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Flow-induced molecular orientation of amphiphile monolayers: Incorporation of hexatic elasticity into Ericksen-Leslie theory

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By introducing the local lattice elasticity into the pure Ericksen-Leslie (EL) theory which only considers the deformation of the director, we developed a more general theory for understanding the behaviors of hexatic liquid crystal under flow. In the cases of amphiphilic monolayers in tilted phases (L_2 and L_2'), the exact solutions of the new EL equation in two types of flow, pure extension and simple shear, explain well most of the features of flow-induced tilt azimuth orientation observed by Fuller's group [Science, **274**, 233 (1996)] and Schwartz's group [Nature (London) **410**, 348 (2001)]. In particular, the "shear band" domain generated by flow discovered by the former is proved theoretically as the result of two-dimensional Wulf construction in L_2 and L_2' phases.

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I. INTRODUCTION

Monolayers have been extensively investigated for more than one century since Langmuir's pioneering works [1]. In the last several years, there has been remarkable progress in understanding the phase transition of monolayers by application of the synchrotron x-ray diffraction method into the observation of molecular packing structure [2,3]. Through traditional surface pressure-area isotherm measurements, abundant phenomena of polymorphism and phase transitions in monolayers of amphiphilic molecules have been revealed by x-ray diffraction technology that have also attracted the attention of many theoretical investigators. In a review article by Kaganer *et al.* [4], the evolution in the experimental and theoretical understanding of structures and phase transitions was summerized. Among the recognized phases, liquid condensed phases L_2 and L_2' are extraordinarily interesting because they happen at the meeting point of two- and three-dimensional (2D and 3D) systems as well as solid (S) and liquid crystal (LC) phases: The polar head groups of the amphiphiles were found to form in average a distorted hexagonal lattice at air/water interface by x-ray diffraction [2,3], and it was as predicted by theory [5] and shown schematically in Fig. 1. The long tails of the molecules are tilted toward a nearest neighbor (NN) for the L_2 phase [i.e., the case of $\phi=0$, schematically shown in Fig. 1(a)], while to the next-nearest neighbor (NNN) for L_2' phase. There are two possible cases for L_2' phases, $\phi=\pi/6$ [as shown in Fig. 1(b)] is one case and the other is $\phi=\pi/2$, however, only the latter has been observed in experiments [3]. Once tilt happens, the symmetry of the hexagonal lattice will be broken and only rectangle symmetry will be held. That means the rectangle symmetry of two states of $\phi=\pi/2$ for NNN phase and $\phi=0$ for NN phase remain even when the monolayers enters the solid phase ($\theta=0$) as well confirmed in the x-ray diffraction experiment [3]. Very recently, the tilting phase transition was studied as a distortion of the orthogonal hexagonal orientation of molecules by a competition among the entropy of both head position and molecular axes orientation distributions, Lenard-Jones potential between two NN molecules, and the work done by surface and bulk pressures [6,7]. The theory predicts a physically reasoning phase portion in a phase diagram between tilting and untilting phases and shows quantitative agreement with the measurement in monolayers of $C_{14}-C_{24}$ acids [8].

The study of monolayers of amphiphilic molecules in L_2 and L_2' phases has been extended from the equilibrium state to the steady state with flow, and the experimental evidence of the existence of a strong coupling between flow and molecular tilt azimuth orientation has been reported [9–13]. Using Brewster angle microscopy (BAM), Fuller's group [9–11] visualized the deformation and orientations of the polydomain structures in two types of flow, pure extension and simple shear (see Fig. 2), generated by a four-roll mill [Fig. 2(a)] and a two-belt channel [Fig. 2(b)]. They speculated that L_2' and S phases experience flow-induced reorientation more obviously than the L_2 phase and the reorientation process was accompanied by the sudden appearance of new domains, called "shear bands," at ±45° to the extension axis of both types. [e.g., see Fig. 5(H) in Ref. [10]]. It was also revealed that the simple shear can fragment the domain structure in L_2' (including the O_v [4]) phase. With the same BAM observation in simple shear flow, Schwartz's group found a different phenomenon [12,13]: The observed domain was gradually skewed with a little distortion shape, and accompanied by a continuous rotation of the molecular orientation that is faster than the domain rotation, regarded as molecular precession (Fig. 2 in Ref. [13]). They also revealed a remarkable discontinuous orientation jump (Fig. 4 in Ref. [13]). The Brewster measurements which show the relation of molecular tilt relative to the flow direction, yet one speculates about the liquid crystalline lattice. Of course, this needs still to be determined independently with x-ray diffraction.

On the theoretical side, a major challenge is to understand the mechanism of the mentioned mysterious effects of flow in monolayer and it has attracted many attempts. Very recently, the shear bands in L_2' phase were modeled by Fuller's

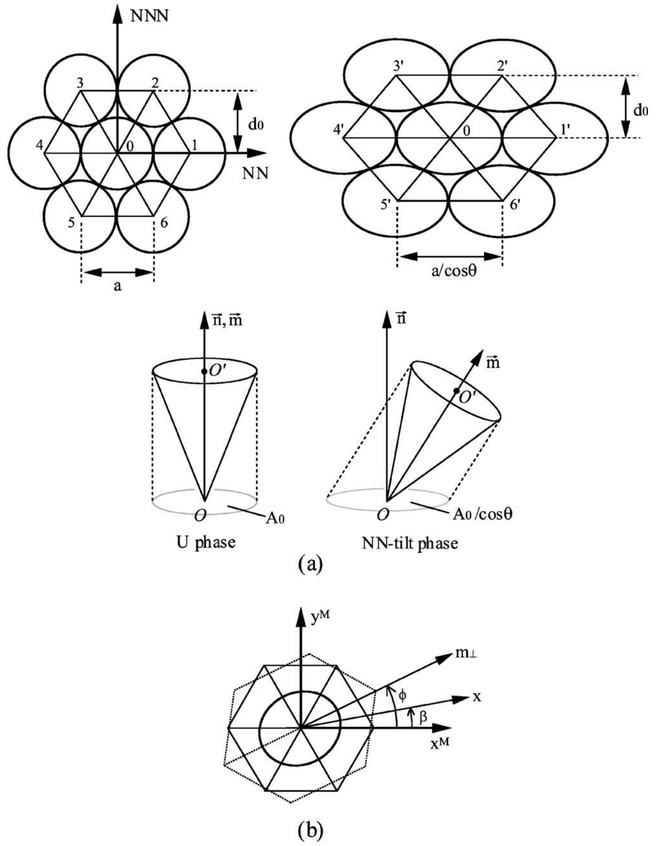


FIG. 1. (a) Model structure for untilt orthorhombic hexagonal phase and its distortion toward a nearest neighbor (NN) regarded as L_2 phase. The structure of L_2' phase is tilted to the next-nearest neighbor (NNN) and has been omitted in the figure. (b) The geometry for a arbitrary tilting domain where $(\vec{x},\vec{y})$ is the laboratory frame, $(\vec{x}^M,\vec{y}^M)$ is one set of (NN, NNN)-tilting directions also the molecular system, and $\vec{m}_\perp$ denotes its tilt azimuthal direction of the monolayer.

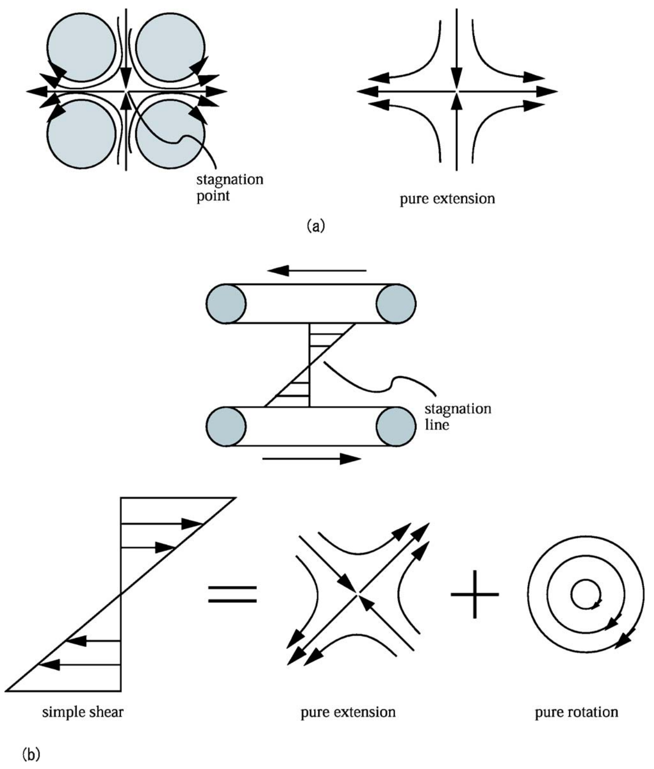


FIG. 2. (Color online) Two types of flow induced by a four-roll mill used by Fuller's group: (a) pure extension and (b) simple shear (after Fig. 1 in Ref. [7])

group by considering the shear-induced elastic distortion of the hexatic lattice as the deformation twinning of crystals in flow [11]. Employing the similar idea, the orientation jump was explained by Schwartz's group as a tight coupling of molecular orientation to the local molecular hexatic lattice (Fig. 5 in [13]) and a flow-induced orientation mechanism different from LC tumbling [14] was argued. However, all these treatments remain in a qualitative framework. Various classical theoretical approaches were employed to clarify the nonequilibrium state pattern formation in monolayers as well. Among them are the theories based on Ginzburg-Landau free energy describing the problem of coupled herring-bone and hexatic degrees of freedom presented by Bruinsma and Aeppli [15,16] and the Landau theory for the pattern formation proposed by Selinger *et al.* [17], etc. These phenomenological theoretical approaches all invoked a free energy expressed as the function of order parameter Ψ. However, it is still not apparent in the relation between the macroscopic physical quantities (such as shear, elasticity, etc.) and the microscopic concepts (such as molecule lattice, order parameter, etc.) from these phenomenological theories. In the present paper, we aim at developing a continuum theory for the quantitative understanding of the behaviors of hexatic liquid crystal under flow. That is, by considering that amphiphilic molecules in monolayers possess both the lattice-structure property related to the positional ordering of polar heads on the water surface and the liquid crystalline property related to the orientational ordering of chains of long tails of amphiphiles pointing towards air, we try to understand the behaviors of monolayers under flow. Especially, we try to reveal the relation between the previous theories applied in LC and monolayers and the experimental observations by Fuller's group [9–11] and Schwartz's group [12,13]. Our approach not only follows both groups' ideas to emphasize the shear-induced elastic deformation of lattice, but also assume that the flow affect the orientations of the long chains of amphiphiles, i.e., a liquid crystal model. In detail, instead of using a distorted "lattice" picture presented by both groups, we use an exact geometrical expression of tilt elastic energy for the hexatic LC phases derived in our previous study (see below for details) [18], and as a key issue, the treatment of flow-induced LC orientation by the Ericksen-Leslie (EL) theory [14] is invoked in the present work by viewing the tilt C_6 axis of the hexatic lattice (the average orientation of the long chains of amphiphiles) appearing in L_2 and L_2' phases as LC director $\vec{m}$ and incorporating the abovementioned tilt elastic energy into the Frank elastic energy of LC. In other words, we introduced the elastic energy of the local lattice deformation into the LC model. Consequently, the EL theory is generalized for both nematic and hexatic LCs. Based on the theory, the tilt equation of director $\vec{m}$ of amphiphilic monolayers in L_2, L_2' and S phases is derived exactly. By solving the equation analytically in the aforementioned two types of flow, most of the features of flow-induced tilt orientation observed by Fuller's group and Schwartz's group are well explained. In particular, as an evidence for the present theory, the precise expression of line tension for a hexatic LC domain induced by both elastic and viscous effects is obtained, by which the mentioned mysterious "shear band" domain is predicted as the exact result of the 2D Wulf construction.

The arrangement of this paper is as follows. In Sec. II, we build a generalized EL theory in which both the deformation of director and the elasticity of the local lattice are concerned. Particularly, in the cases of monolayers in the L_2 and L_2' phases, the free energy and its associated tilt equation are derived exactly. In Sec. III, the solutions of the tilt equation in two types of flow, pure extension and simple shear, are extensively discussed in comparison with the experimental observations of Fuller's group [9–11] and Schwartz's group [12,13]. Section IV gives the discussion and conclusion.

II. THE GENERALIZED EL THEORY

To describe the flow-induced orientation of chains of amphiphiles, we now introduce a 2D flow field $\vec{v}(x,y)$ in the discussed monolayer and the molecular chain orientation is defined as $\vec{m}(x,y)$. By treating, $\vec{m}$ as LC director, its dynamic equation by EL theory is expressed as [14]

$$I\frac{d^2}{dt^2}\vec{m}=\vec{G}+\vec{g}+\vec{\nabla}\cdot\overleftrightarrow{\pi}, \tag{1}$$

where I is the inertia moment of director per volume (usually neglected [14]), $\vec{G}$ is the external force (vanishing in our discussed case), $\vec{g}$ and $\overleftrightarrow{\pi}$ are the intrinsic body force and surface stress, respectively, relating to the Ossen-Zöcher-Frank free energy [19]. They can be written as

$$\vec{g}=\eta\vec{m}-\vec{\zeta}\cdot\vec{\nabla}\vec{m}-\partial F/\partial\vec{m}+\lambda_1\vec{M}+\lambda_2\vec{m}\cdot\overleftrightarrow{d}, \tag{2}$$

$$\overleftrightarrow{\pi}=\vec{\zeta}\vec{m}+\partial F/\partial(\vec{\nabla}\vec{m}), \tag{3}$$

where the Lagrange multipliers η and $\vec{\zeta}$ are the arbitrary constant scale and vector, respectively, and can be determined by the relations $\vec{m}\cdot\vec{m}=1$ and given boundary condition $\lambda_1=\mu_2-\mu_3,\lambda_2=\mu_5-\mu_6$ ($\mu_{1\text{-}6}$ are the Leslie coefficients of viscosity in LC), $\overleftrightarrow{d}$ is the symmetry part of $\vec{\nabla}\vec{v}$ ($\vec{v}$ is the velocity of flow), i.e., $d_{ij}=\frac{1}{2}(v_{i,j}+v_{j,i})$ with $v_{i,j}=\partial_j v_i$, the vector $\vec{M}$ is defined as

$$\vec{M}=\frac{d}{dt}\vec{m}-\overleftrightarrow{w}\cdot\vec{m}, \tag{4}$$

with $w_{ij}=\frac{1}{2}(v_{i,j}-v_{j,i})$ (the antisymmetry part of $\vec{\nabla}v$), and F is the free energy density.

In original EL theory in nematic LC, F takes the Ossen-Zöcher-Frank expression form, denote F_{LC} [20], and serves to describe the elastic energy for deformed director pattern but takes no account of the elasticity of the hexatic lattice deformation. As mentioned in Sec. I, the key step of this paper is to generalize EL theory to involve the effect of this lattice deformation. we consider the free energy as the sum of the energies of both chain orientation and lattice deformation, i.e., $F=F_{\mathrm{LC}}+F_e$ where F_e is the elastic energy density of the local lattice deformation and the LC free energy density F_{LC} describing the chain orientation deformation is given by

$$F_{\mathrm{LC}}=\frac{1}{2}k_{11}(\vec{\nabla}\cdot\vec{m})^2+\frac{1}{2}k_{22}(\vec{m}\cdot\vec{\nabla}\times\vec{m})^2+\frac{1}{2}k_{33}(\vec{m}\cdot\vec{\nabla}\vec{m})^2 - \vec{E}_{\Pi}\cdot(e_1\vec{m}\vec{\nabla}\cdot\vec{m}+e_3\vec{m}\cdot\vec{\nabla}\vec{m}), \tag{5}$$

where k_{ii} are the LC elastic constants [20], e_1 and e_3 are flexoelectric coefficients [21], $\vec{E}_{\Pi}=\overleftrightarrow{\chi}^{-1}:\vec{p}_{\Pi}$ is the local electric field induced by the piezoelectric polarization $\vec{p}_{\Pi}$ in monolayers, and $\overleftrightarrow{\chi}$ is the dielectric tensor of the LC. On the other hand, the elastic energy density of the local lattice deformation $F_e(\vec{m})$ is generally written as

$$F_e=\frac{1}{2}c_{ijkl}s_{ij}s_{kl}, \tag{6}$$

where c_{ijkl} and s_{ij} are the elastic tensor and the strain tensor, respectively (see detained definitions in Refs. [18,22]), and can be rewritten in compact form $F_e=(1/2)c_{\mu\nu}s_{\mu}s_{\nu}$ ($\mu,\nu=1,2,\ldots,6$) with abbreviation conventions $(i,j)\rightarrow\mu$ as $11\rightarrow1$, $22\rightarrow2$, $33\rightarrow3$, $23\rightarrow4$, $31\rightarrow5$, and $12\rightarrow6$ for $c_{ijkl}\rightarrow c_{\mu\nu}, s_{ij}\rightarrow s_{\mu}$ if $i=j$, and $2s_{ij}\rightarrow s_{\mu}$ if $i\neq j$. Hence, the total free energy density F is

$$F=F_{\mathrm{LC}}+F_e=\frac{1}{2}k_{11}(\vec{\nabla}\cdot\vec{m})^2+\frac{1}{2}k_{22}(\vec{m}\cdot\vec{\nabla}\times\vec{m})^2 +\frac{1}{2}k_{33}(\vec{m}\cdot\vec{\nabla}\vec{m})^2-\vec{E}_{\Pi}\cdot(e_1\vec{m}\vec{\nabla}\cdot\vec{m}+e_3\vec{m}\cdot\vec{\nabla}\vec{m}) +\frac{1}{2}c_{\mu\nu}s_{\mu}s_{\nu}. \tag{7}$$

In order to theoretically understand the observations of Fuller's group and Schwartz's group, we will discuss monolayers of amphiphilic molecules in hexatic phases in detail. As mentioned above, the tilt C_6 axis of the hexatic lattice is viewed as LC director $\vec{m}$. F_{LC} is thereby considered to be zero because of the uniform director pattern in monolayers observed in the both groups, i.e., $\vec{\nabla}\cdot\vec{m}=0,\vec{\nabla}\times\vec{m}=\vec{0}$, and $\vec{\nabla}\vec{m}=0$. That means $F=F_e$ and only the hexagonal lattice deformation energy will be calculated in what follows. Considering the symmetry of the hexatic phase, untilt monolayer [Fig. 1(a), left side] or tiltmonolayer [Fig. 1(a), right side], it can be concluded that the nonvanishing components of c_{ijkl} of the elastic constant matrix are (see the elastic constant matrix of hexagonal crystal, Table 9 in Ref. [22])

$$c_{11}=c_{22},\quad c_{44}=c_{55},\quad c_{13}=c_{23}, \tag{8}$$

$$c_{33},\quad c_{66},\ \text{and}\ c_{12}. \tag{9}$$

Thus, for the hexatic phases in monolayer, we have [18]

$$F_e = c_{11}(s_1^2 + s_2^2)/2 + c_{12}s_1s_2 + c_{13}(s_1s_3 + s_2s_3) + c_{44}(s_4^2 + s_5^2)/2 + c_{66}s_6^2/2 + c_{33}s_3^2/2. \tag{10}$$

Following the comment by Sirota [23] that in the condensed phases, a tilting completely determines the monolayer distortion. (i) A stretching of the projected lattice cell along the tilting direction is induced with a ratio of $1/\cos\theta$ [2,3]. (ii) A compression along surface normal happens with a ratio of $\cos\theta$. (iii) The deformed hexagonal lattice is also completely determined by θ and ϕ (see Fig. 1). In other words, the tilting-caused strain, then, the elastic energy as well as the stress are obtained by tilting geometry. Accordingly, the effect of lattice deformation due to tilting of director $\vec{m}$ is described by the elastic energy F_e, but not by the F_{LC} induced by the deformed director pattern. The strain components $s_{ij}(i,j=1,\ 2,\ \text{and}\ 3)$, can be derived as [18] $s_{11}=\frac{1}{2}\tan^2\theta\cos^2\phi, s_{12}=(\sqrt{3}/2)\tan^2\theta\sin\phi\cos\phi, s_{22}=\frac{1}{2}\tan^2\theta\sin^2\phi, s_{13}=\frac{1}{2}\tan^2\theta\cos\phi, s_{23}=\frac{1}{2}\tan\theta\sin\phi$, and $s_{33}=0$. Submitting these strain components and Eqs. (8) and (9) to Eq. (10), we have exactly

$$F_e = \frac{1}{8}(K+\mu)\tan^2\theta + 4c_{44}\tan^2\theta + \frac{1}{4}\left(\frac{-\mu+2c_{66}}{4}\right)\sin^2 2\phi\tan^4\theta, \tag{11}$$

where $K=(c_{11}+c_{12})/2$ and $\mu=(c_{11}-c_{12})/2$ are the plane (hydrostatic) compression modulus and shear modulus, respectively [24], θ is the tilt angle to the surface normal $\vec{n}$, and ϕ is the azimuth from the *NN* direction defined at a molecular system (x^M, y^M, z^M) with $\overrightarrow{x^M}\parallel NN$ direction when the tilt has not happened (Fig. 1). It should be noted that the coefficient $-\mu+2c_{66}$ appearing in the second term of Eq. (11) becomes zero for the hexatic lattice with a tilt angle $\theta=0$, whereas nonzero for the deformed hexatic lattice with a tilt angle $\theta\neq 0$ [see Fig. 1(a) and Table 9 in Ref. [22]].

In fact, in addition to Eq. (11), we could derive the stress tensor σ_{ij} in the laboratory system (x,y,z) by differentiating F_e with s_{ij} using the relation of tensor transformation of $\sigma_{ij}=R_{ik}R_{jl}\sigma_{kl}^M$, where $R_{11}=\cos\beta, R_{12}=-R_{21}=\sin\beta, R_{22}=\cos\beta, R_{33}=1$, others are zero, β is the angle between $\mathbf{x}$ and $\mathbf{x}^M$, and the stress tensor σ_{ij}^M is defined in the molecular system (x^M, y^M, z^M) [18]. The in-(x,y) plane elements of σ_{ij} are found to be the functions of θ, ϕ, and β as

$$\sigma_{11,22} = \frac{1}{2}[K \pm \mu(\cos 2\phi\cos 2\beta + 2\sin 2\phi\cos 2\beta)]\tan^2\theta, \tag{12}$$

$$\sigma_{12} = \sigma_{21} = \frac{1}{2}\mu[2\sin 2\phi\cos 2\beta - \cos 2\phi\sin 2\beta]\tan^2\theta. \tag{13}$$

Obviously, the expression shows σ_{ij} relating the molecular tilt described by θ and ϕ. Here, $\phi-\beta=\gamma$ is the tilt-azimuthal angle of $\vec{m}$ in laboratory frame (see Fig. 1) and, generally speaking, ϕ and β must be the functions of (x,y). However, according to the experimental finding, the 2D domains such as the "shear bands" in [10,11] and the "fished-shaped domain" in Ref. [13] are uniform of orientation, we consider the case of ϕ and β being spatially uniform. In other words, the elastic force associated with Frank free energy, $\vec{\nabla}\cdot\vec{\pi}$, is then not concerned for the moment as mentioned above. On the other hand, the force induced by $F_e, \partial F_e/\partial\vec{m}$, represents only one of elastic effect. To derive an apparent formula for $\partial F_e/\partial\vec{m}$, the following geometric relations: $\sin^2 2\phi = 4\sin^{-4}\theta m_1^{M2} m_2^{M2}, m_1^M = m_1\cos\beta - m_2\sin\beta$, and $m_2^M = m_1\sin\beta + m_2\cos\beta$ are invoked, where $(m_1^m, m_2^m) = (\cos\phi\sin\theta, \sin\phi\cos\theta)^M$ and $(m_1, m_2) = (\cos\gamma\sin\theta, \sin\gamma\sin\theta)$ are the in-plane components of $\vec{m}$ at molecular and laboratory systems, respectively [Fig. 1(b)]. Using these relations and $\partial F/\partial m_i = (\partial F/\partial m_j^M)(\partial m_j^M/\partial m_i)$ we have from Eq. (11) the in-plane elastic force of director per unit area

$$\frac{\partial F}{\partial m_1} = \left(\frac{-\mu+2c_{66}}{4}\right)\cos^{-1}\theta\tan^3\theta\sin 2\phi\sin(\phi+\beta), \tag{14}$$

$$\frac{\partial F}{\partial m_2} = \left(\frac{-\mu+2c_{66}}{4}\right)\cos^{-1}\theta\tan^3\theta\sin 2\phi\cos(\phi+\beta). \tag{15}$$

If the flow field $\vec{v}$ is given, substituting Eqs. (14) and (15) into Eqs. (1)–(3), then it yields the equations to determine ϕ, β (i.e., $\gamma=\phi-\beta$). Thus, the behaviors of monolayers of amphiphilic molecules in hexagonal phase under flow can be calculated theoretically.

III. PURE EXTENSION FLOW AND SIMPLE SHEAR FLOW

First, we consider the case of pure extension [Fig. 2(a)]. The point initially at (x_0, y_0) moves according to $(x,y) = (x_0\exp(\dot{\epsilon}t), y_0\exp(-\dot{\epsilon}t))$ as assumed in Ref. [10], where extension rate $\dot{\epsilon}$ is constant. Thus, the pure extension is steady fluid field $\vec{v}(x,y) = (dx/dt, dy/dt) = (\dot{\epsilon}x, -\dot{\epsilon}y)$, and the nonvanishing components of d_{ij} and w_{ij} are only $d_{11}=-d_{22}=\dot{\epsilon}$. This simplifies Eq. (4) as

$$\vec{M} = \frac{d}{dt}\vec{m} = (-\sin\gamma\sin\theta, \cos\gamma\sin\theta, 0)\frac{d\gamma}{dt}. \tag{16}$$

Substituting Eqs. (14)–(16) into Eq. (1) with $d_{11}=-d_{22}=\dot{\epsilon}$ (i.e., $\vec{g}=\vec{0}$ and $\vec{\nabla}\vec{m}=\vec{0}$ in the present case) and diminishing the Lagrange multiplier η, we have the tilt equation

$$\left(\frac{-\mu+2c_{66}}{4}\right)\tan^2\theta\cos^{-2}\theta\sin 2\phi\cos 2\phi = \lambda_1\dot{\gamma}(t) - \lambda_2\dot{\epsilon}\sin 2\gamma, \tag{17}$$

where $\dot{\gamma}(t)=d\gamma/dt$ and γ is the tilt angle to the x axis. Eq. (17) describes correct equilibrium condition of orientation. When $\dot{\gamma}=\dot{\epsilon}=0$, the equilibrium achieves at $\sin 2\phi=0$ in a manner as predicted from the minimum of $F_e(\phi)$ of Eq. (11), we have thereby $\phi=0$ for NN tilt and $\phi=\pi/2$ for NNN tilt

[4]. This is quite true in physics. Once tilt happens, the distorted hexatic lattice has only rectangle symmetry and it remains even the monolayer enters the *S* phase ($\theta=0$). The *x*-ray experiment by Dutta and co-workers [2,3] confirmed that the head groups remain arranged on the distorted hexagonal lattice at *S* phase. Given these, to discuss the extension flow-induced orientation, we can thereby accept the assumption of ϕ locking at *NN* or *NNN* direction [13], i.e., flow-induced orientation is described by $\lambda_1\dot{\gamma}(t)-\lambda_2\dot{\epsilon}\sin 2\gamma=0$, and its solution can be determined as

$$\gamma(t)=\arctan[\exp(2\dot{\epsilon}t\lambda_2/\lambda_1)\tan\gamma_0], \tag{18}$$

with $\gamma_0=\gamma(0)$. Equation (18) exactly predicts $\gamma(\infty)=0$ for $\dot{\epsilon}>0$ and $\pi/2>\gamma_0>-\pi/2, \pi$ for $\dot{\epsilon}>0$ and $3\pi/2>\gamma_0>\pi/2, \pi/2$ for $\dot{\epsilon}<0$ and $\pi>\gamma_0>0$, and $-\pi/2$ for $\dot{\epsilon}<0$ and $\pi<\gamma_0<2\pi$ because $\lambda_2/\lambda_1<0$ is generally held in LC [14,20]. Comparing with the solution of pure extension (x,y) and its corresponding flow picture shown in Fig. 2(a) we can further conclude that the pure-extension flow always reorients the tilt to along extension direction regardless of its initial γ_0. That is what reported by Fuller's group in Ref. [11].

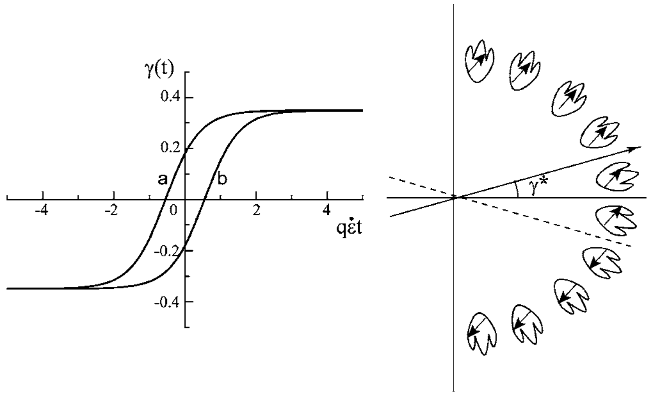
On the other hand, the simple shear flow along the *x* axis is described as $(x,y)=(x_0+\dot{\epsilon}ty_0,y_0)$ and the corresponding velocity is shown as $\vec{v}=(\dot{\epsilon}y_0,0)=(\dot{\epsilon}y,0)$. Therefore, the nonvanishing elements of d_{ij} and w_{ij} are only $d_{12}=d_{21}=\dot{\epsilon}/2$ and $w_{12}=-w_{21}=\dot{\epsilon}/2$. Using these and with the same derivation process as the derivation of Eq. (17), we have the tilt equation for the simple shear flow. Under the same assumption of ϕ-locking at NN or NNN direction the simple shear-induced orientation equation is expressed as

$$\lambda_1\left[\dot{\gamma}(t)+\frac{1}{2}\dot{\epsilon}\right]+\frac{1}{2}\lambda_2\dot{\epsilon}\cos 2\gamma=0. \tag{19}$$

From this equation one can find its asymptotic solution. (i) If $\dot{\epsilon}>0, \gamma(\infty)=\gamma^*$ for $-\gamma^*\leqslant\gamma(0)\leqslant\pi-\gamma^*$ and $\gamma(\infty)=\pi+\gamma^*$ for $\pi-\gamma^*\leqslant\gamma(0)\leqslant 2\pi-\gamma^*$. (ii) If $\dot{\epsilon}<0, \gamma(\infty)=-\gamma^*$ for $-\pi+\gamma^*<\gamma(0)<\gamma^*$ and $\gamma(\infty)=\pi-\gamma^*$ for $\gamma^*<\gamma(0)<\pi+\gamma^*$. Here, $\gamma^*=\arctan(\sqrt{\mu_3/\mu_2})$ and $0<\gamma^*<\pi/4$ because $\mu_2<\mu_3<0$ is generally held [14], and the Parodi's relation of $\mu_2+\mu_3=\mu_6-\mu_5$ is invoked as in LC theory [20]. This result seems remnant of the Poiseulle flow-induced LC alignment because the same asymptotic angle γ^* is revealed in LC [25]. Although Schwartz's group argued that the orientation mechanism in monolayers is different in LC, the solution of Eq. (19) is quite consistent with their observation [13]. In the case of the solution of $\dot{\epsilon}>0$ the solution of Eq. (19) for a given initial value of $\gamma(0)=\gamma_0$ with $-\gamma^*<\gamma_0<\gamma^*$ can be written as

$$\gamma(t)=\arctan\left[\frac{\tan\gamma_0+\tan\gamma^*\tanh(q\dot{\epsilon}t)}{1+(\tan\gamma_0/\tan\gamma^*)\tanh(q\dot{\epsilon}t)}\right], \tag{20}$$

where $q=\sqrt{\mu_2\mu_3}/(\mu_3-\mu_2)$. Figure 3(a) shows numerical examples of $\gamma^*=20°$ for $\tan\gamma_0/\tan\gamma^*=\pm 0.5$. The revealed steep change of flow-orientation is quite similar to the observation on the steep change in the reflectivity of monolayers by Schwartz's group (Fig. 4 in Ref. [13]). Furthermore, if $q\approx 1$ (which is not so far away from the measured values for LC viscosity coefficients [14,20]), we find from Fig. 3(a) the strain ϵ (i.e., $\dot{\epsilon}t$) to induce the steep change of orientation is about 4 that agrees nicely the value $\epsilon=4\sim 5$ measured by grey level observation (Fig. 3 in Ref. [13]). Such a beautiful quantitative evidence shows the validity of the present theory. Moreover, from above asymptotic solution, one can find a small change of $\gamma(0)$ may induce a large reorientation change of γ with magnitude of π, e.g., if $\dot{\epsilon}>0$ and $\gamma(0)$ changes from initial γ^* to $\gamma^*-\delta$ with $\delta\geqslant\gamma^*$ then γ must change from γ^* to $\pi+\gamma^*$. This is the physical feature of molecular precession found by Schwartz's group (Fig. 2 in Ref. [13]): Due to the shear-induced skew of the domain $\gamma(0)$ can have such change as shown in Fig. 3(b).



(a) (b)

FIG. 3. (a) The steep change of simple-shear-induced orientation calculated from Eq. (20) with $\gamma^*=20°$ and $\tan\gamma_0/\tan\gamma^*=0.5$ [(curve (a)] and -0.5 [(curve (b)]. (b) Schematic illustration of simple-shear-induced molecular precession. The fish-shaped domain clockwise skews as the effect of the pure rotation component [Fig. 1(b)]. The arrow in the domain indicates the asymptotic tilt orientation according to the theory, it rotates clockwise but with a steep jump style of 180° at some location.

In what follows we turn to discuss the domain formation affected by flow. Fuller's group revealed L_2 phase domain deformed nearly reversible [9–11]. This can be understood by the expression of stress tensor given by Eqs. (12) and (13). If surrounding domains are assumed isotropic, then σ_{ij} at the boundary of the L_2 domain can be seen as the anisotropic line tension for the discussed domain. Since σ_{ij} is proportional to $\tan^2\theta$, thus domains of L_2 phase possess more significant line tension than L_2' phase. Therefore, the boundary of L_2 domain is stronger than L_2' phase. That is why the domains in the L_2' phase deformed by flow do not relax back to their original shapes and are easy fragmenting as reported in Refs. [9–11]. Viewing σ_{ij} as line tension can be used to discuss the domain shape in L_2' phase. For pure extension flow, the orientation equation (18) predicts that orientation must be along extension axis, i.e., $\gamma=0$. Substituting it (together with the ϕ locking in $\pi/2$ for NNN orientation) into Eq. (13) yields $\sigma_{12}=\sigma_{21}=0$. Thus we have from Eq. (12) the line tension for the domain boundary with normal $\vec{n}_d=(\cos\Phi,\sin\Phi)$

$$\sigma(\Phi) = \overleftrightarrow{\sigma}:\vec{n}_d\vec{n}_d = \sigma_{11}\cos^2\Phi + \sigma_{22}\sin^2\Phi = a_0 + a_2\cos 2\Phi, \tag{21}$$

where $a_0=(K/2)\tan^2\theta$ and $a_2=(-\mu/2)\tan^2\theta$. To find the optimal domain shape, which is a closed planar curve described by $\Phi(x,y)$, we must minimize the energy $F_w = \oint\sigma(\Phi(x,y))dl+\lambda\int dxdy$ with respect to $\Phi(x,y)$. Here the first line integral is along the curve and λ is the Lagrange multiplier to keep the domain area constant. The variation problem has been solved with a geometric method, the classic Wulff construction [26], and with an analytic method for 2D case [27]. For the latter, the minimum distance $R(\Phi)$ between the tangent line through point (x,y) of the boundary and the origin simply satisfies $R(\Phi)=\sigma(\Phi)/\lambda$. This gives a natural role for an existed domain: $\sigma(\Phi)$ must be positive. In our case of Eq. (21) we must require $K>\mu>0$. However, when the external flow is applied, the stress tensor σ_{ij} have to be revised by adding the hydrodynamic (viscous) stress t'_{ij} as treated in LC EL theory [14]. In details, the viscous stress is expressed by

$$\begin{aligned} t'_{ij} = {} & \mu_1 m_k m_m d_{km} m_i m_j + \mu_2 m_i M_j + \mu_3 m_j M_i + \mu_4 d_{ij} \\ & + \mu_5 m_i m_k d_{ki} + \mu_6 m_j m_k d_{ki}. \end{aligned} \tag{22}$$

With the same geometry of asymptotic orientation for L'_2 phase as derivation of σ_{ij}, we have t'_{ij} at pure extension as $t'_{12}=t'_{21}=0$ and $(t'_{11}+t'_{22})/2=\dot{\epsilon}[\mu_1\sin^4\theta+\frac{1}{2}(\mu_5+\mu_6)\sin^2\theta]$ and $(t'_{11}-t'_{22})/2=\dot{\epsilon}[\mu_4+\frac{1}{2}(\mu_5+\mu_6)\sin^2\theta]$. In known data of μ_{1-6} of LC [14,20], $\mu_4>0$ and is the largest one in magnitude. Moreover, θ is generally smaller than 20° in L'_2 phase [4]. Therefore, the influence of t'_{ij} on σ_{ij} is mainly by the μ_4 term. With this approximation, the coefficient a_2 in Eq. (21) should be revised as $a_2=-(\mu/2)\tan^2\theta+\dot{\epsilon}\mu_4$, and the request of $K>\mu>0$ becomes $K>|-\mu+2\mu_4\dot{\epsilon}\cot^2\theta|$. In other words, when $|\dot{\epsilon}|>|\dot{\epsilon}^*|$ with $K=|-\mu+2\mu_4\dot{\epsilon}^*\cot^2\theta|$, old domains will be broken and the only residual shapes of domains, according to Wulff construction and Eq. (21), must be enveloped by straight lines with normal of $\Phi=\pm45°$, where the $\dot{\epsilon}$-induced line tension change has no effect due to $\cos 2\Phi=0$. This is nothing but the "shear bands" found by Fuller's group [9–11].

IV. DISCUSSION AND CONCLUSION

In summary, with above lengthy calculation we have shown that the mysterious and rich phenomena on the flow-induced tilt orientation of amphiphile monolayers observed by several laboratories in the past decade can be understood by incorporation of hexatic elasticity into LC EL theory. It evidently shows that the theoretical concept of soft matter based on LC by de Gennes, Helfrich, Nelson, and many others is capable of dealing with such a complex system. In other words, the present work shows impact in relation to previous theoretical and experimental work. The present model also revealed that the NN (or NNN) locking orientation in microscopic molecular lattice plays important role. The locking can be maintained even the monolayer is subject to a constant shear rate (see the case of pure extension flow in Sec. III) that is due to the monolayer being in LC state. In LC, the molecules can move freely as in a usual liquid but their orientation, the average direction of their long axes can keep during the molecular flow. Therefore, the strain of LC at extension or shear flow does not increase linearly as a function of time as in a solid with the same shear deformation. In physics, the tilt reorientation is described in two folds: Flow induces the reorientation of the tilt of the alkyl chain's tails and it subsequently causes the head groups rearranged on the distorted, hexagonal lattice to fulfill the NN (or NNN) tilt locking. In our theoretical calculation [18], the strains induced by the two fold reorientation has been taken account of the mentioned properties of LC and the obtained strain s_{ij}, is only function of tilting direction and independent of their flow status. Of course the present theory is still based on a phenomenal treatment such as Frank elastic theory and EL dynamic theory of LC, by taking account of the LC symmetry only. One may feel that a molecular theory of flow-induced molecular orientation has to consider molecular interaction potential that is periodic in the molecular distance such that a distance deformation that moves one lattice constant creates zero force. In a recent study on the toughness of biocomposites by de Gennes and co-workers [28] has promoted the similar issue. The treatment may implement the coupling of the hexatic order to the tilt order. With such a molecular-level inspection one can investigate how the orientation acts back on the flow as have been carried out in hexatic and smectic LC by Nelson and Halperin [5]. In fact, as has been mentioned in Sec. I, we have invoked a Lenard-Jones potential to discuss the tilting phase transition in monolayers of $C_{14}-C_{24}$ acids [8]. One would expect hexatic elastic energy and the EL-dynamic theory to be capable of treating the coupling of the hexatic order to the tilt order as well to understand how the orientation acts back on the flow.

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