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Moving contact line of a volatile fluid

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Interfacial flows close to a moving contact line are inherently multiscale. The shape of the interface and the flow at meso- and macroscopic scales inherit an apparent interface slope and a regularization length, both named after Voinov, from the microscopic inner region. Here, we solve the inner problem associated with the contact line motion for a volatile fluid at equilibrium with its vapor. The evaporation or condensation flux is then controlled by the dependence of the saturation temperature on interface curvature—the so-called Kelvin effect. We derive the dependencies of the Voinov angle and of the Voinov length as functions of the parameters of the problem. We then identify the conditions under which the Kelvin effect is indeed the mechanism regularizing the contact line motion.

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The dynamics of a macroscopic solid plunging in a liquid bath [1,2] or withdrawn from it [3–5] depends sensitively on its wetting properties, i.e., on the intermolecular interactions at the nanoscopic scale. The motion of the contact line separating the wet from dry regions is therefore an inherently multiscale problem. Among the important consequences of the coupling between the inner and outer scales (Fig. 1), the speed at which a contact line can recede over a flat solid surface cannot exceed a critical value, associated with a dynamical wetting transition which leads to the formation of a dewetting ridge [6,7], of a V-shaped dewetting corner [1,8–10], or to the entrainment of films [2,10,11] (see Refs. [12,13] for detailed reviews). In many applications, such as coating, imbibition of powders, immersion lithography, or boiling-free heating, these entrainment phenomena are crucial limiting factors for industrial processes.

Figure 1 shows schematically the structure of the flow close to a moving contact line. Even for an infinitesimal velocity U, there exists a range of mesoscopic scales—roughly six decades—separating the microscopic scale from the macroscopic length L, in which the diverging viscous stress is balanced by a gradient of capillary pressure. This balance can be made quantitative in the lubrication approximation, for which the angles are assumed small, and which gives a third-order differential equation for the interface profile $h(x)$:

$$\gamma \frac{d^3h}{dx^3} = -\frac{3\eta U}{h^2}, \tag{1}$$

where η is the liquid dynamic viscosity and γ the surface tension; U is positive for an advancing contact line. This equation has an exact solution [14] which reduces to the asymptotic form proposed by Voinov [15] far from the contact line, but for $x \ll L$:

$$h'(x)^3 - \theta_V^3 = \frac{9\eta U}{\gamma} \ln\left(\frac{x}{\ell_V}\right). \tag{2}$$

θ_V is by definition the apparent contact angle in the static case ($U = 0$), which can be different from the Young angle θ_Y due to out-of-equilibrium processes taking place at a microscopic scale. The Voinov length ℓ_V is also a quantity defined in the mesoscopic range of scales but inherited from the inner region, where the problem is regularized. The mesoscopic solution (2) must also be matched at the macroscopic scale L to an outer solution where viscosity can usually be neglected. Figure 1 features the case of a spreading drop or of a growing bubble but the outer matching problem has been solved for many other geometries including a gravity controlled bath [3,4,16] or a capillary ridge [7]. For receding contact lines, Eq. (2) is an intermediate asymptotic, only valid in the range of scales for which the term on the right-hand side is small compared to θ_V^3, and can only be matched to an outer solution below the dynamical wetting transition [4,13].

Different models have been proposed to solve the moving contact line paradox, i.e., the singularity of Eq. (1) as $x \to 0$. The simplest regularization is obtained by imposing the Navier slip boundary condition based on a slip length ℓ_s that can be expressed using a statistical physics description of liquids [17] and gas [18]. The Voinov angle is then the Young angle θ_Y and the Voinov length reads $\ell_V = 3\ell_s/(e\,\theta_V)$, where e is Euler's number [4]. Alternative descriptions have been proposed, based on disjoining pressure [ℓ_V then scales on the Israelachvili length $(\mathcal{A}/6\pi\gamma)^{1/2}$, where $\mathcal{A}$ is the Hamaker constant] and diffuse interface models (ℓ_V is then set by a diffusion length). Finally, when the substrate presents heterogeneities, the contact line dynamics becomes a thermally activated process in the inner layer [13,19].

This Rapid Communication deals with the the contact line motion of a volatile liquid in contact with an atmosphere of its pure vapor (see Refs. [20–26] and references therein. An evaporation-condensation process has first been proposed as a possible mechanism controlling the contact line motion at the molecular scale by Wayner [27] and Pomeau [28]. The idea that the Kelvin effect, i.e., a dependence of the local interface temperature on the interface curvature, solves the hydrodynamic contact line singularity was first introduced in Ref. [24]. Rednikov and Colinet [29] developed this idea by performing an asymptotic matching of the inner and intermediate regions,

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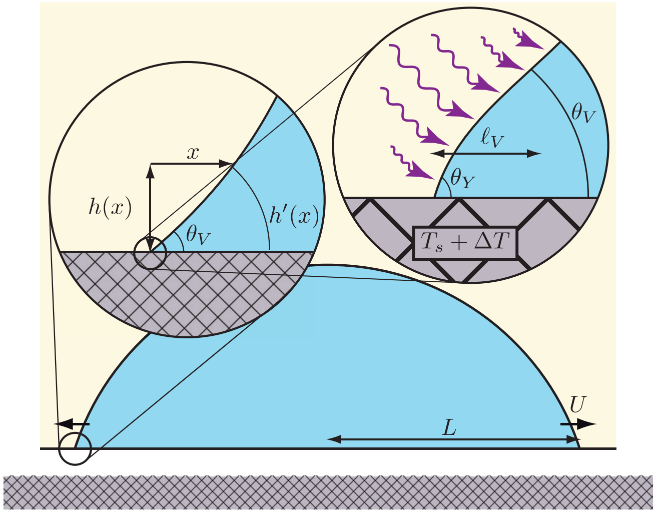

FIG. 1. (Color online) Schematic showing a liquid vapor interface $h(x)$—here, a spreading drop ($U > 0$) on a cooled plate ($\Delta T < 0$)—at different scales. The inner region, close to the moving contact line, is controlled by evaporation or condensation (top right). The slope changes from the Young angle θ_Y to the Voinov angle θ_V across a scale ℓ_V given by the Kelvin length ℓ_K. In a mesoscopic range of scales, the shape of the interface results from the balance between viscous friction and the Laplace pressure gradient, resulting in a slope $h'(x)$ which varies logarithmically in scale [Eq. (2)].

thus showing that the Kelvin effect indeed solves the singularity. In this Rapid Communication we identify and analyze two parameters inherited from the inner region, the Voinov length ℓ_V and the Voinov angle θ_V, as functions of the substrate overheating with respect to the saturation temperature.

Lubrication equations including the Kelvin effect. In this Rapid Communication, we proceed in a hydrodynamical framework, starting from the equation governing the evolution of the interface position h:

$$\partial_t h + \partial_x q = -j, \tag{3}$$

where q is the hydrodynamic flow rate. The rate j at which a liquid evaporates is governed by the energy balance at the liquid-gas interface. Assuming that the vapor pressure is fixed, the interfacial temperature T^i depends on the interface curvature $\kappa \simeq h''(x)$ according to Kelvin's law

$$T^i = T_s\left(1 + \frac{\gamma\kappa}{\rho\mathcal{L}}\right), \tag{4}$$

where T_s is the saturation temperature, $\mathcal{L}$ the latent heat, and ρ the liquid density. In the lubrication approximation, the temperature varies linearly across the liquid layer from the substrate temperature $T_s + \Delta T$, assumed to be imposed (Fig. 1), to the interfacial temperature T_i. Neglecting the energy flux in the vapor phase, the evaporation rate is controlled by the conductive energy flux across the liquid,

$$j = \frac{k}{\rho\mathcal{L}h}\left(\Delta T - \frac{T_s\,\gamma\kappa}{\rho\mathcal{L}}\right), \tag{5}$$

where k is the liquid heat conductivity.

Starting from the Voinov law (2), we define the reduced capillary number [30], using θ_V as a characteristic slope:

$$\delta \equiv \frac{3\eta U}{\gamma\theta_V^3}. \tag{6}$$

The characteristic length ℓ_K is obtained dimensionally by balancing the two fluxes driven by the interface curvature, namely, the evaporation rate j and the divergence of the hydrodynamic flow rate $q = \gamma h^3\kappa'/(3\eta)$:

$$\ell_K \equiv \frac{\sqrt{3\eta k T_s}}{\theta_V^2\rho\mathcal{L}}. \tag{7}$$

We therefore make the solution dimensionless using

$$h(x) = \theta_V\ell_K H(\zeta), \quad \zeta = x/\ell_K.$$

Under the lubrication approximation, the governing equations in the scaled variables then read

$$H'' = \mathcal{K}, \quad \mathcal{K}' = QH^{-3} - \delta H^{-2}, \quad Q' = (\mathcal{K} - \epsilon)/H, \tag{8}$$

where ϵ is the superheating parameter, defined by

$$\epsilon \equiv \frac{\sqrt{3\eta k T_s}}{\gamma\theta_V^3}\,\frac{\Delta T}{T_s} \tag{9}$$

and Q is the dimensionless counterpart of $(q + Uh)$. The fourth-order differential equation (8) must be complemented by the appropriate boundary conditions. We choose $x = 0$ for the contact line position [so $H(0) = 0$] and impose the slope $H'(0) = \theta_Y/\theta_V$ according to Young's law. As we look for regular solutions of the problem, the continuity of the temperature at the contact line requires $\mathcal{K}(0) = \epsilon$. Finally, to make the problem compatible with the asymptotic expansion (2), one assumes a vanishing curvature far from the contact line: $\mathcal{K}(\infty) \to 0$.

Voinov angle. By definition, θ_V is the interface slope for $x \gg \ell_K$ at vanishing capillary number δ. In this limit, the outer boundary condition $\mathcal{K}(\infty) \to 0$ is equivalent to the constant slope condition $H'(\infty) = 1$. The dotted line in Fig. 2 corresponds to a typical solution obtained numerically for

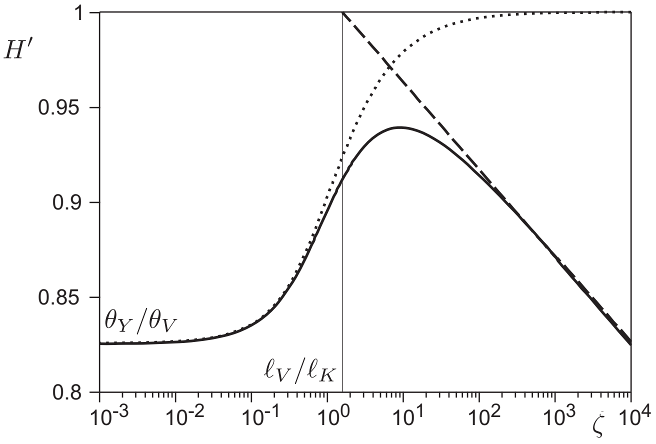

FIG. 2. Solution of the equations for a receding contact line ($\delta = -0.02$), with an overheating $\epsilon = 0.1$. The dotted line corresponds to the static case ($\delta = 0$). The dashed line corresponds to the Voinov outer asymptotics (2). These solutions allow one to obtain the Voinov length ℓ_V and angle θ_V.

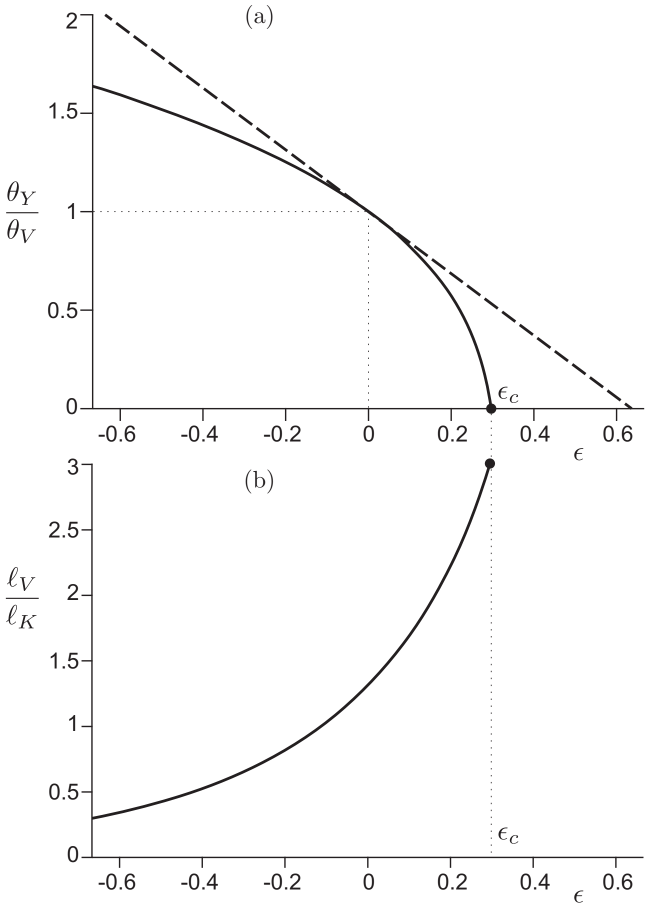

FIG. 3. (a) Ratio of the Young angle to the Voinov angle as a function of overheating parameter ϵ, determined numerically (solid line). The dashed line is the analytical expansion (10). (b) Voinov length ℓ_V rescaled by the Kelvin length ℓ_K as a function of ϵ.

$\delta = 0$ [31]. Overheating ($\epsilon > 0$) induces an evaporation flux that would diverge as h^{-1} at the contact line [cf. Eq. (5)], if not balanced by Kelvin's effect. The induced liquid flow towards the contact line is accompanied by a capillary pressure gradient: The resulting interface curvature leads to an apparent angle θ_V larger than θ_Y. The crossover from θ_Y to θ_V takes place at the microscopic scale, for ζ of the order unity. The ratio θ_Y/θ_V is reported in Fig. 3(a) as a function of ϵ. Following Ref. [24], we perform a linear expansion of the solution in ϵ for $\delta = 0$, writing $H \equiv H_0 = \zeta + \epsilon H_\epsilon + O(\epsilon^2)$. Linearizing Eq. (8), one obtains a differential equation on $\mathcal{K}_\epsilon = H''_\epsilon$, which reads $(\zeta^3 \mathcal{K}'_\epsilon)' - \mathcal{K}_\epsilon/\zeta = -1/\zeta$. The solution verifying the boundary conditions involves the modified Bessel function of the first order K_1: $\mathcal{K}_\epsilon = 1 - \zeta^{-1} K_1(\zeta^{-1})$. Integrating $\mathcal{K}_\epsilon$ from ∞ to 0, one obtains $H'_\epsilon(0) = -\pi/2$, which gives the expansion for the Voinov angle

$$\theta_Y/\theta_V = 1 - (\pi/2)\epsilon + O(\epsilon^2), \tag{10}$$

shown as a dashed line in Fig. 3(a).

The most important feature of the curve $\theta_Y/\theta_V(\epsilon)$ is the existence of a critical value $\epsilon_c \simeq 0.297$ of the overheating parameter—note that the linear approximation (10) overestimates ϵ_c by a factor $\simeq$2. In the limit $\epsilon \to \epsilon_c$, θ_V becomes much larger than θ_Y. Then, the Kelvin effect is just balanced by the maximal available capillary force, so that H' goes from 0 to 1. The equation $\epsilon = \epsilon_c$ gives the large ΔT asymptotic expression of the Voinov angle θ_V, which no longer depends on θ_Y:

$$\theta_V \approx \left(\frac{\sqrt{3\eta k T_s}}{\epsilon_c \gamma} \frac{\Delta T}{T_s} \right)^{1/3}. \tag{11}$$

One may expect this asymptotic regime to be relevant close to the gas-liquid critical point, in particular, to the description of boiling [32,33].

Voinov length. We now consider a contact line moving at a velocity U. We linearize the governing equations with respect to δ, around the solution H_0 obtained for $\delta = 0$ [31]. A typical solution is shown in Fig. 2 (solid line), together with the asymptotic expansions around $\zeta \to 0$ (static solution obtained for $\delta = 0$, dotted line) and $\zeta \to \infty$ (Voinov expansion, dashed line). It shows that a perfectly regular solution is obtained, in spite of the no-slip boundary condition imposed at the solid-liquid interface: At a scale smaller than ℓ_K, the interface advances by the curvature driven condensation (or recedes by evaporation). How can a contact line advance (even at $\epsilon = 0$) in the absence of any regularizing mechanism, leading to a slip of the fluid at the boundary? Consider a perfect wedge initially at rest at the Young angle. Imposing an hydrodynamics flux towards the contact line leads to an increase of the apparent contact angle. However, θ_Y remains the true contact angle at the molecular scale so that a positive curvature κ appears at a small scale, which induces a condensation by the Kelvin effect. As a consequence, the contact line advances, although the liquid velocity vanishes at the contact line: The phase transition flux $j(0) = -U\theta_Y$ balances exactly that induced by the contact line motion.

At distances much larger than the scale ℓ_V, one recovers as expected the Voinov solution $H'(\zeta) \sim 1 + \delta \log(\zeta \ell_K/\ell_V) + O(\delta^2)$. The Voinov length ℓ_V is obtained from the matching to this outer expansion, as shown geometrically in Fig. 2 (intersection between the dashed line and the horizontal line $H' = 1$). Figure 3 shows the dependence of ℓ_V on the overheating parameter ϵ. As expected from dimensional analysis, ℓ_V is on the order of the Kelvin length ℓ_K. The ratio ℓ_V/ℓ_K turns out to increase with the overheating parameter, from $\simeq$1.32 at $\epsilon = 0$ to $\simeq$3.00 at $\epsilon = \epsilon_c$.

Kinetic regime. We have so far assumed that the evaporation process is limited by the energy flux across the interface or, equivalently, that the characteristic time of the kinetics of evaporation was small enough to consider it instantaneous. Actually, the rate of evaporation j must satisfy two conditions simultaneously: the energy conservation (5) at the interface and a kinetic equation based on the Hertz-Knudsen law. The kinetic equation is a balance between desorption at a rate determined by the interfacial temperature T^i and adsorption at a rate proportional to the interfacial vapor density ρ_v^i (Fig. 4). It takes the form

$$j = \frac{\beta\big(\rho_{\text{sat}}(T^i) - \rho_v^i\big)}{\rho}, \tag{12}$$

where β is a thermal velocity, $\rho_{\text{sat}}(T^i)$ the saturation vapor density at the interfacial temperature T^i, and ρ_v^i the actual vapor density at the interface. Importantly, ρ_v^i is defined at the scale of the mean free path $\bar{\ell}$. As Kelvin's effect takes

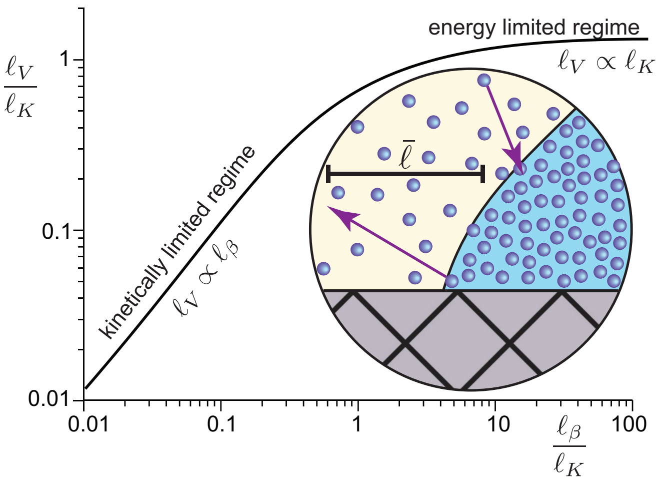

FIG. 4. (Color online) Voinov length ℓ_V as a function of the ratio ℓ_β/ℓ_K for $\epsilon = 0$, as predicted by Eq. (13). Inset: Schematic of the kinetically limited regime. The desorption or adsorption takes place over a scale given by the mean free path $\bar{\ell}$.

place at a scale smaller than $\bar{\ell}$, can ρ_v^i can be considered as a constant determined at the contact line? This effect, often called "interfacial thermal resistance" [20–25,31], regularizes the thermal flux equation (8) according to

$$Q' = \frac{\mathcal{K} - \epsilon}{H + \ell_K/\ell_\beta}. \tag{13}$$

The kinetic length ℓ_β is defined by

$$\ell_\beta \equiv \frac{3\eta T_s \beta}{\theta_V^3 \rho^2 \mathcal{L}} \frac{d\rho_{\text{sat}}}{dT}. \tag{14}$$

Figure 4 shows that the energy controlled regime is recovered when the kinetics of evaporation is fast enough, namely, when $\ell_K \ll \ell_\beta$. In the opposite limit, the kinetics becomes the limiting process and the Voinov length scales on the kinetic length: $\ell_V \simeq 1.17\ell_\beta$ (see the Supplemental Material [31] for the analytic solution).

Discussion. The theory developed above is directly applicable to the microscopic description of boiling, as nucleating bubbles are constituted of pure vapor. It may help solving the demanding problem of the boiling crisis [33]. As long as one aims to address a macroscopic problem involving a moving contact line, the only quantities inherited from the inner molecular-scale region are the Voinov length and the Voinov angle. For a liquid surrounded by its pure vapor with a vanishing slip length, we have shown here that the Voinov length is set by the smallest of the Kelvin length and the kinetic length. In reality, a fluid presents both slip at the solid/liquid interface and evaporation or condensation at the solid/vapor interface. The results obtained in this Rapid Communication are applicable if the Voinov length produced by the Kelvin effect is larger than that induced by the slip length ℓ_s. One therefore needs to compare ℓ_K, ℓ_β, and ℓ_s/θ_V. The slip length ℓ_s is around two molecular sizes when $\theta_Y < \pi/2$ [13,17]. The product $\theta_V^2\, \ell_K$ depends only on the liquid properties and ranges from 0.3 nm for water and methanol to 1 nm for alkanes and refrigerants such as ammonia or fluorocarbon. It can be even larger, for fluids such as glycerol or silicon oils whose large viscosities are due to glassy effects. At ambient temperature, the product $\theta_V^3\, \ell_\beta$ is generically smaller than the nanometer scale. Kelvin's effect can therefore be the mechanism regularizing the stress singularity only for very small contact angles. This can be achieved in low temperature helium, pressurized water, or in refrigerants at ambient temperature, close to a wetting transition. In other situations, the slip length is dominant. In a forthcoming paper, we will address the case of a drop evaporating in a different gas (the so-called "coffee stain" problem), where evaporation also presents a singularity that must be regularized by different physical mechanisms.

Noted added: Recently we became aware of an independent work discussing the regularization of the lubrication equation by the Kelvin effect, now published as Ref. [29].

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