Capillary Emptying and Short-Range Wetting

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We consider a liquid trapped in a narrow horizontal capillary, under the influence of gravity. As the slit is widened, the meniscus, separating the capillary liquid from gas, deforms and develops a long tongue extending along the bottom wall. As a critical slit width is approached, the length of the tongue diverges continuously, leading to the emptying of the capillary. We show that the critical singularities characterizing emptying are the same as those at short-ranged wetting transitions, but at a scale set by the capillary length rather than the bulk correlation length. These meso- or macroscopic versions of both complete and critical wetting are observable in the laboratory and are studied here using a colloid-polymer mixture.

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Phase transitions of inhomogeneous fluids such as wetting, capillary condensation, as well as fluid adsorption at structured walls have received enormous attention recently (see the reviews [1–5]). In most theoretical studies of these transitions, the influence of a gravitational field is either considered secondary or, more often, completely neglected. However, it is clear that gravity plays a role in many situations involving interfaces. Consider a liquid in a tall vertical capillary slit or pore, which is capped at its bottom. What happens when the capillary is turned to the horizontal? Experience tells us the liquid will drain from the open end if the capillary is wide, as when water escapes from a tipped glass, but remains trapped if it is narrow, such as a drinking straw. It is surprising that this basic aspect of capillarity, in particular, the emptying transition that occurs as the slit is widened, has not been investigated. In this Letter, we point out that these phenomena are analogous to phase transitions involving the meniscus shape, and reveal an unexpected connection between phase separation at capillary condensation and the theory of wetting transitions. In particular, we show that capillary emptying are equivalent to meso- or macroscopic short-ranged wetting transitions and provide a simple method of studying these, otherwise rare, phase transitions in the laboratory.

Consider a capped capillary of width L made from two parallel walls of macroscopic height $H \gg L$ and length $N \gg L$, containing a large volume of liquid so that the meniscus is far from the ends (see Fig. 1). One can ask, "What is the meniscus shape when the capillary is tilted?" If we assume that the meniscus is translationally invariant along its length, and let $\ell(z) < H$ denote its distance from the cap along the z axis, the macroscopic free energy per length N is

$$F[\ell] = \sigma\mathcal{A} + g\Delta\rho\mathcal{G} + \Delta p\mathcal{V} + \sigma\mathcal{S}. \qquad (1)$$

Here, σ is the liquid-gas surface tension, $g\Delta\rho$ is the liquid-gas weight density difference, and Δp is a Lagrange multiplier. The functional dependence on ℓ enters through the liquid-gas interfacial area $\mathcal{A}$, volume $\mathcal{V}$, and the gravitational contribution

$$\mathcal{G} = \int_0^L dz\left(\frac{\ell^2}{2}\sin\alpha + \ell z\cos\alpha\right), \qquad (2)$$

where $0 \leq \alpha \leq \pi/2$ is the tilt angle (see Fig. 1). The final term in (1) accounts for the wall-liquid and wall-gas interaction and, on using Young's equation, reduces to $\mathcal{S} = -\cos\theta_0\ell(0) - \cos\theta_L\ell(L)$, where θ_0 and θ_L are the contact angles at the walls. This description is valid provided L and the capillary length, $a = \sqrt{\sigma/g\Delta\rho}$, are much larger than the bulk correlation length ξ_b.

It is clear that, for $\alpha > 0$, the meniscus adopts a certain shape which minimizes free energy (1). However, for the

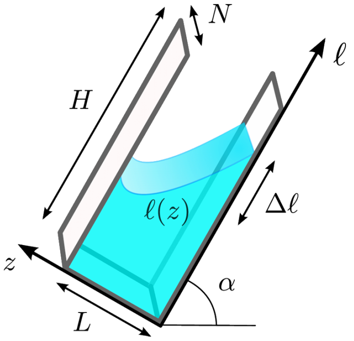

FIG. 1 (color online). Schematic illustration of a meniscus in a tilted capillary.

horizontal capillary ($\alpha = 0$), the existence of a meniscus is only guaranteed for sufficiently narrow capillaries (as in the case of a drinking straw). For capillaries wider than a certain critical size L_E, the liquid drains and no meniscus connecting top and bottom walls is possible (as with the glass of water). This draining can be quantified by determining the equilibrium separation between the front and rear part of the meniscus $\Delta\ell \equiv \ell(0) - \ell(L)$. This acts as an order parameter which diverges as $\alpha \to 0$, provided of course that there is enough volume of liquid, and leads to the phase diagram shown in Fig. 2. Emptying can only occur at $\alpha = 0$, and is represented by the thick line $L \geq L_E$. This state can be approached in two different ways: (a) Complete emptying refers to the limit $\alpha \to 0$ for $L > L_E$ and is the phenomena we are familiar with when we spill a liquid, while (b) Critical emptying refers to the approach to the transition as $L \to L_E$ for $\alpha = 0$. Tilting the capillary ($\alpha \to 0$) for narrower widths ($L < L_E$) does not drain the liquid (if the capillary is sufficiently tall). Note that Fig. 2 is very similar to the phase diagram for wetting transitions, where L and α replace the temperature T and chemical potential μ, respectively, and with the emptying line ($L \geq L_E$) replacing the complete wetting line ($T \geq T_w$), above the wetting temperature T_w [1,2]. As we shall see, the connections between emptying and wetting are much deeper.

In this Letter, we focus on the critical emptying transition, which can be solved analytically. Theoretical and experimental results for complete emptying will be discussed elsewhere. For a horizontal capillary ($\alpha = 0$), minimization of (1) leads to

$$1 + \frac{\ell'(z)}{\sqrt{1 + \ell'(z)^2}} = \frac{z^2}{2a^2} + \frac{\Delta p}{\sigma} z + (1 - \cos\theta_0), \qquad (3)$$

and identifies

$$\Delta p = \sigma \frac{\cos\theta_0 + \cos\theta_L}{L} - \frac{g\Delta\rho L}{2}. \qquad (4)$$

This is just the Kelvin equation for the pressure of shifted phase coexistence (relative to bulk saturation) for the capillary-liquid (CL) and capillary-gas (CG) phases [6]. Indeed, working in the language of a grand-canonical ensemble, the profile $\ell(z)$ describes the interface between CL and CG phases at capillary-phase coexistence. Let us define the right-hand side of (3) to be a function $\Phi(z)$. In zero gravity, this is a straight line, and the meniscus is a section of a circle. As g increases, $\Phi(z)$ develops a minimum at $z = z_T$ (say), implying that the interfacial gradient $\ell'(z_T)$ is large. This bulging of the profile corresponds to the growth of a liquid tongue of height z_T, extending along the lower wall, separating the liquid and gas. As g is increased further, the length of the tongue $\Delta\ell$ increases and *diverges* when $\Phi(z_T) = 0$. This identifies the critical width

$$\frac{L_E}{a} = 2\left(\sin\frac{\theta_0}{2} + \cos\frac{\theta_L}{2}\right) \qquad (5)$$

beyond which there is no solution of (3). At $L = L_E$ the tongue height $z_T = 2a\sin(\theta_0/2)$ and $\Delta\ell = \infty$; i.e., emptying occurs when a macroscopic tongue intrudes between the CL and CG. Note that the free-energy cost of a long tongue (of height z) is simply $\sigma\Phi(z)$ multiplied by its length. Thus, the condition $\Phi(z_T) = 0$ signifies the three-phase coexistence of the tongue, CL and CG. More generally, $\Phi(z)$ belongs to a broader class of functionals studied by Finn (originally, in the absence of gravity), the positivity of which determines the existence of capillary surfaces in confining geometries [7].

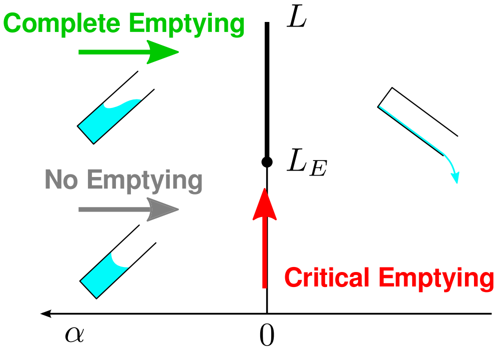

FIG. 2 (color online). Phase diagram showing complete and critical emptying transitions occurring as $\alpha \to 0$ for $L > L_E$, and $L \to L_E$ for $\alpha = 0$.

For a symmetric slit ($\theta = \theta_0 = \theta_L$), Eq. (5) simplifies to $L_E/a = 2\sqrt{1 + \sin\theta}$, which is even about $\theta = \pi/2$ [see Fig. 3(a)]. This means that for walls that preferentially adsorb vapor ($\theta > \pi/2$), emptying occurs due to a tongue of gas that intrudes along the top wall toward the capped end. For an asymmetric slit ($\theta = \theta_0 = \pi - \theta_L$), on the other hand, we have $L_E/a = 4\sin(\theta/2)$, which is simply $L_E = 2z_T(\theta)$. This type of geometry has been used at length in Ising studies of interfacial delocalization (primarily in the absence of gravity), where the asymmetry arises from opposing surface fields [8–10]. In this case, the meniscus is symmetric about the slit midpoint [see Fig. 3(b)]. Note that the critical width becomes microscopic when the lower (upper) wall is completely wet (dry) and takes its maximum possible value ($L_E/a = 4$) when that geometry is inverted.

Critical emptying, that is, crossing the phase boundary (5), can be induced by increasing L, by changing θ (via the temperature or electrowetting, say) or reducing a. However, the nature of the capillary walls leads to two different types of critical emptying transitions, depending on whether the walls are partially or completely wet by the liquid.

(A) Walls showing partial wetting.—In Fig. 3, we illustrate the growth of the tongue in symmetric slits as $\epsilon \equiv (L_E - L)/L_E \to 0$ for $\theta = 0°$ (A)–(C), $\theta = 45°$ (D)–(F), and $\theta = 135°$ (G)–(I). The divergence of $\Delta\ell$ is associated with a singularity $f_{\rm sing}$ in the excess free energy (1). Provided $\theta > 0$, we find

$$\Delta\ell \approx a\ln\epsilon^{-1}, \qquad f_{\rm sing} \approx \sigma a\epsilon\ln\epsilon^{-1}, \qquad (6)$$

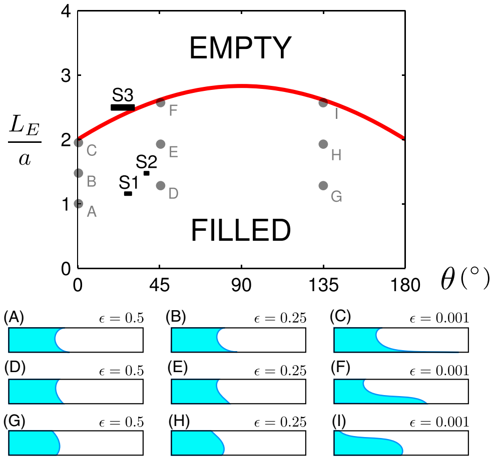

FIG. 3 (color online). Emptying phase boundaries $L_E(\theta)/a$ vs θ for symmetric capillaries. Points $S1$-$S3$ represent the state points of the experimental profiles of Fig. 4 as determined using our fit to the profiles (sizes represent the errors). The obtained values of the capillary length are $a = 52$, 41, and 24 μm, respectively. Representative meniscus profiles for $\theta = 0^\circ$ (A)–(C), $\theta = 45^\circ$ (D)–(F), and $\theta = 135^\circ$ (G)–(I) are shown.

for both the symmetric and asymmetric slits. These singularities can be understood by constructing a constrained free energy $W(\Delta\ell)$ by partially minimizing (1) keeping $\Delta\ell$ fixed. For example, for the asymmetric slit, we find that, for small contact angles,

$$W(\Delta\ell) = \sigma\left(\frac{L_E^2 - L^2}{8a^2}\right)\Delta\ell + B\frac{e^{-\Delta\ell/a}}{1 - e^{-\Delta\ell/a}}. \tag{7}$$

Minimization of (7) determines both f_{sing} and the equilibrium tongue length. The coefficient of $\Delta\ell$ in the first term is equivalent to $\sigma\Phi(z_T) \propto \epsilon$, while the coefficient of the repulsion is $B \propto a\theta^2$, indicating that walls showing complete wetting are a special case. In a long capillary (N and $\mathcal{V} \to \infty$), emptying is also associated with fluctuations due to the wandering of the meniscus, controlled by an effective stiffness σa. These fluctuations are characterized by a correlation length $\xi_x \equiv \sqrt{\sigma a / W''(\Delta\ell)}$ that diverges as $\xi_x \approx a\epsilon^{-1/2}$ when $\epsilon \to 0$.

Thus, for walls that show partial wetting ($0 < \theta < \pi$), the critical emptying transition is equivalent to a short-ranged complete wetting transition occurring on the meso-macroscopic scale of the capillary length. Qualitatively, the intrusion of the liquid tongue between the coexisting CL and CG phases, as $\Phi(z_T)$ vanishes, resembles a fluid intruding between two coexisting bulk phases on approaching a three-phase coexistence. Thus, the field ϵ plays the role of the undersaturation or, in Ising language, a magnetic-field-like scaling variable for wetting. Instead of two interfaces unbinding from each other, emptying refers to the unbinding of the front and rear parts of the meniscus. More tellingly, the quantitative nature of the critical singularities and, indeed, the form of the constrained free energy $W(\Delta\ell)$ are precisely the same as the critical singularities and binding potential for short-ranged complete wetting [1,2]. For example, recall that the mean thickness of a complete wetting film, of liquid for example, at a wall-vapor interface is $\langle\ell\rangle \approx \xi_b \ln\delta p^{-1}$, where δp is the undersaturation (pressure difference from bulk coexistence). This logarithimic divergence is associated with a singularity in the surface tension of the wall-gas interface $\sigma_{\mathrm{sing}} \approx \xi_b \delta p \ln\delta p^{-1}$. Thus, the only difference is that the capillary length a replaces the microsopic bulk correlation length ξ_b (of the intruding phase). These are mean-field-like singularities and, in principle, they could be altered by the wandering of the meniscus, thus leading to fluctuation-dominated behavior akin to two-dimensional complete wetting [11]. However, the macroscopic scale means that the predictions (6) are valid for all practical purposes. This can be quantified by a Ginzburg criterion, based on analysis of $W(\Delta\ell)$, which shows that fluctuations are unimportant unless $\epsilon \ll (\xi_b/L)^4$. Fluctuations are therefore negligible unless we are close to the capillary critical point, marking the end of coexistence between CL and CG [6,12].

(B) Walls showing complete wetting.—Now consider emptying in the symmetric capillary as $\theta \to 0$ and $L \to L_E = 2a$. The tongue length $\Delta\ell$ still diverges even though $z_T = 0$ (see Fig. 3). At fixed $L = L_E$, we find $\Delta\ell \approx a\ln\theta^{-1}$ as $\theta \to 0$. This mimics the growth of a wetting film at a short-ranged critical wetting transition which diverges as $\xi_b \ln\theta^{-1}$ [1,2,13,14]. This is interesting but, of course, presupposes that the capillary walls themselves exhibit a wetting transition. Alternatively, one can use a liquid that completely wets the walls ($\theta = 0$) and, then, increase L or reduce a until $L = L_E$. As earlier, we find that the tongue grows as $\Delta\ell \approx a\ln\epsilon^{-1}$, but the free energy has a different critical exponent (and sign), $f_{\mathrm{sing}} \approx -\sigma a\epsilon^2 \ln\epsilon^{-1}$, indicating that the emptying transition is *higher-order* than for case (A). In fact, these singularities are the same as short-ranged critical wetting as the transition is approached along a thermodynamic path that is initially slightly oversaturated.

These results show that critical emptying is a practical means of studying in the laboratory the experimentally elusive short-ranged complete and critical wetting-like transitions. Recall that continuous wetting transitions are rare—particularly critical wetting, for which only a few examples are known [4,15]. Fluctuation effects are not important for critical emptying, but this is also true, in practice, for short-ranged critical wetting since the asymptotic critical region cannot be easily reached [16–18]. Critical emptying occurs on a scale set by the capillary length a, which is typically millimeters for molecular fluids and microns for phase separating colloid-polymer mixtures [19]. Although molecular fluids are more accessible, colloid-polymer mixtures have the advantage of smaller pinning effects and larger interfacial fluctuations, both due to the colloidal length scale. To illustrate the phenomenon of critical emptying, we report here experimental results for a system of sterically stabilized

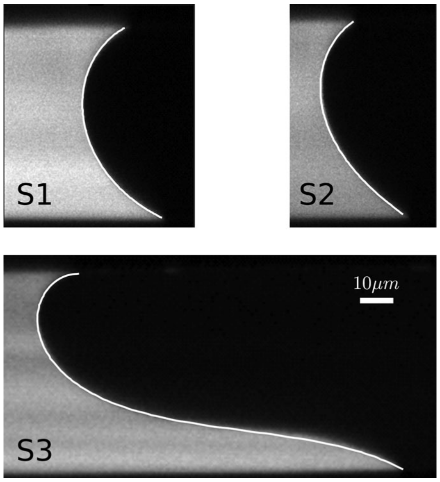

FIG. 4. Confocal microscopy images for meniscii in a colloid-polymer mixture placed in a horizontal capillary for 3 different state points approaching the emptying phase boundary (see Fig. 3). Fits to solutions of Eq. (3) are shown in white.

PMMA colloids (diameter 50 nm, fluorescently labeled) and nonadsorbing polystyrene polymer (molecular weight 233 kg/mol, obtained from FLUKA) dispersed in decalin, similar to the system described in [20]. Because of a depletion interaction [21,22] this system spontaneously phase separates into a colloid-rich phase (a colloidal "liquid") and a polymer-rich phase (a colloidal "gas") at sufficiently high polymer and colloid concentrations [23]. It then behaves as a two fluid system, with an extremely small surface tension. By progressive dilution with decalin, we produced three samples $S1$-$S3$ with decreasing colloid and polymer volume fractions, which reduces the value of the capillary length a. By means of laser scanning confocal microscopy (Zeiss LSM 5 Exciter), we have studied the interfacial profiles of each sample in confinement between two parallel walls of millimeter dimensions $L \times H \times N = 0.062 \pm 0.001 \times 0.5 \times 15$. The length N of the capillary is sufficiently large so that the side walls have little influence on the emptying. This is borne out by the fits to our theoretical predictions for the meniscus profiles. The capillary was initially held vertically before being turned horizontally, and allowed 2 d of equilibration. Since L is much smaller than the gravitational length of the colloids, no complicating factors arise due to the sedimentation-diffusion equilibrium [24]. The ratio L/a increases for samples $S1$-$S3$, which should allow us to cross the emptying phase boundary. The observed profiles (Fig. 4) show precisely this effect with a long liquid tongue, separating the capillary phases, clearly visible in sample $S3$. A quantitative comparison of these profiles with the theoretical result for $\ell(z)$ obtained from integrating (3) is shown in Fig. 4. Here, the fitting parameters are the capillary length, which we can determine to within a micron, and the contact angle, where the latter is introduced via θ_0, θ_L and the Lagrange multiplier Δp. The spread of these three fitted contact angles gives the error bars shown in Fig. 3. We note that sample 3 is so close to capillary emptying that the error in θ spans the phase boundary. Nevertheless, as can be seen, the macroscopic theory reproduces the experimental profiles to high accuracy.

In summary, we have shown that the emptying of a tilted capillary is qualitatively and quantitatively similar to short-ranged complete and critical wetting transitions, depending on whether the capillary walls are partially or completely wet by the liquid. This is a practical means of studying these uncommon transitions in the laboratory, which we have illustrated using a colloid-polymer mixture.

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