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Pressure on the free surface of a liquid film from confined thermally excited sound waves

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Abstract
Recently an acoustic destabilizing pressure was predicted, which could be shown experimentally via a dewetting pattern in thin polymer films. The wavelength λ of the fastest growing mode is a signature of the acting forces. Even in cases with stabilizing van der Waals forces, films became unstable. The present paper also considers thermally excited acoustic waves confined in a thin liquid film of thickness d. A new concept is developed to calculate the acoustic pressure for different boundary conditions: the free-standing film, the film rigid at one surface and the film deposited on a substrate, liquid or solid. For characteristic examples the calculation is carried out numerically. The results for the limiting cases are simple. The acoustic pressure of the free-standing film grows monotonically with d up to a level strongly depending on the temperature, it cannot destabilize the film. The acoustic pressure of the film rigid at one surface rapidly grows with d to a maximum and then decreases monotonically to the same level as for the free-standing film. On the right side of the maximum the film is unstable and λ grows quadratically with d, similar to the case of a destabilizing van der Waals pressure. For a film deposited on a substrate the acoustic pressure comes to a smaller level directly, depending on the excess sound velocity in the substrate: generally it yields a rather linear dependence of λ on d.

1. Introduction

Coatings and their stability have an enormous technological relevance. Lubrication layers, adhesives, protective coatings, membranes and foams are stabilized by the surface tension σ and are further stabilized or destabilized by forces described by their effective interfacial potential $\Phi(d)$, where d is the layer thickness [1]. For very small d there act the prominent van der Waals forces [2, 3]. They exert a pressure

$$P_{\rm vdW}(d) = \Phi'_{\rm vdW} = A/(6\pi d^3). \qquad (1)$$

For a positive Hamaker constant A it destabilizes the film: capillary surface waves are amplified, leading to *spinodal dewetting*. A linear stability analysis yields the wavelength of the mode with the fastest growing amplitude:

$$\lambda(d) = \sqrt{-8\pi^2\sigma/\Phi''(d)}. \qquad (2)$$

λ is a signature of the interface potential and can be used to determine the forces. For example, from the preferred wavelength λ, Seemann *et al* could find precisely the Hamaker constant A for a PS film on an SiO substrate [1]. Otherwise the Hamaker constant is calculated by the refractive indices and dielectric constants of the materials in the layered system. It is positive ($A > 0$) if the refractive indices of the two media bounding the film (air and substrate) are lower as compared to the film [4, 5].

There may act further forces, e.g. electrostatic forces and temperature gradients, and also, as proposed by Schäffer and Steiner [6], the pressure of thermally excited acoustic waves confined in the film. Excluding all other known sources the experiments of Morariu *et al* [4, 7] showed a dewetting pattern even for stabilizing van der Waals forces ($A < 0$). The basic formula for the acoustic pressure used in [4, 7, 8] is

$$P_{\rm ac}(d) = \pi k_{\rm B}T/(18d^3). \qquad (3)$$

It was derived by Schäffer *et al* [6] using the same energy $k_{\rm B}T$ for all states and the Debye approximation for a *free-standing* *film*:

$$\frac{k_B T}{3}\left[\int_0^{\nu_{D,a}} dn_a - \int_{\nu_c}^{\nu_{D,f}} dn_f\right] = P_0 + \frac{\pi k_B T}{18 d^3}, \quad (4)$$

with the density of states for sound waves

$$dn = \frac{4\pi \nu^2 d\nu}{u^3}, \quad (5)$$

and the lower cutoff frequency (u_f being the sound velocity in the film)

$$\nu_c = u_f/(2d). \quad (6)$$

Some questions remain: is P_{ac} destabilizing ($\Phi''_{ac} < 0$) in all cases, and how does it depend on the properties of the film, the substrate and the boundary conditions (see the discussion with Steiner [7])? One of the results of the experiments in [4] is that the influence of P_{ac} vanishes if the film and the substrate are acoustically very similar.

The density of states, equation (5), is an approximation of lower order, which does not reflect the acoustic boundary conditions [9]. Following Landau and Lifshitz [10] and Larraza [11] the radiation pressure on a perfectly reflecting surface of a sound wave (with the mean energy density $\bar{E}$) is given by

$$P = 2\bar{E}\cos^2\Theta, \quad (7)$$

where Θ is the angle of incidence on the surface. The introduction of a limiting frequency $\omega_D = 2\pi\nu_D$ keeps the pressure bounded, if one assumes the same energy $k_B T$ for all states. Using the precise number of confined states below ω_D thus leads to discontinuities of the function $\Phi''(d)$ at $d/d_0 = 1, 2, \ldots,$ where $d_0 = u_f/2\nu_D$. But considering the energy distribution

$$\hbar\omega/(\exp(\hbar\omega/k_B T) - 1) \quad (8)$$

instead of $k_B T$ for each state, the introduction of ν_D is useless and one obtains a finite, smooth curve for the pressure $P_{ac}(d)$.

We proceed in this paper in section 2 by calculating the allowed acoustic states (dispersion curves) for different boundary conditions. P_{ac} will be derived by summing up the contributions of all confined states including the factor $2\cos^2\Theta$ and the energy distribution (8). Section 3 is devoted to the results and discussion. A summary is given in section 4.

2. The pressure from the confined states in a thin liquid film

For a system of flat liquid layers in each layer plane monochromatic sound waves are described by their potential $\varphi = A\cdot\exp(-i\omega t + i\mathbf{kr})$, which is a solution of the wave equation $u^2\ddot{\varphi} - \Delta\varphi = 0$, with the sound velocity u [10]. The variation of the pressure and the particle velocity of the sound wave is given by

$$p = -\rho\dot{\varphi}, \qquad \mathbf{v} = \text{grad}\varphi. \quad (9)$$

With the normal in the x_3 direction one has the boundary conditions for individual layers: (i) at free surfaces the normal component of the stress tensor vanishes, i.e. $p = -\rho\dot{\varphi} = 0$,

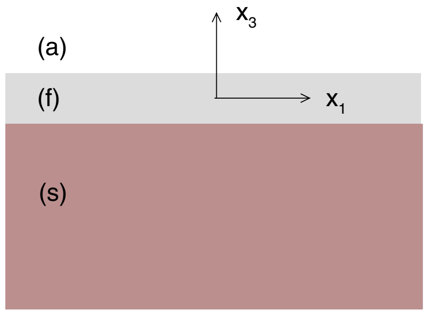

Figure 1. Boundary conditions for a liquid film (f) parallel to the x_1, x_2 plane with one surface bounded by air (a). (I) The other surface is free too. (II) The other surface is fixed. (III) The film is deposited on a liquid substrate (s). (IV) The film is deposited on a solid substrate (s).

(ii) at liquid/liquid interfaces the normal stress $(-\rho\dot{\varphi})$ and the normal component of the particle velocity $(\varphi_{,3})$ should be continuous, (iii) the substrate is regarded as a half-space, so $\varphi(x_3)$ should remain finite and (iv) at rigid surfaces the normal component of the particle velocity vanishes, $v_3 = \varphi_{,3} = 0$. In each layer (film or substrate, see figure 1) the boundary conditions can be fulfilled by superposition of bulk waves. In the film (l = f) and the substrate (l = s)

$$\varphi_l = (A_l \sin(k_{\perp l}x_3) + B_l\cos(k_{\perp l}x_3))\cdot\exp(-i\omega t + i\mathbf{k}_\parallel \mathbf{r}),$$
$$k_{\perp l} = \sqrt{\omega^2/u_l^2 - k_\parallel^2}. \quad (10)$$

The allowed film/substrate states are characterized by their frequency ω, by the wavevector component $k_\parallel \equiv K$ parallel to the surfaces and by the plane of propagation [9, 10, 12].

From the boundary conditions we get the equations for the coefficients:

(1) At the upper free surface of the liquid film ($\dot{\varphi} = 0$):

$$A_f\sin(k_{\perp f}d/2) + B_f\cos(k_{\perp f}d/2) = 0. \quad (11)$$

(2) At the lower surface of the liquid film: if the film is free here too ($\dot{\varphi} = 0$):

$$-A_f\sin(k_{\perp f}d/2) + B_f\cos(k_{\perp f}d/2) = 0. \quad (12)$$

If this surface of the film is rigid ($\varphi_{,3} = 0$):

$$A_f\cos(k_{\perp f}d/2) + B_f\sin(k_{\perp f}d/2) = 0. \quad (13)$$

If the film is deposited on a liquid substrate ($\rho\dot{\varphi}$) and ($\varphi_{,3}$) should be continuous:

$$\rho_f(-A_f\sin(k_{\perp f}d/2) + B_f\cos(k_{\perp f}d/2)) = \rho_s B_s, \quad (14)$$

$$k_{\perp f}\cdot(A_f\cos(k_{\perp f}d/2) + B_f\sin(k_{\perp f}d/2)) = k_{\perp s}A_s, \quad (15)$$

(for the substrate this surface is taken as $x_3 = 0$).

(3) For $x_3 \to -\infty$, φ_s should remain finite. Confined states cannot propagate in the substrate, therefore we require $\omega/k_\parallel < u_s$, so that ($k_{\perp s} \equiv i\cdot a_s$) is imaginary and the boundary condition yields

$$A_s + i\cdot B_s = 0. \quad (16)$$

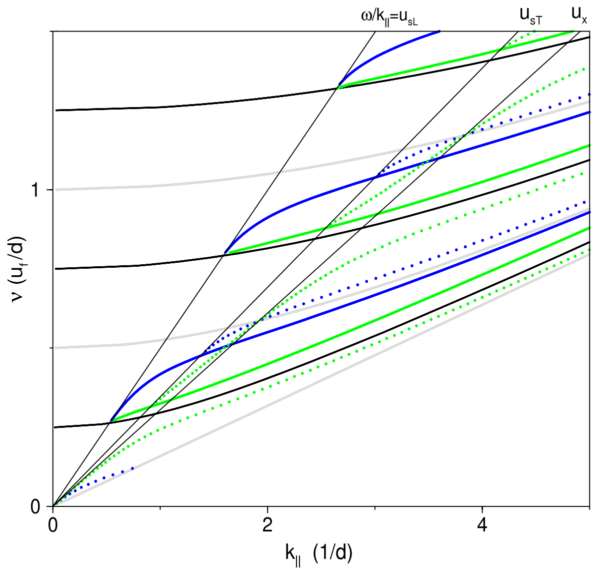

Figure 2. Dispersion curves of the confined modes in a liquid film (d, u_f) with one surface free and different boundary conditions for the other surface. (I) The other surface is free too, grey hyperbola. (II) The other surface is rigid, black hyperbola. (III) The film is deposited on a liquid substrate half-space, solid coloured curves. (IV) The film is deposited on a solid substrate half-space, dotted coloured curves. $R = \rho_s/\rho_f = 1.97$ (green) and $R = 0.197$ (blue).

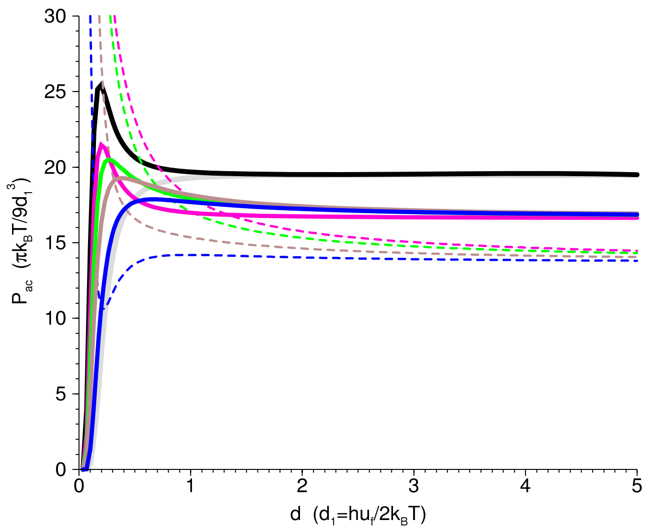

Figure 4. The pressure of the confined sound waves in a liquid film versus film thickness d (with energy distribution (8)). One surface of the film is free. (I) The other surface is free too, solid grey curve. (II) The other surface is rigid, solid black curve. (III) The film is deposited on a liquid substrate, solid coloured curves. (IV) The film is deposited on a solid substrate, dashed coloured curves. $u_f = 2.7$ km s^{-1}, $u_s = 8.4$ km s^{-1}, $u_{sL} = 8.4$ km s^{-1}, $u_{sT} = 5.8$ km s^{-1}, $\rho_f = 1.2$g cm^{-3}, $\rho_s = 2.3$ g cm$^{-3} \cdot F$, $F = 10$ (magenta), $F = 1$ (green), $F = 0.3$ (brown) and $F = 0.1$ (blue).

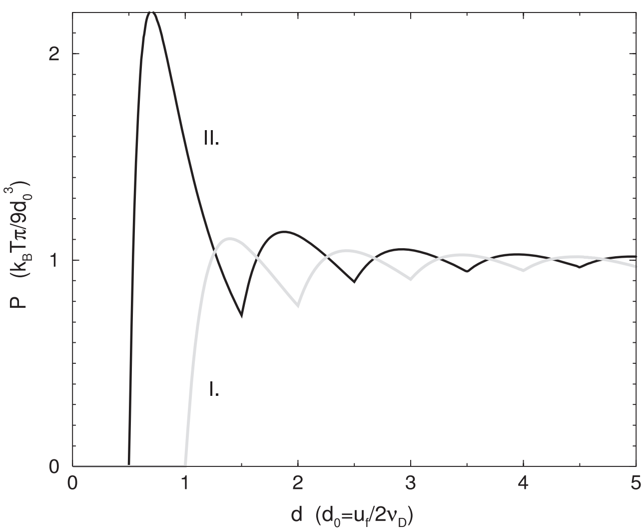

Figure 3. Acoustic pressure for the energy $k_B T$ of each state. (I) Free-standing film, solid grey curve. (II) One surface of the film is free and the other rigid, solid black curve.

2.1. Free-standing liquid film (I)

At both surfaces ($x_3 = \pm d/2$) the normal component of the stress tensor, i.e. $p = -\rho_f \dot{\varphi}_f$, vanishes. The system of equations for A_f, B_f is solvable if its determinant $\sin(k_{\perp f} d)$ vanishes: this yields the dispersion curves (thick grey hyperbola in figure 2)

$$\omega^2/u_f^2 - k_\parallel^2 = (n\pi/d)^2 = k_\perp^2, \qquad k_\perp \equiv k_{\perp f} \quad n = 0, 1, 2, \ldots \tag{17}$$

Each point on these curves represents one state for a fixed plane of propagation. We can count the number of states in the volume $V = L_1 L_2 d$, with frequencies below ω_D (L_1, L_2 being the lengths of the film)

$$A_I(\omega_D) = \sum_{n=0}^{N_I} \frac{L_1 L_2}{4\pi^2} \int_0^{K_{In}} 2\pi K \, dK. \tag{18}$$

The number of curves beginning below ν_D is given by

$$N_I = \lfloor \nu_D/\nu_c \rfloor, \qquad \nu_c = u_f/2d, \tag{19}$$

where $\lfloor \cdots \rfloor$ denotes the maximum natural number below. The intersections of the dispersion curves with $\omega = \omega_D$ are

$$K_{In}^2 = \frac{\omega_D^2}{u_f^2} - \left(\frac{n\pi}{d}\right)^2, \qquad n = 0, 1, \ldots, N_I. \tag{20}$$

To calculate the inside acoustic pressure on the free surface of the film one should multiply each state with its energy density and with

$$2\cos^2\Theta = 2(k_\perp/k)^2, \tag{21}$$

where Θ is the angle of incidence on the surface [10]. If one assumes the energy $k_B T$ for each state [6] one obtains the pressure, which the acoustic states exert on the free surface of the film (thick grey curve in figure 3):

$$P_I = \frac{2k_B T}{V} \sum_{n=0}^{N_I} \frac{L_1 L_2}{4\pi^2} \int_0^{K_{I,n}} \cos^2\Theta 2\pi K \, dK. \tag{22}$$

With the new variable $Z^2 = k^2/k_\perp^2 = 1 + K^2(d/n\pi)^2$ we get

$$P_\mathrm{I} = \frac{\pi k_\mathrm{B} T}{d^3} \sum_{n=0}^{N_\mathrm{I}} n^2 \int_1^{d/d_0 n} \frac{\mathrm{d}Z}{Z}$$

$$= \frac{\pi k_\mathrm{B} T}{d^3} \sum_{n=1}^{N_\mathrm{I}} n^2 \log \frac{d}{n d_0} \longrightarrow \frac{k_\mathrm{B} T \pi}{9 d_0^3}, \qquad d \to \infty \tag{23}$$

where $d_0 = u_\mathrm{f}/2\nu_\mathrm{D}, \qquad N_\mathrm{I} = \lfloor d/d_0 \rfloor.$ (24)

The discontinuities of $\Phi_\mathrm{I}''(d) = P_\mathrm{I}'(d)$ at $d/d_0 = 1, 2, \ldots$ are a result of the limited frequency ν_D; it keeps the pressure on the surface finite for equal energy $k_\mathrm{B}T$ of each state. Introducing the energy distribution (8) instead of $k_\mathrm{B}T$ for each state, the pressure becomes

$$P_\mathrm{I} = \frac{\pi}{d^3} \sum_{n=0}^{N_\mathrm{I}} n^2 \int_1^{d/n d_0} \frac{\mathrm{d}Z}{Z} \cdot \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/k_\mathrm{B}T} - 1}, \tag{25}$$

where $\omega = u_\mathrm{f} k = u_\mathrm{f} k_\perp Z$. With $x = \hbar\omega/k_\mathrm{B}T$ one obtains

$$P_\mathrm{I} = \frac{\pi k_\mathrm{B} T}{d^3} \sum_{n=0}^{N_\mathrm{I} = \lfloor \nu_\mathrm{D}/\nu_\mathrm{C} \rfloor} n^2 \int_{x_{\mathrm{I}n}}^{x_\mathrm{D}} \frac{\mathrm{d}x}{\mathrm{e}^x - 1}, \tag{26}$$

$x_\mathrm{D} = \hbar\omega_\mathrm{D}/k_\mathrm{B}T, \qquad x_{\mathrm{I}n} = n d_1/d$ with the unit

$d_1 = h u_\mathrm{f}/2 k_\mathrm{B} T.$ (27)

(For example, $d_1 = 0.16$ nm if $u_\mathrm{f} = 2000$ m s^{-1} and $T = 300$ K.) We calculate numerically the expression (26) for increasing ν_D until, for a given d interval, the pressure curve $P_\mathrm{I}(d)$ gets sufficiently smooth (thick grey curve in figure 4).

2.2. Liquid film with one surface free and the other rigid (II)

The boundary condition at the free surface ($x_3 = d/2$) remains $\dot\varphi_\mathrm{f} = 0$. At the rigid surface ($x_3 = -d/2$) the normal component of the velocity vanishes, $v_3 = \varphi_{\mathrm{f},3} = 0$. One obtains the dispersion curves (thick black hyperbola in figure 2)

$$\omega^2/u_\mathrm{f}^2 - k_\parallel^2 = ((n - 0.5)\pi/d)^2 = k_\perp^2, \qquad n = 1, 2, \ldots. \tag{28}$$

The calculation of the acoustic pressure on the free surface of the film can be done in the same manner as for the free-standing film, but with the dispersion curves equation (28) instead of equation (17). The intersections of the dispersion curves with $\omega = \omega_\mathrm{D}$ are given by

$$K_{\mathrm{II}n}^2 = \frac{\omega_\mathrm{D}^2}{u_\mathrm{f}^2} - \left(\frac{(n - 0.5)\pi}{d}\right)^2, \qquad n = 1, 2, \ldots, \tag{29}$$

$$N_\mathrm{II} = \lfloor d/d_0 + 0.5 \rfloor = \lfloor \nu_\mathrm{D}/\nu_\mathrm{C} + 0.5 \rfloor.$$

The energy $k_\mathrm{B}T$ for each state [6] leads to the acoustic pressure for the boundary condition (II) (thick black curve in figure 3):

$$P_\mathrm{II}(d) = \frac{2 k_\mathrm{B} T}{V} \sum_{n=1}^{N_\mathrm{II}} \frac{L_1 L_2}{4\pi^2} \int_0^{K_{\mathrm{II}n}} \cos^2\Theta \cdot 2\pi K \,\mathrm{d}K. \tag{30}$$

With the new variable $Z^2 = k^2/k_\perp^2 = 1 + K^2(d/(n - 0.5)\pi)^2$ one obtains

$$P_\mathrm{II}(d) = \frac{\pi k_\mathrm{B} T}{d^3} \sum_{n=1}^{N_\mathrm{II}} (n - 0.5)^2 \times \int_1^{d/d_0(n-0.5)} \frac{\mathrm{d}Z}{Z} \longrightarrow \frac{k_\mathrm{B} T \pi}{9 d_0^3} \qquad d \to \infty. \tag{31}$$

With increasing d, $P_\mathrm{II}(d)$ approaches at the same limit as $P_\mathrm{I}(d)$. The energy distribution (8), yields the smooth, thick black curve in figure 4:

$$P_\mathrm{II}(d) = \frac{\pi k_\mathrm{B} T}{d^3} \sum_{n=1}^{\lfloor \nu_\mathrm{D}/\nu_\mathrm{C} + 0.5 \rfloor} (n - 0.5)^2 \int_{x_{\mathrm{II}n}}^{x_\mathrm{D}} \frac{\mathrm{d}x}{\mathrm{e}^x - 1}, \tag{32}$$

$$x_{\mathrm{II}n} = (n - 0.5) d_1/d.$$

2.3. Liquid film on a liquid substrate (III)

To investigate the influence of a liquid substrate, with the sound velocity $u_\mathrm{s} > u_\mathrm{f}$, we consider the states which fulfil all boundary conditions of the film and the substrate. At the free surface of the film ($x_3 = d/2$), the normal stress should vanish ($\rho_\mathrm{f}\dot\varphi_\mathrm{f} = 0$). At the interface film/substrate, ($x_3 = -d/2$) the normal stress and the normal component of the particle velocity should be continuous: $\rho_\mathrm{f}\dot\varphi_\mathrm{f} = \rho_\mathrm{s}\dot\varphi_\mathrm{s}$ and $\varphi_{\mathrm{f},3} = \varphi_{s,3}$. For the substrate half-space, $\varphi_\mathrm{s}(x_3)$ should remain finite for ($x_3 \to -\infty$).

The dispersion curves (solid coloured curves in figure 2) describe the confined states in the investigated liquid film (d, u_f) on a liquid substrate half-space:

$$\rho_\mathrm{f} \cdot \tan(k_\perp d)/k_\perp + \rho_\mathrm{s} \Big/ \sqrt{K^2 - \omega^2/u_s^2} = 0,$$

$$k_\perp \equiv k_{\perp\mathrm{f}}. \tag{33}$$

We calculate the inside pressure $P_\mathrm{III}(d)$ on the free surface of the film from these dispersion curves $\omega_{\mathrm{III}n}(K)$. With the energy distribution (8) we obtain

$$P_\mathrm{III}(d) = \frac{1}{\pi d} \sum_{n=1}^{N_\mathrm{III}} \int_{K_{sn}}^{K_{\mathrm{III}n}} \cos^2\Theta \cdot K \,\mathrm{d}K \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/k_\mathrm{B}T} - 1}, \tag{34}$$

$$N_\mathrm{III} = \lfloor W \nu_\mathrm{D}/\nu_\mathrm{C} + 0.5 \rfloor, \qquad W = \sqrt{1 - u_\mathrm{f}^2/u_\mathrm{s}^2},$$

$$K_{sn} = \frac{u_\mathrm{f}}{u_\mathrm{s}} \cdot \frac{(n - 0.5)\pi}{W d}. \tag{35}$$

$K_{\mathrm{III}n}$ being the intersections of the dispersion curves with $\omega = \omega_\mathrm{D}$. Using the dispersion curves $\omega_{\mathrm{II}n}$ instead of $\omega_{\mathrm{III}n}$ for $\omega/K < u_\mathrm{s}$, we find the approximation $W^3 P_\mathrm{II}(W d)$. The exact dispersion curves $\omega_{\mathrm{III}n}(K)$ with $x = \hbar\omega/k_\mathrm{B}T$ and $x_{\mathrm{III}n} = (n - 0.5) d_1/W d$ yield

$$P_\mathrm{III}(d) = \frac{k_\mathrm{B} T}{\pi d^3} \sum_{n=1}^{N_\mathrm{III}} \int_{x_{\mathrm{III}n}}^{x_\mathrm{D}} k_\perp^2 d^2 \left(1 - u_\mathrm{f}^2 \cdot \frac{k_\perp}{\omega} \frac{\mathrm{d}k_\perp}{\mathrm{d}\omega}\right) \frac{\mathrm{d}x}{\mathrm{e}^x - 1}. \tag{36}$$

The numerical calculation for sufficiently large ν_D and different elastic properties yields the solid coloured curves in figure 4.

2.4. Liquid film on a solid substrate (IV)

For a solid we start with the equations of linear elasticity. To a given frequency ω and direction of propagation $\mathbf{k}$ in an unbounded isotropic body there are three plane wave solutions for the displacements, two transverse (T) and one longitudinal (L) wave ($j = $ T, L):

$$\mathbf{w} = \mathbf{w_j} \cdot \exp(-\mathrm{i}\omega t + \mathrm{i}\mathbf{k}\mathbf{r}). \tag{37}$$

In a system of solid layers with the normal in the x_3 direction one has the following boundary conditions: (i) vanishing stresses (σ_{i3}) at the free surfaces; (ii) continuous (σ_{i3}) and (w_i) at the interfaces of adjacent layers; (iii) finite displacements if the last layer is the half-space; (iv) vanishing displacements (w_i) at fixed surfaces. The boundary conditions of the layer system can be fulfilled by a superposition of the sound waves in each layer with a common plane of propagation, frequency ω and wavevector component $k_\parallel \equiv K$ parallel to the layers [12].

Now we consider a liquid film with vanishing shear modulus. A linear combination of longitudinal waves propagating in the (x_1, x_3) plane with (ω, K) is given by

$$\begin{pmatrix} w_1 \\ w_3 \end{pmatrix}_{\rm f} = \exp(-\mathrm{i}\omega t + \mathrm{i}Kx_1) \cdot \begin{pmatrix} C_{\rm L} & KS_{\rm L}/\alpha_{\rm L} \\ \mathrm{i}\alpha_{\rm L}S_{\rm L}/K & -\mathrm{i}C_{\rm L} \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix},$$
$$S_j = \sin(\alpha_j x_3), \qquad C_j = \cos(\alpha_j x_3) \qquad j = \mathrm{T, L}$$
$$\alpha_{\rm L} = \sqrt{\omega^2/u_{\rm f}^2 - K^2}. \tag{38}$$

In the substrate we start with a linear combination of transverse and longitudinal waves also polarized in the plane of propagation:

$$\begin{pmatrix} w_1 \\ w_3 \end{pmatrix}_{\rm s} = \exp(-\mathrm{i}\omega t + \mathrm{i}Kx_1) \cdot \left(\begin{pmatrix} C'_{\rm L} & KS'_{\rm L}/\alpha'_{\rm L} \\ \mathrm{i}\alpha'_{\rm L}S'_{\rm L}/K & -\mathrm{i}C'_{\rm L} \end{pmatrix}\begin{pmatrix} A' \\ B' \end{pmatrix} + \begin{pmatrix} \alpha'_{\rm T}S'_{\rm T}/K & -C'_{\rm T} \\ \mathrm{i}C'_{\rm T} & \mathrm{i}KS'_{\rm T}/\alpha'_{\rm T} \end{pmatrix}\begin{pmatrix} C' \\ D' \end{pmatrix}\right),$$
$$\text{with } \alpha'_j = \sqrt{\omega^2/u_{{\rm s}j}^2 - K^2} \quad \text{and}$$
$$a'_j \equiv \mathrm{i}\alpha'_j, \quad j = T, L. \tag{39}$$

In the region $(\omega/K < u_{{\rm s}j})$ the modes cannot propagate in the solid substrate half-space; they are confined in the liquid film. All boundary conditions, without the continuity of w_1 across the interface, can be fulfilled for (ω, K) which solve the dispersion equation

$$\rho_{\rm f} \cdot \tan(\alpha_{\rm L}d)/\alpha_{\rm L} + \rho_{\rm s} \cdot ((1-\kappa)^2/a'_{\rm L} - a'_{\rm T}\kappa^2/K^2) = 0,$$
$$\kappa = 2K^2u_{\rm sT}^2/\omega^2. \tag{40}$$

The dispersion curves $\omega_{{\rm IV}n}(K)$ yield the pressure of the confined modes (dashed curves in figure 4):

$$P_{\rm IV}(d) = \frac{k_{\rm B}T}{\pi d^3}\sum_{n=0}^{N_{\rm IV}}\int_{x_{{\rm IV}n}}^{x_{\rm D}} k_\perp^2 d^2\left(1 - u_{\rm f}^2 \cdot \frac{k_\perp}{\omega}\frac{\mathrm{d}k_\perp}{\mathrm{d}\omega}\right) \times \frac{\mathrm{d}x}{\mathrm{e}^x - 1}, \tag{41}$$

$x_{{\rm IV}n}$ being the first point of the nth dispersion curve at $\omega/K = u_{\rm sT}$. The modes from the region $(u_{\rm sT} < \omega/K < u_{\rm sL})$ are not completely confined in the liquid film. They lose energy into the substrate.

3. Results and discussion

The pressure $P_{\rm ac}(d)$ of confined thermally excited sound waves on the surfaces of a thin liquid film depends on the boundary conditions. From the related dispersion curves the pressure is calculated numerically for characteristic examples. If $P'_{\rm ac}(d) < 0$ the film is acoustically unstable and the dewetting wavelength is calculated:

$$\lambda_{\rm ac}(d) = \sqrt{-8\pi^2\sigma/P'_{\rm ac}(d)}. \tag{42}$$

(I) *For a free-standing film* the acoustic pressure $P_{\rm I}(d)$ grows with d monotonically towards a plateau P_∞, grey curve in figure 4:

$$\lim_{d\to\infty} P_{\rm I}(d) = P_\infty \approx 6.8k_{\rm B}T/d_1^3, \qquad d_1 = hu_{\rm f}/2k_{\rm B}T. \tag{43}$$

Acoustic waves alone cannot destabilize this film, since $P'_{\rm I}(d) > 0$ for all d.

(II) *If one surface of the liquid film is free and the other rigid* the acoustic pressure $P_{\rm II}(d)$ grows rapidly up to a maximum at $d = d_{\rm II} \approx 0.2d_1$. Then it monotonically decreases towards the same plateau P_∞, black curve in figure 4. For $d > d_{\rm II}$ this film is acoustically unstable with the dewetting wavelength, solid black curve in figures 5 and 6:

$$\lambda_{\rm II}(d) = 12d^2 \cdot f(d) \cdot (\pi\sigma/2k_{\rm B}T)^{1/2},$$
$$f(d) \approx 1.3, \qquad d > d_1. \tag{44}$$

If the temperature is high enough, the d-dependent acoustic forces are comparable to the van der Waals forces:

$$\lambda_{\rm II}(d) \approx \lambda_{\rm vdW}(d), \qquad \text{if } A \approx 1.3k_{\rm B}T. \tag{45}$$

(III) *Liquid film with one free surface on a liquid substrate.* The dispersion curves $\omega_{\rm III}(k_\parallel)$ (solid coloured curves in figure 2) lie between the dispersion curves $\omega_{\rm II}(k_\parallel)$ and $\omega_{\rm I}(k_\parallel)$:

$$\omega_{{\rm II}n}(k_\parallel) < \omega_{{\rm III}n}(k_\parallel) < \omega_{{\rm I}n}(k_\parallel), \qquad n = 1, 2, \ldots$$
$$\omega_{\rm I0}(k_\parallel) = u_{\rm f}k_\parallel, \tag{46}$$

for $\omega/k_\parallel \leqslant u_{\rm s}$. There are confined sound waves in the film only if $u_{\rm s} > u_{\rm f}$.

The pressure $P_{\rm III}(d)$ grows up to a maximum at $d = d_{\rm III}(U, R)$ depending on $U = u_{\rm s}/u_{\rm f}$ and $R = \rho_{\rm s}/\rho_{\rm f}$. $d_{\rm III}$ grows for lighter substrates (see table 1). For $d > d_{\rm III}$, $P_{\rm III}(d)$ approaches the plateau

$$\lim_{d\to\infty} P_{\rm III}(d) = W^3P_\infty, \qquad W^2 = 1 - u_{\rm f}^2/u_{\rm s}^2. \tag{47}$$

Table 1. $d = d_{\rm III}$ at the maximum of $P_{\rm III}$ and the coefficient $L_{\rm III}$.

	$U = u_{\rm s}/u_{\rm f} = 3.14$		$U = 1.57$	
$R = \rho_{\rm s}/\rho_{\rm f}$	$d_{\rm III}/d_1$	$L_{\rm III}$	$d_{\rm III}/d_1$	$L_{\rm III}$
0.079	0.79	0.95	0.50	0.644
0.197	0.66	0.85	0.43	0.645
0.395	0.43	0.79	0.40	0.670
1.975	0.26	0.87	0.30	0.879
9.872	0.20	1.46	0.26	1.564
19.75	0.20	1.94	0.26	2.151
49.36	0.20	>3.04	0.23	>3.213

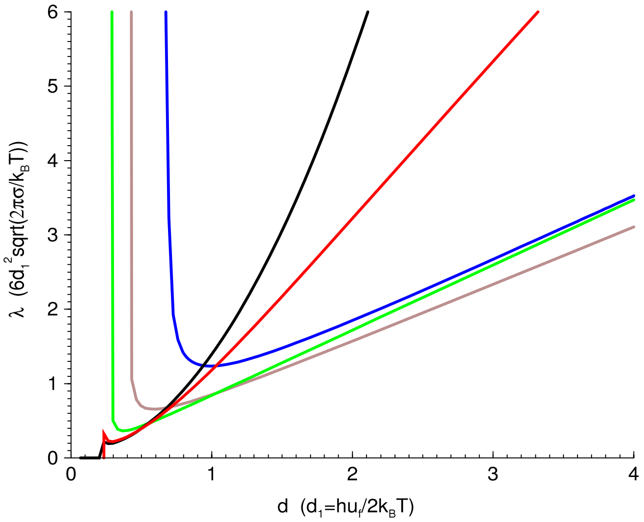

Figure 5. The dewetting wavelength due to confined sound waves in a liquid film with one surface free versus film thickness d. (II) The other surface is rigid, solid black curve. (III) The film is deposited on a liquid substrate, solid coloured curves. $u_f = 2.7$ km s^{-1}, $u_s = 8.4$ km s^{-1}, $\rho_f = 1.2$ g cm^{-3}, $\rho_s = 2.3$ g cm$^{-3} \cdot F$, $F = 10$ (magenta), $F = 1$ (green), $F = 0.3$ (brown) and $F = 0.1$ (blue).

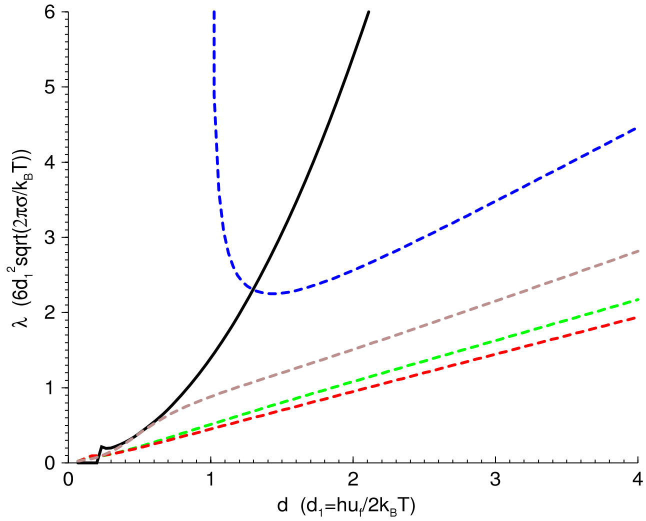

Figure 6. The dewetting wavelength due to confined sound waves in a liquid film with one surface free versus film thickness d. (II) The other surface is rigid, solid black curve. (IV) The film is deposited on a solid substrate, dashed coloured curves. $u_f = 2.7$ km s^{-1}, $u_{sT} = 5.8$ km s^{-1}, $u_{sL} = 8.4$ km s^{-1}, $\rho_f = 1.2$ g cm^{-3}, $\rho_s = 2.3$ g cm$^{-3} \cdot F$, $F = 10$ (magenta), $F = 1$ (green), $F = 0.3$ (brown) and $F = 0.1$ (blue).

Figure 4 shows $P_{\rm III}(d)$ for a fixed $U = 3.14$ and different R as solid coloured curves. With decreasing R the course of $P_{\rm III}(d)$ becomes more similar to that of $P_{\rm I}(d)$, which is stable, and for increasing R to that of $P_{\rm II}(d)$, which is unstable. Only for $d > d_{\rm III}$ can one calculate $\lambda_{\rm III}(d)$, solid coloured curves in figure 5. In a very small interval behind $d_{\rm III}$, $\lambda_{\rm III}(d)$ grows faster than linearly with d. After that $\lambda_{\rm III}(d)$ approaches a linear course $L_{\rm III}(U, R) \cdot d$. This yields an approximation of the acoustic pressure:

$$P_{\rm III}(d) \approx P_\infty W^3 + 8\pi^2\sigma/(L_{\rm III}^2 d), \qquad d > d_{\rm III}. \tag{48}$$

Table 1 lists examples of the coefficient $L_{\rm III}(U, R)$: for fixed $U = u_s/u_f = 3.14$, $L_{\rm III}(U, R)$ grows with R, if $R > 0.395$. For $U = 1.57$, $L_{\rm III}(U, R)$ grows more rapidly with R. Here one finds an example of the same coefficient $L_{\rm III}$ for different situations (i.e. $U = 3.14$ and 1.53).

(IV) *Liquid film with one free surface on a solid substrate*

There are sound waves really confined in the film if $u_f < \omega/k_\parallel < u_{sT}$ (surface acoustic waves—SAWs). For $u_{sT} < \omega/k_\parallel < u_{sL}$ the acoustic waves are leaky: they are not completely confined in the liquid layer and lose energy into the substrate. In this paper we omit the leaky waves.

The dispersion curves $\omega_{\rm IV}(k_\parallel)$ (dotted curves in figure 2) lie between successive dispersion curves $\omega_{\rm II}(k_\parallel)$:

$$\omega_{{\rm II}n}(k_\parallel) < \omega_{{\rm III}n}(k_\parallel) \leqslant \omega_{{\rm IV}n}(k_\parallel) < \omega_{{\rm II}(n+1)}(k_\parallel), \quad n = 1, 2, 3, \ldots \tag{49}$$

They start at $\omega/k_\parallel = u_{sT}$, the transverse sound velocity of the substrate. They intersect the dispersion curves $\omega_{{\rm I}n}$ on the straight line $\omega/k_\parallel = u_{sT} \cdot \sqrt{x}$:

$$(x/2 - 1)^4 = (1 - x)(1 - x \cdot u_{sT}^2/u_{sL}^2). \tag{50}$$

Additionally there exists a dispersion curve $\omega_{\rm IV0}(k_\parallel)$, which starts at the origin and ends when it intersects $\omega_{\rm I0}(k_\parallel)$, where $k_\perp = 0$. The zero dispersion curve is the shorter the smaller $R = \rho_s/\rho_f$. For $R \leqslant 0.02$ it can be neglected. As in the previous cases we sum up the pressure contributions of the allowed states. The dispersion curves $n = 1, 2, 3, \ldots$ yield a pressure with a maximum at $d = d_{\rm IV}$ and the plateau $W_{sT}^3 P_\infty$. The corresponding wavelength approaches a linear course ($L_{\rm IV} \cdot d$). From the $n = 0$ dispersion curve the calculation yields a pressure ($\approx a/d^3$) and a wavelength ($\sim d^2$). The sum of the contributions of all dispersion curves $n = 0, 1, 2, \ldots$, yields the pressure (const $+ a/d^3 + b/d$) with the wavelength

$$\lambda_{\rm IV}(d) = d\sqrt{8\pi^2\sigma/(3a/d^2 + b)} < d\sqrt{8\pi^2\sigma/b} = L_{\rm IV} \cdot d. \tag{51}$$

Figure 4 shows $P_{\rm IV}(d)$ for a fixed $u_{sT}/u_f = 2.17$ and different $R = \rho_s/\rho_f$ as dashed coloured curves. For growing d, $P_{\rm IV}(d)$ approaches the plateau:

$$\lim_{d\to\infty} P_{\rm IV}(d) = W_{sT}^3 P_\infty, \qquad W_{sT}^2 = 1 - u_{sT}^2/u_f^2. \tag{52}$$

The associated wavelengths $\lambda_{\rm IV}(d)$ are plotted as dashed curves in figure 6. They approach a linear course in d.

4. Summary

P_{ac} is the pressure of the thermally excited confined acoustic waves on the surfaces of a thin liquid film (d, u_f, ρ_f). For different boundary conditions we derived the related dispersion curves, which describe all allowed states. Summing up the contributions of the confined states we calculated P_{ac} numerically for some characteristic cases. Generally $P_{ac}(d)$ cannot be described in a simple power law expression such as, for example, the van der Waals pressure. But in the limiting cases the results are simple.

(I) For the free-standing film the pressure $P_{\mathrm{I}}(d)$ monotonically grows with d up to a plateau P_∞ that is strongly dependent on the temperature. Thus the acoustic waves alone cannot destabilize the free-standing film.

(II) For the film with one free and one rigid boundary condition $P_{\mathrm{II}}(d)$ grows rapidly up to a maximum at $d = d_{\mathrm{II}}$ and then descends monotonically for growing d towards the same plateau P_∞ as in case (I). Thus for $d > d_{\mathrm{II}}$ the acoustic pressure can destabilize the film. The related dewetting wavelength grows nearly as d^2.

(III) For the liquid film on a liquid substrate $P_{\mathrm{III}}(d)$ grows to a maximum at $d = d_{\mathrm{III}}$ and then reaches a plateau $W^3 P_\infty$, with $W^2 = 1 - u_{\mathrm{f}}^2/u_{\mathrm{s}}^2$. Only for $d > d_{\mathrm{III}}$ could $P_{\mathrm{III}}(d)$ destabilize the film. d_{III} grows for lighter substrates and the course of $P_{\mathrm{III}}(d)$ is more similar to the course of $P_{\mathrm{I}}(d)$, which is stable. For heavier substrates the course of $P_{\mathrm{III}}(d)$ is more similar to the course of $P_{\mathrm{II}}(d)$, which is unstable.

(IV) We assumed a Newtonian liquid film with vanishing shear modulus μ on a solid substrate. To fulfil the boundary conditions one cannot permit slip. We considered only completely confined sound waves ($u_{\mathrm{sT}} > \omega/k_\parallel > u_{\mathrm{f}}$) and omitted leaky waves ($u_{\mathrm{sL}} > \omega/k_\parallel > u_{\mathrm{sT}}$). The pressure reaches a plateau $W_{\mathrm{sT}}^3 P_\infty$. For a liquid film on a substrate (liquid or solid) the dewetting wavelength approaches a linear course in d. It shows an additional term $\sim 1/d$ in the acoustic pressure.

This is the first calculation of the acoustic pressure including boundary conditions. Until now we have only treated the case of flat layers and isotropic liquids with $\mu = 0$.

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