RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 32, NUMBER 6 DECEMBER 1985

Capillary condensation versus prewetting

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(Received 15 July 1985)

The first-order prewetting transition that has been predicted to occur at the interface between a fluid and a single wall is investigated for the case of a fluid confined between two walls. Prewetting is found to be in competition with capillary condensation of the undersaturated gas to a liquid. The results of density-functional calculations suggest that only for wall separation $H > H_{\text{triple}}(T)$ will prewetting occur at larger undersaturations than condensation. For $H < H_{\text{triple}}(T)$ coexistence between *stable* thick and thin films will not be observed. Since H_{triple} is typically 100 molecular diameters or more, this places restrictions on those adsorption experiments and computer simulations that search for prewetting.

Consider a one-component fluid for which liquid l and gas g phases can coexist for temperatures $T < T_c$, the bulk critical temperature. Suppose that the fluid is in contact with an impenetrable substrate (wall) that exerts a potential V on the fluid molecules. If V is sufficiently attractive, l will be preferentially adsorbed at the wall. In the approach to coexistence from the undersaturated gas, a thick "wetting" film of l may or may not intrude between bulk g and the wall. For $T < T_w$ (partial wetting) the film thickness t remains finite as the chemical potential deviation $(\mu_{\text{sat}} - \mu) \equiv \Delta\mu \rightarrow 0$, while for $T \geqslant T_w$ (complete wetting) t diverges as $(\Delta\mu)^{\beta_s}$ with $\beta_s \leqslant 0$. The interfacial tensions γ, defined at saturation, satisfy Young's equation: $\gamma_{sg} = \gamma_{sl} + \gamma_{lg}\cos\theta$, where s denotes substrate, with contact angle $\theta > 0$ for $T < T_w$ and $\theta = 0$ for $T \geqslant T_w$. If t diverges, and $d(\cos\theta)/dT$ vanishes continuously, the surface phase transition at the wetting temperature T_w is second order (or critical), whereas if t and $d(\cos\theta)/dT$ jump discontinuously, the transition is first order. While both types of wetting transition[1] have been obtained from calculations on model systems[2] and should be observed in appropriate experiments,[2,3] there are good reasons for expecting the first-order transition to be more common.[4-6] The phase diagram for this case is sketched in Fig. 1. For $T > T_w$ and small undersaturations, a first-order transition from a thick to a thin liquid film will occur. Such films, with different thicknesses t, coexist on the "prewetting" or thick-thin transition line. This line terminates in a surface critical point at $T = T_{\text{sc}}$, where the films become identical, and meets tangentially the bulk coexistence curve at $T = T_w$. Several mean-field density-functional calculations of the prewetting line have been reported.[1(b),5,6] All indicate that this line lies very close to bulk coexistence, i.e., the surface critical point corresponds to $\delta \equiv (1 - \rho_b/\rho_{\text{sat}})$ of a few percent. ρ_b is the density of bulk g and ρ_{sat} its value at saturation. (Note that in a second-order wetting transition the prewetting line shrinks to zero.)

Much experimental and computational effort has been expended in the search for the prewetting transition. The only experimental evidence for this transition stems from very recent light scattering measurements on solid spheres immersed in a binary liquid mixture.[7] Prewetting does not appear to have been observed in computer simulations of continuum fluids,[8] although it was found in lattice gas simulations.[9] Given that many adsorption experiments employ solid material in a disperse form (particles) as a substrate and that simulations are usually performed for a fluid confined by *two* adsorbing walls, it is of interest to enquire whether confining geometry effects are important for prewetting and related phase transitions. Here we consider a fluid in contact with a reservoir at at fixed T and μ ($< \mu_{\text{sat}}$) confined by identical parallel walls separated by a finite distance H, but unbounded in the x-y directions. Whereas complete wetting and, hence, the wetting transition, can only occur for a semi-infinite system, since they are associated with infinitely thick films of l at coexistence, prewetting involves films of finite thickness and should occur in a finite system.[10] Thus we ask how the phase diagram of Fig. 1 is modified for finite H. We find that the prewetting transition is in competition with another first-order transition, namely, capillary condensation of the dilute "gas" to a dense "liquid" configuration that fills the slit. For values of $H < H_{\text{triple}}(T)$ condensation occurs for undersaturations $\Delta\mu$ that are larger than those at which prewetting occurs, so the latter cannot be observed except as a transition between metastable states. As the separations H_{triple} are surprisingly large—typically a hundred or more molecular diameters—this has important repercussions for

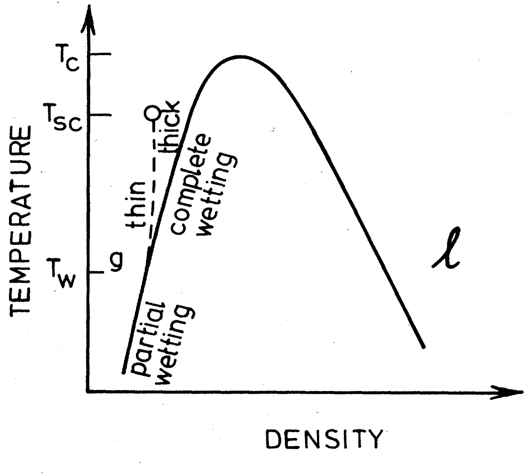

FIG. 1. Schematic temperature-density phase diagram for a semi-infinite system. The dashed curve is the prewetting line where thick and thin films coexist. Partial and complete wetting refers to bulk coexistence (solid curve) below and above T_w, respectively.

adsorption experiments and simulations of wetting transitions.

It is well known that in the limit of large H, condensation occurs when $\Delta\mu \sim 2\gamma_{lg}\cos\theta/H(\rho_l-\rho_g)$, where ρ_l and $\rho_g = \rho_{\mathrm{sat}}$ are the densities of coexisting bulk l and g phases at the given temperature. For $T > T_w$ this implies

$$\Delta\mu_{\mathrm{cond}}(H) \sim 2\gamma_{lg}/H(\rho_l-\rho_g) \ . \tag{1}$$

Equation (1) determines the shift of the bulk coexistence curve resulting from confinement of the fluid.[11] Only for $\Delta\mu < \Delta\mu_{\mathrm{cond}}(H)$ is gas the stable phase in the capillary. If $\Delta\mu_{\mathrm{cond}}(H) > \Delta\mu_{\mathrm{pw}}(H)$, the undersaturation appropriate to the prewetting transition, condensation will occur in preference to prewetting. Provided the interaction between films at different walls is weak, $\Delta\mu_{\mathrm{pw}}(H)$ is unlikely to be substantially different from $\Delta\mu_{\mathrm{pw}}(\infty)$, so we might estimate the separation H_{triple} at which liquid, thick, and thin films coexist by equating $\Delta\mu_{\mathrm{pw}}(\infty)$ with the right-hand side of (1). At low temperatures ($T \ll T_c$) and small undersaturations, $\Delta\mu \approx K_B T\ln(\rho_{\mathrm{sat}}/\rho_b) \sim K_B T\delta$, so that

$$\frac{H_{\mathrm{triple}}}{d} \approx 2\gamma^*_{lg} \Bigg/ \left[\frac{T}{T_c}(\rho^*_l-\rho^*_g)\delta_{\mathrm{pw}}\right] \ , \tag{2}$$

where we have defined dimensionless quantities $\gamma^*_{lg} = \gamma_{lg}d^2/K_BT_c$ and $\rho^* = \rho d^3$ in terms of the molecular diameter d. By use of the results of earlier density functional calculations[12] for a model fluid near a single wall exerting an exponential attractive potential, we can obtain the undersaturation ratio δ_{pw} at various temperatures on the prewetting line ($T_w = 0.58T_c$ and $T_{\mathrm{sc}} = 0.645T_c$ for this particular model system). The maximum value of $\delta_{\mathrm{pw}} = 0.05$ which occurs for $T = T_{\mathrm{sc}}$; the right-hand side of (2) is then ~ 70. For $T = 0.6T_c$, $\delta_{\mathrm{pw}} \approx 0.014$ and $H_{\mathrm{triple}} \sim 300d$.

In order to test this conjecture we performed identical density-functional calculations, but now with the fluid confined by two walls. These exert a total potential equal to $-\epsilon_w(e^{-\lambda_w z}+e^{-\lambda_w(H-z)})$ for $0<z<H$, and ∞ for $z \leq 0$ and $z \geq H$.

The repulsive forces between fluid molecules are modeled by hard spheres of diameter d and their contribution to the free energy is treated in local-density approximation. The attractive pairwise potential $w_2(r)$ is taken to be a Yukawa, $-\lambda_F^3\alpha e^{-\lambda_F r}/4\pi\lambda_F r$, and is treated in mean-field fashion. The parameters of the potentials ($\epsilon_w = 3K_BT_c$, $\lambda_w/\lambda_F = 0.8$, and $\lambda_F^{-1} = d$) were the same as those used earlier.[5] For the two-wall case we found it convenient to compute a dimensionless measure of the adsorption, $\Gamma_m \equiv d^3\int_0^H dz\,\rho(z)/H$. $\rho(z)$ is the density profile of the fluid. Results for $T = 0.60T_c$ and three different values of H are shown in Fig. 2. The adsorption isotherms exhibit loops with stable, metastable, and unstable portions, as is characteristic of capillary condensation.[13] Γ_m jumps discontinuously by a finite amount, from a small gaslike value to a large liquidlike value, at $\Delta\mu = \Delta\mu_{\mathrm{cond}}(H)$. The calculated values $\Delta\mu_{\mathrm{cond}}(H)$ are in reasonable agreement with estimates obtained from (1). For the two smaller separations we could not observe coexistence between thick and thin films in the capillary. Coexistence was found for the largest separation $\lambda_F H = 40$, but is between two distinct gas configurations that have a much higher grand potential than liquid. That is, the prewetting transition occurs between *metastable* films and $\Delta\mu_{\mathrm{pw}}(H) \ll \Delta\mu_{\mathrm{cond}}(H)$, for this H. The density profiles of the two films are almost identical to those calculated[5] for a single wall at the same temperature, and coexistence occurs at almost the same undersaturation ratio $\delta_{\mathrm{pw}} \approx 0.015$. Similar results were calculated for a higher temperature $T = 0.63T_c$; coexisting metastable thick and thin films were obtained for $\lambda_F H = 20$ and 30, but for $\lambda_F H \lesssim 16$ no prewetting was found.

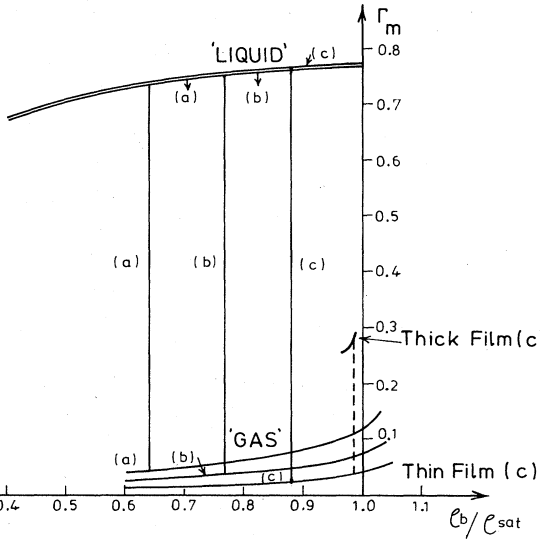

FIG. 2. Adsorption Γ_m as a function of bulk gas density ρ_b for $T = 0.6T_c$. (a) $\lambda_F H = 12$; (b) $\lambda_F H = 20$; and (c) $\lambda_F H = 40$. The vertical lines correspond to capillary condensation. For $\lambda_F H = 40$, a prewetting transition occurs (dashed vertical line) between metastable thick and thin films.

The phase equilibria can most easily be determined by examination of the interfacial free energy $\gamma(H)$, defined[14] as the excess grand potential per unit area of one wall, i.e., $2\gamma(H) = \Omega/A + pH$, where Ω is the total grand potential and p is the (bulk) pressure corresponding to fixed μ and T. A sketch of $\gamma(H)$ for a certain $\Delta\mu$ and T is shown in Fig. 3. Liquid is stable for $H < H_{\mathrm{cond}}$, but since this is metastable in bulk ($\Delta\mu > 0$)$\gamma_{\mathrm{liquid}}(H)$ increases as $H\Delta\mu$ as $H \to \infty$, and gas becomes the stable phase for $H > H_{\mathrm{cond}}$. The gas exhibits two branches corresponding to thick and thin films. When these have equal values of γ, at $H = H_{\mathrm{pw}}$, they coexist. By varying $\Delta\mu$ it is possible to construct the constant-

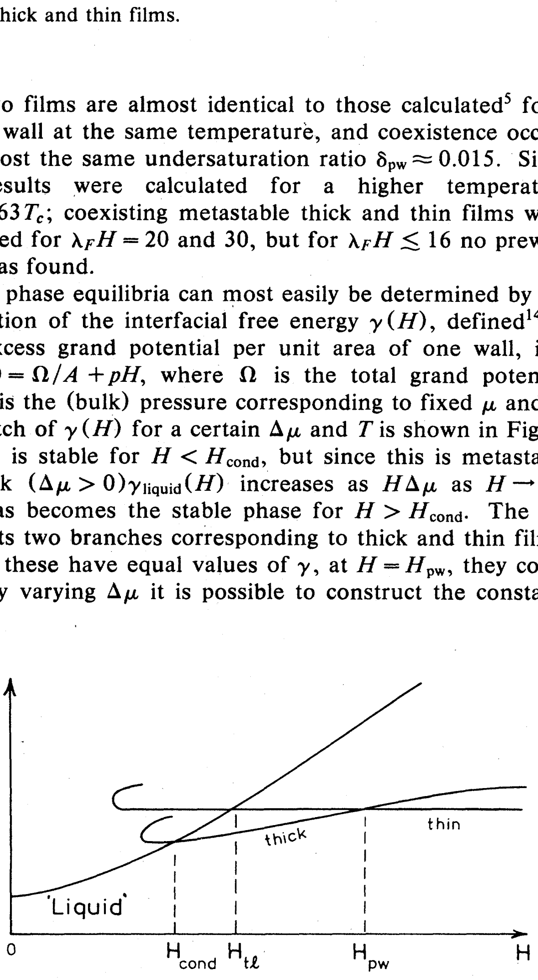

FIG. 3. The interfacial free energy $\gamma(H)$ for fixed $T_w < T < T_{\mathrm{sc}}$ and $\Delta\mu_{\mathrm{triple}} > \Delta\mu \gtrsim \Delta\mu_{\mathrm{pw}}(\infty)$ (schematic).

temperature phase diagram shown in Fig. 4. The condensation line $\Delta\mu_{\text{cond}}(H)$ has the shape suggested by Eq. (1), while the prewetting line is almost parallel to the H axis: $\Delta\mu_{\text{pw}}(H) \gtrsim \mu_{\text{pw}}(\infty)$. A triple point occurs where these lines intersect. Liquid, thin films, and thick films with equal γ or Ω all coexist in the capillary at this point. For $H < H_{\text{triple}}$ liquid is the stable phase, but coexistence between thick and thin metastable films can still occur, as indicated by the dashed line in Fig. 4. This is the situation described for $\lambda_F H = 40$ in Fig. 2. On reducing H further the thick film grows thicker, but eventually this solution disappears (Fig. 3) and no coexistence is possible. For $H > H_{\text{triple}}$ coexistence between the thin film and liquid can occur at $H = H_{tl}$, but both phases are metastable with respect to the thick film—see Fig. 3. The relevant line is marked by dots in Fig. 4; it merges smoothly into the condensation line at $H = H_{\text{triple}}$.

Phase equilibria was also investigated by minimizing a Landau free-energy functional of the type employed in some earlier studies[1(a),2] of prewetting at a single wall. The results are consistent with those described in Figs. 3 and 4.

In Fig. 5 a (tentative) phase diagram is sketched by use of three variables: $1/H$, T, and $\Delta\mu$. The prewetting surface is bounded in the $1/H = 0$ plane by the usual prewetting line AB and by a line of critical points BC. It intersects the surface formed by the lines of capillary condensation in a line of triple points CA. Point C is a critical end point. As $T \rightarrow T_w$, $\Delta\mu_{\text{pw}}(\infty) \rightarrow 0$, and $1/H_{\text{triple}} \rightarrow 0$ at the point A. Thus the "stable" portion of the prewetting surface is restricted to very small values of $1/H$, supporting the argument leading to (2). On the basis of (2) one might suppose that it would be easier to find stable prewetting [small $H_{\text{triple}}(T)$] as $T \rightarrow T_c$, since then $\gamma_{lg}/(\rho_l - \rho_g) \rightarrow 0$. However, calculations[6(b)] show that δ_{pw} becomes smaller at high temperature; $\delta_{\text{pw}} \approx 0.01$ for $T = T_{\text{sc}} = 0.90 T_c$. The length of the prewetting line AB is also much reduced.[6(b)] We conclude that for simple one-component fluids[15] capillary condensation will suppress the prewetting transition except at rather large wall separations.[16]

Our results are relevant for those adsorption experiments that use material such as graphon as a substrate. Typical distances between surfaces of particles[17] are about 100 Å. These are much less than the values H_{triple} estimated here. Computer simulations are currently restricted to $H \lesssim 40d$ and usually employ much smaller separations. Consequently one should not expect to see stable prewetting transitions in grand-canonical Monte Carlo calculations of the type performed in Ref. 8. Indeed, if one was searching for stable prewetting, it would be more efficient to replace one of the wall potentials by an external potential that mimics bulk g,[18] or to work with a fixed number of particles—although the interpretation of the results is less straightforward in this case. Of course, prewetting might occur in a grand-canonical simulation if it were possible to follow the metastable gas branch, $\Delta\mu > \Delta\mu_{\text{cond}}$, in Fig. 2, thereby avoiding condensation. It is likely that complex hysteresis of adsorption would then be observed. Finally, we remark that capillary condensation is also in competition with the formation of thick wetting films for $T > T_{\text{sc}}$ or for $T > T_w$ when the wetting transition is second order. For exponential or finite-ranged potential functions $\lambda_w t \sim -\ln(\Delta\mu/\epsilon_w)$, where ϵ_w is the strength and λ_w^{-1} is the range of the wall potential, assumed longer than that of fluid-fluid interactions λ_F^{-1}. Gas can only exist as the stable phase if $\Delta\mu > \Delta\mu_{\text{cond}}(H)$.

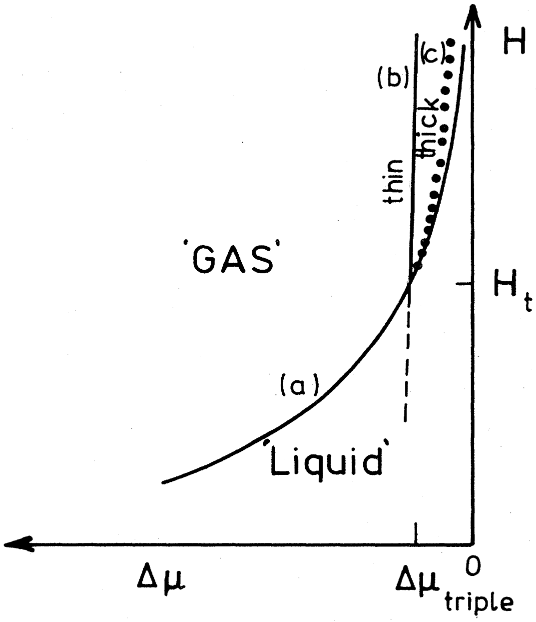

FIG. 4. Coexistence curves for fixed $T_w < T < T_{\text{sc}}$ (schematic). (a) Condensation line $\Delta\mu_{\text{cond}}(H)$; (b) prewetting line $\Delta\mu_{\text{pw}}(H)$ (the dashed portion refers to metastable films); (c) the dotted curve corresponds to coexistence between a metastable thin film and liquid (see text).

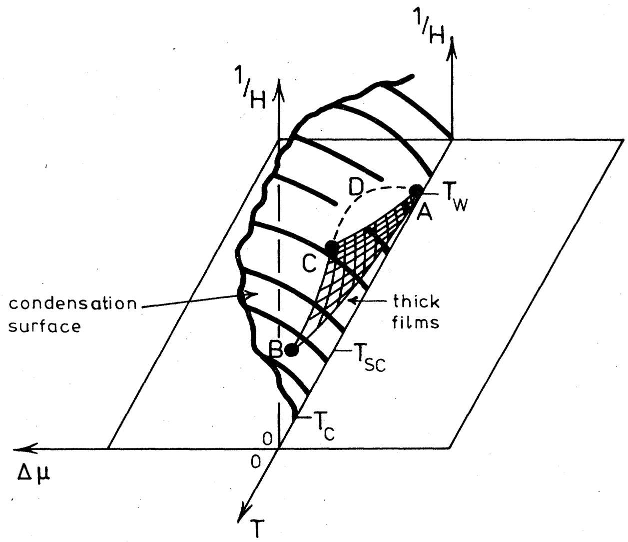

FIG. 5. Schematic phase diagram. Only a small section of the condensation surface is shown; this terminates at the bulk critical point $\Delta\mu = 0$, $T = T_C$, and $1/H = 0$. Thick and thin films coexist on the prewetting surface, and the hatched (stable) portion ABC lies inside, while the remaining (metastable) portion CDA lies outside the condensation surface. The intersection CA is a line of triple points (see text). (This diagram should be compared with Fig. 21 of Ref. 13, which displays the condensation surface in the case where there is no prewetting.)

From (1) it follows that the maximum film thickness t is approximately $\lambda_w^{-1}\ln[H(\rho_l-\rho_g)\epsilon_w/2\gamma_{lg}]$. For smaller $\Delta\mu$ liquid will fill the capillary in a grand-canonical simulation. Similar remarks apply in the complete drying regime.[19]

We have benefited from conversations and correspondence with P. Tarazona, M. M. Telo da Gama, and J. R. Henderson. This research was supported by the Science and Engineering Research Council of the United Kingdom.

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[1] First-order transitions were obtained first by (a) J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977); and (b) C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[2] For a comprehensive review, see D. E. Sullivan and M. M. Telo da Gama, in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1985). Earlier work is reviewed by R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

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[4] See, e.g., R. Lipowsky and D. M. Kroll, Phys. Rev. Lett. **52**, 2303 (1984); D. M. Kroll and T. F. Meister, Phys. Rev. B **31**, 392 (1985); S. Dietrich and M. Schick, *ibid.* **31**, 4718 (1985); T. Aukrust and E. H. Hauge, Phys. Rev. Lett. **54**, 1814 (1985); C. Ebner, W. F. Saam, and A. K. Sen, Phys. Rev. B **31**, 6134 (1985).

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[6] (a) G. F. Teletzke, L. E. Scriven, and H. T. Davis, J. Chem. Phys. **78**, 1431 (1983); (b) R. Evans and P. Tarazona, Phys. Rev. A **28**, 1864 (1983); (c) B. C. Freasier and S. Nordholm, Mol. Phys. **54**, 33 (1985).

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[10] This was also pointed out by H. Nakanishi and M. E. Fisher, J. Chem. Phys. **78**, 3279 (1983).

[11] It is equivalent to the standard Kelvin equation for condensation above T_w. For a recent discussion of its derivation and limitations see R. Evans and U. Marini Bettolo Marconi, Chem. Phys. Lett. **114**, 415 (1985), and Ref. 13.

[12] See Fig. 13 of Ref. 5.

[13] R. Evans, U. Marini Bettolo Marconi, and P. Tarazona (unpublished).

[14] In the limit $H\rightarrow\infty\gamma_{\text{gas}}(H)\rightarrow\gamma_{sg}$, the tension at a single wall—see Refs. 11 and 13.

[15] For a phase-separated binary liquid mixture the liquid-liquid surface tension can be rather small even at temperatures well below the consolute point. This might reduce H_{triple} for such a mixture confined by two walls.

[16] Preliminary results of ours for fluids confined by *cylindrical* pores indicate that stable prewetting should persist to radii R that are considerably smaller than the values of H_{triple} discussed here. The prewetting line $\Delta\mu_{\text{pw}}(R)$ slopes toward large $\Delta\mu$ in a more pronounced fashion than $\Delta\mu_{\text{pw}}(H)$ shown in Fig. 4.

[17] See, for example, S. Blümel and G. H. Findenegg, Phys. Rev. Lett. **54**, 447 (1985).

[18] Such a procedure was used in Ref. 9 where prewetting was observed.

[19] Films of gas can intrude between bulk l and hard walls ($\epsilon_w=0$) as $\mu\rightarrow\mu_{\text{sat}}$ from above. However, capillary evaporation to a gas will occur when $|\Delta\mu|\approx 2\gamma_{lg}/H(\rho_l-\rho_g)$ and the maximum film thickness is $t\sim\lambda_F^{-1}\ln[H(\rho_l-\rho_g)\alpha\rho_g/4\gamma_{lg}]$. Recent simulations of drying [F. van Swol and J. R. Henderson, Phys. Rev. Lett. **53**, 1376 (1984)] for a liquid confined by two hard walls did find thick gas films at very small $|\Delta\mu|$, but these results were for a fixed number of molecules.