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Nonlocal diffuse interface theory of thin films and the moving contact line

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A nonlocal diffuse interface model is explored using the "lubrication approximation" applicable to thin films. We show the inconsistency of the expansion leading to a nonlinear diffusion model, and solve an untruncated integro-differential mean field equation to compute the equilibrium density profile across the fluid-vapor interface. The disjoining potential and effect of interfacial curvature are computed using approximations compatible with the lubrication approximation. We explore the thick film asymptotics, and find it coinciding with the sharp interface limit. These results are further used for computation of the static contact angle and derivation of an evolution equation for flowing films of dynamic menisci in the lubrication approximation. The structure of the evolution equation is identical to that of the sharp interface theory, but it is free from troublesome divergences near the three-phase contact line.

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I. INTRODUCTION

Any interphase boundary is essentially a *mesoscopic* structure. While the material properties vary smoothly at macroscopic distances *along* the interface, the gradients in the *normal* direction are steep, approaching a molecular scale. This brings about a contradiction between the need for a macroscopic description and the necessity to take into consideration microscopic factors that come to influence the motion on incommensurately larger scales.

This contradiction is felt very strongly in the problem of the moving three-phase contact line. It is well known [1,2] that the classical hydrodynamic description of the moving contact line leads to a nonintegrable stress singularity. Numerous ways of resolving this nonphysical divergence have been probed during the last two decades. The approach prevailing in fluid-mechanical computations was to introduce phenomenological corrections, such as effective slip at the solid surface in the vicinity of the three-phase boundary, special rheological properties of the liquid-vapor interface in this region, or an empirical velocity dependence of the contact angle (for a review, see Refs. [3,4]).

The other extreme is a radical departure from the continuum approach, replacing it by direct molecular dynamics simulations in the immediate vicinity of the contact line. Computations based on this method have confirmed the physical importance of the effects of a diffuse boundary and effective slip at molecular distances [5,6]. Such simulations, however, cannot involve macroscopic volumes, and no ways to incorporate them in a macroscopic description are known, although some hybrid computations have been attempted recently [7].

A middle ground is taken by continuum theories introducing intermolecular forces into the hydrodynamic equations of motion. This leads, strictly speaking, to very difficult integro-differential equations even in the sharp interface limit. A computation of the shape of static menisci based on this method has been reported [9], but solution of the formidable problem involving simultaneous computation of both the shape of the free interface and the flow field dependent on intermolecular interactions has never been attempted.

A rational formulation of the sharp interface model with intermolecular interactions is possible in the lubrication approximation [4], where the action of intermolecular forces is reduced to a simple expression for disjoining pressure between parallel vapor-liquid and liquid-solid interphase boundaries [8]. This, however, does not eliminate the stress singularity, except in the case of complete wetting when a sharp contact line is replaced by a gradual transition from a precursor film to a liquid film of macroscopic thickness [2].

The next step toward bridging the gap between macroscopic and microscopic theories is the diffuse interface model, where the density (or other order parameter) is allowed to change continuously in a region interpolating between the two phases. The origin of this approach goes back to Rayleigh [10] and van der Waals [11]. These ideas were further developed in phase field models [12], used mostly in the phenomenological theory of solidification where a fictitious phase field, rather than density, serves as a continuous variable changing across the interphase boundary.

The theory of van der Waals has been widely used for description of equilibrium fluid properties, including surface tension and line tension in three-phase fluid systems [13]. Applications of this theory to dynamical processes in fluids are based on coupling the intermolecular interactions to hydrodynamics through introduction of the capillary tensor into the Stokes equation [14,15]. Numerical computations based on this model have been carried out [16,17], although they involved very small volumes when measured on a macroscopic scale. Here again, a rational analysis matching processes at widely separated scales has been made possible by using the lubrication approximation [18]. The asymptotics of the disjoining pressure in the thick film limit turned out, however, to be different from the respective sharp interface asymptotics, even though both models included physically identical intermolecular interactions.

This prompted us to reexamine the basic assumptions of the diffuse interface model. As explained in more detail in Sec. II, the cause of discrepancy lies in divergences appearing in the commonly used expansion of the interaction term in the expression for free energy, which leads from the original integro-differential equation to the nonlinear diffusion equation of van der Waals [11]. We see no way to eliminate the resulting discrepancy between the qualitative character of solutions of the ‘‘exact’’ and truncated equations, but to return to the original nonlocal formulation.

The aim of this communication is a rational analysis of the *nonlocal* diffuse interface model based on the lubrication approximation, i.e., implying wide separation between characteristic scales across and along the interface. We start (Sec. II) with computation of the equilibrium density profile across the fluid-vapor interface using an untruncated integro-differential mean field equation. It is followed by computation of the disjoining potential (Sec. III) and interfacial curvature correction (Sec. III) using approximations compatible with the lubrication approximation. A remarkable advantage of the nonlocal theory is the possibility of computing density profiles near the solid surface without artificially constructed boundary conditions. We explore the thick film asymptotics, and find it coinciding with the sharp interface limit, as required.

The results of Secs. II–IV are further used for computation of the static contact angle in Sec. V, leading to a specific dependence on the Hamaker constant. The concluding Sec. VI contains the derivation of the evolution equation for flowing films or dynamic menisci in the lubrication approximation. The evolution equation has the same structure as in the sharp interface theory, but is free of troublesome divergences near the three-phase contact line.

II. EQUILIBRIUM DENSITY PROFILE

We consider a one-component van der Waals fluid. It is convenient to use as thermodynamic variables temperature T and number density $\rho = N/V$; N is the number of particles and V is the volume. Further on, we shall restrict ourselves to isothermal processes, while density will be allowed to change in space. In these variables, the Helmholtz free energy is expressed as $F = Nf(\rho,T)$, and pressure p and chemical potential μ are defined as

$$p = -\left(\frac{\partial F}{\partial V}\right)_{N,T} = \rho^2 \frac{\partial f}{\partial \rho}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = \frac{\partial(\rho f)}{\partial \rho}. \tag{1}$$

Our starting point is the expression for the local Helmholtz free energy per molecule $f[\rho(\boldsymbol{x})]$ [19]

$$f[\rho(\boldsymbol{x})] = f_0 - \frac{T}{2}\int (e^{-U(r)/T} - 1)\rho(\boldsymbol{x}+\boldsymbol{r})\, d\boldsymbol{r}. \tag{2}$$

Here U is the pair interaction potential dependent on the distance $r = |\boldsymbol{r}|$; we use units with the Boltzmann constant scaled to unity; $f_0 = T\ln\rho$ is the reference free energy of an ‘‘ideal’’ state with interactions switched off; the factor $\frac{1}{2}$ compensates for counting twice the interacting molecules in each pair. A suitable interaction potential is the modified Lennard-Jones potential with hard-core repulsion:

$$U = \begin{cases} -A_l r^{-6} & (r > d) \\ \infty & (r < d), \end{cases} \tag{3}$$

where d is the nominal hard-core molecular diameter. When the density is constant, the integral in Eq. (2) with hard-core interaction potential gives the free energy of a homogeneous van der Waals fluid. In the hard-core region $r < d$ the exponential term in Eq. (2) vanishes, while at $r > d$ it is expanded in a Taylor series. The result is

$$\overline{f}(\rho,T) = T\ln\rho + \rho(bT - a) \approx T\ln\frac{\rho}{1-b\rho} - a\rho, \tag{4}$$

where $b = \frac{2}{3}\pi d^3$ is the excluded volume and

$$a = -2\pi\int_d^\infty U(r) r^2\, dr = \frac{2\pi A_l}{3d^3}. \tag{5}$$

The approximate expression in (4) yields, by Eq. (1), the van der Waals equation of state $(p + a\rho^2)(1 - b\rho) = \rho T$. The approximation is applicable only at $b\rho \ll 1$, but is used in the van der Waals theory also close to the maximum density $\rho_{\max} = b^{-1}$ as an interpolation formula that yields, as required, two stable states with high and low densities.

It is reasonable to assume that density inhomogeneities are experienced only outside the hard-core radius where the attracting part of the interaction potential is applicable. Separating the homogeneous part, Eq. (2) can be rewritten as [19]

$$f(\boldsymbol{x}) = \overline{f}[\rho(\boldsymbol{x})] + \frac{1}{2}\int_{r>d} U(r)[\rho(\boldsymbol{x}+\boldsymbol{r}) - \rho(\boldsymbol{x})]\, d\boldsymbol{r}. \tag{6}$$

The two terms in the above expression give, respectively, the free energy of a homogeneous state and the distortion energy due to changes of density in space. The equilibrium density is defined by the minimum of $F = \int \rho f\, d\boldsymbol{x}$ subject to the constraint of particle number conservation. This condition is enforced by introducing a Lagrange multiplier — the chemical potential μ. Thus, the integral to be minimized is

$$\mathcal{F} = F - \mu N = \int \rho(\boldsymbol{x})[\overline{f}(\rho) - \mu] d\boldsymbol{x} + \frac{1}{2}\int \rho(\boldsymbol{x})\, d\boldsymbol{x}\int_{r>d} U(r) \times [\rho(\boldsymbol{x}+\boldsymbol{r}) - \rho(\boldsymbol{x})]\, d\boldsymbol{r}. \tag{7}$$

The corresponding Euler-Lagrange equation is

$$g(\rho) - \mu + \int_{r>d} U(r)[\rho(\boldsymbol{x}+\boldsymbol{r}) - \rho(\boldsymbol{x})]\, d\boldsymbol{r} = 0, \tag{8}$$

where $g(\rho) = d[\rho\overline{f}(\rho)]/d\rho$. The first integrand in Eq. (7) should have two minima ρ_l, ρ_v corresponding to the two stable uniform equilibrium states of higher and lower density (liquid and vapor).

A flat interface separating the two phases is at equilibrium when both uniform equilibria are at Maxwell construction, i.e., the minima are of equal depth. This can be achieved at a certain value of chemical potential $\mu = \mu_0$. Under nonequilibrium conditions, the chemical potential serves as a bias parameter that shifts the equilibrium in favor of the dense (dilute) phase when it increases (decreases). The interfacial energy is contributed both by deviations from the equilibrium density levels in the transitional region and by the distortion energy localized there. Thus, the surface tension can be computed, once the density distribution in the transitional layer is known.

The equation for density distribution near a flat boundary normal to the z axis is obtained by assuming ρ to be constant in each lateral plane and integrating Eq. (7) or (8) in the lateral directions. This yields the free energy per unit area,

$$\gamma=\int_{-\infty}^{\infty}\rho(z)[\overline{f}(\rho)-\mu]dz+\tfrac{1}{2}\int_{-\infty}^{\infty}\rho(z)\,dz \times\int_{-\infty}^{\infty}Q(\zeta)[\rho(z+\zeta)-\rho(z)]\,d\zeta, \tag{9}$$

and the one-dimensional (1D) Euler-Lagrange equation

$$g(\rho(z))-\mu+\int_{-\infty}^{\infty}Q(\zeta)[\rho(z+\zeta)-\rho(z)]\,d\zeta=0. \tag{10}$$

The 1D interaction kernel $Q(z)$ lumps intermolecular interaction between layers $z=$const. It is computed by lateral integration using as an integration variable the squared distance $q=r^2=\xi^2+z^2$, where ξ is the radial distance in the lateral plane. Taking note that the lower integration limit for q is $q_0=z^2$ at $|z|>d$, $q_0=d^2$ at $|z|\leqslant d$, we compute

$$Q(z)=-\pi A_l\int_{q_0}^{\infty}q^{-3}\,dq=\begin{cases}-\dfrac{1}{2}\pi A_l z^{-4} & \text{at} \quad |z|>d\\ -\dfrac{1}{2}\pi A_l d^{-4} & \text{at} \quad |z|<d.\end{cases} \tag{11}$$

Computations in the framework of the diffuse interface theory commonly assume that density is changing only slightly over distances comparable with the characteristic interaction length. Then one can expand

$$\rho(\boldsymbol{x}+\boldsymbol{r})=\rho(\boldsymbol{x})+\boldsymbol{r}\cdot\boldsymbol{\nabla}\rho(\boldsymbol{x})+\tfrac{1}{2}\boldsymbol{rr}:\boldsymbol{\nabla\nabla}\rho(\boldsymbol{x})+\cdots. \tag{12}$$

Using this in Eq. (7) we see that the contribution of the linear term to the nonlocal integral vanishes when the system is isotropic and, as a consequence, the interaction term is spherically symmetrical, and the lowest order contribution is due to the quadratic term:

$$F_2(\boldsymbol{x})=-\tfrac{1}{2}K\int\rho(\boldsymbol{x})\nabla^2\rho(\boldsymbol{x})\,d\boldsymbol{x}=\tfrac{1}{2}K\int|\boldsymbol{\nabla}\rho(\boldsymbol{x})|^2\,d\boldsymbol{x}, \tag{13}$$

where

$$K=-\frac{2\pi}{3}\int_d^{\infty}U(r)\,r^4\,dr=-\int_0^{\infty}Q(z)z^2\,dz=\frac{2\pi A_l}{3d}. \tag{14}$$

Thus, Eq. (7) is replaced by

$$\mathcal{F}=\int[\rho\overline{f}(\rho)-\mu\rho+\tfrac{1}{2}K|\boldsymbol{\nabla}\rho(\boldsymbol{x})|^2]d\boldsymbol{x}. \tag{15}$$

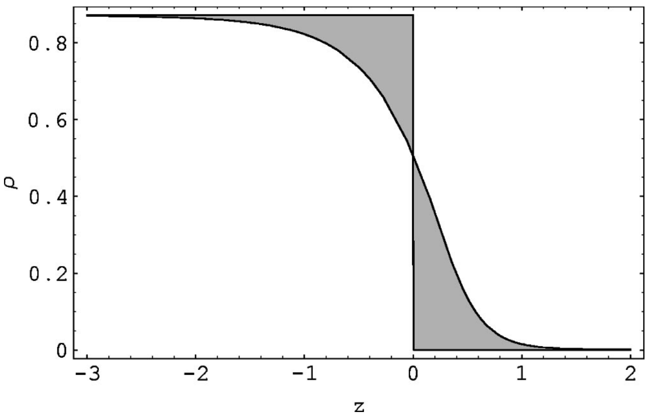

FIG. 1. The density profile obtained by solving Eq. (17) for $\beta=9$. The Gibbs surface is taken as the origin, so that the two shaded areas are equal.

The 1D version of the corresponding Euler-Lagrange equation has the form of a nonlinear reaction-diffusion equation:

$$K\rho''(z)-g(\rho)+\mu=0. \tag{16}$$

This derivation, going back to van der Waals [11], has a disturbing flaw. If the expansion is continued to the next nonvanishing order (fourth), the expression for the corresponding coefficient, computed analogously to Eq. (14), diverges when the common Lennard-Jones potential is used. Such a divergence usually indicates a qualitative difference between the solutions of the "exact" and truncated equations. This, indeed, can be confirmed by considering the asymptotics of Eqs. (10) and (16). The latter has exponential asymptotics, as the deviation from either homogeneous state decays at $|z|\to\infty$ as $\exp(-\lambda|z|)$, where $\lambda=\sqrt{g'(\rho_{l,v})}$. On the other hand, solutions of Eq. (10) exhibit a much weaker power decay, since the integral term perturbing the homogeneous state is proportional at large distances to z^{-3}.

An example of the density profile obtained by solving Eq. (10) numerically with the nonlinear function $g(\rho)$ derived from Eq. (4) is shown in Fig. 1. The dimensionless form of Eq. (10) is

$$\frac{1}{1-\rho(z)}-2\beta\rho(z)-\ln\left(\frac{1}{\rho(z)}-1\right)+\mu+\tfrac{3}{4}\beta \times\int_{-\infty}^{\infty}\hat{Q}(\zeta)[\rho(z+\zeta)-\rho(z)]\,d\zeta=0. \tag{17}$$

Here the length is scaled by the nominal molecular diameter d, the density by b^{-1}, and the chemical potential by T; the interaction kernel is $\hat{Q}(z)=-z^{-4}$ at $z>1$, $\hat{Q}(z)=-1$ at $z<1$; and the only remaining dimensionless parameter is the rescaled inverse temperature $\beta=a/(bT)$. The solution has been obtained through iterations supplemented by some numerical tricks to enhance the convergence. Although, at a first glance, the plot in Fig. 1 may not look very much unlike a typical front solution of Eq. (16), its relatively slow decay leads to a much wider effective interface thickness and to qualitatively different behavior at large (mesoscopic) distances.

III. DISJOINING POTENTIAL

In the proximity of a solid surface, the additional term in the free energy integral (7) is

$$F_s=\int \rho(\boldsymbol{x})\,d\boldsymbol{x}\int_s U_s(r)\rho_s(\boldsymbol{x}+\boldsymbol{r})d\boldsymbol{r}, \tag{18}$$

where U_s is the attractive part of the fluid-solid interaction potential, ρ_s is the solid density, and $\int_s$ means that the integration is carried out over the volume occupied by the solid; all other integrals here and in Eq. (7) are now restricted to the volume occupied by the fluid.

In the following, we shall consider a flat interface parallel to the solid surface $z=0$, and suppose that liquid-solid interactions are also of the van der Waals type with a modified constant $A_s=\alpha_s A_l$. Then the free energy per unit area is expressed, after some rearrangements, as

$$F=\int_0^\infty \rho(z)\{\overline{f}(\rho)+\psi(z)[\alpha_s\rho_s-\tfrac{1}{2}\rho(z)]\}dz$$

$$+\tfrac{1}{2}\int_0^\infty \rho(z)\int_0^\infty Q(z-\zeta)[\rho(\zeta)-\rho(z)]\,d\zeta. \tag{19}$$

The first term contains the same local part as in Eq. (9) complemented by the liquid-solid interaction energy. The latter is computed by integrating the attracting part of the fluid-fluid and fluid-solid interaction energies laterally as in Eqs. (9) and represents the shift of energy compared to the unbounded fluid. The function $\psi(z)$ is computed as

$$\psi(z)=-\pi A_l\int_0^\infty d\zeta\int_{q_0}^\infty q^{-3}\,dq=\int_0^\infty Q(\zeta-z)d\zeta, \tag{20}$$

where the integration limit is $q_0=(z-\zeta)^2$ at $|z-\zeta|>d$, $q_0=d^2$ at $|z-\zeta|\leqslant d$. The result is

$$\psi(z)=\begin{cases}-\dfrac{1}{6}\pi A_l z^{-3} & \text{at} \quad |z|>d\\[2ex] -\pi A_l d^{-3}\left(\dfrac{2}{3}-z/2d\right) & \text{at} \quad |z|<d.\end{cases} \tag{21}$$

The second term in Eq. (19) expresses, as before, the distortion energy, now restricted to the half space $z>0$. The Euler-Lagrange equation derived from Eq. (19) is the familiar Eq. (10) with an additional z-dependent term $\psi(z)[\alpha_s\rho_s-\rho(z)]$.

We shall be further interested in a situation where the perturbation due to the proximity of a solid surface is weak. In this case, the translational invariance of an unbounded two-phase system is weakly broken, and both the shift of the equilibrium chemical potential due to interactions with the solid surface and the deviation from the zero-order density profile computed in the preceding section are small. A necessary condition is smallness of the dimensionless Hamaker constant $\chi=\alpha_s\rho_s/\rho_l-1$. The perturbation, however, ceases to be weak when the density in the layer adjacent to the solid deviates considerably from ρ_l. This means that low densities near the solid surface are strongly discouraged thermodynamically, and a dense "precursor" layer should form on a solid surface in equilibrium with bulk liquid even when the liquid is weakly nonwetting. This layer can be maintained by transport from the gas phase. Since $\rho_l-\rho(z)\propto|z|^{-3}$ at $z\to-\infty$ in an unbounded fluid, the thickness of the precursor layer is estimated as $h_0\propto\chi^{-1/3}$.

The equilibrium chemical potential is shifted from the Maxwell construction $\mu=\mu_0$ in the proximity of the solid surface. In the sharp interface theory, this shift, called the *disjoining potential* [8], is defined as

$$\mu_s=\frac{1}{\rho_l-\rho_v}\,\frac{\partial F}{\partial h}, \tag{22}$$

where h is the distance between gas-liquid and liquid-solid interfaces. In the diffuse interface theory, h has to be defined as a *nominal* interface position relative to the solid, which may be identified with the location of a particular isodensity level. The most natural choice is the Gibbs equimolar surface, which satisfies the relation

$$\int_{-\infty}^h(\rho_l-\rho)dz=\int_h^\infty(\rho-\rho_v)dz. \tag{23}$$

This means that the total mass of an unbounded fluid will not change when the actual profile is replaced by a sharp boundary located at $z=h$ where the density changes abruptly from ρ_l to ρ_v (see Fig. 1).

Returning to Eq. (19), one can observe that only the nonautonomous (z-dependent) part of the first term is responsible for the disjoining potential proper, caused by replacing liquid molecules by solid in the half space $z<0$. The other terms express the energy of the liquid-vapor interface, which is modified when the fluid is restricted to the half space $z>0$. The shift of the chemical potential can be computed, in leading order, by using in Eqs. (19) the zero-order density profile centered at the nominal interface $\rho=\rho_0(z-h)$.

We shall separate several constituent parts of this shift. The derivative of the nonautonomous term is

$$F_h^{(1)}=-\int_0^\infty\psi(z)[\alpha_s\rho_s-\rho_0(z-h)]\rho_0'(z-h)dz. \tag{24}$$

Before differentiating the remaining terms in Eq. (19), it is convenient to transfer the h dependence to the integration limits by using a shifted integration variable $z'=z-h$. The derivative of the local algebraic part is

$$F_h^{(2)}=\rho_0(-h)\overline{f}(\rho_0(-h)). \tag{25}$$

The nonlocal term in Eq. (19) is transformed after differentiating with respect to h using the symmetry of the interaction kernel $Q(z)$, and, after shifting the variable back, integrated by parts with the help of Eq. (20). The result is

$$F_h^{(3)} = -\tfrac{1}{2}\int_0^\infty Q(z)[\rho_0(-h)-\rho_0(z-h)]^2\,dz$$
$$= \int_0^\infty \psi(z)[\rho_0(-h)-\rho_0(z-h)]\rho_0'(z-h)\,dz. \quad (26)$$

The latter expression partly cancels with Eq. (24) when all contributions to μ_s are summed up. It is further convenient to separate the term proportional to the dimensionless Hamaker constant $\chi=\alpha_s\rho_s/\rho_l-1$. The resulting expression for the disjoining potential is

$$\mu_s = \frac{1}{\rho_l-\rho_v}\Bigg\{\rho_0(-h)\overline{f}(\rho_0(-h)) - \chi\rho_l\int_0^\infty \psi(z)\rho_0'(z-h)dz - \int_0^\infty \psi(z)[\rho_l-\rho_0(-h)]\rho_0'(z-h)dz\Bigg\}. \quad (27)$$

In the limit $h \gg d$, when $\rho_0'(z-h)$ can be replaced by the delta function $-(\rho_l-\rho_v)\delta(z-h)$, the second term yields the standard disjoining potential of a liquid layer with sharp interface and uniform density ρ_l:

$$\mu_s^{\mathrm{st}} = -\frac{\pi\chi\rho_l A_l}{6h^3} = -\frac{H}{6\pi h^3\rho_l}, \quad (28)$$

where $H=\pi^2\rho_l A_l(\alpha_s\rho_s-\rho_l)$ is the Hamaker constant defined in the standard way.

The remaining terms vanish in the sharp interface limit when $\rho_0(-h)=\rho_l$. An estimate valid at $h \gg 1$ can be obtained using the asymptotics of $\rho_0(z)$ at $z\to-\infty$, which is obtained from Eq. (10) by replacing the algebraic term there by $[\rho_0(z)-\rho_l]g'(\rho_l)$ and the integral term by its sharp interface limit $(\rho_l-\rho_v)\psi(z)=\frac{1}{6}\pi A_l|z|^{-3}(\rho_l-\rho_v)$. The result is

$$\rho_l-\rho_0(-h) = \frac{\pi A_l\,\rho_l-\rho_v}{6h^3\,g'(\rho_l)}. \quad (29)$$

The first term in Eq. (27), proportional to $[\rho_l-\rho_0(-h)]^2$, decays asymptotically as h^{-6}. The same asymptotics is obtained for the last term in Eq. (27) when the integral is computed in the sharp interface limit. Moreover, the two terms differ by a factor $\frac{1}{2}$ only in this approximation. When $|\chi| \ll 1$, all terms in Eq. (27) are of the same order of magnitude χ^2 when $h=O(|\chi|^{1/3})$. Neglecting the vapor density, we compute in the limit $h \gg 1$

$$\mu_s = -\frac{\pi A_l\chi\rho_l}{6h^3} - \frac{\rho_l}{2g'(\rho_l)}\left(\frac{\pi A_l}{6h^3}\right)^2. \quad (30)$$

The dependence $\mu_s(h)$ defined by this asymptotic formula is nonmonotonic at $\chi<0$, passing a maximum at $h_m = [\pi A_l/6|\chi|g'(\rho_l)]^{1/3}$ and crossing zero at $h_0=2^{-1/3}h_m$. The dependence should remain qualitatively the same at moderate values of χ (see Fig. 2).

The maximum $h=h_m$ corresponds to a minimal thickness of a liquid nucleus condensing on the solid surface. At h larger than the critical thickness h_m, the density profiles are nonmonotonic. Such a solution describes a liquid layer sandwiched between the vapor and the solid, with a weakly depleted density near the solid surface. Nonmonotonic density profiles are unstable with respect to perturbations with a sufficiently long wavelength. This instability is inherent to any nonwetting liquid, but the dynamics is essentially frozen whenever the layer has a macroscopic thickness.

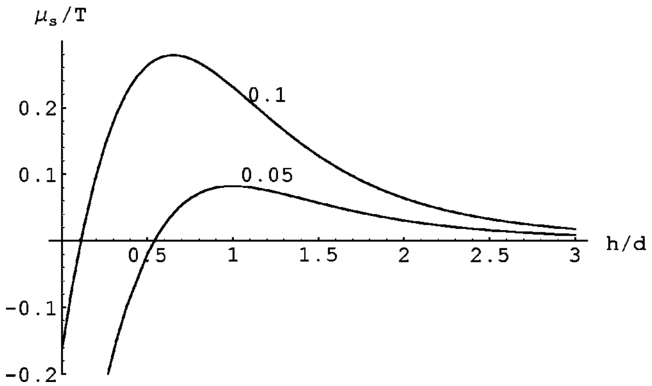

FIG. 2. The dependence of the disjoining potential μ_s on the nominal layer thickness h defined by Eq. (27) for $\beta=9$ and $\chi=0.1$ and 0.05 (as indicated on the respective curves).

At smaller values of h, the maximum disappears, and the solution can be interpreted as a pure vapor phase thickening near the solid wall. The value $h=h_0$ such that $\mu_s(h_0)=0$ corresponds to the nominal interface position on the "dry" surface in equilibrium with the bulk liquid. Clearly, the surface is not literally dry, as even on the nominally "dry" patches the density must be close to bulk liquid density under the specified conditions. At still smaller values of h (which may also be negative) $\mu_s(h)$ sharply decreases to large negative values, and the above approximation is no longer valid. This means that low densities near the solid surface are strongly discouraged thermodynamically, and a dense "precursor" layer with the nominal thickness h_0 should form on a solid surface in equilibrium with bulk liquid; this layer can be maintained by transport from the gas phase. The dependence of h_m and h_0 on the dimensionless Hamaker constant is shown in Fig. 3.

IV. CURVED INTERFACE

Suppose now that the interface is weakly curved, so that isodensity levels no longer coincide with planes $z=\mathrm{const}$. The nominal location of a curved diffuse interface (e.g., the Gibbs equimolar surface) can be used to describe it in the language of differential geometry commonly applied to sharp interfaces. Its spatial position can be defined in a most general way as a vector function $\boldsymbol{X}(\boldsymbol{\xi})$ of surface coordinates $\boldsymbol{\xi}$. A curved interface can be approximated locally by an ellipsoid with the half axes equal to the principal curvature radii. If both radii far exceed the characteristic interface thickness, all isodensity levels are approximated by ellipsoidal segments equidistant from the interface. The density changes along the direction z normal to isodensity surfaces, and the density profile along each normal is defined in the zero order

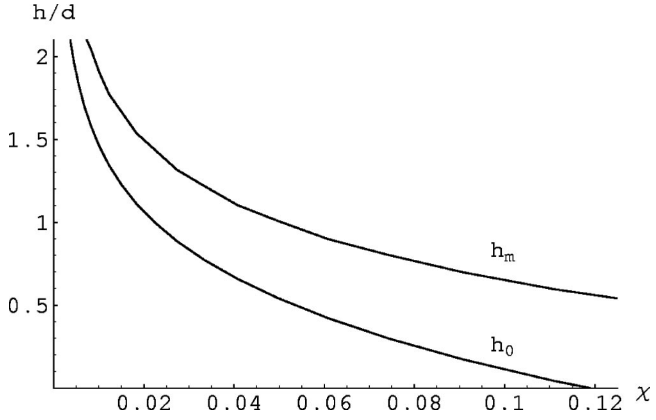

FIG. 3. The dependence of the critical thickness h_m and the thickness of the "precursor" layer h_0 on the dimensionless Hamaker constant $\chi=0.1$ for $\beta=9$.

by the function $\rho=\rho_0(z)$ computed in Sec. II.

A more precise approach is to introduce a coordinate frame aligned with a weakly deformed interface. Given the interface $\mathbf{X}(\boldsymbol{\xi})$, one can find unit tangent vectors along the surface coordinates ξ_α

$$\mathbf{t}_\alpha=\partial\mathbf{X}/\partial\xi_\alpha, \tag{31}$$

the surface metric tensor

$$g_{\alpha\beta}=\mathbf{t}_\alpha\cdot\mathbf{t}_\beta, \tag{32}$$

and the normal vector

$$\mathbf{n}=\tfrac{1}{2}\epsilon^{\alpha\beta}\mathbf{t}_\alpha\times\mathbf{t}_\beta, \tag{33}$$

where $\times$ is the 3D cross product and $\epsilon_{\alpha\beta}$ is the antisymmetric tensor; the Greek indices taking the values (1,2) are lowered and raised with the help of the metric tensor $g_{\alpha\beta}$ and its inverse $g^{\alpha\beta}$. The curvature tensor $\kappa_{\alpha\beta}$ is defined through the covariant derivatives of the tangent or normal vectors with respect to the surface coordinates:

$$\boldsymbol{\nabla}_\beta\mathbf{t}_\alpha=\kappa_{\alpha\beta}\mathbf{n},\quad \boldsymbol{\nabla}_\alpha\mathbf{n}=\kappa_{\alpha\beta}g^{\beta\gamma}\mathbf{t}^\gamma. \tag{34}$$

Next, we define the coordinate axis z directed along $\mathbf{n}$ with the origin on the Gibbs surface. To fix the signs, we assume that the dense phase prevails at $z<0$. The coordinate surfaces $z=\text{const}$ are obtained by shifting the interface along the normal by a constant increment. It is evident that this shift causes the length to increase on convex and to decrease on concave sections. The aligned frame is not well defined far from the interface due to a singularity developing on the concave side at distance about the smallest value of the local curvature radius, i.e., the smallest inverse eigenvalue of the curvature tensor. Since the aligned frame is well defined only sufficiently close to the interface, we have to assume that the curvature is of $O(\epsilon)\ll 1$ when measured on the characteristic scale of intermolecular interactions that defines the effective interface thickness.

The metric tensor of the aligned coordinate system extends the surface metric to the neighboring layers, so that the infinitesimal interval is computed as

$$dr^2=dz^2+(g_{\alpha\beta}+\epsilon z\kappa_{\alpha\beta})\xi^\alpha\xi^\beta+O(\epsilon^2). \tag{35}$$

The free energy integral (7) is rewritten in the aligned frame as a 2D integral along the Gibbs surface. The free energy per unit area γ is a functional of the density profile $\rho(z)$, and is computed in leading order using the standard two-phase solution on the infinite line $\rho_0(z)$. This approximation can be used whenever the density changes between the two extreme values ρ_v and ρ_l within a thin layer where the aligned frame remains well defined. The interfacial curvature induces, however, an $O(\epsilon)$ correction to the local chemical potential, denoted as $\tilde{\mu}(\boldsymbol{\xi})$. Thus, we write

$$\mathcal{F}=\int\left\{\gamma[\rho_0(z)]+\epsilon\tilde{\mu}\int_{-\infty}^{\infty}\rho_0(z)dz\right\}\sqrt{g}\,d^2\xi, \tag{36}$$

where g is the determinant of the surface metric tensor.

The equation defining $\tilde{\mu}(\boldsymbol{\xi})$ (or, after imposing the condition $\tilde{\mu}=\text{const}$, the equilibrium shape of the interface) is obtained by varying Eq. (36) with respect to normal displacements $\delta\mathbf{X}^{(n)}=\mathbf{n}\,\delta z$ reshaping the Gibbs surface. The variation of the area element is expressed through the mean Gaussian curvature $\kappa=g^{\alpha\beta}\kappa_{\alpha\beta}$:

$$\begin{aligned}\delta\sqrt{g}&=\tfrac{1}{2}\sqrt{g}g^{\alpha\beta}\delta g_{\alpha\beta}=\sqrt{g}g^{\alpha\beta}\mathbf{t}_\alpha\cdot\delta\mathbf{t}_\beta=-(\sqrt{g}g^{\alpha\beta}\mathbf{t}_\alpha)_{,\beta}\cdot\mathbf{n}\,\delta z\\ &=-\sqrt{g}g^{\alpha\beta}\kappa_{\alpha\beta}\,\delta z.\end{aligned} \tag{37}$$

The variation of the other term in Eq. (36) is

$$\tilde{\mu}\,\delta z\int_{-\infty}^{\infty}\rho_0'(z)dz=\tilde{\mu}(\rho_l-\rho_v). \tag{38}$$

Assuming, in leading order, $\gamma=\text{const}$, the first-order variation is computed as

$$(\rho_l-\rho_v)\tilde{\mu}-\gamma\kappa=0. \tag{39}$$

First-order terms are added as well when Eq. (36) is varied with respect to ρ; the corresponding Euler-Lagrange equation can be used to compute the first-order correction to the density profile, which we shall not need.

Equation (39) is equivalent to the Gibbs-Thomson law relating the equilibrium chemical potential to the interfacial curvature. This relation is valid only when the surface tension γ is independent of curvature, but curvature-dependent corrections to γ, stemming from corrections to the 1D interaction kernel (11) due to lateral integration along curved isodensity levels, are of $O(\epsilon)$ and do not affect Eq. (39).

V. EQUILIBRIUM CONTACT ANGLE

The results of the two preceding sections can be combined to obtain the conditions of equilibrium of a thin film with a weakly nonplanar interface on a planar support. It is convenient to parametrize the interface by the coordinates $\boldsymbol{\xi}$ in the supporting plane, so that the interface position is defined by a $(2+1)$-vector $\mathbf{X}=\{\boldsymbol{\xi},h(\boldsymbol{\xi})\}$. Then the surface metric tensor is $g_{\alpha\beta}=\delta_{\alpha\beta}+\epsilon\,\partial_\alpha h\cdot\partial_\beta h$, where $\delta_{\alpha\beta}$ are the components of the identity matrix, and the mean Gaussian curvature is $\kappa = \nabla^2 h$.

When the effects of disjoining pressure and interfacial curvature are weak, they are additive; both are of the same order of magnitude when $\chi = O(\sqrt{\epsilon})$. Then Eqs. (27) and (39) can be combined to define the $O(\epsilon)$ chemical potential

$$W = \mu_s - \frac{1}{\rho_l - \rho_v} \gamma \nabla^2 h. \tag{40}$$

The "standard" equilibrium contact angle θ, computed with the help of the Young-Laplace formula, while neglecting the vapor density and presuming the solid surface in contact with vapor to be totally dry, is

$$\cos\theta = 2\alpha_s \rho_s / \rho_l - 1 \quad \text{or} \quad \theta \approx 2\sqrt{-\chi} \ll 1. \tag{41}$$

This expression is, however, inapplicable to the equilibrium solid surface, which is covered by a dense fluid layer even when it is weakly nonwetting.

In the framework of the diffuse interface theory, the equilibrium contact angle has to be defined in a nonstandard way. It is not enough to define a nominal interface position to fix the contact angle unequivocally, since it may then be strongly dependent on the choice of a particular density level for a nominal position. In the weakly nonwetting case considered above, only density levels close to ρ_l can intersect the solid surface at relevant $O(\epsilon)$ values of μ_s, whereas the standard median level never approaches the solid surface. It makes no sense therefore to speak of a "true" contact angle. The contact angle should be defined by its asymptotic value observed at macroscopically large distances, i.e., in the far field limit in terms of Eq. (7) and its offshoots.

This limiting value is determined by balancing the action of interfacial curvature and disjoining potential in accordance with Eq. (40). The curvature of an interface $h(x)$ weakly inclined and curved along the x axis and constant in the spanwise direction is $h''(x)$, and the effective surface tension is defined (in the absence of solid) by Eq. (9). Near the solid surface, the constant density levels are distorted, but the correction is negligible when the disjoining potential is small. Neglecting the vapor density, we write the equation for the nominal interface position

$$\gamma h''(x) - \rho_l \mu_s(h) = 0. \tag{42}$$

In the absence of other external forces, the shape of the interface is determined by solving this equation with the boundary conditions $h = h_0$, $h'(x) = 0$ at $x \to -\infty$, $h'(x) \to \theta = \text{const}$ at $x \to \infty$. As usual, Eq. (42) is transformed, taking as the dependent variable $y(h) = [h'(x)]^2$, to

$$\gamma y'(x) - 2\rho_l \mu_s(h) = 0, \tag{43}$$

with $y(h_0) = 0$, $y \to \theta^2 = \text{const}$ at $x \to \infty$. The asymptotic contact angle is obtained by integration:

$$\theta = \left[\frac{2\rho_l}{\gamma} \int_{h_0}^{\infty} \mu_s(h)\, dh \right]^{1/2}. \tag{44}$$

An estimate valid at $|\chi| \ll 1$ can be obtained using the asymptotic formula (30) and assuming $h \to h_0$ at $z \to -\infty$. Then Eq. (44) reduces to

$$\theta = \frac{\rho_l}{h_0} \left(\frac{\pi A_l |\chi|}{10\gamma} \right)^{1/2} = \frac{\rho_l (2\pi A_l)^{1/6} |\chi|^{5/6} [3g'(\rho_l)]^{1/3}}{(5\gamma)^{1/2}}. \tag{45}$$

Due to the presence of a wet layer on the solid in contact with vapor, the dependence on the dimensionless Hamaker constant χ is qualitatively different from Eq. (41). The exponent at $|\chi|$ is modified due to the dependence of the thickness of the precursor layer on the Hamaker constant.

VI. EVOLUTION EQUATION FOR FLOWING FILMS

The chemical potential computed above enters as a driving force in the hydrodynamic equations of the diffuse interface theory [15]. The equations in the lubrication approximation are derived assuming the characteristic scale in the "vertical" direction (normal to the solid surface) to be much smaller than that in the "horizontal" (parallel) direction. When the interface is weakly inclined and curved, the density is weakly dependent on the coordinate x directed along the solid surface. It is necessary for a consistent scaling of the hydrodynamic equations that the ratio of the characteristic vertical and horizontal length scales or of the characteristic vertical and horizontal velocities v, u be of $O(\sqrt{\epsilon})$, while $\mu_s(h) = O(\epsilon)$.

Equations of motion in the lubrication approximation are obtained following the standard procedure of multiscale expansion [18]. The 2D horizontal velocity vector $\boldsymbol{u}$ is determined by the horizontal component of the Stokes equation:

$$-\rho_0(z-h) \boldsymbol{\nabla} W + (\eta \boldsymbol{u}_z)_z = \boldsymbol{0}, \tag{46}$$

where η is the dynamic viscosity and the driving potential W is defined, in the absence of external forces, by Eq. (40). The solution of Eq. (46) satisfying the no-slip boundary condition on the solid boundary and the no-stress condition at infinity has the general form

$$\vec{u}(z) = \boldsymbol{\nabla} W \int_0^z \frac{d\zeta}{\eta(\zeta)} \int_\zeta^\infty \rho_0(\xi - h)\, d\xi \equiv \Psi(z;h) \boldsymbol{\nabla} W, \tag{47}$$

where the function $\Psi(z;h)$ depends on an assigned dependence of viscosity η on density.

The evolution equation of h is obtained in a standard way using the density profile $\rho_0(z-h)$ and computing the integral balance across the fluid layer. In this way, we obtain the evolution equation in the general form

$$h_t = \boldsymbol{\nabla} \cdot [k(h) \boldsymbol{\nabla} W] \tag{48}$$

with the mobility coefficient

$$k(h)=\int_0^{\infty}\rho_0(z-h)\Psi(z;h)\,dz. \tag{49}$$

When h exceeds the thickness of the precursor film at $\chi \ll 1$, the function $k(h)$ differs only slightly from the standard dependence valid for incompressible Poiseuille flow in a layer of thickness h with a sharp interface:

$$k(h)=\frac{\rho_l h^3}{3\,\eta(\rho_l)}. \tag{50}$$

Taking into account small deviations from the zero-order solution near the wall adds only higher-order corrections.

The structure of Eq. (48) is identical to that of standard equations of motion of thin liquid films [4], which are recovered at large h when the disjoining potential becomes negligible. At small h, the disjoining potential is not singular. At the same time, the viscous stress singularity at the contact line is relaxed as the latter's location becomes indefinite.

One-dimensional steady motion along the x axis can be described by Eq. (48) rewritten in the frame moving with a speed U. The stationary equation can be integrated once, yielding

$$\gamma h'''(x)-\rho_l\mu_s'(h)+\frac{U(h-h_0)}{k(h)}=0. \tag{51}$$

It is assumed here that the liquid layer thickens at $x\to\infty$, and the sign of U is chosen to be positive when the thick layer advances; the integration constant has been introduced allowing for a precursor film with the thickness h_0 at $x\to -\infty$.

Equation (51) is free from singularities which are usually caused by divergences of either viscous stress, or disjoining potential, or both, in a layer of vanishing thickness. The asymptotics at $x,h\to\infty$ is the same as in the sharp interface hydrodynamic theory with van der Waals forces [20], due to the identical asymptotics of the disjoining pressure. Thus, the discrepancy between the asymptotics of sharp and diffuse interface theories is eliminated when the integral formulation is used.

As in the sharp interface theory, a difficulty arises in defining the dynamic contact angle. The asymptotics of Eq. (51) at $h\to\infty$, unlike that of Eq. (42), does not approach any fixed slope, and the growth of the inclination angle is never saturated, as long as macroscopic factors (gravity or volume constraint) are not taken into account. Since $\mu_s \asymp h^{-3}$ at $h\to\infty$, the asymptotics is determined, in the absence of external forces, by a balance of viscous stress and surface tension [20]:

$$h \asymp x\left(3C\ln\frac{h}{h_c}\right)^{1/3}, \tag{52}$$

where $C=(U\eta/\gamma)A^{-3/2}$ is a rescaled capillary number and $A=\pi A_l|\chi|\rho_l^2/\gamma h_0^2=H/\pi\gamma h_0^2$. An indefinite constant h_c should be determined by integrating Eq. (51) with appropriate boundary conditions at $x\to-\infty$ (or small h). There is a unique heteroclinic trajectory of Eq. (51) approaching the asymptotics (52). It is very sensitive to the boundary conditions at or small h, as well as to any kind of molecular-scale factors that may be relevant close to the contact line [21]. The approach to the asymptotics is logarithmically slow, and therefore the value of h_c cannot be determined with a reasonable precision when the shooting method is used, even when the integration is carried out to distances exceeding h_0 by many orders of magnitude, i.e., to films of macroscopic thickness. In realistic computations, external forces, such as gravity, essential at macroscopic distances and determining the far field asymptotics, should be taken into account before the asymptotics (52) is reached [21]. As a result, the dynamic contact angle varies with the distance from the contact line, and its precise definition is to a certain degree a matter of convention.

While the far field asymptotics is common, in the approximation we use, to sharp and diffuse interface theories, the distinction between the two remains substantial near the contact line or in the precursor region. In the sharp interface theory, a nonwetting case cannot be resolved completely in the framework of the lubrication approximation, since the slope has to become large as the contact line is approached. In the present theory, the character of the interaction switches to effective wetting at $h<h_m$, and the lubrication approximation remains valid, as long as the expression for the equilibrium disjoining potential derived above can be used. A more precise theory should take into account nonequilibrium transport processes across isodensity lines, which can be seen as counterparts of evaporation and condensation processes in the sharp interface limit. This problem requires special attention, and will be discussed elsewhere.

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