Nonlinear dilational mechanics of Langmuir lipid monolayers: A lateral diffusion mechanism

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We propose a theoretical model for the nonlinear mechanical response of Langmuir lipid monolayers subjected to a dilational in-plane deformation. Lateral diffusion in conjunction with free convection has been considered to drive nonlinear mass transport in Langmuir lipid monolayers. The present model combines the conservative dynamical equations for lipid transport along the monolayer plane together with a material relationship accounting for nonlinear hypoelasticity, as experimentally observed from high-strain rheological measurements [Hilles *et al.*, Adv. Colloid Interface Sci. **122**, 67 (2007)]. The dynamical equations have been resolved for oscillatory nonlinear motion, the theoretical spectral amplitudes being found in quantitative agreement with the experimental values obtained from surface rheology experiments performed in Langmuir monolayers of two different lipid systems, namely DPPC and native *E. Coli* lipids. The presence of micrometer-sized phase coexistence domains in these lipid systems has been claimed to pump diffusive transport along the monolayer plane. This dynamical scenario defines a relaxation regime compatible with the observed nonlinear mechanical behavior.

I. INTRODUCTION

The picture of the lipid component of biological membranes as passive supporting structures has been revised in recent times due to the growing recognition that these structures can undergo significant density fluctuations leading to nonuniform distributions of chemical composition, mass density, thickness, and mechanical behavior [1–3]. Cell shape is partially encoded in the mechanical properties of the lipid bilayer, particularly bending rigidity and dilational elasticity, which couples stretch and in-plane shear. Because local gradients of lipid concentration and composition are coupled to lateral transport along each monolayer leaflet, the resultant mechanical properties of the membrane are strongly influenced by the diffusive properties of the lipid molecules. At mechanical equilibrium, lipid diffusion is driven by thermal fluctuations restored by the linear viscoelastic response of the lipid assembly. A number of experiments have investigated Brownian diffusion in cell and model membrane systems [4–7]. However, real membranes are subjected to strong stress along their living cycle, thus undergoing large shape fluctuations during division or mass trafficking, for instance. Indeed, a variety of agents, including anionic lipids, high salt, high pH, ATP depletion, and cholesterol enrichment, can strongly modify cell shape systematically and reversibly [8–10]. Equivalently, the sequence of shape changes that a cell undergoes at *in vivo* conditions can be artificially induced by changing its surface area with respect to the equilibrium value [11]. A more complex nonlinear interplay than in the linear case must now underlie the coupling mechanism between microscopic transport and mechanical behavior. This is because nonlinear mechanics emerges relevant to understanding how molecular transport affects the dynamics of membrane deformation in the regime of large deformations.

Lipid diffusion, as modeled in Langmuir lipid monolayers, is of fundamental interest to physics, chemistry, and cell biology [12–14]. Experiments and theory have pointed out the tight interplay between molecular lateral diffusivities and the linear dilational rheology of Langmuir monolayers [15]. However, a nonlinear theory of lateral diffusion on model membranes is not yet available. In the present paper, we address a theoretical study on how lateral diffusion on Langmuir monolayers of lipid systems drives nonlinear mechanics at large dilational deformations. A meaningful study of this influence requires the ability to monitor dilational mechanics in the broad range of displacements covering the linear and nonlinear regimes. Predictions from theory will thus be compared with data obtained from oscillatory barrier experiments performed in Langmuir lipid films [16].

II. DILATIONAL MECHANICS OF LANGMUIR FILMS

A. Linear regime

Surface active substances, most lipids among them, spontaneously adsorb as Langmuir monolayers at the air/water interface. The decrease in free energy upon the spontaneous adsorption of the monolayer is measured by the surface pressure Π ($=\gamma_0-\gamma$, γ being the surface tension of the monolayer-covered surface and γ_0 its value for the bare aqueous surface). Π is indeed the macroscopic descriptor for the monolayer free energy [17], thus $\delta\Pi$ changes caused by a mechanical disturbance can be interpreted as the stress response of the system against the external stimulus [16]. The mechanical behavior of these interfacial monolayers is characterized by surface rheology as they possess large elasticity and viscosity [18]. The Langmuir trough provides the adequate geometry to explore for this surface rheology [17]. A Langmuir monolayer (spread in a rectangular trough of constant width y_0) can be considered as a planar elastic body with rectangular dimensions, $A(x)=y_0x$, defined by the sur-

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face area available between the movable barriers separated at a distance x. Upon lateral stretching or compression along the x axis, a planar Langmuir monolayer experiences a longitudinal dilation u_x. The modulus, $u_x^{(0)}$, of this longitudinal deformation vector ($\vec{u}_x = u_x^{(0)}\vec{i}$, $\vec{i}$ being the unitary vector in the x direction) is easily measured as the displacement of the barriers Δx with respect to their initial position (separated by a distance x_0), i.e., $u_x^{(0)} \equiv \Delta x = x - x_0$ [19]. In this planar elasticity problem, the monolayer is considered as a very thin plate, thus any z displacement, e.g., the capillary fluctuations, is negligible with respect to the in-plane lateral motions [19], i.e., $u_z \sim 0$. Additionally, because the barrier-opposite sides of the Langmuir monolayer are clamped to the trough edges, the in-plane transversal displacement is in this case identically zero, $u_y = 0$. In the theory of elasticity, the generalized strain tensor is defined as $u_{ij} = \frac{1}{2}[(\partial u_i / \partial x_j) + (\partial u_j / \partial x_i) + (\partial u_l / \partial x_i)(\partial u_l / \partial x_j)]$ [19]. In the present planar case ($u_y = 0$, $u_z \sim 0$), thus the longitudinal component reduces simply to $u_{xx} = \partial u_x / \partial x$ [19]. Therefore, the only component of the strain tensor relevant to the present problem is $u_{xx}(x,t)$, in general a function of time and of the x coordinate, with amplitude u. If the monolayer occupying a reference area $A_0 (=y_0 x_0)$ is dilated to a surface area $A (=y_0 x)$ under the action of the barriers of the Langmuir trough, the amplitude of the strain field could be expressed in terms of the compression ratio $\theta \equiv \Delta A / A_0 = (A - A_0)/A_0$. More precisely, because y_0 is constant in the Langmuir trough geometry, the compression ratio is exactly defined by the relative longitudinal dilation, i.e., $\theta \equiv \Delta A / A_0 = (y_0 x - y_0 x_0)/y_0 x_0 = \Delta x / x_0$. After deformation, an arbitrary linear distance x is rescaled to $x' = (1 + 2u)^{1/2} x$ [19], thus the relative dilation actually reads $\Delta x / x_0 \equiv (x' - x)/x = (1 + 2u)^{1/2} - 1$. Consequently, in the limit of small deformations ($u < 1$) one finds $\Delta x / x_0 \approx u$. This is because, for Langmuir monolayers, the amplitude of the longitudinal strain is usually identified with the relative area dilation, $u \approx \theta$ [20]. To first order, this approach is essentially correct, but for larger deformations one has, exactly, $u = \theta + 1/2 \theta^2$.

Upon lateral strain, a Langmuir monolayer experiences a longitudinal stress measured as the change in lateral pressure, $\sigma_{xx} \sim \delta\Pi$. In the limit of small deformations, the viscoelastic free energy takes a quadratic form on the strain function [19,21],

$$\delta F(u_x) = \frac{1}{2}\tilde{\varepsilon} u_{xx}^2. \qquad (1)$$

The viscoelastic coefficient $\tilde{\varepsilon} = \varepsilon + \kappa(\partial/\partial t)$ is termed the linear dilational modulus, which actually contains a pure elastic term (ε), the dilational elasticity, plus a dissipation operator proportional to the dilational viscosity (κ), which accounts for the viscous losses. As a consequence, a linear constitutive relationship is found between the longitudinal viscoelastic stress and the deformation,

$$-\delta\Pi = \sigma_{xx} = \frac{\partial(\delta F)}{\partial u_{xx}} = \tilde{\varepsilon} u_{xx}. \qquad (2)$$

Notice that the viscoelastic stress actually contains two well-separated terms, $\sigma_{xx} = \sigma^{(E)} + \sigma^{(V)}$, the first corresponding to the pure elastic energy storage $\sigma^{(E)} = \varepsilon u_{xx}$ and the second to

the energy dissipated by viscous friction $\sigma^{(V)} = \kappa(\partial u_{xx}/\partial t) = \kappa R$, $R = \partial u_{xx}/\partial t = d(\ln A)/dt$ being the dilation rate. Thus, in the linear regime, if a monolayer at an area A_0 is dilated under the action of the barriers of the Langmuir trough (the amplitude of the strain function actually is $u \approx \theta = \Delta A / A_0$), it consequently experiences an elastic stress $\sigma^{(E)} \equiv \delta\Pi = \Pi - \Pi_0 = -\varepsilon\Delta A / A_0$. If the small dilation is *quasistatic* ($u \to 0$; $R \to 0$) no viscous components are found within the stress response, i.e., $\sigma^{(V)} \sim 0$. Alternatively, if the dilation is exerted at a finite rate, viscous effects might then emerge within the stress function, $\sigma^{(V)} = \kappa(\partial u_{xx}/\partial t) \geq 0$, and $|\sigma| \geq |\delta\Pi|_{R \to 0}$.

Oscillatory barrier experiments appear then as a very convenient method to measure both components of the stress. If the strain function is sinusoidal, $u_{xx}(t) = ue^{i\omega t}$ ($u \approx \Delta A / A_0$), the time-dependent linear viscoelastic response of the monolayer is such that $\sigma(t) = \sigma^{(E)} + \sigma^{(V)} = \varepsilon u_{xx} + \kappa(\partial u_{xx}/\partial t) = (\varepsilon + i\omega\kappa)ue^{i\omega t}$, i.e., the viscous component causes a phase lag, $\phi = \tan^{-1}(\omega\kappa/\varepsilon)$, between the stress function $\sigma(t) = \sigma_0 e^{i(\omega t + \phi)}$ (σ_0 being the stress amplitude) and the applied strain, $u_{xx}(t) = ue^{i\omega t}$. Although the stress amplitude includes both elastic and viscous components summed together, $\sigma_0 = (\varepsilon^2 + \omega^2\kappa^2)^{1/2}u$, each one can be eventually calculated as $\varepsilon = \sigma_0^{(E)}/u = (\sigma_0/u)\cos\phi$ and $\omega\kappa = \sigma_0^{(V)}/u = (\sigma_0/u)\sin\phi$. For Langmuir lipid monolayers, the dilational elastic term usually controls the viscous one ($\varepsilon \gg \omega\kappa$), which is in practice dominated by the intrinsic viscosity of the monolayer. Bulk viscosity effects are neglected with respect to the intrinsic friction [22,23], thus no hydrodynamic coupling between the monolayer and the subphase is explicitly considered.

B. Nonlinear regime

In the linear regime described above, the dilational viscoelastic moduli are strain-independent, however at strains high enough, beyond a threshold value u_C which strongly depends on each system, the monolayer behavior is no longer elastic, and the viscoelastic response becomes nonlinear. Then, a polynomial expansion of the linear relationship in Eq. (2) can be used as a good description of the stress response, $\sigma(u_{xx}) = \varepsilon_1 u_{xx} + \varepsilon_2 u_{xx}^2 + \varepsilon_3 u_{xx}^3 + \cdots$, or equivalently a strain-dependent viscoelastic modulus can be considered in Eq. (2),

$$\tilde{\varepsilon}(u_{xx}) = \tilde{\varepsilon}_1 + \tilde{\varepsilon}_2 u_{xx} + \tilde{\varepsilon}_3 u_{xx}^2 + \cdots . \qquad (3)$$

As a consequence, when the barriers of the Langmuir trough drive the monolayer beyond the linear regime ($u > u_C$), the stress function might contain higher-order harmonics other than the fundamental component, i.e., $\sigma(t) = \sigma_1^{(0)}e^{i\omega t} + \sigma_2^{(0)}e^{2i\omega t} + \sigma_3^{(0)}e^{3i\omega t} + \cdots$, where $\sigma_k^{(0)} = \varepsilon_k u^k$.

Hilles *et al.* [24] have recently adapted the usual methods of Fourier-transform rheology [25] to analyze the nonlinear response of Langmuir monolayers of polymers and colloidal particles. Similarly to bulk systems with a symmetric nonlinear stress tensor, $\sigma(-u_{xx}) = -\sigma(u_{xx})$, only odd harmonics were found in Langmuir monolayers of spherical colloidal particles interacting through Coulombic central force field [24]. However, the complete harmonics sequence was observed by
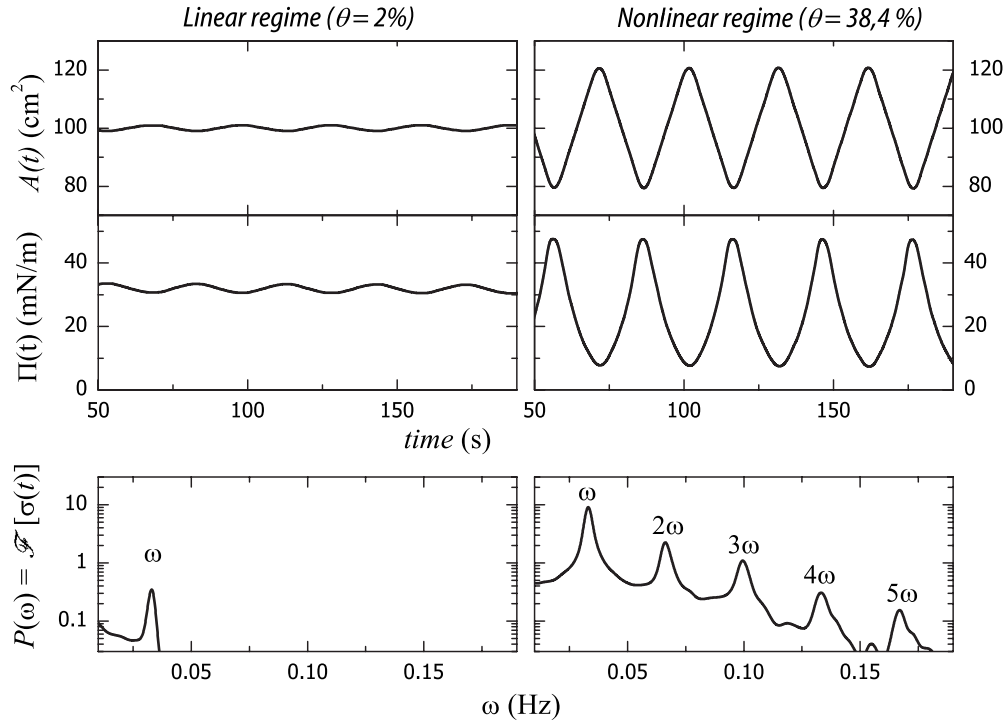
FIG. 1. Stress-strain time traces and mechanical spectra as obtained in oscillatory barrier rheological experiments performed at a frequency ω on Langmuir lipid films of 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) at 25 °C. The monolayer is deformed under an oscillatory strain $u_{xx}(t)=ue^{i\omega t}$ (top), and its mechanical response is monitored as a function of time $\Pi(t)=\Pi_0+\sigma(t)$ (middle). The mechanical spectra are obtained as the Fourier transform of the stress function, $P(\omega)=\mathcal{F}[\sigma(t)]$ (bottom). In the low strain regime (left; $\theta=2\%$, $u=\theta+0.5\theta^2\sim0.02$), the dilational response is linear and only the fundamental mode propagating at a frequency ω is present within the mechanical spectrum. However, the complete series of harmonics at frequencies 2ω, 3ω, 4ω, $5\omega,\ldots$ is present at the high strain nonlinear regime (right; $\theta=38,4\%$, $u=\theta+0.5\theta^2\sim0.42$).

these authors in Langmuir films of entangled polymers [24], likewise analogue bulk systems in which the symmetry of the stress tensor components is broken, $\sigma(-u_{xx})\neq-\sigma(u_{xx})$, e.g., in polymer liquid crystals or elastomer gels [26]. The analysis of the monolayer mechanical response requires the experimental $\sigma(t)=\delta\Pi(t)$ curves to be Fourier-transformed, then the response spectrum is obtained in the frequency domain as $P(\omega)=\int_{-\infty}^{\infty}\sigma(t)e^{-i\omega t}dt$. The numerical methods to carry out the Fourier transform of the experimental data were discussed in detail by Wilhelm [25]. In practice, the digital fast Fourier transform algorithm (FFT) [25,27] is used, but good signal-to-noise ratios are achieved only if (a) the experimental response data contain a large number of periods (more than 10, typically) and (b) the sampling time is minimized (1 s, typically).

Figure 1 shows a typical example obtained for a Langmuir monolayer of a saturated phospholipid, DPPC. At a low deformation ($u\sim2\%<u_C$; see Fig. 1, left), the stress response is linear and accomplishes well the sinusoidal strain wave $\sigma(t)\sim\varepsilon_1ue^{i\omega t}$. However, additional nonlinear features start to be clearly visible within the stress response at larger strains (see Fig. 1, right). These different behaviors are clearly pointed out as the mechanical spectrum is computed from the experimental time traces, $P(\omega)=\int_{-\infty}^{\infty}\delta\Pi(t)e^{-i\omega t}dt$ (see Fig. 1, bottom). Within the linear regime, only the fundamental peak is obtained at the excitation frequency ω, while other, less intense, peaks corresponding to higher har-

monics (2ω, 3ω, $4\omega,\ldots$) are observed in the nonlinear regime beyond θ_C.

These results exemplify how Langmuir lipid monolayers exhibit mechanical behavior characterized by a nonlinear material relationship such as the one described by Eq. (3). To first order, an adequate link between surface mechanics and the microscopic mechanism of mass transport might be provided by surface hydrodynamics. Although the problem of linear dilational mechanics of Langmuir films in the case of small deformations restored by lateral diffusion has been theoretically addressed in the literature [15,28,29], nonlinear extensions describing the regime of large deformations are still lacking. This is indeed the theoretical problem addressed in the present paper. A correct understanding of the nonlinear regime requires a brief description of the linear asymptotic behavior.

III. LINEAR DILATIONAL RHEOLOGY AND LATERAL DIFFUSION

Because any surface dilation exerted on an adsorbed monolayer causes a concentration gradient, as a consequence a surface tension (Marangoni) gradient appears, $\delta\gamma(\Gamma)\sim(d\gamma/d\Gamma)\delta\Gamma$. The mechanical equilibrium imposes the balance between the tangential viscoelastic stress exerted at the fluid interface $f_x=d\sigma_{xx}/dx$ and the restoring Marangoni force exerted by the surface tension gradient, $d\gamma/dx$, thus

$$f_x = \frac{d\gamma}{dx} = \widetilde{\varepsilon}\frac{\partial u_{xx}}{\partial x}. \tag{4}$$

For adsorbed films, e.g., Langmuir lipid monolayers, the Marangoni stress can be conceived as a surface tension gradient caused by a local change in the surface concentration of the surfactant, $\delta\Gamma(u_{xx})$. At a given temperature, and if the changes in lipid concentration $\delta\Gamma$ are assumed to produce an instantaneous change in surface tension $\delta\gamma$ [30], Eq. (4) can be rewritten as follows:

$$\frac{d\gamma}{dx} = \frac{d\gamma}{d\Gamma}\frac{d\Gamma}{dx} = -\frac{\varepsilon_0}{\Gamma_0}\frac{d\Gamma}{dx} = \widetilde{\varepsilon}\frac{\partial u_{xx}}{\partial x}. \tag{5}$$

Here, the Gibbs elasticity modulus $\varepsilon_0 = -\Gamma_0(d\gamma/d\Gamma)_T$ represents the change in surface free energy of the monolayer caused by the increase in lipid density at equilibrium conditions (Γ denotes the lipid density and $\Gamma_0 = 1/A_0$ is its equilibrium value); ε_0 thus corresponds to the equilibrium compression modulus of the monolayer. Equation (5) represents the dilational response function, which establishes that a given surface dilation must be restored by the corresponding density gradient. However, an additional equation accounting for the time dependence of the deformation-density coupling might be written. If molecular transport is restricted to the monolayer plane (i.e., there are no solubilization mechanisms able to transfer molecules across the adjacent bulk phases), lateral diffusion is the only mechanism able to restore the mass-deformation balance mentioned above. In such a case, the mass conservation imposes that diffusive transport exactly balances the flux of matter; then Fick's law for surface diffusion is as follows [31]:

$$\frac{d\Gamma}{dt} = D\frac{\partial^2\Gamma}{\partial x^2}, \tag{6}$$

D being the lateral diffusion coefficient; for lipids, $D \sim 10^{-7}$ cm^2/s typically [15].

Because the surface density is in general a function of time and of the local deformation $\Gamma(t,u_x)$ (u_x being the deformation, and its x derivative $u_{xx} = \partial u_x/\partial x$, the longitudinal component of the strain tensor), the convective term must be considered in the left side of Eq. (6) [32,33],

$$\frac{\partial\Gamma}{\partial t} + \frac{\partial}{\partial x}(\Gamma v_x) = D\frac{\partial^2\Gamma}{\partial x^2}, \tag{7}$$

where $v_x = \partial u_x/\partial t$ stands for the longitudinal velocity function.

For small-amplitude oscillatory motion, $u_x = u_x^{(0)}e^{iqx}e^{i\omega t}$ (ω being the oscillation frequency and q the spatial wave vector), linear solutions to Eq. (7) must be found with the form $\Gamma(x,t) = \Gamma_0 + \delta\Gamma_1 e^{iqx}e^{i\omega t}$ [Γ_0 being the average equilibrium value of the lipid concentration and $\delta\Gamma_1(u_x)$ a linear strain-dependent fluctuation]. After linearization, $\partial(\Gamma v_x)/\partial x \approx \Gamma_0\ (\partial v_x/\partial x)$, one gets the linear relationship between the amplitude of the strain tensor $u = iqu_x^{(0)}$ [fixed by

the external stimulus in the oscillatory barrier experiments, $u = \theta + 1/2\theta^2$ with $\theta = (A - A_0)/A_0$] and the density fluctuation,

$$\frac{\delta\Gamma_1}{\Gamma_0} = -\xi_1(\omega)u, \tag{8}$$

where $\xi_1(\omega)$ is a Maxwell-like relaxation function ($0 \leq \text{mod}[\xi_1(\omega)] \leq 1$) accounting for the frequency dependence of the linear dependence between the applied strain and the density wave,

$$\xi_1(\omega) = \frac{i\omega\tau_D}{1 + i\omega\tau_D}, \tag{9}$$

and τ_D is a diffusion characteristic time,

$$\tau_D = \frac{1}{Dq^2}, \tag{10}$$

which scales quadratically ($\tau_D \sim a^2/D$) with the spatial scale over which lateral diffusion operates, $a \sim q^{-1}$.

Similarly, when Eq. (5) is solved for solutions with the form $\Gamma(x,t) = \Gamma_0 + \delta\Gamma_1 e^{iqx}e^{i\omega t}$, one gets $\delta\Gamma_1/\Gamma_0 = -(\widetilde{\varepsilon}/\varepsilon_0)u$. By comparison with Eq. (8), one can deduce the precise ω dependence of the linear viscoelastic moduli, this is $\widetilde{\varepsilon}(\omega) = \varepsilon + i\omega\kappa = \varepsilon_0\xi_1(\omega)$. These results illustrate that if the monolayer is strained fast enough ($\omega \gg \tau_D^{-1}$, then $\xi_1^{(\text{Re})} = \varepsilon/\varepsilon_0 \sim 1$, $\xi_1^{(\text{Im})} = \omega\kappa/\varepsilon_0 \sim 0$), the system has no time to redistribute the material and its mechanical response turns out to be purely elastic, $\varepsilon \sim \varepsilon_0$, $\kappa \sim 0$. On the contrary, if times longer than the diffusion time are spent to reexpand after the compressing semicycle ($\omega \ll \tau_D^{-1}$), lateral diffusion has enough time to come into play and some stress is relaxed by viscous dissipation; in the limit of zero frequency, $\varepsilon \sim 0$, $\kappa \sim \varepsilon_0\tau_D$. In more general terms, in the linear regime lateral mass fluxes are expected to be directly proportional to the external deformation, where $\xi_1(\omega)$ is the dynamic transference function, which describes the propagation regime of the diffusive modes: a dissipative regime at low frequencies ($\text{mod}[\xi_1] < 0.5$ at $\omega\tau_D < 1$) and a pure elastic one at high frequencies ($\text{mod}[\xi_1] > 0.5$ at $\omega\tau_D > 1$).

Oscillatory lateral strain exerted on a homogeneous monolayer by the barriers of the Langmuir trough causes a longitudinal (Lucassen) wave propagating at a frequency ω and with a wavelength $\lambda = 2\pi/q$. The propagation frequency of the so-created Lucassen wave disperses as $\omega = (3/2)^{1/2}(\varepsilon^2 q^4/\eta\rho)^{1/3}$ (q being the wave vector of the longitudinal wave, ρ the density, and η the viscosity of the subphase on which the monolayer is supported) [22]. Thus, stiffer monolayers develop longer concentration waves; for lipid monolayers strained at frequencies $\omega \sim 1$ Hz, typically $\lambda \sim 20$ cm for $\varepsilon \sim 10$ mN/m and $\lambda > 100$ cm if $\varepsilon \sim 100$ mN/m. Lipid monolayers are very dense assemblies and the surface diffusion coefficient is usually small ($D \sim 10^{-7}$ cm^2/s), thus the concentration gradients associated with Lucassen waves might relax at times so long as $\tau_D \sim \lambda^2/D \gg 10^7$ s. Because this relaxation time far exceeds the experimental time scale, diffusion-driven stress relaxation has never been evidenced on homogeneous lipid monolayers. However, the presence of lipid domains has been recently pointed out as a source of stress relaxation in lipid monolayers [34]. In that work, mi-

crometric sized condensed domains have been hypothesized as lipid reservoirs able to exchange material with the surrounding fluid upon request. In fact, this diffusive exchange is expected to relax at times $\tau_D \sim a^2/D \sim 1-10$ s ($a \sim 1$ μm being the domain size), as experimentally observed [34].

IV. COUPLING BETWEEN LATERAL DIFFUSION AND NONLINEAR DILATIONAL MECHANICS

If the surface dilation exceeds the linear threshold u_C, the concentration gradient might include the nonlinear features of the macroscopic nonlinear response described by Eq. (3). In such a case, the response function in Eq. (4) might be rewritten as follows:

$$\frac{d\gamma}{dx} = -\frac{\varepsilon_0}{\Gamma_0}\frac{d\Gamma}{dx} = (\widetilde{\varepsilon}_1 + \widetilde{\varepsilon}_2 u_{xx} + \widetilde{\varepsilon}_3 u_{xx}^2 + \cdots)\frac{\partial u_{xx}}{\partial x}. \quad (11)$$

In the present case, for large-amplitude oscillatory motion $u_{xx}(x,t) = ue^{iqx}e^{i\omega t}$ ($u > u_C$), nonlinear solutions might be found with the form $\Gamma(x,t) = \Gamma_0 + \delta\Gamma_1 e^{iqx}e^{i\omega t} + \delta\Gamma_2 e^{2iqx}e^{2i\omega t} + \delta\Gamma_3 e^{3iqx}e^{3i\omega t} + \cdots$. After substituting in Eq. (11) and separating terms, one gets

$$\sigma_k^{(0)} = \widetilde{\varepsilon}_k u^k = -\varepsilon_0 k\frac{\delta\Gamma_k}{\Gamma_0}. \quad (12)$$

This equation teaches us that the presence of a given deformation k mode in the mechanical response is only determined by the existence of nonvanishing density fluctuations of a given k symmetry, i.e., $\sigma_k \neq 0$ if $\delta\Gamma_k \neq 0$. From the continuity condition stated in Eq. (11), the presence of any harmonics is not *a priori* forbidden in the response function. On the contrary, while the transport mechanism engenders nonlinear density fluctuation k modes, they will be present in the nonlinear mechanical spectrum of the monolayer. Indeed, when the transport equation in Eq. (7) is resolved for nonlinear solutions $\Gamma(x,t) = \Gamma_0 + \delta\Gamma_1 e^{iqx}e^{i\omega t} + \delta\Gamma_2 e^{2iqx}e^{2i\omega t} + \delta\Gamma_3 e^{3iqx}e^{3i\omega t} + \cdots$, the presence of the convective cross term ($\sim \Gamma u_x$) yields a recurrence relation between the amplitudes of the k modes,

$$\delta\Gamma_1 = -u\frac{i\omega\tau}{1 + i\omega\tau}\Gamma_0,$$

$$\delta\Gamma_2 = -u\frac{i\omega\tau}{2 + i\omega\tau}\delta\Gamma_1,$$

$$\delta\Gamma_3 = -u\frac{i\omega\tau}{3 + i\omega\tau}\delta\Gamma_2,$$

$$\cdots$$

$$\delta\Gamma_k = -u\xi_k(\omega)\delta\Gamma_{k-1} \quad \text{with } \xi_k(\omega) = \frac{i\omega\tau}{k + i\omega\tau}. \quad (13)$$

Obviously, because a given amplitude $\delta\Gamma_k$ depends on $\delta\Gamma_{k-1}$, one deduces that the symmetry of the diffusion is such that every harmonics (odd and even) might be present in the

mechanical response. Finally, if Eqs. (13) are progressively enchained and the result is combined with Eq. (12), one obtains the general relationship for the nonlinear viscoelastic stress amplitudes,

$$\sigma_1^{(0)} = \varepsilon_0 \xi_1 u,$$

$$\sigma_2^{(0)} = -2\varepsilon_0 \xi_1 \xi_2 u^2,$$

$$\sigma_3^{(0)} = 3\varepsilon_0 \xi_1 \xi_2 \xi_3 u^3,$$

$$\cdots$$

$$\sigma_k^{(0)} = (-1)^{k+1} k\varepsilon_0 \left(\prod_{k=1} \xi_k\right) u^k. \quad (14)$$

These formulas illustrate that mass lateral diffusion drives nonlinear mechanics with a singular set of characteristics. (a) The stress function contains both types of harmonics, odd and even. The first are typical of symmetrical constitutive functions, i.e., $\sigma_k(-u) \sim u^k = -\sigma_k(u)$ if $k = 1, 3, 5, \ldots$, but the presence of even harmonics arises from a broken symmetry, i.e., when the system behaves differently under compression than in stretching. Indeed, the symmetry of the diffusion equation [see Eq. (7)] is such that density fluctuations do not remain invariant under sign inversion, $v_x \rightarrow -v_x$. (b) The diffusion-driven nonlinear mechanical response shows unequivocal plasticlike (actually hypoelastic) features; the second-order term is negative, $\sigma_2^{(0)} \sim -\varepsilon_0 \xi_1 \xi_2$, thus leading, under stretching, to an effective elasticity modulus lower than in the linear regime, $\varepsilon_{\text{eff}} \sim \varepsilon_0(1 - \xi_2) < \varepsilon_0$. This behavior was observed in oscillatory barrier experiments performed in Langmuir polymer films [24,35], and more recently in Langmuir monolayers of natural lipids [36]. (c) Because only lateral diffusion has been supposed to underlie nonlinear mechanics, no further constitutive effects other than Marangoni surface tension gradients are contained within each nonlinear coefficient, $\sigma_k \sim (d\gamma/dx)_k \sim (d\gamma/d\Gamma)(d\Gamma/dx) \sim -\varepsilon_0 \delta\Gamma_k$. In other words, the equilibrium compression modulus ε_0 and the diffusion characteristic time τ_D are the only constitutive coefficient included within the present approach [more advanced developments will require further constitutive expansions in the form $\delta\gamma = (d\gamma/d\Gamma)\delta\Gamma + 1/2(d^2\gamma/d\Gamma^2)\delta\Gamma^2 + \cdots$]. For a given ε_0, the absolute value of every nonlinear coefficient is determined by a relaxation function describing the dynamics of the lateral diffusion at the considered frequency ω_k, i.e., $\sigma_k \sim \varepsilon_0 \xi_1 \xi_2 \cdots \xi_k$. As a corollary, a given high-k harmonics contains all of the information about the amplitudes of the $k-1$ preceding modes.

V. VISCOELASTIC RELAXATION WITHIN NONLINEAR MODES

As explained above, if a monolayer is largely strained at a frequency $\omega = \omega_1$, it can eventually respond nonlinearly developing a series of deformation modes at a frequency

$\omega_k = k\omega_1$. Every propagating k-mode is expected to relax diffusively through the dynamic relaxation function,

$$\Theta_k(\omega_k) = \prod_{j=1}^{k} \xi_j(\omega_j). \tag{15}$$

Because the frequency ω_j of a given j harmonics is j times the fundamental frequency ω_1, thus $\xi_j(\omega_j) = \xi_j(j\omega_1) = ji\omega\tau/(j + ji\omega\tau) = i\omega\tau/(1 + i\omega\tau) = \xi_1(\omega)$. The relaxation function in Eq. (15) can be thus expressed as

$$\Theta_k(\omega_k) = \xi_1^k(\omega) = \left(\frac{i\omega\tau}{1 + i\omega\tau} \right)^k. \tag{16}$$

The relaxation function $\Theta(\omega)$ actually represents the "effective" diffusive relaxation function at every k mode.

The modulus of each k-relaxation function, $|\Theta_k(\omega)| = (\omega\tau)^k/(1 + \omega^2\tau^2)^{k/2}$, is plotted in Fig. 2(a). From this figure it appears evident that lateral diffusion relaxes differently for the different modes of deformation. As concerns the ω dependency, for a given k mode the relaxation modulus increases as $\sim \omega^k$, i.e., the relaxation becomes increasingly sharp for the higher harmonics, the relaxation time scale shifting to higher frequencies. This fact is more clearly pointed out by the relaxation losses shown in Fig. 2(b), which are calculated as the imaginary part of the relaxation function, i.e., $\text{Im}[\Theta_k(\omega_k)] = \sin[k \tan^{-1}(1/\omega\kappa)]$. The fundamental mode ($k=1$) relaxes Maxwell-like, i.e., the loss modulus reaches a maximum at the fundamental relaxation frequency $\omega_D = 1/\tau_D$. Higher harmonics display stronger and faster dissipation as k increases (the relaxation maxima progressively enlarge and shift to higher frequencies). The relaxation frequencies scale as $\omega_D^{(k)} \sim k^{0.8}$ [see inset in Fig. 2(b)], weaker than the k mode propagation frequency, $\omega_k \sim k$. As a consequence, if diffusional modes are excited at a frequency lower than the fundamental relaxation one, i.e., at $\omega_1 < 1/\tau_D$, different harmonics are expected to eventually bring about different relaxation states. On the contrary, if excited at a frequency higher than the diffusional one ($\omega_1 > 1/\tau_D$), every surface mode (either the fundamental or the harmonics) might be found propagating at the nondissipative elastic regime, i.e., if $\omega_k < \omega_D^{(k)}$, then $\text{mod}[\Theta_k(\omega)] > 0.5$.

To summarize, nonlinear mechanics is strongly coupled to the diffusion transport mechanism in such a way that each deformation k mode propagates influenced by a frequency-shifted viscoelastic relaxation. Consequently, if dilational modes are excited at a fundamental frequency close to the diffusional relaxation one, $\omega_1 \sim \omega_D^{(1)} \sim 1/\tau_D$, nonlinear harmonics propagating at higher frequencies, $\omega_k = k\omega_1$, far from becoming nonrelaxed, are affected by an enhanced diffusion mechanism. This effect is particularly important with regard to viscous dissipation, which is also efficient for the higher harmonics.

VI. NONLINEAR MECHANICAL SPECTRUM

From Eq. (14), the amplitudes of the mechanical spectrum can be easily obtained. Following Eqs. (15) and (16) for the
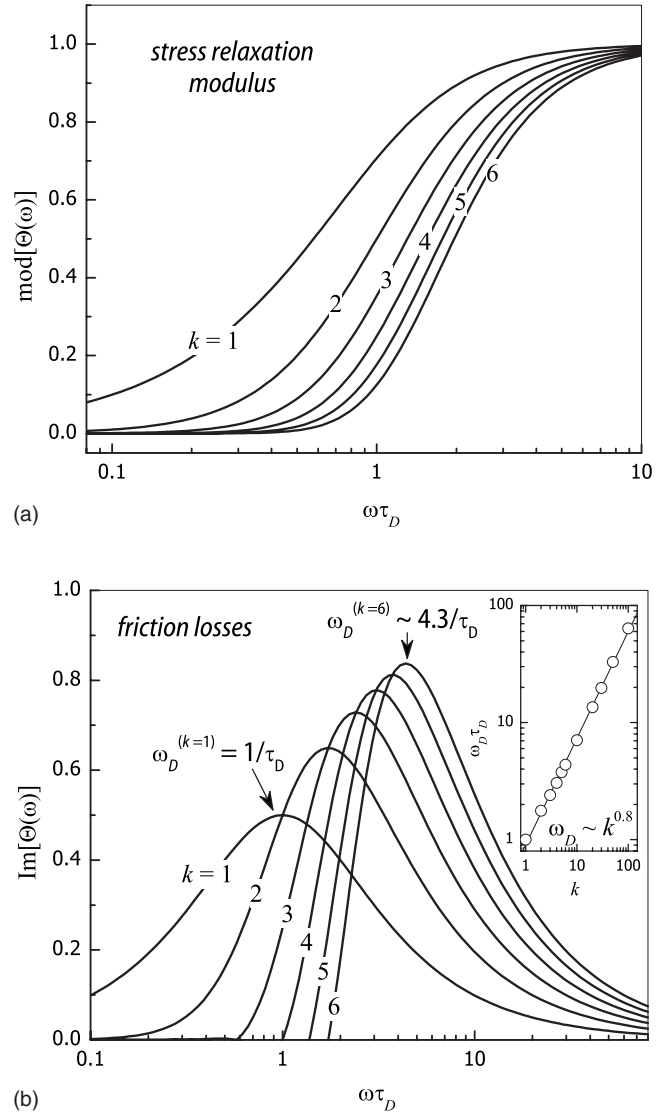

(a)

(b)

FIG. 2. (a) Modulus of the viscoelastic relaxation function $\Theta(\omega)$ for the fundamental diffusive mode ($k=1$) and their nonlinear harmonics (k modes) pumped by a dilational wave. (b) Imaginary part of $\Theta(\omega)$ accounting for the viscous losses within each k mode. The inset plots the k dependence of the effective diffusional relaxation frequency as obtained from the maxima displayed by the loss function.

relaxation function, one gets $|\Theta_k(\omega)| = (\omega\tau)^k/(1 + \omega^2\tau^2)^{k/2}$ and the power spectrum amplitudes are obtained as follows:

$$|\sigma_k^{(0)}| = k\varepsilon_0|\Theta_k|u^k \quad \text{for } k = 1, 2, 3, \ldots . \tag{17}$$

Figure 3 plots experimental data from two different lipid monolayers at a phase coexistence state. These results point out that the nonlinear spectral amplitudes follow powerlike behavior, $\log \sigma_k \sim k$, as predicted by Eq. (17). Although the present data arise from experiments performed at large deformations ($\theta \sim 37\%$), similar nonlinear qualitative behavior is observed to emerge at any deformation beyond the nonlinear threshold ($u > u_C$; in some cases, as *E. Coli* lipid monolayers, $u_C \sim 2\%$) [36].
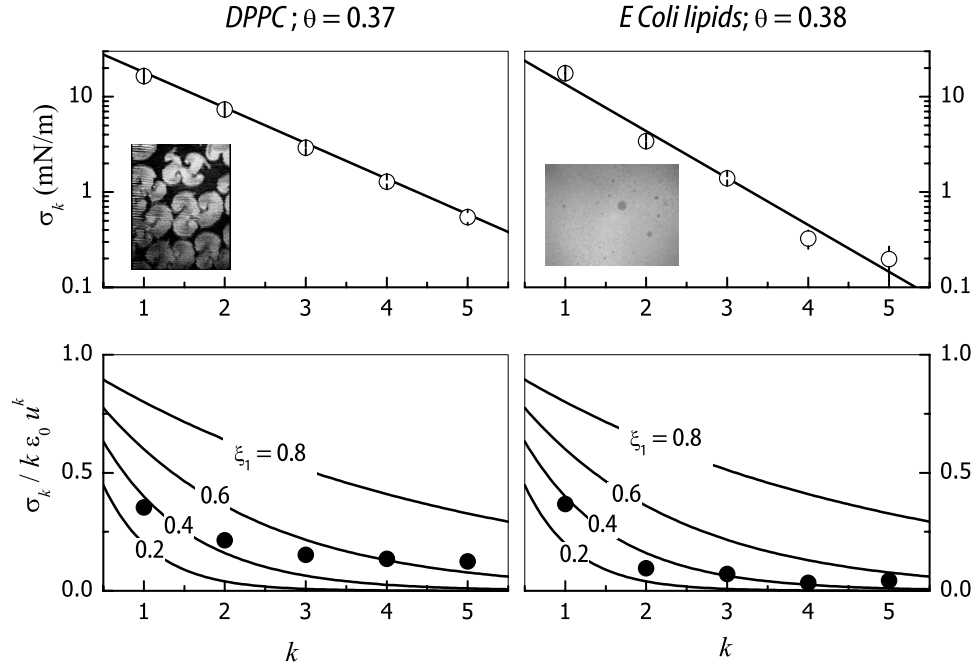
FIG. 3. (Top) Spectral mechanical amplitudes experimentally observed from the Langmuir monolayers of two different lipids when strained in the nonlinear regime. Experimental data depict powerlike $\sigma_k \sim \sigma_1^k$ (straight lines) as predicted by the nonlinear diffusion model [see Eq. (17)]. Inset photos correspond to the monolayer states at which mechanical experiments were performed. They were taken by BAM (DPPC) and fluorescence microscopy (*E. Coli*) pointing out the existence of lipid domains of size $1-10$ μm which could work as mesoscopic lipid reservoirs. (Bottom) Experimental spectral amplitudes (closed symbols) as compared to Eq. (17) for different values of the dynamical function ξ_1 describing different relaxation states; $\xi_1 < 0.5$ implies diffusion mediated viscoelastic relaxation, i.e., $\omega\tau_D < 1$, while a pure elastic nondissipative regime ($\omega\tau_D \gg 1$) is attained when $\xi_1 > 0.5$.

The observed nonlinear powerlike behavior, $\sigma_k \sim u^k$, is found to be concomitant with the presence of coexistence domains, otherwise a near-linear mechanical response extends up to larger deformations. In other words, the present mechanism seems to be relevant only when diffusion comes into operation at the probed timescale, e.g., when lipid domains of size $a \sim 1$ μm exchange material with the surrounding continuous medium with a lower lipid concentration, the characteristic diffusion time is $\tau \sim a^2/D \sim 1$ s [34]. Following Eq. (17), the modulus of the k-relaxation functions can be easily calculated from the spectral amplitudes $\sigma_k^{(0)}$ as $\Theta_k = \sigma_k^{(0)}/\varepsilon_0 k u^k = |\xi_1|^k$. The experimental values of the relaxation function Θ_k have been plotted in Fig. 3(b) as calculated from the spectral amplitudes measured from DPPC and *E. Coli* monolayers [data in Fig. 3(a)]. These experimental data are in quantitative agreement with the theoretical trends expected from the nonlinear diffusional model supposing a dynamical state close to the relaxation frequency [from Eq. (16), $\Theta_k(\omega) = \xi_1^k$, with $\xi_1 = 0.4-0.6$, thus $\omega\tau_D \sim 1$]. In effect, because data in Fig. 3 correspond to experiments performed at a frequency $\omega \sim 0.1$ s^{-1}, values of $\xi_1 \sim 0.5$ are compatible with a diffusional relaxation time of the order of $\tau_D \sim 1/\omega \sim 10$ s, in agreement with the results obtained in dynamical experiments performed in the linear regime and compatible with the hypothesis of lipid domains working as reservoirs dispensing lipids over the microscale (for lipid domains of size $a \sim 1-10$ μm, one gets $\tau_D \sim a^2/D \sim 1-10$ s) [34]. However, because the present theory is actually 1D with no explicit domains, the agreement can only be qualitative.

VII. STRESS-STRAIN RELATIONSHIP

From Eq. (17), the nonlinear stress-strain relationship is expected to follow a polynomial expansion as follows:

$$\sigma(u) = \varepsilon_0 \xi_1 (1 - 2\xi_1 u + 3\xi_1^2 u^2 - 4\xi_1^3 u^3 + \cdots)u. \quad (18)$$

The nonlinear viscoelastic dilational modulus expands thus as a polynomial strain-dependent u^k-response function, $\widetilde{\varepsilon}(u) = \sigma/u = \widetilde{\varepsilon}_1 (1 - 2\xi_1 u + 3\xi_1^2 u^2 - 4\xi_1^3 u^3 + \cdots)$, which is intrinsically hypoelastic and governed by two well-differentiated parameters, the equilibrium modulus ε_0 and the instantaneous value of the relaxation function at the excitation frequency $\xi_1(\omega_1)$. If $|\xi_1 u| < 1$, the infinite geometric series in Eq. (18) converges at $[1 - 2x + 3x^2 - 4x^3 + \cdots = 1/(1+x)^2$ for $x < 1]$

$$\sigma(u) = \varepsilon_0 \frac{\xi_1 u}{(1 + \xi_1 u)^2}. \quad (19)$$

Thus, different nonlinear dynamical regimes can be reached from a given equilibrium state, the instantaneous value of the relaxation function being the dynamical parameter describing how viscoelastic energy is stored and dissipated by the different k modes. If the fundamental mode is excited at a frequency lower than the relaxation one, $\omega_1 \tau_D \ll 1$, lateral diffusion has enough time to fully relax ($\xi_1 \sim i\omega\tau_D$) and the mechanical response might be found to be almost linear and purely viscous, $\sigma(u) \sim i\varepsilon_0 \omega\tau_D u \sim i\omega\kappa u$. Intuitively, if diffusion has time to relax, the energy release on compression is fully dissipated by the fundamental $k=1$ mode itself. On the
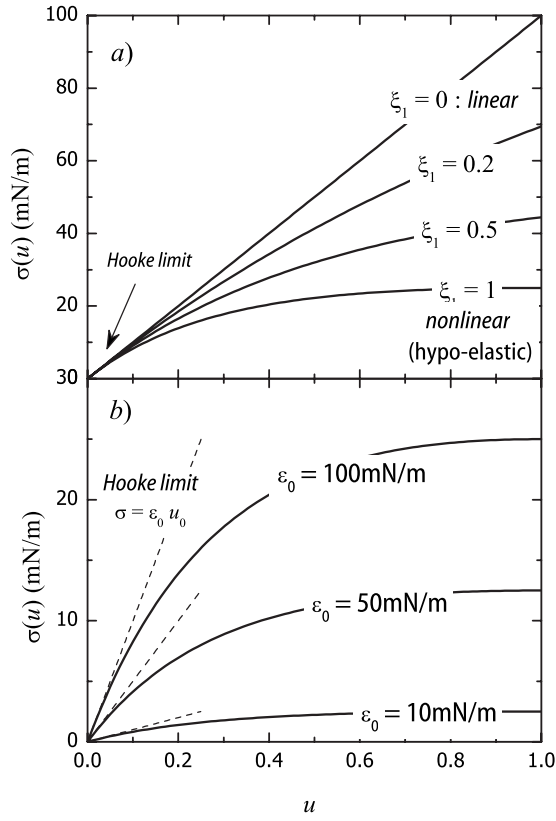
FIG. 4. (a) Stress-strain relationship for different values of the dynamical function ξ_1 describing the relaxation state of the diffusion process: $\xi_1 < 0.5$ since $\omega\tau < 1$, dissipative stress relaxation regime ($\sigma = \sigma_E + \sigma_V$); $\xi_1 > 0.5$ since $\omega\tau > 1$, elastic regime $\sigma_E \gg \sigma_V$. The smaller stress relaxation due to viscous friction is, the larger is the influence of nonlinear elasticity. (b) Compositional effect of the hookean modulus ε_0 on the nonlinear behavior; lateral diffusion engenders similar nonlinear stresses at very low strains ($u_C \ll 0.1$) but stiffer monolayers display yielding at higher stresses ($\sigma_Y = \varepsilon_0/4$).

contrary, if the fundamental mode is excited at higher frequency than the relaxation one, $\omega_1\tau_D \gg 1$, lateral diffusion has no time to become in operation ($\xi_1 \sim 1$) and the mechanical response is found to be purely hypoelastic [$\varepsilon_{\text{eff}} = \varepsilon_0/(1+\xi_1 u)^2 < \varepsilon_0$]. The intermediate cases are properly accounted for by Eq. (19). The stress-strain curves have been plotted in Fig. 4(a) for different values of the dynamic parameter ξ_1 representing different dynamical states.

Figure 4(a) teaches us that if diffusion is fully relaxed, $\xi_1 \sim 0$, the stress-strain curve corresponds to that of a linear viscoelastic body [from Eq. (19), a Hooke-like curve is recovered in this limit, i.e., $\sigma(u) \sim \varepsilon_0\xi_1 u \sim \tilde{\varepsilon}_1 u$]. Nonlinear features start to emerge as lateral diffusion becomes nonrelaxed (i.e., if $0 < \xi_1 < 1$); the higher is ξ_1, the lower is the critical strain u_C at which nonlinearity appears and the lower the stress needed to reach a given deformation state (hypoelasticity). In the nonrelaxation limit ($\omega_1\tau_D \gg 1$, $\xi_1 \sim 1$), the stress-strain curves are characterized by a plasticlike hypoelastic plateau (constant stress at increasing deformation). The yield stress characterizing this plasticlike plateau is reached at a value $\sigma_Y = \varepsilon_0/4$. This plasticlike behavior is more clearly pointed out by Fig. 4(b), where the nonlinear
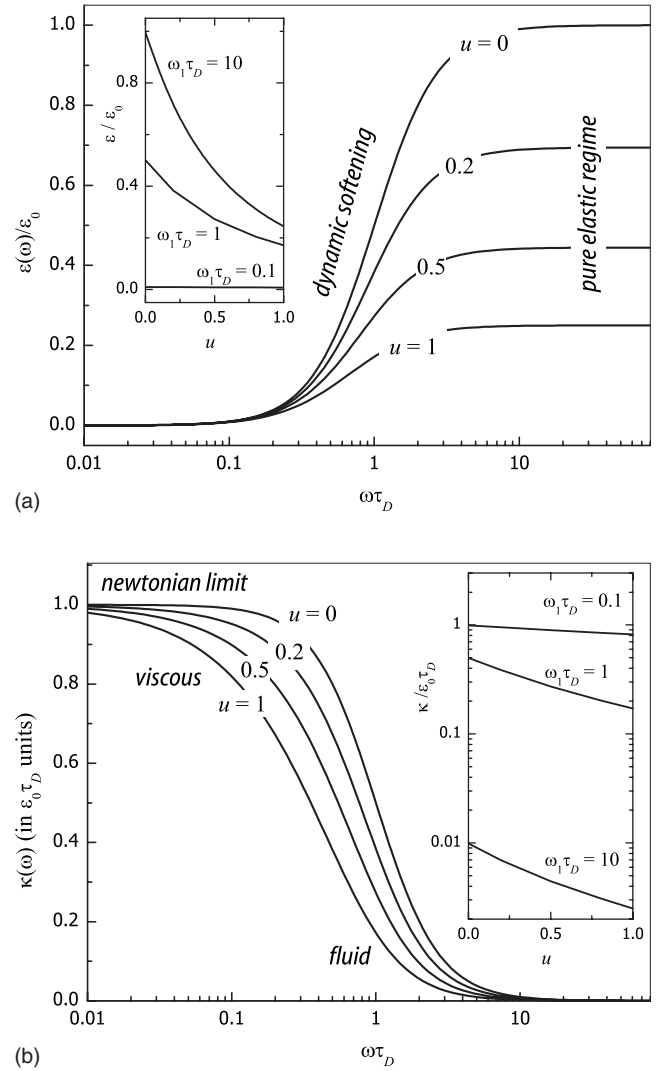

FIG. 5. Effective values of the viscoelastic parameters as dependent on the relaxation state and on the amplitude of the applied strain, u. (a) Reduced dilational elasticity modulus, $\varepsilon/\varepsilon_0$, and (b) reduced dilational viscosity, $\omega/\varepsilon_0\tau_D$. The main figures describe typical viscoelastic relaxation, pure elastic solidlike response at high frequencies ($\varepsilon \sim \varepsilon_0$, $\kappa \sim 0$ at $\omega \gg \tau_D^{-1}$), and dissipative stress relaxation at low frequencies ($\varepsilon < \varepsilon_0$, $\kappa > 0$ at $\omega \leq \tau_D^{-1}$). The effective viscoelastic parameters are largely affected not only by the dynamical state but also by the applied strain. Relaxation of the diffusion process causes the monolayer (a) to soften and (b) to fluidize in dilating at low frequencies, but also, as a consequence of nonlinearity, "thinning" effects emerge when dilating larger (see insets). This nonlinear softening and fluidization happens concomitantly to a larger extent at faster deformations.

stress-strain curves corresponding to the nonrelaxed dynamical state ($\xi_1 \sim 1$) have been plotted for different equilibrium elasticities. Such a hypoelastic material can be conceived to undergo softening behavior under stress. We have recently observed this behavior in *E. Coli* Langmuir monolayers stretched under the action of the trough barriers [36]; in this case, the effective plateau modulus is reached at a value $\sim \varepsilon_0/4$, in agreement with the present model.

In view of the stress-strain relationship, the nonlinear viscoelastic relaxation is discussed again in Fig. 5. The dynamical values of the nonlinear elasticity modulus $\varepsilon(\omega)$ $=\mathrm{Re}[\sigma(u)]/u$ are plotted in Fig. 5(a) and the nonlinear dilational viscosity, calculated as $\kappa(\omega)=\mathrm{Im}[\sigma(u)]/\omega u$, in Fig. 5(b). As expected, the usual linear Maxwell-like relaxation is recovered at zero strain ($u \rightarrow 0$) (see discussion above).

Similar qualitative behavior is observed at increasing strain entering the nonlinear regime, but the viscoelastic parameters take, in general, effective values smaller at higher strain (see insets in Fig. 5). As the system enters the nonrelaxed dynamical regime ($\omega > 1/\tau_D$), the stress softening behavior becomes more and more pronounced, i.e., the effective decrease in elasticity and viscosity as a result of the emergence of modes of nonlinear motion is more efficient at higher frequencies above the diffusional one. The present results point out that the proposed diffusion-driven nonlinear mechanism works in a way such that higher k modes are more efficient than the linear fundamental mode: (a) to redistribute the elastic energy in a variety of modes of motion thus resulting in higher deformations (plasticlike) than if only the hookean mode were present, and (b) to minimize viscous dissipation by flow enhancement. Therefore, a general conclusion can be stated: the k modes developed as a consequence of non-linearity constitute a coupled series of modes of motion able to enhance the viscoelastic response of the system, in a way such that for a given applied stress the deformation is higher and the energy losses lower than if the response was linear.

VIII. CONCLUSIONS

Lateral diffusion in conjunction with natural convection has been considered to drive nonlinear mass transport in Langmuir lipid monolayers. The present model combines the conservative dynamical equations for lipid transport along the monolayer plane together with a material relationship accounting for nonlinear hypoelasticity as experimentally observed in high-strain rheological measurements. For oscillatory motion, nonlinear harmonics are found to be recurrently coupled through a dynamical transfer function governed by the diffusion process, the diffusion characteristic time τ_D being the only controlling parameter. At long times, lateral diffusion is fully relaxed ($t \gg \tau_D$) and the viscoelastic response is found to be essentially linear and characterized by a high viscous dissipation. On the other hand, at deformation times shorter than τ_D, lateral diffusion still has not enough time to become relaxed; then the elastic energy is efficiently distributed by the different nonlinear modes of deformation resulting in a hypoelastic mechanical scenario characterized by larger (plasticlike) deformations and lower viscous friction losses than in the hookean linear regime. In the case of oscillatory motion, the time-dependent viscoelastic relationships arising from this model have been discussed in the context of surface rheology experiments performed in Langmuir monolayers of two different lipid systems, DPPC and native *E. Coli* lipids. The presence of micrometer-sized phase coexistence domains in these lipid systems has been claimed to pump diffusive transport at the experimentally accessible time scales ($t > 1$ s). The nonlinear mechanical response experimentally observed in these lipid systems is found in good quantitative agreement with the theoretical predictions from the model. We hypothesize the present model to appropriately describe the mechanics of lipid membranes under the action of lateral stresses, such as those involved in cell division and motility processes.

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