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Model of a liquid nanofilm on a solid substrate based on the van der Waals concept of capillarity

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Van der Waals attractive forces drastically change the material properties of thin liquid layers several nanometers when in contact with a solid. At this scale, the fluid is no longer homogeneous. Moreover, it has properties which are analogous to those of solids. In particular, in equilibrium the stress tensor is no longer spherical. For such fluids, we use a long-wave approximation to derive the evolution of a liquid nanofilm on a substrate. We establish that the driving pressure in the nanofilm should be associated with the mean value of the component of the pressure tensor tangential to the liquid interface (along the substrate). Finally, we derive the equation for nanofilm dynamics by using a mass conservation formulation. This is not a conventional, conservative equation for the position of the free surface normally used in the theory of thick films where the density is homogeneous, but rather a conservative equation for the liquid mass. The equation turns out to be a nonlinear parabolic equation with a diffusion coefficient of a “good” sign.

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I. INTRODUCTION

Thin liquid films are encountered in a variety of natural phenomena and in many technological applications [1,2].

A mathematical treatment of the dynamics of liquid films on a solid substrate in general has to deal with the fact that film interface represents a free boundary whose configuration evolves both temporally and spatially. This configuration must be determined as a solution for governing equations. The most appropriate analytical method for dealing with the problem is to analyze long-scale phenomena only, in which the characteristic lateral length scale (along the substrate) is much larger than the average film thickness. Such a long-wave theory approach is widely and successfully used to model dynamics of relatively thick liquid films (see Ref. [3] for review). However, this approach cannot be scaled directly down to the nanoscale. That is because liquid in macro and micro films is normally treated as a viscous, incompressible fluid, and Navier-Stokes equations used as the governing equations fail at the nanoscale and have to be revised.

Van der Waals attractive forces drastically change the material properties of thin liquid layers several nanometers when in contact with a solid. At this scale, interfacial transition layers (due to solid-liquid and liquid-gas interactions) completely overlap. The fluid is no longer homogeneous; its density varies in the direction normal to the solid interface. This nonhomogeneity can be taken into account by considering the physical concept where the liquid energy depends on the space derivatives of its density [4,5].

Volume energy dependent on density gradients also appears in the study of the kinetics of phase boundaries, moving contact lines, and other phenomena (see Refs. [6–9] for a comprehensive review).

Rocard [10] introduced the anisotropic stress tensor in such liquids by using the methods of the kinetic theory of gases. The reversible dynamics of such liquids was derived from the Hamilton principle of stationary action in Refs. [11–13] (see also references in Ref. [8]).

These liquids (often called capillary fluids) have peculiar physical properties. In particular, in equilibrium the stress tensor is not spherical, and the fluids have properties analogous to those of solids. The boundary conditions for such fluids represent a correlation between boundary values of the density and its normal derivatives [14–17]. All these peculiarities provide main difficulties in the detailed mathematical treatment of specific physical problems.

We apply this concept to study the motion of liquid nanofilms on a substrate. First, we consider the statics of such liquid nanofilms. We derive an explicit formula for the disjoining pressure, as it was introduced by Derjaguin [18]. This disjoining pressure is exactly the component of the pressure tensor (equal with the sign minus to the stress tensor) normal to the liquid interface which is identically constant in the liquid film. In particular, we show that in static equilibrium, the disjoining pressure should be zero to satisfy the stress-free boundary conditions existing at the free surface (the gas and vapor atmosphere pressure above the nanofilm is neglected here). On the contrary, the component of the stress tensor tangential to the liquid interface (along the substrate) strongly varies inside the liquid film. This was qualitatively predicted by Derjaguin [18]. The tangential pressure compo-

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nent is negative which perfectly corresponds to the nature of van der Waals attractive forces spreading the liquid films.

Then, we use long-wave approximation to describe the evolution (dynamics) of the liquid nanofilm on a substrate. In this approximation the disjoining pressure is always zero. It is worth noting that there is a misleading concept in literature about ultrathin films where the driving pressure for film dynamics is associated with the disjoining pressure. We establish here that the driving pressure in nanofilms should be associated with the mean value of the component of the pressure tensor tangential to the liquid interface (along the substrate), but not disjoining pressure. This tangential pressure is completely different from the disjoining pressure. In particular, the tangential pressure is finite when the film thickness goes to zero.

Finally, we derive the equation for nanofilm dynamics in explicit form, by using mass conservation formulation. This is not a conventional, conservative equation for the position of the free surface normally used in the theory of thick films where the density is homogeneous (see Ref. [3] for review), but rather a conservative equation for the liquid mass. The equation turns out to be a nonlinear parabolic equation with a diffusion coefficient with a "good" sign. This leads us to a different concept of thin film dynamics, and in particular to a different mechanism for film rupture on a substrate.

II. STATIC PROBLEM

Consider a thin liquid film of thickness h occupying the domain Ω which is in equilibrium with a solid substrate. The boundary between the solid and liquid is denoted by S, the upper surface of the film is denoted by Σ. We will suppose that both S and Σ are flat. Gravity is ignored. The total energy of the system $\mathcal{E}_T$ is

$$\mathcal{E}_T = \int_\Omega \left(W(\rho) + \lambda \frac{|\nabla\rho|^2}{2} \right) d\Omega + \int_S \mathcal{E}_S dS + \int_\Sigma \mathcal{E}_\Sigma d\Sigma. \quad (1)$$

Here ρ is the liquid density which is supposed to be not uniform in space due to liquid-substrate and liquid-liquid interactions. $W(\rho)$ is the bulk liquid energy related in general with the kinetic energy of thermal motion of liquid molecules and with the potential energy of interaction between the liquid molecules in uniform liquid of density ρ. The second term, depending on the density gradient $\nabla\rho$, is responsible for the capillary effects (the density nonhomogeneity) due to van der Waals attractive forces. Van der Waals forces are important when the film thickness is in the range of 10–100 nm [7,18–20]. Finally, the last two terms are the energies of the surfaces S and Σ.

A typical expression of $\mathcal{E}_S$ is as follows [7]:

$$\mathcal{E}_S = -\gamma_1 \rho_S + \frac{1}{2}\gamma_2 \rho_S^2.$$

Here ρ_S is the liquid density at the surface $S, \gamma_1 > 0$ corresponds to the attraction between solid and liquid molecules, $\gamma_2 > 0$ is the repulsive component due to the attraction between liquid molecules, which are near the solid, and those in the bulk. For the energy $\mathcal{E}_\Sigma$ we propose an analogous expression

$$\mathcal{E}_\Sigma = \frac{1}{2}\gamma_2 \rho_\Sigma^2.$$

Here ρ_Σ is the liquid density on the upper boundary Σ. The parameter γ_1 is taken to be zero in the last formula because we neglect the interaction between liquid and gas or vapor at the film surface.

The parameters λ, γ_1, and γ_2 can be explicitly calculated in terms of molecular interaction potentials. An example of such a calculation was done in Ref. [21] for semi-infinite liquid in contact with a solid substrate for the Lennard-Jones potentials with hard-core repulsion. If liquid-liquid φ_{ll} and liquid-solid φ_{ls} potentials are given by

$$\varphi_{ll} = \begin{cases} -C_{ll}/r^6, & r > \sigma_l \\ \infty, & r < \sigma_l \end{cases}, \qquad \varphi_{ls} = \begin{cases} -C_{ls}/r^6, & r > \delta \\ \infty, & r < \delta \end{cases}$$

then

$$\gamma_1 = \frac{\pi C_{ls}}{12\delta^2 m_l m_s}\rho_{sol}, \quad \gamma_2 = \frac{\pi C_{ll}}{12\delta^2 m_l^2}. \quad (2)$$

Here $\delta = (\sigma_l + \sigma_s)/2, \sigma_l$, and σ_s are diameters of the liquid and solid molecules, m_l and m_s are masses of the liquid and solid molecules, ρ_{sol} is the density of the solid. The expression for the coefficient λ is [21,22]

$$\lambda = -\frac{2\pi}{3}\int_{\sigma_l}^{\infty} r^4 \varphi_{ll}(r)dr = \frac{2\pi C_{ll}}{3\sigma_l m_l^2}. \quad (3)$$

For nanofilms, the volume energy W can be neglected in Eq. (1). On the contrary, we account for the capillary energy related to the distortion of the density profile due to van der Waals forces. The validity of this approximation will be provided *a posteriori* (see Sec. III). Namely, we will obtain for this approximation an explicit equation for the disjoining pressure and will show that its dependency on film thickness perfectly matches the classical one given in the literature.

In static equilibrium, the total energy of the system is minimal. The solution of the minimization problem for the reduced energy functional

$$\mathcal{E}_T = \int_\Omega \lambda \frac{|\nabla\rho|^2}{2} d\Omega + \int_S \mathcal{E}_S dS + \int_\Sigma \mathcal{E}_\Sigma d\Sigma$$

looks as shown below [14–17]:

$$\nabla(\Delta\rho) = 0, \qquad \lambda \left.\frac{\partial\rho}{\partial n}\right|_S - \gamma_1 + \gamma_2 \rho_S = 0, \qquad \lambda \left.\frac{\partial\rho}{\partial n}\right|_\Sigma + \gamma_2 \rho_\Sigma = 0.$$

Here Δ is the Laplacian operator, and ∇ is the operator gradient. We denoted here $\partial\rho/\partial n$ the normal derivative of the density, and $\mathbf{n}$ is the external normal to the liquid volume.

In the Cartesian coordinates (Oxz), where the x axis is directed along the solid surface, and the z axis is perpendicular to the solid surface direction, we have the following explicit solution:

$$\rho(z) = \rho_S + \alpha_1 z + \alpha_2 \frac{z^2}{2} \quad (4)$$

with boundary conditions

$$\lambda \left.\frac{d\rho}{dz}\right|_{z=0} = -\gamma_1 + \gamma_2\rho_S, \qquad \lambda \left.\frac{d\rho}{dz}\right|_{z=h} = -\gamma_2\rho_\Sigma = -\gamma_2\rho(h).$$

The parameters α_1 and α_2 can easily be determined from the boundary conditions

$$\alpha_1 = \frac{-\gamma_1 + \gamma_2\rho_S}{\lambda}, \quad \alpha_2 = -\frac{\gamma_2\rho_S + \alpha_1(\lambda + \gamma_2 h)}{(\lambda h + \gamma_2 h^2/2)}. \tag{5}$$

In the following, it is convenient to work with the dimensionless variable film thickness,

$$H = \frac{h}{h_*}, \quad h_* = \frac{\lambda}{\gamma_2}.$$

We introduce also the dimensionless parameter α,

$$\alpha = \frac{\lambda\alpha_1}{\gamma_2\rho_S} = 1 - \frac{\gamma_1}{\gamma_2\rho_S}. \tag{6}$$

In dimensionless variables Eq. (5) can be rewritten as follows:

$$\alpha_1 = \frac{\gamma_1}{\lambda}\frac{\alpha}{1-\alpha}, \quad \alpha_2 = \frac{\gamma_1\gamma_2}{\lambda^2}\frac{A(H,\alpha)}{1-\alpha}, \quad A(H,\alpha) = -\frac{1+\alpha(1+H)}{H+H^2/2}. \tag{7}$$

For a fixed dimensionless film thickness H the density profile is

$$\rho(H,Z,\alpha) = \rho_*\frac{(1+\alpha Z + A(H,\alpha)Z^2/2)}{1-\alpha}, \quad Z = \frac{z}{h_*} = \frac{\gamma_2 z}{\lambda}, \quad \rho_* = \frac{\gamma_1}{\gamma_2}. \tag{8}$$

In particular, the fluid density on the upper boundary Σ is

$$\rho_\Sigma(H,\alpha) = \rho_*\frac{2+\alpha H}{(1-\alpha)(2+H)}. \tag{9}$$

In this approach, the liquid density ρ_S on the substrate, which is related with α through Eq. (6), is not yet defined. Defining the density ρ_S is equivalent to defining α. In Sec. IV, we will propose a method to determine ρ_S as a function of the molecular interaction parameters and film thickness.

III. DISJOINING PRESSURE

The energy per unit area of a film of thickness h is

$$\mathcal{E} = \frac{\lambda}{2}\int_0^h \left(\frac{d\rho}{dz}\right)^2 dz + \mathcal{E}_\Sigma + \mathcal{E}_S = \frac{\lambda}{2}\left(\alpha_1^2 h + \alpha_1\alpha_2 h^2 + \alpha_2^2\frac{h^3}{3}\right) + \frac{1}{2}\gamma_2\rho_\Sigma^2 + \mathcal{E}_S.$$

By using Eqs. (6), (7), and (9), we rewrite this energy in dimensionless variables,

$$\mathcal{E} = \frac{\gamma_1^2}{2\gamma_2}\frac{1}{(1-\alpha)^2} \times\left(\frac{12 + 4(1+\alpha)^2 H + \alpha(2+5\alpha)H^2 + \alpha^2 H^3}{3(2+H)^2} + 2\alpha - 1\right). \tag{10}$$

The mass of film per unit area is given by

$$m = \int_0^h \rho dz = \frac{\lambda\gamma_1}{\gamma_2^2}\left(\frac{H(12 + 4H(1+\alpha) + \alpha H^2)}{6(1-\alpha)(2+H)}\right).$$

We introduce the dimensionless mass per unit area,

$$M = \frac{m\gamma_2^2}{\lambda\gamma_1},$$

and express the dimensionless energy per unit area,

$$E = \frac{\mathcal{E}\gamma_2}{\gamma_1^2},$$

as a function of H and M. First, we find α as a function of M and H:

$$\alpha = \frac{2(6M - 6H + 3MH - 2H^2)}{12M + 6MH + 4H^2 + H^3}, \tag{11}$$

and then, we substitute it into Eq. (10) to obtain the energy per unit area as a a function of H and M,

$$E(H,M) = \frac{12M^2(2+H) - 12MH(2+H) - H^3(4+H)}{2H^2(6+H)(2+H)}. \tag{12}$$

The density profile as a function of H, Z, and M is obtained by substituting Eq. (11) into Eq. (8):

$$\frac{\rho(H,Z,M)}{\rho_*} = \frac{6M(2+H)(H+HZ-Z^2) + H(H^3 + 4H^2(1-Z) + 3HZ(Z-4) + 6Z^2)}{H^2(12+8H+H^2)}. \tag{13}$$

The dimensionless disjoining pressure is defined as follows [7,18,19]:

$$\Pi(H,M) = -\left.\frac{\partial E}{\partial H}\right|_{M=const}$$

and is given by

$$\Pi(H,M) = \frac{2[9M^2(2+H)^2(4+H) - 6MH(2+H)^2(3+H) + H^3(12+6H+H^2)]}{H^3(12+8H+H^2)^2}. \tag{14}$$

It can easily be seen that for small H

$$\Pi(H,M) \approx \frac{4M^2}{H^3}.$$

For small film thickness this formula represents the classical H^{-3} equation for the disjoining pressure when electromagnetic retardation can be neglected [7,18–20]. This can be treated as an indirect justification of our assumption (see Sec. II) that volume energy can be neglected for the films of thickness of several nanometers. The typical plot of the disjoining pressure isotherm (14) is shown in Fig. 1.

Now we are going to find how this disjoining pressure is correlated with stress tensor components. Having the explicit expression for the density (13) we can now calculate the stress tensor for such a medium [8,10,12,13]. In the Cartesian coordinates (Oxz) the stress tensor in capillary fluids has the following form (it will appear in Sec. V as well):

$$T = -\lambda\begin{pmatrix} \rho_x^2 - \left(\rho\Delta\rho + \frac{1}{2}|\nabla\rho|^2\right) & \rho_x\rho_z \\ \rho_x\rho_z & \rho_z^2 - \left(\rho\Delta\rho + \frac{1}{2}|\nabla\rho|^2\right) \end{pmatrix}. \tag{15}$$

In static equilibrium (when $\partial/\partial x = 0$) we get

$$-T = \lambda\begin{pmatrix} -\left(\rho\rho_{zz} + \frac{1}{2}\rho_z^2\right) & 0 \\ 0 & \frac{1}{2}\rho_z^2 - \rho\rho_{zz} \end{pmatrix} = \begin{pmatrix} p^{xx} & 0 \\ 0 & p^{zz} \end{pmatrix}.$$

Since we neglect the gas or vapor atmosphere on the film surface, we have to admit that the upper boundary Σ is free of normal stresses. Thus the p^{zz} component of the pressure tensor $-T$ should be zero at the free surface. It is easy to see that p^{zz} does not depend on z. Indeed,

$$\frac{dp^{zz}}{dz} = -\lambda\rho\rho_{zzz} = 0$$

since the density profile is parabolic. Hence p^{zz} should be zero everywhere in the film.

Using Eq. (13) we obtain

$$\frac{p^{zz}}{p_*} = \frac{2[9M^2(2+H)^2(4+H) - 6MH(2+H)^2(3+H) + H^3(12+6H+H^2)]}{H^3(2+H)^2(6+H)^2}$$

with $p_* = \gamma_1^2/\lambda$. This is exactly the equation for the disjoining pressure given by Eq. (14). Thus disjoining pressure represents the normal to substrate component of stress tensor.

There are two roots $M(H)$ where $p^{zz}=0$. They are given by

$$M = \frac{12H + 6H^2 + H^3}{3(8+6H+H^2)} \tag{16}$$

and

$$M = \frac{H^2}{3(2+H)}. \tag{17}$$

That means, for a given mass M, there are two values of possible equilibrium film thickness that fulfill the stress-free boundary condition on a film surface. Additional arguments are needed to decide which solution should be chosen.

IV. DETERMINATION OF THE SURFACE DENSITY

For a given mass M, in equilibrium the energy should be minimal. The critical points of the energy (12) are defined by

$$\left.\frac{\partial E(H,M)}{\partial H}\right|_{M=const} = 0.$$

It corresponds to the disjoining pressure equal to zero. This equation has two roots uniquely defined by Eqs. (16) and (17). One can prove that the first root (16) is stable (the second derivative of the energy is positive) and the second root (17) is unstable (the second derivative of the energy is negative). It is clearly visible in Fig. 1. Now, the fluid density at the bottom is uniquely defined, and the equilibrium density profile in the layer of thickness H corresponding to the stable root is

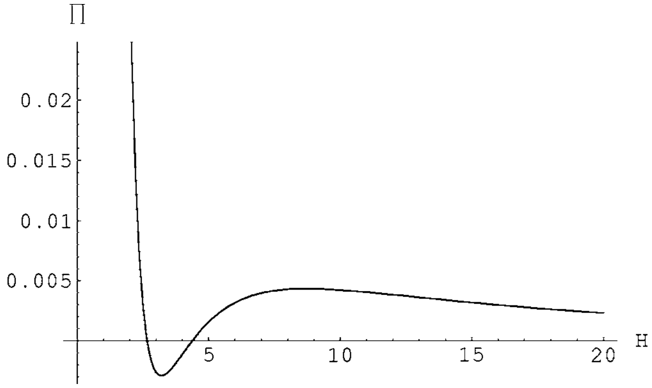

FIG. 1. The normalized disjoining pressure vs normalized film thickness is shown for $M=1$. This curve represents a typical van der Waals isotherm having the classical asymptotics: $\Pi(H)\approx H^{-3}$ as $H\to 0$.

$$\rho(H,Z)=\rho_*\frac{(2+H-Z)^2}{(2+H)(4+H)},\quad Z=\frac{z}{h_*}=\frac{\gamma_2 z}{\lambda}. \tag{18}$$

It is shown in Fig. 2. The density profile $\rho(H,Z)$ is monotonic and concave with respect to Z.

In particular, we obtain from Eq. (18) the fluid density at the substrate and at the surface as functions of H,

$$\rho_S(H)=\rho_*\frac{2+H}{4+H},\quad \rho_\Sigma(H)=\rho_*\frac{4}{(2+H)(4+H)}.$$

If $H\to 0$, the density at the substrate and the density at the surface are both equal to $\gamma_1/2\gamma_2$. Then density at the substrate is growing with H and density at the surface is decreasing with H. When $H\to\infty$, the density at the substrate is equal to γ_1/γ_2 which is the minimum of the surface energy at the substrate $\mathcal{E}_S=-\gamma_1\rho_S+\frac{1}{2}\gamma_2\rho_S^2$, and the density at the surface is equal to 0, which is the minimum of the surface energy at the free surface $\mathcal{E}_\Sigma=\frac{1}{2}\gamma_2\rho_\Sigma^2$. The last limit has a purely mathematical sense, because when $H\to\infty$ our basic assumption that liquid bulk energy is negligible is incorrect.

V. DYNAMIC PROBLEM

The reversible equations of motion can be obtained from the Hamilton principle of stationary action. The Lagrangian for the liquid nanofilm of variable thickness looks as follows:

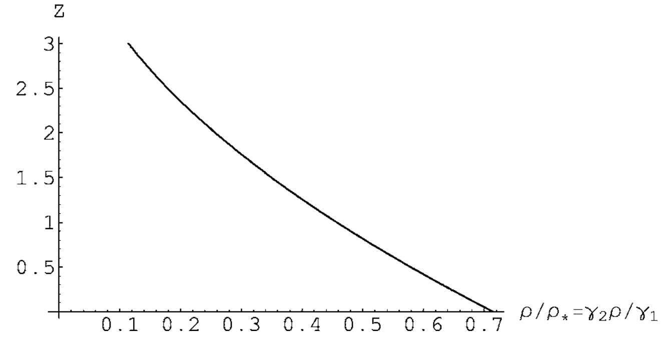

FIG. 2. The normalized density profile is shown for the nanofilm of thickness $H=3$.

$$L=\int\left[\int_0^{h(t,x)}\left(\rho\frac{|\mathbf{u}|^2}{2}-\lambda\frac{|\nabla\rho|^2}{2}\right)dz-\mathcal{E}_S-\mathcal{E}_\Sigma\right]dx.$$

Here $z=h(t,x)$ is the equation of the upper boundary Σ which is supposed to be a contact interface. The equations of motion derived from this Lagrangian are

$$\rho_t+\boldsymbol{\nabla}\cdot(\rho\mathbf{u})=0, \tag{19}$$

$$(\rho\mathbf{u})_t+\boldsymbol{\nabla}\cdot(\rho\mathbf{u}\otimes\mathbf{u}-T)=0.$$

Here $\mathbf{u}=(u,w)$ is the velocity field and T is the stress tensor defined previously in Eq. (15),

$$-T=\lambda\left[\boldsymbol{\nabla}\rho\otimes\boldsymbol{\nabla}\rho-\left(\rho\Delta\rho+\frac{1}{2}|\boldsymbol{\nabla}\rho|^2\right)I\right].$$

We denoted by I the unit tensor, and by $\otimes$ the tensor product. We define $-T$ as the pressure tensor.

We have shown in Secs. III and IV that in static equilibrium p^{zz} is identically zero. This is in accordance with the fact that the gas pressure is zero on the free surface. The tangential to substrate pressure component $p^{xx}=p^{zz}-\lambda\rho_z^2=-\lambda\rho_z^2$ depends on z and h. It can be calculated from Eq. (18),

$$\frac{\lambda p^{xx}}{\gamma_1^2}=-\frac{4(2+H-Z)^2}{(2+H)^2(4+H)^2}.$$

We see that p^{xx} is negative, minimal at the bottom, and maximal at the upper surface. Therefore since the density is nonuniform in the film, it creates tension in x direction (along the substrate) which is nonhomogeneous (in the z direction).

We can calculate the *mean pressure* in the nanofilm by the following equation:

$$\bar{p}=\frac{1}{2}\mathrm{tr}(-\bar{T})=\frac{1}{2}(\overline{p^{zz}}+\overline{p^{xx}}), \tag{20}$$

where

$$\overline{p^{zz}}=\frac{\int_0^h p^{zz}dz}{h}=0,\quad \overline{p^{xx}}=\frac{\int_0^h p^{xx}dz}{h}.$$

An explicit form of $\bar{p}$ as a function of H is

$$\frac{\bar{p}(H)}{p_*}=\frac{\lambda\bar{p}(H)}{\gamma_1^2}=\frac{\lambda\overline{p^{xx}}}{2\gamma_1^2}=-\frac{2(12+6H+H^2)}{3(2+H)^2(4+H)^2}.$$

One can see that the mean pressure is negative. It is shown in Fig. 3.

VI. LONG WAVE APPROXIMATION

The nonconservative form of system (19) is

$$\rho_t+\boldsymbol{\nabla}\cdot(\rho\mathbf{u})=0,$$

$$(\rho\mathbf{u})_t+\boldsymbol{\nabla}\cdot(\rho\mathbf{u}\otimes\mathbf{u})=\lambda\rho\,\boldsymbol{\nabla}\,(\Delta\rho).$$

We will use now the approximation of "long waves" by employing that the vertical scale length (film thickness) is much

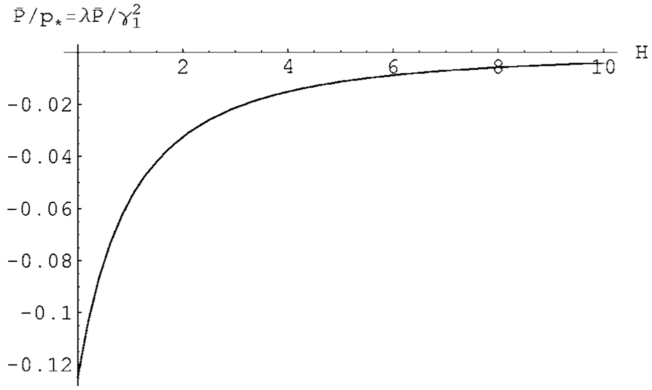

FIG. 3. The mean pressure is a concave and monotonic function of the film thickness H.

smaller than the horizontal scale length (wavelength of perturbation of the film). This is reminiscent of the “shallow water” approximation used in the theory of gravity waves (see, for example, Ref. [23]). In this limit we obtain

$$\rho_t + (\rho u)_x + (\rho w)_z = 0,$$

$$(\rho u)_t + (\rho u^2)_x + (\rho u w)_z = \lambda \rho (\rho_{zz})_x,$$

$$0 = \lambda (\rho_{zz})_z. \tag{21}$$

The last equation in Eq. (21) can be integrated as follows:

$$\rho(z) = \rho_S + \alpha_1 z + \alpha_2 \frac{z^2}{2}.$$

Here the constants α_1, α_2 are determined by Eq. (5). Finally, the density profile has the same form as in Eq. (18). The difference between the static equilibrium case considered in Secs. II–IV and the case obtained now is that the position of the surface Σ depends on time and space.

We integrate now system (21) with respect to the vertical coordinate to obtain

$$\left(\int_0^h \rho dz\right)_t + \left(\int_0^h \rho u dz\right)_x = 0,$$

$$\left(\int_0^h \rho u dz\right)_t + \left(\int_0^h \rho u^2 dz\right)_x = \lambda \int_0^h \rho (\rho_{zz})_x dz = \lambda (\alpha_2)_x \int_0^h \rho dz. \tag{22}$$

In this derivation we took into account that the surface $z = h(t,x)$ is a contact surface, i.e., at this surface the kinematic boundary condition

$$h_t + u h_x = w,$$

and the boundary condition for the vertical velocity on the solid substrate should be satisfied,

$$w|_{z=0} = 0.$$

The last equation of Eq. (22) determines the *driving pressure* $p_d(h)$ defined by

$$\frac{dp_d(h)}{dh} = -\lambda \frac{d\alpha_2(h)}{dh} \frac{\int_0^h \rho dz}{h}, \quad p_d \to 0 \text{ as } h \to \infty. \tag{23}$$

Next, we introduce the average velocity U defined by

$$U = \left(\int_0^h \rho u dz\right) \Big/ \left(\int_0^h \rho dz\right).$$

Now mass conservation equation looks as follows:

$$\left(\int_0^h \rho dz\right)_t + \left(U \int_0^h \rho dz\right)_x = 0. \tag{24}$$

To determine U we have to add friction into our system through the classical solution of the Navier-Stokes equation in which we neglect the liquid inertia in the momentum equation,

$$U = -\frac{h^2}{3\mu_*} p_d(h)_x. \tag{25}$$

Here μ_* is the effective liquid viscosity. It is known that liquid viscosity in nanofilms is very different from its viscosity in bulk liquid. Moreover, liquid slipage on the solid wall is possible at the nanoscale. Current experimental and theoretical data about slip phenomena in liquid nanofilms are controversial now [24–28]. That is why we use the effective viscosity concept in this study, although more advanced viscosity models can easily be incorporated at this point.

Taking into account that

$$\int_0^h \rho dz = \frac{\lambda \gamma_1}{\gamma_2^2} M(H) = \frac{\lambda \gamma_1}{\gamma_2^2} \frac{12H + 6H^2 + H^3}{3(8 + 6H + H^2)}$$

the dimensionless driving pressure $\lambda p_d / \gamma_1^2$ (denoted as Π_d) can be calculated from Eq. (23) in explicit form,

$$\Pi_d(H) = -\frac{2}{3} \frac{10 + 6H + H^2}{(8 + 6H + H^2)^2}. \tag{26}$$

Finally, we can rewrite the evolution equation (24) in explicit form for dimensionless variable H,

$$(M(H))_t - \left(\frac{\lambda \gamma_1^2}{3\mu_* \gamma_2^2} H^2 M(H) (\Pi_d(H))_x\right)_x = 0, \tag{27}$$

where $M(H)$ is determined by Eq. (16).

Equation (27) is parabolic with the diffusion coefficient of “good” sign because

$$\frac{d\Pi_d(H)}{dH} > 0$$

We compared the driving pressure defined by Eqs. (23) and (26) (shown by a solid curve in Fig. 4) and the mean pressure defined by formula (20) (shown by a dash line in Fig. 4). The results show that the curves are almost nondistinguishable for large H. For large H both curves have the same asymptotic,

$$\bar{P}(H) \approx \Pi_d(H) \approx -\frac{2}{3H^2}.$$

So, the driving pressure can be seen as the average pressure obtained as the averaged trace of the pressure tensor $-T$.

Since

$$\frac{d\Pi_d}{dH}(0) = \frac{3}{32},$$

for small H, the parabolic equation will look as follows:

$$H_t - \left(\frac{\lambda\gamma_1^2}{32\mu_*\gamma_2^2}H^3H_x\right)_x = 0.$$

Assuming that μ_* is approximately constant, we can obtain in new dimensionless variables x and t (we denoted them by the same letters) the equation

$$H_t - (H^3H_x)_x = 0.$$

This is the classical porous medium equation (see, for example, Refs. [29,30]). In particular, it has the following self-similar solution, which in our case may be used to describe the spreading of a nanodroplet on a substrate:

$$H = \begin{cases} t^{-1/5}\left[C - \frac{3}{10}\left(\frac{x}{t^{1/5}}\right)^2\right]^{1/3}, & \left(\frac{x}{t^{1/5}}\right)^2 < \frac{10}{3}C \\ 0, \quad \left(\frac{x}{t^{1/5}}\right)^2 > \frac{10}{3}C \end{cases}.$$

Here the constant C is determined by the total mass of the nanodroplet.

VII. DISCUSSION

Let us calculate some characteristic parameters introduced and employed in this study. For estimation, we consider a liquid argon film on a pure silicon substrate. The masses of liquid and substrate molecules are $m_l = 59.78 \times 10^{-27}$ kg and $m_s = 46.50 \times 10^{-27}$ kg, respectively. The density of the substrate is $\rho_{sol} = 2330$ kg/m^3. The effective diameter of a liquid molecule is $\sigma_l = 0.34$ nm. The effective diameter of a substrate molecule can be estimated as $\sigma_s = [M_s/(\rho_{sol}N_A)]^{1/3} = 0.27$ nm, where M_s is the molecular weight of the substrate and N_A is the Avogadro number.

Then a characteristic film thickness h_* (see Sec. II) may be estimated as

$$h_* = \frac{\lambda}{\gamma_2} = \frac{8\delta^2}{\sigma_l} = 2.19 \text{ nm}.$$

A characteristic liquid density ρ_* (see Sec. II) is

$$\rho_* = \frac{\gamma_1}{\gamma_2} = \rho_{sol}\frac{m_l}{m_s}\frac{C_{ls}}{C_{ll}} = 2996\frac{C_{ls}}{C_{ll}} \text{ kg/m}^3.$$

A characteristic liquid pressure p_* (see Sec. III) is estimated as the following:

$$p_* = \frac{\gamma_1^2}{\lambda} = \frac{3\pi}{288}\frac{\sigma_l\rho_{sol}^2}{\delta^4 m_s^2}\frac{C_{ls}{}^2}{C_{ll}} = 3158\frac{C_{ls}{}^2}{C_{ll}}\text{Pa}.$$

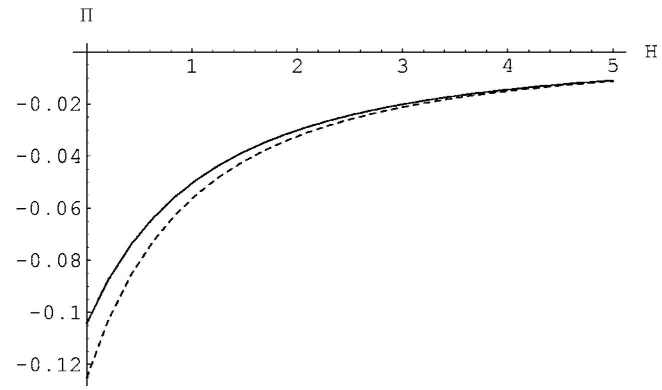

FIG. 4. The normalized driving pressure is shown by a solid line and the normalized average pressure is shown by a dash line.

The constant C_{ll} for the intermolecular potential can be estimated from the attractive part of the classic Lennard-Jones potential as follows: $C_{ll} = 4\epsilon\sigma_l^6$, where ϵ is a characteristic energy of the intermolecular interaction. For the argon $\epsilon = 1.65 \times 10^{-21}$ J, and one can get that $C_{ll} = 10^{-77}$ J m^6.

Since the information about the argon-silicon intermolecular interaction is not available now, for rough estimation purposes we take here $C_{ls} = C_{ll}$. Then we can get the following values for the characteristic density and pressure: $\rho_* = 2996$ kg/m^3, $p_* = 324$ atm.

These characteristic values help to better read the plots presented in Figs 2–4. Namely, Fig. 2 shows that in 7 nm thickness, the argon film liquid density changes from 2100 kg/m^3 at the substrate (higher than the liquid argon bulk density) to 360 kg/m^3 at the film free surface (lower than the liquid argon bulk density). For thicker films, the liquid density at the substrate is gradually approaching its limit of 2996 kg/m^3, which is even higher than the density of the substrate itself.

Figures 3 and 4 show that the liquid in a nanofilm expresses a very strong tension along the substrate. For example, in 7-nm-thickness film, the tension is about 7 atm. The tension increases when the film thickness decreases and approaches its upper limit at about 35 atm, when the film thickness tends to zero.

The disjoining pressure is equal to zero everywhere in the film, assuming that the atmospheric pressure is compensated by the bulk component of pressure. Both of these pressures are neglected in this study.

We have obtained evolution equation (27) for describing the free surface of a nanofilm. This equation is basically a nonlinear diffusion equation with a "good" sign of the diffusion coefficient. That means a nanofilm driven solely by capillary forces is unconditionally stable. It is found that the nanofilm is driven by the tension along the substrate (a negative pressure). It is proposed here that although the film is unconditionally stable, such a strong tension may cause the film to spontaneously break up.

In the case of very thin films, an effective film diffusion coefficient is derived as

$$\kappa = \frac{\lambda \gamma_1^2}{32\mu_* \gamma_2^2}\left(\frac{h}{h_*}\right)^3. \quad (28)$$

For given parameters of argon and silicon this coefficient is calculated as

$$\kappa = \frac{5 \times 10^{-12}}{\mu_*}\left(\frac{h}{h_*}\right)^3 \mathrm{m}^2/\mathrm{s}. \quad (29)$$

For example, for $\mu_* = 10^{-2}$ kg/(m s) and $h = 7$ nm we get $\kappa = 1.35 \times 10^{-8}$ m^2/s.

It should be noted that the use of the self-similar solution presented in Sec. VI is not systematic, because Eq. (27) describing the free surface evolution is derived only for the case of finite depth of the film. More research is needed to study the physics of the triple line in the frame of the proposed approach.

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