Surface dynamics of a freely standing smectic-*A* film

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A theoretical analysis of surface fluctuations of a freely standing thermotropic smectic-*A* liquid-crystal film is provided, including the effects of viscous hydrodynamics. We find two surface dynamic modes (undulation and peristaltic). For long wavelengths and small frequencies in a thin film, the undulation mode is the dominant mode. Permeation enters the theory only through the boundary conditions. The resulting power spectrum is compared with existing experiments. It is also shown that feasible light scattering experiments on a freely standing smectic-*A* film can reveal viscosity and elastic coefficients through the structure of the power spectrum containing contributions from both the undulation and peristaltic modes. [S1063-651X(98)12805-2]

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Recent experiments on the dynamics and instabilities of soap [1] and smectic-*A* films [2] have raised interest in the general question of dynamics of freely standing films. The interactions between bulk elasticity and surface tension make freely standing smectic-*A* films (FSSF's) suitable systems for studying finite-size and surface effects; hence fluctuations in FSSF's are an important subject for both theoretical and experimental study [3]. However, during the past decade only static properties of these systems have been considered. Recent x-ray-scattering [4] experiments probed details of static in-plane correlations in a smectic-*A* film. To our knowledge, however, studies on dynamic light scattering of freely standing liquid films were concentrated on soap films, two-dimensional orientational fluctuations in liquid crystal films [5], or other systems without internal structure [6]. The only experimental work on dynamic light scattering of FSSFs to our knowledge [7] was carried out without a systematic theoretical analysis. Hence a theoretical investigation of the dynamics of smectic-*A* liquid crystals in the presence of free surfaces can help us to gain deeper insight into the physics of FSSF's and to provide a basis for understanding recent experiments [2].

At free surfaces, smectic layers always orient parallel to the smectic-air interface [8]. When the system is driven out of equilibrium, surface and bulk elasticity and hydrodynamic effects give the film very complicated dynamical properties. In this paper we give a theoretical calculation of the power spectrum of thermal fluctuations of the surfaces in equilibrium by studying the linearized hydrodynamic equations developed by Martin *et al.* [9]. We show that for thin films, long-wavelength surface fluctuations have two normal modes: an *undulation mode* in which the two interfaces moving in phase and a *peristaltic mode* corresponding to a ''breathing'' motion. The undulation mode is the dominant mode at low frequency and long wavelength. The amplitude of the peristaltic mode is expected to be very small. Only when the thickness of the film becomes very large and the motions of the two interfaces decouple do the two modes become comparable. Permeation processes are important within the boundary layer [10,11] in order that the proper boundary conditions are satisfied. However, our calculation shows that, in the wavelength and frequency range considered, the power spectrum of the surface fluctuations is independent of the permeation constant. We also show that the earlier experimental study of dynamic light scattering on a FSSF [7] was performed in the limit of a very thin film such that the power spectrum has the same form as that of a soap film, i.e., bulk elasticity making no contribution to the power spectrum. The scaling relations suggested in Ref. [7] for the peak position are not valid in general, especially when the thickness of the film is increased, thus allowing the bulk elasticity of the smectic material to play a role in the dynamics. For a reasonably thick film, the power spectrum can have, in addition to a single undulation peak, some additional structure that reveals the interaction between the two free surfaces and the contribution from bulk properties. We suggest that more light scattering experiments on a FSSF will be great help for an understanding of the interplay between surface and bulk properties in this layered system.

In the ground state, an ideal smectic-*A* phase consists in a uniform piling of planar, parallel and equidistant layers of molecular thickness. We use a continuum description and take the average layer normals parallel to the z axis. When small fluctuations are present, the bulk elastic free energy of smectic-*A* phase is given by [10]

$$F=\int d^3\mathbf{r}\frac{1}{2}\left\{B\left(\frac{\partial u}{\partial z}\right)^2+K_1\left(\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right)^2\right\}, \tag{1}$$

where $u(\mathbf{r},t)$ is the layer displacement from the equilibrium position at position $\mathbf{r}$ at time t and B and K_1 are, respectively, the the layer compression and undulation elastic moduli. The characteristic length $\lambda\equiv\sqrt{K_1/B}$ is typically of the order of the layer spacing ($\sim 10^{-7}$ cm) [10].

The equations for viscous flow in smectic-*A* liquid crystals were written down by Martin *et al*. [9] In the absence of topological defects, the system satisfies the equations of motion in bulk

$$\rho\frac{\partial v_i}{\partial t}=-\partial_i p+\partial_j\sigma'_{ij}+h\,\delta_{iz} \tag{2}$$

and

$$\frac{\partial u}{\partial t}=v_z+\zeta_p h, \tag{3}$$

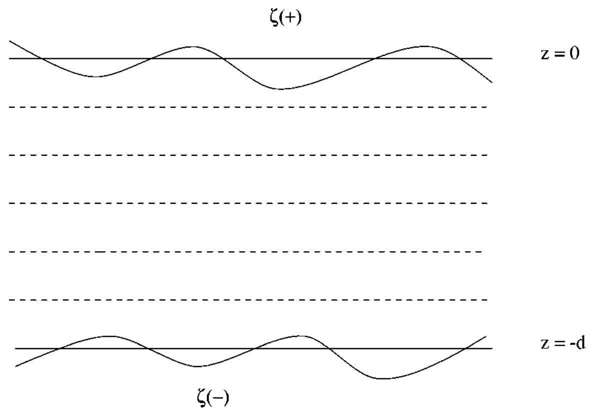

FIG. 1. Schematic of a freely standing smectic-*A* film of thickness d.

where, as usual, ρ, v_i, and p are the density, velocity components, and pressure, respectively, σ' is the viscous stress tensor, ζ_p is the permeation constant, and h is defined by

$$h \equiv \partial_i \left(\frac{\delta F}{\delta \partial_i u} \right). \tag{4}$$

In Eq. (2) we sum on repeated indices and $\partial_j = \partial / \partial x_j$. An important length scale associated with permeation is the boundary layer δ. Within this distance to the boundary, permeation takes place to satisfy proper boundary conditions of the system under consideration [10–12]. We will show that the boundary layer is associated with the ''permeation modes.'' The boundary conditions for free surfaces are discussed below.

We consider a freely standing smectic-*A* liquid crystal film with film normal in the z direction. As noted, in equilibrium, the layers are parallel to the free surfaces. When the surfaces are perturbed by an external force, elastic forces and dissipative effects act to drive the system back to the equilibrium configuration. In this paper we study such a system by including the hydrodynamics in the film.

The geometry of the film is shown in Fig. 1; the film extends from $z=-d$ to $z=0$, but is otherwise without boundaries in the x,y directions. The displacements of the upper and lower free surfaces from their equilibrium values are described by two functions $\zeta^+(x)$ and $\zeta^-(x)$. We consider surface light scattering experiments [13] with momentum transfer vector $\mathbf{q}$ in the x direction; we further assume translational invariance in the y direction. The quantities we are interested in are the response functions and the shape of the power spectrum of the surface displacement, which can be measured directly in experiments.

We look for surface wave solutions in the form of a traveling wave parallel to the surface with amplitude exponentially damped in the perpendicular (z) direction, i.e.,

$$v_z = \sum_k \{A_k^+ e^{S_k q z} + A_k^- e^{-S_k q (z-d)}\} e^{i\omega t + iqx}, \tag{5}$$

where the real parts $\mathrm{Re}(S_k) \geqslant 0$. The index $k=1,2,\ldots,n$ runs over a finite number of solutions to a characteristic equation such as given below. All the S_k's are in principle complex. Since both ω and q are real, a purely imaginary S_k indicates oscillatory behavior without damping, while a purely real S_k indicates purely damped behavior. In the zero-frequency limit, S_3 reduces to its static value, which is real (see below). A^+ and A^- are the respective amplitudes at the surfaces $z=0$ and $z=-d$. For given q and ω we look for S_k's yielding a velocity field that satisfies the equations of motion. We assume the film is incompressible so that the pressure is chosen to satisfy the incompressibility. The system is left with three hydrodynamic variables (v_x, v_z, and u), which gives three solutions for $S_k, k=1,2,3$. When the incompressibility condition is satisfied, only two combinations of viscosities η' and η_3 [12], enter the expressions for the S_k's. A length scale associated with the permeation process is $\kappa^{-1} \equiv \sqrt{\zeta_p \eta_3} \sim 10^{-7}$ cm [10–12]. A dimensionless (and pure imaginary) frequency Ω is conveniently defined as $\Omega = -i\omega\rho/\eta_3 q^2$. The characteristic frequency $K_1 q^2/\eta_3$ for the decay rate of the bulk undulation mode, divided by $\eta_3 q^2/\rho$, yields a dimensionless combination of material constants $\mu = K_1 \rho/\eta_3^2$, which plays an important role in what follows. We consider low frequencies and long wavelengths satisfying conditions $(\kappa/q)^2 \gg 1$, $\lambda q \ll 1$, $(|\Omega|/\mu)(\lambda q)^2 \ll 1$, and $(|\Omega|^2/\mu)(\lambda q)^2 \ll 1$. These conditions mean that we consider a regime in which the velocity of the surface wave is slow compared to the typical velocity of ''second sound'' $\sqrt{B/\rho}$ [10]. Furthermore, since then the frequency cannot be as large as $K_1 \lambda^{-2}/\eta_3$, permeation cannot have a significant contribution to the bulk undulation mode [10]. In this frequency and wave-number domain the three spatially decaying modes in the z direction can be found. One of them yields a long spatial relaxation length and is given by

$$S_3^2 = (\lambda q)^2 \left[\frac{1 - \dfrac{\Omega}{\mu}(1-\Omega)}{1 + \dfrac{\Omega}{\mu}(\lambda q)^2 \left(\Omega - \dfrac{\eta'}{\eta_3} - 2 \right)} \right] \tag{6}$$

$$\equiv (\lambda q)^2 [f(\Omega, q)]^2. \tag{7}$$

The other two solutions (S_1 and S_2) have $|\mathrm{Re}S|, |\mathrm{Im}S| \gg 1$ and satisfy

$$S^4 + \frac{\Omega}{\mu}(\kappa\lambda)^2 S^2 + \left(\frac{\kappa}{q} \right)^2 = 0. \tag{8}$$

In typical light scattering experiments $q \sim 10^2 - 10^4$ cm^{-1} and $\omega \leqslant 10^8$ rad/s. For typical materials $\eta_3 \sim 1$ P, so that the long-wavelength, low-frequency conditions above are satisfied. We note that when the denominator of the (complex) function $f(\Omega, q)$ defined above is significantly different from unity, one cannot separate the solutions for S_1, S_2, S_3 in the way mentioned above. The relaxation governed by S_3 is related to the dynamic generalization of the penetration length of layer distortion in the bulk due to surface undulation [10,14]. Following the terminology of Rapini [14], from now on we refer to the S_3 solution as the *elastic mode*. Since S_1 and S_2 depend on the permeation constant ζ_p through the parameter κ, their respective solutions are called *permeation modes*. For $d \gg [\mathrm{Re}(S_1 q)]^{-1}$, $[\mathrm{Re}(S_2 q)]^{-1} \sim \delta$, the film thickness is large compared to the boundary layer δ (identified as the exponential decay length), and the permeation modes relax in the bulk.

The surface displacements ζ^+, ζ^- satisfy the boundary condition for the normal component of the velocity in linear theory

$$\frac{\partial \zeta^{+(-)}}{\partial t} = v_z|_{z=0(-d)}. \tag{9}$$

The other boundary conditions can be understood from the covariant elasticity theory of smectic-A systems developed by Kléman and Parodi [15]. For free surfaces the force vanishes and the normal component of the permeation force [16] should also vanish. The condition that $\sigma_{xz}=0$ on the free surfaces reveals $A_k^{+(-)} \ll A_3^{+(-)}$ for $k=1,2$, which indicates that the permeation modes have negligible contributions to the dynamics of the system. The condition that $\sigma_{zz}=0$ yields the following relation between the surface displacements and the infinitesimal external forces P_{ext}^+, P_{ext}^- which are assumed to act on the free surfaces:

$$P_{ext}^{+(-)} = \left[p - \sigma'_{zz} + B\frac{\partial u}{\partial z} + \alpha \frac{\partial^2 \zeta^{+(-)}}{\partial x^2} \right]_{z=0(-d)}, \tag{10}$$

where α is the air-film surface tension. The normal component of the permeation force, in the system under consideration, is

$$B\frac{\partial u}{\partial z} = 0 \tag{11}$$

at $z=0,-d$ for all x. Finally, the linear response function X, which connects the surface displacements with the external forces, is defined through

$$\boldsymbol{\zeta}(q,\omega) = -\mathbf{X}(q,\omega)\mathbf{P}_{ext}(q,\omega)A, \tag{12}$$

where A is the surface area $\boldsymbol{\zeta}$, $\mathbf{P}_{ext}$ are vectors for surface displacement and external force, respectively, e.g., $\boldsymbol{\zeta} = (\zeta^+, \zeta^-)$, and $\mathbf{X}$ is a 2×2 matrix for the response function.

Putting Eqs. (10)–(12) together, diagonalization of the response matrix leads to two linear combinations: the *undulation mode* with amplitude

$$\zeta^U = \frac{1}{2}(\zeta^+ + \zeta^-) \tag{13}$$

and the *peristaltic mode* with amplitude

$$\zeta^P = \frac{1}{2}(\zeta^+ - \zeta^-). \tag{14}$$

The corresponding response functions (i.e., eigenvalues of the response matrix) are in turn given by

$$X^U = \frac{1}{2\alpha q^2 A} \frac{1}{1 + g f(\Omega,q)\ \tanh\left(\frac{\lambda q^2 d}{2} f(\Omega,q)\right)} \tag{15}$$

and

$$X^P = \frac{1}{2\alpha q^2 A} \frac{1}{1 + g f(\Omega,q)\ \coth\left(\frac{\lambda q^2 d}{2} f(\Omega,q)\right)}, \tag{16}$$

where $g \equiv \sqrt{BK_1}/\alpha$ is a dimensionless coefficient involving elasticity coefficients and surface tension. In typical materials g is of order unity. Nonetheless, the term involving g in Eq. (16) can be much greater than unity. Equations (15) and (16) are the central results of our calculation.

In the limit of infinite thickness $d\to\infty$, the response functions X^U and X^P become equal, which indicates that the correlation between the two free surfaces vanishes for large thickness, i.e., $\langle \zeta^+(q,\omega)\zeta^-(-q,\omega)\rangle \to 0$. For low frequency ($|\Omega| \ll 100$) and infinite thickness, our results reduce to the earlier calculation by Rapini [14] for an infinitely thick smectic-A material with a free surface.

We now introduce a natural frequency of surface motion as $\omega_0^2 = (2\alpha/\rho d)q^2$ and dissipation coefficient $\gamma = \eta_3 q^2/\rho$. In the range of the only available experiment [7] (thin film $d\sim 100$ nm and small wave number $q \sim 10^4$ cm^{-1}), one has $|\lambda q^2 d f(\Omega,q)/2| \ll 1$. The response function is approximately

$$X^U \sim \frac{1}{1+\frac{1}{2}g[f(\Omega,q)]^2 \lambda q^2 d} \sim \frac{1}{(\omega_0^2 - \omega^2) + i\gamma\omega}, \tag{17}$$

which is the same as the response function of a damped, driven simple harmonic oscillator. The peak position in the range of weak damping $[(\eta_3 q^2/\rho)\omega \ll \sqrt{2\alpha/\rho d}q]$ is

$$\omega = q\sqrt{\frac{2\alpha}{\rho d}}. \tag{18}$$

(In general, we may not have a system with weak damping and the peak position should be slightly modified.) This response is the same as for a soap film and it gives the scaling relation that the experimental data satisfy. However, the experiment does not probe the full nature of a structured film. Nonetheless, for the experiment referred to, the width of the undulation mode peak $(\eta_3 q^2/\rho)$ does provide information about the viscosity η_3.

The peristaltic mode changes the layer spacing much more significantly than the undulation mode; hence we expect that the peak in the peristaltic power spectrum (ImX^P) occurs when the term proportional to g in Eq. (16) dominates. Also in the range of interest, the relation $|\Omega|/\mu \gg 1$ is valid. A straightforward calculation leads to an estimate of the peak position of the peristaltic response

$$\lambda q^2 d f_I(\Omega,q) \approx \pi, \tag{19}$$

where $f_I(\Omega,q)$ is the imaginary part of the function f we defined via Eq. (7). In this approximation the surface tension plays no role and the peak position is essentially independent of g and has the form

$$\Omega \approx -i\frac{2\mu\pi^2}{\lambda q^2 d\sqrt{\lambda^2 q^4 d^2 + 4\mu\pi^2}}. \tag{20}$$

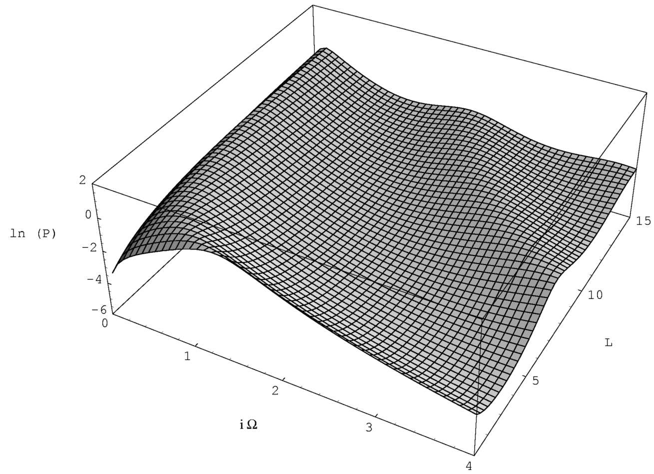

FIG. 2. Dimensionless power spectrum (natural logarithm) for a typical choice of parameters with increasing thickness of the film: $\lambda q = 10^{-3}$, $\mu = 10^{-4}$, $g = 0.1$, and $\eta' = \eta_3$. $L = qd$ is dimensionless. As the thickness increases, we can easily see that the peristaltic mode and the extra structure of the undulation mode provide additional contributions to the power spectrum.

For typical material parameters the above approximation yields the peristaltic peak within 5% when compared to our full calculation. From this relation we can estimate the bulk elastic coefficients K_1 and B by fitting the value μ and λ to measurements over a range of thickness and wave number.

One may ask whether it is possible to observe the peristaltic mode and the special features of a smectic-*A* liquid crystal in a free-standing film experiment. Figure 2 shows the total (dimensionless) power spectrum of the displacement of one free surface, i.e., $P = \mathrm{Im} 2\alpha q^2 A(X^U + X^P)$, for a typical choice of parameters with increasing film thickness. As the film gets thicker we observe that a peak develops in the higher-frequency range. This peak is due to the peristaltic mode. When $L = qd \geqslant 12$ and $|\Omega| \geqslant 3$, there is some extra structure arising from sources other than the peristaltic mode. Figure 3 shows the dimensionless power spectrum for the same choice of parameters with $qd = 15$. The contributions from both undulation and peristaltic modes are plotted in long and short dashed lines, respectively. We find that the power spectrum of the peristaltic mode is about one order of magnitude smaller than the contribution of the undulation mode. Notice that there is a second peak of the undulation mode in the high-frequency region. It comes from the oscillating behavior of the hyperbolic tangent function when the argument $\lambda q^2 d f(\Omega, q)/2$ is complex. This extra structure in the power spectrum at high $|\Omega|$ is a result of the interplay of bulk elasticity and the existence of the two free surfaces; it is

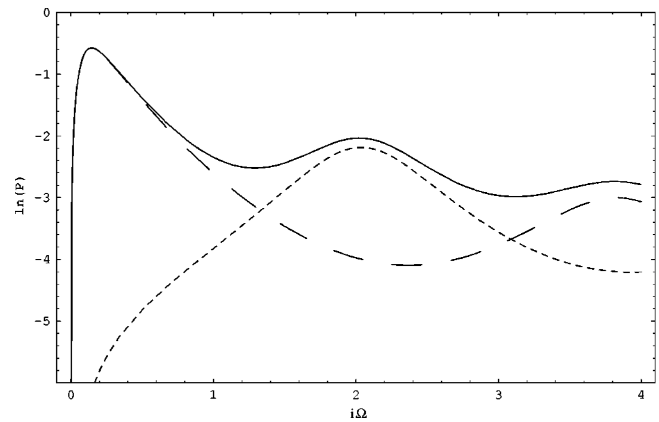

FIG. 3. Dimensionless power spectrum (natural logarithm) for a typical choice of parameters: $\lambda q = 10^{-3}$, $qd = 15.0$, $\mu = 10^{-4}$, $g = 0.1$, and $\eta' = \eta_3$. The long dashed line is the undulation mode contribution, the short dashed line the peristaltic mode, and the solid line the total power spectrum. Notice that there is a small peak in the undulation mode contribution at $|\Omega| \simeq 4$.

a special feature of a structured fluid. Hence we conclude that for reasonable choices of material parameters and for an experiment with typical dynamic range, it should be possible to observe the peristaltic mode. Combinations of material parameters can be extrapolated from the shape of the undulation peak and the peristaltic peak. However, the detailed shape of the power spectrum is sensitive to the specific material parameters used in a laboratory experiment.

In conclusion, we have derived the power spectrum of a freely standing smectic-*A* film within linear hydrodynamics and assuming the absence of topological defects. The dynamics of this system are dominated by the elastic mode and the permeation constant does not show up in the power spectrum of the surfaces. The permeation process is important near the surfaces and helps the system to satisfy proper boundary conditions. When the thickness of the film is small enough, bulk elasticity does not contribute to the undulation mode and the peristaltic mode is not observable. However, for a reasonably thick film the power spectrum does show the interplay of surface tension and bulk elasticity. The extra structure in the power spectrum is a special feature due to the existence of two free surfaces and the contribution from the bulk elasticity. We suggest that further experimental work on FSSFs over a wider range of film thickness and wave number can reveal these interesting features.

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[1] X.-l. Wu, B. Martin, H. Kellay, and W.I. Goldburg, Phys. Rev. Lett. **75**, 236 (1995).
[2] D. Dash and X.L. Wu, Phys. Rev. Lett. **79**, 1483 (1997).
[3] E.A.L. Mol, J.D. Shindler, A.N. Shalaginov, and W.H. de Jeu, Phys. Rev. E **54**, 536 (1995); A. Poniewierski and R. Hołyst, Phys. Rev. B **47**, 9840 (1993), and references therein.
[4] E.A.L. Mol, G.C.L. Wong, J.M. Petit, F. Rieutord, and W.H. de Jeu, Phys. Rev. Lett. **79**, 3439 (1997). In this work static in-plane correlations of a smectic-*A* film were examined over a range of wave numbers. At sufficiently short wavelength, approaching molecular dimensions, deviations from ''undulatory'' behavior were observed.

[5] D. Langevin, in *Light Scattering by Liquid Surfaces and Complementary Techniques*, edited by D. Langevin (Dekker, New York, 1992); J. G. H. Joosten, in *Thin Liquid Films*, edited by I. B. Ivanov (Dekker, New York, 1988).

[6] See, for example, F. Brochard, and J.F. Lennon, J. Phys. (Paris) **36**, 1035 (1975), where the thermal fluctuations of the thickness of red blood cells were studied. The free energy associated with deformations involved only the squared curvature of the bounding membranes $\sim(\nabla_{\perp}^2 u)^2$, with u the membrane displacement. Further, the interior of the cell was treated as a simple fluid.

[7] A. Böttger and J.G.H. Joosten, Europhys. Lett. **4**, 1297 (1987).

[8] J.B. Fournier, J. Phys. II **6**, 985 (1996).

[9] P.C. Martin, O. Parodi, and P.S. Pershan, Phys. Rev. A **6**, 2401 (1972).

[10] P.G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[11] Orsay Group on Liquid Crystals, J. Phys. (Paris) Colloq. **36**, C1-305 (1975).

[12] The viscosity coefficient η_3 is defined in Ref. [9]. In their notation, $\eta' = \eta_1 + \eta_2 - 4\eta_3 - 2\eta_5 + \eta_4$.

[13] See, for example, *Light Scattering by Liquid Surfaces and Complementary Techniques* (Ref. [5]), Chap. 2, for an introduction to surface light scattering experiments.

[14] A. Rapini, Can. J. Phys. **53**, 968 (1975).

[15] M. Kléman, *Points, Lines, and Walls* (Wiley, New York, 1983); M. Kléman and O. Parodi, J. Phys. (Paris) **36**, 617 (1975).

[16] In Kléman's notation, the permeation force on the surface is the vector **S** (defined in Ref. [15]), which happens to be $B(\partial u/\partial z)$ when the normal to the surface is in the z direction. The torque acting on the surface is always zero in the system under consideration.