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Disjoining pressure for nonuniform thin films

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The effect of the attractive forces originating from van der Waals interactions on the dynamics of thin films ($\leqslant \sim 100$ nm) is often approximated in fluid dynamics as the disjoining pressure between two unbounded parallel interfaces. However, it is known that this concept of the disjoining pressure, as a force per unit area between parallel interfaces, cannot generally be extended to films of nonuniform thickness. In this paper, we derive a formula for the disjoining pressure for a film of nonuniform thickness by minimizing the total Helmholtz free energy for a thin film residing on a solid substrate. Comparing to the augmented Young-Laplace equation, the disjoining pressure for a thin film of small slope on a flat substrate is shown to take the form $\Pi = -\frac{A_{123}(4-3h_x^2+3hh_{xx})}{24\pi h^3}$, where A_{123} is the Hamaker constant for phases 1 and 3 interacting through phase 2; h, h_x, and h_{xx} are the local film thickness, slope and second order derivative, respectively. For the limiting case of parallel interfaces (e.g., $h_x = h_{xx} \equiv 0$), the disjoining pressure reduces to $\Pi = -\frac{A_{123}}{6\pi h^3}$ in agreement with the classical Lifshitz expression for the van der Waals force. The derivation can be readily extended to more general nonuniform films by constructing tangential planes at both interfaces of the films. Because of steric effects that prevent molecules from overlapping each other, the molecular size cannot be neglected when applying the mesoscopic concept of the disjoining pressure to films of thickness comparable to molecular scales.

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I. INTRODUCTION

This paper is concerned with a generalization of the theoretical approach, pioneered by Deryagin [1] and Lifshitz [2,3] and discussed more recently by Israelachvili [4], for the inclusion of van der Waals forces in a theoretical framework suitable for fluid dynamics studies of thin liquid films via the introduction of the so-called disjoining pressure. It builds upon the recent study of Wu and Wong [5] but differs from it in important fundamental aspects, and leads to a different result.

There are two approaches that have been developed for continuum-based fluid mechanics studies of free boundary problems involving the motion of fluid interfaces. One is the so-called "diffuse interface" approach [6], which is usually based on a phenomenological model due to Cahn and Hilliard [7]. If we define a phase-field variable ϕ such that the concentrations of the two components in the interfacial region are $(1+\phi)/2$ and $(1-\phi)/2$, the Cahn-Hilliard theory postulates a functional for the free energy of "mixing" of the two components in the interfacial region that is truncated at a square-gradient dependence $|\nabla \phi|^2$. This truncation of the Cahn-Hilliard free energy means that it can only represent "weakly" nonlocal interactions, and thus does not properly capture the attractive van der Waals forces across a thin film [8,9]. Hence, although the diffuse interface theories have been successfully used for free boundary problems such as the motion of a single macroscopic drop in flow where van der Waals forces do not play a significant role, they are currently unable to cope with problems such as coalescence that involve the rupture of a thin film due to the attractive van der Waals forces.

In the alternative (and older) continuum mechanics view, interfaces or boundaries between two macroscopic phases are treated as pure mathematical surfaces of zero thickness and zero mass, across which macroscopic properties such as the density of viscosity may jump discontinuously from the value for one phase to the value for the other.[1] The macroscopic property of interfacial tension or interfacial free energy per unit area accounts for the difference in the collective molecular interactions for a heterogeneous system containing a fluid interface with respect to those interactions that would exist if the system were homogeneous [4,7,9]. In the continuum mechanical framework, the interfacial tension is often interpreted as an effective force per unit length that acts in the direction tangent to the interface [12]. In a system in which all phase boundaries and interfaces are sufficiently far apart, the incorporation of interfacial tension into the stress balance at fluid interfaces is sufficient, together with the macroscopic Navier-Stokes equations and the additional conditions of continuity of velocity and the kinematic condition at the interface, for a complete description of fluid motion and interface shapes [13]. However, if the distance between interfaces or boundaries approaches mesoscopic dimensions (100 nm or less), the collective effect of molecular interactions across this mesoscopic region must be taken into account. Examples where this is relevant include the three-phase region near a contact line [5,14–16] or the thin film that separates a pair of drops just prior to coalescence [17–19].

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[1] It was pointed out by one of the referees that some statistical physicists refer to this as a "sharp-kink" approximation, a terminology introduced in this context by Dietrich and colleagues [10,11].

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The difference between the complete molecular interactions and the interactions that are accounted for as interfacial tension are modeled as additional intermolecular based forces. The most familiar example is the van der Waals force. Two approaches have been pursued for the incorporation of these forces in the macroscopic, continuum formulation. One incorporates the additional intermolecular potential directly into the Navier-Stokes equation as a body force term [20–22], but this approach is extremely unwieldy for free boundary problems where the shapes of the interfaces (and thus the fluid domains) change with time.

The second, more commonly adopted approach, utilizes the disjoining pressure approximation, as originally developed by Lifshitz [2,3] for the case of a thin film. In this approach, the additional intermolecular forces are replaced by an attractive force per unit area, which can be thought of as a pressure applied at the boundaries of the film, known as the disjoining pressure. An exact expression for the disjoining pressure developed by Lifschitz [2,3], is available for a thin film between two unbounded parallel flat surfaces, which may be either interfaces or solid boundaries. In the simplest (nonretarded) approximation, this expression is $\Pi = -A/(6\pi h^3)$, where h is the distance between the interfaces and A is the Hamaker constant (which depends on the fluids involved and can be evaluated via the Lifshitz theory [2,3]). This simple expression for the disjoining pressure has been applied in a number of papers to study the stability and rupture of thin liquid films [11,23–25], even though the boundaries are generally neither flat nor unbounded.

However, as already noted, the simple formula for the disjoining pressure is exact only for the force per unit area between two unbounded parallel interfaces, and thus should strictly be applied only to thin films of uniform thickness. A number of efforts to derive expressions for the disjoining pressure for films of nonuniform thickness have been reported [5,14,15,26–29]. Moreover, in the limit as the film thickness goes to zero, $h \to 0$, the classical formula for the disjoining pressure becomes unbounded. As argued in some references [5,14], this leads to problems with the description of a thin film ending on a substrate. Hocking [14], based on the work of Miller and Ruckenstein [30], tried to resolve this problem by deriving a nonsingular expression for the disjoining pressure for a liquid wedge with a small contact angle residing on a solid substrate and neglecting the vapor effects. Hocking's expression [14] takes the form $\Pi = -B_H(\psi_H^4 - h_x^4)/h^3$, where B_H and ψ_H are material functions defined in Hocking's paper and h and h_x are the local film thickness and slope, respectively. Based on Hocking's expression, as long as $\psi_H^4 - h_x^4 \to 0$ faster than h^3 as we approach the edge of the film, the disjoining pressure Π converges to a finite value. However, in a more recent study, Wu and Wong [5] have correctly noted that Hocking's derivation contains fundamental flaws. The most important is that Hocking applied an "equilibrium" condition, namely, $\Phi = \text{const}$ only at the interface, which does not guarantee equilibrium for the system as a whole.

In a completely independent and separate series of studies, beginning with the work of Robbins *et al.* [27], a theoretical framework that is similar to Hocking's analysis was developed by the statistical physics community, most notably Dietrich and co-workers [28,29]. As in the work of Hocking, these investigators mistakenly used an equilibrium condition applied only at the fluid interface.

Wu and Wang [5] considered a liquid drop (i.e., a nearly parallel thin film) on a solid substrate. By minimizing the total free energy, and calculating a quantity that they reported to be the excess free energy within a wedge shaped region above that for a "bulk" fluid, they obtained an alternative expression for the disjoining pressure in the small-slope limit containing a second-order derivative $\Pi = -B_w(\alpha^4 - h_x^4 + 2hh_x^4 h_{xx})/h^3$, where $B_w \equiv 3\pi\eta_f^2\beta_{ff}(1-\rho)/16$ and $\alpha \equiv [8(1-\lambda)/(9-9\rho)]^{1/4}$ is the contact angle. The parameters that appear in these expressions are $\lambda = \eta_s\beta_{fs}/\eta_f\beta_{ff}$ and $\rho = \eta_g\beta_{fg}/\eta_f\beta_{ff}$, where η_s, η_f, and η_g, are the number densities of solid, liquid, and vapor molecules, and β_{ff}, β_{fg}, and β_{fs} are the liquid-liquid, liquid-vapor, and liquid-solid van der Waals potential constants, respectively. Unlike Hocking's [14] theory, which explicitly neglects the vapor effects, Wu and Wong's derivation [5] is intended as a general formulation for arbitrary three-phase systems. Although their approach is a step in the right direction, there are issues with the details. An indication of this is the fact that their expression for the disjoining pressure does not have the correct form for the limiting case of two parallel interfaces $h_x = h_{xx} \equiv 0$. In particular, their expression in this case reduces to

$$\Pi = -B_w\alpha^4/h^3 = -\pi\eta_f^2\beta_{ff}\left(1 - \frac{\eta_s\beta_{fs}}{\eta_f\beta_{ff}}\right) \Bigg/ 6h^3,$$

which depends only on the fluid-fluid and fluid-solid van der Waals constants but is independent of the properties of the third phase. This suggests that there is some problem with their calculation.

In this paper, we have followed the same approach as outlined by Wu and Wong [5], but with several fundamental differences. In particular, we define the disjoining pressure based on the equilibrium condition of Yeh *et al.* [15,16] for a liquid thin film residing on a flat solid substrate, but we modify it to include the excess energy outside the film. Assuming a van der Waals hard sphere interaction at the molecular level [see Eq. (2)], the crucial difference is that we start with the total intermolecular potential, obtained by integrating throughout the whole heterogeneous system, and obtain the excess energy associated with the disjoining pressure by subtracting the interfacial tension potential from the total intermolecular potential. In the limit of a small slope, the disjoining pressure given by this approach takes the relatively simple form

$$\Pi = -\frac{\partial E_1}{\partial h} + \frac{\partial}{\partial x}\left(\frac{\partial E_1}{\partial h_x}\right) = -A_{123}(4 - 3h_x^2 + 3hh_{xx})/24\pi h^3, \tag{1}$$

where E_1 is the excess energy per substrate area within the thin film region, A_{123} is the Hamaker constant for the interactions between phase 1 and 3 through phase 2, and we use the numbers 1, 2, and 3 to denote the vapor, liquid, and solid phases. In Eq. (1), h, h_x, and h_{xx} are the local film thickness, slope and second-order derivative, respectively. A key point is that the form for the Hamaker constant depends on the properties of all three phases, and is completely consistent with the Lifshitz theory for nonretarded van der Waals forces [2–4,31] [i.e., in the limiting case of two parallel interfaces, $h_x = h_{xx} = 0$, we get the classical Lifshitz result $\Pi = -A_{123}/(6\pi h^3)$].

The extension to more general nonuniform thin films, for example, those that are not necessarily bounded by solid substrates, is more or less trivial, and can be achieved by constructing tangential planes along the top and the corresponding bottom interfaces of the film. As expected from Eq. (1), the disjoining pressure for a nonuniform thin film is a function of the film thickness, the local slopes and the second order derivative of both interfaces.

One needs to be very careful when trying to extrapolate the concept of disjoining pressure, basically a mesoscopic concept, to molecular scales. The main problem arises from the characteristic length scales at which molecules are prevented from overlapping because of steric effects. Such steric effects automatically preclude extrapolation of the thickness of the film to zero values; they actually provide a minimum thickness which is of the order of molecular dimensions and this prevents infinite self-interactions as well as infinite interactions between molecules at the boundaries between different phases.

II. INTERFACIAL TENSION

The basic idea in the recent work of Wu and Wong [5] was to screen out the disjoining pressure for a thin film by subtracting the contribution that corresponds to the interfacial tension from the total intermolecular potential. Conceptually, this is clearly the correct approach. Both the van der Waals force and the interfacial tension (or the interfacial free energy) originate from molecular interactions, and hence both are included in the total intermolecular potential. But Wu and Wong calculate the intermolecular potential only within the liquid region, and the term they subtract, which they term the "bulk" value of the interfacial potential does not completely correspond to the interfacial free energy. It is these factors that lead to the disagreement of their result with the Lifshitz's theory for the van der Waals forces as discussed in Sec. I.

To provide a clear basis for distinguishing the disjoining pressure from the interfacial tension, we begin by briefly reviewing the concept of interfacial tension from the viewpoint of intermolecular interaction potential [4,32]. For simplicity, we assume that the molecules are equal-sized spherical particles that interact via a van der Waals–like attractive potential of the form

$$W(r) = \begin{cases} -C/r^6, & r > \sigma, \\ \infty, & r < \sigma, \end{cases} \tag{2}$$

where σ is the molecular diameter, r is the center to center distance between two molecules and C is the potential constant. The hard wall part of the pair potential prohibits molecules from overlapping with each other. As one of the referees suggested, one would not choose such a simple model if the objective was to obtain a formula valid for calculating the interfacial tension even as the separation distance actually tends to zero. However, this model is sufficient for the present goal of a modified formula for the disjoining pressure. Our objective in this section is a formula for the interfacial tension, consistent with the model (2), which can be subtracted from the total intermolecular potential to obtain a formula for the disjoining pressure.

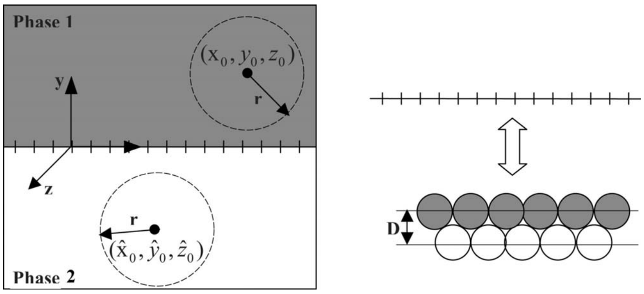

FIG. 1. The left panel represents a nonuniform system consisting of two macroscopic phases with a sharp interface; the right figure represents the microscopic structure of the sharp interface where a molecular cutoff length D is introduced to prevent the molecules from overlapping with each other.

Let us first consider a uniform phase, denoted by the number 1, occupying all space, e.g., phase 1 contains molecules of diameter σ_1 with number density n_1. The potential energy per molecule is obtained by summing the potentials of all pairs of molecules over all of space and thus the intermolecular potential per unit volume of the uniform phase 1 is given by [4,5,14]

$$\Phi_1^* = \frac{n_1}{2}\int_{\sigma_1}^{\infty} -\frac{C_{11}}{r^6}(4\pi r^2 n_1)\,dr = -\frac{2\pi C_{11} n_1^2}{3\sigma_1^3} = -\frac{2A_{11}}{3\pi\sigma_1^3}, \tag{3}$$

where $A_{11} = \pi^2 C_{11} n_1^2$ is the Hamaker constant [3] and C_{11} is the van der Waals force constant. Similarly, the intermolecular potential per unit volume of a uniform phase 2 is $\Phi_2^* = -2A_{22}/(3\pi\sigma_2^3)$ with $A_{22} = \pi^2 C_{22} n_2^2$.

In order to determine the expression for interfacial tension at the interface between bulk fluid phases 1 and 2 in terms of intermolecular interactions, we consider the idealized system shown in Fig. 1, which has pure phase 1 for $y > 0$ and pure phase 2 for $y < 0$. Strictly speaking, for vapors and liquids, the system in Fig. 1 does not lead to the lowest free energy and, hence, does not exist in reality. In the real system, all interfaces have a definite structure and thickness. However, for the purpose of simplification, we assume the phases are sharply divided, neglect the mixing entropy and kinetic energy, and focus only on the effects of molecular interactions on interfacial tension. The reader is referred to the papers of Cahn and Hilliard [7,33,34] for a much more complete thermodynamic description.

The intermolecular potential per unit volume of phase 1 at the point of (x_0, y_0, z_0) in the nonuniform system in Fig. 1 can be calculated by subtracting the 1-1 potential in the region for $y < 0$ from the expression (3) for an unbounded phase 1 and adding the 1-2 potential.

$$\Phi_1 = -\frac{2A_{11}}{3\pi\sigma_1^3} + \frac{(A_{11}-A_{12})}{2\pi^2}\int_{-\infty}^{0} dy \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} \frac{1}{[(x-x_0)^2+(y-y_0)^2+(z-z_0)^2]^3}dz$$
$$= -\frac{2A_{11}}{3\pi\sigma_1^3} + \frac{(A_{11}-A_{12})}{12\pi y_0^3}, \qquad (4)$$

where $A_{12}=\pi C_{12}n_1n_2$. The corresponding expression for the intermolecular potential per unit volume of phase 2 at $(\hat{x}_0,\hat{y}_0,\hat{z}_0)$ in Fig. 1 is given by

$$\Phi_2 = -\frac{2A_{22}}{3\pi\sigma_2^3} - \frac{(A_{22}-A_{12})}{12\pi\hat{y}_0^3}. \qquad (5)$$

The interfacial free energy or interfacial tension is, by definition, the difference per unit area of interface between the actual free energy of the system and that which it would have if the properties of the phases were continuous throughout [7]. The interfacial tension for the nonuniform system in Fig. 1 is therefore given by

$$\gamma_{12} = \int_{+D}^{+\infty}(\Phi_1-\Phi_1^*)dy_0 + \int_{-\infty}^{-D}(\Phi_2-\Phi_2^*)d\hat{y}_0$$
$$= \frac{1}{24\pi D^2}(A_{11}+A_{22}-2A_{12}), \qquad (6)$$

where, for both integrals, we integrate from the interface outward to obtain a result that is invariant under rotations about an axis along the interface.

In the integrals in Eq. (6), we set a cutoff length D, of the scale of the larger of σ_1 or σ_2, because of the steric effects we mentioned above. This cutoff avoids unphysical unbounded molecular interactions, and is commonly applied for this type of calculation. According to Eq. (6), the interfacial tension involves integrations extending to infinity and, in this sense, it is a collective effect involving molecular interactions throughout the whole macroscopic nonuniform system.

III. DISJOINING PRESSURE FOR A TWO-DIMENSIONAL THIN FILM RESIDING ON A FLAT SUBSTRATE

We now consider a two-dimensional liquid thin film in the form of a "drop" on a flat solid substrate shown in Fig. 2, the same system discussed by Wu and Wong [5]. We also denote the vapor, liquid, and solid phases with the numerals 1, 2, and 3. We assume the phases are made up of equal-sized, spherical molecules and are characterized by self-interaction van der Waals potentials leading to Hamaker constants A_{11}, A_{22}, and A_{33}.

The thermal equilibrium condition given by minimizing the total Helmholtz free energy for the two-dimensional drop shown in Fig. 2 was studied thoroughly by Yeh and his coworkers [15] and applied in Wu and Wong's derivation [5] for a slope-dependent disjoining pressure. In addition to the interfacial tension of Eq. (6) for the liquid-vapor interface (obtained by assuming a single interface with a semi-infinite body on either side), there is an excess energy per unit substrate area within the thin film region because of the proximity of the interface between the solid substrate and the liquid, as argued in Yeh's analysis [15]. It is this quantity that is associated with the disjoining pressure. We follow the precedent from Wu and Wong's analysis [5], and assume that this excess energy can be approximated as a function of the local film thickness h and the local film slope h_x, i.e., $E(h,h_x)$. The excess energy is most important in the film region where the interfaces 2-3 and 1-2 are very close to each other. Outside the droplet, along interface 1-3, there is also an excess energy, because of the nearby presence of the liquid molecules in the drop, which becomes significant upon approach to the contact line. We will assume that the excess energy beyond the liquid thin film region is a function of the contact angle $h_x|_{x=\pm x_0}$ as well as the distance to the contact line and that it decays to zero at infinity $x \to \pm\infty$ (see Fig. 2).

Accounting for the excess energy both inside and outside the thin film region, the thermal equilibrium condition, in the spirit of Yeh's derivation [15], for a thin film residing on a flat substrate that is symmetric about the axis y as shown in Fig. 2, is given by

$$\delta\left\{\int_{-x_0}^{0}[\gamma_{12}\sqrt{1+h_x^2}+\gamma_{23}-\gamma_{13}+E_1(h,h_x)+p_ch]dx + \int_{-\infty}^{-x_0}E_2(|x_0+x|,\, h_x|_{x=x_0})dx\right\}=0, \qquad (7)$$

where δ represents the variation of the whole function inside the outer parentheses with respect to h,h_x and the position of

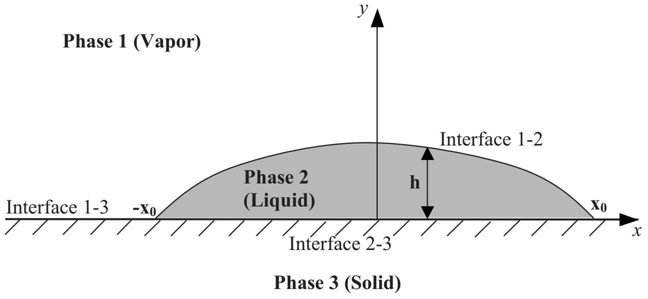

FIG. 2. Schematic representation of a two-dimensional thin film residing on a flat substrate and the common contact lines are located at x_0 and $-x_0$. The film thickness is denoted by h.

the contact line x_0; $E_1(h,h_x)$ is the excess energy per unit substrate area in the film region $(-x_0 \leqslant x \leqslant x_0)$ while $E_2(|x_0+x|,\, h_x|_{x=x_0})$ is the same quantity outside the film region $(|x| > x_0)$; p_c is a Lagrange multiplier for mass conservation, and γ_{12}, γ_{13}, and γ_{23} are the interfacial tensions for interfaces 1-2, 1-3, and 2-3, respectively. Expanding Eq. (7) yields the governing equation in the film region, that is, phase 2

$$\frac{\gamma_{12}h_{xx}}{(1+h_x^2)^{3/2}} - \left[\frac{\partial E_1}{\partial h} - \frac{d}{dx}\left(\frac{\partial E_1}{\partial h_x}\right)\right] = p_c \tag{8}$$

together with the symmetry boundary condition at $x=0$

$$\frac{\gamma_{12}h_x}{(1+h_x^2)^{1/2}} + \frac{\partial E_1}{\partial h_x} = 0 \tag{9}$$

and the boundary condition at $x=-x_0$

$$\frac{\gamma_{12}}{(1+h_x^2)^{1/2}} + \gamma_{23} - \gamma_{13} + \left[E_1 - h_x\frac{\partial E_1}{\partial h_x}\right] - \int_{-\infty}^{x_0} h_{xx}\frac{\partial E_2}{\partial h_x}\bigg|_{x=-x_0} dx = 0. \tag{10}$$

The disjoining pressure can be defined from Eq. (8), by comparing with the augmented Young-Laplace equation [15], as

$$\Pi = -\frac{\partial E_1}{\partial h} + \frac{d}{dx}\left(\frac{\partial E_1}{\partial h_x}\right). \tag{11}$$

It can be seen that the excess energy outside of the film region [i.e., E_2 in the region $x \in (-\infty, -x_0)$] does not affect the disjoining pressure. However, E_2 does affect the boundary condition at the contact line $x=-x_0$ [see Eq. (10)]. The consequences of this modification are not clear to us at this time. It is most likely important in determining the contact angle, but may also be related to the concept of a "line tension" at the contact line. Since the objective of this paper is the disjoining pressure, we do not pursue this issue here.

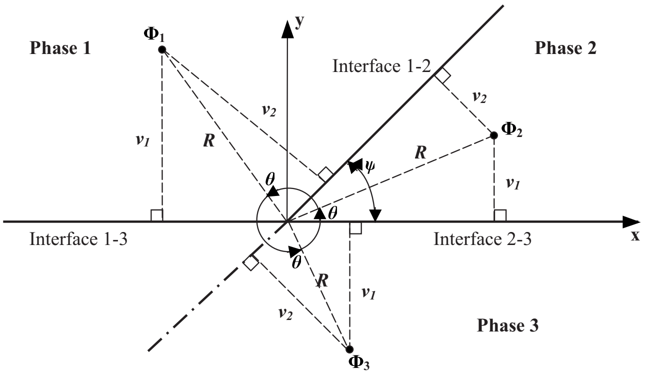

FIG. 3. Schematic of a three-phase thin film system near the contact line; phase 1 corresponds to $\theta \in (\psi, \pi)$, phase 2 corresponds to $\theta \in (0, \psi)$, phase 3 corresponds to $\theta \in (\pi, 2\pi)$, where ψ is the contact angle; v_1 and v_2 are the distances of a point to the horizontal interface, e.g., interface 1-3 or 2-3, and to the inclined interface 1-2, respectively.

The result, Eq. (11), is the same as obtained by Wu and Wong [5]. However, our calculation of the excess energy per unit substrate area E_1 differs fundamentally from their approach. First, we sum the intermolecular potentials in all three of the bulk phases, rather than just the intermolecular potential for the molecules in the liquid phases. Second, we subtract the portion of the intermolecular potential that corresponds exactly to the interfacial tension, rather than subtracting the "bulk" form of the intermolecular potential as done in the Wu and Wong analysis. The result obtained in this way is exactly the excess energy E_1. In particular, we avoid mixing effects of the intermolecular potentials attributed to interfacial tension from those of other van der Waals forces.

The thin film near the contact line, at $x=-x_0$ in Fig. 2, is schematically shown in Fig. 3. Assuming van der Waals interactions only, we sum the pairwise potentials between a molecule and all the other molecules throughout the system to obtain the total intermolecular potential per unit volume

$$\Phi_1 = -\frac{2A_{11}}{3\pi\sigma_1^3} + \frac{1}{12\pi}\left[\frac{a_1(A_{12}-A_{11}) + (A_{11}-A_{13})}{v_1^3} + \frac{a_2(A_{12}-A_{11})}{v_2^3}\right], \tag{12}$$

$$\Phi_2 = -\frac{2A_{22}}{3\pi\sigma_2^3} + \frac{1}{12\pi}\left[\frac{a_1(A_{22}-A_{21}) + (A_{21}-A_{23})}{v_1^3} + \frac{a_2(A_{22}-A_{21})}{v_2^3}\right], \tag{13}$$

$$\Phi_3 = -\frac{2A_{33}}{3\pi\sigma_3^3} + \frac{1}{12\pi}\left[\frac{a_1(A_{32}-A_{31}) + (A_{31}-A_{33})}{v_1^3} + \frac{a_2(A_{32}-A_{31})}{v_2^3}\right], \tag{14}$$

where $a_1=\frac{1}{2}+\frac{3}{4}\cos\theta-\frac{1}{4}\cos^3\theta$, $a_2=\frac{1}{2}+\frac{3}{4}\cos(\psi-\theta)-\frac{1}{4}\cos^3(\psi-\theta)$, $v_1=R\sin\theta$, $v_2=R\sin(\psi-\theta)$; phase 1 corresponds to $\theta\in(\psi,\pi)$; phase 2 corresponds to $\theta\in(0,\psi)$; and phase 3 corresponds to $\theta\in(\pi,2\pi)$. In addition, $A_{11}=\pi C_{11}n_1^2$, $A_{22}=\pi C_{22}n_2^2$, $A_{33}=\pi C_{33}n_3^2$, $A_{12}=A_{21}=\pi C_{12}n_1n_2$, $A_{13}=A_{31}=\pi C_{13}n_1n_3$, $A_{32}=A_{23}=\pi C_{23}n_2n_3$ are the Hamaker constants as discussed above; σ_1,σ_2, and σ_3 are the diameters of the molecules of phase 1, 2, and 3 respectively; their number densities are denoted by n_1, n_2, and n_3. The result given by Eq. (13) is the intermolecular potential for the liquid phase, and is the same as that calculated by Wu and Wong [5]. The pairwise additivity of the intermolecular interactions that is inherent in Eqs. (12)–(14) ignores many-body effects of neighboring molecules. The effects from the immediate neighborhood could alter the molecular polarizabilities and make the van der Waals potentials for macroscopic bodies actually nonadditive [4]. The nonadditivity of van der Waals potential for multiphase systems, however, can be circumvented using the Lifshitz theory of van der Waals forces, as discussed below.

Without loss of generality, we subtract the constant intermolecular potential of a uniform phase $[\Phi_1^*=-2A_{11}/(3\pi\sigma_1^3)$; $\Phi_2^*=-2A_{22}/(3\pi\sigma_2^3)$; $\Phi_3^*=-2A_{33}/(3\pi\sigma_3^3)]$ since it plays no role in determining the excess energy. We obtain the energy per unit substrate area by integrating the remaining part throughout the complete heterogeneous system, along the vertical y direction in Fig. 3,

$$\Lambda_1=\int_{-\infty}^{-D}(\Phi_3-\Phi_3^*)dy+\int_{D}^{h-D\sqrt{1+h_x^2}}(\Phi_2-\Phi_2^*)dy+\int_{h+D\sqrt{1+h_x^2}}^{+\infty}(\Phi_1-\Phi_1^*)dy, \tag{15}$$

$$\Lambda_2=\int_{-\infty}^{-D}(\Phi_3-\Phi_3^*)dy+\int_{D}^{+\infty}(\Phi_1-\Phi_1^*)dy. \tag{16}$$

Here, Λ_1 and Λ_2 represent the energy per unit substrate area inside and outside the thin film region, respectively. Inside the thin film region, that is, for $x>-x_0$ in Fig. 3, the integration along y crosses two interfaces, namely, the 1-2 and 2-3 interfaces, while outside ($x<-x_0$), the integration crosses the 1-3 interface only. As discussed previously, we follow standard protocol, and introduce a molecular "cutoff" length D at the interface to exclude molecular overlaps (and infinite interactions). For simplicity, we assume the characteristic molecular length scales for the 1-2, 2-3, and 1-3 interfaces have the same value D. In Eq. (15), the integration limit at the interface 1-2 contains the term $\sqrt{1+h_x^2}$ to account for its slope.

In the asymptotic limit $D/h\to 0$ (the film thickness is by far larger than the molecular cutoff length D), the energy per unit substrate area defined in Eqs. (15) and (16) reduces to

$$\begin{aligned}\Lambda_1&=\frac{1}{24\pi D^2}(A_{22}+A_{33}-2A_{23})+\frac{\sqrt{1+h_x^2}}{24\pi D^2}(A_{11}+A_{22}-2A_{12})\\&\quad+E_1(h,h_x)\\&=\gamma_{23}+\sqrt{1+h_x^2}\gamma_{12}+E_1(h,h_x),\end{aligned} \tag{17}$$

$$\begin{aligned}\Lambda_2&=\frac{1}{24\pi D^2}(A_{11}+A_{33}-2A_{13})+E_2(x_0-x,\,h_x|_{x=x_0})\\&=\gamma_{13}+E_2(x_0-x,\,h_x|_{x=x_0}).\end{aligned} \tag{18}$$

The energy per unit substrate area presented in Eqs. (17) and (18) clearly consists of two parts: one arising from the interfacial tension and the other from excess energy. The first two terms of Λ_1 correspond to the 2-3 and 1-2 interfacial tension contributions, respectively, and $\sqrt{1+h_x^2}$ in the second term of Λ_1 accounts for the slope of the 1-2 interface. For Λ_2, the first term is the 1-3 interfacial tension. The expressions for the excess energy per substrate area E_1 and E_2 are presented in the Appendix; they are complicated nonlinear functions of the film thickness, the local film slope, the contact angle, and the distance to the contact line. However, for the small slope limit $h_x \ll 1$ (which is consistent with the assumption that E_1 is a function only of h and h_x and not higher order derivatives), E_1 and E_2 reduce to simpler forms

$$E_1(h,h_x)=-\left(\frac{1}{12\pi h^2}+\frac{h_x^2}{16\pi h^2}\right)(A_{22}+A_{13}-A_{12}-A_{23}), \tag{19}$$

$$E_2(|x_0-x|,\,h_x|_{x=-x_0})=\frac{(A_{11}+A_{23}-A_{12}-A_{13})}{48\pi|x_0-x|^2}\,h_x|_{x=-x_0}. \tag{20}$$

From the Lifshitz theory of the non-retarded van der Waals force [2–4,31], the Hamaker constant for two phases interacting through a third phase can be approximated via the combining relations [4]

$$\begin{aligned}A_{123}&\approx(\sqrt{A_{11}}-\sqrt{A_{22}})\times(\sqrt{A_{33}}-\sqrt{A_{22}})\\&\approx(A_{22}+\sqrt{A_{11}A_{33}}-\sqrt{A_{11}A_{22}}-\sqrt{A_{22}A_{33}})\\&\approx(A_{22}+A_{13}-A_{12}-A_{23}),\end{aligned} \tag{21}$$

$$\begin{aligned}A_{213}&\approx(\sqrt{A_{22}}-\sqrt{A_{11}})\times(\sqrt{A_{33}}-\sqrt{A_{11}})\\&\approx(A_{11}+\sqrt{A_{22}A_{33}}-\sqrt{A_{11}A_{22}}-\sqrt{A_{11}A_{33}})\\&\approx(A_{11}+A_{23}-A_{12}-A_{13}).\end{aligned} \tag{22}$$

Here, A_{123} represents the Hamaker constant for phase 1 and phase 3 interacting through phase 2 while A_{213} represents the Hamaker constant for phase 2 and phase 3 interacting through phase 1. Substituting Eqs. (21) and (22) into Eqs. (19) and (20), the excess energies per unit area reduce to

$$E_1(h,h_x)=-A_{123}\left(\frac{1}{12\pi h^2}+\frac{h_x^2}{16\pi h^2}\right), \tag{23}$$

$$E_2(|x_0-x|,\,h_x|_{x=-x_0})=\frac{A_{213}}{48\pi|x_0-x|^2}\,h_x|_{x=-x_0}. \tag{24}$$

The disjoining pressure defined in Eq. (11) is then calculated as

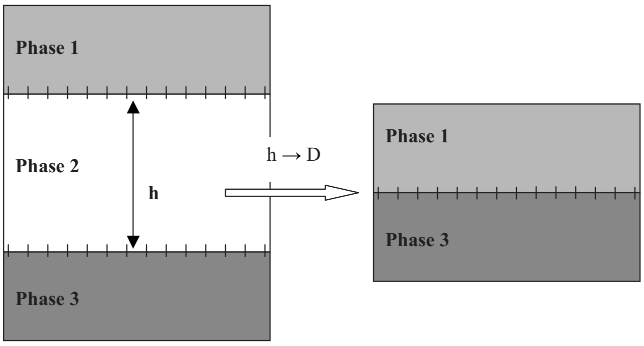

FIG. 4. As the film thickness approaches to the cutoff molecular scale $h \rightarrow D$, a three-phase system with two parallel interfaces switches to a two-phase system. This implies that the film thickness cannot go directly to zero since molecules are not allowed to overlap each other.

$$\Pi = -\frac{\partial E_1(h,h_x)}{\partial h} + \frac{d}{dx}\left(\frac{\partial E_1(h,h_x)}{\partial h_x}\right)$$

$$= -\frac{A_{123}(4 - 3h_x^2 + 3hh_{xx})}{24\pi h^3}. \quad (25)$$

The integral corresponding to the boundary condition at $x=-x_0$, e.g., Eq. (10), with a cutoff molecular length D is $\int_{-\infty}^{-x_0} h_{xx}\frac{\partial E_2}{\partial h_x}\big|_{x=-x_0}\,dx=\frac{A_{213}}{48\pi D}\,h_{xx}\big|_{x=-x_0}$.

In the limiting case of two parallel interfaces, i.e., for $h_x=h_{xx}\equiv 0$, the disjoining pressure reduces to $\Pi=-A_{123}/(6\pi h^3)$ which is the expected form for the disjoining pressure between two parallel, plane interfaces based on the Lifshitz theory [2–4,31]. As $h \rightarrow 0$, the disjoining pressure $\Pi=-A_{123}(4-3h_x^2+3hh_{xx})/(24\pi h^3)$ appears to be unbounded. The characteristic molecular length D implicitly built into the film thickness h, however, will not allow $h=0$, since the molecules cannot overlap. Thus, the lower limit for the film thickness is D instead of zero. The cutoff molecular length D is also built into the interfacial tension as discussed in the previous section. By the same reasoning, the distance to the contact line $|x_0-x|$ cannot be smaller than the cutoff distance D. The excess energy E_2 outside the thin film region in Eqs. (20) and (24) is therefore bounded.

Let us now consider a three-phase system with two parallel interfaces, Fig. 4. The energy per unit area consists of two interfacial tensions: γ_{12} and γ_{23}, and an excess energy $E=-A_{123}/(12\pi h^2)$, so that according to Eq. (23):

$$\Lambda = \gamma_{12} + \gamma_{23} + \frac{-A_{123}}{12\pi h^2}. \quad (26)$$

Let $h \rightarrow D$ and substitute the interfacial tension defined in Eq. (6) and the Hamaker constant A_{123} in Eq. (21) into Eq. (26):

$$\Lambda \rightarrow \frac{A_{11}+A_{22}-2A_{12}}{24\pi D^2} + \frac{A_{22}+A_{33}-2A_{23}}{24\pi D^2}$$

$$- \frac{A_{22}+A_{13}-A_{12}-A_{23}}{12\pi D^2}$$

$$= \frac{A_{11}+A_{33}-2A_{13}}{24\pi D^2} = \gamma_{13}. \quad (27)$$

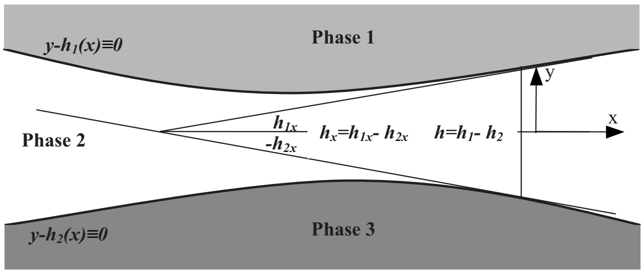

FIG. 5. The disjoining pressure for a nonuniform thin film in the small slope limit is approximated by constructing the tangential planes at the top and bottom interfaces of the thin film.

Thus, as one would expect, when $h \rightarrow D$, the three-phase system reduces to a two-phase system. Interfaces 1-2 and 2-3 disappear and a new interface 1-3 is generated, leading to a system energy per unit area given by Eq. (27).

Both Hocking [14] and Wu and Wong [5] adopted the point of view that the cutoff length was so small that the limit $h \rightarrow 0$ is meaningful, which is equivalent to saying that $D \ll h$ as h approaches zero. The expressions that these investigators obtained are well behaved in this limit provided that the local slope at the contact line is approaching the contact angle. This results from canceling terms that eliminate the singularities that otherwise would have appeared had they not assumed that $D \ll h$ as $h \rightarrow 0$.

IV. DISJOINING PRESSURE FOR GENERAL TWO-DIMENSIONAL NONUNIFORM THIN FILMS

Based on Eq. (25), the disjoining pressure is a function of the local film thickness, the slope and the second order derivative of the film. The film thickness term corresponds to the disjoining pressure between two parallel interfaces while the slope and the second order derivative are introduced to correct for the deviation from the parallel interface configuration. If the film thickness varies linearly with the lateral position, the only correction needed is given by the term that depends on the slope. The second order derivative term accounts for curvature effects. The disjoining pressure in Eq. (25) was obtained in the limit of small film slope h_x and the characteristic length scale for the curvature term is generally chosen as the film width, which is usually much larger than the film thickness.

The formulation of disjoining pressure discussed so far is for a thin film with at least one flat interface. However, the derivation for that special case can be readily extended to the general nonuniform thin film in the small slope limit.

Let us consider a two-dimensional nonuniform thin film, as shown schematically in Fig. 5. Consider two tangential planes at the top (1-2) and bottom (2-3) interfaces. The two tangential planes (see Fig. 5) are arranged in the geometry of the three-phase contact line problem we discussed in the previous section, where the contact angle is $h_{1x}-h_{2x}$. Thus, in the small slope limit, we can approximate the disjoining pressure for the nonuniform thin film with the disjoining pressure for the three-phase contact line problem. Substituting $h=h_1-h_2$, $h_x=h_{1x}-h_{2x}$, and $h_{xx}=h_{1xx}-h_{2xx}$ into Eq. (25), we obtain a new expression for the disjoining pressure for the nonuniform thin film

$$\Pi = -\frac{A_{123}[4-3(h_{1x}-h_{2x})^2+3(h_1-h_2)(h_{1xx}-h_{2xx})]}{24\pi(h_1-h_2)^3}. \tag{28}$$

Based on Eq. (28), the disjoining pressure for a general nonuniform thin film is a function of the local film thickness, the local slope and the second order derivative at both interfaces. The second order derivative term corrects for the deviation of the interface from its tangential plane.

During the coalescence of equal-sized deformable drops in a suspending fluid via a head-on collision [17–19], the thin film has a reflection symmetry [e.g., in Fig. 5, at the interfaces $y-h_1(x)\equiv 0$ and $y-h_2(x)\equiv 0$, with respect to the plane of $y=0$]. By utilizing this symmetry, namely, $h(x)=h_1(x)=-h_2(x)$, the disjoining pressure can be further simplified to obtain

$$\Pi = -\frac{A_{123}(1-3h_x^2+3hh_{xx})}{48\pi h^3}. \tag{29}$$

In this approximation the disjoining pressure of a nonuniform thin film is given by the disjoining pressure between the two tangential planes along the interfaces. This expression goes beyond the usual approximation for the disjoining pressure for a nonuniform thin film which only accounts for the local film thickness (equivalent to the disjoining pressure between two parallel interfaces, effectively a zeroth order approximation). Following the procedure described herein one can develop other approximations involving higher order derivatives in the limiting case of small slopes. For large slopes, one expects significant nonlinear terms where a full numerical evaluation is likely to be necessary.

V. CONCLUDING REMARKS

We have presented a thermodynamics equilibrium condition for a thin liquid film on a solid substrate based on the formulation of Yeh *et al.* [15]. Our condition was obtained by accounting for the excess energy outside the thin film region; we showed that this excess energy affects the boundary condition at the contact lines. By comparing to the augmented Young's equation, an expression for the disjoining pressure is given in Eq. (11) which depends on the variations of the excess energy as a function of the local film thickness and the local film shape.

To obtain the excess energy due to the proximity of interfaces across a thin film, originating from van der Waals forces, we integrated the total intermolecular potential throughout the whole system to obtain the total energy per unit area, and then subtracted the contributions due to the interfacial tension. Applying the combining law for the Hamaker constants based on the Lifshitz theory for van der Waals forces [2–4,31], the nonadditive expression for the van der Waals potential for a macroscopic multiphase system was reduced to a simpler expression leading to a new formula for disjoining pressure in the small slope limit $\Pi=-\frac{A_{123}(4-3h_x^2+3hh_{xx})}{24\pi h^3}$. This expression takes into account the local film slope and the curvature of the thin film. In the limiting case of two parallel interfaces, $h_x=h_{xx}\equiv 0$, the disjoining pressure reduces to $\Pi=-\frac{A_{123}}{6\pi h^3}$, a well known result from the classical Lifshitz theory [2–4,31] for the disjoining pressure.

The disjoining pressure for a thin film on a flat substrate was then extended to a general nonuniform thin film by constructing the tangential planes along both interfaces. The disjoining pressure obtained by this approach is a function of the local film thickness, the slope and the second order derivative of both interfaces of the thin film.

In our analysis we introduced a molecular cutoff length D to account for the steric effects between individual molecules at the interfaces. We have, however, ignored the effects of mixing entropy and molecular kinetic energy, which lead to the "so-called" diffuse interface [7,33,34]. In this spirit, a self-consistent multiscale approach was developed to include molecular-scale effects in mesoscopic formulations of disjoining pressure.

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APPENDIX: THE EXCESS ENERGY PER UNIT SUBSTRATE AREA

The total energy per unit substrate area inside (Λ_1) and outside (Λ_2) the thin film region is obtained by integrating the molecular potential throughout the whole heterogeneous system, along the vertical y direction, as schematically shown in Fig. 3,

$$\Lambda_1 = \int_{-\infty}^{-D}(\Phi_3-\Phi_3^*)dy + \int_{D}^{h-D\sqrt{1+h_x^2}}(\Phi_2-\Phi_2^*)dy + \int_{h+D\sqrt{1+h_x^2}}^{+\infty}(\Phi_1-\Phi_1^*)dy, \tag{A1}$$

$$\Lambda_2 = \int_{-\infty}^{-D}(\Phi_3-\Phi_3^*)dy + \int_{D}^{+\infty}(\Phi_1-\Phi_1^*)dy. \tag{A2}$$

In the limit $D/h\to 0$, where the local film thickness h is much larger than the molecular cutoff length D, Eqs. (A1) and (A2) are calculated by following the integration strategy described in Wu and Wong's paper [5]:

$$\Lambda_1 = \frac{1}{24\pi D^2}(A_{22}+A_{33}-2A_{23}) + \frac{\sqrt{1+h_x^2}}{24\pi D^2}(A_{11}+A_{22}-2A_{12}) + E_1(h,h_x), \tag{A3}$$

$$\Lambda_2 = \frac{1}{24\pi D^2}(A_{11}+A_{33}-2A_{13}) + E_2(x_0-x,\, h_x|_{x=x_0}), \tag{A4}$$

where

$$E_1(h,h_x) = \frac{(A_{23}-A_{13})[2h_x^2+2(3+\sqrt{1+h_x^2})+h_x^2(3+2\sqrt{1+h_x^2})]}{96\pi h^2} + \frac{(A_{12}-A_{11})[2+h_x^2+2h_x^4+2(1-h_x^3)\sqrt{1+h_x^2}]}{96\pi h^2\sqrt{1+h_x^2}} + \frac{(A_{12}-A_{22})[4+4h_x^4+h_x^2(5+3\sqrt{1+h_x^2})]}{96\pi h^2\sqrt{1+h_x^2}} - \frac{A_{22}}{24\pi h^2} \tag{A5}$$

and

$$E_2(|x_0-x|,h_{x|x=-x_0}) = \left[2h_{x|x=-x_0}+[2\sqrt{1+(h_{x|x=-x_0})^2}-3]+\frac{2}{1+\sqrt{1+(h_{x|x=-x_0})^2}}\right]\frac{(A_{11}+A_{23}-A_{12}-A_{13})}{96\pi|x_0-x|^2}. \tag{A6}$$

Here, $E_1(h,h_x)$ corresponds to the excess energy per unit substrate area within the film region ($x>-x_0$ in Fig. 3) and it is a function of the local film thickness h and the local film slope h_x. Similarly, $E_2(|x_0-x|,h_{x|x=-x_0})$ corresponds to the same quantity outside the film region. It is determined by the contact angle $h_{x|x=-x_0}$ and the distance to the contact line $|x_0-x|$. The local film thickness h and the distance to the contact line from outside the thin film region $|x_0-x|$ cannot be exactly equal to zero because the closest approach distance is restricted to the molecular cutoff length D, leading to bounded expressions in Eqs. (A5) and (A6).

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