

Classification

Physics Abstracts

61.30 — 82.70 — 75.50M

Elasticity and hydrodynamic properties of « doped solvent » dilute lamellar phases

Frédéric Nallet ⁽¹⁾, Didier Roux ⁽¹⁾, Catherine Quilliet ^(2, *), Pascale Fabre ⁽²⁾ and Scott T. Milner ⁽³⁾

⁽¹⁾ Centre de recherche Paul-Pascal, CNRS, Avenue du Docteur-Schweitzer, 33600 Pessac, France

⁽²⁾ Laboratoire des fluides organisés (**), Collège de France, 11 place Marcelin-Berthelot, 75231 Paris Cedex 05, France

⁽³⁾ Exxon Research & Engineering Co., Annandale, NJ 08801, U.S.A.

(Received 23 March 1994, revised 31 May 1994, accepted 14 June 1994)

Résumé. — Les fluctuations à l'équilibre ainsi que la relaxation des états légèrement en dehors de l'équilibre des phases lamellaires à « solvant dopé » sont étudiées, aussi bien d'un point de vue théorique qu'expérimental, dans la limite de basses fréquences et de grandes longueurs d'onde. Les systèmes décrits sont des cristaux-liquides smectiques A lyotropes formés de trois constituants : un tensioactif en solution dans une suspension *colloïdale* forme des bicouches de grande extension latérale qui s'empilent de façon périodique le long d'une direction dans l'espace. Avec de tels systèmes anisotropes et à plusieurs constituants deux modes présents dans la partie à basse fréquence du spectre des fluctuations (associés à la relaxation d'ondes, couplées, de concentration colloïdale et de déplacement des couches smectiques) ont une certaine importance expérimentale. Dans la limite d'un couplage faible, l'un des deux modes est similaire au mode barocline des phases lamellaires à deux constituants ; le second s'identifie au mouvement brownien de diffusion d'un colloïde dans un substrat anisotrope. Les constantes élastiques du cristal liquide smectique de même que le coefficient de diffusion du colloïde peuvent en principe être déduits de la mesure des relations anisotropes de dispersion de ces deux modes ; cela est illustré par des expériences de diffusion quasi-élastique de la lumière sur des *ferrosmectiques*.

Abstract. — The equilibrium fluctuations and weakly out-of-equilibrium relaxation properties of « doped solvent » dilute lamellar phases are investigated, both theoretically and experimentally, in the low-frequency, long-wavelength limit. The physical system of interest is a three-component smectic A lyotropic liquid crystal where surfactant bilayers infinite in extent are periodically stacked along one direction in space and separated by a *colloidal* solution. Two experimentally relevant modes are found in the lowest frequency part of the fluctuation spectrum of such multicomponent systems. Both are associated to the relaxation of *coupled* layer displacement and

(*) *Present address* : Laboratoire de minéralogie-cristallographie, URA CNRS 9, université Pierre-et-Marie-Curie, 4 place Jussieu, 75252 Paris Cedex 05, France.

(**) URA CNRS 792.

colloid concentration waves. In the limit of small coupling, one mode is close to the well-known undulation/baroclinic mode of *two-component* lamellar phases, while the other corresponds to the Brownian diffusive motion of the colloid in an anisotropic medium. Elastic constants of the smectic liquid crystal and diffusion parameters of the colloidal solution may be deduced from a measurement of the anisotropic dispersion relation of these two modes, as illustrated by dynamic light scattering experiments on the *ferrosmectic* system.

Introduction.

Lamellar L_α phases are the liquid crystalline smectic A phases one often encounters in the phase diagram of surfactant/solvent systems [1]. Although from a physico-chemical point of view they may be quite complex, since prepared by mixing not only a surfactant with one solvent but most often by also adding co-surfactants, co-solvents, salts, etc., an idealization of the structure both convenient and realistic in many cases, especially in the dilute regime is that of a *two-component* smectic A phase (Fig. 1) [2-4] : surfactant *bilayers* (perhaps holding a co-surfactant or slightly swollen by a co-solvent) are periodically stacked in space, separated by a *solvent* (which may be itself a multicomponent mixture). In some particular cases, however, this idealization is no longer relevant. For instance, one may think of *three* distinct types of lamellar phases that require a description in terms of *three-component* smectic A systems. The first type occurs when the amount of co-solvent swelling the surfactant bilayers becomes comparable to the amount of solvent separating them (Fig. 2a). The three components to be considered are the surfactant *monolayer* (which may still be a composite object), and the two solvents. We call such a system a *two-solvent* lamellar phase. A second type arises when the surfactant bilayer hosts a colloidal component (a protein, for instance ; see Fig. 2b). We call it a *doped-bilayer* lamellar phase. The third type is dual to the second one : while the surfactant bilayer is « pure », the solvent is now hosting a colloidal component (Fig. 2c). Accordingly, its denomination is a *doped-solvent* lamellar phase.

All the three types have been experimentally prepared [5-7]. As far as their *macroscopic* (i.e. elastic or hydrodynamic) properties are concerned, the two-solvent, doped-bilayer and doped-solvent lamellar phases are on a phenomenological basis quite similar. They are three-component smectic A phases, and therefore the elastic free energy density has to be written (for incompressible systems) in terms of *three* variables, coupled in general, namely the

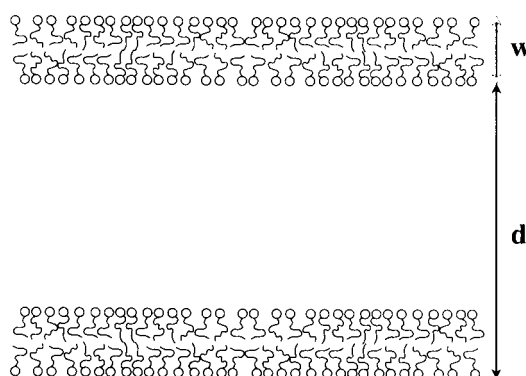


Fig. 1. — Schematic drawing for a two-component lyotropic smectic A phase ; surfactant bilayers with thickness w are periodically stacked (period d) along a direction z .

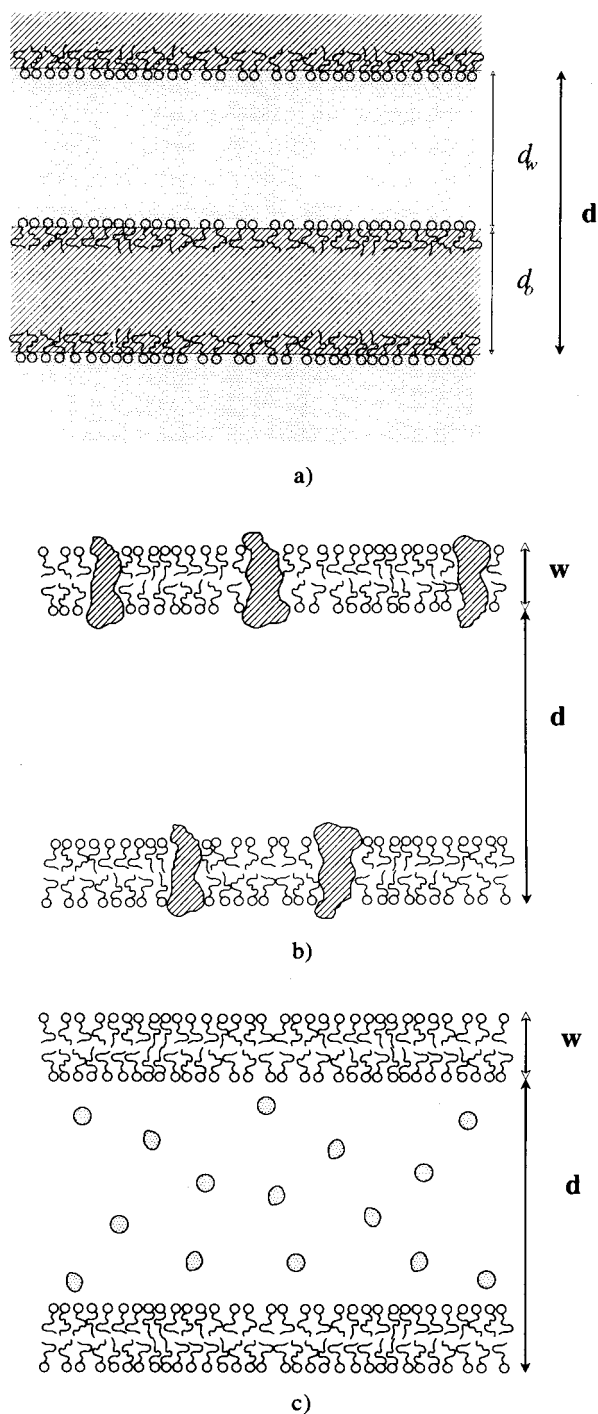


Fig. 2. — Schematic drawings for various kinds of three-component lyotropic smectic A phases ; a) two-solvent lamellar phase, where surfactant monolayers are separated by polar or hydrophobic regions, with thicknesses respectively d_w and d_0 ; b) doped-bilayer lamellar phase ; c) doped-solvent lamellar phase ; in the last two cases, a colloid is added to either the bilayer or the solvent component.

smectic layer displacement field and two composition variables (for instance, the surfactant and colloid concentrations, for the two *doped* systems ; the solvent 1 and solvent 2 concentrations, for *two-solvent* systems). Moreover, on account of the symmetry of the phase and of the number of locally conserved variables one expects *eight* hydrodynamic modes [8] in the long wavelength, low frequency part of the collective motion spectrum.

However, in view of the system we are experimentally dealing with (see below) we focus our attention in this paper to the specific case of *doped-solvent* lamellar phases. As will be apparent soon, this restriction amounts to assuming that some coupling terms that are in principle present in any elastic or hydrodynamic description of a three-component smectic A phase are small and may therefore be equated to zero. Our conclusions, though built within the general framework pertaining to three-component smectic A systems, are thus not of completely general validity.

The paper is divided into three main parts. In the first part we give the elastic free energy density of our system. With the help of a very schematic microscopic description of the doped-solvent lamellar phase, we extract from the *a priori* numerous coefficients in the free energy expansion a small number of relevant elastic constants. In the second part, we expose the hydrodynamic properties of the system. We show in particular that the (anisotropic) dispersion relations of the two lowest frequency modes are controlled by experimentally relevant elastic constants and hydrodynamic parameters. The third and last part is devoted to the quasi-elastic light scattering experiment we have performed on the « ferrosmectic » system [7], one of the first examples of a doped-solvent lamellar phase. We show how the experimental spectra may be described by the full hydrodynamic theory and extract from them values or estimates of elastic or hydrodynamic parameters, complementing a previous work on this system [9].

Elasticity of doped-solvent lamellar phases.

In addition to temperature T and total mass density ρ , *two* composition variables are required in order to characterize the macroscopic state at thermal equilibrium of any three-component system. In the case of the doped-solvent lamellar phase, we choose them as mass fractions of surfactant, c_i and colloidal particles, c_p . With the simplifying assumption of an *incompressible* system, the free energy per unit mass \tilde{f} does not depend on the total mass density and the free energy F of a doped-solvent lamellar phase with smectic period d is given by :

$$F = \int \rho \tilde{f}(T, c_p, c_i; d) d^3x. \quad (1)$$

One obtains the equilibrium smectic spacing d_{eq} by minimizing F with respect to local variations in spacing $\delta d(\mathbf{x})$, at fixed temperature and global composition of the system, i.e. as a solution of : $\frac{\partial \tilde{f}}{\partial d} = 0$. The equilibrium smectic spacing d_{eq} therefore depends *a priori* on temperature, as well as on both composition variables c_p and c_i .

The (harmonic) elastic free energy describing isothermal *fluctuations* around this equilibrium state is found by expanding F , up to second order in the fluctuating variables. Since the total mass, as well as the masses of each species are conserved quantities, and with d_{eq} given by the above minimum equation one gets :

$$F = F_{eq} + \int d^3x \frac{\rho}{2} \left[\frac{\partial^2 \tilde{f}}{\partial d^2} \delta d^2 + \frac{\partial^2 \tilde{f}}{\partial c_p^2} \delta c_p^2 + \frac{\partial^2 \tilde{f}}{\partial c_i^2} \delta c_i^2 + 2 \frac{\partial^2 \tilde{f}}{\partial d \partial c_p} \delta d \delta c_p + \right. \\ \left. + 2 \frac{\partial^2 \tilde{f}}{\partial d \partial c_i} \delta d \delta c_i + 2 \frac{\partial^2 \tilde{f}}{\partial c_p \partial c_i} \delta c_p \delta c_i \right]. \quad (2)$$

With the identification $\delta d(\mathbf{x})/d = \partial_z u$ (u is the layer displacement field), taking into account the smectic layer curvature energy [10] and with convenient notations we recast the elastic energy in the following form :

$$F = F_{\text{eq}} + \int d^3x \frac{1}{2} [B(\partial_z u)^2 + K(\nabla_{\perp}^2 u)^2 + \chi_p^{-1} \delta c_p^2 + \chi_t^{-1} \delta c_t^2 + 2 C_p \partial_z u \delta c_p + 2 C_t \partial_z u \delta c_t + 2 C \delta c_p \delta c_t] \quad (3)$$

where B is the smectic layer compression modulus (at constant surfactant and particle concentrations), K is the smectic bending modulus (expressed in terms of the *bilayer* bending modulus κ through the relation $K = \kappa/d$ [11]), χ_p^{-1} (resp. χ_t^{-1}) is related to the particle (resp. surfactant) osmotic compressibility and the C 's are coupling constants.

It will later prove convenient to handle a reduced (diagonal) form of this free energy expansion. Using as normal coordinates :

$$\partial_z u, \delta \tilde{c}_p = \delta c_p + C \chi_p \delta c_t + C_p \chi_p \partial_z u \quad \text{and} \quad \delta \tilde{c}_t = \delta c_t + \frac{C_t \chi_p^{-1} - C C_p}{\chi_t^{-1} \chi_p^{-1} - C^2} \partial_z u$$

we get :

$$F = F_{\text{eq}} + \int d^3x \frac{1}{2} [\bar{B}(\partial_z u)^2 + K(\nabla_{\perp}^2 u)^2 + \bar{\chi}_p^{-1} \delta \tilde{c}_p^2 + \bar{\chi}_t^{-1} \delta \tilde{c}_t^2] \quad (4)$$

with, in particular, the elastic constant \bar{B} expressed as :

$$\bar{B} = B - \frac{C_p^2 \chi_t^{-1} + C_t^2 \chi_p^{-1} - 2 C C_p C_t}{\chi_t^{-1} \chi_p^{-1} - C^2} \quad (5)$$

From equation (4) the layer displacement correlation function is readily computed, using equipartition :

$$\langle u(\mathbf{q}) u(-\mathbf{q}) \rangle \propto \frac{k_B T}{\bar{B} q_z^2 + K q_{\perp}^4} \quad (6)$$

which shows that the elastic constant \bar{B} here defined has the same meaning as usually for smectic A liquid crystals. Besides, it results from equations (3) and (5) that \bar{B} is equal to the smectic compression modulus at constant surfactant *and* particle chemical potentials. The other two constants are given by :

$$\begin{aligned} \bar{\chi}_p^{-1} &= \chi_p^{-1} \\ \bar{\chi}_t^{-1} &= \chi_t^{-1} - C^2 \chi_p \end{aligned} \quad (7)$$

More insight into the meaning of the numerous elastic constants entering the above formal expansion of the free energy may be gained by introducing the following microscopic, simplified model of a doped-solvent lamellar phase : we describe the structure as an ensemble of surfactant bilayers, with thickness w [12], separated by a solvent containing an amount ϕ (volume fraction) of colloid particles and periodically stacked in space along a direction z , with

period d (see Fig. 2c). The bilayer thickness and colloid volume fraction are related to the compositions through :

$$c_p = \frac{\rho_p \phi (d - w)}{\rho_t w + [\rho_s(1 - \phi) + \rho_p \phi](d - w)} \tag{8}$$

$$c_t = \frac{\rho_t w}{\rho_t w + [\rho_s(1 - \phi) + \rho_p \phi](d - w)}$$

with ρ_s , ρ_p and ρ_t standing respectively for the (constant) mass densities of the solvent, colloidal particles and surfactant.

In terms of the variables d , ϕ and w three simple, distinct types of fluctuations around the equilibrium state may be considered, as hinted in figure 3 : figure 3a schematically displays a fluctuation in bilayer thickness at constant smectic spacing and colloid volume fraction figure 3b, a fluctuation in smectic spacing, at constant bilayer thickness and colloid volume fraction ; figure 3b, a fluctuation in colloid volume fraction at constant smectic spacing and bilayer thickness. Note in particular that the fluctuations in smectic spacing (at constant bilayer thickness and colloid volume fraction) depicted in figure 3b also modulate surfactant and colloid concentrations is space.

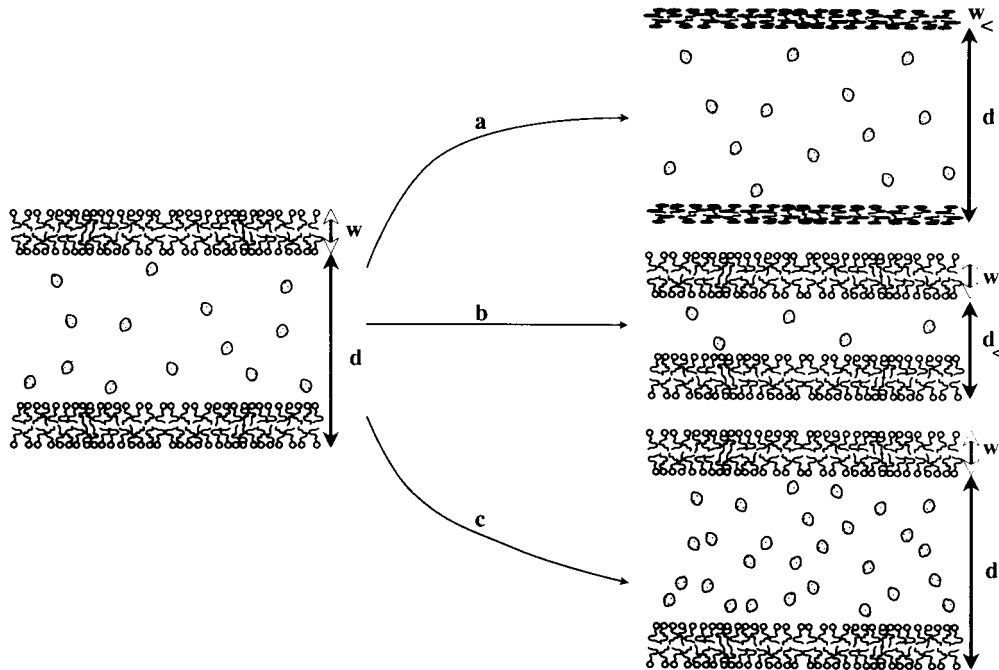


Fig. 3. — Canonical fluctuations in a doped-solvent lamellar phase ; a) modulation of the bilayer thickness w at constant smectic period and colloid volume fraction ; relevant elastic constant : χ_t^{-1} ; b) modulation of the smectic period d at constant bilayer thickness and colloid volume fraction (in the *dilute* limit the surfactant chemical potential is very nearly proportional to the surfactant bilayer thickness and the elastic constant associated to this deformation is : $B - C_t^2 \cdot \chi_t$) ; c) modulation of the colloid volume fraction ϕ at constant smectic period and bilayer thickness (elastic constant in the dilute limit $\chi_p^{-1} - C^2 \cdot \chi_t$).

The restoring forces have basically their origin in, respectively, surfactant-solvent interfacial energy (or *curvature* energy, for *crumpled* membranes ; see Ref. [12]), (Fig. 3a) ; bilayer-bilayer interactions (either direct or entropy-driven interactions) (Fig. 3b) ; and colloidal solution osmotic compressibility (Fig. 3c). In the following, we describe these restoring forces in very simplified terms, leaving to Appendix A a more elaborate approach. The bilayer-bilayer interactions are assumed to stem from a potential energy V , per bilayer and per unit bilayer area which depends on the smectic spacing d *only* ; we thus neglect here a plausible dependence on the colloid volume fraction ϕ . The dependence on bilayer thickness may always be safely neglected, since it is essentially constant in the dilute limit. The energy for changes in bilayer thickness, implying both changes in area per surfactant head and stretching or compression of surfactant tails is represented, in the harmonic approximation and per surfactant molecule, by the following expression : $\frac{1}{2} \varepsilon \left(\frac{w}{w_0} - 1 \right)^2$ where w_0 is the thickness

the bilayer would have when bilayer-bilayer interactions are negligible, i.e. in a very dilute lamellar phase and ε is a constant characteristic energy. We assume here that both ε and w_0 are independent on colloid volume fraction. The colloid contribution is given by the excess free energy per unit volume of the colloidal solution, $g(\phi)$ assumed here not to depend on the confinement within finite thickness layers.

With these assumptions, the free energy F of a volume $\Omega = Ah$ -area along bilayer plane A ; height along the stacking axis h - of the doped-solvent lamellar phase may be written as :

$$F = V(d) A \frac{h}{d} + \frac{1}{2} \varepsilon \left(\frac{w}{w_0} - 1 \right)^2 \frac{wA}{v_t} \frac{h}{d} + g(\phi)(d-w) A \frac{h}{d} \quad (9)$$

(with v_t the volume of one surfactant molecule) or, in terms of the free energy f per unit volume (and with $W(w) = \frac{1}{2} \varepsilon \left(\frac{w}{w_0} - 1 \right)^2 \frac{w}{v_t}$) :

$$f = \frac{V(d) + W(w)}{d} + g(\phi) \left(1 - \frac{w}{d} \right). \quad (10)$$

The free energy per unit mass \tilde{f} may now be easily expressed. For the sake of simplicity, the (constant) mass densities of the solvent, particles and surfactant will be taken as equal : we shall therefore neglect the differences between mass and volume fractions. We thus get the identification :

$$\tilde{f}(d, c_p, c_t) = \frac{1}{\rho} \left[\frac{V(d) + W(dc_t)}{d} + (1 - c_t) g \left(\frac{c_p}{1 - c_t} \right) \right]. \quad (11)$$

The equilibrium smectic spacing d_{eq} is given by the solution of the minimization equation :

$$V(d) + W(dc_t) = d(V' + c_t W') \quad (12)$$

which is $d_{eq} \approx w_0/c_t$ in the dilute limit. In this (over) simplified model the spacing d_{eq} is independent on c_p , as expected from our starting assumptions ; note that this is at contrast with experimental findings on « ferrosmectic » systems [13].

A simple computation yields the following expressions for the elastic constants :

$$B = d(V'' + c_t^2 W'') ; \quad \chi_p^{-1} = \frac{g''}{1 - c_t} ; \quad \chi_t^{-1} = dW'' + \frac{\phi^2 g''}{1 - c_t} \quad (13)$$

$$C_p = 0 ; \quad C_t = dc_t W'' ; \quad C = \frac{\phi g''}{1 - c_t}.$$

The diagonal form for the elastic free energy density is obtained using as normal variables :

$$\partial_z u, \delta \tilde{c}_p = \delta c_p + C \chi_p \delta c_t \quad \text{i.e.} \quad (1 - c_t) \delta \phi$$

and

$$\delta \tilde{c}_t = \delta c_t + \frac{C_t}{\chi_t^{-1} - C^2 \chi_p} \partial_z u \quad \text{i.e.} \quad \frac{\delta w}{d}$$

and the reduced elastic constants are in this case :

$$\bar{B} = dV''; \quad \bar{\chi}_p^{-1} = \frac{g''}{1 - c_t}; \quad \bar{\chi}_t^{-1} = dW''. \quad (14)$$

In particular, the smectic layer compression modulus \bar{B} (the one that appears in the correlation function $\langle u(\mathbf{q})u(-\mathbf{q}) \rangle$) is related to the bilayer-bilayer interaction potential V through the expression $\bar{B} = dV''$ already valid with two-component lamellar phases [3, 14]. This result is not general, however, as may be seen in Appendix A where a more complex model is considered, leading to a less transparent link between elastic constants B , C_p , etc. and the microscopic energies V , W and g .

Hydrodynamics of doped-solvent lamellar phases.

On general grounds [8] *eight* hydrodynamic modes are to be expected in the long wavelength, low frequency part of the spectrum of any *three*-component, *smectic A* phase. If one concentrates on the very low frequency part of the spectrum, three modes may at once be neglected, namely sound (that couples longitudinal momentum and pressure, and accounts for two modes) and heat diffusion, because they relax quickly towards equilibrium. This is equivalent to considering an *incompressible* and *athermal* system. Moreover, among the five remaining modes the relaxation of a shear wave that is transverse to both the optical axis of the smectic phase and the mode wave vector is always decoupled. We thus consider only the four hydrodynamic equations that describe the time evolution of the transverse component of the momentum which lies in the optical axis-wave vector plane, g_t ; the fluctuations in particle and surfactant compositions, δc_p and δc_t ; and the layer displacement, u . Drawing an analogy with similar equations for (incompressible, athermal) two-component smectics A valid when the wave vector modulus q is much smaller than the reciprocal smectic spacing $1/d$ [2, 3, 15], we get :

$$\begin{aligned} \dot{g}_t &= -\frac{\eta}{\rho} q^2 g_t - i \frac{q_x}{q} \mathbf{q} \cdot \Phi \\ \delta \dot{c}_p &= -\frac{\alpha_p}{\rho} q_x^2 \delta \tilde{\mu}_p - \frac{\alpha}{\rho} q_x^2 \delta \tilde{\mu}_t \\ \delta \dot{c}_t &= -\frac{\alpha_t}{\rho} q_x^2 \delta \tilde{\mu}_t - \frac{\alpha}{\rho} q_x^2 \delta \tilde{\mu}_p \\ \dot{u} &= -\frac{q_x}{\rho q} g_t. \end{aligned} \quad (15)$$

In these equations for the spatial Fourier components of the dynamic variables (with the x - z plane containing both the wave vector \mathbf{q} and the normal to the layers z) we have made use of simplifying assumptions on the anisotropies of the viscosity and diffusion coefficient tensors (*isotropic* viscous dissipation, with viscosity η ; mass diffusion-quantified by the dissipative parameters α_i , etc. along the plane of the layers *only*) and on the values of the « flexodiffu-

The diagonal form for the elastic free energy density is obtained using as normal variables :

$$\partial_z u, \delta \tilde{c}_p = \delta c_p + C \chi_p \delta c_t \quad \text{i.e.} \quad (1 - c_t) \delta \phi$$

and

$$\delta \tilde{c}_t = \delta c_t + \frac{C_t}{\chi_t^{-1} - C^2 \chi_p} \partial_z u \quad \text{i.e.} \quad \frac{\delta w}{d}$$

and the reduced elastic constants are in this case :

$$\bar{B} = dV''; \quad \bar{\chi}_p^{-1} = \frac{g''}{1 - c_t}; \quad \bar{\chi}_t^{-1} = dW''. \quad (14)$$

In particular, the smectic layer compression modulus \bar{B} (the one that appears in the correlation function $\langle u(\mathbf{q}) u(-\mathbf{q}) \rangle$) is related to the bilayer-bilayer interaction potential V through the expression $\bar{B} = dV''$ already valid with two-component lamellar phases [3, 14]. This result is not general, however, as may be seen in Appendix A where a more complex model is considered, leading to a less transparent link between elastic constants B , C_p , etc. and the microscopic energies V , W and g .

Hydrodynamics of doped-solvent lamellar phases.

On general grounds [8] *eight* hydrodynamic modes are to be expected in the long wavelength, low frequency part of the spectrum of any *three*-component, *smectic A* phase. If one concentrates on the very low frequency part of the spectrum, three modes may at once be neglected, namely sound (that couples longitudinal momentum and pressure, and accounts for two modes) and heat diffusion, because they relax quickly towards equilibrium. This is equivalent to considering an *incompressible* and *athermal* system. Moreover, among the five remaining modes the relaxation of a shear wave that is transverse to both the optical axis of the smectic phase and the mode wave vector is always decoupled. We thus consider only the four hydrodynamic equations that describe the time evolution of the transverse component of the momentum which lies in the optical axis-wave vector plane, g_t ; the fluctuations in particle and surfactant compositions, δc_p and δc_t ; and the layer displacement, u . Drawing an analogy with similar equations for (incompressible, athermal) two-component smectics A valid when the wave vector modulus q is much smaller than the reciprocal smectic spacing $1/d$ [2, 3, 15], we get :

$$\begin{aligned} \dot{g}_t &= -\frac{\eta}{\rho} q^2 g_t - i \frac{q_x}{q} \mathbf{q} \cdot \Phi \\ \delta \dot{c}_p &= -\frac{\alpha_p}{\rho} q_x^2 \delta \tilde{\mu}_p - \frac{\alpha}{\rho} q_x^2 \delta \tilde{\mu}_t \\ \delta \dot{c}_t &= -\frac{\alpha_t}{\rho} q_x^2 \delta \tilde{\mu}_t - \frac{\alpha}{\rho} q_x^2 \delta \tilde{\mu}_p \\ \dot{u} &= -\frac{q_x}{\rho q} g_t. \end{aligned} \quad (15)$$

In these equations for the spatial Fourier components of the dynamic variables (with the x - z plane containing both the wave vector \mathbf{q} and the normal to the layers z) we have made use of simplifying assumptions on the anisotropies of the viscosity and diffusion coefficient tensors (*isotropic* viscous dissipation, with viscosity η ; mass diffusion-quantified by the dissipative parameters α_i , etc. along the plane of the layers *only*) and on the values of the « flexodiffu-

and eliminate g_i and $\delta\tilde{c}_i$. We then get a set of hydrodynamic equations for the two slow variables u and $\delta\tilde{c}_p$, valid when q_x is not too small, of the following form :

$$\begin{aligned} \left[\frac{\eta q^3}{q_x} + \mu^{-1} \frac{q_z^2}{qq_x} \right] \dot{u} + (\bar{B}q_z^2 + Kq_x^4) \frac{q_x}{q} u - i \frac{q_x q_z}{q} \Delta \chi_p^{-1} \delta\tilde{c}_p = 0 \\ \delta\tilde{c}_p - i q_z \Delta u + D_{\perp} q_x^2 \delta\tilde{c}_p = 0 \end{aligned} \quad (19)$$

with $D_{\perp} = \frac{\alpha_t \alpha_p - \alpha^2}{\rho^2 \alpha_t} \chi_p^{-1}$ the colloid diffusion coefficient in the plane of the layers (see below), $\mu^{-1} = \frac{\rho^2}{\alpha_t} \left(\frac{C_t \chi_p^{-1} - C C_p}{\chi_p^{-1} \chi_t^{-1} - C^2} \right)^2$ a parameter analogous to the inverse surfactant mobility in two-component smectic hydrodynamics [2, 3, 15], and Δ a parameter expressing the dynamic coupling between particle and layer motions in doped-solvent lamellar phases :

$$\Delta = \frac{\alpha_t (\chi_t^{-1} C_p - C_t C) - \alpha (\chi_p^{-1} C_t - C_p C)}{\alpha_t (\chi_p^{-1} \chi_t^{-1} - C^2)} .$$

These equations have a simple solution when $q_z = 0$, i.e. when the wave vector \mathbf{q} lies in the plane of the membranes. There is no longer any coupling between the two dynamic variables u and $\delta\tilde{c}_p$: for this particular orientation of the wave vector, the layer displacement modulation is an *undulation*, with no changes in the *local spacing* between surfactant membranes. The two uncoupled modes are therefore : i) the usual undulation mode of one- and two-component smectic A phases, where the layer displacement u relaxes with frequency : $\omega_u = -i \frac{K}{\eta} q^2$; ii) the in-plane particle diffusion mode, with a characteristic frequency for the relaxation of concentration fluctuations given by [9] : $\omega_d = -i D_{\perp} q^2$.

For a general, *oblique* orientation of the wave vector \mathbf{q} the two modes both mix layer displacement u with concentration fluctuations $\delta\tilde{c}_p$, except of course if one may assume that the dynamic coupling coefficient Δ is negligible (as would be the case for c_t and ϕ small, using equation (13) as a simple model of the elastic constants, for instance). One would then get an u -mode, the baroclinic mode of two-component smectics A [3], with a dispersion relation :

$$\omega_b = -i \frac{\bar{B}q_z^2 + Kq_x^4}{\eta q^4 + \frac{q_z^2}{\mu}} q_x^2 \quad (20)$$

and a concentration mode, corresponding to the anisotropic, in-plane diffusion of the particles, with frequency :

$$\omega_d = -i D_{\perp} q_x^2 . \quad (21)$$

With non zero dynamic coupling Δ and for a given oblique orientation of the wave vector \mathbf{q} one mode has a baroclinic-like behaviour whereas the other one is closer to the anisotropic particle diffusion mode. Both are qualitatively depicted in figure 4, which schematically displays the superposition of a layer displacement wave with a particle concentration one. The relative amounts of particle concentration and layer displacement modulations are different for the two modes. As may be seen from equation (19), the amplitudes of the layer displacement and particle concentration waves in a mode with relaxation frequency Ω are related by : $\partial_z u = \delta\tilde{c}_p (\omega_d - \Omega) / \Omega \cdot \Delta$ or, equivalently, by : $\delta\tilde{c}_p = \partial_z u \Delta (\Omega - \omega_b) / \omega_c$ (the frequency ω_c is defined in the Appendix B Eq. (B.5)).

The anisotropic dispersion relations of the high and low frequency modes may be obtained from the general solution of the coupled hydrodynamic equations (Appendix B, Eq. (B.6)).

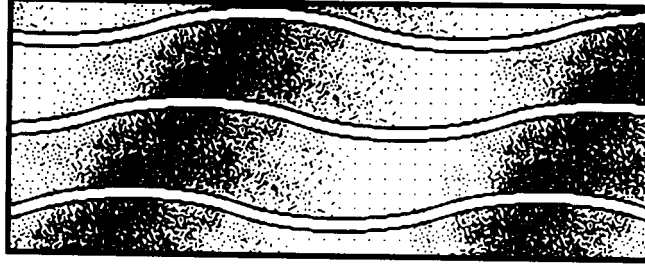


Fig. 4. — Schematic drawing of any of the two low-frequency modes, where layer displacement fluctuations at constant bilayer thickness are coupled to colloid concentration fluctuations (*oblique* wave vector orientation).

For small Δ (i.e. when $\mu \Delta^2 / \chi_p$ is much smaller than $|\mu \bar{B} - D_\perp|$), and in the limit $q_x \ll q_z$, the two frequencies are given by :

$$\begin{aligned}\Omega_1 &= -i \mu \bar{B} \left(1 - \frac{\mu \Delta^2 \chi_p^{-1}}{D_\perp - \mu \bar{B}} \right) q_x^2 \\ \Omega_2 &= -i D_\perp \left(1 - \frac{\mu \Delta^2 \chi_p^{-1}}{\mu \bar{B} - D_\perp} \right) q_x^2.\end{aligned}\quad (22)$$

The baroclinic (resp. particle-diffusion)-like mode is then identified with the eigenmode with frequency Ω_1 (resp. Ω_2). In fact, three generic cases obtain, according to whether $\mu \bar{B} < D_\perp < \frac{K}{\eta}$ or $D_\perp < \mu \bar{B}$ or $\frac{K}{\eta} < D_\perp$, with corresponding dispersion relations plotted in figures 5a, b and c. In figure 5a, the high-frequency mode is baroclinic (undulation)-like when q_z is close to zero (Ω close to ω_b , and therefore $\delta \tilde{c}_p$ small compared to $\partial_z u$) but particle-diffusion-like for q_x close to zero (Ω close to ω_d ; $\partial_z u$ small compared to $\delta \tilde{c}_p$); in figure 5b, the high-frequency mode has a baroclinic (undulation) character for all orientations of the wave vector, when it is particle-diffusion-like in figure 5c.

As mentioned previously, the above analysis cannot be correct when q_x becomes close enough to zero. We have indeed neglected all the dissipative phenomena, like permeation and surfactant or particle diffusion that occur along the z -axis; these processes relax at small but *finite* frequencies elastic strain or concentration fluctuations with wave vector perpendicular to the plane of the layers. Moreover, the distinction between « fast » (g_t and $\delta \tilde{c}_t$) and « slow » (u and $\delta \tilde{c}_p$) variables is no longer obvious when $q_x = 0$.

In this limit, the general hydrodynamic equations for a three-component smectic A take the following form :

$$\begin{aligned}\dot{g}_t &= -\frac{\eta}{\rho} q^2 g_t \\ \delta \dot{c}_p &= -\frac{\alpha_{pz}}{\rho} q^2 \delta \tilde{\mu}_p - \frac{\alpha_z}{\rho} q^2 \delta \tilde{\mu}_t - \frac{\Gamma_p}{\rho} q^2 \Phi_z \\ \delta \dot{c}_t &= -\frac{\alpha_z}{\rho} q^2 \delta \tilde{\mu}_p - \frac{\alpha_{tz}}{\rho} q^2 \delta \tilde{\mu}_t - \frac{\Gamma_t}{\rho} q^2 \Phi_z \\ \dot{u} &= i \Gamma_p q \delta \tilde{\mu}_p + i \Gamma_t q \delta \tilde{\mu}_t + i \zeta q \Phi_z\end{aligned}\quad (23)$$

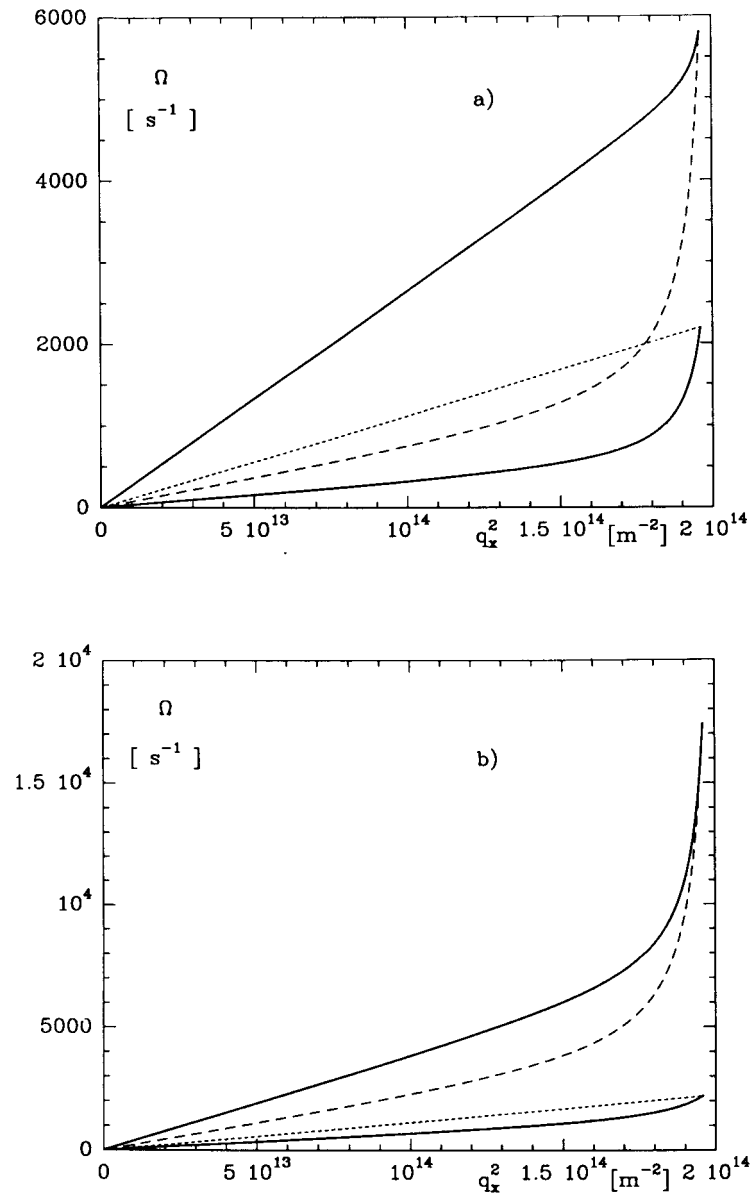


Fig. 5. — Anisotropic dispersion relations of the two low-frequency modes (continuous curves), compared to the uncoupled *baroclinic* mode (dashed curve) or *particle-diffusion* mode (broken curve), as a function of q_x^2 , for a fixed value of the wave vector modulus q . We have chosen parameters as follows : $q = 1.4 \times 10^7 \text{ m}^{-1}$; smectic spacing $d = 40 \text{ nm}$; solvent viscosity $\eta = 1.35 \text{ mPa}\cdot\text{s}$; mobility $\mu = 9.7 \times 10^{-14} \text{ m}^2\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$; and layer compression modulus $\bar{B} = 235 \text{ Pa}$ (Figs. 5a and c) or $\bar{B} = 78 \text{ Pa}$ (Fig. 5b); layer bending modulus $K = 1.2 \times 10^{-13} \text{ N}$ (Figs. 5a and c) or $K = 4 \times 10^{-14} \text{ N}$ (Fig. 5b); particle in-plane diffusion coefficient $D_{\parallel} = 1.12 \times 10^{-11} \text{ m}^2\cdot\text{s}^{-1}$ (Figs. 5a and b) or $D_{\parallel} = 1.12 \times 10^{-10} \text{ m}^2\cdot\text{s}^{-1}$; reduced dynamic coupling $\left(r = \frac{d^2 \Delta^2 \chi_p^{-1}}{\eta D_{\perp}} \right) r = 12.3$ (Figs. 5a and b) or $r = 1.23$ (Fig. 5c); the parameters chosen in figure 5a are typical in a light scattering study of ferrosmectic samples (see text below, experimental part).

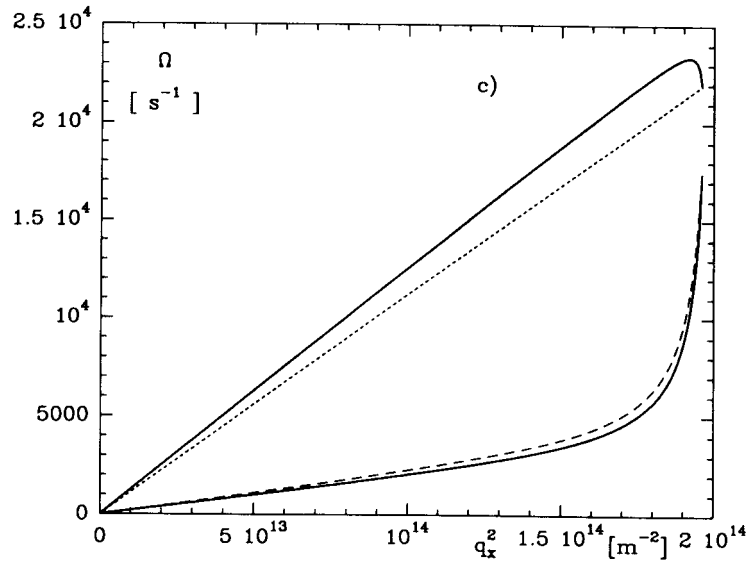


Fig. 5 (continued).

where the α_z 's are dissipative coefficients for particle or surfactant diffusive motions along the z -axis, the Γ 's « flexodiffusion » dissipative coefficients (link between elastic strain with matter flows) and ζ the smectic permeation coefficient.

A qualitative discussion is possible without explicitly solving these equations. The transverse momentum variable q_t becomes uncoupled; it yields a high-frequency shear wave, which is one $q_x = 0$ limit of second sound. The other three variables yield three modes that couple layer displacement with particle and surfactant concentrations. One of these modes, at a comparatively « high » frequency, has presumably a permeation character and is very schematically depicted in figure 6a; it is the other $q_x = 0$ limit of second sound, and its frequency therefore increases very rapidly as the wave vector \mathbf{q} becomes oblique. The last two modes are the $q_x = 0$ limits of the slow modes that were discussed in some detail above. At medium frequency one probably finds a mode with a particle-diffusion character (Fig. 6b), whereas at low frequency the mode may be associated to surfactant diffusion (Fig. 6c). The anisotropic dispersion relations in the vicinity of $q_x = 0$ are easily guessed from the previous considerations and are plotted in figure 7, where the dashed lines are the dispersion relations for the baroclinic-like and particle-diffusion-like modes for negligible dissipative processes along the z -axis.

These modes have no *quantitative* incidence on our analysis where permeation and other z -axis dissipative processes are altogether neglected: indeed, the fastest $q_x = 0$ mode is probably permeation as mentioned above, associated to the « leakage » of the solvent through the surfactant bilayer (Fig. 6a). Its frequency should be of the order of $\omega_{\text{perm}} \approx \zeta \bar{B} q^2$, i.e. with a rough estimate for the permeation coefficient ζ in lyotropic smectics ($\zeta \approx 10^{-33} \text{ m}^2 \text{ Pa}^{-1} \text{ s}^{-1}$ [17] or $\zeta \approx 10^{-19} \text{ m}^2 \text{ Pa}^{-1} \text{ s}^{-1}$ [18]) and typical values for \bar{B} (a few hundred Pa) and q (about 10^7 m^{-1}) a frequency much too small to be within the range of intensity correlation spectroscopy: in light scattering experiments, z -axis dissipative phenomena are infinitely slow.

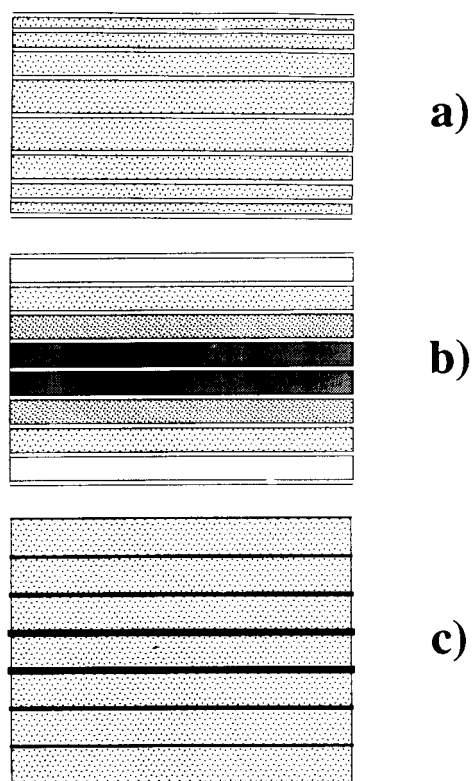


Fig. 6. — Schematic drawing of the three, presumably low-frequency excitations when the wave vector is normal to the smectic layers ; a) layer displacement wave ; b) colloid concentration wave ; c) surfactant concentration wave ; the three eigenmodes presumably couple these three waves.

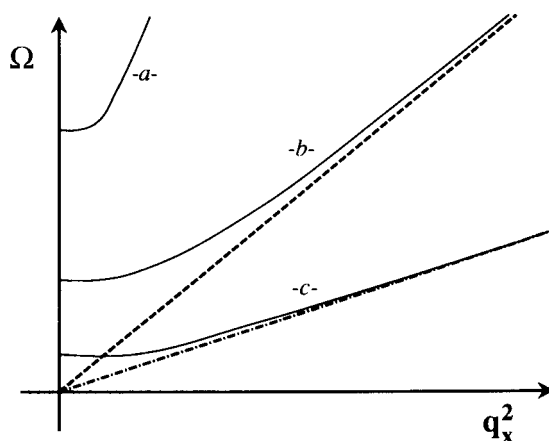


Fig. 7. — Schematic drawing of the anisotropic dispersion relations of the three low-frequency modes, for (fixed-modulus) wave vectors \mathbf{q} nearly perpendicular to the smectic layers ; the a-branch, with a presumably solvent-permeation character for q_x close to zero, evolves towards the (high frequency) second sound mode when q_x increases ; the b-branch (resp. c-branch) has a presumably particle-permeation (resp. surfactant-permeation) character at small q_x and evolves towards one of the two coupled modes described for *oblique* orientations of the wave vector (Fig. 5).

Quasi-elastic light scattering.

A light scattering experiment is sensitive to fluctuations in the dielectric tensor of the studied medium. For multicomponent smectic A phases, which are on symmetry grounds birefringent (uniaxial) media, layer displacement and concentration fluctuations both modulate strongly the dielectric tensor. Polarized scattering is to be expected from concentration fluctuations, and both polarized and depolarized scattering, in general, from layer displacement fluctuations. In the particular case of ferrosmectic phases, which are doped solvent, dilute lamellar phases, it seems reasonable to assume that the *polarized* scattering originates from colloid concentration fluctuations alone and that *depolarized* scattering is negligible. Indeed, owing to their size the colloid particles are far more efficient in scattering light than the surfactant membrane, and dilute lamellar phases are only weakly birefringent. For such a system, the quasielastic (polarized) light scattering is thus described by the correlation function $S(\mathbf{q}, t)$ defined as :

$$S(\mathbf{q}, t) = \langle \delta c_p(\mathbf{q}, t) \delta c_p(-\mathbf{q}, 0) \rangle \quad (24)$$

which may be expressed, introducing the normal variables u , $\delta \tilde{c}_p$ and $\delta \tilde{c}_1$, as the sum of various auto- or cross-correlation functions, each one being easily (though tediously, see Appendix B) computed from the hydrodynamic equations established above, using linear response theory [19].

In the particular case where $q_z = 0$, there is no coupling between the slow normal variables u and $\delta \tilde{c}_p$ and the correlation function is simply expressed :

$$S(q_z = 0, \mathbf{q}_\perp ; t) = k_B T \chi_p \exp(-D_\perp q^2 |t|). \quad (25)$$

This result was already used for measuring the colloid in-plane diffusion coefficient D_\perp in a previous work [9]. For *oblique* orientations of the wave vector \mathbf{q} , u and $\delta \tilde{c}_p$ are coupled but if one further assumes that the main contribution to $S(\mathbf{q}, t)$ comes from the correlation function $\langle \delta \tilde{c}_p(\mathbf{q}, t) \delta \tilde{c}_p(-\mathbf{q}, 0) \rangle$ (see the Appendix B, Eq. (B.4), for a complete expression), the light scattering signal is given by :

$$S(\mathbf{q}, t) = \frac{k_B T \chi_p}{\Omega_1 - \Omega_2} \{ (\Omega_1 - \omega_b) \exp(-i \Omega_1 |t|) + (\omega_b - \Omega_2) \exp(-i \Omega_2 |t|) \} \quad (26)$$

where ω_b is the baroclinic mode relaxation frequency (Eq. (20)) and Ω_1, Ω_2 are the relaxation frequencies of the two slow modes (Appendix B, Eq. (B.6)). Its time decay is therefore controlled in general by *two* characteristic frequencies. Note that in the particular case where the dynamic coupling parameter Δ is small, the frequency of the baroclinic-like mode, say Ω_1 , is close to ω_b for all the orientations of the scattering wave vector \mathbf{q} and the correlation function reduces to the very simple following form :

$$S(\mathbf{q}, t) \approx k_B T \chi_p \exp(-i \Omega_2 |t|) \quad (27)$$

with Ω_2 close to ω_d ; hence, the experimental relevance of the two-mode superposition obtains only for strong enough dynamic coupling Δ .

Quasi-elastic light scattering experiments on various oriented ferrosmectic samples, varying both the modulus q and the orientation \mathbf{q}_\perp of the scattering wave vector \mathbf{q} , have been performed. We give here our results for one sample [20], with a reversed sodium dodecylsulphate-water-pentanol membrane (water over surfactant mass ratio 2.5 ; membrane thickness 5 nm), swollen with a cyclohexane-pentanol solvent containing a volume fraction $\phi = 0.8\%$ of the magnetic colloid (surfactant-coated Fe_2O_3 - γ maghemite particle of radius

about 3 nm); its smectic period is $d = 38$ nm [7, 13]. The good-quality orientation required for light scattering is achieved through a thermal treatment of the sample held in a sealed glass capillary with rectangular cross-section ($2 \text{ mm} \times 200 \mu\text{m}$); smectic layers are laid parallel to the glass plates. We also prepared a reference sample, by swelling the same reversed membrane with the same amount of *pure* solvent.

In our light-scattering experiment, fully described elsewhere [3], the normal to the broad sides of the capillary (also normal to the smectic layers) may be tilted out of the scattering plane, with a fixed tilt angle $\psi = 25$ degrees; its projection onto the scattering plane is freely orientable. The scattering angle varies between 10 and 150 degrees. The incident light (Coherent IK-90 Kr⁺ ion laser, $\lambda = 647.1$ nm; note that a red line has to be used, to avoid as much as possible absorption by the brownish colloid suspension) is polarized perpendicular to the scattering plane and an analyser may be set in front of the detector. A 72-channel Brookhaven Instruments digital correlator, operated in its multiple-sample-time mode to span the longest possible time range is used to build the autocorrelation function of the scattered light.

With the reference sample, the time dependence of the autocorrelation function is very close to a single exponential (Fig. 8) with small departures, especially when the scattering wave vector is close to being parallel or perpendicular to the layers attributed to an imperfect orientation of the sample. The light scattering signal originates here in the usual baroclinic-undulation mode [3]. The anisotropic dispersion relation is well described by equation (20), which yields (using the simple Poiseuille flow model [2] for the surfactant mobility μ and a solvent viscosity $\eta = 1.0$ mPa.s) elastic constants K about 8×10^{-14} N and $\bar{B} = 38$ Pa.

With the doped sample, the time dependence of the correlation function always departs from a single exponential, whatever the orientation of the scattering wave vector \mathbf{q} . As noted in a

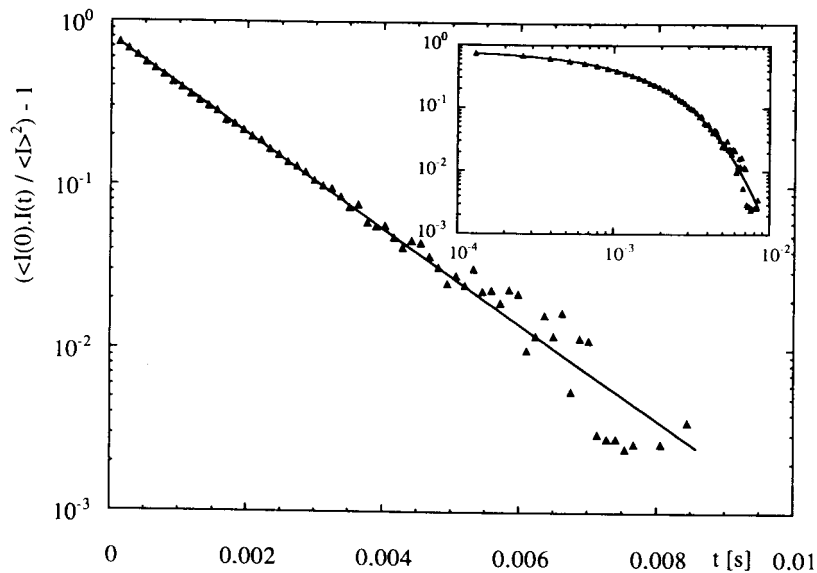


Fig. 8. — Autocorrelation function $\frac{\langle I(0)I(t) \rangle}{\langle I \rangle^2} - 1$ of the scattered light intensity as a function of time, in single or double-logarithmic (insets) coordinates. Points : data from the reference, undoped sample ($q = 1.4 \times 10^7 \text{ m}^{-1}$, $q_z = 7.8 \times 10^6 \text{ m}^{-1}$); line : fit to an exponential test function, with frequency $\Omega = 6.74 \times 10^2 \text{ s}^{-1}$.

previous work [9] this occurs also when the wave vector is parallel to the layers ($q_z = 0$) though one should expect, according to equation (25) a single mode contribution to the light scattering signal. It was shown [9] that the size distribution of the magnetic colloid explains this apparent inconsistency ; the single mode analysis was thus simply replaced by the

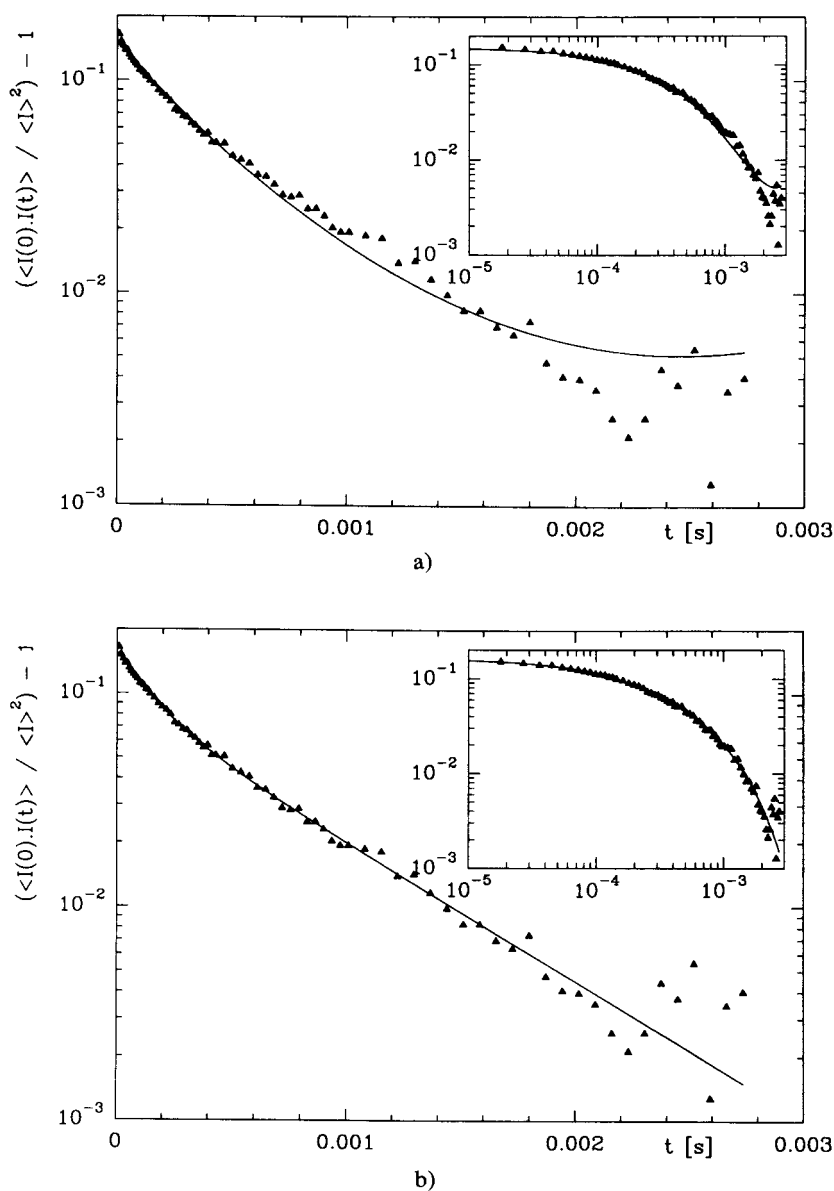


Fig. 9. — Autocorrelation function $\frac{\langle I(0)I(t) \rangle}{\langle I \rangle^2} - 1$ of the scattered light intensity as a function of time, in single or double-logarithmic (insets) coordinates. Points: data from the doped sample ($q = 1.4 \times 10^7 \text{ m}^{-1}$, $q_z = 7.8 \times 10^6 \text{ m}^{-1}$); lines: fits to cumulant (Fig. 9a; initial frequency $\bar{\Omega} = 1.37 \times 10^3 \text{ s}^{-1}$) or two-exponential (Fig. 9b; high frequency $\Omega_+ = 5.23 \times 10^3 \text{ s}^{-1}$; low frequency $\Omega_- = 774 \text{ s}^{-1}$) test functions.

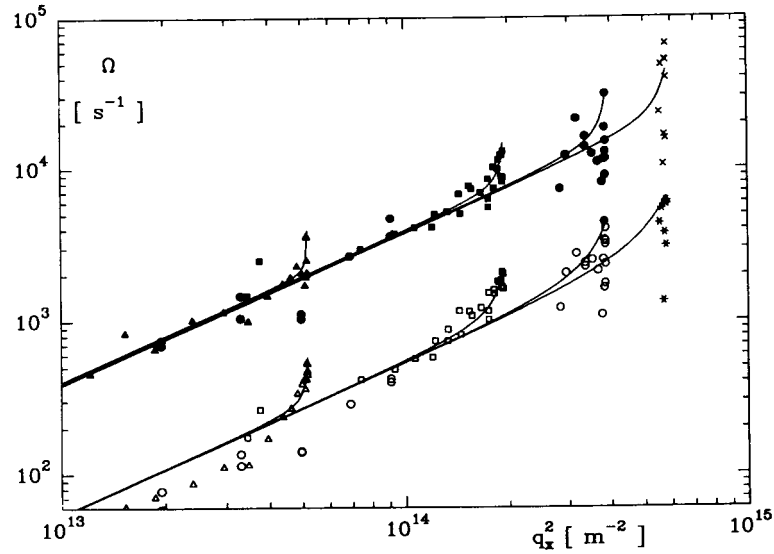


Fig. 10. — Anisotropic dispersion relations of the low and high frequency components of the light scattering signal, displayed as a function of q_{\perp}^2 for various scans at fixed values q of the scattering wave vector modulus \mathbf{q} ; $q = 7.2 \times 10^6 \text{ m}^{-1}$: open and filled triangles; $q = 1.4 \times 10^7 \text{ m}^{-1}$: open and filled squares; $q = 2.0 \times 10^7 \text{ m}^{-1}$: open and filled circles; $q = 2.4 \times 10^7 \text{ m}^{-1}$: stars and crosses. The lines come from a fit of the complete set of data to the roots of equation (19).

cumulant analysis appropriate for polydisperse colloid solutions. For *oblique* wave vectors \mathbf{q} we analyze the data using one of the following two procedures: i) fit to a (second order) cumulant expansion or ii) fit to (the square of) the sum of two single exponentials (homodyne detection). Close to $q_z = 0$, both procedures give a comparable agreement between the model functions and the data. One frequency of the two-exponential fit is always close to the initial frequency of the cumulant fit whereas the remaining one, often with an at least ten times less weight, may be much higher or much smaller and seems meaningless. Far enough from $q_z = 0$, the cumulant fit is seemingly worse than the two-exponential one, as illustrated in figure 9. We may therefore consider that the data reasonably support our theoretical expectation of a two-mode superposition (Eq. (26)), indicating a non negligible dynamic coupling parameter Δ .

We get from procedure ii), when it is reliable, two relaxation frequencies, $\Omega_>$ and $\Omega_<$. Their anisotropic dispersion relations are displayed in figure 10, for various *constant* wave vector *modulus* scans, as a function of q_{\perp}^2 . The lines come from a single fit of the *complete set* of frequencies to the roots of the coupled hydrodynamic equations, (Eq. (19)), using as adjustable parameters the elastic constants \bar{B} and K , the particle in-plane diffusion coefficient D_{\perp} and a reduced, dimensionless dynamic coupling parameter $r = \frac{\Delta^2 \chi_p^{-1} d^2}{D_{\perp} \eta}$. The

viscosity is taken equal to the solvent viscosity $\eta = 1.0 \text{ mPa}\cdot\text{s}$; the dissipative parameter μ is identified, in the absence of a more adequate microscopic model for it, to the value it would have according to the Poiseuille flow model in a two-component lamellar phase [2] (here, μ about $9 \times 10^{-14} \text{ s}\cdot\text{kg}^{-1}\cdot\text{m}^{-3}$). Indeed, the expressions given equation (13) for the elastic constants in the most simple model of a doped-solvent lamellar phase lead to similar forms for μ in binary and ternary lamellar systems. The resulting values of elastic and hydrodynamic

parameters for the doped system are : $D_{\perp} = 1.1 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$; $\bar{B} = 2.3 \times 10^2 \text{ Pa}$; $r = 12$; K in the range 10^{-13} N .

Among these parameters, the bending modulus K is probably the least well-defined parameter since it describes the dispersion relation of the *high-frequency* mode in the vicinity of $q_z = 0$, that is to say in the range where its contribution to the light scattering signal vanishes. The values for \bar{B} and r stem from an analysis of the signal far from $q_z = 0$ and are thus on a better ground. One should however remember that the quoted values are linked to our *assumption* about the (model-dependent) mobility μ . As a final word of caution, note that the analysis we perform is not entirely self-consistent. According to our description of the light scattering signal (Eq. (26)), two characteristic frequencies (Ω_1 and Ω_2) and an amplitude ratio ($[\Omega_1 - \omega_b]/[\omega_b - \Omega_2]$) are determined by the hydrodynamic model (Eq. (19)). Unfortunately, it is not possible to get satisfactory results when we try to fit simultaneously the experimental relaxation frequencies $\Omega_>$ and $\Omega_<$ and the experimental amplitude ratio to the three corresponding hydrodynamic functions : the experimental amplitude of the high frequency part of the signal tends to be smaller than is predicted for a given amplitude of the low frequency part. This may mean that some of the simplifying assumptions that led to equations (24) and (26) are incorrect. The basic conclusion (see Appendix) that the low frequency part of the spectrum of light scattered by a doped-solvent lamellar phase contains two frequencies Ω_1 and Ω_2 which are the roots of the characteristic equation (Eq. (19)), is left unaffected, however.

Conclusion.

In this paper we have shown how the framework of the general elastic and hydrodynamic theory of ordered condensed phases [8], already used successfully to describe simple lamellar [2, 3] and other [15] two-component smectic A phases may be applied with three-component smectic A systems belonging to the class of « doped solvent » lamellar phases. As was the case with (two-component) dilute lamellar phases, we find that the value of the elastic constant \bar{B} directly stems, in the most simple case, from bilayer interactions. Together with the mode originating in the relaxation of layer displacement fluctuations, i.e. the undulation-baroclinic mode in two-component lamellar systems, one finds a new mode in doped-solvent systems that arises from the colloid diffusive motion. Layer displacement and colloid concentration fluctuations are coupled in general, except in the particular case where the wave vector \mathbf{q} of the disturbance lies in the plane of the smectic layers. The anisotropic dispersion relation of each mode is sensitive to elastic and dissipative parameters such as the smectic elastic constants \bar{B} and K and the in-plane colloid diffusion coefficient D_{\perp} , which allows in principle an experimental measurement of these parameters through dynamic light scattering, for instance. The dynamic light scattering study of ferrosmectic samples, though sensitive to the colloid concentration fluctuations only, illustrates the validity of this scheme, even if an experiment devoted to the measurement of the *layer displacement* fluctuations remains desirable to get a reliable estimate of the splay modulus K . While previous, simpler experiments devoted to the measurement of the particle in-plane diffusion coefficient D_{\perp} showed the influence of the quasi-two-dimensional confinement of the particles [9], our present experiment mainly corroborates the strong increase in the smectic compression modulus \bar{B} induced by the presence of the colloidal component that was observed with other experimental techniques [13, 21]. More work is obviously required in order to get precisely the functional dependence of \bar{B} on smectic spacing and colloid volume fraction. New systems, such as polymer doped lamellar phases for instance [22-24], with \bar{B} a decreasing function of the dopant concentration, are also promising for further studies.

Appendix A.

Possible extensions of the simple microscopic model for a doped-solvent lamellar phase.

The free energy of a doped-solvent lamellar phase considered in the text (Eq. (10)), is built as an addition of free energy contributions for a *two-component* lamellar system and a binary mixture. A consequence of this assumption is that the equilibrium smectic period d_{eq} and, as a result, the compression modulus at constant surfactant and particle chemical potentials \bar{B} do not depend on the colloid concentration c_p . This is not true experimentally for ferrosmectics, as demonstrated by structural studies of such systems [13] as well as by the light scattering results presented here. More realistic models should therefore incorporate the coupling between layer spacing and colloid concentration, i.e. a non-zero C_p . One way to introduce such a coupling is to consider that the colloid has some affinity with the surfactant bilayer. This may change the bilayer flexibility κ and therefore the *strength* of bilayer-bilayer interactions in sterically-stabilized lamellar phases but this effect is reputed small [25, 26]. If the affinity is strong, with colloid particles stuck to the membranes the *range* of the Helfrich repulsion is also modified, with an increased hard core exclusion zone. Besides, a weak affinity changes in a controlled way the colloid excess free energy owing to the induced colloid concentration *profile* between the bilayers. In the following, we consider in some details this last effect.

The total free energy G of an incompressible colloidal solution contained between two walls of area A a distance h apart may be written as [27] :

$$G = A \left\{ 2 \gamma_0 - 2 \gamma_1 \phi_s + \int_{-h/2}^{h/2} \left[g(\phi) + \frac{m^2}{2} (\partial_z \phi)^2 \right] dz \right\} \quad (\text{A.1})$$

where $g(\phi)$ is the *bulk* free energy of the colloidal solution, m^2 is an energy per unit length and the wall-solvent interfacial energy is written, in the weak-coupling limit as the sum of a pure solvent term γ_0 and a term $\gamma_1 \phi_s$, linear in colloid volume fraction at the walls.

The equilibrium concentration profile $\phi(z)$ for given wall separation h and mean colloid concentration $\bar{\phi}$ is found by the minimization of the free energy G with respect to small variations in bulk $\delta \phi(z)$ and surface $\delta \phi_s$ concentrations, with the colloid conservation constraint :

$$\int_{-h/2}^{h/2} \phi(z) dz = \bar{\phi} h \quad (\text{A.2})$$

and symmetry property : $\phi(z) = \phi(-z)$. This leads to the profile equation :

$$m^2 \partial_z^2 \phi = \frac{\partial g}{\partial \phi} - \lambda \quad (\text{A.3})$$

where a Lagrange multiplier λ has been introduced, with the boundary conditions :

$$\partial_z \phi \Big|_{z=h/2} = \frac{\gamma_1}{m^2}; \quad \partial_z \phi \Big|_{z=0} = 0. \quad (\text{A.4})$$

Integrating once and eliminating the Lagrange multiplier leads to a first order profile equation :

$$\frac{m^2}{2} (\partial_z \phi)^2 = g(\phi) - g(\phi_0) - \frac{g(\phi_s) - g(\phi_0)}{\phi_s - \phi_0} (\phi - \phi_0) + \frac{(\phi - \phi_0)}{\phi_s - \phi_0} \frac{\gamma_1^2}{2 m^2} \quad (\text{A.5})$$

with boundary conditions $\phi(z=0) = \phi_0$ and $\phi(z=h/2) = \phi_s$. It can be solved explicitly if one assumes the following simple model for the bulk free energy of the colloid solution :

$$g(\phi) = \bar{g} + \mu(\phi - \bar{\phi}) + \frac{1}{2\chi}(\phi - \bar{\phi})^2 \quad (\text{A.6})$$

with the parameters μ (chemical potential) and χ (osmotic compressibility $\phi \cdot \partial\phi/\partial\pi = \chi$) taken as constant. This yields the equilibrium profile :

$$\phi(z) = \bar{\phi} - \frac{2\gamma_1\chi}{h} \left[1 - \frac{h}{2\xi \text{sh}(h/2\xi)} \text{ch}(z/\xi) \right] \quad (\text{A.7})$$

where the correlation length ξ is given by $\xi = m\sqrt{\chi}$. Substituting the equilibrium profile into the total free energy G of the colloid solution we get :

$$G = 2A \left\{ \gamma_0 - \gamma_1 \bar{\phi} + \bar{g} \frac{h}{2} + \frac{\gamma_1^2 \xi}{2m^2} \left[\frac{2\xi}{h} - \coth\left(\frac{h}{2\xi}\right) \right] \right\}. \quad (\text{A.8})$$

This result for G implies that the free energy f per unit volume of a doped-solvent lamellar phase should now be given by :

$$f = \frac{V(d) + W(w)}{d} + g(\phi) \left(1 - \frac{w}{d} \right) - 2\gamma_1 \frac{\phi}{d} + \frac{\gamma_1^2 \xi}{m^2 d} \left[\frac{2\xi}{d-w} - \coth\left(\frac{d-w}{2\xi}\right) \right] \quad (\text{A.9})$$

instead of equation (10), where the (constant) wall-solvent interfacial energy γ_0 has been incorporated into the energy $V(d)$. The equilibrium smectic spacing d_{eq} then becomes a function of the colloid concentration c_p as well as of the surfactant concentration c_t . The coupling constant C_p defined in the elastic free energy expansion (Eq. (3)) is no longer identically zero : from equation (A.9) we get $C_p = 2\gamma_1/[(1 - c_t) d_{\text{eq}}]$. Besides, repeating the steps that led to equation (14), one in particular finds for the elastic constant \bar{B} (up to second order in γ_1) :

$$\bar{B} = dV'' - \frac{\chi\gamma_1^2 d \text{ch}[d(1-c_t)/2\xi]}{2\xi^3 \text{sh}^3[d(1-c_t)/2\xi]} \quad (\text{A.10})$$

which shows that \bar{B} is no longer determined by the bilayer-bilayer interactions *alone*. Note that the very presence of a colloid concentration profile *reduces* \bar{B} , whatever the sign of the colloid-wall interaction γ_1 . Thus, the mechanism described here cannot be the dominant one with ferrosmectic systems, where one finds an *increase* in \bar{B} .

Appendix B.

Time-dependent correlation functions.

Our dynamic light scattering experiments probe the time relaxation of the particle concentration correlation function $S(\mathbf{q}, t)$ defined equation (24). In terms of normal variables, and taking into account that correlation functions involving the « fast » variable $\delta\tilde{c}_t$ decay quickly we get in the long time limit :

$$S(\mathbf{q}, t) = \langle \delta\tilde{c}_p(\mathbf{q}, t) \delta\tilde{c}_p(-\mathbf{q}, 0) \rangle + q_z^2 \left(\frac{CC_t - C_p\chi_t^{-1}}{\chi_p^{-1}\chi_t^{-1} - C^2} \right)^2 \langle u(\mathbf{q}, t) u(-\mathbf{q}, 0) \rangle + \\ + iq_z \frac{CC_t - C_p\chi_t^{-1}}{\chi_p^{-1}\chi_t^{-1} - C^2} (\langle u(\mathbf{q}, t) \delta\tilde{c}_p(-\mathbf{q}, 0) \rangle - \langle \delta\tilde{c}_p(\mathbf{q}, t) u(-\mathbf{q}, 0) \rangle). \quad (\text{B.1})$$

Linear response theory [19] relates the time Fourier transforms $S_{pp}(\mathbf{q}, \omega)$, $S_{uu}(\mathbf{q}, \omega)$ and $S_{pu}(\mathbf{q}, \omega)$ of, respectively, $\langle \delta \tilde{c}_p(\mathbf{q}, t) \delta \tilde{c}_p(-\mathbf{q}, 0) \rangle$, $\langle u(\mathbf{q}, t) u(-\mathbf{q}, 0) \rangle$ and $\langle \delta \tilde{c}_p(\mathbf{q}, t) u(-\mathbf{q}, 0) \rangle$ to generalized susceptibilities that may be constructed from our (linear) hydrodynamic equations, equation (19). With $H(\mathbf{q})$ the two-by-two matrix built from equation (19) recast in the form :

$$\begin{aligned} \dot{u} &= H_{uu} u + H_{up} \delta \tilde{c}_p \\ \delta \dot{\tilde{c}}_p &= H_{pu} u + H_{pp} \delta \tilde{c}_p \end{aligned} \quad (\text{B.2})$$

and $S(\mathbf{q})$ defined by :

$$S(\mathbf{q}) = \begin{bmatrix} \langle u(\mathbf{q}) u(-\mathbf{q}) \rangle & \langle u(\mathbf{q}) \delta \tilde{c}_p(-\mathbf{q}) \rangle \\ \langle \delta \tilde{c}_p(\mathbf{q}) u(-\mathbf{q}) \rangle & \langle \delta \tilde{c}_p(\mathbf{q}) \delta \tilde{c}_p(-\mathbf{q}) \rangle \end{bmatrix} \quad (\text{B.3})$$

a new matrix $C(\mathbf{q}, z)$ is constructed : $C(\mathbf{q}, z) = -[H(\mathbf{q}) + iz]^{-1} S(\mathbf{q})$. One gets frequency-dependent correlation functions as : $S_{pp}(\mathbf{q}, \omega) = 2 \text{Re} \{C_{pp}(\mathbf{q}, \omega + i\varepsilon)\}$, etc. This procedure, supplemented by the use of equipartition theorem in equation (4), leads to the final result :

$$\begin{aligned} S(\mathbf{q}, t) &= \frac{kT}{\Omega_1 - \Omega_2} [\chi_p \{(\Omega_1 - \omega_b) \exp(-i\Omega_1|t|) + (\omega_b - \Omega_2) \exp(-i\Omega_2|t|)\} + \\ &+ \left(\frac{CC_t - C_p \chi_t^{-1}}{\chi_p^{-1} \chi_t^{-1} - C^2} \right)^2 \frac{q_z^2}{\bar{B}q_z^2 + Kq_x^4} \{(\Omega_1 - \omega_d - \omega_c) \exp(-i\Omega_1|t|) \\ &+ (\omega_d + \omega_c - \Omega_2) \exp(-i\Omega_2|t|)\} \\ &+ 2 \frac{CC_t - C_p \chi_t^{-1}}{\chi_p^{-1} \chi_t^{-1} - C^2} \chi_p \Delta^{-1} \omega_c \{ \exp(-i\Omega_1|t|) - \exp(-i\Omega_2|t|) \}] \quad (\text{B.4}) \end{aligned}$$

where ω_b is the baroclinic mode frequency (Eq. (20)), ω_d is the particle in-plane diffusion mode frequency (Eq. (21)) and ω_c is defined by :

$$\omega_c = -i \Delta^2 \chi_p^{-1} \frac{q_x^2 q_z^2}{\eta q^4 + \frac{q_z^2}{\mu}} \quad (\text{B.5})$$

The light scattering signal $S(\mathbf{q}, t)$ is therefore the sum of two exponentially-decaying components with characteristic relaxation frequencies Ω_1 and Ω_2 , roots of the hydrodynamic equation (Eq. (19)), i.e.

$$\begin{aligned} \Omega_1 &= \frac{1}{2} [\omega_b + \omega_d + \omega_c + i \sqrt{4 \omega_p \omega_d - (\omega_b + \omega_d + \omega_c)^2}] \\ \Omega_2 &= \frac{1}{2} [\omega_b + \omega_d + \omega_c - i \sqrt{4 \omega_p \omega_d - (\omega_b + \omega_d + \omega_c)^2}] \end{aligned} \quad (\text{B.6})$$

The simpler form (Eq. (26)), given in the text for $S(\mathbf{q}, t)$ arises if one further assumes that the $u - u$ and $u - \delta c_p$ contribution to the light scattering correlation function are negligible. This is the case within the framework of our simplified model for a dilute, doped solvent lamellar phase ; indeed, from equation (13), we get :

$$\frac{CC_t - C_p \chi_t^{-1}}{\chi_p^{-1} \chi_t^{-1} - C^2} = \phi c_t \quad (\text{B.7})$$

which is of course small in the dilute limit ($c_t \ll 1$) and at low particle volume fraction ϕ .

References

- [1] Ekwall P., *Advances in Liquid Crystals*, G. M. Brown Ed. (Academic, New York, 1975).
- [2] Brochard F. and de Gennes P.-G., *Pramana Suppl.* **1** (1975) 1.
- [3] Nallet F., Roux D. and Prost J., *J. Phys. France* **50** (1989) 3147.
- [4] Nallet F., Roux D. and Milner S. T., *J. Phys. France* **51** (1990) 2333.
- [5] Kahlweit M., Strey R. and Firman P., *J. Phys. Chem.* **91** (1986) 671.
- [6] Ott A., Urbach W., Langevin D., Ober R. and Waks M., *Europhys. Lett.* **12** (1990) 395.
- [7] Fabre P., Casagrande C., Veyssié M., Cabuil V. and Massart R., *Phys. Rev. Lett.* **64** (1990) 539.
- [8] Martin P. C., Parodi O. and Pershan P. S., *Phys. Rev. A* **6** (1972) 2401.
- [9] Fabre P., Quilliet C., Veyssié M., Nallet F., Roux D., Cabuil V. and Massart R., *Europhys. Lett.* **20** (1992) 229.
- [10] de Gennes P.-G., *J. Phys. Colloq. France* **30** (1969) C4-65.
- [11] Helfrich W., *Z. Naturforsch.* **33a** (1978) 305.
- [12] In what follows, we do not take into account the *crumpling* that may arise from the short wavelength undulations of the membrane. Its relevance in the surfactant concentration fluctuation mechanism is described in : Lubensky T. C., Prost J. and Ramaswamy S., *J. Phys. France* **51** (1990) 933.
- [13] Ponsinet V., Fabre P., Veyssié M. and Auvray L., *J. Phys. II France* **3** (1993) 1021.
- [14] Roux D. and Safinya C. R., *J. Phys. France* **49** (1988) 307.
- [15] Xin Wen and Meyer R. B., *J. Phys. France* **50** (1989) 3043.
- [16] Permeation should also be considered in principle when the wave vector \mathbf{q} is parallel to the layers (i.e. $q_z = 0$) ; it affects the relaxation frequency of the transverse shear mode for wave vectors of the order of, or greater than $q_{\text{shear}}^* = \sqrt{\eta/\zeta K\rho}$ and the undulation mode relaxation frequency above $q_{\text{und}}^* = \sqrt{2/\zeta\eta}$. With reasonable estimates for the parameters (see Refs. [17, 18] for the permeation coefficient ζ), these cross-over wave vectors q^* are *orders of magnitude* larger than light scattering wave vectors ; neglecting permeation for such orientations of the wave vector is thus definitely reasonable.
- [17] Chan W. K. and Webb W. W., *J. Phys. France* **42** (1981) 1007.
- [18] Oswald P. and Allain M., *J. Phys. France* **46** (1985) 831.
- [19] Forster D., *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (W. A. Benjamin Inc., Reading, 1975).
- [20] The complete set of data may be found in : Quilliet C., thèse de l'université Pierre-et-Marie-Curie, Paris (unpublished).
- [21] Quilliet C., Fabre P. and Veyssié M., *J. Phys. II France* **3** (1993) 1371.
- [22] Singh M., Ober R. and Kléman M., *J. Phys. Chem.* **97** (1993) 11108.
- [23] Ligoure C., Bouglet G. and Porte G., *Phys. Rev. Lett.* **71** (1993) 3600.
- [24] Ficheux M.-F., Bellocq A.-M. and Nallet F., unpublished results.
- [25] Brooks J. T., Marques C. M. and Cates M. E., *J. Phys. II France* **1** (1991) 673.
- [26] Podgornik R., *Europhys. Lett.* **21** (1993) 245.
- [27] Cahn J., *J. Chem. Phys.* **66** (1977) 3667.