

Hydrodynamic modes of viscoelastic polymer films

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We discuss the hydrodynamic modes of a thin viscoelastic film of polymeric material at the interface between two Newtonian fluids. The mode dispersion relations and the dynamic structure factor of thermally induced (transverse) modes are obtained by the method of fluctuating hydrodynamics utilizing generalized boundary conditions derived for a thin viscoelastic interface. Specific examples appropriate to liquidlike films of entangled polymers are presented, and possible relevance to existing experimental studies of dynamic light scattering from insoluble polymeric monolayers is discussed.

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I. INTRODUCTION

The properties of fluid interfaces in the presence of surface-active materials has been a very active area of research in the last few decades [1–3]. Studies of such systems have implications in physics, chemistry, and biology, as well as many technological applications. The hydrodynamics of such interfaces is one of the most active and interesting areas of study. The qualitative effects of impurities at a liquid-vapor interface have been known for many years [4,5]; very small amounts of surface-active material strongly damp surface fluctuations. Early theoretical studies identified Gibbs elasticity of the surface impurity as the cause of capillary wave damping, and experimental studies of mechanically generated surface waves on monolayer covered interfaces were carried out [6]. The subsequent development of quasielastic surface light-scattering techniques made possible noninvasive studies of surface hydrodynamics. Recent refinements of this technique allow for extremely precise measurements of the thermally induced modes of fluid interfaces [7,8].

Extensive theoretical studies of the surface light scattering from monolayers at liquid interfaces have been made [9,10]. In a seminal paper, Kramer [9] developed a general theory of light scattering from surface modes of membranes and monolayers. This theory is based on interfacial stress-strain relations for membranes and monolayers with two-dimensional isotropic or hexagonal rotational symmetry and postulated forms for the three independent interfacial viscoelastic moduli. In Ref. [9], the transverse modulus, \mathcal{P} , and the in-plane shear and compressional moduli, \mathcal{S} and \mathcal{K} , respectively, were assumed to have a Voigt form [11]: $\mathcal{S}(\omega) = \mathcal{S}_0 + i\omega\mathcal{S}_1$,

$\mathcal{K}(\omega) = \mathcal{K}_0 + i\omega\mathcal{K}_1$, and $\mathcal{P}(\omega) = \mathcal{P}_0 + i\omega\mathcal{P}_1$; where \mathcal{S}_0 , \mathcal{K}_0 , and \mathcal{P}_0 are the elastic moduli of in-plane shear and compression, and transverse displacement of the membrane, respectively, and where \mathcal{S}_1 , \mathcal{K}_1 , and \mathcal{P}_1 are the associated viscosities [12]. Most other theoretical treatments have followed this approach, although some have excluded the possibility of a transverse viscosity, \mathcal{P}_1 . Experimental light-scattering studies of monolayers of low molecular weight surfactant molecules at liquid-vapor and liquid-liquid interfaces are in good agreement with this picture [13–19]. Similar experiments on monolayers of insoluble polymers have also been carried out [16–24]. These experiments are also in basic accord with existing theory, although some unusual viscoelastic features were observed [22,23]. For a recent review of such experiments, see Ref. [24].

Monolayers, however, are only one class of viscoelastic polymer film that may be present at a liquid-liquid or liquid-vapor interface. One may imagine various types of viscoelastic interfacial films of finite but small thickness. Examples include wetting layers of entangled flexible polymers, insoluble films of entangled polymeric surfactants, and smectic layers of polymer liquid-crystalline materials. The internal structure of such surface films is expected to result in more complex viscoelastic behavior than in the case of classical monolayers discussed above. A more general approach for studying the interfacial viscoelastic behavior of more complex films is to start with a proper hydrodynamic description of the three-component system consisting of two liquid phases and an intermediate viscoelastic phase of finite thickness. This point of view has recently been adopted to discuss the related problem of hydrodynamic modes of a freely suspended soap film containing a viscoelastic liquid [25]. In the limit of a very thin film, however, one may reduce the full three-phase hydrodynamic problem to an effective two-phase problem with interfacial boundary conditions that are derived from the bulk viscoelastic properties of the interfacial material rather than postulat-

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ed *a priori*. This approach allows one to systematically deduce the effect of interfacial structure on the hydrodynamic modes of a viscoelastic interface.

In this paper, we illustrate this scheme by considering the case of a thin isotropic film of viscoelastic material at the interface between two Newtonian liquids. Such a film may serve as a model of an entangled polymer film (e.g., a melt, a concentrated solution, or a gel) at the interface between two dilute polymer solutions. In Sec. II, we present the general hydrodynamic description of the three-phase system consisting of a viscoelastic film and two Newtonian liquids. We then show how this description in the thin-film limit reduces to the equations of motion for two Newtonian liquids with generalized boundary conditions at the liquid-film-liquid interface. Derivation of these boundary conditions is presented in Appendix A. In Sec. III, we present general results for the dispersion relations $\omega(k)$ of the interfacial modes and the structure factor $S(k, \omega)$ of thermally induced transverse modes. Derivation of these results is presented in Appendix B. We illustrate these results by considering two special cases: (i) fluctuations of a polymeric film separating two fluids of the same viscosity and density (the "symmetric interface"), and (ii) fluctuations of a polymeric film at the interface between a Newtonian liquid and vapor (the "free interface"). We compare these results to those of the classical monolayer model discussed in Refs. [9] and [10]. Finally, in Sec. IV, we conclude with a discussion of possible applications of our general model, and with suggestions for possible experiments to check our predictions. A preliminary report of our findings has been published in a recent proceedings volume [26].

II. HYDRODYNAMIC MODEL

We consider two semi-infinite incompressible Newtonian liquids separated by a film of viscoelastic material of thickness d . For the sake of argument, we assume liquid 1 occupies the region $z > d/2$, while liquid 2 occupies the region $z < -d/2$ in equilibrium. We characterize each liquid by its viscosity η_i and density ρ_i for $i=1,2$. Thermal fluctuations or weak externally applied forces will induce small-amplitude modes on the upper and lower boundaries of the film. Under these assumptions, the appropriate linearized equations of motion have the form

$$\rho_i \frac{\partial \mathbf{v}^{(i)}}{\partial t} = \nabla \cdot \boldsymbol{\sigma}^{(i)} + \rho_i \mathbf{g}, \quad (1)$$

$$\nabla \cdot \mathbf{v}^{(i)} = 0, \quad (2)$$

$$\rho_m \frac{\partial \mathbf{v}^{(m)}}{\partial t} = \nabla \cdot \boldsymbol{\sigma}^{(m)} + \rho_m \mathbf{g}, \quad (3)$$

where $\mathbf{v}^{(i)}$ and $\boldsymbol{\sigma}^{(i)}$ for $i=1,2$ are, respectively, the Newtonian liquid velocities and stress tensors; where ρ_m , $\mathbf{v}^{(m)}$, and $\boldsymbol{\sigma}^{(m)}$ denote, respectively, the density, velocity, and stress tensor of the viscoelastic material; and where $\mathbf{g} \parallel -\hat{\mathbf{z}}$ is the acceleration of gravity. Equation (1) is the usual linearized Navier-Stokes equation if $\sigma_{\alpha\beta}^{(i)} = -P^{(i)}\delta_{\alpha\beta} + \eta_i(\nabla_{\alpha}v_{\beta}^{(i)} + \nabla_{\beta}v_{\alpha}^{(i)})$, where we denote components of vectors and tensors by greek indices and

where $\nabla_{\beta} \equiv \partial/\partial x_{\beta}$. Equation (2) is the incompressibility condition for the Newtonian fluids. Equation (3) is the generalization of the Navier-Stokes equation to a linear viscoelastic medium; it must be amended by dynamical equations for the internal degrees of freedom of the viscoelastic medium as discussed in Appendix A.

The solutions to these equations of motion are subject to appropriate boundary conditions on the upper and lower film interfaces. As is usual in hydrodynamic theories, we characterize these interfaces by step-function density profiles and surface tensions γ_i . Then, in addition to requiring continuity of velocity at the interfaces, we also require continuity of shear stress, and the balance of normal stress difference with the Laplace pressure at each deformed interface.

In the limit of a very thin film ($d \rightarrow 0$), the equation of motion of the viscoelastic material and the boundary conditions at the fluid-film interfaces may be replaced by effective boundary conditions between the Newtonian fluids 1 and 2. These are obtained by enforcing conservation of momentum across the viscoelastic interface separating the fluids. As we are interested in relatively long wavelength modes of very thin films ($kd \ll 1$, where k is the mode wave number), we may restrict our attention to transverse undulation modes of the film, i.e., modes in which the upper and lower interfaces fluctuate in phase, approximately maintaining the constant thickness of the film [27]. Then, we may consider the film as a membrane of negligible thickness and characterize its modes by the local transverse and in-plane displacements from equilibrium, ξ and ξ , respectively. In Appendix A, we show that the effective dynamic boundary conditions for such membrane modes have the form

$$[\sigma_{\alpha z}]_{1,2} = P_{\alpha}^{(m)}, \quad (4)$$

where $[f]_{1,2}$ denotes the discontinuity of f across the membrane and $P_{\alpha}^{(m)}$ is the total interfacial force density (given below), including the contributions from the viscoelasticity of the film and from the Laplace pressure of the perturbed fluid-membrane-fluid interface with an effective surface tension γ . Note that the viscoelastic contribution to the boundary conditions is determined in part by the choice of a bulk dynamical constitutive equation for the membrane material. One may use an empirically determined bulk constitutive equation for $\sigma_{\alpha\beta}^{(m)}$, such as a Maxwell model [11], to obtain $P_{\alpha}^{(m)}$. Alternatively, we discuss a very general form of $\sigma_{\alpha\beta}^{(m)}$ appropriate for homogeneous, isotropic viscoelastic materials from the point of view of macroscopic hydrodynamics [28], in which the elastic degrees of freedom are taken to be additional macroscopic slow variables that, however, relax in finite time. Thus, in addition to the usual static elastic and liquidlike viscous responses discussed in the Introduction, we allow for extra frequency-dependent viscoelastic response, the origin of which is in the relaxation of entanglements in a concentrated polymeric film. We also include higher-order viscoelastic bending moduli, for the sake of completeness. This approach is introduced and developed extensively in Appendix A.

As for kinematic boundary conditions, we require sur-

face modes to be localized at the membrane surface, i.e., we impose $v^{(i)} \rightarrow 0$ as $z \rightarrow \pm \infty$; and we require the continuity of velocity at the fluid-membrane-fluid interface,

$$\mathbf{v}^{(1)} = \mathbf{v}^{(2)} = \mathbf{v}^{(m)}. \quad (5)$$

In a linearized theory such as ours, Eqs. (4) and (5) are to be evaluated at $z = \zeta(\mathbf{x}) \approx 0$. Since we are neglecting the thermal degree of freedom, we do not need boundary conditions for heat flow.

In order to study both the mode spectrum and the amplitude-amplitude correlation function of thermally induced membrane fluctuations, we employ the usual method of linear fluctuating hydrodynamics, in which the hydrodynamic currents in fluids 1 and 2 are amended by fluctuating parts with zero means and variances given by generalized fluctuation dissipation relations [29]. The stress tensors in the bulk liquid phases then take the form

$$\sigma_{\alpha\beta}^{(i)} = -P^{(i)}\delta_{\alpha\beta} + \eta_i(\nabla_\alpha v_\beta^{(i)} + \nabla_\beta v_\alpha^{(i)}) + \Sigma_{\alpha\beta}^{(i)}, \quad (6)$$

where $\Sigma_{\alpha\beta}^{(i)}$ are random sources of stress related to dissipation in liquid i through the generalized fluctuation dissipation theorem for incompressible classical fluids

$$\langle \Sigma_{\alpha\beta}^{(i)}(\mathbf{r}, t) \Sigma_{\mu\nu}^{(j)}(\mathbf{r}', t') \rangle = 2k_B T \eta_i (\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}) \times \delta_{ij} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (7)$$

where k_B is Boltzmann's constant, T is the absolute temperature, δ_{ij} is the Kronecker delta function, and $\delta(x - x')$ is the Dirac delta function. We have suppressed the effects of extensional viscosity in Eq. (7) since we are considering the limit of incompressible liquids in regions 1 and 2.

Equations (1), (2), and (4)–(7), together with a dynamical constitutive equation for the viscoelasticity of the membrane material, provide the necessary equations of motion and boundary conditions to determine the membrane mode spectrum and fluctuation amplitude correlations.

It suffices to consider the case of plane waves of wave vector k and frequency ω propagating along, say, the x direction. Then, the macroscopic dynamics approach leads to $P_\alpha^{(m)}$ in the boundary conditions [Eq. (4)] of the form $P_\alpha^{(m)} = \mathcal{C}^{(\alpha)}(k, \omega)(ik^2/\omega)v_\alpha^{(m)}$ with

$$\mathcal{C}^{(x)}(k, \omega) = \varepsilon + i\omega v_\parallel + \frac{i\omega\tau_\parallel c_\parallel}{1 + i\omega\tau_\parallel}, \quad (8)$$

$$\mathcal{C}^{(y)}(k, \omega) = i\omega v_s + \frac{i\omega\tau_s c_s}{1 + i\omega\tau_s}, \quad (9)$$

$$\mathcal{C}^{(z)}(k, \omega) = \gamma + i\omega(v_\perp + v_b k^2) + \frac{i\omega\tau_\perp}{1 + i\omega\tau_\perp}(c_\perp + c_b k^2), \quad (10)$$

where γ is the effective surface tension of the fluid-membrane-fluid interface; ε is the static uniaxial compressional modulus; v_\parallel , v_s , and v_\perp are, respectively, the liquidlike uniaxial dilational viscosity, surface shear viscosity, and transversal viscosity; and where the

dynamical contribution to the film viscoelasticity due to polymer entanglements is characterized by transient uniaxial-compressional, shear, and transverse moduli, c_\parallel , c_s , and c_\perp , and by associated relaxation times, τ_\parallel , τ_s , and τ_\perp , as discussed in Appendix A. In addition to these terms, we include in the surface viscoelasticity term corresponding to transverse displacements [Eq. (10)] the possibility of a transverse-bending mode viscosity v_b , and a dynamic viscoelastic bending modulus c_b with corresponding relaxation time τ_\perp , i.e., the same relaxation time as for c_\perp . Note that the dynamic viscoelastic terms in Eqs. (8)–(10) corresponding to relaxation of entanglements are equivalent to those obtained within the context of a Maxwell rheological model.

III. RESULTS

Localized surface mode solutions of Eqs. (1), (2), and (4)–(10) include in-plane shear modes, in-plane compressional modes, and transverse modes. Due to the isotropic rotational symmetry of the polymer films under consideration, the shear modes decouple from the others. Furthermore, in-plane shear modes are not easily observable with conventional radiation scattering techniques. So, we ignore the shear modes, and assume $\mathbf{v} = \mathbf{v}(x, z)$ and $\mathbf{v} \cdot \hat{\mathbf{y}} = 0$. In general, however, the transverse modes and in-plane compressional modes are coupled. The general film dispersion relation $\omega(k)$, and the dynamic structure factor $S(k, \omega)$ of thermally induced transverse modes are derived in Appendix B. The resulting expressions for $\omega(k)$ and $S(k, \omega)$ are given by Eqs. (B24) and Eqs. (B26)–(B28). These are rather involved so we will not reproduce them here. Rather, in the next two subsections, we discuss two interesting limiting cases. The first case (the symmetric interface) corresponds to the limit of equal fluid viscosities $\eta_1 = \eta_2$ and equal fluid densities $\rho_1 = \rho_2$. In this limit, transverse and compressional modes are decoupled, and $S(k, \omega)$ is independent of $\mathcal{C}^{(x)}(k, \omega)$. This is a consequence of reflection symmetry with respect to the x - y plane; from a hydrodynamic point of view fluids 1 and 2 are identical in this limit. The second case (the free interface) corresponds to the limit of vanishing η and ρ for the fluid in one region. This limit is essentially the case of a viscoelastic film at a liquid-vapor interface, an often studied situation [16–23]. In this limit, the coupling between transverse and compressional modes is maximized.

A. Modes of a symmetric interface

In the limit of equal fluid viscosities and densities, the compressional and transverse modes of the film are independent, with dispersion relations obtained from Eq. (B24) in the limit $\eta_1 = \eta_2 = \eta$ and $\rho_1 = \rho_2 = \rho$. These are given by

$$\omega^2 = \frac{k^2(q - k)\mathcal{C}^{(x)}(k, \omega)}{2\rho}, \quad (11)$$

$$\omega^2 = \frac{k^3(q - k)\mathcal{C}^{(z)}(k, \omega)}{2\rho q}, \quad (12)$$

where $q/k = (1 + i\rho\omega/\eta k^2)^{1/2}$ and where $\mathcal{C}^{(x)}$ and $\mathcal{C}^{(z)}$

are given by Eqs. (8) and (10). Equation (11) is the implicit dispersion relation of uniaxial compression modes, while Eq. (12) is that of the transverse modes. The corresponding dynamic structure factor of thermally induced transverse modes is obtained from Eqs. (B26)–(B28) in the limit $\eta_1 = \eta_2 = \eta$ and $\rho_1 = \rho_2 = \rho$; we find

$$S(k, \omega)_{\text{sym}} = \frac{k_B T \Lambda_{\text{sym}}(k, \omega)}{|\omega^2 - \mathcal{C}^{(z)}(k, \omega) k^3 / 2\rho + ik(q+k)\eta\omega/\rho|^2}, \quad (13)$$

where $\Lambda_{\text{sym}}(k, \omega) = \eta k^2 |q+k|^2 / (2\rho^2 \text{Re}[q])$ and where the subscript label sym indicates the symmetric interface limit. Notice that $S(k, \omega)_{\text{sym}}$ is independent of all *in-plane* viscoelastic moduli and viscosities. In the absence of viscoelastic material at the liquid-liquid boundary, Eqs. (12) and (13) reduce to expressions for the capillary fluctuations of a symmetric liquid-liquid interface [30], in which case the dynamic structure factor $S(k, \omega)_{\text{sym}}$ in the low fluid viscosity limit has a peak at $\omega_0 = (\gamma/2\rho)^{1/2} k^{3/2}$ of width $\Delta\omega_0 = 4\eta k^2 / \rho$. The presence of viscoelastic material can modify the mode spectrum in interesting ways. Consider the case of a thin film of concentrated polymer solution at a liquid-liquid interface as might occur, for example, when it is energetically favorable for polymers in solution to wet the interface between two immiscible solvents. In the simplest model of such a scenario, the viscoelastic interface may be characterized by an effective surface tension γ , and by a transient modulus c_\perp and relaxation time τ_\perp due to polymer entanglements (a Maxwell model). Thus, for simplicity, we ignore the viscoelastic bending modulus and interfacial viscosities in $\mathcal{C}^{(z)}$, and write $\mathcal{C}^{(z)}(k, \omega) = \gamma + c^*(\omega)$ with $c^*(\omega) = i\omega\tau_\perp c_\perp / (1 + i\omega\tau_\perp)$. Qualitatively, the viscoelastic contribution $c^*(\omega)$ provides an effective transverse viscosity at moderate frequencies ($\omega \approx 1/\tau_\perp$) and augments the effective surface tension at high frequencies. Thus, the peak width $\Delta\omega$ is anomalously broadened at intermediate k and the peak position ω_p is shifted to higher frequencies at high k . In Fig. 1, we give plots of ω_p and $\Delta\omega$ vs k for $\gamma = 40$ dyn/cm, $\eta = 10^{-2}$ poise, $\rho = 1$ g/cm³, $\tau_\perp = 3 \times 10^{-5}$ sec, and $c_\perp = 2, 4, 6,$ and 8 dyn/cm. Figure 1(a) shows ω_p normalized by the peak position for a bare symmetric interface, $\omega_0 = (\gamma/2\rho)^{1/2} k^{3/2}$, and plotted against k . Notice that the peak position is essentially unaffected by interfacial viscoelasticity for $k < 200$ cm⁻¹, but that ω_p increases monotonically with k for $k > 200$ cm⁻¹. Figure 1(b) shows $\Delta\omega$ normalized by the intrinsic peak width for a bare symmetric interface, $\Delta\omega_0 = 4\eta k^2 / \rho$, and plotted against k . Notice that the peak width increases sharply at $k \approx 350$ cm⁻¹, corresponding to the crossover frequency $\omega(k) \approx 1/\tau_\perp$. In both the plots of ω_p and $\Delta\omega$, the viscoelastic effects become more pronounced for larger values of the transient stretching modulus c_\perp . We note, however, that in realistic situations c_\perp is probably quite small, and that the effects shown in Fig. 1 might be difficult to observe in practice.

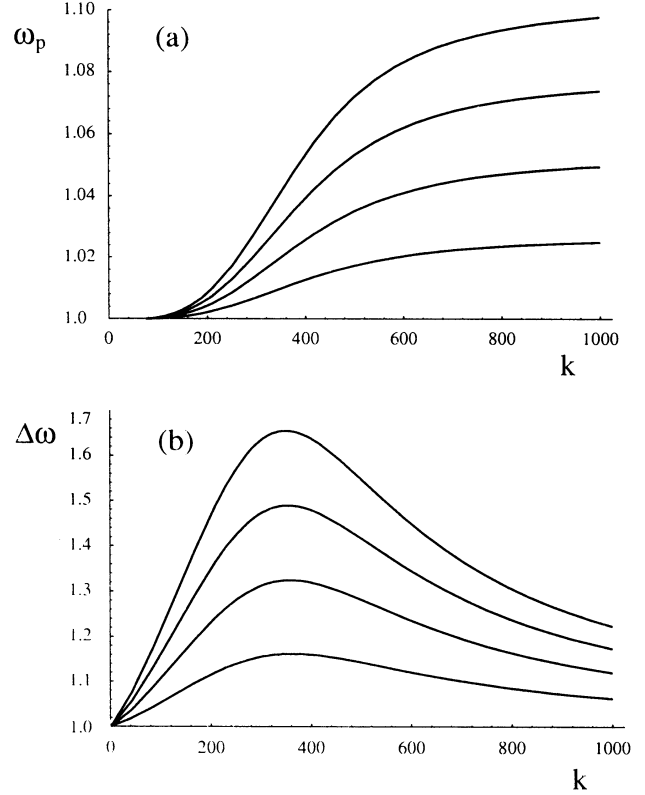


FIG. 1. Plots of dimensionless ω_p and $\Delta\omega$ vs k in units of cm⁻¹ for $\gamma = 40$ dyn/cm, $\eta = 10^{-2}$ poise, $\rho = 1$ g/cm³, $\tau_\perp = 3 \times 10^{-5}$ sec and $c_\perp = 2, 4, 6,$ and 8 dyn/cm (bottom to top). (a) shows ω_p normalized by the peak position for a bare symmetric interface, $\omega_0 = (\gamma/2\rho)^{1/2} k^{3/2}$, and plotted against k . (b) shows $\Delta\omega$ normalized by the intrinsic peak width for a bare symmetric interface, $\Delta\omega_0 = 4\eta k^2 / \rho$, and plotted against k .

B. Modes of a free interface

The limit of vanishing density and viscosity in one fluid region corresponds to the case of a viscoelastic film at a liquid-vapor interface. The interface mode dispersion relation in this limit is obtained from Eq. (B24) with $\rho_1 \rightarrow 0$ and $\eta_1 \rightarrow 0$; we find an implicit dispersion relation $D(k, \omega)_{\text{fr}} = 0$ with

$$D(k, \omega)_{\text{fr}} = [\tilde{\mathcal{C}}^{(z)}(k, \omega) k^3 + i\eta k(q+k)\omega - \rho\omega^2] \times [\mathcal{C}^{(x)}(k, \omega) k^3 + i\eta k(q+k)\omega] + \eta^2 k^2 (q-k)^2 \omega^2 \quad (14)$$

where $\tilde{\mathcal{C}}^{(z)}(k, \omega) = \mathcal{C}^{(z)}(k, \omega) + g/k^2$, $\rho_2 = \rho$, $\eta_2 = \eta$, $q/k = (1 + i\rho\omega/\eta k^2)^{1/2}$, and where $\mathcal{C}^{(x)}$ and $\mathcal{C}^{(z)}$ are given by Eqs. (8) and (10). Equation (14) is the generalization of the well-known Lucassen mode dispersion relation [6,9,10] to more general viscoelastic interfaces. The corresponding dynamic structure factor of thermally induced transverse modes obtained from Eqs. (B26)–(B28) in the limit $\rho_1 \rightarrow 0$ and $\eta_1 \rightarrow 0$ is given by

$$S(k, \omega)_{\text{fr}} = \frac{k_B T \Lambda_{\text{fr}}(k, \omega)}{|D(k, \omega)_{\text{fr}}|^2} \quad (15)$$

where the subscript label fr indicates the free interface

limit, and $D(k, \omega)_{\text{fr}}$ is given in Eq. (14) and $\Lambda_{\text{fr}}(k, \omega)$ is given by

$$\Lambda_{\text{fr}}(k, \omega) = \frac{8\rho^2\eta k^5}{|q-k|^2} \left\{ \omega^4\lambda_1 - \omega^2(\lambda_2 \text{Re}[\mathcal{C}^{(x)}]) - \lambda_3 \text{Im}[\mathcal{C}^{(x)}] + \lambda_4 |\mathcal{C}^{(x)}|^2 \right\} \quad (16)$$

with

$$\begin{aligned} \lambda_1 &= 1 - \text{Im}[q]/(\beta k), \\ \lambda_2 &= k^2|q-k|^2/(2 \text{Re}[q]\rho), \\ \lambda_3 &= k^2|q-k|^2/(\text{Im}[q]\rho), \\ \lambda_4 &= \beta \text{Im}[q]k^5/(4\rho^2), \end{aligned} \quad (17)$$

where $\text{Re}[f]$, $\text{Im}[f]$, and $|f|$ denote, respectively, the real part, the imaginary part, and the modulus of f ; and $\beta \equiv \rho\omega/\eta k^2$. Equations (14)–(17) reduce to the classical theory for the surface hydrodynamics of monolayers discussed in the Introduction [6,9,10] if $\mathcal{C}^{(x)} = \varepsilon + i\omega\nu_{\parallel}$ and $\mathcal{C}^{(z)} = \gamma + i\omega\nu_{\perp}$. The general viscoelastic response is more complex, however. Consider the idealized case where $\mathcal{C}^{(x)} = \varepsilon + i\omega\nu_{\parallel} + c^*(\omega)$ and $\mathcal{C}^{(z)} = \gamma + i\omega\nu_{\perp} + c^*(\omega)$ with $c^*(\omega) = i\omega\tau c_0/(1+i\omega\tau)$. Here we assume, for simplicity, a single characteristic viscoelastic response $c^*(\omega)$ due to entanglements for both transverse and compressional modes of the film. In Figs. 2 and 3, we give plots of peak position ω_p and peak width $\Delta\omega$ vs ε/γ at $k=200$

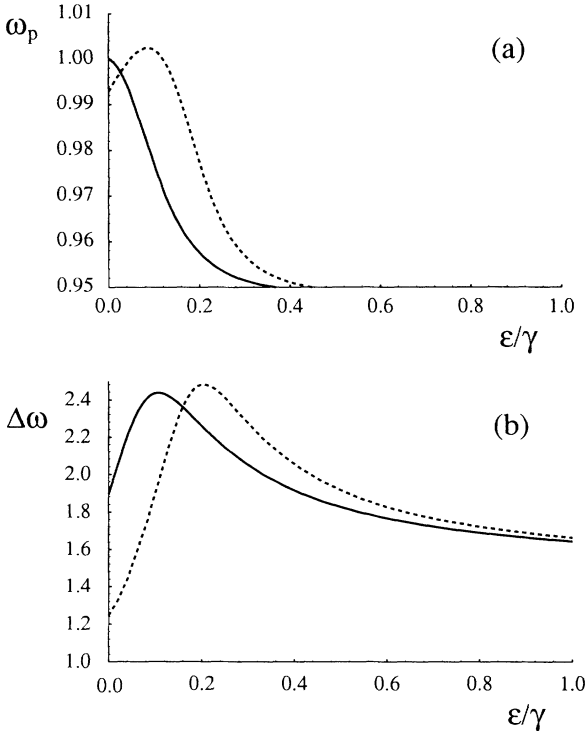


FIG. 2. Plots of dimensionless peak position ω_p and peak width $\Delta\omega$ vs ε/γ at $k=200 \text{ cm}^{-1}$ for $c_0=4 \text{ dyn/cm}$, $\gamma=40 \text{ dyn/cm}$, $\eta=10^{-2} \text{ poise}$, $\rho=1 \text{ g/cm}^3$, $\nu_{\parallel}=10^{-4} \text{ surface poise}$, and $\nu_{\perp}=0 \text{ surface poise}$. (a) shows a plot of ω_p for $\tau=10^{-3} \text{ sec}$ normalized by the peak position for a bare free interface, $\omega_0=(\gamma/\rho)^{1/2}k^{3/2}$. (b) shows the corresponding plot of $\Delta\omega$ normalized by the intrinsic peak width for a bare free interface, $\Delta\omega_0=4\eta k^2/\rho$. The dashed curves are those corresponding to $c^*(\omega)=0$, i.e., the analogous classical results.

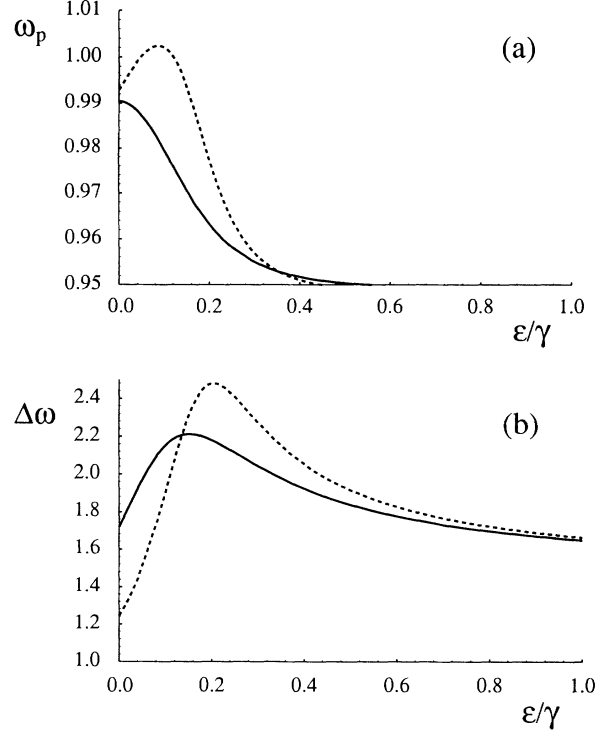


FIG. 3. Plots of dimensionless peak position ω_p and peak width $\Delta\omega$ vs ε/γ at $k=200 \text{ cm}^{-1}$. Parameters are chosen as in Fig. 2, except that $\tau=10^{-4} \text{ sec}$.

cm^{-1} for $c_0=4 \text{ dyn/cm}$, $\gamma=40 \text{ dyn/cm}$, $\eta=10^{-2} \text{ poise}$, $\rho=1 \text{ g/cm}^3$, $\nu_{\parallel}=10^{-4} \text{ surface poise}$, and $\nu_{\perp}=0 \text{ surface poise}$. Figure 2(a) shows a plot of ω_p for $\tau=10^{-3} \text{ sec}$ normalized by the peak position for a bare free interface, $\omega_0=(\gamma/\rho)^{1/2}k^{3/2}$; while Fig. 2(b) shows the corresponding plot of $\Delta\omega$ normalized by the intrinsic peak width for a bare free interface, $\Delta\omega_0=4\eta k^2/\rho$. Figure 3 shows analogous plots of ω_p and $\Delta\omega$ for $\tau=10^{-4} \text{ sec}$. In both plots, the dashed curves are those corresponding to $c^*(\omega)=0$, i.e., the analogous classical results. Notice that while the anomalous film viscoelasticity has only a small effect on the peak positions, it has a significant effect on the broadening of the peaks; the apparent static Gibbs modulus ε at which peak width is maximized decreases in the presence of viscoelasticity due to entanglements. This behavior is inherently frequency dependent, as can be seen by comparing Figs. 2(b) to Fig. 3(b). At a given frequency ω , the film depicted in Fig. 2 (with $\tau=10^{-3}$) is more solidlike (elastic) than the film depicted in Fig. 3 (with $\tau=10^{-4}$). We should add that the qualitative behavior in Figs. 2 and 3 is unchanged if we suppress transverse viscoelastic effects and write $\mathcal{C}^{(z)} = \gamma + i\omega\nu_{\perp}$; the broadening of the peak in $S(k, \omega)_{\text{fr}}$ is controlled primarily by the coupling of the propagating transverse and in-plane modes of the film, and hence is most sensitive to the entanglement contribution to the compressional viscoelasticity.

IV. DISCUSSION

We have presented a general theoretical approach for the hydrodynamics of thin viscoelastic films at liquid-

liquid and liquid-vapor interfaces based on the method of linear fluctuating hydrodynamics utilizing generalized boundary conditions obtained from the bulk viscoelastic properties of the interface material. We have illustrated this approach for the case of homogeneous and isotropic polymeric films characterized by an idealized constitutive equation modeling the effects of polymer entanglements on film viscoelasticity.

In Sec. III A, we showed that at finite frequencies the viscoelastic stretching modulus of the film augments the effective interfacial tension and provides an extra source of dissipation. As a result, the peak of the dynamic structure factor of the thermally induced transverse-mode shifts to higher frequency with increasing k [i.e., $\omega(k)$ grows with k somewhat faster than $k^{3/2}$ at high k ; cf. Fig. 1(a)]. Also, the peak width $\Delta\omega(k)$ is anomalously broadened at intermediate k [cf. Fig. 1(b)]. For realistic films, these effects may be quite modest since c_{\perp} is expected to be quite small.

In Sec. III B, we considered the effect of film viscoelasticity on the coupling between transverse modes and in-plane compressional modes. In the conventional Lucassen picture of monolayer hydrodynamics [6,9,10], coupling between transverse and in-plane compressional modes results in broadening of the peak in the transverse-mode dynamic structure factor, $S(k, \omega)$. This broadening is maximized for a static Gibbs modulus $\varepsilon \approx 0.2\gamma$. However, in the present case the complex, frequency-dependent contribution to the in-plane compressional modulus due to entanglements significantly alters the *apparent* maximizing value of ε [cf. Figs. 2(b) and 3(b)]. Such interfacial viscoelasticity due to entanglements could complicate the interpretation of dynamic light-scattering data.

The theory we have presented may have some relevance to recent dynamic light-scattering studies of insoluble polymer monolayers at liquid-liquid and liquid-vapor interfaces [16–22]. In these experiments, the surface tension γ and static Gibbs elasticity ε of polymeric monolayers as a function of surface coverage Γ were monitored in a Langmuir trough simultaneously with dynamic light-scattering studies of transverse interfacial modes. In these studies, dynamic light-scattering results were analyzed using the classical theory discussed in the Introduction [9,10]; and for the most part, theory and experiment were consistent, especially at low to moderate surface coverages. Some unusual features were observed in several studies, however, especially at high surface coverage including (i) a significant discrepancy between measured static and dynamic surface elasticities at high Γ , and (ii) an unusual double maximum in the transverse-mode peak width $\Delta\omega$ vs surface coverage Γ [22]. The former feature is quite plausibly a viscoelastic effect of the sort discussed in this work. The latter feature was explained in terms of a nonmonotonic dependence of ε on Γ [22]. However, we suggest that a viscoelastic interpretation is also possible. Very recent electrocapillary wave diffraction studies of cellulose-based polymer monolayers have reported effective compressional moduli and surface viscosities, $\varepsilon(\omega)$ and $\kappa(\omega)$, with unusual frequency dependencies, and have qualitatively

analyzed the viscoelastic properties of these monolayers in terms of a phenomenological Maxwell model of surface viscoelasticity [23]. We should note that chain entanglements are relatively ineffective in true two-dimensional (2D) polymer monolayers. However, at sufficiently high Γ monolayers may buckle, leading to films of finite thickness in which entanglements might play a role in the surface viscoelasticity. Alternatively, films subjected to high surface pressures may also respond by formation of loops in the solvent subphase(s). Hydrodynamic and direct interactions between such loops might also contribute to the effective viscoelastic properties of the films [23].

There are several interesting experimental scenarios in which our hydrodynamic model may be applied. For instance, dynamic light scattering might be used to monitor the process of adsorption or wetting of polymer at a liquid-vapor interface from solution as a function of solvent quality and polymer concentration. The viscoelastic behavior of very thin films would be essentially like that of monolayers, while for thicker films viscoelastic effects due to chain entanglements would play an increasing role [31]. Another interesting possibility would be to use dynamic light scattering to study the gel-sol transition in polymer wetting films. In this case, the characteristic relaxation times associated with chain entanglements diverge at the gel transition, leading to essentially different viscoelastic behavior in the gel and sol regimes. This effect perhaps could be probed by dynamic light-scattering techniques.

The theoretical approach described in this paper may be extended to include anisotropic films and membranes with internal structure such as films of copolymeric surfactants, liquid crystalline polymer materials, or hybrid macromolecular materials. One must then modify the procedure described in Appendix A to deduce the appropriate generalized boundary conditions from the known viscoelastic properties of the analogous bulk phase of the material.

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APPENDIX A

We consider a thin film separating two Newtonian fluids. On hydrodynamic length scales, we may regard the film as a membrane of negligible thickness which we assume lies in the $z=0$ plane. The region $z > 0$ contains fluid 1, while the region $z < 0$ contains fluid 2. The conservation of linear momentum in both regions implies [32]

$$\dot{g}_{\alpha}^{(i)} = \nabla_{\beta} \sigma_{\alpha\beta}^{(i)}, \quad (\text{A1})$$

where $\dot{g}_{\alpha}^{(i)}$ and $\sigma_{\alpha\beta}^{(i)}$ are, respectively, the components of

the linear momentum density and the stress tensor in fluid i , and where the Einstein convention on summation over repeated greek indices is implied everywhere. Consider a cylinder of volume V containing a small area ΔA of membrane and aligned parallel to the z axis, as shown in Fig. 4. Integration of Eq. (A1) inside the cylinder using the divergence theorem of vector calculus yields

$$\int_V \dot{g}_\alpha^{(i)} dV = \int_{\partial V} \sigma_{\alpha\beta}^{(i)} df_\beta, \quad (\text{A2})$$

where ∂V denotes the surface of the cylinder, and df_β are the components of the local surface normal multiplied by an infinitesimal area element. The contribution to the surface integral in Eq. (A2) from the cylindrical mantle vanishes by symmetry, giving

$$\int_{\partial V} \sigma_{\alpha\beta}^{(i)} df_\beta = (\sigma_{\alpha z}^{(1)} - \sigma_{\alpha z}^{(2)}) \Delta A. \quad (\text{A3})$$

In the limit $V \rightarrow 0$, the volume integral in Eq. (A2) is governed solely by the momentum density at the membrane surface and we have

$$\int_V \dot{g}_\alpha^{(i)} dV = \nabla_\beta \sigma_{\alpha\beta}^{(m)} \Delta A, \quad (\text{A4})$$

where $\sigma_{\alpha\beta}^{(m)}$ is the surface stress tensor of the membrane (i.e., a surface energy per unit area), and where we have used the equation of linear momentum conservation in the membrane $\dot{g}_\alpha^{(m)} = \nabla_\beta \sigma_{\alpha\beta}^{(m)}$. Putting together Eqs. (A3) and (A4), we obtain an effective boundary condition

$$(\sigma_{\alpha z}^{(1)} - \sigma_{\alpha z}^{(2)}) = \nabla_\beta \sigma_{\alpha\beta}^{(m)} \quad (\text{A5})$$

for the discontinuity of stress across the membrane.

In order to complete the derivation of the stress boundary conditions, we must relate the viscoelastic surface stress tensor $\sigma_{\alpha\beta}^{(m)}$ to the corresponding bulk material constitutive relation. For purely elastic materials, the usual approach to this problem amounts to obtaining the strain energy per unit area \mathcal{E} by integration of the deformation free energy per unit volume e across the film [33–35]. The deformation energy per unit volume is assumed to be a function of the spatial derivatives of the film deformation profile $u_\alpha(x, y, z)$, i.e., $e = e(\nabla_\beta u_\alpha)$. If the film deformation profile is homogeneous, there are only shear,

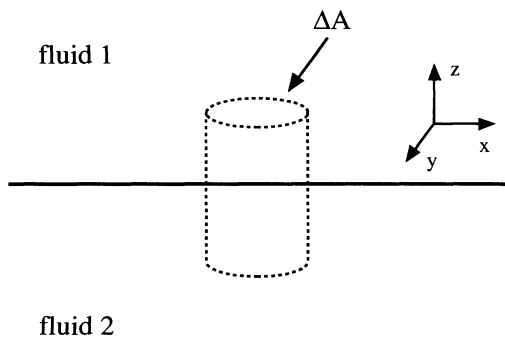


FIG. 4. Sketch of a small cylinder of volume V intersecting a thin film which separates two Newtonian fluids. On hydrodynamic length scales, we may regard the film as a membrane of negligible thickness positioned at the $z=0$ plane. The cylinder is assumed to be aligned parallel to the z axis, and contain a small area ΔA of membrane.

stretching, and compressional terms in the corresponding strain energy per unit area. However, for more general deformations there are also bending energy contributions which depend on the local film curvature. One may see this by considering a deformation profile that depends linearly on z , with a coefficient that depends on the local film deformation: $u_\alpha(x, y, z) = u_\alpha(x, y) + f[\nabla_\beta u_\alpha]_z$ for $\beta=1, 2$. Expansion of such an $e(\nabla_\beta u_\alpha)$ around the film midpoint $z=0$ to second order in z and integration of the resulting expression across the film yields an \mathcal{E} which is the sum of in-plane elastic terms proportional to the film thickness d multiplied by e , and bending energy terms proportional to d^3 and depending on second derivatives $\nabla_\alpha \nabla_\beta u_\gamma$. A general mathematical discussion of this approach including a detailed discussion of membrane mechanical stability issues can be found in Ref. [35] and references therein.

For the case of linear elasticity, this procedure is equivalent to the classical theory of thin elastic plates and shells (see, for instance, Ref. [33]), in which $\mathcal{E} = \mathcal{E}_p + \mathcal{E}_b$ with in-plane and bending contributions given by

$$\mathcal{E}_p = \frac{d}{2} \sigma_{\alpha\beta} \epsilon_{\alpha\beta}, \quad (\text{A6})$$

$$\mathcal{E}_b = \frac{\mu d^3}{24(1-\sigma)} (\Delta_\perp \xi)^2 + \frac{\mu d^3}{12} [(\nabla_x \nabla_y \xi)^2 - \nabla_x^2 \xi \nabla_y^2 \xi], \quad (\text{A7})$$

where $\sigma_{\alpha\beta} = 2\mu \epsilon_{\alpha\beta} + (K - 2\mu/3) \epsilon_{\gamma\gamma} \delta_{\alpha\beta}$ is the usual stress tensor of a linear elastic solid with shear modulus μ , compression modulus K , and $\epsilon_{\alpha\beta}$ is the 2D membrane strain tensor

$$\epsilon_{\alpha\beta} = \frac{1}{2} (\nabla_\beta u_\alpha + \nabla_\alpha u_\beta)_{z=0} \quad (\text{A8})$$

and where σ is Poisson's ratio, and $\Delta_\perp \equiv \nabla_x^2 + \nabla_y^2$.

The analysis for isotropic linear viscoelastic materials is analogous to the case of linear elasticity presented above. The principle difference is that the deformation energy density $e(t)$ is a history-dependent quantity which relaxes for sufficiently long times. The terms in the strain energy per unit area \mathcal{E} inherit their history dependence from the bulk deformation energy density [e.g., $\mathcal{E}_p(t) = e(t)d$]. There are many schemes used to model the bulk viscoelastic properties of materials. The traditional approach is to use a phenomenological constitutive equation relating stress to strain history, which is either postulated *a priori* or obtained empirically. In this case, one generally has $\sigma_{\alpha\beta}(t) = \int_{-\infty}^t G(t-t')_{\alpha\beta\gamma\delta} \dot{\epsilon}_{\gamma\delta}(t')$ for the bulk viscoelastic material. The Maxwell model, with $G(t)_{\alpha\beta\gamma\delta} \sim \exp(-t/\tau)$, is a typical example of such a constitutive equation [11]. In frequency space, this approach entails frequency dependent moduli, e.g., $\mu = \mu(\omega)$, $K = K(\omega)$, etc. Then for the case of thin viscoelastic films, one simply obtains $\mathcal{E}(\omega)$ from Eqs. (A6) and (A7) with the relevant $\mu(\omega)$ and $K(\omega)$. The corresponding interfacial force densities, $P_\alpha^{(m)}$, due to film viscoelasticity are then easily obtained from $\mathcal{E}(\omega)$.

We adopt an alternative approach in the following which is somewhat less phenomenological. Rather than assuming a dynamical constitutive equation $\sigma_{\alpha\beta}(\omega)$ for

the membrane stress tensor, we treat the displacement field u_α as a slowly relaxing field within the context of macroscopic dynamics [28], in which very slowly relaxing fields are included among the list of true hydrodynamic variables of a system in the formulation of its linear irreversible thermodynamics. This approach has been utilized to describe the dynamics of the λ transition in ^4He [36], and more recently has applied to the dynamics of polymeric liquids [28] and liquid crystalline polymeric elastomers [37]. In the present context, this approach reduces to the usual Maxwell model of rheological behavior. We utilize the macroscopic dynamics approach, however, since it is less *ad hoc* than the traditional rheological modeling and since it is rather a general approach which may be extended to nonisotropic materials with additional internal degrees of freedom. As this approach is developed extensively for bulk polymeric liquids in Ref. [28], and the connection between bulk and interfacial viscoelasticity is discussed above, we only present an abbreviated derivation in the following.

In an isotropic single-component viscoelastic membrane, the rigorous hydrodynamic variables corresponding to conserved quantities are the membrane density ρ_m , the interfacial linear momentum density $g_\alpha^{(m)}$, and the energy density \mathcal{E} . In the case that the viscoelastic membrane is a two-component mixture (as in the case of a thin film of semidilute polymer solution) we would also include the local concentration ϕ of one constituent as a hydrodynamic variable. In addition to these true hydrodynamic variables, we also keep the elastic displacement field u_α as a quasihydrodynamic variable which relaxes in a large but finite time. Since the membrane separates two bulk samples of immiscible liquids, the thermodynamic state of the interfacial region also depends on the area A of the membrane. We treat this dependence separately from the thermodynamic description of the membrane itself. Thus, in the hydrodynamic regime, the membrane is locally in thermodynamic equilibrium and satisfies the following Gibbs-Duhem relation:

$$T ds = d\mathcal{E} - \mu d\rho_m - v_\alpha dg_\alpha^{(m)} - \psi_{\alpha\beta} d\epsilon_{\alpha\beta}, \quad (\text{A9})$$

where s is the local entropy per unit area. Equation (A9) gives the variation of the entropy per unit area s with the changes in the other thermodynamic variables. Since the properties of the system are invariant under homogeneous displacements and rotations, the appropriate quasihydrodynamic variable appearing in Eq. (A9) and below is the symmetrized 2D strain tensor $\epsilon_{\alpha\beta}$ rather than the displacement field u_α . The quantities T , μ , v_α , and $\psi_{\alpha\beta}$ are the thermodynamic forces that are conjugate to the above thermodynamic variables. Note that all quantities are independent of the z coordinate within an infinitesimally thin film, and in particular that $\nabla_z u_\alpha = 0$. The thermodynamic forces are generally obtained by variation of the total free energy of the film $E = \int \mathcal{E}(x, y) dx dy$ with respect to the relevant thermodynamic variable. For instance, the surface stress $\psi_{\alpha\beta}$ conjugate to $\epsilon_{\alpha\beta}$ is given by $\psi_{\alpha\beta} = \delta E / \delta \epsilon_{\alpha\beta} | \dots$, where $| \dots$ indicates that all other thermodynamic variables are held constant. Within

linear thermodynamics, the total energy is the most general bilinear function of the thermodynamic variables that is consistent with all fundamental invariance properties of the system (e.g., time-reversal symmetry, translational and rotational symmetry, symmetry under spatial parity transformations, etc.). Thus, the corresponding thermodynamic forces are linear functions of the thermodynamic variables. Of particular interest in our case is the form of the surface stress $\psi_{\alpha\beta}$. In the absence of cross couplings to thermodynamic variables other than $\epsilon_{\alpha\beta}$, we find

$$\psi_{\alpha\beta} = (c_k + c_s) \epsilon_{\gamma\gamma} \delta_{\alpha\beta} + 2c_s \epsilon_{\alpha\beta} + (c_\perp - c_b \Delta_\perp) \epsilon_{\alpha z} \delta_{\beta z}, \quad (\text{A10})$$

where $\Delta_\perp \equiv \nabla_x^2 + \nabla_y^2$ and where c_k and c_s are, respectively, the in-plane compression and shear elastic constants, and c_\perp and c_b are, respectively, the transverse stretching and bending elastic constants. It is convenient in the following to define a uniaxial compressional modulus $c_\parallel \equiv c_k + c_s$. The membrane elastic constants are given in terms of the corresponding transient bulk elastic constants of compression and shear, K and μ , Poisson's ratio σ of the material, and the film thickness d by $c_\parallel = (K + \mu)d$, $c_s = \mu d$, $c_\perp \sim c_s$, and $c_b = \mu d^3 / 12(1 - \sigma)$ [cf. Eqs. (A6)–(A8)]. There is only one curvature elastic contribution (c_b), related to the mean curvature of the surface, since the second part of Eq. (A7) does not contribute to $\psi_{\alpha\beta}$.

We will now discuss the appropriate dynamic equations. The conservation laws for the areal density and density of linear momentum are given by

$$\dot{\rho}^{(m)} + \nabla_\alpha g_\alpha^{(m)} = 0, \quad (\text{A11})$$

$$\dot{g}_\alpha^{(m)} = \nabla_\beta \sigma_{\alpha\beta}^{(m)}, \quad (\text{A12})$$

where $\sigma_{\alpha\beta}^{(m)}$ is the membrane surface stress tensor, the sign of which is chosen to conform to the usual Navier-Stokes equation in the case of a viscous liquid film. Note that the density of linear momentum $g_\alpha^{(m)}$ is both a hydrodynamic variable and the current of the areal density [cf. Eqs. (A9) and (A12)]. The corresponding dynamical equations for the nonconserved variables $\epsilon_{\alpha\beta}$ and s are

$$\dot{\epsilon}_{\alpha\beta} + X_{\alpha\beta} = 0, \quad (\text{A13})$$

$$\dot{s} + \nabla_\alpha j_\alpha = \frac{R}{T}, \quad (\text{A14})$$

where j_α is the entropy current, R/T is the entropy production ($R \geq 0$, as required by the second law of thermodynamics), and $X_{\alpha\beta}$ is the quasicharge associated with the strain tensor field $\epsilon_{\alpha\beta}$. In a Newtonian fluid the dynamical equation for $\epsilon_{\alpha\beta}$ would be absent, since there the strains relax on a microscopic time scale. The conservation equation for membrane energy density \mathcal{E} is obtained from Eqs. (A10)–(A14). In the following, howev-

er, we focus on the dynamical equations (A11)–(A13) for density, momentum density and strain field.

In order to close our set of equations (A10)–(A14), we must relate the currents and quasicurrents $g_\alpha^{(m)}$, $\sigma_{\alpha\beta}^{(m)}$, s , and $X_{\alpha\beta}$ to the thermodynamic forces T , μ , v_α , and $\psi_{\alpha\beta}$, taking into account all symmetries of the system. Within linear macroscopic dynamics, these currents are linearly related to the thermodynamic forces, and in general are the sum of reversible and dissipative contributions. The reversible parts may be obtained using general symmetry and invariance arguments alone. Their dissipative counterparts are obtained from functional derivatives of the dissipation function R , which is the most general bilinear function of the thermodynamic forces that is consistent with all symmetry and invariance properties of the system, and the requirement of positive definite entropy production $R \geq 0$. For example, the dissipative part of the strain quasicurrent $X_{\alpha\beta}^D$ is given by $X_{\alpha\beta}^D = \delta R / \delta \psi_{\alpha\beta} | \dots$. This procedure is discussed in detail in Ref. [28], so we simply give the results here. The momentum $g_\alpha^{(m)} = \bar{\rho}_m v_\alpha^{(m)}$ is a purely reversible current, while the stress $\sigma_{\alpha\beta}^{(m)}$ and strain quasicurrent $X_{\alpha\beta}$ have both reversible and dissipative parts. The resulting membrane contribution to the surface stress (excluding the contribution from the fluid-membrane-fluid surface tension) is given by

$$\sigma_{\alpha\beta}^{(m)} = -p\delta_{\alpha\beta} + \psi_{\alpha\beta} + v_\parallel \delta_{\alpha\beta} \nabla_\gamma v_\gamma^{(m)} + v_s A_{\alpha\beta} + (v_\perp - v_b \Delta_\perp) \delta_{\alpha z} \nabla_\beta v_z^{(m)}, \quad (\text{A15})$$

where p is the hydrostatic pressure, $\psi_{\alpha\beta}$ is the elastic contribution of the transient polymer network to the stress tensor, $A_{\alpha\beta} = (\nabla_\alpha v_\beta^{(m)} + \nabla_\beta v_\alpha^{(m)})/2$ is the symmetrized velocity gradient tensor, and v_\parallel , v_s , v_\perp , and v_b are, respectively, the viscosities corresponding to uniaxial compression, shear, transverse stretching and bending motions of the membrane. Changes in the pressure δp are related to variations in density $\delta \rho_m$ via $\delta p = \varepsilon \delta \rho_m / \bar{\rho}_m$, where ε is the liquidlike compressibility of the membrane. This relation provides a connection between pressure and spatial variation of the momentum density through the continuity equation Eq. (A11).

The quasicurrent $X_{\alpha\beta}$ is given by

$$X_{\alpha\beta} = -A_{\alpha\beta} + \frac{1}{2} \mathcal{T}_{\alpha\beta\gamma\delta}^{-1} \psi_{\gamma\delta}, \quad (\text{A16})$$

where the $\mathcal{T}_{\alpha\beta\gamma\delta}^{-1}$'s are relaxation coefficients of the viscoelastic material, i.e., each is a product of a relaxation time and an appropriate elastic constant. The tensor of these coefficients has the same symmetries as the elastic strain field $\varepsilon_{\alpha\beta}$. We should note that while $v_z^{(m)} = \xi$ in the above, $\varepsilon_{\alpha z} \neq \nabla_\alpha \xi$ from the point of view of macroscopic dynamics; internal rearrangement of material within a thin viscoelastic film is not necessarily connected to its geometric transverse displacement ξ . Equations (A11)–(A16) give the divergence of the membrane stress tensor components $\nabla_\beta \sigma_{\alpha\beta}^{(m)}$ in terms of spatial derivatives of membrane velocity and strain. For our purposes it suffices to consider the simplified case of one-dimensional membrane modes, in which all quantities are assumed to vary as $\exp(ikx + i\omega t)$. Then the above analysis simplifies considerably; all spatial derivatives with respect

to y and z vanish, while $\nabla_x \rightarrow ik$ and $\partial/\partial t \rightarrow i\omega$. After some algebraic manipulations, we find a total interfacial force density of the form

$$P_\alpha^{(m)} = \mathcal{C}^{(\alpha)}(ik^2/\omega)v_\alpha^{(m)} \quad (\text{A17})$$

with $\mathcal{C}^{(\alpha)}$ for $\alpha = x, y, z$ given by

$$\mathcal{C}^{(x)}(k, \omega) = \varepsilon + i\omega v_\parallel + \frac{i\omega \tau_\parallel c_\parallel}{1 + i\omega \tau_\parallel}, \quad (\text{A18})$$

$$\mathcal{C}^{(y)}(k, \omega) = i\omega v_s + \frac{i\omega \tau_s c_s}{1 + i\omega \tau_s}, \quad (\text{A19})$$

$$\mathcal{C}^{(z)}(k, \omega) = \gamma + i\omega(v_\perp + v_b k^2) + \frac{i\omega \tau_\perp}{1 + i\omega \tau_\perp} (c_\perp + c_b k^2), \quad (\text{A20})$$

where we have included in Eq. (A20) the contribution to the surface force density from the Laplace pressure of the fluid-film-fluid interface, $P_L = \gamma \nabla_x^2 \xi = \gamma (ik^2/\omega)v_z^{(m)}$; and where we have explicitly written the relaxation coefficients as products of macroscopic relaxation times and elastic constants, e.g., $\mathcal{T}_\parallel = \tau_\parallel c_\parallel$, $\mathcal{T}_s = \tau_s c_s$, and $\mathcal{T}_\perp = \tau_\perp c_\perp$, in order to make a connection with the classical Maxwell model. Equations (A17)–(A20) are the boundary conditions given in Eqs. (8)–(10) of Sec. II. The $\mathcal{C}^{(x)}(k, \omega)$ and $\mathcal{C}^{(z)}(k, \omega)$ in Eqs. (A18) and (A20) can be interpreted as a generalized ω - and k -dependent compressional modulus $\varepsilon_{\text{eff}}(k, \omega)$ and surface tension $\gamma_{\text{eff}}(k, \omega)$, respectively, both of which contain dissipative contributions due to internal viscoelastic effects.

APPENDIX B

To obtain the membrane-mode dispersion relation $\omega(k)$ and the transverse-membrane-mode structure factor $S(k, \omega)$, one must solve the linearized equations of motion and boundary conditions given in Sec. II. The techniques used in this appendix are very similar to those used in a previous work to calculate the surface modes of a semi-infinite viscoelastic liquid [38,39]. Hence, we give only an abbreviated derivation in the following. For our purposes, it suffices to consider one-dimensional membrane modes, for which all quantities vary as $\exp(ikx + i\omega t)$. Then, Eqs. (1), (2), and (6) for fluid i become

$$i\omega \rho_i v_x^{(i)} = -ikP^{(i)} + \eta_i \hat{D}v_x^{(i)} + ik\Sigma_{xx}^{(i)} + \nabla_z \Sigma_{xz}^{(i)}, \quad (\text{B1})$$

$$i\omega \rho_i v_z^{(i)} = -\nabla_z \hat{P}^{(i)} + \eta_i \hat{D}v_z^{(i)} + ik\Sigma_{zz}^{(i)} + \nabla_z \Sigma_{zz}^{(i)}, \quad (\text{B2})$$

$$ikv_x^{(i)} + \nabla_z v_z^{(i)} = 0, \quad (\text{B3})$$

where $\hat{D} \equiv \nabla_z^2 - k^2$ and where $\Sigma_{\alpha\beta}^{(i)}$ are the components of the fluctuating stress tensor in each liquid. In Eq. (B2), we have implicitly included the gravitational contribution to the hydrostatic pressure by writing $\hat{P}^{(i)} = P^{(i)} + \rho_i g z$. These equations of motion are subject to the requirement that mode amplitudes vanish far from the membrane, i.e., $v_\alpha^{(i)} \rightarrow 0$ as $z \rightarrow \pm \infty$, and subject to the effective kinematic and dynamic boundary conditions at the membrane surface

$$\mathbf{v}^{(1)}|_{z=0} = \mathbf{v}^{(2)}|_{z=0} = \mathbf{v}^{(m)}, \quad (\text{B4})$$

$$[2\eta_i \nabla_z v_z^{(i)} + \Sigma_{zz}^{(i)} - \hat{P}^{(i)}]_{1,2} + \mathcal{C}^{(z)}(k, \omega)(k^2/i\omega)v_z^{(m)} = 0, \quad (\text{B5})$$

$$[\eta_i (\nabla_z v_x^{(i)} + ikv_z^{(i)}) + \Sigma_{xz}^{(i)}]_{1,2} + \mathcal{C}^{(x)}(k, \omega)(k^2/i\omega)v_x^{(m)} = 0, \quad (\text{B6})$$

where $[f^{(i)}]_{1,2}$ denotes the discontinuity of f across the liquid-membrane-liquid interface, and where $\mathcal{C}^{(x)}(k, \omega)$ and $\mathcal{C}^{(z)}(k, \omega)$ are given by Eqs. (A18) and (A20). The Fourier-transformed components of the random stress tensors $\Sigma_{\alpha\beta}^{(i)}(k, z, t)$ are related to the fluid viscosities η_i through the generalized fluctuation-dissipation theorem for classical fluids [29]

$$\langle \Sigma_{\alpha\beta}^{(i)}(k, z, t) \Sigma_{\mu\nu}^{*(j)}(k', z', t') \rangle = 8\pi^2 k_B T \eta_i (\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}) \delta_{ij} \delta(z-z') \delta(k-k') \delta(t-t') \quad (\text{B7})$$

where $k_B T$ is the thermal energy, the asterisk denotes complex conjugation, and where we define the Fourier transform by $f(k, \omega) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dt f(x, z, t) \exp(ikx + i\omega t)$. It is convenient to express all equations of motion and boundary conditions in terms of $v_z^{(i)}$. The incompressibility condition, Eq. (B3), gives $v_x^{(i)}$ in terms of $v_z^{(i)}$. Then, taking the curl of the Navier-Stokes equation by subtracting ik times Eq. (B2) from ∇_z of Eq. (B1) gives an equation of motion for $v_z^{(i)}$,

$$(\rho_i \omega + i\eta_i \hat{D}) \hat{D} v_z^{(i)} = -ik^2 \nabla_z (\Sigma_{xx}^{(i)} - \Sigma_{zz}^{(i)}) - k \hat{D}_+ \Sigma_{xz}^{(i)}, \quad (\text{B8})$$

where $\hat{D}_+ \equiv \nabla_z^2 + k^2$. Solving Eq. (B1) for the pressure $P^{(i)}$ and using Eq. (B3) to eliminate $v_x^{(i)}$ yields

$$P^{(i)} = \frac{1}{k^2} [\eta_i \hat{D} - i\omega \rho_i] \nabla_z v_z^{(i)} + \Sigma_{xx}^{(i)} - \frac{i}{k} \nabla_z \Sigma_{xz}^{(i)}. \quad (\text{B9})$$

Substitution of Eq. (B9) into Eq. (B5) gives the normal stress boundary condition in terms of the $v_z^{(i)}$

$$\{[\eta_i (\hat{D} - 2k^2) - i\rho_i \omega] \nabla_z v_z^{(i)}\}_{1,2} - \frac{k^2}{i\omega} [\mathcal{C}^{(z)}(k, \omega) k^2 + \Delta\rho g] v_z^{(i)}|_{z=0} = [k^2 (\Sigma_{zz}^{(i)} - \Sigma_{xx}^{(i)}) + ik \nabla_z \Sigma_{xz}^{(i)}]_{1,2}, \quad (\text{B10})$$

where $\Delta\rho = \rho_2 - \rho_1$, and where we have used $\zeta(x) = v_z^{(i)}(x, 0)/i\omega$ (for the gravitational contribution), $v_z^{(m)} = v_z^{(i)}|_{z=0}$, and $[f^{(i)}]_{1,2} = (f^{(1)} - f^{(2)})|_{z=0}$ here and in the following. Similarly, elimination of $v_x^{(i)}$ in Eq. (B6) gives the shear stress boundary condition as

$$[\eta_i \hat{D}_+ v_z^{(i)}]_{1,2} + \frac{k^2}{i\omega} \mathcal{C}^{(x)}(k, \omega) \nabla_z v_z^{(i)}|_{z=0} = [ik \nabla_z \Sigma_{xz}^{(i)}]_{1,2}, \quad (\text{B11})$$

where we have used $v_x^{(m)} = v_x^{(i)}|_{z=0} = i \nabla_z v_z^{(i)}|_{z=0}/k$.

The most general solution to the equations of motion is the sum of a particular solution of Eq. (B8) and the solution of the associated homogeneous equations with $\Sigma_{\alpha\beta} = 0$ which satisfies the boundary conditions, Eqs. (B10) and (B11). To obtain a particular solution in region i , it is convenient to Laplace transform Eq. (B8) with respect to the z coordinate using

$$\tilde{f}^{(i)}(q_i) = \begin{cases} \int_0^\infty dz \exp(-q_1 z) f^{(1)}(z) \\ \int_{-\infty}^0 dz \exp(+q_2 z) f^{(2)}(z) \end{cases}. \quad (\text{B12})$$

Since we seek any particular solution of Eq. (B8) that is consistent with the boundary conditions, we have the freedom to choose the values of $v_z^{(i)}$, and its derivatives with respect to z , $v_z^{(i)'}$, $v_z^{(i)''}$, and $v_z^{(i)'''}$ on $z=0$. For convenience we take these to be

$$\begin{aligned} v_z^{(i)}(0) &= 0, \\ v_z^{(i)'}(0) &= 0, \\ v_z^{(i)''}(0) &= ik \Sigma_{xz}^{(i)}(0)/\eta_i, \\ v_z^{(i)'''}(0) &= \{ik \Sigma_{xz}^{(i)}(0) - k^2 [\Sigma_{xx}^{(i)}(0) - \Sigma_{zz}^{(i)}(0)]\}/\eta_i. \end{aligned} \quad (\text{B13})$$

Then after the Laplace transformation of Eq. (B8) using Eq. (B12), one finds $\tilde{v}_z^{(i)}(q_i)$ in region i given by

$$\tilde{v}_z^{(i)}(q_i) = \frac{-\{q_i k^2 [\tilde{\Sigma}_{xx}^{(i)}(q_i) - \tilde{\Sigma}_{zz}^{(i)}(q_i)] - ik(q_i^2 + k^2) \tilde{\Sigma}_{xz}^{(i)}(q_i)\}}{\eta_i q_i^4 - (i\rho_i \omega + 2\eta_i k^2) q_i^2 + (i\rho_i \omega + \eta_i k^2) k^2}. \quad (\text{B14})$$

These $\tilde{v}_z^{(i)}(q_i)$ are easily inverted into real-space expressions using the convolution theorem of Laplace transformations. The general solution for $v_z^{(i)}$ is then the sum of the homogeneous solution $[v_z^{(i)}]_h$ and the particular solution obtained by

inverse Laplace transformation of Eq. (B14); we find

$$\begin{aligned} v_z^{(1)}(k, z, \omega) &= [v_z^{(1)}]_h + \int_0^z dz' \lambda_{\alpha\beta}^{(1)}(z-z') \Sigma_{\alpha\beta}^{(1)}(z'), \\ v_z^{(2)}(k, z, \omega) &= [v_z^{(2)}]_h + \int_z^0 dz' \lambda_{\alpha\beta}^{(2)}(z-z') \Sigma_{\alpha\beta}^{(2)}(z'), \end{aligned} \quad (\text{B15})$$

where $\lambda_{\alpha\beta}^{(1)}(z)$ is given by

$$\begin{aligned} \lambda_{\alpha\beta}^{(1)}(z) &= \frac{k^2 \exp(kz)}{2\eta_1(k^2 - q_1^2)} \{ -(\delta_{\alpha x} \delta_{\beta x} - \delta_{\alpha z} \delta_{\beta z}) + 2i \delta_{\alpha x} \delta_{\beta z} \} + \frac{k^2 \exp(-kz)}{2\eta_1(k^2 - q_1^2)} \{ -(\delta_{\alpha x} \delta_{\beta x} - \delta_{\alpha z} \delta_{\beta z}) - 2i \delta_{\alpha x} \delta_{\beta z} \} \\ &+ \frac{k^3 \exp(q_1 z)}{2\eta_1 q_1 (k^2 - q_1^2)} \left\{ \frac{q_1}{k} (\delta_{\alpha x} \delta_{\beta x} - \delta_{\alpha z} \delta_{\beta z}) + \frac{k^2 + q_1^2}{ik^2} \delta_{\alpha x} \delta_{\beta z} \right\} \\ &+ \frac{k^3 \exp(-q_1 z)}{2\eta_1 q_1 (k^2 - q_1^2)} \left\{ \frac{q_1}{k} (\delta_{\alpha x} \delta_{\beta x} - \delta_{\alpha z} \delta_{\beta z}) - \frac{k^2 + q_1^2}{ik^2} \delta_{\alpha x} \delta_{\beta z} \right\} \end{aligned} \quad (\text{B16})$$

and where $\lambda_{\alpha\beta}^{(2)}(z) = \lambda_{\alpha\beta}^{(1)}(-z)$ with $q_1 \rightarrow q_2$ and $\eta_1 \rightarrow \eta_2$. The homogeneous solutions $[v_z^{(i)}]_h$ have the form

$$[v_z^{(i)}]_h = a_i \exp(kz) + b_i \exp(-kz) + c_i \exp(q_i z) + d_i \exp(-q_i z), \quad (\text{B17})$$

where $q_i^2 = k^2 + i\rho_i \omega / \eta_i$, and where the coefficients a_i , b_i , c_i , and d_i are to be determined by the boundary conditions. The requirement that the modes are localized at the membrane surface ($v_z^{(i)} \rightarrow 0$ as $z \rightarrow \pm \infty$) implies that

$$\begin{aligned} a_1 &= -I_k^{(1)}, \\ c_1 &= +I_q^{(1)}, \\ b_2 &= -I_k^{(2)}, \\ d_2 &= +I_q^{(2)}, \end{aligned} \quad (\text{B18})$$

with $I_k^{(i)}$ and $I_q^{(i)}$ given by

$$\begin{aligned} I_k^{(i)} &= \frac{k^2}{2i\omega} \int_0^\infty dz' \exp(-kz') [\Sigma_{xx}^{(i)}(z') - \Sigma_{zz}^{(i)}(z') - 2i \Sigma_{xz}^{(i)}(z')], \\ I_q^{(i)} &= \frac{k^2}{2i\omega} \int_0^\infty dz' \exp(-q_i z') \left[\Sigma_{xx}^{(i)}(z') - \Sigma_{zz}^{(i)}(z') + \frac{k^2 + q_i^2}{ikq_i} \Sigma_{xz}^{(i)}(z') \right]. \end{aligned} \quad (\text{B19})$$

Due to our judicious choice of derivatives of $[v_z^{(i)}]_p$ on the membrane surface $z \simeq 0$ [cf. Eq. (B13)], the general solution for $v_z^{(i)}$ given by Eqs. (B15) and (B16) will satisfy the kinematic and dynamic boundary conditions provided $[v_z^{(i)}]_h$ satisfy the associated homogeneous boundary conditions, i.e., Eq. (B4), and Eqs. (B10) and (B11) with $\Sigma_{\alpha\beta}^{(i)} = 0$. These homogeneous boundary conditions are

$$[v_z^{(1)}(0)]_h = [v_z^{(2)}(0)]_h = v_z^{(m)}, \quad (\text{B20})$$

$$\nabla_z [v_z^{(1)}]_h |_{z=0} = \nabla_z [v_z^{(2)}]_h |_{z=0} = -ikv_x^{(m)}, \quad (\text{B21})$$

$$\{ [\eta_i (\hat{D} - 2k^2) - i\rho_i \omega] \nabla_z [v_z^{(i)}]_h \}_{1,2} - \frac{k^2}{i\omega} [\mathcal{C}^{(z)}(k, \omega) k^2 + \Delta \rho g] v_z^{(i)}(0)_h = 0, \quad (\text{B22})$$

$$[\eta_i \hat{D} + [v_z^{(i)}]_h]_{1,2} + \frac{k^2}{i\omega} \mathcal{C}^{(x)}(k, \omega) [\nabla_z v_z^{(i)}]_h |_{z=0} = 0, \quad (\text{B23})$$

where in Eq. (B21) we have used the incompressibility relation to write $-ik[v_x^{(i)}(z)]_h = \nabla_z [v_z^{(i)}(z)]_h$. Substitution of the form of $[v_z^{(i)}(z)]_h$ from Eqs. (B17) and (B18) into Eqs. (B20)–(B23) yields four inhomogeneous linear equations for $\{a_2, b_1, c_2, d_1\}$ in terms of $I_k^{(i)}$ and $I_q^{(i)}$.

The determinant of the matrix of coefficients of $\{a_2, b_1, c_2, d_1\}$ gives the implicit membrane mode dispersion relation $D(k, \omega) = 0$. After substantial algebraic manipulation we find

$$\begin{aligned}
D(k, \omega) = & (k - q_1)(k - q_2) \mathcal{E}^{(x)}(k, \omega) \left[\mathcal{E}^{(z)}(k, \omega) + \frac{g}{k^2} \right] k^6 - 2(k - q_1)(k - q_2) [\eta_1^2 q_1 + \eta_2^2 q_2 - \eta_1 \eta_2 (q_1 + q_2) - (\Delta\eta)^2 k] \omega^2 k^3 \\
& + \left[\rho_1 q_1 + \rho_2 q_2 - 2\bar{\rho} \frac{q_1 q_2}{k} \right] \mathcal{E}^{(x)}(k, \omega) - (\rho_1 q_2 + \rho_2 q_1 - 2\bar{\rho} k) \left[\mathcal{E}^{(z)}(k, \omega) + \frac{g}{k^2} \right] \omega^2 k^4 \\
& - \left[2\bar{\rho} \frac{q_1 q_2}{k} (\eta_1 q_1 + \eta_2 q_2) - 2(\rho_2 \eta_1 q_1 + \rho_1 \eta_2 q_2) k + \Delta\rho [\eta_1 (q_1^2 - q_2 k) - \eta_2 (q_2^2 - q_1 k) - \Delta\eta k^2] \right] i \omega^3 k^2, \quad (\text{B24})
\end{aligned}$$

where $2\bar{\rho} = \rho_1 + \rho_2$, $\Delta\rho = \rho_2 - \rho_1$ and $\Delta\eta = \eta_2 - \eta_1$. In the limit $\eta_1 = \eta_2$ and $\rho_1 = \rho_2$ the compressional and transverse modes decouple, and Eq. (B24) reduces to the product of the compressional and transverse membrane mode dispersion relations given in Eqs. (11) and (12) of Sec. III A. On the other hand, for $\rho_1 \rightarrow 0$ and $\eta_1 \rightarrow 0$, we recover the limit of a film at a liquid-vapor interface, and Eq. (B24) reduces to the generalized Lucassen mode dispersion relation given by Eq. (14) of Sec. III B.

Solving the inhomogeneous equations for $\{a_2, b_1, c_2, d_1\}$ gives $\zeta(k, \omega) = v_z^{(i)}(k, 0, \omega) / i\omega$ in terms of $I_k^{(i)}$ and $I_q^{(i)}$. The dynamic structure factor $S(k, \omega) = (2\pi)^{-3} \langle |\zeta(k, \omega)|^2 \rangle$ of thermally excited membrane modes is then determined by the thermal averages of $I_k^{(i)}$ and $I_q^{(i)}$. These are obtained with the aid of the generalized fluctuation-dissipation theorem given in Eq. (B7) as

$$\begin{aligned}
\langle I_k^{(i)} I_k^{*(j)} \rangle &= (2\pi)^3 2k_B T \eta_i \frac{k^3}{\omega^2} \delta_{i,j}, \\
\langle I_q^{(i)} I_q^{*(j)} \rangle &= \frac{k}{q_i + q_i^*} \left[1 + \frac{|k^2 + q_i^2|^2}{4k^2 |q_i|^2} \right] \langle I_k^{(i)} I_k^{*(j)} \rangle, \quad (\text{B25}) \\
\langle I_k^{(i)} I_q^{*(j)} \rangle &= \frac{k}{k + q_i^*} \left[1 + \frac{(k^2 + q_i^2)^*}{2k q_i^*} \right] \langle I_k^{(i)} I_k^{*(j)} \rangle,
\end{aligned}$$

where no summation convention on repeated roman indices is implied. With the use of Eq. (B25), one eventually obtains $S(k, \omega)$ in the form

$$S(k, \omega) = \frac{2k_B T \omega^2 \Lambda(k, \omega)}{|D(k, \omega)|^2}, \quad (\text{B26})$$

where $D(k, \omega)$ is given by Eq. (B24), and where $\Lambda(k, \omega)$ is

$$\Lambda(k, \omega) = 4 \text{Re}[\mathcal{E}^{(x)}(k, \omega)] \Lambda_1(k, \omega) - 8 \text{Im}[\mathcal{E}^{(x)}(k, \omega)] \Lambda_2(k, \omega) + |\mathcal{E}^{(x)}(k, \omega)|^2 \Lambda_3(k, \omega) + 4\Lambda_4(k, \omega) \quad (\text{B27})$$

with the $\Lambda_i(k, \omega)$ given by

$$\Lambda_1(k, \omega) = (\rho_1 \eta_2 |k - q_2|^2 + \rho_2 \eta_1 |k - q_1|^2) \text{Im}[q_1] \text{Im}[q_2] k^2 + (\eta_1 \text{Im}[q_1] - \eta_2 \text{Im}[q_2]) |k - q_1|^2 |k - q_2|^2 \Delta\eta \frac{k^3}{\omega},$$

$$\Lambda_2(k, \omega) = (\rho_1 \text{Im}[q_1] |k - q_2|^2 - \rho_2 \text{Im}[q_2] |k - q_1|^2) \Delta\eta k^3 + \rho_1 \rho_2 \text{Im}[q_1] \text{Im}[q_2] \omega k^2 + |k - q_1|^2 |k - q_2|^2 (\Delta\eta)^2 \frac{k^4}{\omega},$$

$$\Lambda_3(k, \omega) = (\rho_1 \text{Im}[q_1] |k - q_2|^2 + \rho_2 \text{Im}[q_2] |k - q_1|^2) \frac{k^4}{\omega},$$

$$\begin{aligned}
\Lambda_4(k, \omega) = & \rho_1 \rho_2 (\rho_2 \text{Im}[q_1] + \rho_1 \text{Im}[q_2]) \omega^3 - (\rho_1^2 |k - q_2|^2 - \rho_2^2 |k - q_1|^2) \Delta\eta \omega^2 k \\
& - (\rho_1 \text{Im}[q_1] |k - q_2|^2 + \rho_2 \text{Im}[q_2] |k - q_1|^2) (\Delta\eta)^2 \omega k^2, \quad (\text{B28})
\end{aligned}$$

where $\text{Re}[f]$, $\text{Im}[f]$, and $|f|$ denote, respectively, the real part, the imaginary part, and the modulus of f . Equations (B24), (B26), (B27), and (B28) for the implicit dispersion relation $D(k, \omega) = 0$ and the dynamic structure factor $S(k, \omega)$ are our central results. In the limit $\eta_1 = \eta_2$ and $\rho_1 = \rho_2$, Eqs. (B26)–(B28) reduce to the symmetric interface dynamic structure factor $S(k, \omega)_{\text{sym}}$ given in Eq. (13) of Sec. III A. On the other hand, for $\rho_1 \rightarrow 0$ and $\eta_1 \rightarrow 0$, we recover the limit of a film at a liquid-vapor interface, and Eqs. (B26)–(B28) reduce to the generalized Lucassen mode dynamic structure factor $S(k, \omega)_{\text{fr}}$ given by Eqs. (15)–(17) of Sec. III B.

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