h , which would be proportional to q^2 (since ϕ is conserved, and the Onsager matrix is symmetric). Since these variables are already coupled thermodynamically, we will neglect these crossterms for simplicity in the present work. Finally, h itself can be relaxed by conservative transport (diffusion of handles) as well as activated local processes; this suggests that Λ_{hh} should have a permeation-like term similar to $\Lambda_{\psi\psi}$ and $\Lambda_{\phi\phi}$.

Hence we have, for the symmetric state,

$$\Lambda = \begin{bmatrix} \psi_0^2[\beta\tau_\psi^{-1} + a(q\xi)^2\eta^{-1}] & 0 & 0 \\ 0 & b\phi_0^2(q\xi)^2\eta^{-1} & 0 \\ 0 & 0 & h_0^2[\beta\tau_h^{-1} + c(q\xi)^2\eta^{-1}] \end{bmatrix}, \quad (10)$$

where a , b , and c are coefficients of order unity, and $\tau_\psi = \infty$ for microemulsions. The inverse susceptibility matrix is

$$\chi^{-1} \equiv \begin{bmatrix} F_{\psi\psi} & 0 & 0 \\ 0 & F_{\phi\phi} & F_{h\phi} \\ 0 & F_{\phi h} & F_{hh} \end{bmatrix}. \quad (11)$$

The linearized hydrodynamic equations for our microemulsion degrees of freedom are then (in matrix form)

$$\dot{\Phi} = M\Phi \equiv \Lambda\chi^{-1}\Phi. \quad (12)$$

3.2 DYNAMIC LIGHT SCATTERING PREDICTIONS. — In a dynamic light-scattering experiment, we may observe most easily in microemulsions the autocorrelations of ψ , and in the L_3 phase (where there is no contrast between inside (ψ) and outside ($1 - \psi$) regions, which contain identical solvent) the autocorrelations of ϕ [11]. Hence we are interested in the decomposition of the oil or surfactant volume fractions in terms of the hydrodynamic eigenmodes of the system. In the symmetric state, the ψ autocorrelation function $S_{\psi\psi}(q, t)$ decouples, and gives for microemulsions the simple diffusive behavior anticipated in equation (6):

$$S_{\psi\psi}(q, t) \sim \chi_{\psi\psi}(q) \exp[-D_\psi q^2 t], \quad (13)$$

$$D_\psi = a\xi^2 \eta^{-1} \psi_0^2 F_{\psi\psi}. \quad (14)$$

The autocorrelation of the surfactant volume fraction ϕ is more complicated ; its coupling to a nearly-conserved handle density gives a q -dependence to the apparent diffusion constant for ϕ . The effect may be summarized as follows. For q such that the relaxation time τ_h is short compared to the timescale $(D_\phi q^2)^{-1}$ of conservative relaxation of surfactant density, the handle density may be regarded as annealed. This would be the conventional hydrodynamic assumption, and gives

$$D_\phi |_{\mu_h} = b\xi^2 \eta^{-1} \phi_0^2 F_{\phi\phi} |_{\mu_h}. \tag{15}$$

In contrast, for q large enough that $D_\phi q^2 \geq \tau_h^{-1}$, the relevant susceptibility is that found at fixed h , and we have

$$D_\phi |_h = b\xi^2 \eta^{-1} \phi_0^2 F_{\phi\phi} |_h. \tag{16}$$

The ratio of the two results for D_ϕ is given by the thermodynamic relation

$$F_{\phi\phi} |_h = [1 + F_{\phi h}^2 / (F_{\phi\phi} F_{hh})] F_{\phi\phi} |_{\mu_h}. \tag{17}$$

Hence there should be a crossover from the quenched prediction $D_\psi |_h$ to the annealed expression $D_\psi |_{\mu_h}$, which is smaller by a factor of order unity [12], on the timescale τ_h .

Note finally that when the dependence of $F_{\phi\phi}$ and $F_{\psi\psi}$ on cell size ξ is taken into account, both D_ϕ and D_ψ scale as

$$D_\alpha \sim \frac{kT}{\eta\xi} \ln \left(\frac{\xi}{\xi_K x_\alpha} \right).$$

Here α stands for either ϕ or ψ , ξ_K is the persistence length, and the $\{x_\alpha\}$ are constants. This scaling holds because the dimensionless inverse susceptibilities $a^2 F_{\alpha\alpha}$ both scale [8, 13] as $kT/\xi_K^3 \times \ln(x/x_\alpha)/x^3$, with $x \equiv \xi/\xi_K$ and $\{x_\alpha\}$ as above. Except for the logarithmic corrections [8, 13], this is evident from dimensional analysis, as the thermodynamic derivatives are both energy densities, and the scales of energy and length in these systems are kT and ξ respectively.

3.3 BROKEN SYMMETRY. — The oil-water or inside-outside symmetry may be broken, either spontaneously in the L₃ phase, or by the imposition of a nonzero spontaneous curvature of the surfactant monolayers in a microemulsion. There is no longer a $\psi \rightarrow (1 - \psi)$ symmetry, hence there are off-diagonal couplings involving ψ in the thermodynamic and Onsager matrices. One may guess that for the L₃ phase, these couplings will be of order $\varepsilon \equiv (2\langle\psi\rangle - 1)$ times the appropriate coupling scale. That is, we expect

$$F_{\psi\phi} \sim \varepsilon [F_{\psi\psi} F_{\phi\phi}]^{1/2}. \tag{18}$$

For a « minimal » thermodynamic model, we may take such an off-diagonal coupling between ψ and the surfactant volume fraction in the free energy. For simplicity we assume an annealed handle density in the broken symmetry case. This is equivalent to taking a linear coupling, of the form given above, between ψ and an annealed variable $\tilde{\phi} \equiv \phi - hF_{h\phi}/(2F_{\phi\phi})$, and omitting a separate coupling between ψ and h .

At the same level of approximation, we assume in the Onsager matrix that symmetry-breaking introduces only off-diagonal couplings between ϕ and ψ , of the form

$$\Lambda_{\phi\psi} = -d\varepsilon (q\xi)^2 \eta^{-1}, \tag{19}$$

where d is a positive coefficient of order unity. (Here the sign is determined by the supposition that the surfactant current will tend to follow the current of the minority fluid phase; this is motivated by a picture of moving droplets.)

With these assumptions, we may summarize the effect of the symmetry-breaking on the eigenmodes (in the case of annealed topology) as follows. The $O(\varepsilon)$ couplings shift the two eigenvalues of the hydrodynamic matrix by an amount of order $O(\varepsilon^2)$, and split the modes by a similar amount. The eigenvectors are also changed, such that the mode which was for $\varepsilon = 0$ purely surfactant transport at fixed oil volume fraction now involves oil flow at $O(\varepsilon)$.

This mixing may be difficult to see experimentally, for the following reason. As remarked above, the dimensionless inverse susceptibilities $\alpha^2 F_{\alpha\alpha}$ for $\alpha = \phi, \psi$ scale [8, 13] in the same way with ξ ; similarly, the permeabilities for oil and surfactant transport were argued to be of the same order, $(q\xi)^2 \eta^{-1}$. Hence the two eigenvalues which are being mixed may not be widely separated, and have the same scaling dependence on ξ etc. The symmetry breaking introduces an $O(\varepsilon)$ admixture of a relaxational mode of a comparable decay rate to the mode already observed for the symmetric state. Because separation of the sum of two exponentials of similar decay rate can be experimentally difficult, this effect could be misinterpreted as an $O(\varepsilon)$ shift in the decay rate, with a decrease in the goodness of fit.

In addition, if we examine an asymmetric L_3 phase in which τ_ψ (presumed here $\gg \tau_h$) falls in the experimental timescale, we should expect to see a q -dependent crossover in D_ϕ as we pass from wavenumbers with $\tau_\psi \ll (D_\psi q^2)^{-1}$, at which ψ is quickly relaxing (annealed) compared to ϕ fluctuations, to wavenumbers at which ψ is slowly relaxing (quenched). This fractional shift in D_ϕ for q crossing $D_\phi q^2 \sim \tau_\psi^{-1}$ will be $O(\varepsilon^2)$.

4. Estimating τ_h .

As a final topic, we turn to the question of how we can determine the timescale τ_h for relaxation of the microemulsion topology. We have already argued that the kinetics of this relaxation is activated, according to the process shown in figure 1b. The attempt frequency for the activated process should be set by the so-called «Zimm time» $\tau_0 \sim \xi^2 D(\xi)^{-1}$ required for a fluid region of size ξ to diffuse its own length. The relaxation time τ_h then has the form ($\beta \equiv (k_B T)^{-1}$)

$$\tau_h \sim \tau_0 \exp[\beta \Delta E], \quad (20)$$

where the diffusion constant for a region of size ξ is simply

$$D(\xi) \sim \frac{kT}{6\pi\eta\xi}. \quad (21)$$

Rather than trying to determine ΔE from some microscopic model of the surfactant layer, we will try to bound this τ by considering 1) the viscosity of the microemulsion or L_3 phase, and 2) the sensitivity of the system to shear. (Our numerical estimates are pertinent to the very dilute SDS-dodecane-pentanol-water L_3 phase of Ref. [3].)

We expect a contribution to the viscosity from the long relaxation time τ to go as $\delta\eta \sim G(0)\tau$, where the instantaneous modulus $G(0)$ of the mesophase is of order $G(0) \sim kT/\xi^3$ (by a scaling argument, which maintains that the characteristic energy of a cell of size ξ is of order kT). This gives rise to a contribution to the viscosity which is simply $\delta\eta \sim \eta \exp[\beta \Delta E]$, where η is the solvent viscosity. Because microemulsions and L_3 phases are not extremely viscous, $\beta \Delta E$ cannot be very large, and so τ is bounded above. For the very

dilute L₃ phases of reference [3], we may take $\delta\eta \leq 100 \eta_0$, and $\xi \sim 1\,000 \text{ \AA}$; then we find $\tau_h \leq 10^{-1} \text{ s}$.

On the other hand, preliminary experiments [14] in most of these dilute L₃ phases indicate that characteristic shear rates for shear-induced birefringence (and possibly a transition to lamellar order) are on the order of $\gamma \sim 100 \text{ s}^{-1}$. This suggests some relaxation time τ_h which is no *shorter* than about 10^{-2} s . The two estimated bounds taken together suggest that the topological relaxation time τ in the dilute L₃ phase is in the neighborhood of 10^{-2} s (though perhaps much shorter in microemulsions, which are usually less viscous and less dramatically affected by shear). This estimate implies an energetic barrier to creation of handles of around $5kT$ for the most dilute L₃ phases of reference [3].

Relaxation times of order 10^{-2} s are readily observable, for example in temperature-jump experiments [15]. (Shorter time scales, as might arise in microemulsions or less dilute sponge phases, can also be easily resolved by this technique.) Furthermore, the crossover in the q -dependence of the decay rate for surfactant fluctuations may give evidence of the size of τ_h . We may compare a relaxation time of order 10^{-2} s with the conserved relaxation rate to determine the magnitude of q for which the diffusion constant and amplitude of fluctuations might be expected to change; we obtain

$$q^2 \sim (kT)^{-1} \eta \xi \tau_h^{-1}, \quad (22)$$

which for the typical L₃ parameters used above gives $q \sim 10^4 \text{ cm}^{-1}$, which should be accessible by dynamic light scattering.

5. Conclusions.

We have described the hydrodynamic modes associated with fluctuations of oil and surfactant volume fractions (ψ, ϕ) in microemulsions. For the analogous « sponge » or L₃ phase, ψ is not « oil » but the volume fraction of « inside » solvent [2]. Two relevant timescales are: 1) τ_ψ , the « leakage » time of solvent across the bilayer in the L₃ phase ($\tau_\psi = \infty$ in microemulsions, where solvents on opposite sides of a surfactant interface are distinct); and 2) τ_h , the relaxation time for the topology of the surfactant interface, which may be very long in phases with sharply-defined interfaces and high activation barriers.

In the simplest case, in which the phase respects the oil/water or inside/outside symmetry ($\langle \psi \rangle = 1/2$), the hydrodynamic decay rates for ψ and ϕ fluctuations are displayed in figure 3. To summarize: fluctuations of ψ decay as $D_\psi q^2$ for large q , and as τ_ψ^{-1} for small q . Fluctuations of ϕ decay as $D_\phi(q) q^2$, with $D_\phi(q)$ crossing over from a value at small q appropriate to an annealed topology, to a larger value at large q corresponding to a quenched topology. The crossovers occur when the relaxation rates of ψ and ϕ fluctuations equal τ_ψ^{-1} and τ_h^{-1} respectively. In the broken-symmetry phase ($\langle \psi \rangle \neq 1/2$), ψ and ϕ fluctuations are coupled at $O(\langle \psi \rangle - 1/2)^2$, and the resulting fluctuation decays are not single-exponential.

By considering the observed sensitivity to shear and moderate viscosity of L₃ phases, we conclude that τ_h for the dilute L₃ phases of reference [3] should be of order 10^{-2} s . This relaxation time may be observed either in small- q crossover of relaxation rates of ϕ fluctuations in L₃ phases, or in temperature-jump experiments [15].

A magnetic birefringence measurement, in which a square wave pulse of magnetic field is applied to the system, would give striking behavior for the optical signal as the duration τ of the pulse is increased beyond τ_h . For short pulses with $\tau \ll \tau_h$, the topology would be unable to adjust to the imposed field before it was removed again; in this case the decay of the

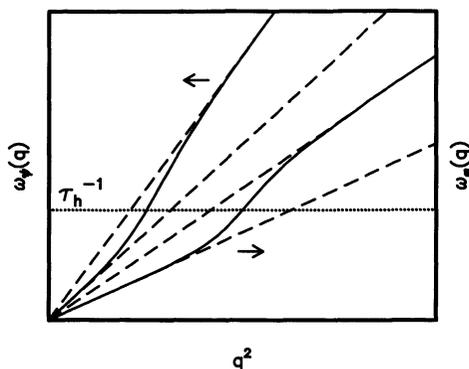


Fig. 3. — Shown are the different wavenumber-dependences at small q^2 ($q\xi \ll 1$) of the characteristic decay rates ω_ψ and ω_ϕ for the volume fractions of oil and surfactant in a symmetric microemulsion. The dashed curves are asymptotic diffusive behaviors; the dotted line indicates the crossover frequency τ_h^{-1} , near which the apparent diffusion constants of the two modes changes from the « quenched topology » (high-frequency) value to the « annealed topology » (low-frequency) value. (We have assumed arbitrarily for this figure that $\omega_\psi(q)$ lies above $\omega_\phi(q)$.) In the symmetric sponge phase, the timescale τ_ψ is finite, and the « oil » mode (unobservable by scattering) decay rate approaches τ_ψ^{-1} as q approaches zero. In the broken-symmetry phase, the modes are mixed as described in section 3.3.

optical signal should be governed by local solvent and surfactant flow with a relaxation time of order $\tau_0 \sim \xi^2/D_\phi(\xi^{-1}) \sim 6\pi\eta\xi^3/T$. The topology could adjust to a new equilibrium value if the duration of the pulse exceeded τ_h ; then the decay of the optical signal after the removal of the field would show the slow relaxation time $\tau_h \sim \tau_0 \exp(\beta \Delta E)$ in addition to a fast part with time τ_0 . As discussed above, these times may be well separated if the activation energy for topological change is large enough.

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