

Hydrodynamic Modes of Viscoelastic Soap Films

P. Sens, C. Marqués, and J. F. Joanny*

Institut Charles Sadron, 6, rue Boussingault, 67083 Strasbourg Cedex, France

Received April 22, 1993. In Final Form: July 15, 1993*

We discuss the dispersion relation of the undulation modes of a soap film containing a viscoelastic Maxwell fluid modeling a water soluble polymer. Two types of modes exist, bending modes and squeezing modes. In addition to the modes existing for a usual viscous soap film, we find Rayleigh waves driven by the bulk elasticity E of the liquid. The dispersion relation of the undulation modes strongly depends on the value of the surface elastic modulus of the surfactant layers ϵ_s . We study in detail the limit where the surface elastic modulus vanishes and the limit where it is of the same order of magnitude as the surface tension. In this last case the Rayleigh waves are observed if $Eh \gg \epsilon_s$ where h is the thickness of the film. We also discuss briefly the existence of higher harmonics due to the coupling of the undulation modes to compressional elastic modes of the film.

I. Introduction

A large number of industrial processes require the simultaneous use of polymers and surfactants. The interplay between the properties of the polymer and that of the surfactant is in general very subtle and is difficult to describe theoretically. A typical example is the stabilization of foams or soap films by addition of hydrosoluble polymers.

In order to understand the role of a water-soluble polymer on the properties of a soap film, detailed experimental studies have been performed in particular by di Meglio and collaborators.¹⁻³ They have shown that the drainage of the soap film is strongly affected by the polymer and that the classical drainage law proposed by Frankel and Mysels⁴ which describes well the drainage of simple soap films is qualitatively not followed. Tentative explanations based on the existence of normal viscous stresses or on the slip of the polymer on the surfactant layer have been proposed.⁵

In order to test the hydrodynamic properties of soap films, one can also measure their undulation modes by quasielastic light scattering. A very thorough study of the undulations of soap films from both the experimental and the theoretical point of view has been performed by Joosten.⁶⁻⁸ His hydrodynamic theory is in good agreement with the experimental results obtained by light scattering and shows the important role of both the surface elastic modulus and the direct interactions between the surfaces of the film characterized by the so-called disjoining pressure.

In this work we want to discuss the effect of the polymer on the undulation modes of the soap film. As a first step, we consider the polymer solution confined between the surfaces of the soap film as a homogeneous viscoelastic medium. We thus ignore the effect of the polymer-surfactant interaction which induces an adsorption or a

depletion of the polymer close to the surfaces of the film (giving thus a contribution to the disjoining pressure) and we investigate only the role of the elasticity of the polymeric liquid.^{9,10}

We use the simplest possible model of a viscoelastic fluid, the Maxwell model where the complex viscosity at a frequency ω varies as

$$\eta(\omega) = E\tau/(1 + i\omega\tau) \quad (1)$$

This model has a single relaxation time τ and a plateau modulus E . The liquid behaves as a viscous medium with a viscosity $\eta_0 = E\tau$ at long times and as an elastic medium at short times. The spectrum of the waves on the surface of a semiinfinite viscoelastic Maxwell liquid¹¹ has been studied in detail by Harden et al.^{11,12} who showed the existence of elastic Rayleigh waves in addition to the usual capillary waves. Our model can thus also be considered as a generalization of their results to liquid slabs of finite thicknesses.

The paper is organized as follows. In the next section we derive the hydrodynamic equations for a viscoelastic soap film taking into account the molecular interactions between the surfaces (described here by the DLVO disjoining pressure) following closely the work of Joosten⁶⁻⁸ for viscous soap films. In section III, we discuss the dispersion relation of the various undulation modes of the soap film both for bending modes and for squeezing modes. We present explicit calculations for the cases where the Gibbs surface elastic modulus vanishes and where it is large. The last section presents some concluding remarks and discusses some possible future directions.

II. Bending and Squeezing Modes

The soap film is a thin liquid slab of thickness h stabilized by the adsorption of an ionic surfactant on its surfaces. In the following, the z axis is normal to the film and the origin is at the middle of the film. The equilibrium thickness of the film is due to the balance between the disjoining pressure characterizing the molecular interactions in the film and the hydrostatic pressure head $P_h = \rho gH$ that can be imposed between the film and a bulk reservoir (ρ is the liquid density, g the gravity acceleration, and H the height difference between the film and the

* Abstract published in *Advance ACS Abstracts*, September 15, 1993.

(1) Cohen-Addad, S.; di Meglio, J. M. *Langmuir* 1992, 8, 324.

(2) Cohen-Addad, S. These Université Paris VI 1992 unpublished.

(3) Cohen-Addad, S.; di Meglio, J. M.; Ober, R. C. R. *Seances Acad. Sci., Ser. 2* 1992, 315, 39.

(4) Mysels, K.; Shinoda, K.; Frankel, S. *Soap films, studies of their thinning*; Pergamon Press: London, 1959.

(5) Bruinsma, R.; di Meglio, J. M.; Quere, D.; Cohen-Addad, S. Preprint.

(6) Joosten, J. *J. Chem. Phys.* 1984, 80, 2363.

(7) Joosten, J. *J. Chem. Phys.* 1984, 80, 2383.

(8) Joosten, J. In *Liquids at Interfaces*; Les Houches summer school; Charvolin, J., Joanny, J. F., Zinn-Justin, J., Eds.; North Holland: Amsterdam, 1990.

(9) Bird, R.; Armstrong, R.; Hassager, O. *Dynamics of Polymeric Liquids*; Wiley: New York, 1977.

(10) Ferry, J. *Viscoelastic properties of Polymers*; Wiley: New York, 1980.

(11) Harden, J.; Pleiner, H.; Pincus, P. *Europhys. Lett.* 1988, 7, 383.

(12) Harden, J.; Pleiner, H.; Pincus, P. *J. Chem. Phys.* 1991, 94, 5208.

reservoir). If we ignore the steric forces due to the polymer, the molecular interactions in the film are well accounted for by the classical DLVO theory: the disjoining pressure $\Pi = \Pi_{vdW} + \Pi_{DL}$ is the sum of a van der Waals and an electrostatic contribution.¹³ In the absence of retardation effects, the van der Waals disjoining pressure is attractive and decays with the thickness of the film as

$$\Pi_{vdW} = -A/6\pi h^3 \quad (2)$$

where the Hamaker constant A is positive and of the order of the thermal excitation kT . The electrostatic contribution to the disjoining pressure is repulsive and due to the interaction between the electrical double layers on the surfaces of the film. In the limit where the two surfaces overlap only weakly, it can be written as

$$\Pi_{DL} = 64kTn\sigma^2 \exp(-\kappa h) \quad (3)$$

Here, n is the concentration of monovalent salt in the film, κ^{-1} the associated Debye screening length ($\kappa^2 = 2e^2n/\epsilon kT$, where e is the elementary charge and ϵ the dielectric constant of water), and σ is a dimensionless number characterizing the electrostatic potential of the surfaces ψ_0 , $\sigma = th(e\psi_0/4kT)$.

The equilibrium thickness of the film is in general in the range 5–90 nm. The film is stable only if the disjoining pressure is a decreasing function of thickness, i.e. if $\partial\Pi/\partial h < 0$.

1. Hydrodynamic Equations. We now discuss the dynamics of small undulations of the surfaces of the film around the equilibrium configuration of a flat film of thickness h . Each point on the two surfaces has a displacement ξ and we shall only consider the hydrodynamics of the film at linear order in ξ . The velocity field $\mathbf{v}(\mathbf{r}, t)$ inside the film is given by the momentum conservation equation where we neglect the convective terms and the gravity effects

$$\rho \frac{\partial \mathbf{v}}{\partial t} = \nabla(\sigma + \mathbf{T}) - \rho \nabla W \quad (4)$$

where ρ is the mass density of the liquid.

The stress tensor σ is the sum of the pressure and of the viscoelastic stress. The viscoelastic stress is more easily expressed in terms of the Fourier components in time

$$\sigma(\mathbf{r}, \omega) = -p\mathbf{I} + \eta(\omega)[\nabla\mathbf{v}(\mathbf{r}, \omega) + {}^T\nabla\mathbf{v}(\mathbf{r}, \omega)] \quad (5)$$

where η is the complex viscosity given by eq 1.

The electrostatic interactions are described via the electrostatic Maxwell tensor \mathbf{T} and W is the van der Waals potential, i.e. the difference in van der Waals energy between a molecule at position \mathbf{r} in the film and a molecule in an infinite film.

For an undulation of pulsation ω , the momentum equation can be recast as

$$\rho i\omega \mathbf{v} = \eta(\omega)\nabla^2 \mathbf{v} - \nabla P \quad (6)$$

where P is an effective pressure calculated by Joosten⁶ which contains the effect of both the van der Waals and the electrostatic interactions.

The momentum equation must be supplemented by the incompressibility condition

$$\text{div } \mathbf{v} = 0 \quad (7)$$

On the surface of the film the molecules follow the velocity and the surface displacement is such that $\mathbf{v} = \partial\xi/\partial t$.

The exact boundary conditions on the stress are rather complicated and can be found in ref 6, we use here approximate boundary conditions replacing the effective pressure P in the film by $p - \Pi$ where Π is the disjoining pressure calculated for the local thickness of the film and p the actual pressure. The spirit of this approximation is the same as the Derjaguin approximation used in colloid science, it assumes that the film is locally flat and that the interactions are local in the directions parallel to the film. Our boundary conditions are thus valid in the limit where the wave vector of the undulation q is small enough that $qh \ll 1$. This is the interesting limit since if $qh > 1$, the two surfaces of the film are not coupled and the undulation modes are the simple capillary modes of each surface studied in refs 11 and 12.

In doing so, we also neglect the contribution of the van der Waals¹⁴ and electrostatic interactions¹⁵ to such quantities as the surface tension or the surface elastic modulus of the film. In the following these quantities must thus be understood as the total surface tension or the total surface elastic modulus including the van der Waals and electrostatic contributions.

On the upper surface of the film, the generalized pressure can then be written as

$$P = p_0 + \gamma C - \Pi + 2\eta\partial v_z/\partial z \quad (8)$$

where p_0 is the external pressure. The second term on the right-hand side is the Laplace pressure, γ is the surface tension, and C the local curvature.

The tangential stress at the surface of the film is due to the Marangoni effect and the corresponding boundary condition can be written as^{16,17}

$$\eta(\partial v_x/\partial z + \partial v_z/\partial x) = \epsilon_S \partial^2 \xi_x / \partial x^2 \quad (9)$$

The transverse undulation waves that we want to discuss have two types of eigenmodes, squeezing modes in which the two interfaces move antiparallel with respect to the z axis and bending modes in which the two interfaces move parallel with respect to the z axis (see Figure 1); we now discuss separately the velocity field for the two types of modes in the long wavelength limit $qh \ll 1$.

2. Squeezing Modes. In a squeezing mode of wave vector q , the two surfaces of the film move out of phase and the amplitude of the mode can be characterized by $u = (\xi_z^u - \xi_z^d)/2$, where ξ_z^u and ξ_z^d are respectively the deformation of the upper ($z = h/2$) and the lower ($z = -h/2$) surfaces in the z direction. The symmetry of the mode also imposes that $v_z(z, t) = -v_z(-z, t)$ and $v_x(z, t) = v_x(-z, t)$.

As is usually done to study surface waves,^{16,17} we decompose the velocity field as a sum of a longitudinal and a transverse field $\mathbf{v} = \nabla\phi + \mathbf{v}'$, where the longitudinal component is the gradient of a velocity potential ϕ .

The potential ϕ satisfies a Laplace equation $\nabla^2\phi = 0$ so that

$$\phi = A e^{iqx} \cosh(qz) \quad (10)$$

where A is an integration constant. The longitudinal component of the momentum equation gives the correction

(14) The effect of undulations on van der Waals interactions has been studied in Robbins, M.; Andelman, D.; Joanny, J. F. *Phys. Rev. A* 1991, 43, 4344.

(15) The effect of undulations on electrostatic interactions has been studied in Harden, J.; Marques, C.; Joanny, J. F.; Andelman, D. *Langmuir* 1992, 8, 1170.

(16) Lucassen, J. *Trans. Faraday Soc.* 1968, 64, 1221.

(17) Kramer, L. *J. Chem. Phys.* 1971, 55, 2097.

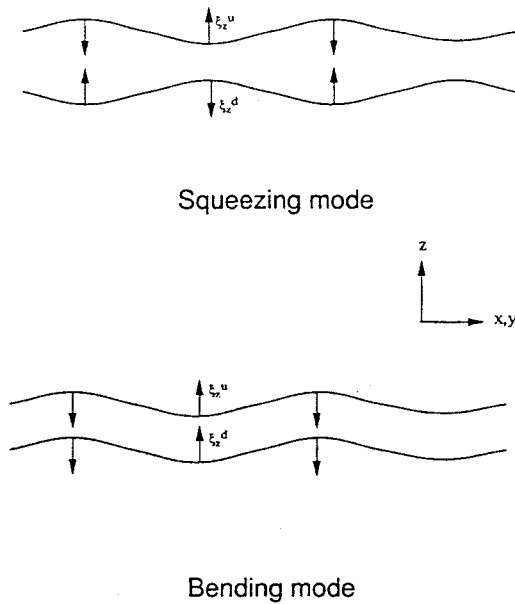


Figure 1. Geometry of the squeezing and bending modes.

to the pressure as

$$P = -\rho i \omega \phi = -\rho i \omega A e^{iqx} \cosh(qz) \quad (11)$$

The transverse velocity is the solution of the transverse component of the momentum equation (6)

$$v_x^t = \alpha_x e^{iqx} \cosh(mz), \quad v_z^t = \alpha_z e^{iqx} \sinh(mz) \quad (12)$$

where the wave vector m is such that $m^2 = q^2 + \rho i \omega / \eta(\omega)$; the two amplitudes α_x and α_z are related by the incompressibility equation, $m \alpha_z = -i q \alpha_x = -i m q B$, where B is another integration constant.

The two remaining integration constants are found from the boundary conditions on the stress. The tangential stress condition gives

$$\eta(\omega) \{ 2i q^2 A \sinh(qh/2) + B [m^2 + q^2] \sinh(mh/2) \} = -q^2 \epsilon_S / i \omega \{ i q A \cosh(qh/2) + m B \cosh(mh/2) \} \quad (13)$$

The normal stress boundary condition is obtained from eq 8 by expanding the disjoining pressure around the equilibrium value of a film of constant thickness h ($\Pi(h + 2u) = \Pi(h) + 2u \partial \Pi / \partial h$)

$$-\rho i \omega A \cosh(qh/2) = \gamma (q^2 + 2/L^2) [q A \sinh(qh/2) - i q B \sinh(mh/2)] / (i \omega) + 2 \eta(\omega) [q^2 A \cosh(qh/2) - i q m B \cosh(mh/2)] \quad (14)$$

We have introduced here the so-called healing length¹⁴ defined as $L^2 = -\gamma / (\partial \Pi / \partial h)$. The healing length characterizes the competition between surface tension and disjoining pressure and is in general larger than the thickness h .

Equations 13 and 14 are a homogeneous linear system in the variables A and B , a nonvanishing solution exists only in the limit where the determinant vanishes: this gives the dispersion relation of the squeezing mode. In the limit where $qh < 1$ and $|mh| < 1$, it reads

$$\omega^3 - 4i \nu(\omega) q^2 \omega^2 - \omega(\omega_c^2 + \omega_s^2) + i h^2 \omega_c^2 \omega_s^2 / 12 \nu(\omega) = 0 \quad (15)$$

We have introduced in eq 15 the complex kinematic viscosity $\nu(\omega) = \eta(\omega) / \rho$ and two characteristic pulsations: $\omega_c^2 = \gamma q^2 h (q^2 + 2/L^2) / 2\rho$ characterizes the surface waves

dominated by the surface tension or the disjoining pressure and $\omega_s^2 = 2q^2 \epsilon_S / \rho h$ represents the effect of the surface elasticity.

3. Bending Modes. The dispersion relation of the bending modes can be obtained in a similar manner as that of the squeezing mode. For a bending mode, the two surfaces oscillate in phase and the amplitude of the mode is defined as $u = \xi_z^u = \xi_z^d$; the symmetry imposes that $v_z(z, t) = v_z(-z, t)$. It is clear that the thickness of the film remains constant and thus that the disjoining pressure remains constant and plays no role in the bending mode.

In the limit of small thickness the dispersion relation is

$$\omega^3 - i \omega^2 [\nu(\omega) q^4 h^2 / 3 + \omega_s^2 h^2 / 4 \nu(\omega)] - \omega(\omega_c'^2 + \omega_s^2 q^2 h^2 / 4) + i \omega_c'^2 \omega_s^2 h^2 / 4 \nu(\omega) = 0 \quad (16)$$

We have here introduced the capillary frequency $\omega_c'^2 = 4\omega_c^2 / q^2 h^2 = 2\gamma q^2 / \rho h$. Note also that this relation is not exactly identical to that of ref 6, we have an extra term corresponding to the diffusion of vorticity in the ω^2 term in eq 16.

Both for the bending and the squeezing mode, one must check a posteriori for consistency that $|mh| < 1$ whenever $qh < 1$. In the following, we discuss the various asymptotic regimes of the dispersion relations (14 and 15) when the properties of the soap film are varied.

III. Dispersion Relation

The work of Joosten⁶⁻⁸ has shown the major importance of the surface elasticity for the properties of soap films. If the surface elastic modulus ϵ_S is very large, the surface of the soap film is rigid and the parallel velocity vanishes at the surface of the film. If the surface elasticity is small, the molecules are free to move on the interface and the parallel velocity is finite. The surface elastic modulus of a soap film can be varied in a broad range.¹⁸ For a sake of simplicity, we do not study here the general case but we study the two limits where the surface elastic modulus vanishes or has a large value of the order of the surface tension γ .

1. Films with No Surface Elasticity. We first discuss the squeezing modes. In the limit where ω_s vanishes, the dispersion relation takes the particularly simple form

$$\omega_c^2 - 4i \nu(\omega) q^2 \omega - \omega_c^2 = 0 \quad (15')$$

We now distinguish the two limits where the soap film has a viscous behavior $\omega \tau < 1$ and where it has an elastic behavior $\omega \tau > 1$. In the viscous limit, the kinematic viscosity is $\nu = E \tau / \rho = \nu_0 = \eta_0 / \rho$ and there are two squeezing modes

$$\omega = 2i q^2 \nu_0 \pm \{ \omega_c^2 - 4 \nu_0^2 q^4 \}^{1/2} \quad (17)$$

At a low value of the kinematic viscosity, ν_0 , the two modes are propagating and $\omega^2 = \omega_c^2 = \gamma q^2 h (q^2 + 2/L^2) / 2\rho$. They correspond to standard capillary waves in the shallow water approximation ($\omega^2 = \gamma q^4 h / 2\rho$) if the wavelength is smaller than the healing length ($qL > 1$) and to waves driven by the DLVO potential that we call DLVO waves if $qL < 1$ ($\omega^2 = \gamma q^2 h / L^2 \rho$). At high wave vector the two modes are overdamped and correspond to a viscous liquid mode due to the diffusion of vorticity ($\omega = 4i q^2 \nu_0$) and to an overdamped capillary wave ($\omega = \gamma q^2 h / 8 \eta_0$). The crossover between the propagating capillary wave and the overdamped modes occurs when $\nu_0 = (\gamma h / \rho)^{1/2}$ or $E = E_2$

(18) Lucassen, J. In *Anionic Surfactants*; Lucassen, E., Ed.; Marcel Dekker: New York, 1981; Chapter 6.

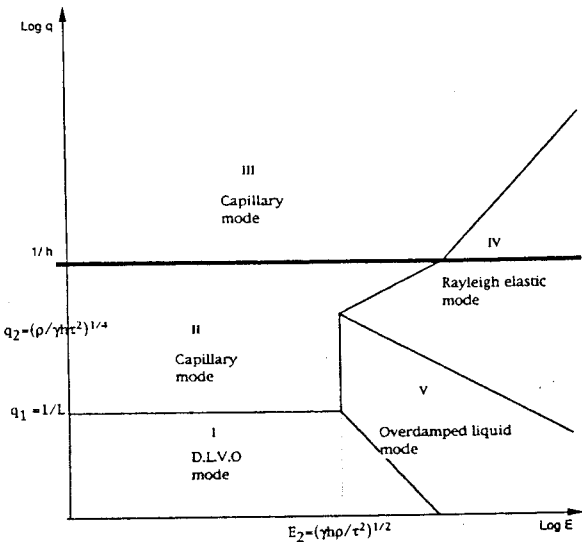


Figure 2. Asymptotic domains for the dispersion relation of the squeezing modes when the surface elastic modulus vanishes in the case where $1 < N = \gamma\tau^2/\rho h^3 < (L/h)^4$. In region I the undulation mode is a DLVO wave $\omega^2 = \gamma q^2 h/L^2 \rho$, in region II it is a capillary wave $\omega^2 = \gamma q^4 h/2\rho$, in region III a capillary wave $\omega^2 = \gamma q^3/\rho$, in region IV an elastic Rayleigh wave $\omega^2 = 4Eq^2/\rho$, and in region V the modes are overdamped $\omega = i\nu_0 q^4 h^2/3$ and $\omega = 6i\gamma/\eta_0 q^2 h^3$. The boundary between regions III and IV is given by $q = E/\gamma$, the boundary between regions II and IV by $q = (E/\gamma h)^{1/2}$, the boundary between regions IV and V by $q = (\rho/E\tau^2 h)^{1/2}$, and the boundary between regions V and I by $q = (\gamma\rho h)^{1/2}/(\tau LE)$.

$= (\gamma h \rho / \tau^2)^{1/2}$ and the crossover between the DLVO wave and the overdamped mode for a wavevector $q = (\gamma h \rho / L^2)^{1/2} / \eta$.

In the high frequency elastic range, the kinematic viscosity is $\nu = E/i\omega\rho$, the dispersion relation becomes in this limit

$$\omega^2 - (\omega_c^2 + 4Eq^2/\rho) = 0 \quad (18)$$

The two modes are propagative and correspond either to a capillary wave or to an elastic Rayleigh wave $\omega^2 = 4Eq^2/\rho$. Note that in this confined geometry the dispersion relation of the Rayleigh wave has the same structure as in an infinite medium.¹⁹ The crossover between Rayleigh and capillary waves occurs for a wave vector $q = (E/\gamma h)^{1/2}$.

It is useful to represent graphically the various possible asymptotic regimes for the squeezing modes in a plane elastic modulus wave vector. The relative importance of the various regions depends on the dimensionless number $N = \gamma\tau^2/\rho h^3$ which compares a capillary time, the period of a capillary wave of wave vector h^{-1} , and the viscoelastic relaxation time τ . Figure 2 corresponds to values of N such that, $1 < N < (L/h)^4$.

It is interesting to note that our results for small values of qh match smoothly with those of Harden et al. which have been obtained for waves at the surface of a semiinfinite viscoelastic liquid and thus correspond to the limit $qh \gg 1$. They found three types of modes, an elastic Rayleigh mode and an overdamped viscous liquid mode with the same dispersion relation as in the confined geometry above and a classical capillary mode (corresponding to the deep water limit) for which $\omega^2 = (\gamma/\rho)q^3$. The large wavelength limit is also represented in Figure 2.

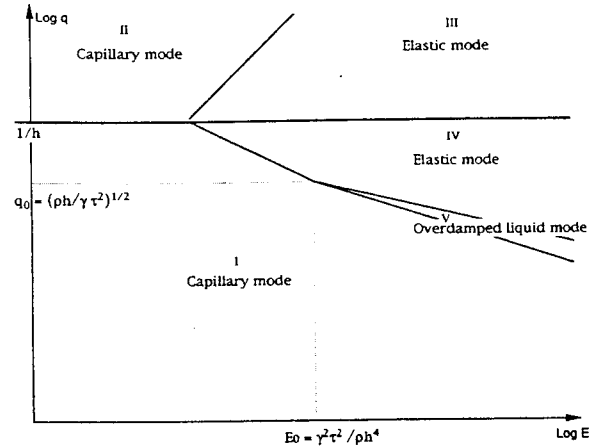


Figure 3. Asymptotic domains for the dispersion relation of the bending modes when the surface elastic modulus vanishes in the case where $1 < N = \gamma\tau^2/\rho h^3 < (L/h)^4$. In region I the undulation mode is a capillary wave $\omega^2 = 2\gamma q^2/\rho h$, in region II it is a usual capillary wave $\omega^2 = \gamma q^3/\rho$, in region III it is an elastic Rayleigh wave $\omega^2 = Eq^2/\rho$ and in region IV a Rayleigh wave in a confined geometry $\omega^2 = Eq^4 h^2/3$, and in region V the modes are overdamped $\omega = i\nu_0 q^4 h^2/3$ and $\omega = 6i\gamma/\eta_0 q^2 h^3$. The boundary between regions II and III is $q = E/\gamma$, the boundary between regions IV and I $q^2 = \gamma/Eh^3$, the boundary between regions IV and V $q^4 = \rho/(\tau^2 h^2 E)$, and the boundary between regions V and I $q^3 = \gamma\rho/(\tau^2 h^5 \rho)$.

The bending modes are studied along the same lines as the squeezing modes. The dispersion relation is

$$\omega^2 - i\omega \nu(\omega) q^4 h^2/3 - \omega_c^2 = 0 \quad (16')$$

The capillary waves have a high frequency than for the squeezing modes $\omega^2 = \omega_c^2 = 2\gamma q^2/\rho h$. The Rayleigh waves have the same dispersion relation as that of the bending modes of a thin solid plate, $\omega^2 = Eq^4 h^2/3$ and the overdamped modes are such that $\omega = i\nu_0 q^4 h^2/3$ and $\omega = 6i\gamma/\eta_0 q^2 h^3$. The various possible asymptotic regimes for the bending modes are displayed in Figure 3 for the same dimensionless number N as in Figure 2.

2. Films with a Finite Surface Elasticity. When the surface elastic modulus is finite, the properties of the soap film depend on many variables and it is difficult to present a general discussion. A dimensional analysis on the dispersion relations (15 and 16) shows that there are four dimensionless numbers to be considered

$$N_\gamma = \epsilon_s/\gamma, \quad N_{DLVO} = h/L, \quad N_\epsilon = \epsilon_s h/\rho\nu_0^2, \quad x = \nu_0\tau/h^2 \quad (19)$$

The relative importance of surface tension and surface elasticity is measured by N_γ ; in many cases N_γ is of the order 1 or larger, and we make this assumption below. As already mentioned above, in general $N_{DLVO} < 1$. N_ϵ measures the relative importance of the surface elasticity and of the viscous dissipation; if we introduce reasonable orders of magnitude ($\epsilon_s = 100$ dyn/cm, $h = 50$ nm, $\nu_0 = 10^{-2}$ cm²/s), we find that N_ϵ is of order 1. If the polymer concentration in the soap film is high enough, the kinematic viscosity is much larger than that of the water and it is reasonable to assume that $N_\epsilon \ll 1$. In the following, we consider that the three numbers N_ϵ , N_γ , and N_{DLVO} have a fixed value with these constraints and we look at the dispersion relation of the undulation modes of the viscoelastic soap film when the dimensionless number x varies. This number characterizes the viscoelasticity of the soap film and can be changed at constant value of the kinematic viscosity (i.e. at constant value of all the other numbers) by changing the viscoelastic relaxation time, the purely viscous fluid corresponding to $\tau = 0$.

(19) Landau, L.; Lifschitz, E. *Théorie de l'Elasticité* Ed Mir (Moscou 1967). For our isotropic fluid, the Poisson ratio is equal to 1/2.

a. Squeezing Modes. The dispersion relation of the squeezing mode is given by eq 15. In the limit where $N_\gamma \leq 1$ and $N_{DLVO} < 1$, as long as $qh < 1$, the capillary contribution ω_c^2 can be neglected compared to the surface elasticity term $\omega_s^2 = 2q^2\epsilon_s/\rho h$. We first discuss the small ω regime where the fluid has a viscous behavior and then the large ω regime where it exhibits an elastic behavior.

When $\omega\tau < 1$, it is useful to define a dimensionless pulsation $s = \omega/\omega_s$, and the dispersion relation becomes

$$s^3 - s^2 4i\nu_0 q^2/\omega_s - s + ih^2\omega_c^2/(12\nu_0\omega_s) = 0 \quad (20)$$

The constant term in this equation is always smaller than 1. The coefficient of s^2 can be smaller or larger than 1. If the wave vector is small ($y = qh < N_\epsilon^{1/2}$), this coefficient is smaller than 1 and the three modes are given by $s = \pm 1$ and $s = ih^2\omega_c^2/(12\nu_0\omega_s)$ or

$$\omega_{12} = \pm\omega_s, \quad \omega_3 = ih^2\omega_c^2/(12\nu_0) = ih^2\gamma q^2 h(q^2 + 2/L^2)/24\eta_0 \quad (21)$$

The first two modes are propagative and dominated by the surface elastic modulus. The third mode is overdamped and is identical to the surface waves of a thin liquid film of viscosity η_0 and thickness h on a solid surface (the difference in numerical prefactor corresponds to the existence of the two surfaces). Its dispersion relation can be easily obtained by approximating the Navier–Stokes equation by a lubrication approximation.^{20,21} The crossover to the elastic regime occurs when $\omega\tau = 1$ or $y \sim 1/(xN_\epsilon^{1/2})$.

If the wave vector is large ($N_\epsilon^{1/2} < y = qh < 1$) the coefficient of the s^2 term is larger than 1 and the three modes are overdamped $s = 4i\nu_0 q^2/\omega_s$, $s = i\omega_s/4\nu_0 q^2$, and $s = ih^2\omega_c^2/(12\nu_0\omega_s)$. Their dispersion relations are

$$\omega_1 = 4i\nu_0 q^2, \quad \omega_2 = i\epsilon_s/2\eta_0 h, \quad \omega_3 = ih^2\omega_c^2/(12\nu_0) \quad (22)$$

The fastest mode is a viscous liquid mode corresponding to the diffusion of vorticity, the slowest one is the overdamped capillary mode, and the intermediate one is an overdamped mode driven by surface elasticity with a constant relaxation time independent of the wave vector. The crossover to the elastic regime occurs when $y \sim 1/x^{1/2}$.

In the elastic range, all the modes are propagative and the dispersion relation is

$$\omega^2 = \omega_s^2 + 4E q^2/\rho + \rho\omega_c^2\omega_s^2/12E \quad (23)$$

Within the approximations ($|mh| < 1$) that we used to derive the dispersion relation (23), the coupling term is always negligible and the wave is an elastic wave driven by either the surface or the bulk elasticity. The surface elasticity is dominant ($\omega^2 = \omega_s^2$) if $\epsilon_s \gg Eh$ or $x > N_\epsilon^{-1}$ and the bulk elasticity is dominant (Rayleigh wave $\omega^2 = 4E q^2/\rho$) if $x < N_\epsilon^{-1}$. The limit $|mh| < 1$ corresponds to $y < 1/(x^{1/2}N_\epsilon^{1/2})$. If the wave vector is larger ($y > 1/(x^{1/2}N_\epsilon^{1/2})$) no mode can be found with $|mh| < 1$. There are however elastic modes such that $|mh| > 1$. These are purely elastic wave propagating in the direction perpendicular to the surface and coupled to the surface undulation waves. These modes are briefly discussed in the Appendix. As they are transverse modes, their dispersion relation is only weakly depending on q and there is a series of harmonics corresponding to standing waves with a given

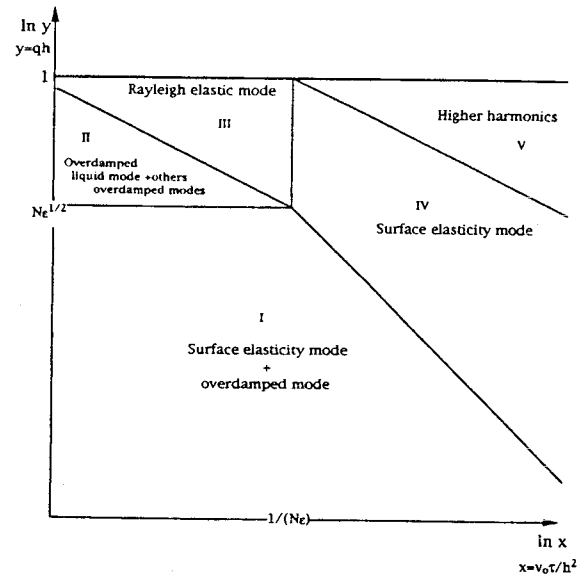


Figure 4. Asymptotic domains for the dispersion relation of the squeezing modes when the surface elastic modulus is large ($\epsilon_s = \gamma$). In regions I and IV the propagative modes are dominated by the surface elasticity $\omega = \omega_s$, in region I there is also an overdamped capillary mode $\omega = ih^2\omega_c^2/(12\nu_0)$. In region II the three modes are overdamped with a dispersion relation given by eq 22. In region III the squeezing mode is an elastic Rayleigh wave. In region V there are no modes such that $|mh| < 1$ (see text). The boundary between regions II and III is $y = 1/x^{1/2}$; the boundary between regions I and IV is $y = 1/(xN_\epsilon^{1/2})$. The boundary between regions IV and V is $y = 1/(x^{1/2}N_\epsilon^{1/2})$.

number of nodes. The dispersion relation of the lowest harmonic is $\omega^2 = \text{const } E/\rho h^2$, where the constant is only weakly depending on the wave vector q .

All these asymptotic regimes are displayed in a plane [$y = qh$, $x = \nu_0\tau/h^2$], in Figure 4. In the limit where $\tau \rightarrow 0$, we recover the viscous soap film behavior discussed by Joosten in the limit $y < N_\epsilon^{1/2}$.

b. Bending Modes. A similar analysis can be carried out for the bending mode, we will assume here for simplicity that $N_\gamma \approx 1$, i.e. that the surface tension and the surface elastic modulus are of the same order of magnitude.

In the viscous range we choose as the unit frequency ω'_c ($\omega'_c{}^2 = 2\gamma q^2/\rho h$) and define $s = \omega/\omega'_c$; the dispersion relation can be approximated by

$$s^3 - is^2[\nu_0 q^4 h^2/3\omega'_c + \omega_s^2 h^2/4\nu_0\omega'_c] - s + ih^2\omega_s^2/(4\nu_0\omega'_c) = 0 \quad (24)$$

The constant term is always smaller than unity. If $y < N_\epsilon^{1/6}$ the term proportional to s^2 is also smaller than unity. The three roots of this equation are $s = \pm 1$ and $s = ih^2\omega_s^2/(4\nu_0\omega'_c)$ corresponding to two propagative and one overdamped modes

$$\omega_{12} = \pm\omega'_c, \quad \omega_3 = ih^2\omega_s^2/(4\nu_0) = ih\epsilon_s q^2/2\eta_0 \quad (25)$$

The propagative modes are now capillary waves and the overdamped mode is an elastic surface mode. The crossover to the elastic regime occurs for $\omega'_c\tau = 1$ or $y \sim 1/(N_\epsilon^{1/2}x)$.

If $y > N_\epsilon^{1/6}$, $\nu_0 q^4 h^2/3\omega'_c > 1$ and the three modes are overdamped and correspond to $s = i\nu_0 q^4 h^2/3\omega'_c$, $s = 3i\omega'_c/\nu_0 q^4 h^2$, and $s = ih^2\omega_s^2/(4\nu_0\omega'_c)$ or

$$\omega_1 = i\nu_0 q^4 h^2/3, \quad \omega_2 = 6i\gamma/\eta_0 q^2 h^3, \quad \omega_3 = ih^2\omega_s^2/(4\nu_0) \quad (26)$$

The viscous diffusion mode has a much lower frequency than in the squeezing mode, the slowest mode is an

(20) Batchelor, G. *An Introduction to Fluid Dynamics*; Cambridge University Press: Cambridge, 1971.

(21) Levich, B. *Physicochemical hydrodynamic*; Prentice Hall: Englewood Cliffs, NJ, 1962.

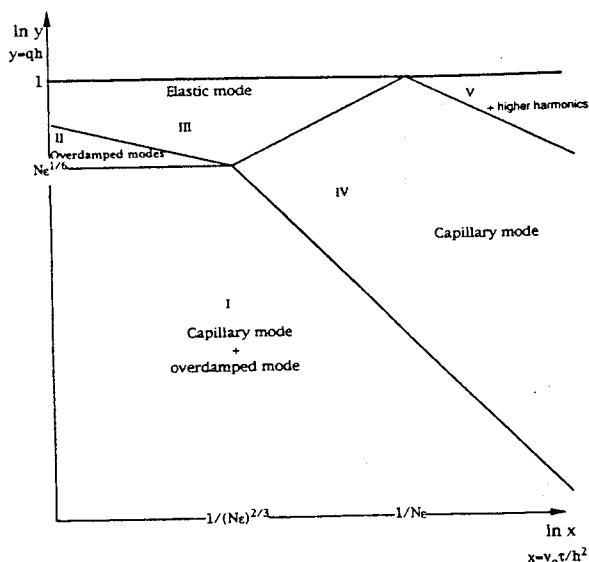


Figure 5. Asymptotic domains for the dispersion relation of the bending modes when the surface elastic modulus is large ($\epsilon_s = \gamma$). In regions I, IV, and V the propagative modes are capillary waves; in region III there is an overdamped surface elastic mode $\omega_3 = ih\epsilon_s q^2/2\eta_0$. In region III the bending mode is a confined Rayleigh elastic wave. In region II the three modes are overdamped and their dispersion relation is given by eq 26. The boundary between regions II and III is $y = 1/x^{1/4}$, the boundary between regions III and IV is $y = x^{1/2}N_e^{1/2}$, the boundary between regions I and IV is $y = 1/(xN_e^{1/2})$, and the boundary between regions IV and V is $y = 1/(x^{1/2}N_e^{1/2})$.

overdamped capillary wave, and the intermediate mode is an overdamped surface elastic wave with a relaxation time which decreases with the wave vector. The crossover with the elastic regime occurs for $y \sim x^{-1/4}$.

In the elastic range, the dispersion relation can be written as

$$\omega^2(1 + \omega_s^2 h^2 \rho / 4E) - [\omega_c'^2 + E q^4 h^2 / 3\rho + \omega_s^2 \gamma q^2 h^2 / 2Eh] \quad (27)$$

In the limit where $qh < 1$, two cases must be distinguished, if $y > N_e^{1/2} x^{1/2}$ the wave is a confined Rayleigh wave $\omega^2 = E q^4 h^2 / 3\rho$ and in the reverse limit $y < N_e^{1/2} x^{1/2}$, it is a capillary wave $\omega^2 = \omega_c'^2$. It should be noted that it is possible that $|m\hbar|$ be larger than unity for the capillary waves but we show in the Appendix that the capillary wave still exists in this limit. The perpendicular elastic modes are also coupled to the bending modes and there are also higher frequency modes with $\omega^2 = \text{const } E/\rho h^2$ or higher harmonics. All these asymptotic regimes are summarized in Figure 5 in a plane $x - y$.

The major difference between the bending and squeezing modes comes from the relative roles of the surface tension and the surface elastic modulus. The surface elasticity plays a dominant role in the squeezing modes and the surface tension plays a dominant role in the bending modes.

IV. Concluding Remarks

We have discussed the undulation modes of a soap film containing a viscoelastic fluid such as a water soluble polymer solution. As for usual viscous soap films there are two types of modes, squeezing modes and bending modes. The new feature introduced by the viscoelasticity of the fluid is the existence of Rayleigh waves driven by the bulk elasticity of the fluid.

We have found an extremely rich variety of behaviors. One of the most important parameters is the surface elastic modulus of the surfactant monolayers on the surface of

the film. This parameter is known to vary in a broad range.¹⁸ When the soap film contains polymers, the adsorption of polymers on the surfaces of the film is also likely to modify the value of the surface elastic modulus. We have assumed here that this parameter is known and we have discussed two limits. The limit where there is no surface elasticity is summarized in Figures 2 and 3. Although this is probably not a very realistic limit, it gives a generalization to thin films of the study of the surface waves on a viscoelastic liquid done by Harden et al. A similar study for a gel (with different boundary conditions) has recently been done by Kumaran.²²

The more realistic case seems to be the case where the surface elastic modulus is of the same order of magnitude as the surface tension. As for a viscous soap film, the surface tension plays a dominant role for the bending modes and the surface elasticity for the squeezing modes. Here also Rayleigh waves can be observed whenever the bulk elastic modulus E is larger than ϵ_s/h for the squeezing mode. Our results are summarized in Figures 4 and 5.

One important result is the existence of elastic modes showing a whole series of harmonics. These correspond to elastic waves propagating in the direction perpendicular to the surface of the film and coupled to the undulation modes. These modes have been discussed in the case where the surface elastic modulus is large but certainly exist in all cases.

The important question is then to decide whether these modes are possible to observe experimentally. In the limit of infinite thickness, i.e. at the surface of a semiinfinite semidilute polymer solution in an organic solvent, Rayleigh waves have recently been observed.²² Figure 2 suggests that when the surface elasticity is small, the Rayleigh waves could be observed for a lower value of the plateau modulus on a thinner film. When the surface elasticity is finite, the criterion for the observation of Rayleigh waves is $Eh > \epsilon_s$. For reasonable values of ϵ_s (10 mN/m) and h (50 nm) this gives rather high values of E of order 10^6 Pa. The observation of the Rayleigh waves will thus require either concentrated polymer films or a small surface elasticity.

Our model of a soap film containing polymer has been that of a simple viscoelastic liquid. Although this might be a reasonable assumption for thick films, the detailed structure of the polymer solution is relevant when the film is thin and can considerably modify the hydrodynamics. The dispersion relation of the undulation modes could then give information on the interaction between the polymer and the surfactant monolayers. We wish to come back to this problem in a future work.

We also have neglected the viscoelasticity of the surfaces. It is shown in ref 18 that the exchange of surfactant molecules between the bulk of the film and the surface contributes to this viscoelasticity: the surface elastic modulus ϵ_s is then complex and frequency dependent. The variation of ϵ_s with frequency could however be more complex for a soap film containing polymers since the surface polymer layer certainly contributes significantly to the viscoelasticity. The imaginary part of the surface elastic modulus (the surface viscosity) increases the dissipation and thus enhances the damping of the surface waves; it is not clear however whether this is an important effect.

Finally we have considered the polymer solution as a homogeneous liquid ignoring the relative motion of the polymer and the solvent. One could improve our model

(22) Kumaran, V. *J. Chem. Phys.* 1993, 98, 3429.

(23) Dorshow, R.; Turkevich, L. *Phys. Rev. Lett.* 1993, 70, 2439; 1993, 98, 8349.

by considering a two-fluid model as in ref 12, but it then seems that the solvent viscosity is only relevant at high wave vectors.

Experimentally the undulation modes that we discuss could be observed by inelastic light scattering, the propagating waves give rise to side peaks at nonzero frequency, and the overdamped modes contribute to the width of the central quasielastic peak. A very detailed study has been conducted for viscous soap films, but to our knowledge no experiment has been conducted with soap films containing polymers.

Appendix: Coupling to the Perpendicular Elastic Modes

In sections II and III we only have considered undulation modes such that $|mh| < 1$, modes such that $|mh| > 1$ (even though $qh < 1$) also exist when the fluid has an elastic behavior ($\omega\tau > 1$). In this Appendix, we briefly discuss these modes in the limit where $\epsilon_s > Eh$ or $\nu\tau/h^2 > N_c^{-1}$.

The dispersion relation is obtained by expansion in powers of qh only. We obtain for squeezing modes

$$\omega^4 - \omega^2[\omega_c^2 + \omega_s^2 mh/2 \coth mh/2] + \omega_s^2 \omega_c^2 [mh/2 \coth mh/2 - 1] = 0 \quad (A-1)$$

In the range of parameters considered, m^2 is negative and m is a pure imaginary number, we thus define $m = im'$. Equation A-1 can be rewritten as an equation for $m'h$ only by noting that $\omega^2 \approx (m'h)^2 E/\rho h^2$.

$$z^2(m'h)^4 - z(m'h)^2 [m'h/2 \cot m'h/2] + q'^2 h^2 [m'h/2 \cot m'h/2 - 1] = 0 \quad (A-2)$$

where we have introduced $q'^2 = q^2 + 2/L^2$ and $z = E/(\rho h^2 \omega_s^2)$. The value $z = 1$ gives precisely the curve in the diagram of Figure 3 where $|mh|$ becomes larger than 1: $y \sim 1/(x^{1/2} N_c^{1/2})$.

This equation can be solved for $m'h$ giving

$$m'h/2 \cot m'h/2 = [q'^2 h^2 - z^2(m'h)^4]/[q'^2 h^2 - z(m'h)^2] \quad (A-3)$$

Equation A-3 is solved graphically in Figure 6. The function f on the right-hand side has two branches and diverges for $m'h = q'h/z^{1/2}$. The left branch is positive for $q'h > 1$ (if $m'h > 0$) and the function is always larger than 1. The right branch (large $m'h$) is negative in the vicinity of $m'h = q'h/z^{1/2}$. The function on the left-hand side of eq A-3 has an infinity of branches corresponding to the divergences of the cotangent for $m'h = 2k\pi$. The lowest branch starts from 1 when $m'h = 0$ and is monotonically decreasing.

Two cases must be considered. If $q'h/z^{1/2} < 2\pi$ (Figure 6a) the smallest solution of eq A-3 is given by the intersection of the smallest branch of the cotangent and the negative branch of f ; when $z > 1$ the solution is such that $m'h < 1$ and gives back the surface elastic wave $\omega = \omega_s$. When z decreases, $m'h$ increases and becomes equal to 2π when $q'h/z^{1/2} = 2\pi$. The other branches of the

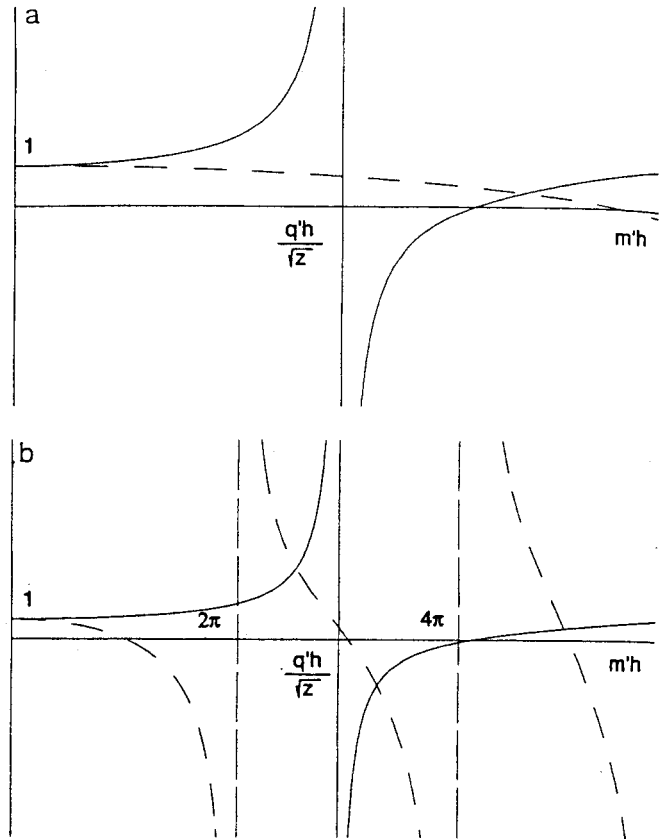


Figure 6. Graphic solution of eq A-3: (a) corresponds to the case $(q'h)^2/z < 1$; (b) corresponds to the case $(q'h)^2/z > 1$.

cotangent each give one mode such that $2n\pi < m'h < 2(n+1)\pi$. The order of magnitude of the pulsation of the n th mode is thus $\omega^2 = 2n\pi E/\rho h^2$. This clearly corresponds to compressional elastic waves of the gel propagating perpendicular to the surface and coupled to the undulation waves that we study. The various harmonics correspond to waves with a varying number of nodes. If $q'h/z^{1/2} > 2\pi$, the first branch of the cotangent does not give any solution to eq A-3 and the smallest solution is $m'h > 2\pi$ (Figure 6b).

The dispersion relation of the bending modes can be written as

$$\omega^4 - \omega^2[\omega_c^2 - \omega_s^2 m'h/2 \tan m'h/2] - \omega_s^2 \omega_c^2 [m'h/2 \tan m'h/2] = 0 \quad (A-4)$$

Rewriting this as a function of $m'h$ we find two types of solutions for any value of $m'h$

$$\omega = \omega_c, \quad \tan(m'h/2)/(m'h/2) = 4z' \quad (A-5)$$

where z' is defined as $z' = E/(\rho h^2 \omega_c^2)$. The capillary wave thus exists even if $m'h > 1$ and the bending modes are also coupled to the elastic compressional modes. The higher harmonics have a dispersion relation $\omega^2 = (2n+1)\pi E/\rho h^2$.