Theory of Condensation in Narrow Capillaries

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By means of a density functional approach, the phase equilibria of a fluid confined between two adsorbing walls, i.e., in a slitlike capillary, have been investigated. The theory provides a microscopic basis for the phenomenon of capillary condensation and, for fluids in narrow slits, predicts a line of critical points marking the end of the lines of coexistence between "liquid" and "gas" phases.

A fluid whose chemical potential is less than its value at saturation, and is, therefore, a gas *in bulk*, can condense to form a liquid inside a narrow capillary. This phenomenon of capillary condensation plays a major role in the adsorption of gases by mesoporous solids. Such materials contain a network of capillaries whose radii lie, typically, in the range 10 to 250 Å. The measured adsorption isotherms for mesoporous solids exhibit characteristic features which are attributed to capillary condensation and which are made to yield information concerning the surface area and pore structure of the solid.[1] The pressure at which condensation (or evaporation) occurs is related to the pore radius by use of the *macroscopic* Kelvin equation for the pressure of a gas in equilibrium with a liquid meniscus. Despite several attempts[1,2] to develop versions of the Kelvin equation appropriate for small radii, the physics of capillary condensation and, in particular, the regime of validity of the Kelvin equation remain poorly understood. In this Letter we report some results of a (mean-field) microscopic theory for the phase equilbria of fluids in a *single*[3] slitlike capillary. Our analysis takes proper account of solid-fluid interactions, or "adsorption forces" as they are termed in the literature.[1,2] We believe this to be the first statistical treatment[4] of capillary condensation and evaporation and the first theory appropriate for narrow capillaries. The capillary phase diagram exhibits a surprisingly rich structure when the slit is a few molecular diameters wide and our results indicate that fluids between adsorbing walls can undergo phase transitions which are different from, but no less diverse than, the wetting transition[5] that occurs at a single wall.

Consider a model capillary consisting of two adsorbing solid walls located at $z = 0$ and $z = H$, and unbounded in the x and y directions. The capillary is in contact with a reservoir at temperature T and chemical potential μ. For a given separation H the fluid in the capillary will adopt the configuration which minimizes the grand potential per unit area, $\omega(H) = -pH + 2\gamma(H)$. Here p is the (bulk) pressure corresponding to (μ, T) and $\gamma(H)$ is the interfacial free energy per unit area. In the limit $H \to \infty$, $\gamma(H) \to \gamma_{sf}$, the solid-fluid or wall-fluid surface tension. The fluid can be liquid or gas.

We examine first the situation where $\mu = \mu_{sat}$, the chemical potential at saturation, so that *bulk* liquid and gas coexist. It is clear that in the limit $H \to \infty$ the equilibrium configuration in the capillary is that which corresponds to the lower surface tension. At high temperatures it is expected that most fluids will wet or partially wet most solids,[5] i.e., the contact angle θ should be less than $\pi/2$, so that Young's equation implies $\gamma_{sl} < \gamma_{sg}$ and the fluid should adopt a "liquid" configuration. The latter is characterized by a high, liquidlike, density for most values of z inside the capillary. At low temperatures, however, it is possible to find systems for which $\theta > \pi/2$ and $\gamma_{sl} > \gamma_{sg}$ so that a "gas" configuration, in which the density exhibits small, gaslike, values, is the stable one. We denote by T_s the temperature at which a transition between the two configurations will occur[6] (for $H = \infty$). Evidently $\gamma_{sg}(T_s) = \gamma_{sl}(T_s)$ or $\theta(T_s) = \pi/2$. For *finite* separations the phase equilibrium is determined by the difference $\gamma_{liq}(H) - \gamma_{gas}(H)$, where the subscripts refer to the possible configurations. The theory we have developed allows us to compute this difference for a particular model.

Our model is a direct generalization to two walls of that introduced by Sullivan[7] in his elegant analysis of wetting transitions and contact angles at a single wall. The equilibrium density profile of the fluid, $\rho(z)$, is obtained by minimizing the grand potential functional,

$$\Omega_V[\rho] = \int d^3r \, f_H(\rho(z)) + \tfrac{1}{2} \int\int d^3r \, d^3r' \, w_2(|\vec{r} - \vec{r}'|)\rho(z)\rho(z') - \int d^3r[\mu - V(z)]\rho(z). \tag{1}$$

The first two terms in (1) represent the free energy arising from fluid-fluid interactions. Repulsive forces are treated in a local density approximation[8]: $f_H(\rho)$ is the Helmholtz free energy density of a uniform hard-sphere fluid of density ρ. Attractive forces are treated in mean-field fashion: $w_2(r)$ is the attractive part of the pairwise potential between fluid molecules. The integral equation for $\rho(z)$ which results from the minimization of (1) can be transformed into a nonlinear differential equation of precisely the same form as that given by Sullivan,[7] provided that we set $w_2(r) = -\alpha\lambda^3\exp(-\lambda r)/4\pi\lambda r$ and the solid-fluid potential $V(z) = V_s(z) + V_s(H - z)$, where $V_s(z)$ is the single-wall–fluid potential of Sullivan. That is, $V_s(z) = -\epsilon_w\exp(-\lambda z)$ for $z > 0$ and $= \infty$ for $z < 0$. The parameters α and ϵ_w are positive and characterize the strength of the attractive fluid-fluid and wall-fluid potentials, respectively. λ^{-1} is a measure of the range of both potentials. The boundary conditions on $\rho(z)$ differ from those of the single-wall problem and the method of solving the equation will be discussed elsewhere.

We find that the solutions exhibit different branches corresponding to gas and liquid configurations. The interfacial free energy associated with each branch, $\gamma_{gas}(H)$ and $\gamma_{liq}(H)$, can be evaluated following a procedure similar to that of Sullivan.[7] Both branches exist for large H but as $H \to 0$ the metastable branch terminates and only the stable branch, corresponding to the smaller $\gamma(H)$, persists to $H = 0$. If, for given (μ, T), the functions $\gamma_{liq}(H)$ and $\gamma_{gas}(H)$ intersect with different slopes at a certain value of $H = H_t(T)$ there will be a first-order transition from one equilibrium configuration to the other. At $H = H_t(T)$ the gas and liquid configurations coexist. If, on the other hand, these functions meet contiguously at the value of H which marks the end of the metastable branch there will be a continuous, second-order, transition at that point and the latter will be the critical point at the end of the coexistence line. In the present model, $\gamma(H) \sim \gamma_{sf} - C\exp(-\lambda aH)$ for large H. Here C is a positive constant and $a = (1 + \alpha\kappa_T\rho_f^2)^{-1/2}$, where κ_T is the isothermal compressibility of the bulk fluid of density ρ_f. Since at low temperatures the density of the coexisting bulk liquid ρ_l is very much larger than that of the bulk gas, ρ_g, $a_{liq} \ll a_{gas}$ and $\gamma_{liq}(H)$ decreases much more rapidly with decreasing H than does $\gamma_{gas}(H)$. Thus for all $T > T_s$, $\gamma_{liq}(H) < \gamma_{gas}(H)$ for all H and the liquid configuration is stable for all separations. At $T = T_s$ liquid and gas coexist for $H = \infty$ but for all

finite H the liquid is stable. For $T < T_s$ the gas is stable for large H but at $H = H_t(T)$ there is a first-order transition to a liquid which then persists as the stable configuration for all $H < H_t(T)$. If T is reduced further, $H_t(T)$ decreases until eventually, at the capillary critical temperature T_{cc}, $\gamma_{gas}(H)$ and $\gamma_{liq}(H)$ meet contiguously at $H = H_{cc}(T_{cc})$. The relevant phase diagram is plotted in Fig. 1. This is calculated for a wall potential[9] with $\epsilon_w = 2.114k_B T_c$, where T_c is the bulk critical temperature.[10] The temperature for which $\theta = \pi/2$ is $T_s = 0.57T_c$ which is well below the temperature $(T_w = 0.96T_c)$ at which the transition[7] to complete wetting occurs $(\theta = 0)$ in this model. At $T = T_{cc} = 0.439T_c$ and $H = H_{cc}(T_{cc}) \sim 1.45\lambda^{-1}$ the density profiles $\rho(z)$ of gas and liquid are identical. For $T < T_{cc}$ the gas configuration is stable for all H. If we interpret λ^{-1} as the correlation length of the bulk fluid it follows that $H_{cc} \sim 2$ or 3 molecular diameters and we must expect the distinction between gas and liquid to disappear at such small separations.[11]

The phenomenon of capillary condensation is usually associated with undersaturated gases, i.e., $\mu < \mu_{sat}$. In this case the gas is always the stable configuration as $H \to \infty$ since the difference in grand potentials now contains a contribution which increases linearly with H:

$$\omega_{liq}(H) - \omega_{gas}(H)$$
$$= (p - p_l^\dagger)H + 2[\gamma_{liq}(H) - \gamma_{gas}(H)]. \tag{2}$$

p is the pressure of the bulk gas and $p_l^\dagger$ is the pressure of the metastable bulk liquid at the same chemical potential μ. For large H (and small
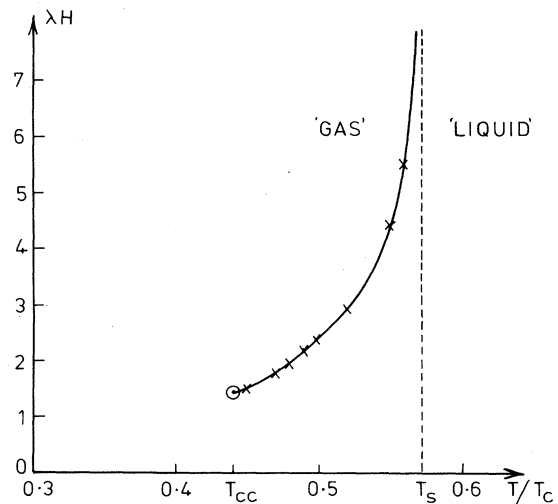

FIG. 1. The coexistence curve for $p = p_{sat}$.

undersaturations) $\gamma_{liq}(H) \sim \gamma_{sl}$ and $\gamma_{gas}(H) \sim \gamma_{sg}$. Equation (2) then implies that the fluid will condense to a liquid when

$$p - p_l^\dagger = 2\gamma_{lg} \cos\theta/H, \qquad (3)$$

where we have used Young's equation to introduce θ and the liquid-gas surface tension, γ_{lg}. This result has an immediate macroscopic interpretation. The right-hand side is the pressure difference across the concave cylindrical meniscus[12] that forms when the slit is filled with wetting liquid ($\theta < \pi/2$). As μ is increased $p - p_l^\dagger$ decreases until it reaches this value; then condensation will occur. [For small undersaturations $p - p_l^\dagger = (\mu_{sat} - \mu)(\rho_l - \rho_g)$.] If we make the additional assumption that the gas is ideal, (3) reduces to the Kelvin equation[13]:

$$\ln(p_{sat}/p) = 2\gamma_{lg} \cos\theta/H k_B T(\rho_l - \rho_g), \qquad (4)$$

where p_{sat} is the saturated vapor pressure. This derivation should clarify the status of the Kelvin equation for capillary condenstation; Eq. (4) constitutes a rigorous criterion for condensation in the limit $H \to \infty$—provided that the gas is sufficiently dilute to be treated as ideal. At high temperatures, where ρ_g is larger, the "Laplace" form will be more accurate.

For smaller values of H it is necessary to calculate the detailed behavior of $\gamma_{gas}(H)$ and $\gamma_{liq}(H)$. We have performed calculations for the model described above for various undersaturations (and supersaturations) at temperatures in the neighborhood of T_s. Results for the capillary phase eq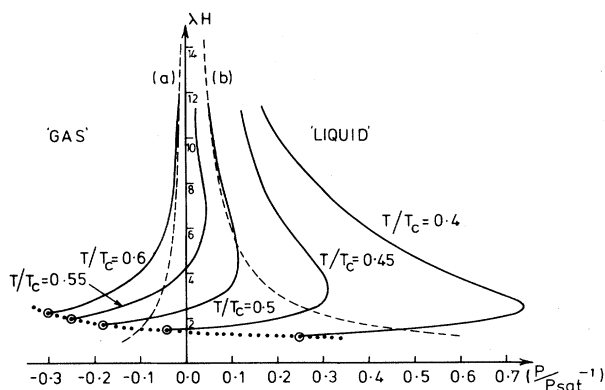uilibria are shown in Fig. 2. The liquid-gas coexistence curve for $T = 0.6 T_c$ ($> T_s$) follows accurately curve a, the Kelvin prediction [Eq. (4)] for $H \gtrsim 10\lambda^{-1}$. For smaller H the Kelvin equation grossly overestimates the pressure required to induce condensation. The coexistence curve terminates in a critical point at $H = H_c(T)$ and a critical pressure $p = p_c(T)$. Only gas is stable for $p < p_c(T)$. If $T > T_s$ the liquid is always the stable configuration for $p > p_{sat}$ and there is no transition in the supersaturated fluid.

The other coexistence curves refer to $T < T_s$ and these exhibit more structure. For $p < p_{sat}$ the gas is the stable configuration for most values of H; note $\gamma_{sg} < \gamma_{sl}$. Condensation does occur, however, at finite undersaturation, for small values of H, provided $T > T_{cc}$. The rapid decrease of $\gamma_{liq}(H)$ with decreasing H stabilizes the liquid. At all $T > T_{cc}$ there is a critical point with a critical pressure $p_c(T) < p_{sat}(T)$. At temperatures below T_s the coexistence curves of the *supersaturated* fluids follow the Kelvin prediction[15] rather accurately for $H \gtrsim 8\lambda^{-1}$. This is illustrated for $T = 0.5 T_c$. These curves exhibit loops for smaller H so that for $T_s > T > T_{cc}$ and a small supersaturation the fluid will undergo two transitions —from liquid to gas to liquid as H is reduced. Above a certain pressure, which depends on T, the liquid is always stable. For $T < T_{cc}$ the critical pressure $p_c(T)$, which marks the end of the coexistence curve, is greater than $p_{sat}(T)$ and there is only one transition from liquid to gas as H is reduced for $p_c(T) > p(T) > p_{sat}(T)$.

These results and, in particular, the *shapes* of the coexistence curves will probably be strongly model dependent. It is the rapid decrease of $\gamma_{liq}(H)$ with decreasing H which produces a positive gradient in Fig. 1 and loops for $p > p_{sat}$. Allowing the wall-fluid potential to be longer ranged than the fluid-fluid potential will change the form[16] of $\gamma_{liq}(H)$ and might yield loops for $p < p_{sat}$. We should note, moreover, that the incorporation of short-ranged correlations, which are absent from the present theory,[8] might modify our results at very small H. Nevertheless, our prediction of a line of critical points should remain valid.

As mentioned earlier, physical chemists have often speculated on the limit of validity of the Kelvin equation (4). Our present results indicate that this will be accurate for slits wider than 10–15 molecular diameters. For narrower slits our theory predicts significant deviations from the Kelvin result and complex phase equilibria. While it will be difficult to test these predictions by adsorption measurements on real materials

FIG. 2. The coexistence curves, at different temperatures T, as a function of gas pressure p (see Refs. 14 and 15). The dotted line marks the line of critical points $H_c(T)$. The dashed lines a and b are the results of the Kelvin equation (4) for $T/T_c = 0.6$ and 0.5, respectively.

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it should be possible to carry out computer simulations of model capillaries. Indeed Lane and Spurling[17] have performed Monte Carlo calculations of an undersaturated gas between two adsorbing walls and observed a first-order transition to a liquid when H was reduced to about 5 molecular diameters. Their calculation corresponds to $\theta \ll \pi/2$. It would be interesting to perform similar calculations for lower temperatures where $\theta \sim \pi/2$. On the experimental side it would be useful to measure the force f between the two "walls" with the technique pioneered by Israelachvili.[18] Since $f = -[\partial\gamma(H)/\partial H]_{\mu, T}$ the force will change discontinuously at a first-order transition.

[1]See, for example, S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity* (Academic, London, 1982), Chap. 3.

[2]J. C. P. Broekhoff and J. H. de Boer, J. Catal. 9, 8 (1967). See also the review by D. H. Everett and J. M. Haynes, in *Colloid Science Vol. 1: Specialist Periodical Reports* (Chemical Society, London, 1973), p. 123.

[3]We do not consider the effects of a network structure nor do we discuss hysteresis of adsorption isotherms in this article.

[4]Several authors have considered the effects of confining walls on the *critical* behavior of fluids; see, for example, H. Nakanishi and M. E. Fisher, J. Chem. Phys. 78, 3279 (1983), and references therein. Here we are concerned with temperatures well below the bulk critical temperature.

[5]J. W. Chan, J. Chem. Phys. 66, 3667 (1977); C. Ebner and W. F. Saam, Phys. Rev. Lett. 38, 1486 (1977), and many recent papers.

[6]In any real or model system T_s might lie below the triple point.

[7]D. E. Sullivan, Phys. Rev. B 20, 3991 (1979), and J. Chem. Phys. 74, 2604 (1981).

[8]This approximation (see Ref. 7) neglects short-ranged correlations so that the density profiles do not exhibit oscillatory behavior near the wall.

[9]This value of ϵ_w would be appropriate for a model of Ar at a solid CO_2 substrate.

[10]Our calculations make use of the Carnahan and Starling result for $f_H(\rho)$. T_c is then given by $k_B T_c d^3 = 0.0901\alpha$, where d is a hard-sphere diameter (see Ref. 7).

[11]Capillaries of this size would be classified as micropores (see Ref. 1).

[12]Equation (3) follows directly from the Laplace equation; the mean radius of curvature is $H/\cos\theta$ (Ref. 1).

[13]For the more common example of an open cylindrical capillary the same result is obtained with H replaced by r, the radius of the cylinder. Both formulas have been applied to *desorption* (evaporation of the condensate) in mesopores (see Ref. 1).

[14]For supersaturated fluids p is $p_g{}^\dagger$.

[15]Since $\theta > \pi/2$ the meniscus is now convex and (3) is replaced by $p - p_g{}^\dagger = -2\gamma_{lg}\cos\theta/H$, where p is the pressure of the bulk liquid and $p_g{}^\dagger$ is the pressure of the (metastable) gas at the same chemical potential. In (4) p must be replaced by $p_g{}^\dagger$.

[16]The range of the wall-fluid potential plays a crucial role in the theory of wetting transitions [see P. Tarazona and R. Evans, Mol. Phys. 48, 799 (1983)] since it determines the form of the free energy of a thick film.

[17]J. E. Lane and T. H. Spurling, Aust. J. Chem. 33, 231 (1980), and 34, 1529 (1981). Our work provides an immediate explanation of their result.

[18]See, for example, R. G. Horn and J. N. Israelachvili, Chem. Phys. Lett. 71, 192 (1980).