Condensation in a Capped Capillary is a Continuous Critical Phenomenon

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We show that condensation in a capped capillary slit is a continuous interfacial critical phenomenon, related intimately to several other surface phase transitions. In three dimensions, the adsorption and desorption branches correspond to the unbinding of the meniscus from the cap and opening, respectively, and are equivalent to 2D-like complete-wetting transitions. For dispersion forces, the singularities on the two branches are distinct, owing to the different interplay of geometry and intermolecular forces. In two dimensions we establish precise connection, or covariance, with 2D critical-wetting and wedge-filling transitions: i.e., we establish that certain interfacial properties in very different geometries are identical. Our predictions of universal scaling and covariance in finite capillaries are supported by extensive Ising model simulation studies in two and three dimensions.

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Capillary condensation (CC) is central to our understanding of confined fluids and has received much attention over the last few decades [1]. As is well known, vapor confined in a slit of width L condenses at a pressure $p_{co}(L)$, less than the value p_{sat} at bulk saturation, given by the macroscopic *Kelvin equation*,

$$p_{sat} - p_{co}(L) = \frac{2\sigma \cos\theta}{L} + \dots, \qquad (1)$$

where σ is the liquid-vapor surface tension and θ the contact angle. Studies of CC, based on Landau or modern density functional methods, usually consider confining walls of infinite area and assume translational invariance parallel to these [1,2]. In this case, CC is certainly a first-order transition and mean-field treatments yield adsorption isotherms with a van der Waals loop. Far less attention has been given to CC in slits of finite-depth D which are capped at one end and open into a reservoir (see Fig. 1). This scenario is certainly experimentally accessible and is similar to recent analysis of adsorption on grooved and pitted substrates [3,4]. Three numerical studies [5–7], restricted to complete wetting ($\theta = 0$), have reported the same basic finding: In a finite capillary, CC is a sharp but continuous transition (Fig. 1) and adsorption isotherms exhibit no van der Waals loops for any finite D (see also [8,9]). However, the physical reason behind this striking change and the quantitative aspects of the transition have not been elucidated.

Here we show that CC in such capped capillaries is a continuous interfacial critical phenomenon exhibiting observable critical singularities which are intimately related to several other surface phase transitions. Our two main findings are: (i) In three dimensions, adsorption and desorption in a deep capillary correspond to the continuous unbinding of the meniscus from the bottom and top, respectively, and map onto two-dimensional complete wet-

ting [10,11] with relevant scaling field $\Delta p = p_{co}(L) - p$. The divergence of the average meniscus height on these branches is described by the respective critical singularities $\langle \ell \rangle \sim \Delta p^{-\beta_A}$, $D - \langle \ell \rangle \sim |\Delta p|^{-\beta_D}$ which are, in general *distinct*. In particular, for dispersion forces, $\beta_A = \frac{1}{4}$ while $\beta_D = \frac{1}{3}$ implying that the adsorption (isotherm) is steeper than the desorption. For a finite-depth capillary, the meniscus has large-scale fluctuations at $p = p_{co}$ equivalent to those of an interface in a 2D infinite capillary with *opposing* walls for which there are long-standing predictions [12–15]. (ii) In a 2D capped slit (or a 3D capillary pore), one can proceed further and relate CC to *critical-wetting* transitions occurring at 2D planar substrates [10,16]. This precise connection is an extension of the geometrical covariance known for the filling of wedges [17,18], cones
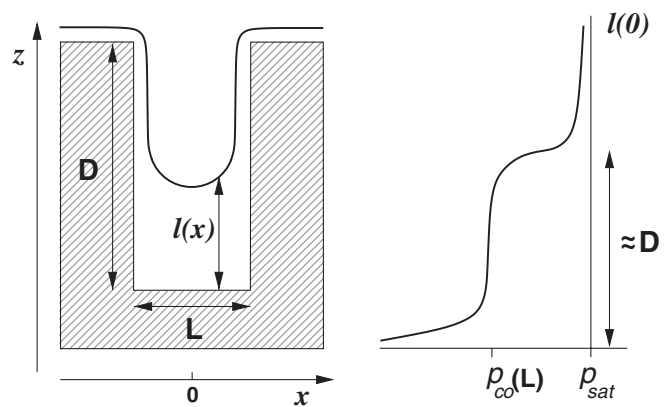

FIG. 1. Schematic cross section of a capped capillary of depth D and width L illustrating the local interfacial height $\ell(\mathbf{x})$. The slit is infinitely long in the y direction. A typical adsorption isotherm is also sketched showing the rapid but continuous rise in the midpoint height near CC [$p \approx p_{co}(L)$] and the complete wetting as saturation is approached.

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[19] and apexes [20] and implies that some (universal) interfacial properties in very different geometries are identical. These predictions, based primarily on analysis of interfacial Hamiltonians, are supported fully by our Ising model simulation studies in two and three dimensions.

In an infinite capillary, the two phases, referred to as capillary-liquid and capillary-vapor, coexist when $p = p_{co}(L)$. Any meniscus separating these phases is delocalized and has large-scale fluctuations, analogous to those of a planar interface between coexisting bulk phases, but in one lower dimension. Now in a capped system, geometry necessitates the formation of a meniscus whose location is determined, in part, by the capillary thermodynamics. For $p < p_{co}(L)$ the meniscus must be located near the bottom because the capillary-liquid phase is metastable, while for $p > p_{co}(L)$, the capillary-vapor is metastable and the meniscus must reside near the capillary opening. The fundamental question is, what happens to the meniscus as $p \to p_{co}$?

We first follow [6] and introduce an interfacial model based on the local interfacial height $\ell(x, y)$, where y is the variable along the capillary. The free energy is

$$H[\ell] = \sigma S[\ell] + \delta p V[\ell] + W[\ell]. \quad (2)$$

Here S is the fluid interfacial area, V the volume of liquid, $\delta p = p_{sat} - p$, and W is the binding potential accounting for the (dispersion) intermolecular forces. For confining walls which are completely wet ($\theta = 0$), one can use

$$W[\ell] = \frac{12A}{\pi} \iint d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|^6}, \quad (3)$$

where $A > 0$ is the Hamaker constant, an energy, and $\mathbf{r}$ and $\mathbf{r}'$ denote points in the substrate and vapor, respectively. The numerical prefactor is chosen so that (3) recovers the usual binding potential per unit area $W(\ell) = A\ell^{-2}$ for planar walls [10]. The model (2) describes the whole adsorption isotherm including the CC and the complete wetting of the entire substrate as $p \to p_{sat}$. The latter is not of interest so we seek an effective Hamiltonian which will allow us to study the CC more easily. Accordingly, we integrate out degrees of freedom keeping only the long-wavelength fluctuations in the meniscus height *along* the capillary. Close to CC, the meniscus must be of semicircular cross section at local height $\ell(y) \equiv \ell(0, y) < D$. The fluctuations of the meniscus are then described by a *capillary* Hamiltonian, obtained via a constrained minimization of (2). After some algebra we find [21]

$$H_{cap}[\ell(y)] = \int dy \left\{ \frac{\sigma L}{2} \left(\frac{d\ell}{dy} \right)^2 + W_{cap}(\ell; D) \right\}, \quad (4)$$

where the capillary binding potential is

$$W_{cap}(\ell; D) = \Delta p L \ell + \frac{5}{24} \frac{AL^2}{\ell^3} + \frac{AL}{(D - \ell)^2} + \cdots. \quad (5)$$

The model is only valid near CC and does not describe the complete wetting as $p \to p_{sat}$. Nevertheless it describes

accurately the interplay of the geometry, forces, and fluctuations for $p \approx p_{co}$, providing a more transparent view of the interfacial behavior.

Equation. (5) is one of our central results and highlights some intriguing properties of CC: (i) The first term, conjugate to $\ell(y)$, is proportional to $\Delta p \equiv p_{co}(L) - p$, measuring the *deviation from capillary coexistence*. This establishes the connection with complete-wetting phenomena, in one lower dimension, with the meniscus acting as the unbinding interface. (ii) Intermolecular forces repel the meniscus from the capillary cap and opening. At CC, the capillary cap wishes to be ''wet'' by the capillary liquid while the capillary opening is wet by the capillary vapor. The finite-size (FS) effects mimic therefore those of an interface in a capillary with *opposing* walls that are wet by different fluid phases [22–24]. This connection is deeper in two dimensions as we shall see later. (iii) While the repulsion from the top is similar to the planar wall [22], that from the bottom is *shorter ranged* due to a geometry-induced cancellation of intermolecular forces. This is the reason behind the asymmetry in the adsorption isotherm seen in numerical studies [6] and is a general feature of CC in systems with long-ranged (dispersion) forces. For short-ranged forces the (direct) repulsions from the top and bottom are similar to exponential decays.

To continue, consider the critical behavior in the semi-infinite limit $D \to \infty$. The adsorption and desorption branches of the 3D capillary isotherm become analogous to 2D-like complete-wetting phase transitions describing the unbinding of the meniscus from the cap and open end, respectively. The associated critical singularities are well understood [11] and reflect the long-ranged forces presented in $W_{cap}(\ell)$ and fluctuation effects associated with the wandering of the meniscus controlled by the surface tension term in (4). The dependence on the slit width is significant since increasing L effectively suppresses the role of fluctuations. For example, the entropic repulsion from the bottom effectively adds a term $\propto (k_B T)^2 / \sigma L \ell^2$ to (5). While, in principle, the asymptotic divergence of ℓ is ultimately determined by this entropic repulsion, in practice it is irrelevant for slits more than a few angstroms in width because the amplitude is negligible compared to that of the long-range forces. The latter dominate for all practical purposes and we anticipate mean-field-like behavior with $\langle \ell \rangle \sim (AL/\Delta p)^{1/4}$, as quoted earlier. On the desorption branch, fluctuation effects are similarly negligible, even though they are marginal, and we predict $D - \langle \ell \rangle \sim (A/|\Delta p|)^{1/3}$. For systems with short-ranged forces, on the other hand, the influence of fluctuations can no longer be neglected and both the adsorption and desorption branches show the same critical behavior. Thus, for example, on the adsorption branch $\langle \ell \rangle \sim (L^2 \Delta p)^{-1/3}$. All these results are supported fully by transfer-matrix analysis of the Hamiltonian (4).

Condensation (or rather pseudocondensation) in a 2D capped capillary is particularly interesting. Here we focus

solely on systems with short-ranged forces since long-ranged forces are not pertinent for all physical scenarios. However, we broaden our discussion to the case of nonzero contact angle θ. First, as above, the adsorption and desorption in a semi-infinite capillary are related to the 1D limit of complete wetting. The probability of finding the meniscus at a given height is simply proportional to the Boltzmann weight of W_{cap}, implying that on the adsorption branch $\langle \ell \rangle \sim (L\Delta p)^{-1}$ and similarly for desorption. Thus the critical exponent $\beta_A = 1$ can be identified as the $d \rightarrow 1^+$ limit of the general result $\beta_{\text{co}}^s(d) = (3 - d)/(d + 1)$ appropriate to short-ranged complete wetting in dimension $d \leq 3$ [10].

To see the deep connection with 2D critical wetting we introduce what at first appears to be an artificial geometry, and adopt a magnetic notation also useful for comparison with our Ising model simulation results. Consider a planar Ising-like system, with spontaneous magnetization m_0 and a boundary (wall) in the shape of a trough. That is the height of the wall above some reference line is $\Psi(x) = 0$ for $|x| < L/2$ and $\Psi(x) = (|x| - L/2)\tan\alpha$ otherwise. The spins on the boundary are subject to a surface field $h_1 > 0$. The spins away from the wall are subject to a position dependent external field $h(x) = h$ for $|x| < L/2$ and $h(x) = 0^-$ otherwise. In general these boundary conditions induce a fluctuating interface at height $\ell(x)$, which defines the "wetting" layer of up spins adsorbed near the wall.

The trough has limiting geometries, each having distinct transitions. For $\alpha = \frac{\pi}{2}$, we have a capped capillary with spins subject to bulk field h exhibiting continuous CC when $h \equiv h_{\text{co}}(L) \approx -\sigma \cos\theta/(m_0 L)$. In the limit $L \rightarrow 0$ we recover a wedge, which at bulk two-phase coexistence exhibits a 2D filling transition [17,18,25,26] when $\theta(T_{\text{fill}}) = \alpha$, whereby the thickness of the adsorbed layer at the bottom diverges: $l_w \sim (T_{\text{fill}} - T)^{-\beta_w}$. Finally, if α, $L \rightarrow 0$ we recover a planar geometry with a critical transition at temperature T_{wet}, at which the mean layer thickness diverges: $l_\pi \sim (T_{\text{wet}} - T)^{-\beta^s}$, and $\theta \rightarrow 0$ [10].

The trough exhibits a generalized filling transition which can be studied using the effective Hamiltonian

$$H_{\text{tr}}[\ell] = \int dx \left\{ \sigma \sqrt{1 + \left(\frac{d\ell}{dx}\right)^2} + W_{\text{tr}}(\ell, x; h, \alpha) \right\}. \quad (6)$$

The binding potential for the trough, W_{tr}, has a contact (attractive) interaction at the wall and a term $2m_0 h\ell(x)$ for $|x| < \frac{L}{2}$ which models the bulklike field acting on spins in the strip vertically above the bottom. The model is amenable to transfer-matrix analysis similar to that used for filling in acute wedges [18]. In particular, one can establish that, for all $\alpha \leq \pi/2$, close to the transition the probability distribution function (PDF) for the midpoint ($x = 0$) interfacial height has the simple scaling form $P_{\text{tr}}(\ell) \propto e^{-\ell/\langle \ell \rangle}$, where the mean height is given by

$$\langle \ell \rangle = \frac{k_B T}{2(\sigma \sin(\theta - \alpha) - m_0 hL)}. \quad (7)$$

This result identifies correctly the phase boundaries for CC, filling and wetting in the limits discussed above. When $L = 0$, we recover the covariance between the PDFs at 2D wedge filling and planar critical wetting written, in an obvious notation, $P_w(\ell; \theta, \alpha) = P_\pi(\ell; \theta - \alpha)$ [17]. The covariance of the PDF therefore extends to 2D CC and establishes a dimensional reduction between 2D critical wetting and 1D complete wetting for thermal systems. This has a number of consequences. First, the 2D exponents satisfy $\beta_A = \beta_w = \beta^s = 1$ and are identified with the 1D complete-wetting result $\beta_{\text{co}}^s(1^+)$ noted earlier. Second, the invariance of the PDF necessarily implies that the thermal interfacial wandering exponent $\zeta(d)$ must satisfy $\zeta(2) = 1/2$ and $\zeta(1^+) = 1$. These last results are not new but they point to a very deep connection between substrate geometry and interfacial fluctuations which is not yet fully explored.

Our discussion has focused so far on the critical singularities in a semi-infinite capillary. Fluctuation effects and covariances are also apparent in a capillary of finite depth, particularly if the pressure (or bulk field for Ising systems) is tuned to the condensation value, $p = p_{\text{co}}(L)$, of the infinite capillary. Here we focus on systems with short-ranged forces where the geometrical covariances are most striking and we can compare with simulation studies. We consider only the case of strongly adsorbing walls ($\theta = 0$), although the 2D case is insensitive to θ and show that the fluctuations of the meniscus in both two and three dimensions capillaries are related, via geometrical covariance, to universal FS effects in an entirely different 2D geometry.

Consider an infinitely long, 2D Ising magnet with boundaries at $z = 0$, D along which the spins are subject to fields h_1 and $-h_1$ respectively [12]. In zero bulk field, the lower wall is wet by up spins for $T \geq T_{\text{wet}}$ while the upper is wet by down spins. The FS effects are known to fall into two universality classes. Exactly at the critical-wetting temperature $T = T_{\text{wet}}$ the profile contains a scaling contribution [12]

$$\frac{m(z)}{m_0} = 1 - \frac{2z}{D}, \quad (8)$$

while for $T_c^{\text{bulk}} > T > T_{\text{wet}}$,

$$\frac{m(z)}{m_0} = 1 - \frac{2z}{D} + \frac{1}{\pi} \sin\left(\frac{2\pi z}{D}\right). \quad (9)$$

These results are valid in the scaling limits $z, D \rightarrow \infty$ with z/D arbitrary and are verified by exact Ising calculations [14,15]. Both are indicative of large-scale interfacial fluctuations where the roughness scales with the separation D.

Now consider the magnetization profile $m(z)$ measured along the central axis $x = 0$ of a finite-depth capped capillary at bulk field tuned to condensation, i.e., $h = h_{\text{co}}(L)$. If the capillary is 2D, covariance with 2D critical wetting implies we should expect (8). In a 3D capillary, on the other hand, transfer-matrix analysis of (4), with short-ranged forces, leads us to the prediction (9).
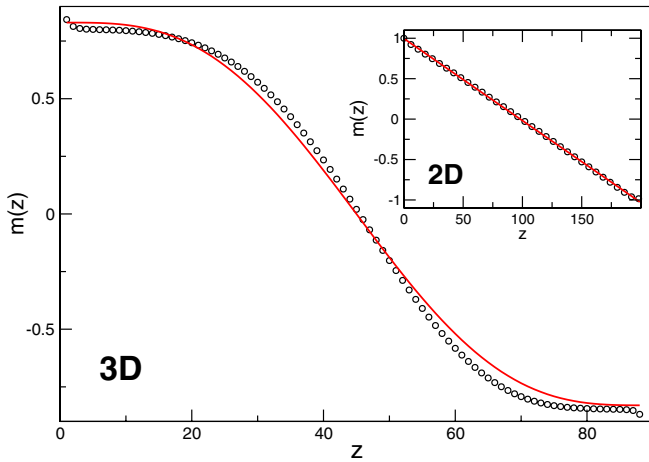
FIG. 2 (color online). Representative Monte Carlo simulation results (points) for the midpoint magnetization profile in 2D and 3D capped capillaries compared with theoretical predictions (8) and (9) (curves). The temperatures, $T = 0.741 T_c^{\text{bulk}}$ (2D) and $T = 0.830 T_c^{\text{bulk}}$, respectively, were chosen to avoid the bulk critical region and also the roughening transition (3D).

In order to test these predictions Monte Carlo simulations were performed using a Metropolis algorithm for system sizes $L = 13$, $D = 200$ (2D) and $L = 11$, $D = 88$, $M = 9000$ (3D). The length M in the direction along the 3D capillary is sufficiently large to preclude FS. More quantitatively, transfer-matrix analysis shows these are negligible if $\exp(-\frac{6\pi^3 \omega M}{L(\kappa D)^2}) \ll 1$ where ω is the dimensionless wetting parameter [10] and κ the inverse bulk correlation length. We mimic the capillary cap geometry by fixing all spins on all surfaces to $+1$ except along the top line or plane $z = D$ where they are fixed to -1. Periodic boundary conditions apply (in three dimensions) along the capillary. First we determined the CC line $h_{\text{co}}(L)$ for the 2D and 3D open capillaries, where periodic boundary conditions apply at the top ($z = L$) and bottom ($z = 0$), using standard multicanonical and histogram reweighting techniques. The measured form of the axial magnetization profiles at h_{co} are shown in Fig. 2. The comparison with the theoretical prediction is good in both dimensions but particularly so in two dimensions, confirming the covariance with critical wetting. Residual discrepancies in the 3D case are attributable to a failure to fully attain the scaling limit $D \to \infty$ which, in view of the requirement $M > D^2$, is computationally intractable.

We have shown that continuous CC is intimately related to a number of other surface phase transitions and highlights the deep connection between interfacial behavior, fluctuation effects, and substrate geometry. Our predictions of distinct critical singularities for adsorption and desorption in deep capillaries should be verifiable in experiments similar to those reported in [3]. Finally, we remark that the present discussion has been largely limited (in three dimensions) to the most experimentally accessible case where confining walls are completely wet ($\theta = 0$). The phenomenology will be significantly enriched if one con-

siders walls with nonzero contact angle since the unbinding of the meniscus at CC for adsorption and/or desorption may become first order. This intriguing possibility requires further study.

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