

The dynamics of liquid films, as described by the diffuse-interface model

Cite as: Phys. Fluids 32, 112103 (2020); doi: 10.1063/5.0027152

Submitted: 27 August 2020 • Accepted: 21 October 2020 •

Published Online: 5 November 2020



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AFFILIATIONS

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ABSTRACT

The dynamics of a thin layer of liquid between a flat solid substrate and an infinitely thick layer of saturated vapor is examined. The liquid and vapor are two phases of the same fluid governed by the diffuse-interface model. The substrate is maintained at a fixed temperature, but in the bulk of the fluid, the temperature is allowed to vary. The slope ε of the liquid/vapor interface is assumed to be small, as is the ratio of its thickness to that of the film. Three asymptotic regimes are identified, depending on the vapor-to-liquid density ratio ρ_v/ρ_l . If $\rho_v/\rho_l \sim 1$ (which implies that the temperature is comparable, but not necessarily close, to the critical value), the evolution of the interface is driven by the vertical flow due to liquid/vapor phase transition, with the horizontal flow being negligible. In the limit $\rho_v/\rho_l \rightarrow 0$, it is the other way around, and there exists an intermediate regime, $\rho_v/\rho_l \sim \varepsilon^{4/3}$, where the two effects are of the same order. Only the $\rho_v/\rho_l \rightarrow 0$ limit is mathematically similar to the case of incompressible (Navier–Stokes) liquids, whereas the asymptotic equations governing the other two regimes are of different types.

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I. INTRODUCTION

The diffuse-interface model (DIM) originates from the idea of van der Waals¹ and Korteweg² that intermolecular attraction in fluids can be modeled by relating it to macroscopic variations of the fluid density. Recently, this approach was incorporated into hydrodynamics: more comprehensive models have been developed for multi-component fluids with variable temperature^{3,4} and simpler ones for single-component isothermal fluids⁵ or single-component isothermal and incompressible fluids^{6–9} [in the last case, the van der Waals force does not depend on the (constant) density, but on a certain “order parameter” satisfying the Cahn–Hilliard equation].

Various versions of the DIM have been used in applications, such as nucleation, growth, and collapse of vapor bubbles,^{10–13} drops impacting on a solid wall,¹⁴ and contact lines in fluids.^{8,15–23}

When studying contact lines, a boundary condition describing the interaction of the fluid and substrate is needed. Two versions of such a condition have been suggested: one involving the near-substrate density¹⁵ and its normal derivative, and another prescribing just the density.⁵ The former is based on minimization of the wall free energy,⁵ whereas the latter can be obtained through an asymptotic expansion of the non-local representation of the van der Waals

force.²⁴ In the present paper, the latter (simpler) boundary condition is used.

The DIM has been also adapted for the case of liquid films, where the liquid phase is confined to a thin layer bounded by a liquid/vapor interface and a solid substrate. Assuming that the flow is isothermal and the saturated-vapor density ρ_v is much smaller than the liquid density ρ_l , Pismen and Pomeau⁵ derived an asymptotic version of the DIM similar to the thin-film approximation of the Navier–Stokes equations for incompressible fluids.

It has been argued, however, that in some, if not most, common fluids, including water, liquid/vapor interfaces are *not* isothermal. Using a non-isothermal version of the DIM, Refs. 24 and 25 estimated the density and pressure change near the interface and showed that the resulting temperature change is order-one. It is unclear, however, whether this conclusion affects liquid films, as a *thin* liquid layer can behave differently from the general case—especially if the substrate is maintained at a fixed temperature acting as a thermostat for the adjacent fluid.

There are two more omissions in the existing literature on liquid films with a diffuse interface. First, no thin-film models exist for the regime with $\rho_v \sim \rho_l$ observed at medium and high temperatures. Second, no-one has examined the implications for films of a recently identified contradiction between the DIM and the

Navier–Stokes equations: as shown in Ref. 26, the former does not admit solutions describing static two-dimensional sessile drops (also called liquid ridges), whereas the latter do. A similar comparison between the thin-film asymptotics of the two models should clarify the nature of the discrepancy, as asymptotic models are much simpler than the exact ones.

The present paper tackles the above omissions. It is shown that if $\rho_v \sim \rho_l$, the heat released (consumed) due to the fluid compression (expansion) near the interface makes non-isothermality important, so the thin-film asymptotics in this case differs from that derived in Ref. 5. In the limit $\rho_v/\rho_l \rightarrow 0$, however, liquid films are essentially isothermal and the thin-film approximation of the DIM coincides with that of the Navier–Stokes equations. This implies that liquid ridges exist in the former model as quasi-static states, i.e., they evolve, but so slowly that the evolution is indistinguishable from, say, evaporation.

The present paper is structured as follows: In Sec. II, the problem is formulated mathematically, and in Sec. III, the simplest case of static interfaces is examined. The regimes $\rho_v \sim \rho_l$ and $\rho_v \ll \rho_l$ are examined in Secs. IV and V, respectively. Since these sections include a lot of cumbersome algebra, a brief summary of the results, plus their extensions to three-dimensional flows, is presented in Sec. VI.

II. FORMULATION

Consider a compressible fluid flow characterized by density $\rho(\mathbf{r}, t)$, velocity $\mathbf{v}(\mathbf{r}, t)$, and temperature $T(\mathbf{r}, t)$, where \mathbf{r} is the position vector and t , the time. Let the pressure p be related to ρ and T by the van der Waals equation of state,

$$p = \frac{RT\rho}{1 - b\rho} - a\rho^2, \quad (1)$$

where R is the specific gas constant, and a and b are fluid-specific constants (b is the reciprocal of the maximum allowable density). Equation (1) was chosen for its simplicity, with all of the results obtained below being readily extendable to general non-ideal fluids.

The diffuse-interface model in application to compressible Newtonian fluid is³

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (2)$$

$$\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] + \nabla p - \nabla \cdot \mathbf{\Pi} = K\rho \nabla^2 \rho, \quad (3)$$

$$\rho c_V \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) + [\mathbf{I}(p + a\rho^2) - \mathbf{\Pi}] : \nabla \mathbf{v} - \nabla \cdot (\kappa \nabla T) = 0, \quad (4)$$

where \mathbf{I} is the identity matrix,

$$\mathbf{\Pi} = \mu_s \left[\nabla \mathbf{v} + (\nabla \mathbf{v})^T - \frac{2}{3} \mathbf{I}(\nabla \cdot \mathbf{v}) \right] + \mu_b \mathbf{I}(\nabla \cdot \mathbf{v}) \quad (5)$$

is the viscous stress tensor, K is the so-called Korteweg parameter, μ_s (μ_b) is the shear (bulk) viscosity, c_V is the specific heat capacity, and κ is the thermal conductivity. Note that, generally, μ_s , μ_b , c_V , and κ depend on ρ and T , whereas K is a constant.

In what follows, two-dimensional flows will be mainly explored, so $\mathbf{r} = [x, z]$ and $\mathbf{v} = [u, w]$, where x and u are the horizontal

components of the corresponding vectors, and z and w are their vertical components. The three-dimensional extensions of the results obtained will be presented without derivation in Sec. VI.

Assume that the fluid is bounded below by a solid substrate located at $z = 0$, so the flow is constrained by

$$\mathbf{v} = \mathbf{0} \quad \text{at} \quad z = 0, \quad (6)$$

$$T = T_0 \quad \text{at} \quad z = 0, \quad (7)$$

$$\rho = \rho_0 \quad \text{at} \quad z = 0. \quad (8)$$

Equation (6) is the no-flow boundary condition, (7) implies that the substrate is maintained at a fixed temperature T_0 , and the near-wall density ρ_0 in (8) is a phenomenological parameter (in the diffuse-interface model,^{5,24} it is assumed to be known). Note that the parameter ρ_0 is specific to the fluid–substrate combination under consideration and is uniquely related to the contact angle.

Given a suitable initial condition, the boundary-value problem (1)–(8) determines the unknowns $\rho(\mathbf{r}, t)$, $\mathbf{v}(\mathbf{r}, t)$, and $T(\mathbf{r}, t)$.

III. STATIC FILMS

Before examining the evolution of liquid films, it is instructive to briefly review the properties of static films.

Letting $\mathbf{v} = \mathbf{0}$ and $\partial \rho / \partial t = 0$, and taking into account that only isothermal films can be static (hence, $T = T_0$), one can reduce Eqs. (1)–(5) to a single equation,

$$RT_0 \left(\ln \frac{b\rho}{1 - b\rho} + \frac{1}{1 - b\rho} \right) - 2a\rho - K\nabla^2 \rho = G, \quad (9)$$

where G is a constant of integration (physically, the free-energy density). Once Eq. (9) is complemented with boundary conditions, one can determine G together with the solution ρ .

The one- and two-dimensional solutions of Eq. (9) will be examined in Secs. III A and III B, respectively.

A. Films with flat interfaces

Let ρ be independent of x , so that $\rho(z)$ describes a flat interface parallel to the substrate. The following nondimensional variables will be used:

$$\rho_{nd} = b\rho, \quad z_{nd} = \frac{z}{z_0}, \quad (10)$$

where

$$z_0 = \sqrt{\frac{K}{a}} \quad (11)$$

is, physically, the characteristic thickness of liquid/vapor interfaces. Estimates of z_0 for specific applications presented in Refs. 11 and 24 show that z_0 is on a nanometer scale; hereinafter, it will be referred to as “microscopic.”

It is convenient to also introduce the nondimensional analogues of the parameters ρ_0 and G ,

$$(\rho_0)_{nd} = b\rho_0, \quad G_{nd} = \frac{b}{a}G. \quad (12)$$

In the nondimensional form, Eq. (9) is (the subscript nd omitted)

$$\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \frac{d^2\rho}{dz^2} = G, \quad (13)$$

where the first two terms on the left-hand side represent the nondimensional free-energy density of the van der Waals fluid, and

$$\tau = \frac{RT_0 b}{a} \quad (14)$$

is the nondimensional temperature. The nondimensional version of the boundary condition (8) will not be presented as it looks exactly as its dimensional counterpart. One should also impose the requirement of zero Korteweg stress at infinity,

$$\frac{d\rho}{dz} \rightarrow 0 \quad \text{as} \quad z \rightarrow \infty. \quad (15)$$

Due to the presence of the undetermined constant G , Eq. (13) and the boundary conditions (8) and (15) do not fully determine the solution. The most convenient way to fix $\rho(z)$ consists of prescribing the height h of the interface through the requirement

$$\rho(h) = \frac{\max\{\rho(z)\} + \min\{\rho(z)\}}{2}. \quad (16)$$

In what follows, the solution of the boundary-value problem (13), (8), (15), and (16) will be denoted by $\rho(z|h)$. Several examples of $\rho(z|h)$ with increasing h are shown in Fig. 1.

In this work, the following properties of $\rho(z|h)$ will be needed:

(1) Since z was [nondimensionalized] on a microscopic scale, macroscopic films correspond to $h \gg 1$, making this limit important for applications—both industrial (e.g., paint or polymer coating) and natural (e.g., rainwater flowing down a [rockface]).

For large h , the interface is located far from the substrate, so the interfacial profile is similar to that in an unbounded fluid. Mathematically, this means

$$\rho(z|h) \rightarrow \bar{\rho}(z-h) \quad \text{as} \quad z, h \rightarrow \infty, \quad (17)$$

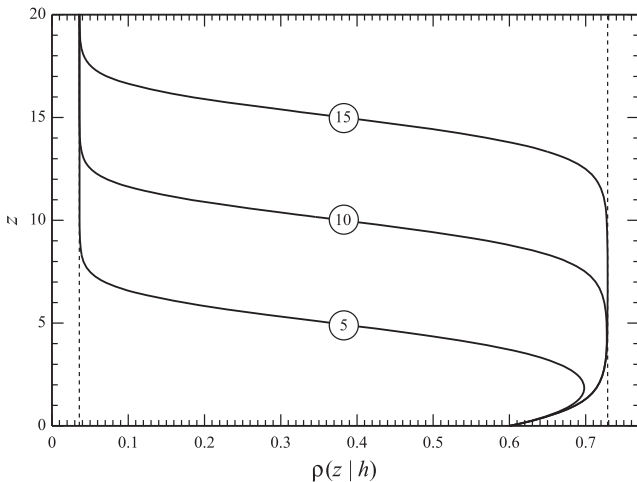


FIG. 1. The function $\rho(z|h)$ [determined by (13), (8), (15), and (16)] for $\tau = 0.2$ and $\rho_0 = 0.6$. The curves are labeled with the corresponding values of h . The dotted lines show ρ_v and ρ_l .

where $\bar{\rho}(z)$ satisfies the same equation as $\rho(z, h)$ and the open-space boundary conditions,

$$\tau \left(\ln \frac{\bar{\rho}}{1-\bar{\rho}} + \frac{1}{1-\bar{\rho}} \right) - 2\bar{\rho} - \frac{d^2\bar{\rho}}{dz^2} = G, \quad (18)$$

$$\bar{\rho}(z) \rightarrow \rho_l \quad \text{as} \quad z \rightarrow -\infty, \quad (19)$$

$$\bar{\rho}(z) \rightarrow \rho_v \quad \text{as} \quad z \rightarrow \infty, \quad (20)$$

$$\bar{\rho}(0) = \frac{\rho_l + \rho_v}{2}. \quad (21)$$

Equations (18)–(21) fix $\bar{\rho}(z)$, as well as ρ_v and ρ_l (which represent the nondimensional densities of saturated vapor and liquid, respectively).

As observed in Ref. 5, the influence of the substrate decays exponentially with the distance, which implies that the asymptotic formula (17) is accurate even for moderate (logarithmically large) h . However, even though $\bar{\rho}(z-h)$ approximates $\rho(z|h)$ well in the interfacial region, $\bar{\rho}(z-h)$ does not generally satisfy the boundary condition at the substrate. The only exception is the case where ρ_0 is close to ρ_l , which implies that near the substrate, $\rho(z|h) \approx \bar{\rho}(z-h) + \mathcal{O}(\varepsilon)$, where $\varepsilon = \rho_l - \rho_0$. Merging this result with (17) (which is exponentially accurate in both $1/h$ and ε), one obtains

$$\rho(z|h) = \bar{\rho}(z-h) + \mathcal{O}(\varepsilon) \quad \text{if} \quad h \gg 1, \quad (22)$$

which applies to all z . Note also that the limit of small ε is important as it corresponds to the approximation of small contact angle (more details are given below).

(2) ρ_l and ρ_v can be computed without calculating $\bar{\rho}(z)$, through the so-called Maxwell construction. In the low-temperature limit $\tau \rightarrow 0$, it yields (see Appendix A)

$$\rho_l = \frac{1 + \sqrt{1-4\tau}}{2} + \mathcal{O}(e^{-1/\tau}), \quad (23)$$

$$\rho_v = \frac{1 + \sqrt{1-4\tau}}{1 - \sqrt{1-4\tau}} e^{-1/\tau} + \mathcal{O}(\tau^{-1} e^{-2/\tau}). \quad (24)$$

Thus, if τ is small, ρ_v is exponentially small.

If τ increases, ρ_v grows and ρ_l decays; eventually, they merge at the critical point $(\rho_v)_{cr} = (\rho_l)_{cr} = 1/3$, $\tau_{cr} = 8/27$. For larger τ , only one phase exists; so, liquid films do not exist.

For $\tau \ll 1$, one can also obtain an exponentially accurate expression for the whole solution $\bar{\rho}(z)$, but it is bulky and implicit. In what follows, an algebraically accurate but explicit expression will be used:

$$\bar{\rho}(z) = \begin{cases} 1 + \mathcal{O}(\tau \ln \tau) & \text{if } z \leq -2^{-3/2}\pi, \\ \frac{1}{2} (1 - \sin 2^{1/2}z) + \mathcal{O}(\tau \ln \tau) & \text{if } z \in [-2^{-3/2}\pi, 2^{-3/2}\pi], \\ 0 + \mathcal{O}(\tau \ln \tau) & \text{if } z \geq 2^{-3/2}\pi. \end{cases} \quad (25)$$

This solution follows from Eq. (18) with $\tau = 0$ and the boundary conditions (19) and (20) with $\rho_l = 1$ and $\rho_v = 0$.

The low-temperature limit is important, as τ is indeed small for many common liquids. For water at 20 °C, for example, estimates of

τ vary from 0.064 to 0.14 (depending on the equation of state used—see Refs. 24 and 25).

(3) In what follows, the function

$$\rho'(h) = \frac{1}{\rho_l - \rho_0} \left[\frac{d\rho(z|h)}{dz} \right]_{z=0} \quad (26)$$

plays an important role. It can be readily computed—see examples shown in Fig. 2. Evidently, $\rho'(h)$ is bounded above, and its precise upper bound is (see Appendix B)

$$\rho'(h) < \frac{\sqrt{2}}{\rho_l - \rho_0} \sqrt{\tau \left[\rho_0 \ln \frac{\rho_0(1 - \rho_v)}{\rho_v(1 - \rho_0)} - \frac{\rho_0 - \rho_v}{1 - \rho_v} \right] - (\rho_0 - \rho_v)^2}. \quad (27)$$

As shown in Fig. 2, $\rho'(h)$ tends to its maximum as $h \rightarrow \infty$. What happens in this limit with $\rho(z|h)$ is illustrated in Fig. 1.

Note that $\rho'(h)$ remains order-one in the limit $\rho_0 \rightarrow \rho_l$. Indeed, letting

$$\rho_0 = \rho_l - \varepsilon \quad (28)$$

and expanding estimate (27) in powers of ε , one can take into account the Maxwell construction (A1) and (A2) and see that the

first two orders of the expansion in ε vanish, so that (27) becomes

$$\rho'(h) < \sqrt{\frac{\tau}{\rho_l(1 - \rho_l)^2} - 2} + \mathcal{O}(\varepsilon). \quad (29)$$

The limit $\varepsilon \ll 1$ is particularly important, as it corresponds to the contact angle being small.⁵

B. Films with slightly curved interfaces

Consider the full (two-dimensional) equation (9) and assume that the interface is curved, but its slope is small. This can only occur if the contact angle is small—which, in turn, implies that ρ_0 is close to, but still smaller than, the liquid density ρ_l .

Given scaling (10) of the vertical coordinate z , the scaling of the horizontal coordinate should be

$$x_{nd} = \frac{\varepsilon x}{z_0}, \quad (30)$$

where $\varepsilon \ll 1$ is related to the physical parameters by (28), but also plays the role of the slope of the interface. Rewriting Eq. (9) in terms of the nondimensional variables (10)–(12) and (30), one obtains (the subscript nd omitted)

$$\tau \left(\ln \frac{\rho}{1 - \rho} + \frac{1}{1 - \rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} = G. \quad (31)$$

In addition to the boundary condition (8) at the wall, a condition is required as $z \rightarrow \infty$. Assuming that the liquid film is bounded above by an infinite layer of saturated vapor, let us require

$$\rho \rightarrow \rho_v \quad \text{as} \quad z \rightarrow \infty. \quad (32)$$

This boundary condition is consistent with Eq. (31) only if

$$G = \tau \left(\ln \frac{\rho_v}{1 - \rho_v} + \frac{1}{1 - \rho_v} \right) - 2\rho_v. \quad (33)$$

The difference between Eq. (31) and its one-dimensional counterpart (13) is $\mathcal{O}(\varepsilon^2)$ —hence, the solution of the former can be sought using that of the latter,

$$\rho(x, z) = \rho(z|h) + \mathcal{O}(\varepsilon^2), \quad (34)$$

where $h = h(x)$ is an undetermined function. Physically, solution (34) describes a liquid film with a slowly changing thickness.

Let $h \gg 1$, in which case, expressions (34) and (22) yield

$$\rho = \bar{\rho}(z - h) + \mathcal{O}(\varepsilon). \quad (35)$$

This approximation will be used everywhere in this paper. It applies to films whose dimensional thickness exceeds the thickness z_0 of the liquid/vapor interface given by (11)—hence, since z_0 is on a nanometer scale, this assumption is not very restrictive.

There are two ways to determine $h(x)$. First, one can expand the solution in ε , with the leading order determined by (35)—then, try to find the next-to-leading-order solution. The latter is likely to exist only subject to $h(x)$ satisfying a certain differential equation.

Second, one can try to rearrange the exact boundary-value problem in such a way that all leading-order terms cancel; then, substitute the leading-order solution (35) in the resulting equation(s). For the static case, the second approach is only marginally simpler—but, for evolving films, it is *much* simpler, and so will be used in both cases.

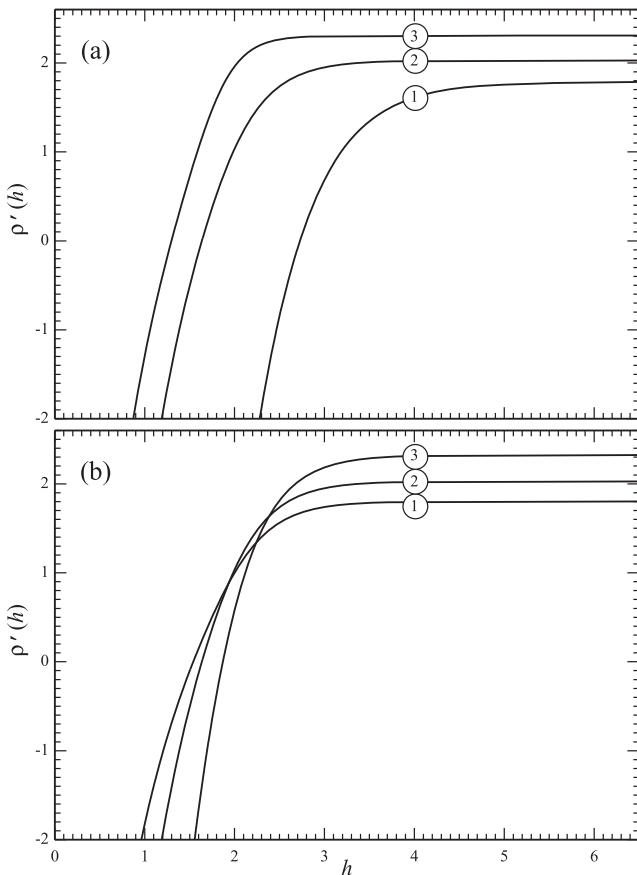


FIG. 2. The function $\rho'(h)$. Panel (a): $\rho_0 = 0.8$, curves 1–3 correspond to $\tau = 0.15, 0.1, 0.05$; Panel (b): $\tau = 0.1$, curves 1–3 correspond to $\rho_0 = 0.75, 0.8, 0.85$.

To eliminate the leading-order terms from Eq. (31), multiply it by $\partial\rho/\partial z$, integrate from $z = 0$ to $z = \infty$, and then take into account the boundary conditions (32), (8) and expression (33) for G . After straightforward algebra, one obtains

$$-\varepsilon^2 \frac{d}{dx} \int_0^\infty \frac{\partial\rho}{\partial x} \frac{\partial\rho}{\partial z} dz = C - \frac{1}{2} \left[\left(\frac{\partial\rho}{\partial z} \right)_{z=0} \right]^2, \quad (36)$$

where

$$C = \tau \left[\rho_0 \left(\ln \frac{\rho_0}{1-\rho_0} - \ln \frac{\rho_v}{1-\rho_v} \right) - \frac{\rho_0 - \rho_v}{1-\rho_v} \right] - (\rho_0 - \rho_v)^2. \quad (37)$$

Next, substitute (28) into (37), expand it in ε , take into account the Maxwell construction (A1) and (A2), and thus obtain

$$C = \varepsilon^2 \left[\frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 \right] + \mathcal{O}(\varepsilon^3). \quad (38)$$

Observe that, even though the exact expression for C involves ρ_v , the approximate one involves ρ_l (which occurs due to the use of the Maxwell construction inter-relating these parameters).

Now, substitute the leading-order solution (35) into Eq. (36) and take into account (38). Omitting small terms, one obtains

$$\frac{d}{dx} \left(\sigma \frac{dh}{dx} \right) = \frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2} \rho'^2(h), \quad (39)$$

where the function $\rho'(h)$ is defined by (26) and (28), and

$$\sigma = \int_0^\infty \left[\frac{\partial\hat{\rho}(z-h)}{\partial z} \right]^2 dz.$$

Since $h \gg 1$, one can extend the above integral to $-\infty$ (without altering significantly its value),

$$\sigma = \int_{-\infty}^\infty \left[\frac{\partial\hat{\rho}(z)}{\partial z} \right]^2 dz. \quad (40)$$

This expression does not depend on h and coincides with the capillary coefficient (see Ref. 5).

Finally, substituting (38) into (39), one obtains

$$2\sigma \frac{d^2h}{dx^2} = \frac{\tau}{\rho_l(1-\rho_l)^2} - 2 - \rho'^2(h). \quad (41)$$

This equation determines the profile $h(x)$ of a liquid film. Bar notation, it coincides with Eq. (42) of Ref. 5, and they both are thin-film reductions of the requirement that a steady distribution of density must have homogeneous chemical potential.

C. Does Eq. (41) admit ridge solutions?

The most surprising feature of Eq. (41) is that it does not admit solutions describing two-dimensional sessile drops (also called liquid ridges). This conclusion is highly counter-intuitive, as the Navier–Stokes equations do admit such solutions. This paradox will be resolved in Sec. V.

To prove the nonexistence of ridge solutions, note that the DIM does not allow the substrate to be completely dry.⁵ Hence, ridge solutions should involve a “precursor film,” i.e.,

$$h \rightarrow h_{pf} \quad \text{as} \quad x \rightarrow \pm\infty, \quad (42)$$

where h_{pf} is the precursor film’s thickness. This boundary condition is consistent with Eq. (41) only if h_{pf} satisfies either

$$\rho'(h_{pf}) = -\sqrt{\frac{\tau}{\rho_l(1-\rho_l)^2} - 2} \quad (43)$$

or

$$\rho'(h_{pf}) = \sqrt{\frac{\tau}{\rho_l(1-\rho_l)^2} - 2}. \quad (44)$$

It can be deduced from the Maxwell construction that

$$\frac{\tau}{\rho_l(1-\rho_l)^2} > 2 \quad \text{if} \quad \tau < \frac{8}{27},$$

hence, Eq. (43) admits a real solution for h_{pf} . Equation (44), on the other hand, does *not* admit real solutions due to inequality (29).

The mere fact that there exists only one value of h such that the right-hand side of Eq. (41) vanishes disallowing the existence of ridge solutions. Indeed, let the ridge’s crest be located at $x = 0$, i.e.,

$$\frac{dh}{dx} = 0, \quad h > h_{pf} \quad \text{at} \quad x = 0,$$

and assume that $h(x)$ monotonically grows in $(-\infty, 0)$ and decays in $(0, \infty)$. This implies existence of two inflection points, where $d^2h/dx^2 = 0$ and $h > h_{pf}$. The former condition can only hold if the right-hand side of Eq. (41) vanishes at the inflection points—which is, however, impossible since it vanishes only if $h = h_{pf}$.

If the ridge profile involves oscillations and, thus, several pairs of inflection points, the same argument applies to the farthest one from the crest (because h at this inflection point certainly differs from h_{pf}). Overall, the conclusion about the nonexistence of *thin* ridges agrees with a similar result proved in Ref. 26 for *arbitrary* ridges. The physical implications of the nonexistence of steady ridge solutions will be discussed in the end of Sec. V C.

Equation (41) still admits solutions such that

$$h \sim \theta x \quad \text{as} \quad x \rightarrow +\infty, \quad (45)$$

where the constant θ can be identified with the contact angle (strictly speaking, the contact angle equals $\arctan \theta$, but under the thin-film approximation $\arctan \theta \approx \theta$). Examples of the solution of the boundary-value problem (41), (42), and (45) have been computed numerically and are shown in Fig. 3. Evidently, with increasing temperature, the precursor film becomes thicker [see Fig. 3(a)], whereas the contact angle becomes smaller [see Fig. 3(b)]. The latter conclusion agrees with the results of Ref. 24 obtained for a realistic equation of state for water.

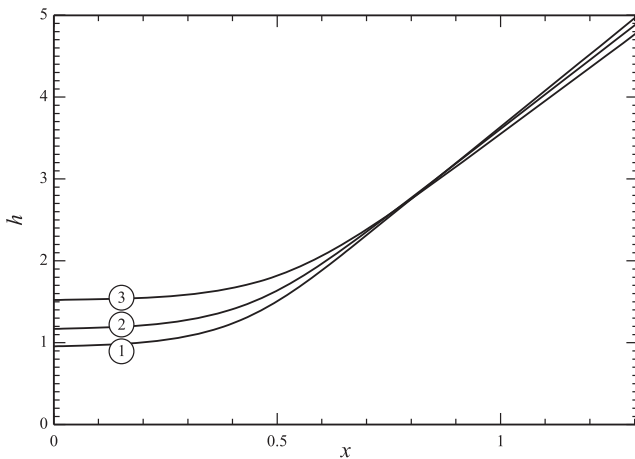


FIG. 3. The solution of the boundary-value problem (41), (42), and (45) for $\rho_0 = 0.85$ and (1) $\tau = 0.05$, (2) $\tau = 0.1$, and (3) $\tau = 0.15$.

IV. EVOLVING INTERFACES: THE REGIME WITH $\rho_v \sim \rho_l$

Dynamics of liquid films depends strongly on the vapor-to-liquid density ratio. The regime $\rho_v/\rho_l = \mathcal{O}(1)$ —which occurs if $\tau = \mathcal{O}(1)$ (i.e., the dimensional temperature T is comparable to the fluid's critical temperature T_{cr})—will be examined first. The reader will see that, in this case, diffuse-interface films behave very differently from their Navier–Stokes counterparts.

The asymptotic limit $T \ll T_{cr}$ will be examined in Sec. V.

A. Nondimensionalization

In addition to the nondimensional versions of coordinates (10), density (12), and parameter ρ_0 (30), introduce

$$t_{nd} = \frac{\varepsilon^2 v_0}{z_0} t, \quad u_{nd} = \frac{u}{\varepsilon^3 v_0}, \quad w_{nd} = \frac{w}{\varepsilon^2 v_0}, \quad (46)$$

$$T_{nd} = \frac{T}{T_0}, \quad p_{nd} = \frac{b^2}{a} p, \quad (47)$$

$$(\mu_s)_{nd} = \frac{\mu_s}{\mu_0}, \quad (\mu_b)_{nd} = \frac{\mu_b}{\mu_0}, \quad \kappa_{nd} = \frac{\kappa}{\kappa_0}, \quad (48)$$

where the shear and bulk viscosities are assumed to be of the same order ($\mu_s \sim \mu_b \sim \mu_0$) and

$$v_0 = \frac{az_0}{\mu_0 b^2} \quad (49)$$

is the general-case velocity scale (which applies when the film's slope ε and thickness h are both order-one). Note that the powers of ε in (46) have been chosen through the trial-and-error approach, so that a consistent asymptotic model would be obtained in the end.

In terms of the nondimensional variables, the boundary-value problem (1)–(8) becomes (the subscript nd omitted)

$$\frac{\partial \rho}{\partial t} + \varepsilon^2 \left[\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho w)}{\partial z} \right] = 0, \quad (50)$$

$$\begin{aligned} & \alpha \varepsilon^4 \left(\frac{\partial u}{\partial t} + \varepsilon^2 \left[u \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} \right] + \frac{1}{\rho} \frac{\partial}{\partial x} \left(\frac{\tau}{1-\rho} T \rho - \rho^2 \right) \right. \\ & \quad \left. - \frac{\partial}{\partial x} \left(\varepsilon^2 \left[\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2} \right] \right) \right) \\ & = \frac{\varepsilon^2}{\rho} \frac{\partial}{\partial x} \left[2 \varepsilon^2 \mu_s \frac{\partial u}{\partial x} + \left(\mu_b - \frac{2}{3} \mu_s \right) \left(\varepsilon^2 \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \right] \\ & \quad + \varepsilon^2 \frac{\partial}{\partial z} \left[\mu_s \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \right], \end{aligned} \quad (51)$$

$$\begin{aligned} & \alpha \varepsilon^4 \left(\frac{\partial w}{\partial t} + \varepsilon^2 \left[u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right] + \frac{1}{\rho} \frac{\partial}{\partial z} \left(\frac{\tau}{1-\rho} T \rho - \rho^2 \right) \right) \\ & \quad - \frac{\partial}{\partial z} \left(\varepsilon^2 \left[\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2} \right] \right) \\ & = \frac{\varepsilon^4}{\rho} \frac{\partial}{\partial x} \left[\mu_s \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right) \right] + \varepsilon^2 \frac{\partial}{\partial z} \\ & \quad \times \left[2 \mu_s \frac{\partial w}{\partial z} + \left(\mu_b - \frac{2}{3} \mu_s \right) \left(\varepsilon^2 \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \right], \end{aligned} \quad (52)$$

$$\begin{aligned} & \alpha \gamma \varepsilon^2 \rho C_V \left(\frac{\partial T}{\partial t} + \varepsilon^2 \left[u \frac{\partial T}{\partial x} + w \frac{\partial T}{\partial z} \right] \right) \\ & \quad + \beta \varepsilon^2 \frac{\tau}{1-\rho} \left(\varepsilon^2 \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \\ & = \beta \varepsilon^4 \left\{ \mu_s \left[2 \varepsilon^4 \left(\frac{\partial u}{\partial x} \right)^2 + \varepsilon^2 \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \right)^2 + 2 \left(\frac{\partial w}{\partial z} \right)^2 \right] \right. \\ & \quad \left. + \left(\mu_b - \frac{2}{3} \mu_s \right) \left(\varepsilon^2 \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right)^2 \right\} \\ & \quad + \varepsilon^2 \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right), \end{aligned} \quad (53)$$

$$u = 0, \quad w = 0 \quad \text{at} \quad z = 0, \quad (54)$$

$$\rho = \rho_0, \quad T = 1 \quad \text{at} \quad z = 0, \quad (55)$$

where τ is given by (14) and

$$\alpha = \frac{K}{\mu_0^2 b^3}, \quad \beta = \frac{aK}{\mu_0 \kappa_0 T_0 b^4}, \quad (56)$$

$$\gamma = \frac{c_V \mu_0}{\kappa_0}, \quad C_V = \frac{c_V}{R}. \quad (57)$$

Physically, α is the Reynolds number, γ is the Prandtl number, C_V is the nondimensional heat capacity, and β characterizes heat

release due to viscosity and fluid compression or cooling due to fluid expansion.

The parameter β was first introduced in Refs. 24 and 25 for the case where the flow’s aspect ratio was order-one. It was concluded that β is an “isothermality indicator”: if $\beta \sim 1$, the effect of variable temperature is strong. The same is true for liquid films—despite the fact that Eq. (53) and the boundary condition (55) suggest that the temperature is almost uniform—i.e.,

$$T = 1 + \varepsilon^2 \tilde{T}(x, z, t). \tag{58}$$

Yet, as shown below, the small variation \tilde{T} affects the leading-order film dynamics.

There is still a slight difference between liquid films and the general case: in the latter, the heat production/consumption due to compressibility is comparable to the heat production due to viscosity. In the liquid-film equation (53), on the other hand, the compressibility term exceeds the viscosity term by an order of magnitude ($\varepsilon^2\beta$ to $\varepsilon^4\beta$, respectively).

In what follows, β is assumed to be order-one—which it indeed is for many common fluids (including water) at room temperature.²⁵ As for α and γ , they appear in the governing equations only in a product with a power of ε —so their values are unimportant as long as they are not large (and, for common fluids, they are not²⁵). Finally, the nondimensional heat capacity C_V will be assumed to be order-one.

Another important feature of the proposed scaling is that the divergence terms in the density Eq. (50) are *not* of the same order (as they would be for Navier–Stokes films). This is due to the fact that, under the regime considered, the interface is not driven by horizontal advection—but rather by evaporation and condensation, making it move vertically.

B. The asymptotic equation

Assume that the flow far above the substrate is not forced, so the viscous stress is zero,

$$\frac{\partial u}{\partial z} \rightarrow 0, \quad \frac{\partial w}{\partial z} \rightarrow 0 \quad \text{as} \quad z \rightarrow \infty, \tag{59}$$

and, as before, let

$$\rho \rightarrow \rho_v \quad \text{as} \quad z \rightarrow \infty. \tag{60}$$

In the study of static films in Sec. III B, an “asymptotic shortcut” has been used, and a similar one will be used for evolving films.

To derive it, multiply Eq. (52) by $(\rho - \rho_0)$ and integrate it from $z = 0$ to $z = \infty$. Integrating the viscous term for w by parts and taking into account ansatz (58) and the boundary conditions (54), (55), (59), and (60), one obtains

$$\begin{aligned} \varepsilon^{-2} \left\{ C - \frac{1}{2} \left[\left(\frac{\partial \rho}{\partial z} \right)_{z=0} \right]^2 \right\} + \frac{\partial}{\partial x} \int_0^\infty \frac{\partial \rho}{\partial z} \frac{\partial \rho}{\partial x} dz \\ + \tau \int_0^\infty \frac{\rho - \rho_0}{\rho} \frac{\partial}{\partial z} \left(\frac{\tilde{T} \rho}{1 - \rho} \right) dz + \int_0^\infty \frac{\rho_0}{\rho^2} \frac{\partial \rho}{\partial z} \mu \frac{\partial w}{\partial z} dz = \mathcal{O}(\varepsilon^2), \end{aligned} \tag{61}$$

where C is given by (37) and

$$\mu = \mu_b + \frac{4}{3} \mu_s.$$

Next, observe that, to leading order, the dynamics equations (51) and (52) coincide with their static counterparts. As a result, the density field of an evolving film is quasi-static and described by the static-film expressions (34) and (17). The only difference is that, the *evolving*-film thickness h should depend on t as well as x , so

$$\rho = \bar{\rho}(z - h(x, t)) + \mathcal{O}(\varepsilon). \tag{62}$$

To obtain a closed-form equation for $h(x, t)$, it remains to express \tilde{T} and w through ρ and insert them into Eq. (61).

To find w , substitute (62) into Eq. (53) and, taking into account the boundary condition (54), obtain

$$w = \frac{\partial h}{\partial t} \frac{\bar{\rho}(z - h) - \rho_0}{\bar{\rho}(z - h)} + \mathcal{O}(\varepsilon). \tag{63}$$

Substitution of this expression and (62) into Eq. (53) yields

$$\beta \tau \frac{\partial h}{\partial t} \frac{\rho_0 \bar{\rho}(z - h)}{1 - \bar{\rho}(z - h)} \frac{\partial \bar{\rho}(z - h)}{\partial z} = \frac{\partial}{\partial z} \left[\kappa(\bar{\rho}(z - h), 1) \frac{\partial \tilde{T}}{\partial z} \right] + \mathcal{O}(\varepsilon), \tag{64}$$

where it has been taken into account that the dependence of the thermal conductivity on the temperature is weak due to the near-isothermality condition (58).

One should assume that heat is neither coming from, nor going to, infinity,

$$\frac{\partial \tilde{T}}{\partial z} \rightarrow 0 \quad \text{as} \quad z \rightarrow \infty,$$

and also substitute (58) into (55) which yields

$$\tilde{T} = 0 \quad \text{at} \quad z = 0.$$

Solving Eq. (64) with these boundary conditions, one obtains

$$\begin{aligned} \tilde{T} = \beta \tau \frac{\partial h}{\partial t} \int_0^z \frac{\rho_0}{\kappa(\bar{\rho}(z_1 - h), 1)} \\ \times \left[\ln \frac{\bar{\rho}(z_1 - h)}{1 - \bar{\rho}(z_1 - h)} - \ln \frac{\rho_v}{1 - \rho_v} \right] dz_1 + \mathcal{O}(\varepsilon). \end{aligned} \tag{65}$$

Substituting expressions (63) and (65) into Eq. (61) and keeping the leading-order terms only (which implies replacing ρ_0 with ρ_l), one obtains, after cumbersome but straightforward algebra,

$$\begin{aligned} \frac{\tau}{2\rho_l(1 - \rho_l)^2} - 1 - \frac{1}{2}\rho_l^2 - \frac{\partial^2 h}{\partial x^2} \int_0^\infty \left[\frac{\partial \bar{\rho}(z - h)}{\partial z} \right]^2 dz \\ + \frac{\partial h}{\partial t} \int_0^\infty \frac{\rho_l^2 \mu (\bar{\rho}(z - h), 1)}{\bar{\rho}^4(z - h)} \left[\frac{\partial \bar{\rho}(z - h)}{\partial z} \right]^2 dz \\ + \beta \tau^2 \frac{\partial h}{\partial t} \int_0^\infty \frac{\rho_l}{\kappa(\bar{\rho}(z - h), 1)} \left[\ln \frac{\bar{\rho}(z - h)}{1 - \bar{\rho}(z - h)} - \ln \frac{\rho_v}{1 - \rho_v} \right] \\ \times \left\{ \rho_l \left[\ln \frac{\bar{\rho}(z - h)}{1 - \bar{\rho}(z - h)} - \ln \frac{\rho_v}{1 - \rho_v} \right] - \frac{\rho_l - \rho_v}{1 - \rho_v} \right\} dz = 0, \end{aligned} \tag{66}$$

where $\rho'(h)$ is the same function as its static-film counterpart defined by (26).

The integrals in this equality can be simplified using the assumption that h exceeds the interfacial thickness. In the first two

integrals, one can simply move the lower limit to $-\infty$ and then replace $z - h$ with z [the first integral after that becomes equal to the surface tension σ given by (40)].

If, however, the same procedure is applied to the third integral in Eq. (66), it will diverge. To avoid the divergence and still take advantage of h being large, one should first use integration by parts (so that the integrand is replaced by its derivative multiplied by z) and only after that move the lower limit to $-\infty$. Eventually, one can transform Eq. (66) into

$$\frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2}\rho^{r^2}(h) - \sigma \frac{\partial^2 h}{\partial x^2} + [A_1 + \beta(A_2 + Bh)] \frac{\partial h}{\partial t} = 0, \tag{67}$$

where

$$A_1(\tau) = \int_{-\infty}^{\infty} \frac{\rho_l^2 \mu(\bar{\rho}(z), 1)}{\bar{\rho}^4(z)} \left[\frac{d\bar{\rho}(z)}{dz} \right]^2 dz, \tag{68}$$

$$A_2(\tau) = -\tau^2 \int_{-\infty}^{\infty} z \frac{d}{dz} \left(\frac{\rho_l^2}{\kappa(\bar{\rho}(z), 1)} \left\{ \frac{\bar{\rho}(z)(1-\rho_v)}{\rho_v[1-\bar{\rho}(z)]} - \frac{\rho_l - \rho_v}{\rho_l(1-\rho_v)} \right\} \times \ln \frac{\bar{\rho}(z)(1-\rho_v)}{\rho_v[1-\bar{\rho}(z)]} \right) dz, \tag{69}$$

$$B(\tau) = \frac{\tau^2 \rho_l^2}{\kappa(\rho_l, 1)} \left[\ln \frac{\rho_l(1-\rho_v)}{\rho_v(1-\rho_l)} - \frac{\rho_l - \rho_v}{\rho_l(1-\rho_v)} \right] \ln \frac{\rho_l(1-\rho_v)}{\rho_v(1-\rho_l)}. \tag{70}$$

Equation (67) is the desired asymptotic equation governing $h(x, t)$; physically, it describes diffusion of chemical potential on its way toward homogeneity.

C. Discussion

- (1) Let us identify the physical meaning of the time-derivative term of Eq. (67) [the rest of the terms are the same as in the steady state equation (41)].

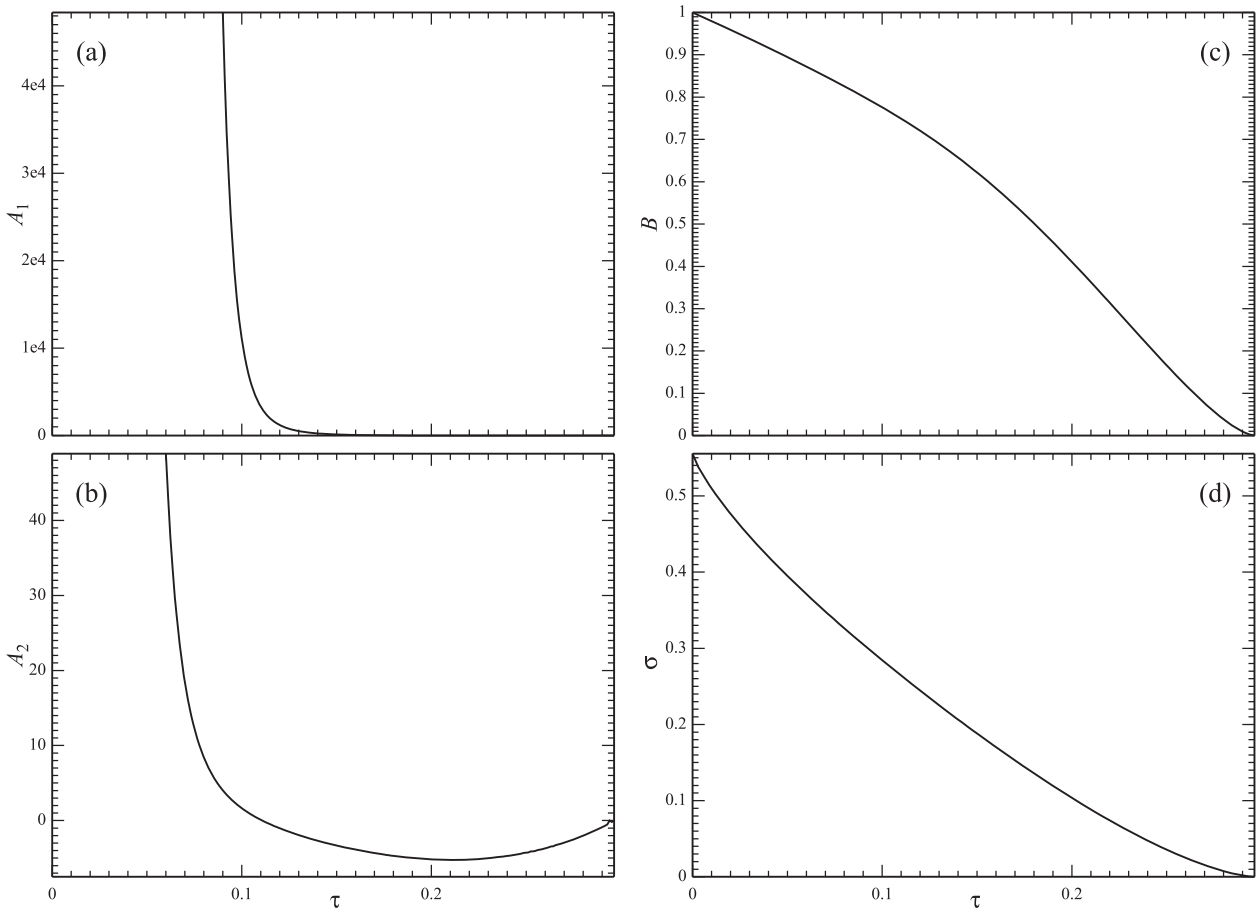


FIG. 4. The coefficients of Eq. (67) [with μ and κ given by (71)] vs the nondimensional temperature τ . (a) A_1 given by (68), (b) A_2 given by (69), (c) B given by (70), and (d) σ (the surface tension) given by (39).

The term involving A_1 describes the interface’s vertical motion driven by evaporation and condensation, and the two terms multiplied by β describe heating/cooling of the fluid caused by its expansion/compression. Neither of these effects is present in the Navier–Stokes films.

- (2) Mathematically, Eq. (67) is also very different from the equation describing Navier–Stokes films. Even if the latter accounts for variable temperature [as Eq. (1) of Ref. 27], it does not involve anything like the above-mentioned factor in front of $\partial h/\partial t$; besides, it is of the fourth order in x , whereas Eq. (67) is of the second order. The dynamics described by the two models should be completely different (this work is in progress).
- (3) It is instructive to compute the coefficients of Eq. (67). To do so, one has to specify the effective viscosity μ and thermal conductivity κ —for example, assume that they are proportional to the fluid density. The proportionality coefficients should generally depend on the temperature, but due to the near-[isothermality] ansatz (58), the temperature is close to being constant, hence can be eliminated by a proper choice of the [nondimensionalization] scales μ_0 and κ_0 . Thus, one can simply let

$$\mu(\rho, 1) = \rho, \quad \kappa(\rho, 1) = \rho. \quad (71)$$

The coefficients A_1 , A_2 , B , and σ —given by (68)–(70) and (40), respectively—have been computed and are plotted in Fig. 4. Observe that, as $\tau \rightarrow 0$, the coefficient A_1 grows, as does A_2 (although much slower than A_1)—whereas B and σ remain finite. The limits of the latter two can be calculated using the small- τ asymptotics (23)–(25), which yield

$$B \rightarrow 1, \quad \sigma \rightarrow 2^{-5/2}\pi \quad \text{as} \quad \tau \rightarrow 0. \quad (72)$$

The reason why A_1 and A_2 are singular as $\tau \rightarrow 0$ can be readily seen from expressions (68) and (69), which both involve division by $\bar{\rho}(z)$ —whose minimum value, ρ_v , tends to zero as $\tau \rightarrow 0$. In fact, one can derive asymptotically (see Appendix C) that

$$A_1 \approx 0.36994 \tau^{1/2} \rho_v^{-3/2} \quad \text{if} \quad \tau \ll 1, \quad (73)$$

$$A_2 \approx 0.75918 \tau^{3/2} \rho_v^{-1/2} \quad \text{if} \quad \tau \ll 1. \quad (74)$$

The singular behavior of A_1 and A_2 indicates that Eq. (67) fails when the temperature is low enough to make ρ_v small; in terms of the dimensional variables, Eq. (67) fails when the vapor-to-liquid density ratio is small. What happens in this case is examined in Sec. V.

V. REGIME(S) WITH $\rho_v \ll \rho_l$

It turns out that the asymptotic regime corresponding to the limit

$$\rho_v \rightarrow 0, \quad \varepsilon = \text{const} \quad (75)$$

does not “overlap” with the limit

$$\rho_v = \text{const}, \quad \varepsilon \rightarrow 0$$

examined previously. This suggests that there exists an intermediate regime, where ρ_v is small, but is still comparable to, say, a certain power of ε .

It is worth noting that, in all three regimes, the leading-order solution is represented by $\bar{\rho}(z - h)$ where $\bar{\rho}(z)$ describes a liquid/vapor interface in an unbounded space. The difference in the value of τ , however, makes $\bar{\rho}(z)$ specific to the corresponding regime—which, in turn, affects higher orders.

In what follows, limit (75) will be examined in Secs. V A–V C, whereas the intermediate regime will be examined in Secs. V D and V E.

A. Regime (75): The nondimensionalization

As seen earlier, smallness of τ implies exponential smallness of ρ_v ; thus, when they appear in the same expression, the former should be, by comparison, treated as an order-one quantity. Another important point is that the smallness of ρ_v does not affect the scaling of $\rho(x, z, t)$ whose maximum value remains to be order-one. In fact, only the velocity and time need to be rescaled—by switching to the same scaling as that for the Navier–Stokes films.

Summarizing the above, one should revise the finite- ρ_v scaling by replacing (46) with

$$t_{nd} = \frac{\varepsilon^4 v_0}{z_0} t, \quad u_{nd} = \frac{u}{\varepsilon^3 v_0}, \quad w_{nd} = \frac{w}{\varepsilon^4 v_0}. \quad (76)$$

The resulting nondimensional equations are

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho w)}{\partial z} = 0, \quad (77)$$

$$\begin{aligned} & \alpha \varepsilon^6 \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + w \frac{\partial u}{\partial z} \right) + \frac{1}{\rho} \frac{\partial}{\partial x} \left(\frac{\tau T \rho}{1 - \rho} - \rho^2 \right) \\ & - \frac{\partial}{\partial x} \left(\varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2} \right) \\ & = \frac{\varepsilon^4}{\rho} \frac{\partial}{\partial x} \left[2\mu_s \frac{\partial u}{\partial x} + \left(\mu_b - \frac{2}{3}\mu_s \right) \left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \right] \\ & + \frac{\varepsilon^2}{\rho} \frac{\partial}{\partial z} \left[\mu_s \left(\frac{\partial u}{\partial z} + \varepsilon^2 \frac{\partial w}{\partial x} \right) \right], \quad (78) \end{aligned}$$

$$\begin{aligned} & \alpha \varepsilon^8 \left(\frac{\partial w}{\partial t} + u \frac{\partial w}{\partial x} + w \frac{\partial w}{\partial z} \right) + \frac{1}{\rho} \frac{\partial}{\partial z} \left(\frac{\tau T \rho}{1 - \rho} - \rho^2 \right) \\ & - \frac{\partial}{\partial z} \left(\varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2} \right) \\ & = \frac{\varepsilon^4}{\rho} \left\{ \frac{\partial}{\partial x} \left[\mu_s \left(\frac{\partial u}{\partial z} + \varepsilon^2 \frac{\partial w}{\partial x} \right) \right] \right. \\ & \left. + \frac{\partial}{\partial z} \left[2\mu_s \frac{\partial w}{\partial z} + \left(\mu_b - \frac{2}{3}\mu_s \right) \left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \right] \right\}, \quad (79) \end{aligned}$$

$$\begin{aligned}
 & \alpha\gamma\varepsilon^4 \rho C_V \left(\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + w \frac{\partial T}{\partial z} \right) + \beta\varepsilon^4 \frac{\tau T \rho}{1-\rho} \left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right) \\
 &= \beta\varepsilon^6 \left\{ \mu_s \left[2\varepsilon^2 \left(\frac{\partial u}{\partial x} \right)^2 + \left(\frac{\partial u}{\partial z} + \varepsilon^2 \frac{\partial w}{\partial x} \right)^2 \right. \right. \\
 & \quad \left. \left. + 2\varepsilon^2 \left(\frac{\partial w}{\partial z} \right)^2 \right] + \varepsilon^2 \left(\mu_b - \frac{2}{3}\mu_s \right) \left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right)^2 \right\} \\
 & \quad + \varepsilon^2 \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial z} \left(\kappa \frac{\partial T}{\partial z} \right), \quad (80)
 \end{aligned}$$

where the parameters τ , α , β , γ , and C_V are determined by (14), (56), and (57). The boundary conditions look the same as those for the finite- ρ_v regime—see (54), (55), (59), and (60).

B. Regime (75): The asymptotic equation

Equation (80) suggests that

$$T = 1 + \varepsilon^4 \tilde{T}(x, z, t). \quad (81)$$

Comparison of ansatz (81) and its the finite- ρ_v analogue (58) shows that the temperature variations are now weaker than those in the finite- ρ_v regime.

Substituting (81) into Eqs. (78) and (79), one can rewrite them in the form

$$\begin{aligned}
 & \frac{\partial}{\partial x} \left[\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} \right] \\
 &= \frac{\varepsilon^2}{\rho} \frac{\partial}{\partial z} \left[\mu_s(\rho, 1) \frac{\partial u}{\partial z} \right] + \mathcal{O}(\varepsilon^4), \quad (82)
 \end{aligned}$$

$$\frac{\partial}{\partial z} \left[\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} \right] = \mathcal{O}(\varepsilon^4), \quad (83)$$

Observe that \tilde{T} does not appear in the leading and next-to-leading orders of these equation, with the implication that the non-isothermality effect is now too weak to affect interfacial dynamics.

It follows from Eq. (83) that, to leading order, the expression in the square brackets is a function of x and t (but not z), with Eq. (82) suggesting that this function is $\mathcal{O}(\varepsilon^2)$. Thus, denoting it by $\varepsilon^2 F(x, t)$, one can rewrite Eqs. (82) and (83) in the form

$$\varepsilon^2 \frac{\partial F(x, t)}{\partial x} = \frac{\varepsilon^2}{\rho} \frac{\partial}{\partial z} \left[\mu_s(\rho, 1) \frac{\partial u}{\partial z} \right] + \mathcal{O}(\varepsilon^4), \quad (84)$$

$$\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} = \varepsilon^2 F(x, t) + \mathcal{O}(\varepsilon^4). \quad (85)$$

Assuming as before that $h \gg 1$, one can replace ρ with $\bar{\rho}(z-h)$ and then use Eq. (85) to relate F to h . To do so, multiply (85) by $\partial \rho / \partial z$, integrate with respect to z from 0 to ∞ , and use the boundary conditions, which yields

$$F(x, t) = \frac{1}{\rho_0 - \rho_v} \left[\sigma \frac{\partial^2 h}{\partial x^2} + \frac{1}{2} \rho_0''(h) \right] + \text{const} + \mathcal{O}(\varepsilon^2), \quad (86)$$

where the surface tension σ is given by (40) and the specific expression for const will not be needed.

Under the same assumption $h \gg 1$, one can let $\rho = \bar{\rho}(z-h) + \mathcal{O}(\varepsilon)$ and $\bar{\rho}(-h) = \rho_l + \mathcal{O}(\varepsilon)$. Keeping in mind these equalities, one can use Eqs. (77) and (85), and the boundary conditions, to deduce

$$u = -\frac{\partial F}{\partial x} \int_0^z \frac{1}{\mu_s(\bar{\rho}(z_2-h), 1)} \int_{z_2}^{\infty} [\bar{\rho}(z_1-h) - \rho_v] dz_1 dz_2 + \mathcal{O}(\varepsilon), \quad (87)$$

$$\begin{aligned}
 w &= \frac{1}{\bar{\rho}(z-h)} \left\{ [\rho_l - \bar{\rho}(z-h)] \frac{\partial h}{\partial t} \right. \\
 & \quad \left. + \frac{\partial}{\partial x} \int_0^z \bar{\rho}(z_1-h) u(x, z_1, t) dz_1 \right\} + \mathcal{O}(\varepsilon). \quad (88)
 \end{aligned}$$

Substituting the former expression into the latter and introducing an auxiliary function

$$\bar{q}(z) = \int_z^{\infty} [\bar{\rho}(z_1) - \rho_v] dz_1, \quad (89)$$

one can obtain (after straightforward algebra)

$$\begin{aligned}
 w &= -\frac{1}{\bar{\rho}(z-h)} \left\{ [\bar{\rho}(z-h) - \rho_l] \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \right. \\
 & \quad \left. \times \left[\frac{\partial F}{\partial x} \int_0^z \frac{\bar{q}(z-h) - \bar{q}(z_1-h)}{\mu_s(\bar{\rho}(z_1-h), 1)} \bar{q}(z_1-h) dz_1 \right] \right\} + \mathcal{O}(\varepsilon). \quad (90)
 \end{aligned}$$

One can now take advantage of the assumption $\tau \ll 1$ and, thus, replace $\bar{\rho}$ with asymptotic (25). Among other things, it implies that $\bar{\rho}(z-h) \rightarrow 0$ as $z \rightarrow h + 2^{-3/2}\pi$ —which gives rise to a singularity in expression (90). To avoid the singularity, one has to assume

$$\rho_l \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[\frac{\partial F}{\partial x} \int_0^{h+2^{-3/2}\pi} \frac{\bar{q}^2(z_1-h)}{\mu_s(\bar{\rho}(z_1-h), 1)} dz_1 \right] = 0. \quad (91)$$

To simplify this equation, observe that expressions (23) and (28) imply

$$\rho_l = 1 + \mathcal{O}(\tau), \quad \rho_0 = 1 + \mathcal{O}(\tau, \varepsilon).$$

Now, replacing in Eq. (91) F and q with expressions (86) and (89), respectively, and keeping the leading-order terms only, one obtains

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[Q(h) \frac{\partial}{\partial x} \left(\sigma \frac{\partial^2 h}{\partial x^2} + \frac{1}{2} \rho'' \right) \right] = 0, \quad (92)$$

where

$$Q(h) = \int_{-h}^{2^{-3/2}\pi} \left[\int_z^{2^{-3/2}\pi} \bar{\rho}(z_1) dz_1 \right]^2 \frac{dz}{\mu_s(\bar{\rho}(z), 1)}, \quad (93)$$

and $\bar{\rho}(z)$ is given by (25). Equation (92) is the desired asymptotic equation for $h(x, t)$.

It is instructive to calculate the function $Q(h)$ for a particular case—say

$$\mu_s(\rho, 1) = q\rho,$$

where q is a constant. Then, expression (93) yields

$$\begin{aligned}
 Q(h) &= q^{-1} \left[\frac{1}{3} h^3 + 2^{-1/2} \pi (1 - \ln 2) - 2^{-9/2} 3^{-1} \pi^3 \right] \\
 &\approx q^{-1} \left(\frac{1}{3} h^3 + 0.22489 \right). \quad (94)
 \end{aligned}$$

Even though this expression was derived under the assumption that h is large, h may be *logarithmically* large; hence, the retainment of the constant in the above expression is justified. For the same reason, one may want to keep in Eq. (92) σ instead of replacing it with its small- τ limit (72).

C. Regime (75): Existence of liquid ridges

Steady-state solutions of Eq. (92) satisfy

$$\sigma \frac{d^2 h}{dx^2} + \frac{1}{2} \rho'^2 = D, \tag{95}$$

where $h = h(x)$ and $D > 0$ is a constant of integration. The mere fact that Eq. (95) involves an arbitrary constant [unlike its finite- ρ_v counterpart (41)] allows the ridge solution to exist. It can be readily shown that, if

$$0 < (2D)^{1/2} < \max\{\rho'(h)\},$$

(95) admits a symmetric solution such that

$$h \rightarrow h_{pf} \quad \text{as} \quad x \rightarrow \pm\infty,$$

where h_{pf} is the smaller root of the equation

$$\rho'^2(h_{pf}) = 2D.$$

In addition to h_{pf} , this equation has another (larger) root—say, h_i . Recalling Fig. 2 [which shows what the graph of the function $\rho'(h)$ looks like], one can see $\rho'(h_{pf}) < 0$, whereas $\rho'(h_i) > 0$. Obviously, h_i corresponds to the inflection point of $h(x)$.

The ridge solution can be found in an implicit form by reducing (95) to a first-order separable equation.

Thus, the asymptotic model for the case $\rho_v/\rho_l \ll 1$ admits steady solutions, whereas the $\rho_v/\rho_l \sim 1$ model (examined in Sec. III C) does not. This suggests that, in the exact equations, the ridges exist as *quasi*-steady solutions: generally, they evolve (so are *not* steady)—but if $\rho_v/\rho_l \ll 1$, their evolution is slow and indistinguishable from, say, evaporation. Given that, for a drop of water on one’s kitchen table, ρ_v/ρ_l is indeed small, this argument should help to reconcile the unexpected mathematical results obtained in this study and Ref. 26 with one’s everyday intuition.

D. The intermediate regime: The asymptotic equation

Note that the small- ρ_v Eq. (92) cannot be obtained from its finite- ρ_v counterpart (67) by letting $\rho_v \rightarrow 0$. This suggests that there may exist an intermediate regime.

Finding this regime is not straightforward, however. First, there are three small parameters in the problem: ε , ρ_v , and $1/h$, making a formal expansion cumbersome even if τ [related to ρ_v through equality (24)] is treated as an order-one parameter. Second, the regions where $\rho \sim 1$ and $\rho \ll 1$ are to be examined differently, implying a convoluted matching procedure.

To find a reasonably simple approach to exploring the intermediate regime, recall that the finite- and small- ρ_v limits differ by the scaling of the vertical velocity w [compare (46) and (76)]. Thus, the intermediate regime can be found by considering the small- ρ_v Eqs. (77)–(80), but retaining the terms involving w even if they appear to be of a higher-order in ε .

Accordingly, rewrite Eqs. (78) and (79) in the form

$$\begin{aligned} \frac{\partial}{\partial x} \left[\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} \right] \\ = \frac{\varepsilon^4}{\rho} \frac{\partial}{\partial x} \left[\left(\mu_b - \frac{2}{3} \mu_s \right) \frac{\partial w}{\partial z} \right] \\ + \frac{\varepsilon^2}{\rho} \frac{\partial}{\partial z} \left[\mu_s(\rho, 1) \left(\frac{\partial u}{\partial z} + \varepsilon^2 \frac{\partial w}{\partial x} \right) \right] + \mathcal{O}(\varepsilon^4, \varepsilon^6 w), \end{aligned} \tag{96}$$

$$\begin{aligned} \frac{\partial}{\partial z} \left[\tau \left(\ln \frac{\rho}{1-\rho} + \frac{1}{1-\rho} \right) - 2\rho - \varepsilon^2 \frac{\partial^2 \rho}{\partial x^2} - \frac{\partial^2 \rho}{\partial z^2} \right] \\ = \frac{\varepsilon^4}{\rho} \frac{\partial}{\partial z} \left[\mu(\rho, 1) \frac{\partial w}{\partial z} \right] + \mathcal{O}(\varepsilon^4, \varepsilon^6 w), \end{aligned} \tag{97}$$

where, as before, $\mu = \mu_b + 4\mu_s/3$. Equation (97) can be used to derive the “asymptotic shortcut”: multiplying (97) by $(\rho - \rho_0)$ and carrying out straightforward algebra [similar to that in Secs. III B and IV B], one obtains

$$\begin{aligned} \frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2} \rho'^2 - \sigma \frac{\partial^2 h}{\partial x^2} + \varepsilon^2 \int_0^\infty \frac{\rho_l}{\bar{\rho}^2(z-h)} \\ \times \frac{\partial \bar{\rho}(z-h)}{\partial z} \mu(\bar{\rho}(z-h), 1) \frac{\partial w}{\partial z} dz = \mathcal{O}(\varepsilon^2, \varepsilon^4 w). \end{aligned} \tag{98}$$

To reduce Eq. (98) to a closed-form equation for h , one should first use Eq. (77) to relate w to $\bar{\rho}(z-h)$ and u , and then use Eq. (96) to relate u to $\bar{\rho}(z-h)$. Unfortunately, the latter equation—unlike its small- ρ_v counterpart (82)—includes w , making it impossible to eliminate it after all.

Luckily, the contribution of w to Eq. (96) turns out to be negligible.

To understand why, recall that expression (88) for w applies to both previously considered limits; hence, it applies to the intermediate regime also. Using it and the leading-order solution (25) for $\bar{\rho}$, one obtains

$$w = \mathcal{O}(\rho_v^{-1}) \quad \text{at} \quad z \approx h + 2^{-3/2} \pi,$$

$$w = \mathcal{O}(1) \quad \text{at} \quad z \not\approx h + 2^{-3/2} \pi.$$

Thus, w has a peak near $z = h + 2^{-3/2} \pi$, and it can be further estimated (see Appendix D) that the characteristic width of this peak is $\tau^{-1/2} \rho_v^{1/2}$.

Next, the expression in the square brackets in Eq. (96) can be denoted (as before) by $\varepsilon^2 F(x, t)$. Considering the resulting equation as a means of finding u , one can see that it involves two components:

1. a contribution of the term involving F (this component is of order-one and is spread between $z = 0$ and $z \approx h + 2^{-3/2} \pi$) and
2. a contribution of the term involving w (of amplitude $\varepsilon^2 \rho_v^{-1}$ and width $\tau^{-1/2} \rho_v^{1/2}$ localized near the point $z = h + 2^{-3/2} \pi$).

Once u is substituted into Eq. (88), both components are multiplied by $\bar{\rho}(z-h)$ and integrated; thus, component 1 contributes $\mathcal{O}(1)$, whereas component 2 contributes $\mathcal{O}(\varepsilon^2 \rho_v^{1/2} \tau^{-1/2})$. The latter is smaller—which effectively means that the w -involving terms in Eq. (96) can be omitted—which effectively means that, in the

intermediate regime, w can still be approximated by the small- ρ_v expression (90).

Substituting (90) into Eq. (98), one obtains

$$\frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2}\rho'^2 - \sigma \frac{\partial^2 h}{\partial x^2} + \varepsilon^2 A_1 \times \left\{ \frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left[Q(h) \frac{\partial}{\partial x} \left(\sigma \frac{\partial^2 h}{\partial x^2} + \frac{1}{2}\rho'^2 \right) \right] \right\} = 0, \quad (99)$$

where A_1 is given by expression (68) and $Q(h)$ by (93).

Equation (99) is the asymptotic equation governing the intermediate regime.

E. The intermediate regime: Discussion

- (1) In principle, ρ_l , σ , and A_1 in Eq. (99) can be replaced with their small- τ estimates (23), (72), and (73), respectively. Using the last of the three estimates and, for simplicity, treating τ as an order-one parameter, one can see that the last term in (99) is order-one when

$$\rho_v \sim \varepsilon^{4/3}. \quad (100)$$

This is the applicability condition of the intermediate regime examined in this section, whereas the finite- ρ_v regime and the small- ρ_v limit are valid if $\rho_v \gg \varepsilon^{4/3}$ and $\rho_v \ll \varepsilon^{4/3}$, respectively.

- (2) Note that Eq. (99) was obtained under the assumption that the near-[isothermality] ansatz (81) used for the small- ρ_v regime applies to the intermediate regime as well. This can be verified through an asymptotic analysis of the temperature Eq. (80), in a manner similar to how Eq. (96) was analyzed.
- (3) It is unlikely that Eq. (99) admits solutions describing liquid ridges, but their nonexistence is not easy to prove.

VI. THREE-DIMENSIONAL LIQUID FILMS

Even though the asymptotic equations (67), (92) and (99) have been derived for two-dimensional films, they can be readily extended to three dimensions. In what follows, these 3D extensions are summarized.

In the main body of the paper, two of the asymptotic equations derived are written in nondimensional variables that are different from those of the third equation. In this section, all equations are written in terms of the variables for the small- ρ_v regime [i.e., those given by (10), (11), (30), (76), and (47)–(49)].

The nondimensional parameter space of the problem involves the vapor-to-liquid density ratio, ρ_v/ρ_l , and the parameter ε defined by (28) (physically, the latter is proportional to the contact angle). Since this paper deals with *thin* liquid films, $\varepsilon \ll 1$.

The limit $\rho_v/\rho_l \gg \varepsilon^{4/3}$ was examined in Sec. IV, and the 3D extension of the asymptotic equation (67) derived there is

$$\varepsilon^2 [A_1 + \beta(A_2 + Bh)] \frac{\partial h}{\partial t} - \sigma \nabla^2 h + \frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2}\rho'^2(h) = 0, \quad (101)$$

where the nondimensional temperature τ is given by (14), and the surface tension σ and the coefficients A_1 , A_2 , and B depend on τ and are given by expressions (40) and (68)–(70), respectively. The function $\rho'(h)$ (see examples in Fig. 2) is defined by (26) and determined by the boundary-value problem (18)–(21).

The regime $\rho_v/\rho_l \sim \varepsilon^{4/3}$ was examined in Secs. V D and V E. The 3D extension of the asymptotic Eq. (99) is

$$\varepsilon^2 A_1 \left(\frac{\partial h}{\partial t} + \nabla \cdot \left\{ Q(h) \nabla \left[\sigma \nabla^2 h + \frac{1}{2}\rho'^2(h) \right] \right\} \right) - \sigma \nabla^2 h + \frac{\tau}{2\rho_l(1-\rho_l)^2} - 1 - \frac{1}{2}\rho'^2(h) = 0, \quad (102)$$

where the function $Q(h)$ is determined by (93).

Finally, the limit $\rho_v/\rho_l \ll \varepsilon^{4/3}$ was examined in Secs. V A–V C, and the 3D extension of the asymptotic equation (92) is

$$\frac{\partial h}{\partial t} + \nabla \cdot \left\{ Q(h) \nabla \left[\sigma \nabla^2 h + \frac{1}{2}\rho'^2(h) \right] \right\} = 0. \quad (103)$$

For macroscopic films—such that the film thickness exceeds that of the liquid/vapor interface by several order of magnitude—one can assume in expression (93) that $\bar{\rho} \approx \rho_l$ and thus obtain

$$Q(h) \approx \frac{\rho_l^2}{3\mu_s} h^3,$$

where μ_s is the nondimensional shear viscosity of the liquid phase. Furthermore, in the limit $h \rightarrow \infty$, the function $\rho'(h)$ tends to a constant (see Fig. 2). As a result, Eq. (103) reduces to the equation for the usual Navier–Stokes films,

$$\frac{\partial h}{\partial t} + \frac{\rho_l^2 \sigma}{3\mu_s} \nabla \cdot (h \nabla \nabla^2 h) = 0.$$

This conclusion helps to understand why the Navier–Stokes equations follow from the DIM in the incompressibility limit, but—unlike the DIM—admit solutions describing liquid ridges.

Indeed, for common fluids at room temperature, ρ_v/ρ_l is very small: for water at $T = 20^\circ\text{C}$, for example, $\rho_v/\rho_l \approx 1.7 \times 10^{-5}$. An estimate of ε , in turn, can be deduced from the fact that contact angles of common fluids on commonly used substrates are unlikely to be smaller than 5° . This implies that liquid ridges can be modeled using Eq. (102) with (sic!) $\varepsilon^2 A_1 \gg 1$. Consequently, the terms in Eq. (102) that prevent liquid ridges from being steady are small and the resulting evolution is slow—probably indistinguishable from evaporation and other effects not taken into account by the present model.

VII. CONCLUDING REMARKS

Thus, three parameter regimes have been identified and three asymptotic models have been derived for liquid films. Two points are still in order: one on the results obtained and another on how to improve them.

- (1) One should realize that the diffuse-interface model (used to derive all of the results of the present work) does not include any adjustable parameters, i.e., it could be used to optimize the results to fit a specific phenomenon. In addition to the equation of state (typically, known from thermodynamics handbooks), the DIM includes only the Korteweg parameter K and the near-wall density ρ_0 . The former is uniquely linked to the surface tension of the fluid under consideration and the latter to the static contact angle.
- (2) Before applying the present results to a specific fluid, one should make them more realistic—by extending them to a mixture of several fluids and assume the temperature to be

subcritical for one fluid and supercritical for all the others. Such a model should provide a sufficiently accurate description of, say, a water droplet surrounded by air, at room temperature.

APPENDIX A: THE MAXWELL CONSTRUCTION

It follows from (18)–(20) that

$$\tau \left(\ln \frac{\rho_v}{1-\rho_v} + \frac{1}{1-\rho_v} \right) - 2\rho_v = \tau \left(\ln \frac{\rho_l}{1-\rho_l} + \frac{1}{1-\rho_l} \right) - 2\rho_l. \quad (\text{A1})$$

Physically, Eq. (A1) means that the free-energy density of the vapor phase equals that of the liquid.

Another equation inter-relating ρ_v and ρ_l can be obtained by considering

$$\int_{-\infty}^{\infty} \bar{p} \times \frac{d}{dz} (18) dz.$$

Integrating the term involving $d^2\bar{p}/dz^2$ by parts and taking into account the boundary conditions (19) and (20), one obtains

$$\frac{\tau\rho_v}{1-\rho_v} - \rho_v^2 = \frac{\tau\rho_l}{1-\rho_l} - \rho. \quad (\text{A2})$$

Physically, (A2) is the condition of equality of the pressure in the vapor phase to that in the liquid phase. In this paper, Eqs. (A1) and (A2) are referred to as the Maxwell construction.

In the low-temperature limit, one expects

$$\rho_v \rightarrow 0, \quad \rho_l \rightarrow 1, \quad \tau \rightarrow 0. \quad (\text{A3})$$

Under the assumption that, as $\tau \rightarrow \infty$, ρ_v becomes exponentially small (to be verified later), Eq. (A2) yields

$$\rho_l = \frac{1 + \sqrt{1 - 4\tau}}{2} + \mathcal{O}(\tau\rho_v). \quad (\text{A4})$$

Next, rearranging Eq. (A1) using (A3), one obtains

$$\rho_v = \frac{\rho_l}{1-\rho_l} \exp \left[-\frac{2\rho_l}{\tau} + \frac{\rho_l}{1-\rho_l} + \mathcal{O}(\rho_v) \right]. \quad (\text{A5})$$

Using the leading-order term of (A4) to rearrange the leading-order term of (A5) and using the leading-order term of the latter to rearrange the error in both expressions, one obtains (23) and (24) as required.

APPENDIX B: PROPERTIES OF $\rho(z|h)$

The function $\rho(z|h)$ is determined by the boundary-value problem (13), (8), (15), and (16)—which can actually be solved analytically, albeit in an implicit form. To do so, multiply (13) by $d\rho/dz$, integrate with respect to z , and recalling condition (8) and definition (26) of $\rho'(h)$, one obtains

$$\left(\frac{d\rho}{dz} \right)^2 = F(\rho), \quad (\text{B1})$$

where

$$F(\rho) = (\rho_l - \rho_0)^2 \rho'^2 + 2 \left[\rho_0^2 - \rho^2 - G(\rho - \rho_0) + \tau \left(\rho \ln \frac{\rho}{1-\rho} - \rho_0 \ln \frac{\rho_0}{1-\rho_0} \right) \right]. \quad (\text{B2})$$

Equation (B1) is separable (hence, can be solved analytically), but it involves an unknown constant G . To determine it, introduce

$$\rho_\infty = \lim_{z \rightarrow \infty} \rho(z|h) \quad (\text{B3})$$

(note that, generally, $\rho_\infty \neq \rho_v$), and observe that Eq. (13) implies that

$$G = \tau \left(\ln \frac{\rho_\infty}{1-\rho_\infty} + \frac{1}{1-\rho_\infty} \right) - 2\rho_\infty. \quad (\text{B4})$$

Note also that (B3) is consistent with Eq. (B1) only if $F(\rho_\infty) = 0$ —which yields [together with expressions (B2) and (B4)]

$$(\rho_l - \rho_0)^2 \rho'^2 + 2(\rho_0 - \rho_\infty)^2 + 2\tau \left[\rho_0 \ln \frac{\rho_\infty(1-\rho_0)}{\rho_0(1-\rho_\infty)} + \frac{\rho_0 - \rho_\infty}{1-\rho_\infty} \right] = 0. \quad (\text{B5})$$

This equation relates ρ_∞ to ρ_0 and ρ' . If $\rho' < 0$, $\rho(z|h)$ monotonically decays with z —but, if $\rho' > 0$, $\rho(z|h)$ has a maximum. Common sense and numerical experiments suggest that, when increasing ρ' , this maximum approaches ρ_l , whereas ρ_∞ approaches ρ_v (while the distance h between the substrate and interface tends to infinity). Thus, denoting the upper bound of ρ' by ρ'_{max} , one can find it by substituting $\rho' = \rho'_{max}$ and $\rho_\infty = \rho_v$ into (B5). Finally, expressing ρ'_{max} from the resulting equation, one can obtain estimate (27) as required.

APPENDIX C: ESTIMATES (73) AND (74)

In a manner similar to how Eqs. (B1) and (B2) were obtained, one can use Eq. (18) and the boundary condition (20) to obtain

$$\frac{d\bar{p}}{dz} = -2^{1/2} \left\{ \tau \left[\bar{p} \ln \frac{\bar{p}(1-\rho_v)}{\rho_v(1-\bar{p})} - \frac{\bar{p} - \rho_v}{1-\rho_v} \right] - (\bar{p} - \rho_v)^2 \right\}^{1/2}.$$

Using this equality and omitting overbars, one can rewrite (68), (69), and (71) in the form

$$A_1 = 2^{1/2} \rho_l^2 \int_{\rho_v}^{\rho_l} \frac{1}{\rho^3(1-\rho)} \left\{ \tau \left[\rho \ln \frac{\rho(1-\rho_v)}{\rho_v(1-\rho)} - \frac{\rho - \rho_v}{1-\rho_v} \right] - (\rho - \rho_v)^2 \right\}^{1/2} d\rho, \quad (\text{C1})$$

$$A_2 = \tau^2 \rho_l^2 \int_{\rho_l}^{\rho_v} \frac{z(\rho)}{\rho^2} \left\{ \left[\ln \frac{\rho(1-\rho_v)}{\rho_v(1-\rho)} - \frac{\rho_l - \rho_v}{\rho_l(1-\rho_v)} - \frac{2}{1-\rho} \right] \times \ln \frac{\rho(1-\rho_v)}{\rho_v(1-\rho)} + \frac{\rho_l - \rho_v}{\rho_l(1-\rho_v)(1-\rho)} \right\} d\rho. \quad (\text{C2})$$

Observe that, in (C2), z is a function of ρ .

In the limit $\tau \rightarrow 0$, the main contribution in integrals (C1) and (C2) comes from the neighborhood of the point $\rho = \rho_v$, which suggests the substitution $\rho = \rho_v \xi$. Keeping in (C1) and (C2) the leading order only, one obtains

$$A_1 = \frac{2^{1/2} \tau^{1/2}}{\rho_v^{3/2}} \int_1^\infty \frac{1}{\xi^3} [\xi(\ln \xi - 1) + 1]^{1/2} d\xi, \quad (\text{C3})$$

$$A_2 = -\frac{\tau^2}{\rho_v} \int_1^\infty \frac{z(\rho_v \xi)}{\xi^2} [(\ln \xi - 3) \ln \xi + 1] d\xi, \quad (\text{C4})$$

and evaluating the integral in (C4) numerically, one obtains (73).

To derive (74), observe that it follows from the linearized version of Eq. (18) that

$$\tilde{\rho} \sim \rho_v + \Delta \exp\left[-\sqrt{\frac{\tau}{\rho_v(1-\rho_v)^2}} z\right] \quad \text{as } z \rightarrow \infty, \quad (C5)$$

whereas monotonicity of $\tilde{\rho}(z)$ implies that the constant Δ is positive. Letting $\tilde{\rho} = \rho_v \xi$ and taking into account that $\rho_v \ll 1$, one obtains

$$z \sim \rho_v^{1/2} \tau^{-1/2} \ln(\xi - 1) - \ln \Delta. \quad (C6)$$

Substituting (C6) into (C4), one can verify that the integral involving D vanishes, and

$$A_2 = \rho_v^{-1/2} \tau^{3/2} \int_1^\infty \frac{\ln(\xi - 1)}{\xi^2} [(\ln \xi - 3)\ln \xi + 1] d\xi.$$

Finally, evaluating the integral in the above expression numerically, one obtains (74), as required.

APPENDIX D: THE ASYMPTOTICS OF $\tilde{\rho}(z)$ AS $\tilde{\rho} \rightarrow \rho_v$

The asymptotics of the peak of w [given by expression (88)] is determined by the region where $\tilde{\rho}(z)$ is small. To examine it, consider Eq. (18) for $\tilde{\rho}(z)$ and let $\tilde{\rho} = \rho_v \tilde{\rho}$. Then, taking into account (33) and keeping the leading-order terms only, one obtains

$$\ln \tilde{\rho} + \frac{\rho_v}{\tau} \frac{d^2 \tilde{\rho}}{dz^2} = 0.$$

Evidently, all small parameters can be scaled out from this equation by changing z to ξ such that

$$\xi = \left(\frac{\tau}{\rho_v}\right)^{1/2} (z - 2^{-3/2}).$$

This effectively means that the characteristic width of the small- $\tilde{\rho}$ region is $(\rho_v/\tau)^{1/2}$.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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