

Critical Point Wedge Filling

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We present results of a microscopic density functional theory study of wedge filling transitions, at a right-angle wedge, in the presence of dispersionlike wall-fluid forces. Far from the corner the walls of the wedge show a first-order wetting transition at a temperature T_w which is progressively closer to the bulk critical temperature T_c as the strength of the wall forces is reduced. In addition, the meniscus formed near the corner undergoes a filling transition at a temperature $T_f < T_w$, the value of which is found to be in excellent agreement with macroscopic predictions. We show that the filling transition is first order if it occurs far from the critical point but is continuous if T_f is close to T_c even though the walls still show first-order wetting behavior. For this continuous transition the distance of the meniscus from the apex grows as $\ell_w \approx (T_f - T)^{-\beta_w}$ with the critical exponent $\beta_w \approx 0.46 \pm 0.05$ in good agreement with the phenomenological effective Hamiltonian prediction. Our results suggest that critical filling transitions, with accompanying large scale universal interfacial fluctuation effects, are more generic than thought previously, and are experimentally accessible.

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There is now direct experimental evidence for the thermal excitation of the gravity stabilized capillary-wave-like fluctuations at the interface between coexisting fluid phases [1]. Over the last few decades theory has predicted that such fluctuation effects are particularly important at certain types of interfacial phase transitions such as critical wetting [2–6]. Wetting refers to the unbinding of a fluid interface from a solid substrate (or another fluid interface) on approaching a temperature T_w , at which the contact angle θ vanishes. The order of these transitions is determined by the subtle interplay between wall-fluid and fluid-fluid intermolecular forces and also interfacial fluctuations. The original macroscopic argument for wetting transitions had predicted that the transition would be first order, and should necessarily occur on approaching the bulk critical temperature T_c [7]. Model calculations soon revealed that the location and order of the transition are more general than this. In particular, Nakanishi and Fisher showed that, for systems with short-ranged forces, the transition should change from first order to continuous, if the surface forces are weakened and T_w approaches T_c [8]. While this has been fully tested in Ising model studies [9], this scenario is altered by the presence of long-ranged, dispersionlike intermolecular forces. In order to see continuous (now referred to as “critical”) wetting transitions one requires a fine tuning of the range and strengths of the solid-fluid and fluid-fluid forces [2,10]. Consequently while there are many examples of first-order wetting, there are no unambiguous experimental examples of critical wetting for solid-fluid interfaces, although the transition has been seen in a few binary mixtures [5].

One way around this, which would allow one to see the strong influence of interfacial fluctuations on a continuous phase transition, is to consider fluid adsorption in a linear wedge for which there is an analogous transition referred to as filling [11–15]. This transition is far more common in nature than the wetting transition and was first studied experimentally almost 40 years ago [16] although the order of the transition was not considered. Recent phenomenological effective Hamiltonian models have predicted that fluctuation effects are enhanced compared to wetting and also that the requirements that the transition can be continuous are more relaxed [17–19]. While this has been studied extensively in the Ising model [20–24], the more realistic case of long-ranged forces has not been studied in detail. In this Letter we present the results of a study of filling in the presence of dispersion forces, based on a microscopic classical density functional theory (DFT). The latter has been instrumental in developing our understanding of inhomogeneous fluids but is most usually applied to systems in which the equilibrium density depends on only one coordinate [25–28]. Here we use a two-dimensional DFT to study filling transitions and compare with the predictions of thermodynamic arguments and effective Hamiltonian theory. We find that close to T_c the filling transition is continuous even though the walls of the wedge themselves still exhibit first-order wetting. This result allows us to check interfacial Hamiltonian predictions for the critical behavior and offers strong encouragement that continuous filling transitions may be found in the laboratory similar to experiments on complete wedge filling [29].

Consider a wedge geometry formed by two identical infinite planar walls that meet at an opening angle 2ψ in contact with a bulk vapor at the chemical potential μ , tuned to saturation $\mu = \mu_{\text{sat}}^-$ at a temperature $T < T_c$. The wedge may be thought as being a missing link between a planar wall ($\psi = \pi/2$) and a capillary slit ($\psi = 0$) and shows a phase transition (filling) which is distinct from wetting and capillary condensation. Far from the apex the thickness of the liquid wetting layer ℓ_π is the same as for a planar wall. However near the apex, the thickness of the meniscus can be much greater. Macroscopic arguments dictate that the wedge is completely filled above a filling transition temperature T_f which occurs when the contact angle of a liquid drop satisfies [11–14]

$$\theta(T_f) = \frac{\pi}{2} - \psi. \quad (1)$$

The wedge filling transition corresponds to the change from microscopic to macroscopic adsorption, as $T \rightarrow T_f$, and may be first order or continuous (critical filling) corresponding to the discontinuous or continuous divergence of the adsorption. Because Eq. (1) is an exact requirement, the filling transition is ubiquitous in nature for all fluids that form drops with a finite contact angle.

Within classical DFT the equilibrium density profile is found by minimizing the grand potential functional $\Omega[\rho] = F[\rho] + \int d\mathbf{r} \rho(\mathbf{r})[V(\mathbf{r}) - \mu]$, where $V(\mathbf{r})$ is the external potential [30]. We consider a right angle wedge ($\psi = \pi/4$) so that the potential $V(\mathbf{r}) = V(x, z)$ is a function of Cartesian coordinates $x, z > 0$ and is translationally invariant along the wedge. Here $F[\rho]$ is the intrinsic free energy functional of the fluid one-body density $\rho(\mathbf{r})$, which can be split into ideal and excess parts. Modern DFT often divides the latter into a hard-sphere part $F_{\text{hs}}[\rho]$ and an attractive contribution $F_a[\rho] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) u_a(r_{12})$ where $u_a(r)$ is the attractive part of the fluid-fluid potential. We take this to be a Lennard-Jones (LJ) potential $u_a(r) = -4\epsilon(\sigma/r)^6 H(r - \sigma)$ which is truncated at $r_c = 2.5\sigma$, where σ is the hard-sphere diameter and $H(x)$ is the Heaviside function. For $F_{\text{hs}}[\rho]$ we use Rosenfeld's fundamental theory which accurately models packing effects if the density is high close to the walls [31,32]. The external potential arises from a uniform distribution of wall atoms, with density ρ_w , which for $r > \sigma$ interact with the fluid atoms via the LJ potential $\phi_w(r) = -4\epsilon_w(\frac{\sigma}{r})^6$, leading to

$$V(x, z) = \alpha_w \left[\frac{1}{z^3} + \frac{2z^4 + x^2 z^2 + 2x^4}{2x^3 z^3 \sqrt{x^2 + z^2}} + \frac{1}{x^3} \right], \quad (2)$$

where $\alpha_w = -(1/3)\pi\epsilon_w\rho_w\sigma^6$. There is a hard-wall repulsion if $x, z < \sigma$. Infinitely far from the wedge apex, the potential close to either surface recovers that of a planar wall, e.g., $V(\infty, z) = 2\alpha_w/z^3$. The functional $\Omega[\rho]$ is minimized numerically on an $L \times L$ grid where the lateral dimension of our box is $L = 50\sigma$ and the grid has a

discretization size 0.05σ . To mimic the bulk boundary conditions we impose $\rho(L, z) = \rho_\pi(z)$ and $\rho(x, L) = \rho_\pi(x)$ where $\rho_\pi(z)$ is the equilibrium profile for a planar wall-fluid interface with $\rho_\pi(L)$ fixed to the bulk gas density ρ_g . In our model DFT $k_B T_c / \epsilon = 1.414$ and temperature is expressed either in fractions of T_c or in dimensionless units $T^* = k_B T / \epsilon$.

We have considered a variety of wall strengths and present results for $\epsilon_w = 1.2\epsilon$, $\epsilon_w = \epsilon$, and $\epsilon_w = 0.8\epsilon$. For each, we first considered the planar wall with the potential $V_\pi(z) = 2\alpha_w/z^3$ and determined the density profile $\rho_\pi(z)$ and surface tensions γ_{wg} , γ_{wl} , and γ of the wall-gas, wall-liquid and liquid-gas interfaces, respectively. From Young's equation $\cos\theta = (\gamma_{\text{wg}} - \gamma_{\text{wl}})/\gamma$ we determined $\theta(T)$ for each of these systems (see Fig. 1). Each system exhibits a wetting transition, with T_w determined from the crossing of γ_{wg} and $\gamma_{\text{wl}} + \gamma$. These occur at $T_w = 0.83T_c$, $T_w = 0.93T_c$ and $T_w = 0.99T_c$ as ϵ_w is reduced. The wetting transitions are all first order; that is, the thickness of the liquid layer ℓ_π jumps from a microscopic to macroscopic value at T_w . This is to be expected since the wall-fluid potential is long ranged but the truncated LJ fluid-fluid interaction is effectively short ranged [2]. This prohibits critical wetting, which is important for our study. Also, as expected, the strength of the first-order transition decreases as T_w approaches T_c . This is apparent when one determines the interfacial binding potential $W(\ell)$ corresponding to the excess grand potential of a wetting film constrained to be of thickness ℓ . The global minimum of this determines the equilibrium film thickness ℓ_π . This is shown in Fig. 2 for the case $\epsilon_w = 0.8\epsilon$ close to the wetting temperature and shows an activation barrier, characteristic of first-order wetting, at $\ell_B \approx 10\sigma$. For comparison the barrier for the binding potential for $\epsilon_w = \epsilon$ is an order of magnitude larger and located at $\ell_B \approx 4\sigma$.

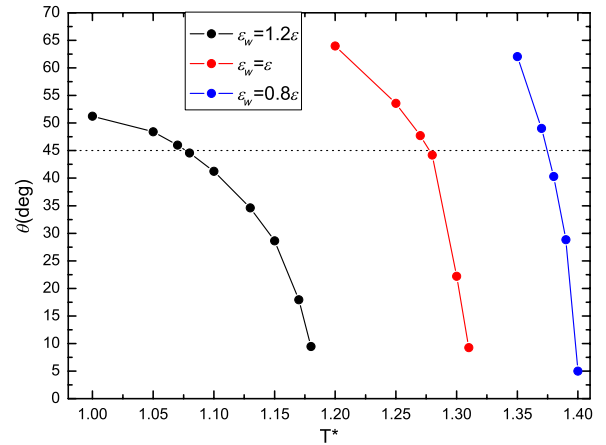


FIG. 1 (color online). Variation of the contact angle with T for different wall strengths. The intersection with the dashed line at $\theta = 45^\circ$ is the thermodynamic prediction for T_f .

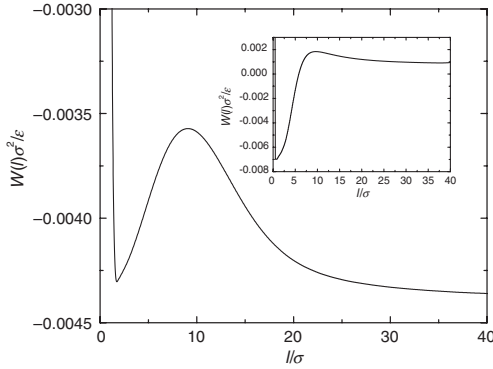


FIG. 2. Binding potential function $W(l)$ for $\epsilon_w = 0.8\epsilon$ close to a first-order wetting transition at $T_w^* = 1.4$ showing an activation barrier at $\ell_B \approx 10\sigma$. In the inset we show the binding potential at a lower temperature close to $T_f^* \approx 1.38$ for which the activation barrier is still present. In both cases the results correspond to a bulk coexistence.

According to the thermodynamic prediction Eq. (1), the location of the filling transitions can be determined from the intersection of the contact angle curves with $\psi = \pi/4$ and gives $T_f = 0.76T_c$, $T_f = 0.90T_c$, and $T_f = 0.97T_c$ as ϵ_w decreases in strength. To check this we set $\mu = \mu_{\text{sat}}^-$ and minimize $\Omega[\rho]$ to a global or local minimum Ω , starting from different high density and low density configurations. For first-order filling these will converge to different equilibrium profiles, corresponding to microscopic and macroscopic adsorptions, which coexist at T_f . This is what is found for the two strongest walls as illustrated in Fig. 3 where we plot the excess grand potential $\Omega^{\text{ex}} = \Omega + pV$ per unit volume as a function of T . The values for T_f obtained are in near exact agreement with the thermodynamic predictions and differ from them only due to the limitations of numerical discretization and finite size. In Fig. 4 we show the coexisting density profiles $\rho(x, z)$, corresponding to macroscopic (left) and

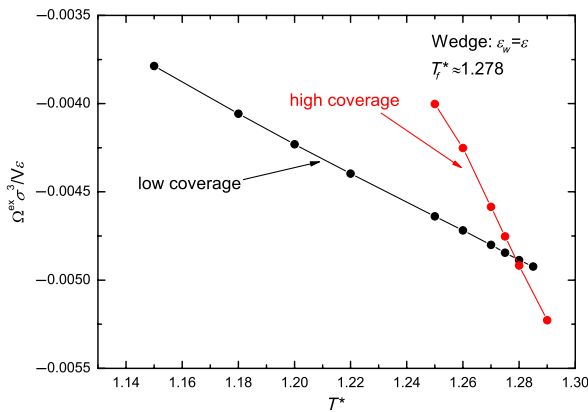


FIG. 3 (color online). Location of a first-order filling transition for $\epsilon_w = \epsilon$. Here V is the available volume which is the length of the wedge multiplied by $(L - \sigma)^2$.

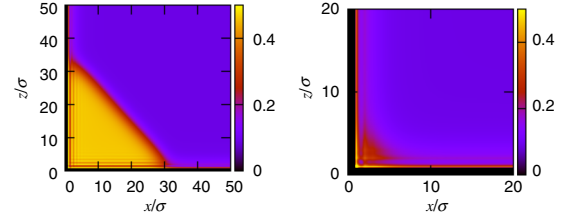


FIG. 4 (color online). Coexisting macroscopic (left) and microscopic (right) density profiles at a first-order filling transition for $\epsilon_w = \epsilon$.

microscopic (right) states, for $\epsilon_w = \epsilon$. From these we can determine the thickness ℓ_w of the meniscus above the wedge apex defined as the distance from the origin to a point on a diagonal where $\rho(x, x) = (\rho_l + \rho_g)/2$. The macroscopic meniscus is nearly flat (as it should be since we are at bulk coexistence) and meets each wall at the correct contact angle $\theta \approx \pi/4$. Of course the size of this macroscopic state is limited by our numerical grid and scales with the system size L . For the microscopic configuration the meniscus thickness ℓ_w is larger than the wetting layer thickness ℓ_π but of the same order as the distance of the activation barrier $\ell_B \approx 4\sigma$ for the corresponding binding potential for the wetting transition. This is precisely the expectation for first-order filling from effective Hamiltonian theory [18]. Both microscopic and macroscopic profiles show layering behavior close to the apex.

For the weakest wall strength $\epsilon_w = 0.8\epsilon$, however, both initial coverages converge to a unique phase indicating that the transition, which is of course rounded by the finite size of our system, is continuous. A plot of the adsorption $\Gamma = \iint dx dz (\rho(x, z) - \rho_g)$ vs T is shown in Fig. 5 and shows a dramatic but continuous increase in the adsorption near the anticipated $T_f^* \approx 1.38$. A cross section of the density

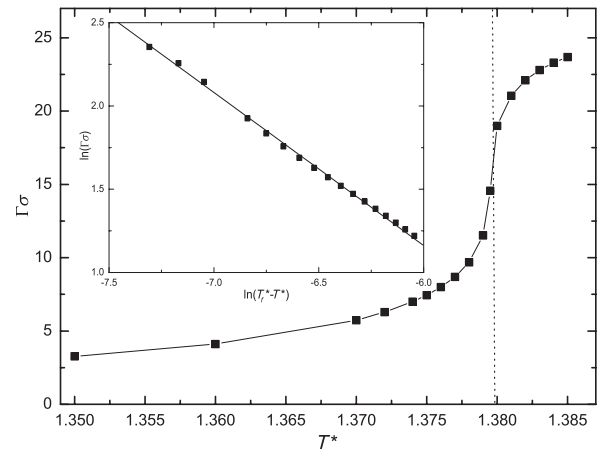


FIG. 5. Temperature dependence of the adsorption in the wedge with the weakest wall interaction $\epsilon_w = 0.8\epsilon$. The inset shows the log-log plot of the adsorption vs the scaling field $T_f - T$. The slope of the straight line is -0.92 .

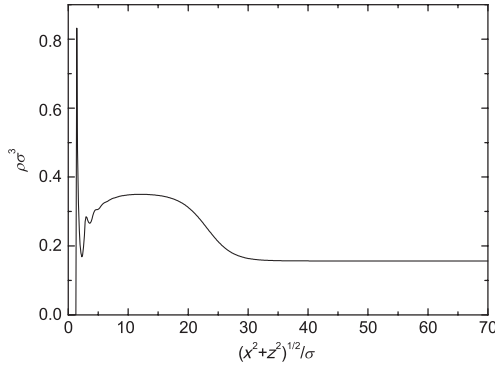


FIG. 6. Density profile along the diagonal from $(0, 0)$ to (L, L) at the filling temperature T_f for $\varepsilon_w = 0.8\varepsilon$.

profile along the diagonal $\rho(x, x)$ for $T \approx T_f$ is also shown (see Fig. 6). This indicates that the order of the filling transition is changed near the vicinity of T_c . Support for this comes from the two sources. First, near T_f the meniscus height $\ell_w \approx 22\sigma$ is considerably larger than the location of the activation barrier $\ell_B \approx 10\sigma$ associated with the wetting binding potential (see the inset in Fig. 2). This is not at all expected for first-order filling [18]. Second, we can compare quantitatively with predictions for critical filling. If the transition is critical then in an infinite wedge we expect that $\ell_w \sim (T_f - T)^{-\beta_w}$ with $\Gamma \propto \ell_w^2$ owing to the triangular shape of the meniscus. Effective Hamiltonian theory predicts that the critical singularities depend on the power law describing the dominant wall-fluid or fluid-fluid interaction which we may write more generally as $V(z) \approx 1/z^{p+1}$. The critical behavior falls into two regimes with $\beta_w = 1/p$ for $p < 4$ and $\beta_w = 1/4$ for $p > 4$ [18]. Thus we anticipate $\beta_w = 1/2$ in our model since $p = 2$. The inset in Fig. 5 shows a log plot of the adsorption for $T < T_f$, in which we use an unfitted estimate of the filling temperature $T_f^* = 1.38$ obtained from Eq. (1). This gives $\beta_w = 0.46 \pm 0.05$ in good agreement with the predicted value.

The presence of a critical (or at least effectively critical) filling transition when T_f is close to T_c , when the walls still exhibit first-order wetting, and in the presence of realistic long-ranged interactions is the main new result of our Letter, and is we believe encouraging for experimental studies. To date there have only been detailed laboratory studies of complete filling in linear wedges corresponding to the approach to coexistence when the walls are completely wet ($\theta = 0$) [29]. However the observation of critical filling would be more interesting because fluctuation effects are much stronger. For example, we expect that beyond mean-field level, capillary-wave fluctuations do not alter the divergence of $\ell_w \approx (T_f - T)^{-1/2}$ but do lead to a universal interfacial roughness (width) $\xi_\perp \approx (T_f - T)^{-1/4}$ which is much bigger than for complete filling and also critical wetting [18]. These fluctuations are not

captured by the present DFT and consequently the density profiles will be broader than predicted here. However our DFT should be otherwise extremely accurate regarding the location of the transition, its order, and the adsorption. The observed change in order from first order to continuous filling has only been partially anticipated by the previous effective Hamiltonian theory. This had been predicted on the basis of a simple interfacial model, valid only for shallow wedges, but the proposed mechanism required that both the wall-fluid and fluid-fluid forces be of the same range. Then it was noted that even for first-order wetting, the filling transition would be continuous if it occurs at a temperature below which the activation barrier forms in the binding potential $W(\ell)$ [18]. However in the present DFT study a small activation barrier is still present at T_f (see the inset in Fig. 2), indicating that the prediction of the simple, shallow wedge, effective Hamiltonian theory is not completely correct. Nevertheless we believe that the substantial reduction in the size of the barrier as T approaches T_c plays a prominent role in the change of order of the filling transition. Finally it would be interesting to know if the change in order occurs via a tricritical or critical end point and also what happens for more acute wedges with stronger wall potentials.

In this Letter we have presented our results of numerical studies of first-order and critical filling transitions in a rectangular wedge using a nonlocal density functional theory. This is the first time that filling transitions have been studied using modern microscopic DFT in the presence of long-ranged wall-fluid interactions, and the results show that close to the bulk critical temperature the wedge filling transition may be continuous even though the walls themselves exhibit first-order wetting.

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