J. Phys. France **51** (1990) 1733-1747 15 AOÛT **1990**, PAGE 1733

Classification
Physics Abstracts
64.60H — 61.25H — 64.70M

Hexagonal and lamellar mesophases induced by shear

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(*Received on January 15, 1990, revised on April 10, 1990, accepted on April 26, 1990*)

Abstract. — The role of a shear flow in the formation of an hexagonal mesophase is investigated and the transition between the isotropic, lamellar and hexagonal phases described in a three dimensional phase diagram $[\tilde{\tau}, \tilde{\mu}, \Delta]$ where $\tilde{\tau}$ is a temperature-related parameter, $\tilde{\mu}$ a measure of the intrinsic asymmetry of the system and Δ the strength of the shear rate. At zero shear rate the microphase separation transition (M.S.T.) is dominated by fluctuations but it acquires a strong mean-field character as Δ is increased. We find a region in the phase diagram where the same isotropic phase may undergo a transition to a lamellar or an hexagonal structure according to whether is cooled or sheared. The relevance of our results for diblock copolymers and for microemulsions is discussed.

1. Introduction.

Blends [1, 2] or solutions [3] of diblock copolymers are a classic example [4] of systems undergoing a microphase separation transition (M.S.T.). At high temperatures the mixing entropy of the two blocks is enough to overcome the natural tendency for separation as dictated by the positive heat of mixing of monomers A and B. Thus the system is isotropic for such temperatures. Under cooling, a point is reached where separation is favoured over mixing and the two blocks tend to stay as far apart as possible in order to reduce the number of A-B contact points. However, since they are chemically bonded, a macroscopic phase separation is not possible as it would be in the case of blends or solutions of two chemically different polymers. The connectivity implies that the structures which the polymers are able to form have a typical size of the order of the radius of gyration of the chains R_G. Consequently, the Fourier transform of the two point correlation function, $S(\mathbf{k})$, shows a well-pronounced peak at $k = |\mathbf{k}| = k_0 \sim R_G^{-1}$, where it can be approximated by

$$S(\mathbf{k}) = \frac{1}{c^2} \frac{1}{\tau + (k - k_0)^2} \tag{1.1}$$

τ being is a temperature-like control variable.

Several different ordered structures can result from the M.S.T., depending upon the asymmetry of the diblock copolymer (usually measured by the ratio of the chemical lengths of the blocks, $f = N_A/N_B$). Very asymmetric copolymers tend to form spherical objects, packed in a three-dimensional body-centre cubic lattice. For smaller asymmetries the tendency is to form cylinder-like aggregates, packed in a two-dimensional hexagonal lattice, or one dimensional lamellar structures. More exotic phases, such as bicontinuous ordered structures, have been also reported [5].

Many other systems, like lyotropic liquid crystals [6-9] or microemulsions [10-12] undergo a microscopic mesophase separation as well. Here the asymmetry is a more complicated function of the system parameters. For microemulsions, for example, the intrinsic asymmetry is controlled not only by the spontaneous curvature of the surface of an ordered domain but also by the ratio of water and oil contents. In suitable systems, hexagonal liquid crystalline phases, as well as lamellar (smectic) ones, are seen [13]. The onset of the ordering at finite values of wave vector has also turned out to be a useful tool in explaining the phase transitions observed in colloidal crystals [14] or even in convective systems [15] (Rayleigh-Bénard instabilities).

In all these cases the transition is second order or weakly first order and this has motivated a description of the M.S.T. based upon a Landau-Ginsburg free-energy, which is expected to correctly account for the phase diagram in the regions close to the transition lines. At the level of the mean-field approximation the isotropic-lamellar transition is predicted to be second order [16, 2] for symmetric systems (for instance, for diblock copolymers which have blocks of equal lengths or for microemulsions with no spontaneous curvature and equals amounts of water and oil). Taking into account the role of fluctuations at the Hartree level [17] leads to a negative shift into the temperature at which the transitions occur [17, 1] : under cooling, the fluctuations *delay* the ordering. Furthermore the transition becomes first order even for symmetric systems and the spinodal point is shifted formally to an infinite negative temperature τ.

As mentioned above, when the system approaches the transition the fluctuations of the order parameter become large. Since the microscopic mobility remains essentially unchanged, this means that the lifetime of such fluctuations, also becomes large near the transition. It is then interesting to investigate the effect of a dynamical perturbation imposed on the system, because the relaxation frequencies become experimentally accessible [18, 19]. The typical example is that of an applied shear flow (for example in a Couette geometry) which imposes an average velocity flow $\mathbf{u}_x = (Dy, 0, 0)$. For small enough shear rates D, the time for a fluctuation to be convected away from the critical shell ($|\mathbf{k}| = k_0$) is longer than its spontaneous relaxation time, and the flow has only a weak effect on the phase transition. However, for large shear rates the fluctuations are convected away before they would otherwise have time to relax, and are less and less effective in suppressing the phase transition which, at high shear rates, therefore acquires a strong mean-field character.

In a recent letter [20] Cates and Milner investigate the role of a shear-flow on the isotropic-lamellar phase transition. Their results show that the transition temperature increases with shear rate and, for large enough shear rates, approaches exponentially its mean-field value. Hence, close to the static transition temperature, there is a region where the disordered homogeneous phase becomes unstable to a lamellar phase at high enough shear rate. Cates and Milner argued that the lamellar phase should order in the direction which better avoids the constraints of the flow, i.e., with the wavevector perpendicular to both the flow and its gradient.

Obviously, two dimensional structures are also good candidates for phases that can arise under shear flow conditions. In this paper we study the formation of a two-dimensional hexagonal phase, and the corresponding isotropic-hexagonal (I-H) and hexagonal-lamellar (H-L) phase transitions. In section 2 we review some well known results on the M.S.T. within the framework of both a mean-field [2] and the Hartree approximation of Brazovskii [17].

The role of the shear field on the I-H and H-L phase transitions is discussed in section 3. In section 4 we outline the practical relevance of this work for diblock copolymers and microemulsions. Section 5 summarizes our results and presents our conclusions.

2. The microphase separation transition.

A second order or weakly first order phase transition can be described [21] by the Landau-Ginsburg expansion for the free-energy density as a function of the order parameter $\phi(\mathbf{r})$ (in units of $k_B T$):

$$F[\psi] = \frac{1}{2!} \int_V \int_V A(\mathbf{r} - \mathbf{r}') \, \phi(\mathbf{r}) \, \phi(\mathbf{r}') \frac{\mathrm{d}\mathbf{r}}{V} \frac{\mathrm{d}\mathbf{r}'}{V} + \frac{\mu}{3!} \int_V [\phi(\mathbf{r})]^3 \frac{\mathrm{d}\mathbf{r}}{V} + \frac{\lambda}{4!} \int_V [\phi(\mathbf{r})]^4 \frac{\mathrm{d}\mathbf{r}}{V} \quad (2.1)$$

where

$$A(\mathbf{r}) = \frac{1}{(2\pi)^3} \int \exp\{i\mathbf{k} \cdot \mathbf{r}\} \, [c^2 S(\mathbf{k})]^{-1} \, \mathrm{d}\mathbf{k} \quad (2.2)$$

and $S(\mathbf{k})$ is approximated by (1.1). The order parameter is chosen to vanish on average in the homogeneous disordered phase and has a non-zero value in the ordered phases. In this formulation the coefficients of the third and quartic order terms are taken as constants which corresponds to a local approximation for the vertex functions in the expansion of the free energy as a function of the order parameter [1]. This approximation has so far proved accurate enough for the systems of interest in the present work. The third order coefficient μ is a measure of the intrinsic asymmetry, being zero for completely symmetric systems. The Landau-Ginsburg free-energy is invariant under the transformation $\{\phi \to -\phi \, ; \mu \to -\mu\}$. Thus, we assume, without lost of generality, that μ is positive. Throughout this section we shall discuss the predictions of the Landau-Ginsburg free-energy from its general formulation, we specify the physical meaning of the order parameter and of the several coefficients when analyzing the diblock copolymer and microemulsion cases, in section 4.

2.1 THE MEAN-FIELD APPROXIMATION. — In the limit of high shear rates the transition is expected to become mean-field in character, we therefore first recall the predictions of the mean-field theory for the formation of the lamellar and hexagonal mesophases. The one dimensional lamellar phase along the z-axis is described by

$$\phi(\mathbf{r}) = 2 a_\ell \cos(k_0 z) \quad (2.3)$$

and for the two dimensional hexagonal phase in the Y-Z plane we have

$$\phi(\mathbf{r}) = 2 a_\mathrm{h} \left\{ \cos(k_0 z) + \cos\left(k_0 \frac{\sqrt{3}\,y - z}{2}\right) + \cos\left(k_0 \frac{-\sqrt{3}\,y - z}{2}\right) \right\}. \quad (2.4)$$

Inserting these forms of the order parameter in the Landau-Ginsburg free energy (2.1) one obtains

$$F_\ell = \tau a_\ell^2 + \frac{\lambda}{4} a_\ell^4 \quad (2.5)$$

for the lamellar structure and

$$F_\mathrm{h} = 3 \tau a_\mathrm{h}^2 + 2 \mu a_\mathrm{h}^3 + \frac{15 \lambda}{4} a_\mathrm{h}^4 \quad (2.6)$$

for the hexagonal phase. The isotropic-lamellar (I-L), isotropic-hexagonal (I-H) and lamellar-hexagonal (L-H) phase transitions are determined by the minimization of these free energies, and the comparison of their respective values at the minimum.

The phase diagram may be displayed in a convenient way in the $[\tau/\lambda, \mu/\lambda]$ plane (Fig. 1). As expected we have an homogeneous disordered phase at high temperatures. For symmetric systems ($\mu = 0$) there is a second-order phase transition from the isotropic to the lamellar phase at $\tau = 0$. For asymmetric systems ($\mu \neq 0$) the transitions are first order. Under cooling the hexagonal phase appears first, at temperatures given by [2] $\tau = (4/45)\,\mu^2/\lambda \simeq 0.089\,\mu^2/\lambda$. At lower temperatures there is a first order phase-transition from hexagonal to lamellar. The H-L line satisfies the equation $\tau = -\frac{7+3\sqrt{6}}{5}\,\mu^2/\lambda \simeq -2.87\,\mu^2/\lambda$.

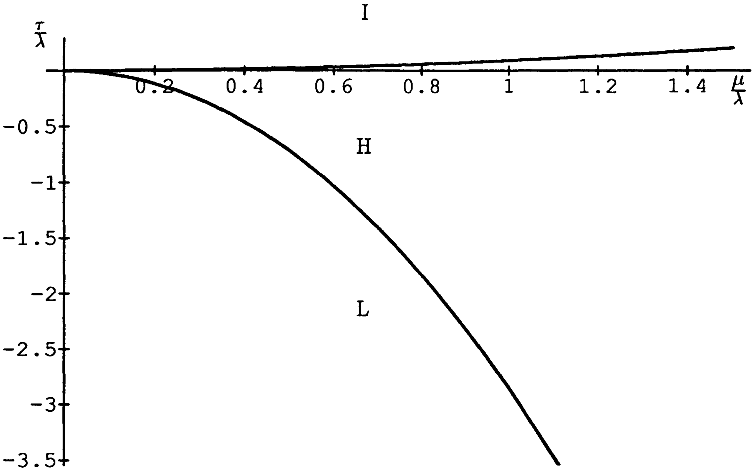

Fig. 1. — Mean-field phase diagram of the isotropic (I), hexagonal (H) and lamellar (L) structures. τ is a temperature related parameter and μ the measure of the intrinsic asymmetry. λ is the fourth coefficient of the Landau-Ginsburg free-energy and accounts for the relative importance of the spontaneous fluctuations. The I-H and H-L lines are parabolas of equations $\tau = (4/45)\,\mu^2/\lambda \simeq 0.089\,\mu^2/\lambda$ and $\tau = -\frac{7+3\sqrt{6}}{5}\,\mu^2/\lambda \simeq -2.87\,\mu^2/\lambda$, respectively [2].

2.2 THE HARTREE APPROXIMATION. — The role of the fluctuations on the phase transition has been previously considered by Brazovskii [17] who shown that, within a self-consistent Hartree approximation, the thermodynamic potentials for the lamellar and hexagonal phases are

$$\begin{cases} \Phi_\ell(a_\ell) = (1/2\,\lambda)\,(r_\ell^2 - r_0^2) + \alpha\,(r_\ell^{1/2} - r_0^{1/2}) - \frac{\lambda}{4}\,a_\ell^4 \\ \Phi_h(a_h) = (1/2\,\lambda)\,(r_h^2 - r_0^2) + \alpha\,(r_h^{1/2} - r_0^{1/2}) + 2\,\mu a_h^3 - \frac{3\,\lambda}{4}\,a_h^4 \end{cases} \tag{2.7}$$

where $\alpha = k_0^2/(4\,\pi)$. The renormalized inverse susceptibilities of the isotropic (r_0), lamellar (r_ℓ) and hexagonal (r_h) phases satisfy the following equations [1, 17]:

$$\begin{cases} r_0 = \tau + \sigma_0 = \tau + \frac{\alpha\lambda}{r_0^{1/2}} \\ r_\ell = \tau + \sigma_\ell + \lambda a_\ell^2 = \tau + \frac{\alpha\lambda}{r_\ell^{1/2}} + \lambda a_\ell^2 \\ r_h = \tau + \sigma_h + 3\,\lambda a_h^2 = \tau + \frac{\alpha\lambda}{r_h^{1/2}} + 3\,\lambda a_h^2 . \end{cases} \tag{2.8}$$

The difference to the mean-field picture resides in the presence of the σ-terms and it is easy to check that by formally setting $\alpha = 0$, the potentials (2.7) reduce to their mean-field form. These terms are the explicit contributions of the fluctuations, self-consistently calculated from

$$\sigma_i = \frac{1}{2}\frac{\lambda}{(2\pi)^3}\int \mathrm{d}\mathbf{k}\, S(\mathbf{k}) \simeq \frac{\alpha\lambda}{r_i^{1/2}} \tag{2.9}$$

where $S(\mathbf{k}) = [r_i + (k - k_0)^2]^{-1}$. The phase diagram can be obtained, as in the preceding section, by minimization of these three thermodynamic potentials and by comparison of their values at the minimum [1]. We summarize in figure 2 the results plotted in the plane $\tilde{\tau}$, $\tilde{\mu}$ where $\tilde{\tau} = \tau\alpha^{-2/3}\lambda^{-2/3}$, $\tilde{\mu} = \mu\lambda^{-5/6}\alpha^{-1/3}$.

There are two main differences with the mean-field phase-diagram. First, the isotropic-lamellar phase transition is shifted to negative values of the temperature ($\tilde{\tau}_c = -2.03$) and the transition is first order even for symmetric systems. This can be easily seen from the equation for the renormalized susceptibility in the homogeneous phase. Indeed, the spinodal line, given by $r_0 = 0$ is shifted to $\tau = -\infty$. In the symmetric case the lamellar structure first appears from the isotropic phase with a finite amplitude $a_\ell = 1.45\,\alpha^{1/3}\lambda^{-1/6}$.

The second difference is the existence of a finite region of small $\tilde{\mu}$ for which the hexagonal phase is never stable. Only for asymmetries larger than $\tilde{\mu}_c = 0.564$ does this structure appear.

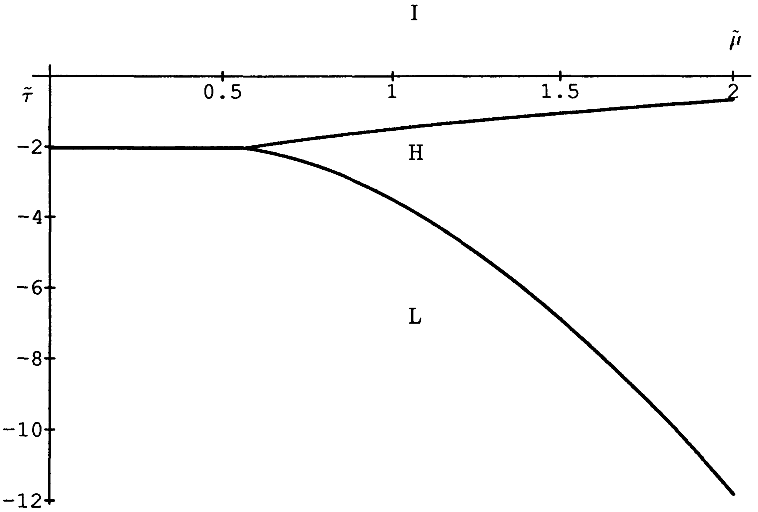

Fig. 2. — Hartree phase-diagram of the isotropic (I), hexagonal (H) and lamellar (L) structures. The coordinates of the triple point are $\tilde{\tau}_c = -2.308$, $\tilde{\mu}_c = 0.564$. For high values of $\tilde{\mu}$ the transition lines approach their mean-field values.

3. The microphase separation under a shear flow

We now investigate how an applied shear flow modifies the M.S.T. described above. We closely follow a previous letter of Cates and Milner [20], and the works of Frederickson [22] and Onuki [23]. The starting point is the convective Langevin equation for the order parameter

$$\frac{\partial\phi(\mathbf{r},t)}{\partial t} = -Dy\frac{\partial\phi(\mathbf{r},t)}{\partial x} + \int_V \kappa(\mathbf{r}-\mathbf{r}')\nabla_{\mathbf{r}'}^2\frac{\delta F[\phi(\mathbf{r}',t)]}{\delta\phi(\mathbf{r}',t)}\,\mathrm{d}\mathbf{r}' + \theta(\mathbf{r},t) \tag{3.1}$$

where $\theta(\mathbf{r}, t)$ is the usual random noise source and $\kappa(\mathbf{r} - \mathbf{r}')$ the kernel for the driving force. The main assumption in this equation is that the flow field $\mathbf{u}_x = (Dy, 0, 0)$ is fixed by an externally imposed perturbation. This completely neglects any reaction of the flow field to local fluctuations in the order parameter, but it is a good approximation for the disordered state and presumably also in weakly ordered phases (since the order parameter is small everywhere).

The Langevin equation (3.1) is equivalent to the following Fokker-Planck equation for the probability of the $\mathbf{k}$ Fourier component of the order parameter [24]

$$\frac{\partial P\{\phi(\mathbf{k}, t)\}}{\partial t} = \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \frac{\delta}{\delta\phi(\mathbf{k}, t)} \left\{ \zeta \left[\frac{\delta}{\delta\phi(-\mathbf{k}, t)} + \frac{\delta F[\phi(\mathbf{k}, t)]}{\delta\phi(-\mathbf{k}, t)} \right] - Dk_x \frac{\partial\phi(\mathbf{k}, t)}{\partial k_y} \right\} \times \\ \times P\{\phi(\mathbf{k}, t)\} \qquad (3.2)$$

if the Onsager mobility coefficient $\zeta(\mathbf{k}) = k^2 \kappa(\mathbf{k})$ is approximated by its value ζ at k_0. To completely solve this equation in steady state $(\partial P\{\phi(\mathbf{k}, t)\}/\partial t = 0)$ is a rather formidable task, since the functional derivative of the free-energy include terms up to third order. Two main approximations will be used to deal with this strong nonlinearity.

3.1 THE EFFECT OF SHEAR FLOW ON THE FLUCTUATIONS.

— First we remark that, for a flow field along the x-axis, all the fluctuations with $k_x \neq 0$ will be strongly convected. Indeed, any ordered structure involving a wavevector with non-zero k_x cannot exist, in steady state, at nonzero shear rate D [20]. This is because we have assumed a uniform shear field that is imposed externally and does not react to the ordering : a finite amplitude density wave with $k_x \neq 0$ is simply convected away from $|\mathbf{k}| = k_0$ and so cannot be part of a time-independent solution. This rules out triply-periodic structures, for example the body centered cubic phase (BCC), even though these are present on the static phase diagram. (Since it cannot persist under flow, this phase was omitted from our previous discussions.) Lamellar and hexagonal states can exist, but only with wavevector(s) transverse to the flow. In the hexagonal case, this means that the symmetry axis lies along the streamlines.

In the disordered (I) state, we can under flow expect a strongly anisotropic $S(\mathbf{k})$. We now calculate this fluctuation spectrum by writing the « Hartree version » of equation (3.2) in the Gaussian form

$$\int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \frac{\delta}{\delta\phi(\mathbf{k}, t)} \left\{ \zeta \left[\frac{\delta}{\delta\phi(-\mathbf{k}, t)} + [r + (k - k_0)^2]\, \phi(-\mathbf{k}, t) \right] - Dk_x \frac{\partial\phi(\mathbf{k}, t)}{\partial k_y} \right\} \times \\ \times P\{\phi(\mathbf{k}, t)\} = 0 \qquad (3.3)$$

which gives an equation for the flow-distorted $S(\mathbf{k})$ [22, 23]

$$[r + (k - k_0)^2]\, S(\mathbf{k}) - \frac{D}{2\zeta} k_x \frac{\partial S(\mathbf{k})}{\partial k_y} = 1 \,. \qquad (3.4)$$

The method of characteristics gives a formal solution [19, 22] which reads

$$S(\mathbf{k}) = \zeta \int_0^\infty \mathrm{d}t \exp\left[-\zeta \int_0^t \{r + [k(t') - k_0]^2\}\, \mathrm{d}t' \right] \qquad (3.5)$$

with $k(t')^2 = k_x^2 + (k_y + Dt'\, k_x/2)^2 + k_z^2$. This shows clearly the origin of the distortion in the correlation function $S(\mathbf{k})$. The equation can be understood by noting that a randomly excited Fourier component at wavevector $\mathbf{k}(t)$, injected at time $-t$, is convected to a present (time zero) wavevector $\mathbf{k}$. At all intermediate times $-t'$ $(0 < t' < t)$ its amplitude has decayed at an (instantaneous) rate $-\zeta\left\{r+\left[k(t')-k_0\right]^2\right\}$, appropriate to the thermodynamic force acting on it at this intermediate time. The susceptibility $S(\mathbf{k})$ at time zero can be viewed as the superposition of a sequence of random Fourier components (supplied by thermal noise), which have been injected at past time $-t$ and convected to the present wavevector $\mathbf{k}$. Note that, in accordance with our previous discussion, only Fourier components with $k_x = 0$ escape convection and it is only in these components that order (i.e. finite values of the amplitude) can develop.

We now consider the possibility of ordered states. Since those with $k_x \neq 0$ cannot persist in a flow field, any ordered states must be steady state solutions of (3.2) with $k_x = 0$. However, setting $k_x = 0$ in that equation removes any direct effect of the flow field through the convective (D) term [20]. We are thus left with an equivalent static problem, whose solution, within Hartree theory, is straightforward (since the steady state of a static Fokker-Planck equation is given by the Boltzmann distribution). Of course, the flow field does enter indirectly, because the Hartree renormalization parameter $r = \tau + \sigma$ depends (self-consistently) on the flow-distorted $S(\mathbf{k})$, and hence on the flow rate. Nonetheless [20], the search for ordered states under flow is reduced to that of minimizing self-consistently an effective free energy that contains the flow-dependent parameter $\sigma = \frac{1}{2}\frac{\lambda}{(2\pi)^3}\int \mathrm{d}\mathbf{k}\, S(\mathbf{k})$.

To determine σ it is possible, in principle, to find a complete numerical solution for the equation (3.5). However, the most relevant information may be obtained more directly, at least in the limit of small and large shear rates. In the limit of small shear rates we obtain the perturbative correction to the fuctuation integral (2.9), which now reads, to the leading order in D and small r

$$\sigma(D) = \sigma(0) + \frac{\pi}{24}\left(\frac{D}{D^*}\right)^2\left(\frac{|\tau_c|}{r}\right)^{7/2}\tau_c \tag{3.6}$$

where $\tau_c = -2.03\,(\alpha\lambda)^{2/3}$ and $D^* = \zeta\lambda\alpha^{1/2}$. The negative sign of this contribution shows that, as expected, the shear flow reduces the fluctuations. The functional form (3.6) for $\sigma(D)$ is as given by Cates and Milner, who did not, however, calculate the prefactor.

In the limit of large shear rates, since we are interested in the solutions with vanishing k_x, it is not permissible to treat (3.3) perturbatively in $1/D$. Instead, the memory kernel in (3.5) may be approximated by an « effective lifetime » for injected Fourier components, which is dependent on both $\mathbf{k}$ and D [20, 23]. Using this approach one finds for the susceptibility $S(\mathbf{k})$ the following interpolation formula [20, 23]

$$S(\mathbf{k}) = \frac{1}{r + (k-k_0)^2 + b\left(\dfrac{Dk_xk_y}{\zeta\alpha^{1/2}}\right)^{2/3}} \tag{3.7}$$

with b a constant of order unity. This leads to the fluctuation integral [20] (at the leading order in r)

$$\sigma(D) \simeq \left(\frac{D}{D^*}\right)^{-1/3}|\tau_c| - \left(\frac{D}{D^*}\right)^{-1} r[\ln \beta r]^2 \tag{3.8}$$

with $\beta \simeq |\tau_c|^{-1}(D/D^*)^{2/3}$. This integral vanishes with increasing shear rates, even in the limit $r \to 0$. Accordingly the behaviour approaches that of mean-field theory, as D/D^* approaches infinity. The crossover from the Hartree to the mean-field description is roughly at $D = D^*$.

In the next section, we calculate the resulting phase diagram which contains lamellar and hexagonal phases along with the isotropic phase. Triply-periodic structures are excluded since they are unstable under an imposed uniform shear flow, as discussed above. Also excluded are, for example, distorted near-hexagonal phases in which the three Fourier components have different amplitudes. These are possible in principle, since the shear flow $\mathbf{u}_x = (Dy, 0, 0)$ fully breaks rotational symmetry, as is reflected in the form of $S(\mathbf{k})$ (3.7). However, when $k_x = 0$, (3.3) recovers rotational symmetry in the k_y, k_z plane. In other words, although $S(\mathbf{k})$ is highly anisotropic in general, it is isotropic in the $k_x = 0$ subspace of wavevectors at which order can actually develop [25].

Of course, this assertion, along with the rest of our results for the phase diagram under flow (presented below) are only true within the limits of the approximations we have made. The main ones are : locality of the third and fourth order terms in the free energy expansion (2.1) ; conditions such that the Hartree treatment holds in the static regime ; and the existence of a convective velocity field that is imposed externally (with no local fluctuations that might be coupled to those of the order parameter). The first assumption is not very severe, and has (for all static purposes) proved to be accurate enough for the systems of interest here. The Hartree factorization, if valid in the static case, holds even better under flow since this only *reduces* the fluctuations [20]. The third assumption (passive convection) should hold for systems that order sufficiently weakly since the density variations that arise are then unlikely to perturb the flow field. In contrast, under conditions of strong ordering, structures that we have ruled out (such as BCC) can survive under flow by completely distorting the flow-lines ; this regime presumably requires an entirely different approach, which we do not attempt here.

3.2 THE PHASE DIAGRAM UNDER A SHEAR FLOW. — As described in the preceding section, the Hartree and mean-field phase-diagrams can be represented in a two-dimensional space of reduced parameters. These parameters are related to the coefficients of the Landau-Ginsburg free-energy : the temperature τ, the asymmetry μ, the strength of the fluctuations λ and, additionally for the Hartree representation, the wavevector k_0 and c, the curvature of the susceptibility at its maximum. In order to have a common representation for both phase diagrams we chose the Hartree set $[\tilde{\tau}, \tilde{\mu}]$ (Sect. 2.2) which is simply related to the mean field representation by $[\tilde{\tau} = (\lambda^{1/2} \alpha^{-1})^{2/3} \tau / \lambda,\ \tilde{\mu} = (\lambda^{1/2} \alpha^{-1})^{1/3} \mu / \lambda]$ (notice that the mean-field transition lines $\tau / \lambda = \text{const.} \times (\mu / \lambda)^2$ keep the same form in this representation).

Following the above scheme, in the presence of a dimensionless flow rate $\Delta \equiv D / D^*$, the phase diagram for the crystallization of the lamellar and hexagonal structures is still obtained by minimization of the « static » thermodynamic potentials of equations (2.7), where the contributions from the fluctuations to the renormalized susceptibilities (Eqs. (2.1) and (2.9)) are now flow-dependent (Eqs. (3.6) and (3.8)). In the regime of small shear rates we solve these equations by a perturbation method, to first order in Δ^2. For large shear rates we indicate the general trends of the solutions, which may be determined largely by applying topological arguments to the phase diagram.

The new phase diagram which accounts for the role of the shear flow is set in a three-dimensional space $[\tilde{\tau}, \tilde{\mu}, \Delta]$. The $\Delta = 0$ and $\Delta = \infty$ planes correspond, respectively, to the static Hartree (Fig. 2) and mean-field (Fig. 1) phase-diagrams.

The $\tilde{\mu} = 0$ plane (Fig. 3) corresponds to the situation previously analyzed by Cates and Milner [20]. This situation arises for completely symmetric systems, and the only two possible phases are the lamellar and the isotropic. The I-L transition temperature $\tilde{\tau}$ departs continuously from $\tilde{\tau}_c = -2.03$ for zero shear rate, to reach the infinite shear rate value of $\tilde{\tau}_c = 0$. in the region of small flow rate the first correction to the temperature is quadratic in the flow rate

$$\tilde{\tau}_c(\Delta) - \tilde{\tau}_c = 3.323\, \Delta^2 . \tag{3.9}$$

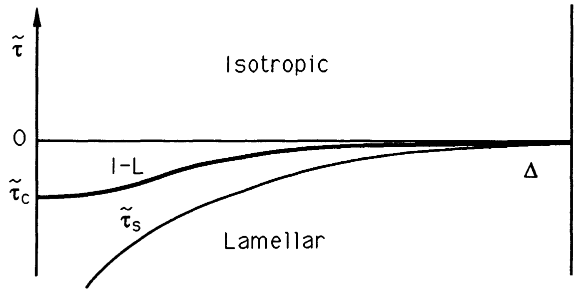

Fig. 3. — Role of the shear rate in the isotropic-lamellar phase transition for symmetric systems $\tilde{\mu} = 0$. As the shear rate Δ goes to large values the I-L line exponentially approaches the spinodal $\tilde{\tau}_s$. The transition remains first order [20].

For large values of Δ the transition line approaches exponentially the spinodal line τ_s :

$$\tilde{\tau}_c(\Delta) - \tilde{\tau}_s \sim \Delta^{-5/6} \exp\{-\Delta^{1/2}\} \tag{3.10}$$

where $\tilde{\tau}_s$, the solution of $r_0 = 0$, is given by

$$\tilde{\tau}_s \sim \Delta^{-1/3} . \tag{3.11}$$

Since the transition line always lies above the spinodal, the I-L phase transition for symmetric systems remains first order. However, all the relevant quantities, such as the amplitude or the transition temperature, are exponentially close to their values on the spinodal and thus may be, at high enough shear, indistinguishable from a second order transition for practical purposes.

When $\tilde{\mu} \neq 0$ the planes $[\tilde{\tau}, \Delta]$ at constant $\tilde{\mu}$ are qualitatively different for values of $\tilde{\mu}$ larger or smaller than $\tilde{\mu}_c = 0.564$.

In the large $\tilde{\mu}$ case ($\tilde{\mu} > \tilde{\mu}_c$) three different phases already exist at zero shear rate : the homogeneous disordered phase at high temperatures, the hexagonal phase at intermediate temperatures and the lamellar phase at lower temperatures. Thus, by increasing the shear rate at constant $\tilde{\mu}$ the only effect is to shift each of the two correspondent transition lines (Fig. 4).

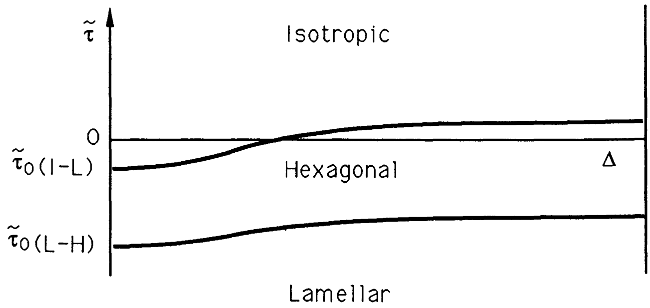

Fig. 4. — Schematic phase diagram for the transition between the isotropic, hexagonal and lamellar mesophases for systems with large asymmetry ($\tilde{\mu} > \tilde{\mu}_c = 0.564$).

Again, for small shear rates there is a parabolic departure from the Hartree values :

$$\begin{cases} \tilde{\tau}_c(\Delta) - \tilde{\tau}_0(\tilde{\mu}) = C_{\mathrm{IH}}(\tilde{\mu})\,\Delta^2 & \text{I-L} \\ \tilde{\tau}_c(\Delta) - \tilde{\tau}_0(\tilde{\mu}) = C_{\mathrm{HL}}(\tilde{\mu})\,\Delta^2 & \text{H-L} \end{cases} \tag{3.12}$$

where $\tilde{\tau}_0(\tilde{\mu})$ are the I-L and H-L transition temperatures for a given $\tilde{\mu}$ at zero shear. We list some values of the coefficients $C(\tilde{\mu})$ in table I. C_{HL} is smaller than C_{IH} and thus, on increasing values of the asymmetry $\tilde{\mu}$, the Hartree H-L transition line approaches its mean-field limit much faster than the I-L line. For large shear rates each of the transition lines approaches its respective mean-field value following an equation similar to (3.11).

In the intermediate $\tilde{\mu}$ case $(0 < \tilde{\mu} < \tilde{\mu}_c)$, only two phases are present in the static Hartree phase diagram, but three phases do exist in the mean field limit. Therefore the I-L transition line must split in the two I-L and H-L lines for some value of Δ (Fig. 5). Correspondingly, the triple point located at $[\tilde{\tau}_c, \tilde{\mu}_c, \Delta = 0]$ in the static case moves towards its $[\tilde{\tau} = 0, \tilde{\mu} = 0, \Delta = \infty]$ position in the mean-field diagram. We sketch in figure 6a the $\tilde{\mu}$ coordinate of the triple point as a function of Δ. Figure 6b shows this line calculated perturbatively for small shear rates : curves are shown for both the intersection of the I-L/H-L and of the I-L/I-H sheets ; these must of course coincide in any exact calculation. We can see from the extension of the region where the lines almost coincide that the perturbation method works very well up to shear rates of $\Delta \simeq 0.1$.

Table I. — *Some numeric values for the coefficients of the temperature shift with shear rate.*

$\tilde{\mu}$	0.564	0.6	0.7	0.8	0.9	1.0
C_{IH}	6.77	5.93	4.17	2.99	2.18	1.62
C_{HL}	0.309	0.198	0.067	0.027	0.012	0.006

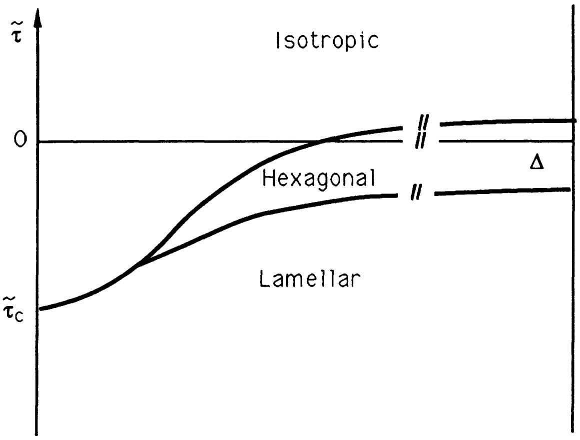

Fig. 5. — Schematic phase diagram for the transition between the isotropic, hexagonal and lamellar mesophases for systems with small asymmetry $(0 < \tilde{\mu} < \tilde{\mu}_c = 0.564)$. This diagram implies that a isotropic system which, under cooling, would form a lamellar phase may nonetheless crystallize, upon increasing the shear rates, into an hexagonal structure.

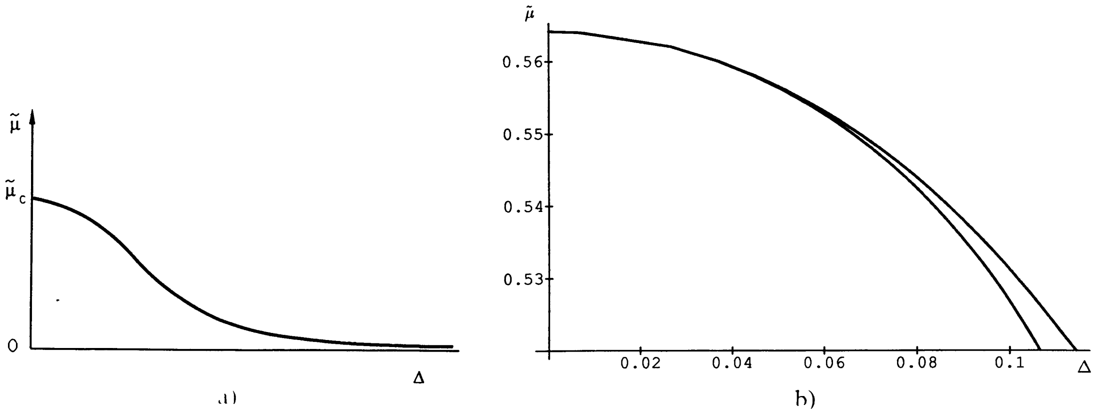

Fig. 6. — a) Schematic representation of the I-H-L triple line. b) The triple line calculated from the intersection of the I-H/I-L and H-L/I-L surfaces. The region where the two lines reasonably coincide gives a measure of the accuracy of the perturbation method.

The special geometry of the phase diagram near the static triple point allows for a very interesting situation where the same isotropic system can transform either into the lamellar or into the hexagonal phase according to whether is cooled or sheared. The optimal position in the static phase diagram ($\Delta = 0$) to observe this particular behaviour is for $\tilde{\mu}$ smaller than but close to the triple point value ($\tilde{\mu}_c = 0.56$), and for temperatures such that $\tilde{\tau}$ is greater than but close to its I-L value $\tilde{\tau}_c = -2.03$.

4. Applications to copolymer and surfactant systems.

The results presented above determine the effect of shear on systems whose phase transitions are well described by a Landau-Ginsburg expansion with small quartic nonlinearity λ. In this sense they can be straightforwardly applied to blends of diblock copolymers and, with some extra input from experimental results, to microemulsions. We believe also that the explanation of flow induced striped phases in colloidal crystals [14] may well be related to the present work, but a detailed discussion of this is beyond our scope. The same remark applies to the possibility of hexagonal crystalline order being induced by shear in wormlike or rodlike micellar systems [26].

4.1 THE M.S.T. OF DIBLOCK COPOLYMERS UNDER A SHEAR FLOW. — We follow in this subsection the definitions and notation used in the paper by Fredrickson and Helfand [1] hereafter denoted by FH. The system consists on a blend of AB diblock copolymers with polymerization index N. The A block is a sequence of fN monomers and the B block has $(f - 1) N$ segments. The unperturbed radius of gyration of the chains is $R = b\sqrt{N/6}$ where b is the statistical size of both monomers A and B. The interaction between monomers A and B is expressed by the Flory interaction parameter χ. Combining our results and equations (4.3), (4.4) and (2.16) of FH one gets the following shear induced shift for the values of χ at the I-L transition line

$$(\chi N)_t = 10.495 + 41.022\, N^{-1/3}\,[1 - 1.636\, \Delta^2] \tag{4.1}$$

and for the amplitude

$$a_\ell = 0.814\, N^{-1/6}[1 - 2.805\, \Delta^2]\,. \tag{4.2}$$

It is already clear from the FH paper (see also Refs. [22, 27]) that the region around the triple point is easily accessible from the experimental point of view, its particular position in the phase diagram being essentially a function of the ratio f and of the polymerization index N. The last relevant parameter to be determined is then the crossover frequence $D^* = \zeta \lambda \alpha^{1/2}$ (related to the dimensionless shear rate by $\Delta = D/D^*$). From its definition $\alpha^{1/2}$ is proportional to the dominant wavevector k_0 and thus proportional to $N^{-1/2}$. The coefficient λ is of order of N^{-1} and, assuming that the dynamics of the individual chains is governed by reptation, the Onsager mobility ζ is proportional to the reptation frequency [27, 28]. This last can already be, for large enough chains, of the order of 1 s^{-1}, and thus well in the range of the Couette flow experiments. Note that because of the enhancement factor $N^{-3/2}(D^* \sim N^{-3/2} \zeta)$ a flow induced transition may arise at flow rates small even compared to the reptation frequency [22, 27]. Numerical predictions for D^* can be calculated by combining equation (2.10) of reference [27] and the results of table I in FH (note that in this table λ is N times larger than λ in our paper).

4.2 THE ORDERING OF MICROEMULSIONS UNDER A SHEAR FLOW. — We consider in this paragraph mixtures of oil, water and surfactant which form thermodynamically stable phases. Although no complete derivation of a Landau-Ginsburg free-energy from a microscopic Hamiltonian is available, we may estimate the coefficients on which our phase diagram depends by combining phenomenological expressions of the free-energy in the isotropic state with existing experimental results. A convenient form for the free-energy per unit volume of the isotropic state $G(\phi, \phi_s, x_0, \delta)$, has been obtained by Andelman *et al.* [12] within a random mixing approximation. This free-energy depends on four independent parameters : ϕ the volume fraction of water ; ϕ_s the volume fraction of the surfactant (which resides in the surface dividing the water and oil domains) ; $\delta = \xi_k/a$ where ξ_k is the persistence length of that surface and a its thickness, and x_0 which is the ratio of the persistence length to the spontaneous radius of curvature of the interface. By minimizing this free-energy the authors obtain a phase diagram which qualitatively explains the main features of microemulsions. We now concentrate on the region of the phase diagram where only one isotropic phase is present (avoiding the complexity of coexisting oil-rich and water-rich phases). Specializing to the role of the fluctuations in the water/oil contents we expand the free-energy $G(\phi, \phi_s, x_0, \delta)$ in powers of the order parameter $\psi = \phi - \bar{\phi}$ and its gradients

$$F[\psi] = \frac{1}{2!} \int_V \int_V \left\{ A(\nabla_r \psi(\mathbf{r})^2) + B(\nabla_r^2 \psi(\mathbf{r})^2) + \frac{f_2}{2} \psi(\mathbf{r})^2 \right\} \frac{d\mathbf{r}}{V} + \\ + \frac{f_3}{3!} \int_V [\psi(\mathbf{r})]^3 \frac{d\mathbf{r}}{V} + \frac{f_4}{4!} \int_V [\psi(\mathbf{r})]^4 \frac{d\mathbf{r}}{V} \tag{4.3}$$

where $f_i = \partial_\phi^{(i)} G(\phi)|_{\phi = \bar{\phi}}$. Here $\bar{\phi}$ is the average value of the water contents in the homogeneous disordered phase and ϕ its spatially dependent value in an ordered phase. The coefficients f_3 and f_4 can be identified with parameters μ and λ of equation (3.1). Parameters A and B can be eliminated in favour of experimentally determined quantities, namely the maximum of the susceptibility (at the static transition) $S(k_0)$, the wavevector k_0 for which it occurs and the compressibility $f_2 = S^{-1}(0)$. It is thus easy to estimate the asymmetry parameter $\tilde{\mu}$

$$\tilde{\mu} = 2\pi^{1/3} \frac{(1 - \beta)^{1/6}}{k_0} f_2^{1/6} f_4^{-5/6} f_3 \tag{4.4}$$

where $\beta = S(0)/S(k_0)$, a coefficient which for microemulsions is of order unity [29]. Within the framework of the model of Andelman *et al.* the value of k_0 is of the order of [29]

$\pi \phi_s/(6 \bar{\phi}(1-\bar{\phi}))$. We display in figure 7 the values of $\tilde{\mu}$ as a function of $\bar{\phi}$ for $\beta = 0.5$, $\phi_s = 0.2$, $\delta = e^{10}$ and $x_0 = 0$ (see Ref. [12]). The asymmetry parameter can easily be in the region of $\tilde{\mu}_c$ even for quite small asymmetries of the water/oil contents. This does not contradict the original assumption of Cates and Milner [20] that $\mu = 0$, since the systems studied in that paper (namely « spongelike » bilayer phases) have under suitable conditions a special symmetry (inside/outside symmetry [30]) that ensures the vanishing of a cubic term in the analogue of equation (4.4).

To investigate the possibility of a microemulsion exhibiting a shear-induced hexagonal or lamellar phase, we need to estimate the crossover shear rate D^*. This was done by Cates and Milner [20] on the basis of a hydrodynamic estimate of the relaxation time for piece of surfactant film of the characteristic size (related to the persistence length). However, their estimate neglects the fact that full structural relaxation requires topological reconnections of the film, for which there is a significant energy barrier [31]. Incorporation of this effect may allows a reduction of D^* from rather high rates of order 10^4-$10^6\ \mathrm{s}^{-1}$ toward values more readily accessible experimentally. In particular for suitable sponge phases [6] the I-L transition appears to be induced by simple agitation of the test tube ; while this is an extreme case, D^* values of order a few hundred for normal microemulsions might easily be attainable.

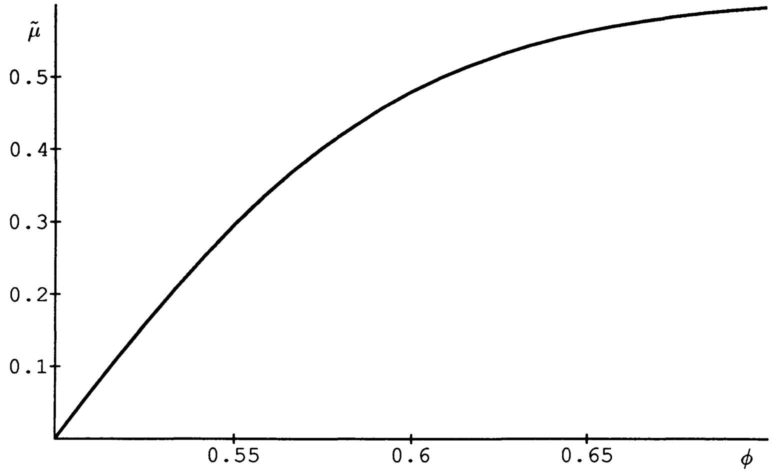

Fig. 7. — Variation of the asymmetry parameter $\tilde{\mu}$ as a function of ϕ in a microemulsion. Here $\phi_s = 0.2$, $\delta = e^{10}$ and $x_0 = 0$ (see Ref. [12]). The value of $\tilde{\mu}$ can be easily in the region of $\tilde{\mu}_c$ even for relatively small asymmetries of the water/oil contents.

5. Conclusions.

In this paper we have studied the effect of shear on the transition from isotropic (I) to hexagonal (H) and lamellar (L) phases in weakly ordering systems, such as block copolymers, microemulsions, and lyotropic surfactant. The work differs from earlier studies [20] in including a cubic term in the appropriate Landau expansion, thus allowing systems to be described that do not have reflection symmetry of the order parameter. In such systems hexagonal phases can arise as well as lamellar ones. (Cubic order can also arise in the static case but is, within the present theoretical framework, unable to survive even an infinitesimal shear rate, which is why we have not discussed it above).

Our work confirms the earlier conclusion of Cates and Milner [20] that, by suppressing nonlinear fluctuation effects, the role of shear is to move the system away from Hartree and toward mean-field behaviour. For the case of the I-L phase transition this leads to a transition temperature that increases with flow rate ; thus for suitable temperatures a shear induced I-L transition is predicted. In the more general case considered here, the same tendency to suppress fluctuations can lead to more subtle effects on the phase diagram. When the cubic coefficient $\tilde{\mu}$ is large enough, a hexagonal phase is stabilized relative to lamellae at all flow rates ; its stabilization (relative to the isotropic phase) by a shear flow is qualitatively similar to that found previously for lamellae. However, the most interesting case arises when there is a relatively *small* cubic term. Under these conditions a mean field calculation (valid at high flow rate) show that the hexagonal phase is stable whereas the Hartree results for the static case show that the lamellar phase is preferred. This results in the phase diagram of figure 5, which shows that hexagonal order may be induced under shear in systems that have no phase of this symmetry in their static phase diagram.

Whereas the observation of static hexagonal order in some microemulsion forming systems [13] provides ample motivation for our study, the above comments show that the results are relevant to many other systems for which only lamellar ordered phases are seen statically. For surfactant systems the characteristic flow rates required to induce a change of symmetry may depend strongly on the energy barriers for topological reconnection of the surfactant layers [31], but flow rates of order a hundred s^{-1} should be sufficient to see a transition in many cases. For block copolymer systems the flow rates required are very much smaller (at least for long chains) although for large molecular weights the temperature range in which the flow-induced transition can occur (namely the range between the Hartree and mean-field predictions of the static transition temperature) becomes increasingly narrow.

Finally we point out that in the low flow rate regime our perturbative results should be amenable to quantitative experimental test. For, although there are several free parameters (μ, λ, c, etc.), most of these can be fixed by performing suitable static measurements (e.g. of $S(\mathbf{k})$ at more than one temperature). The Onsager coefficient ζ (which *via* D^* sets the time scale for dynamics) is estimable theoretically, as indicated above, but it should be possible in any case to eliminate this parameter between two different dynamics measurements (for example the dependence on flow rate of the structure factor [22], and that of the transition temperature) so as to obtain a quantitative test of the theory. (The measurement of a dynamic structure factor in the absence of flow would also give the needed information.) The accuracy of our approach of course depends on the correctness of the Hartree approximation ; roughly speaking this is valid near the transition to whatever extent there is a large peak in the structure factor ($S(k_0)/S(0) \equiv \beta^{-1} \gg 1$). By this measure, we expect close agreement for block copolypers [1] but only qualitative validity in the microemulsion case, for which β values of order 0.5 are more typical.

Acknowledgements.

The authors wish to thank Scott Milner and Didier Roux for very helpful discussions. This work was funded in part by EEC grant No. SC1*0288-C (EDB).

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