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Metastable wetting layers

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In the two-phase region of a critical binary liquid mixture a wetting layer of the heavier phase can occur at the upper liquid-vapor surface sufficiently close to the critical temperature. This wetting layer can be either *stable* or *metastable* to long-wavelength capillary wave fluctuations on the adjacent critical interface. The stability depends upon the sign and slope of the dispersion force curve $F(d)$. We classify the four main generic shapes for $F(d)$, which determines the stability or metastability of the wetting layer, in terms of the relative magnitudes of the static and visible dielectric constants for the two liquid components. For realistic values of the liquid-mixture parameters we calculate the critical wavelength beyond which fluctuations are unstable and also determine the lifetime of the metastable state. The lifetime can vary from seconds to many hours.

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I. INTRODUCTION

Wetting layers have been the subject of intense study for many years [1], ever since Cahn [2] predicted a first-order wetting transition at the noncritical surface of a critical binary liquid mixture (of A and B molecules) on approaching the critical temperature T_c. In Fig. 1 we show the heavier β phase (with the B the majority component) wetting the upper αs surface, where the noncritical phase s can be either a vapor or a solid. The typical equilibrium thickness d_0 of the wetting layer is $\sim 20-200$ nm. The equilibrium properties of wetting layers are well understood.

There are three conditions that must be satisfied in order that a wetting layer exist at the αs surface:

(i) $\sigma_{\beta s} < \sigma_{\alpha s}$, where σ_{ij} is the surface tension between phases i and j. This condition is obviously necessary in order that B molecules lower the αs surface free energy.

(ii) The temperature must be greater than the wetting transition temperature T_w. Below T_w, $\sigma_{\beta s}+\sigma_{\alpha\beta} > \sigma_{\alpha s}$, while at T_w and above Antonow's rule holds, namely, $\sigma_{\beta s}+\sigma_{\alpha\beta}=\sigma_{\alpha s}$ [3].

(iii) The thickness of the wetting layer is determined by gravity which thins the wetting layer and dispersion forces $F(d)$, which thicken the wetting layer according to the equation [4,5]

$$F(d_0)+\Delta\rho g L=0 . \tag{1}$$

Here the mass density difference $\Delta\rho=\rho_\beta-\rho_\alpha$, g is the acceleration due to gravity, L is the height of the bulk α phase, and the wetting-layer thickness has a value of d, which in equilibrium will be denoted by d_0. For an equilibrium wetting layer to exist *$F(d)$ must be negative* [5].

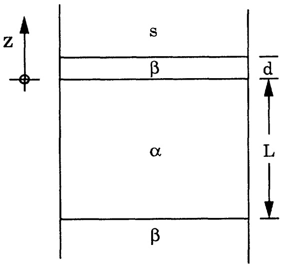

FIG. 1. Schematic diagram of the heavier β phase wetting the upper αs surface. The wetting layer has a thickness d, while the height of the bulk α phase is L.

If any of the conditions (i)–(iii) are not met then the structure of the αs surface is governed by critical adsorption rather than wetting [6,7]. In critical adsorption the composition at the αs surface is a function of distance into the liquid where the composition profile scales with the bulk correlation length ξ. In contrast to critical adsorption, a wetting layer of thickness d has a constant composition equal to the bulk β-phase composition.

It is perhaps less well known that if (i) and (ii) hold but (iii) does not hold that a long-lived *metastable* wetting layer of the β phase (with zero contact angle) can still exist at the αs surface. We will examine the conditions under which this occurs in this paper and determine the lifetime of the metastable wetting layer. The results in this paper can be readily extended to metastable wetting layers in other systems such as at microemulsion surfaces [8].

This paper is organized as follows: In Sec. II we determine the main shapes for the dispersion force curve $F(d)$ as a function of the wetting-layer thickness d. At a binary liquid-vapor surface there are four main dispersion force curves determined by the sign of $\Delta\epsilon_0=\epsilon_{\alpha 0}-\epsilon_{\beta 0}$ and $\Delta\epsilon_v=\epsilon_{\alpha v}-\epsilon_{\beta v}$, where the subscript 0 (v) indicates the static (visible) dielectric constant. Specifically, (i) $\Delta\epsilon_0>0$ and $\Delta\epsilon_v>0$, $F(d)<0$, and the wetting layer is always stable; (ii) $\Delta\epsilon_0<0$ and $\Delta\epsilon_v>0$, $F(d)$ changes from negative to positive with increasing d, and at large d the wetting layer is metastable; (iii) $\Delta\epsilon_0>0$ and $\Delta\epsilon_v<0$, $F(d)$ changes from positive to negative with increasing d, and at small d the wetting layer is metastable; finally, (iv) $\Delta\epsilon_0<0$ and $\Delta\epsilon_v<0$, $F(d)>0$, and the wetting layer is always metastable. Metastable wetting layers are unstable to capillary-wave fluctuations greater than a critical wavelength Λ_c. We determine the critical wavelength and lifetime τ_m of the metastable state for realistic binary-liquid-mixture parameters. The lifetime can vary from seconds to many hours. Our results are discussed in Sec. III.

The equations for Λ_c and τ_m used in Sec. II were obtained from Vrij and Overbeek [9], who considered the rupture of a film of total surface tension γ. It is not clear how their results apply to our situation where the wetting layer is very asymmetric with $\sigma_{\beta v} \gg \sigma_{\alpha\beta}$. In the Appendix we show that the wetting layer is unstable to long-wavelength capillary-wave fluctuations on the critical $\alpha\beta$ surface and therefore Vrij and Overbeek's analysis is valid with $\gamma/2$ replaced by $\sigma_{\alpha\beta}$.

II. STABLE AND METASTABLE WETTING LAYERS

Whether an equilibrium wetting layer can exist depends upon the sign and slope of $F(d)$. It has often been assumed in the literature that the dispersion force can be modeled by a simple power-law function of the form

$$F(d)=\frac{A}{6\pi d^3} \tag{2}$$

for nonretarded van der Waals forces, where A is the Hamaker constant. Such a model is correct for very thin wetting layers ($d \le 5$ nm) [10]; however, for the wetting-layer thicknesses observed in practice (≥ 20 nm), this is not a good approximation. For real systems $F(d)$ is often far more complicated and can even change sign as a function of d. $F(d)$ must be calculated from the Dzyaloshinskii-Lifshitz-Pitaevskii (DLP) theory of dispersion forces [11], which requires as inputs the order parameter for the binary liquid mixture of interest and dispersion data for the pure liquid components [5]. According to the DLP theory for arbitrary media, 1, 2, and 3 corresponding to s, α, and β above,

$$F(d)=\frac{k_B T}{\pi c^3}\sum_{j=0}^{\infty}{}' \epsilon_3^{3/2}\xi_j^3 \int_1^{\infty} p^2 dp\,\{[f_1(1)f_2(1)\exp(2p\xi_j\epsilon_3^{1/2}d/c)-1]^{-1}+[f_1(\epsilon_1/\epsilon_3)f_2(\epsilon_2/\epsilon_3)\exp(2p\xi_j\epsilon_3^{1/2}d/c)-1]^{-1}\}\ , \tag{3a}$$

where

$$f_i(x)=(s_i+px)/(s_i-px) \tag{3b}$$

and

$$s_i=(\epsilon_i/\epsilon_3-1+p^2)^{1/2}\ , \quad i=1,2\ . \tag{3c}$$

The quantity k_B is Boltzmann's constant, c is the speed of light, $\xi_j=2\pi j k_B T/\hbar$, $2\pi\hbar$ is Planck's constant, and ϵ_1, ϵ_2 and ϵ_3 are the frequency-dependent dielectric constants of the three media evaluated at the imaginary frequencies $\omega=i\xi_j$. The prime attached to the summation denotes that the term with $j=0$ is to be given half weight. The excellent pedagogical paper of Kayser [5] demonstrates how to calculate $F(d)$ for critical binary liquid mixtures using (3).

As mentioned previously the sign of $F(d)$ is very important in determining the stability or metastability of a wetting layer. It is difficult to obtain an intuitive understanding of the behavior of $F(d)$ from (3) because of the complexity of this equation. Israelachvili [12] has presented an approximate expression for $F(d)$, which is valid for nonretarded van der Waals forces. His expression allows us to qualitatively interpret the main features of $F(d)$. In the nonretarded regime the Hamaker constant is given approximately by

$$A=A_{j=0}+A_{j>0}\ , \tag{4a}$$

where

$$A_{j=0}\sim k_B T(\epsilon_{\alpha 0}-\epsilon_{\beta 0})(\epsilon_{s0}-\epsilon_{\beta 0})\ , \tag{4b}$$

$$A_{j>0}\sim \hbar\omega_{\rm uv}(\epsilon_{\alpha v}-\epsilon_{\beta v})(\epsilon_{sv}-\epsilon_{\beta v})\ , \tag{4c}$$

where ϵ_{i0} and ϵ_{iv} are, respectively, the static and visible dielectric constants of medium i and $\omega_{\rm uv}$ is a characteristic electronic absorption frequency ($\sim 2\times 10^{16}$ Hz). If one of the components of the liquid mixture is polar the static dielectric constants $\epsilon_{\alpha 0}$ and $\epsilon_{\beta 0}$ may be very different and the zero-frequency component ($j=0$) can be very important and make a significant contribution to $F(d)$. At small $d \ll c/\omega_{\rm uv}$ all contributions to $F(d)$ are nonretarded and decay as d^{-3}. For most liquid mixtures the dominant contribution comes from the visible component so that $A_{j>0}$ determines the sign of $F(d)$ for small d. At larger $d \gtrsim c/\omega_{\rm uv}$ (~ 10 nm) the visible contribution to $F(d)$ becomes retarded and decays as d^{-4} while the zero-frequency contribution remains nonretarded and eventually dominates $F(d)$ for sufficiently large d. Therefore at large d the sign of $F(d)$ is determined by $A_{j=0}$.

For a binary liquid-vapor surface ($\epsilon_s=1$) four main possibilities can occur, depending upon the relative magnitudes of $\epsilon_{\alpha v}$, $\epsilon_{\beta v}$, $\epsilon_{\alpha 0}$, and $\epsilon_{\beta 0}$ (Fig. 2).

(i) $\epsilon_{\beta v}<\epsilon_{\alpha v}$ and $\epsilon_{\beta 0}<\epsilon_{\alpha 0}$. In this case $F(d)$ is negative and a monotonic increasing function of d. For any value of the gravitational force there is one equilibrium value of the wetting-layer thickness given by the intersection of $-\Delta\rho g L$ with $F(d)$. If the wetting layer is prepared in a state with a thickness other than d_0, the wetting layer will approach d_0 via diffusion-limited growth [13].

(ii) $\epsilon_{\beta v}<\epsilon_{\alpha v}$ and $\epsilon_{\beta 0}\gg\epsilon_{\alpha 0}$. The static contribution is positive while the visible contribution is negative. For this situation $F(d)$ changes from negative to positive with increasing d. The static term makes a significant contribution at small d and a dominant contribution at large d so that there is a maximum in $F(d)$. For all values of the

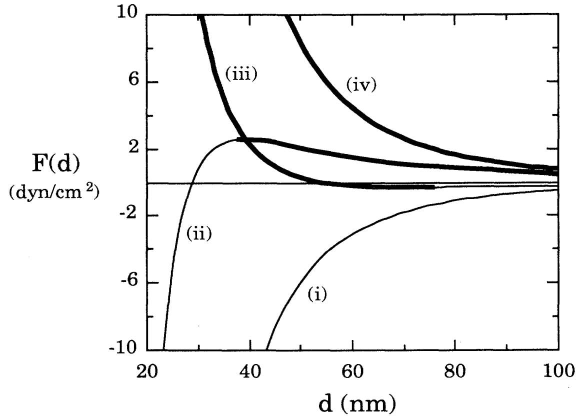

FIG. 2. Dispersion force curves $F(d)$ as a function of the wetting-layer thickness d calculated using the parameters for critical hexadecane plus acetone at a reduced temperature of $t=10^{-2}$. The static, microwave, and visible dielectric constants have been permuted in generating curves (i)–(iv); their values are listed in Ref. [15]. Curve (i) $\Delta\epsilon_0>0$ and $\Delta\epsilon_v>0$; (ii) $\Delta\epsilon_0<0$ and $\Delta\epsilon_v>0$; (iii) $\Delta\epsilon_0>0$ and $\Delta\epsilon_v<0$; and (iv) $\Delta\epsilon_0<0$ and $\Delta\epsilon_v<0$. Metastable wetting layers with $\partial F/\partial d<0$ are indicated by the heavier line.

gravitational force there is a corresponding equilibrium wetting-layer thickness given by the intersection of $F(d)$ with $-\Delta\rho g L$. However, if a wetting layer is prepared with sufficiently large d such that $\partial F/\partial d<0$ [indicated by the heavier line in Fig. 2, curve (ii)], then this wetting layer will be unstable to long-wavelength capillary-wave fluctuations, as will be discussed below. Such a wetting layer would be metastable with a lifetime given by τ_m below.

(iii) $\epsilon_{\beta v}>\epsilon_{\alpha v}$ and $\epsilon_{\beta 0}\ll\epsilon_{\alpha 0}$. The static contribution is negative while the visible contribution is positive. In this case $F(d)$ is positive for small d; however, at large d it changes sign and passes through a minimum in $F(d)$. For small $\Delta\rho g L$ below a minimum $F_G(\mathrm{min})$ (~ 0.24 dyn/cm^2 in Fig. 2) there are two solutions to Eq. (1): one which is metastable (indicated by the heavier line in Fig. 2 where $\partial F/\partial d<0$) with a lifetime τ_m and the other which is stable. For $\Delta\rho g L>F_G(\mathrm{min})$ no wetting layer can exist in equilibrium.

(iv) $\epsilon_{\beta v}>\epsilon_{\alpha v}$ and $\epsilon_{\beta 0}>\epsilon_{\alpha 0}$. $F(d)$ is positive for all d and a wetting layer cannot exist in equilibrium. All wetting layers are metastable with lifetime τ_m.

In calculating Fig. 2 we have used the DLP theory with the parameters for hexadecane plus acetone [14] where we have interchanged either $(\epsilon_{i0}/\epsilon_{io+})$ and/or ϵ_{iv} between liquid A and liquid B, where ϵ_{io+} is the microwave dielectric constant for liquid i. The notation $(\epsilon_{i0}/\epsilon_{io+})$ means that both ϵ_{i0} and ϵ_{io+} are interchanged. The critical liquid mixture hexadecane plus acetone at a reduced temperature $t=10^{-2}$ is represented by curve (ii) in Fig. 2, while curves (i), (iii), and (iv) have $(\epsilon_{i0}/\epsilon_{io+})$ and/or ϵ_{iv} interchanged. In [15] we list the various values for ϵ_{i0}, ϵ_{io+}, and ϵ_{iv} used in generating the curves in Fig. 2.

Vrij and Overbeek [9] previously considered the metastability of films, of total surface tension γ, to capillary-wave fluctuations. We demonstrate, in the Appendix, that wetting layers are unstable to long-wavelength fluctuations on the $\alpha\beta$ interface and that therefore Vrij and Overbeek's results are applicable with $\gamma/2$ replaced by $\sigma_{\alpha\beta}$.

In the metastable wetting region (heavier curves in Fig. 2), where $\partial F/\partial d<0$ capillary wavelengths Λ, larger than a critical wavelength

$$\Lambda_c=\left[-\frac{4\pi^2\sigma_{\alpha\beta}}{\partial F/\partial d}\right]^{1/2}, \tag{5}$$

are unstable to fluctuations on the $\alpha\beta$ interface. The characteristic lifetime for a particular capillary wave vector k $(=2\pi/\Lambda)$ is given by [9]

$$\tau(k)=-\frac{12\eta}{d^3}\left[\frac{\partial F}{\partial d}k^2+\sigma_{\alpha\beta}k^4\right], \tag{6}$$

where η is the film viscosity. The lifetime τ depends upon k and has a sharp minimum when $\Lambda=2^{1/2}\Lambda_c$, where the minimum lifetime is

$$\tau_m=\frac{48\sigma_{\alpha\beta}\eta}{d^3\left[\dfrac{\partial F}{\partial d}\right]^2}. \tag{7}$$

We have plotted the critical wavelength Λ_c, (Fig. 3) and the minimum lifetime τ_m (Fig. 4) for the metastable regions of Fig. 2 [curves (ii)–(iv)]. One observes from Fig. 4 that the lifetime τ_m can vary from seconds to many hours, depending on the signs of $\Delta\epsilon_0$ and $\Delta\epsilon_v$ and depending on the thickness of the metastable film. The breaking time τ_b of a metastable film is a simple multiple of τ_m [9],

$$\tau_b\sim f\tau_m, \tag{8}$$

where $f\sim 7$ for $d\sim 50$ nm and $\sigma_{\alpha\beta}\sim 0.15$ erg/cm^2. The critical liquid mixture hexadecane plus acetone is de-

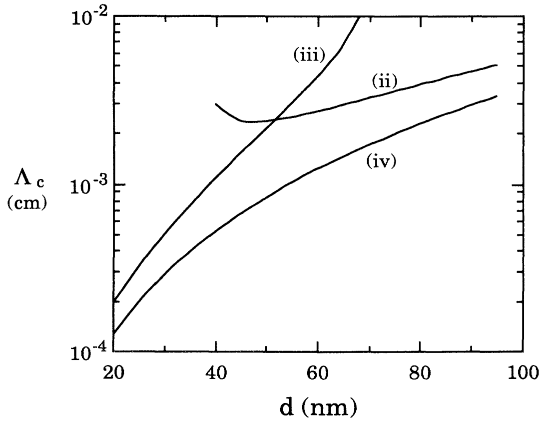

FIG. 3. Plot of the critical wavelength Λ_c for the metastable regions of Fig. 2 above which capillary-wave fluctuations are unstable. The designations (ii), (iii), and (iv) correspond to the same designations in Fig. 2.

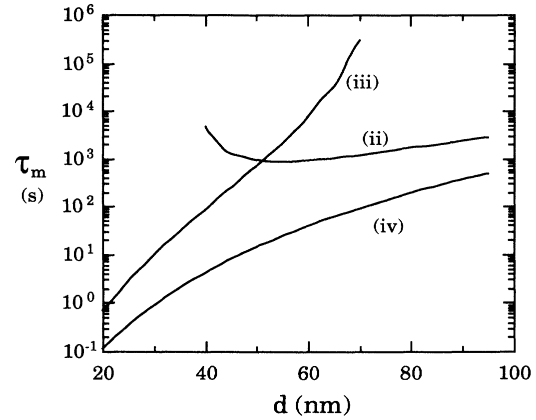

FIG. 4. Plot of the minimum lifetime τ_m for the metastable regions of Fig. 2. The designations (ii), (iii), and (iv) correspond to the same designations in Fig. 2

scribed by curve (ii) in Fig. 4; the observed breaking time qualitatively agrees in magnitude with the observations in a previous publication [14].

III. CONCLUSION

For highly polar liquid mixtures the zero-frequency contribution to the dispersion force can be very large at all thicknesses of the wetting layer. The stability or metastability of a wetting layer depends upon the sign and slope of the dispersion force at each thickness. From the relative magnitudes of the static and visible dielectric constants of the two components in a binary liquid mixture we have determined the four major forms for the dispersion force $F(d)$, which can occur in the two-phase region at the binary liquid-vapor surface.

With the advent of the technique of reflectance fluctuation spectroscopy [16], which allows one to measure the viscosity of the wetting layer and $\partial F/\partial d$, it should be possible to quantitatively test the theory of film rupture as presented in (7) and (8). A critical binary liquid mixture is particularly convenient for tests on film rupture because the critical surface tension $\sigma_{\alpha\beta}=\sigma_0 t^{\mu}$, where $\mu=1.24$, appearing in (7) is a sensitive function of temperature. For critical liquid mixtures which obey (2), where $A \sim t^{\beta}$ with the critical exponent $\beta=0.33$, the critical wavelength $\Lambda_c \sim t^{(\mu-\beta)/2}$ while the minimum lifetime $\tau_m \sim t^{\mu-2\beta}$ and metastable wetting films rupture more quickly at smaller reduced temperatures.

A quantitative examination of film rupture would aid in the understanding of foams whose stability is not well understood [17]. Surfactant solutions which constitute foams and also microemulsions [8] have an additional contribution from double-layer forces where the total surface force per unit area is given by [12,18]

$$F=F_{\text{disp}}+F_{\text{DL}} , \quad F_{\text{DL}}=-B\kappa_D^2\exp(-\kappa_D d) , \tag{9}$$

where F_{disp} is the dispersion force given in (3) and F_{DL} is the double-layer force, with κ_D the inverse Debye length and $B>0$. Therefore the double-layer force always stabilizes the wetting layer against capillary-wave fluctuations on the $\alpha\beta$ surface, namely, $\partial F_{\text{DL}}/\partial d>0$.

Throughout this paper we have ignored the effects from diffusion-limited growth of the wetting layer [13]; in reality the wetting film will slowly approach the equilibrium wetting-layer thickness via diffusion. For critical binary liquid mixtures the diffusion time constant is usually very large [13].

Finally, we note in passing that Dietrich and Latz [19] and Getta and Dietrich [20] have published some important related work where they classify interfacial wetting behavior from a somewhat different perspective than presented here.

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APPENDIX

In this appendix we consider the dispersion relation for a wetting layer in contact first with a solid and second with a vapor.

1. Wetting layer in contact with a solid

The surface wave has a spatial and temporal dependence of $\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]$, where $\mathbf{k}=(k_x,k_y)$ is a two-dimensional surface wave vector, $\mathbf{r}=(x,y)$, ω is the frequency of the wave, and $k=(k_x^2+k_y^2)^{1/2}$. One can readily show [21] that, for an inviscid liquid of constant density, the linearized hydrodynamic equations reduce to

$$(D^2-k^2)w=0 , \tag{A1}$$

where w is the velocity of the liquid in the vertical z direction and $D=d/dz$. Consequently

$$w=\begin{cases} A\cosh(kz)+B\sinh(kz) , & 0<z<d \quad \text{(A2a)} \\ C\exp(kz) , & z<0 , \quad \text{(A2b)} \end{cases}$$

where A, B, and C are constants.

For a solid surface

$$w_{\beta s}=w(z=d)=0 , \tag{A3}$$

while the boundary condition at the $\alpha\beta$ surface is [21,22]

$$\Delta_0(\rho D w)=\frac{k^2}{\omega^2}\left\{\left[g\Delta_0(\rho)-k^2\sigma_{\alpha\beta}-\frac{\partial F}{\partial d}\right]w_{\alpha\beta}+\frac{\partial F}{\partial d}w_{\beta s}\right\} . \tag{A4}$$

In this equation $\partial F/\partial d$ is often represented as $-\partial\pi/\partial d$, where π is the disjoining pressure [22] and the notation $\Delta_s(f)=f(z=s+)-f(z=s-)$ represents the jump in quantity f at interface $z=s$, while $w_{\alpha\beta}$ is the common value of the vertical velocity at $z=0$. We necessarily have no discontinuity in the vertical velocity at this surface,

$$w_{\alpha\beta}=w(0+)=w(0-) . \tag{A5}$$

From the three boundary conditions (A3)–(A5) we can eliminate the three constants A, B, and C in (A2) to obtain the dispersion relation [23]

$$\omega^2 = \frac{-k\left[g\Delta\rho - k^2\sigma_{\alpha\beta} - \frac{\partial F}{\partial d}\right]\tanh(kd)}{\rho_\beta + \rho_\alpha \tanh(kd)} . \tag{A6}$$

The wetting layer is unstable to fluctuations on the $\alpha\beta$ surface when $\omega^2 < 0$, namely, for capillary wavelengths Λ greater than

$$\Lambda_c = \left[\frac{4\pi^2\sigma_{\alpha\beta}}{g\Delta\rho - \frac{\partial F}{\partial d}}\right]^{1/2} . \tag{A7}$$

This equation agrees with the results in Sec. II and with Ref. [9]. In Sec. II we have ignored the gravitational term because it is, in general, at least two orders of magnitude smaller than $\partial F/\partial d$ except very near a maximum or minimum in $F(d)$.

2. Wetting layer in contact with a vapor

We generalize the analysis of the preceding section to the case where the βs surface has capillary-wave fluctuations. For such a situation the boundary condition (A3) is no longer valid; the condition on the βs surface takes a form similar to (A4), namely,

$$\Delta_d(\rho D w) = \frac{k^2}{\omega^2}\left\{\left[g\Delta_d(\rho) - k^2\sigma_{\beta s} - \frac{\partial F}{\partial d}\right] w_{\beta s} + \frac{\partial F}{\partial d} w_{\alpha\beta}\right\} . \tag{A8}$$

The bulk-fluid equations (A2) continue to hold in this situation where the boundary conditions (A4), (A5), and (A8) are used to eliminate A, B, and C. The most general dispersion equation is very complicated. It is necessary to make some approximations. We assume the following.

(i) $\zeta_{\alpha\beta} = w_{\alpha\beta}/\omega \gg \zeta_{\beta s} = w_{\beta s}/\omega$, where ζ_i is the magnitude of the fluctuations on boundary i. This is a reasonable approximation as the restoring forces on the $\alpha\beta$ surface are much smaller than on the βs surface.

(ii) $k^2\sigma_{\beta s} \gg \Delta\rho g, \partial F/\partial d$. The surface tension provides most of the restoring force at the βs surface for wavelengths less than the βs capillary length.

(iii) $k^2\sigma_{\alpha\beta} \gg \Delta\rho g$.

(iv) $kd \ll 1$. This is the most important limit in practice because the critical wavelength Λ_c is much larger than the wetting-layer thickness d.

One can show that with these assumptions the dispersion relation reduces to

$$\omega^4\rho_\alpha\rho_\beta - \omega^2 k^3\rho_\beta(\sigma_{\beta s} + \sigma_{\alpha\beta}) + \left[k^2\sigma_{\alpha\beta} + \frac{\partial F}{\partial d}\right] k^5\sigma_{\beta s} h = 0 , \tag{A9}$$

which has, to a good approximation, the following two solutions:

$$\omega_+^2 \approx \frac{k^3(\sigma_{\beta s} + \sigma_{\alpha\beta})}{\rho_\alpha} \tag{A10a}$$

and

$$\omega_-^2 \approx \frac{k^2 h}{\rho_\beta}\left[k^2\sigma_{\alpha\beta} + \frac{\partial F}{\partial d}\right] . \tag{A10b}$$

The ω_+ solution is the dispersion relation for waves on a liquid-vapor surface with surface tension $(\sigma_{\alpha\beta} + \sigma_{\beta s})$. It describes the "undulatory mode," where the upper and lower surfaces move in phase with essentially equal amplitudes [24]. The ω_- solution describes the "peristaltic mode," where the upper and lower surfaces move out of phase and the upper surface wave amplitude is much smaller than the lower surface wave amplitude [24]. The dispersion relation (A10b) again leads to the critical wavelength given in (5).

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and for curve (iv) the respective values are 2.04, 2.04, 1.819, 21.2, 2.2, and 2.025.

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[23] This dispersion relation is similar to that quoted by S. Chatterjee, V. Vani, S. Guha, and E. S. R. Gopal, J. Phys. (Paris) **46**, 1533 (1985), for the same physical situation, except that they omit the $\partial F/\partial d$ term and also do not have the term $\tanh(kd)$ in the denominator. The $\tanh(kd)$ term in the denominator is required. For example, consider the case when $\rho_\beta=0$ and $F=0$ in (A6); then the dispersion relation must reduce to that of a free liquid surface. They also state in their paper that wetting layers are unstable to the Rayleigh-Taylor instability on the $\alpha\beta$ interface sufficiently close to T_c. This may be true for very thick wetting layers far from the equilibrium thickness where $\partial F/\partial d$ is small. However, for *equilibrium wetting layers* described by Eqs. (1) and (2), $\partial F/\partial d = 3\Delta\rho g L/d_0$, which always dominates the gravitational term in (A6) so that $\omega^2 > 0$ and, in this situation, the wetting layer is never unstable to capillary-wave fluctuations on the critical interface.

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