Three-Phase Fluid Coexistence in Heterogenous Slits

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We study the competition between local (bridging) and global condensation of fluid in a chemically heterogeneous capillary slit made from two parallel adjacent walls each patterned with a single stripe. Using a mesoscopic modified Kelvin equation, which determines the shape of the menisci pinned at the stripe edges in the bridge phase, we determine the conditions under which the local bridging transition precedes capillary condensation as the pressure (or chemical potential) is increased. Provided the contact angle of the stripe is less than that of the outer wall we show that triple points, where evaporated, locally condensed, and globally condensed states all coexist are possible depending on the value of the aspect ratio $a = L/H$, where H is the stripe width and L the wall separation. In particular, for a capillary made from completely dry walls patterned with completely wet stripes the condition for the triple point occurs when the aspect ratio takes its maximum possible value $8/\pi$. These predictions are tested using a fully microscopic classical density functional theory and shown to be remarkably accurate even for molecularly narrow slits. The qualitative differences with local and global condensation in heterogeneous cylindrical pores are also highlighted.

Confined fluids can exhibit dramatically different phase behavior and associated phase transitions to that occurring in the bulk [1–3]. Even for a single wall (substrate), the presence of the wall-fluid interaction induces rich new surface phase phenomena: wetting transitions are a very well-known example of this [4–7]. The complexity of the fluid phase behavior is further enriched if the wall is geometrically or chemically heterogeneous [8]. Wedge filling [9–12], step wetting [13], bridging [14–16], and the change from Cassie's [17] to Wenzel's [18] state are but a few examples of phase transitions directly induced by the substrate geometry. Another related phenomenon is capillary condensation referring to the shift of the bulk liquid-gas phase boundary, when a fluid is confined between two parallel walls separated by a distance L. Macroscopically, the shift in the chemical potential, relative to saturation, at which capillary condensation (CC) occurs is given by Kelvin's equation

$$\delta\mu_{\mathrm{CC}} \equiv \mu_{\mathrm{sat}} - \mu_{\mathrm{CC}} = \frac{2\gamma\cos\theta}{L\Delta\rho}, \qquad (1)$$

where γ is the liquid-gas surface tension, θ is Young's contact angle, and $\Delta\rho$ is the difference between the number densities of coexisting liquid and gas. Here, the Laplace pressure δp due the curved interface separating liquid and gas phases has been approximated by $\delta p \approx \delta\mu_{\mathrm{CC}}\Delta\rho$ valid for small undersaturation [19]. Studies based on microscopic density functional theory (DFT) models [5,20] have shown that the Kelvin equation is remarkably robust. This is particularly true for partial wetting ($\theta > 0$), where thick wetting layers are absent at each wall.

There have also been a number of studies of fluid confinement between walls that are themselves geometrically sculpted or patterned, that is when translational invariance is broken both across and along the slit [21–29]. In particular, numerical DFT studies have established that capillary condensation, which must still be present, competes with other types of phase transition induced by the patterning or equivalently that the condensation occurs in two steps. In this Letter, we show that this problem can be studied analytically and derive results characterizing the two step condensation which apply to capillaries of all scales from the macroscopic down to the molecular. To do this we consider the case in which each wall is chemically heterogeneous and has a macroscopically long stripe or
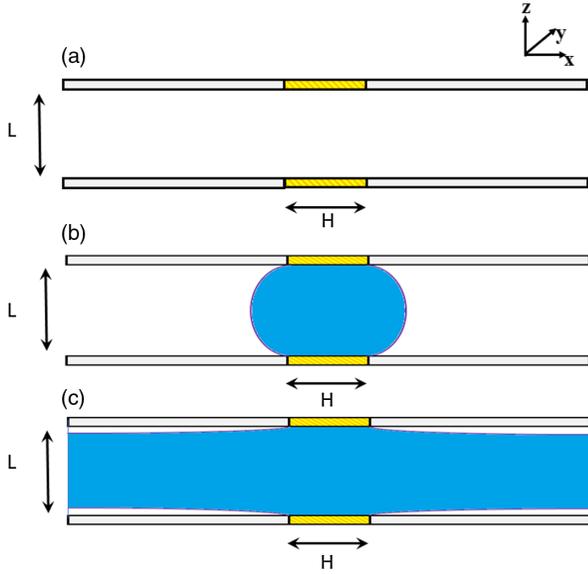
FIG. 1. Illustration of (a) gaslike, (b) locally condensed bridge-like, and (c) liquidlike states in a chemically heterogenous slit. Possible configurations depend on μ.

patch of width H for which the local contact angle is θ_p. Outside of this region the wall is made from a different material where the contact angle is θ. The stripes are adjacent and parallel (see Fig. 1). Since the outer wall area is macroscopically large the location of the global capillary condensation from a gaslike to a liquidlike phase as the chemical potential is increased is unaffected by the presence of the stripes. However, if $\theta_p < \pi/2$ (so there is greater affinity to liquid than to gas) *and* $\theta_p < \theta$, so that it preferentially adsorbs the liquid relative to the outer wall, it is also possible that the fluid locally condenses forming a liquid bridge between the patches. This is a third possible phase for the confined fluid which competes with the evaporated (gaslike) and globally condensed (liquidlike) fluid states (see Fig. 1). Here, we establish the conditions under which local condensation (bridging) precedes capillary condensation as the chemical potential is increased towards saturation. Our analysis uses a modified Kelvin equation not considered in previous works which allows for an edge contact angle θ_E which describes the shape of the menisci pinned at the edges of both patches. Our main new result is that for a slit maximum wetting contrast in which a completely wet stripe is embedded within completely dry wall, the value of the aspect ratio determining the triple point is maximum and takes a universal value $8/\pi$. This prediction is tested using microscopic DFT and is shown to be extraordinarily accurate even for molecularly narrow slits.

Let us begin with mesoscopic considerations. As mentioned above, since the outer wall area is infinitely greater than that of the patch the global condensation from a gaslike to liquidlike state occurs at the same chemical

potential $\delta\mu_{CC}$ identified by the standard Kelvin equation. We next need to determine the chemical potential at which a gaslike phase locally condenses forming a bridge between the patches. Here, we use a modified Kelvin equation similar to one recently proposed for opened slits. This bridge phase is characterized by two circular menisci of Laplace radius $R = \gamma/\delta p$ which separate the liquid within the bridge from the gas in the outer regions of the capillary. These menisci are necessarily pinned at the edges of the patch and meet the walls with an edge contact angle θ_E whose value depends on the thermodynamic state, as well as the properties of the heterogenous slit. However, exactly at the bridging transition, the value of θ_E depends only on the contact angle of the patch θ_p and the aspect ratio $a \equiv L/H$; there is no dependence on the outer contact angle θ since the exposed wall surface area to the vapor phase is the same for the evaporated and bridge phases.

The situation is closely analogous to condensation in an open slit and balancing the bulk and surface free-energy contributions of the evaporated and bridge phases determines that a local condensation to the bridge phase occurs at the chemical potential $\mu_b \equiv \mu_{sat}(T) - \delta\mu_b$ where the shift is determined by the modified Kelvin equation

$$\delta\mu_b = \frac{2\gamma \cos \theta_E}{L\Delta\rho}. \qquad (2)$$

Here, θ_E is the edge contact angle whose value at the bridging transition is given by [30,31]

$$\cos\theta_p = \cos\theta_E + \frac{a}{2}\left[\sin\theta_E + \sec\theta_E\left(\frac{\pi}{2} - \theta_E\right)\right] \qquad (3)$$

which, as mentioned above, is independent of the properties of the outer wall.

Comparing the chemical potential shifts (1) and (2) immediately determines what phases are stable and metastable in the heterogeneous capillary slit. It follows that on increasing the chemical potential a bridging transition precedes the global condensation only if $\theta_E < \theta$ since the chemical potential shift $\delta\mu_b > \delta\mu_{CC}$. In this case on increasing μ the gaslike phase in capillary first locally condenses (bridges the walls) near the patch at the chemical potential μ_b. On further increasing the chemical potential the bridge phase eventually condenses to a liquidlike phase when the chemical potential reaches μ_{CC}. During this process the value of the edge contact angle increases continuously from its value given by (3) at μ_b taking the value θ exactly at μ_{CC}. This means that at the condensation the menisci are no longer pinned at the edges by the macroscopic forces of tension, i.e., translating the menisci away from the patch does not alter the macroscopic free energy. We return to this later in our discussion of fluctuation effects. On the other hand, if $\theta_E > \theta$ the global condensation occurs prior to the bridging which is only

ever a possible metastable phase. These two possibilities are separated by the case $\theta_E = \theta$ which is the condition for a triple point where all three phases coexist.

It follows that for given contact angles θ_p and θ, the value of the aspect ratio a_T at which a triple point occurs is given by

$$a_T = \frac{2(\cos\theta_p - \cos\theta)}{\sin\theta + \left(\frac{\pi}{2} - \theta\right)\,\sec\theta}. \quad (4)$$

Only if the aspect ratio $a < a_T$ does a bridging transition precede global capillary condensation. Therefore, as anticipated, bridging is only possible if the contact angle in the patch $\theta_p < \theta$. It is only in this case that the free-energy cost of creating two menisci is compensated by the greater affinity of the patches for the liquid. We can also identify that the condition for the maximum value of the triple-point aspect ratio. This corresponds to a heterogeneous slit of maximum contrast (MC) comprising a completely wet patch ($\theta_p = 0$) embedded within a completely dry outer wall ($\theta = \pi$). These values of the contact angles minimize the denominator and maximize the numerator in (4) leading to the intriguing value

$$a_T^{\mathrm{max}} = \frac{8}{\pi}. \quad (5)$$

Thus, only for $a < 8/\pi$ will a MC slit exhibit a bridging transition which precedes a global capillary condensation. We also note that for $a < 1$ the value of μ_b at which this occurs is less than μ_{sat} meaning that the menisci are concave. For aspect ratio $a = 1$ the bridging transition occurs exactly at μ_{sat} and the menisci are flat. For $a > 1$ the menisci are convex and the bridging transition occurs at $\mu_b > \mu_{\mathrm{sat}}$.

We test these predictions using a microscopic DFT to determine equilibrium density profiles $\rho_{\mathrm{eq}}(\mathbf{r})$ and the corresponding free energies of possible stable or metastable states. These are obtained by minimization of the grand potential functional

$$\Omega[\rho] = F[\rho] - \int d\mathbf{r}[\mu - V(\mathbf{r})]\rho(\mathbf{r}), \quad (6)$$

where $V(\mathbf{r})$ is the external potential exerted by the heterogenous slit and $F[\rho]$ is the intrinsic free energy functional of the one-body density $\rho(\mathbf{r})$. We concentrate on the maximum contrast slit geometry and the prediction (4) for the value of a_T^{max}. Explicit expressions for the corresponding external potential as well as the approximative free-energy functional adopted are shown in the Supplemental Material [31].

We have considered two different values of the patch width $H = 10\sigma$ and $H = 20\sigma$ and for each varied the slit width L, thus varying the aspect ratio a. For a given aspect
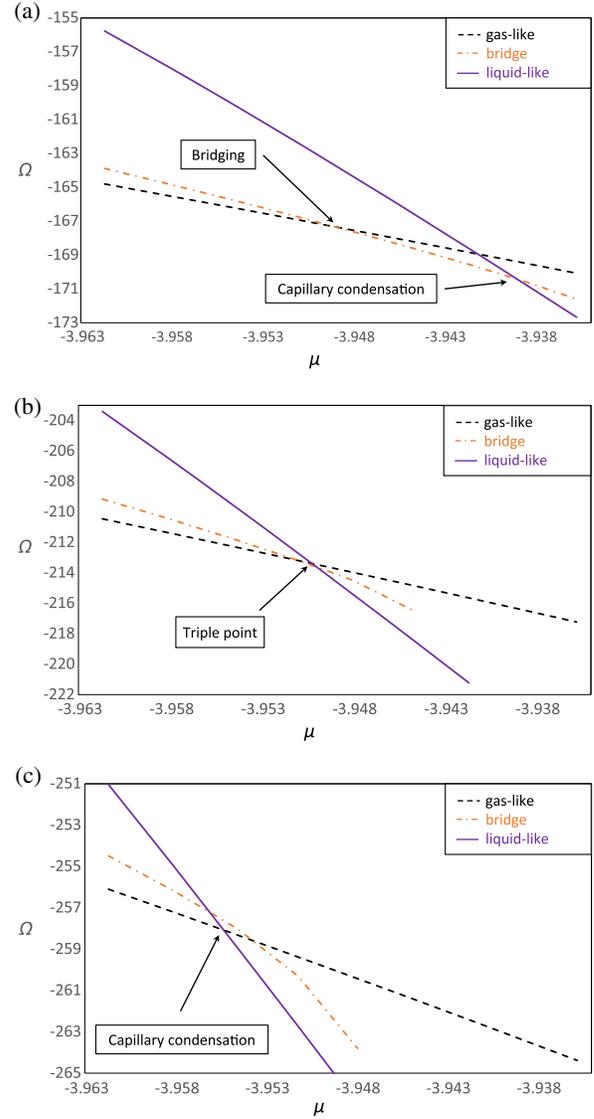
FIG. 2. DFT results for the grand potential as a function of the chemical potential (both in units of ε) for the maximum contrast slit with $\theta_p = 0$ and $\theta = \pi$ and $H = 10\sigma$. Three values of L are shown corresponding to the aspect ratios (a) $a = 2.3$ for which bridging precedes the global capillary condensation, (b) $a = 2.6$ our best estimate of the triple point, and (c) $a = 2.8$ where only single capillary condensation transition is stable and the bridge configurations are always metastable. Our estimate to the triple point $a = 2.6$ is very close to the predicted value a_T as given by (5).

ratio we varied the chemical potential and determined the equilibrium stable and metastable phases corresponding to evaporated, bridged, and condensed states. This is achieved by determining numerically the minimal grand potential using Picard's iteration starting from an initial configuration corresponding to these phases. In Fig. 2 we present results for the grand potential as a function of the chemical potential for $a = 2.3$, $a = 2.6$, and $a = 2.8$ for the smallest system size $H = 10\sigma$. For the smallest value of a we

observe two kinks in the minimum value of the grand potential corresponding to bridging and global capillary condensation transitions as the chemical potential is increased. On increasing the value of a the kinks move closer and eventually merge at a value $a = 2.6$ which, even for this microscopically small patch, is very close to the prediction (4). For the largest value of a shown there is only one kink which corresponds to single capillary condensation. Bridge states also exist but have a higher grand potential and are therefore metastable. Similar results have been obtained for larger values of H with the aspect ratio corresponding to the triple point always very close to the predicted value $8/\pi$.

To finish our Letter we mention three further points. First, so far we have supposed that the contact angle of the patch is less than that of the outer wall. If we reverse this scenario, so that $\theta_p > \theta$ and $\theta_p > \pi/2$, then the patch has greater affinity for the gas compared to the outer wall. In this case, analogous bridging transitions take place but involve a bubble of gas that with two menisci separating the bubble from the outer liquid. Thereafter, the analysis of the bridging and global condensation transitions remains the same including the location of the triple point, although the numerator in (4) is replaced by $\cos\theta - \cos\theta_E$.

Second, we mention that qualitatively similar phenomena occur in a heterogenous cylindrical pore of radius $\mathcal{R}$ containing a patch of width H for which the local contact angle is θ_p. For this we define an aspect ratio $a^{cyl} = 2\mathcal{R}/H$. Again, assuming that θ_p is less than the contact angle θ of the outer wall, we must consider the possibility of a local bridging transition occurring at $\delta p = 2\gamma \cos\theta_E^{cyl}/\mathcal{R}$ and a global condensation occurring at $\delta p = 2\gamma \cos\theta/\mathcal{R}$. The value of θ_E^{cyl} at the transition is again known from previous studies of condensation in open pores [30]. The analysis is analogous to that for the heterogenous slit and setting $\theta_E^{cyl} = \theta$ leads to the condition for the value of the aspect ration a_T^{cyl}. For example, when the patch is completely wet ($\theta_p = 0$) the triple point occurs for

$$a_T^{cyl} = \sqrt{\frac{1 - \cos\theta}{1 + \cos\theta}}. \quad (7)$$

It is interesting to compare this with the result for the slit geometry obtained by setting $\theta_p = 0$ in (4) displayed in Fig. 3. Unlike the slit geometry for which the aspect ratio reaches a maximum value with maximum contrast ($\theta = \pi$) the triple-point value of a_T^{cyl} diverges as θ is increased to π. A triple point therefore does not exist for the maximum contrast cylinder. This reflects the fact that the for the cylindrical geometry the surface tension contributions for the wall-gas and the wall-liquid interfaces scale with the radius $\mathcal{R}$. There is no such dependence on the wall separation L for capillary slits.
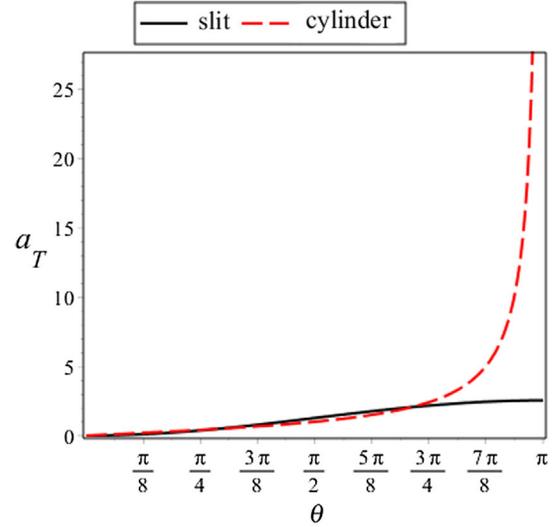
FIG. 3. Predicted triple-point aspect ratios for the heterogenous slit and the pore geometries for the completely wet patch θ_p as a function of the contact angle θ of the outer wall.

Finally, we turn our attention to possible fluctuation effects which are not captured by macroscopic arguments or our model DFT. Fluctuations do not effect the direct capillary condensation from a gaslike to a liquidlike state (occurring for $\theta_E < \theta$ or equivalently $a > a_T$) since the capillary is pseudo–two dimensional. However, they do, at least in principle, affect the two other possible transitions in rather different ways. Here, we argue however that they are not quantitative important. Consider the bridging transition first. Since the patch width H and wall separation L are finite the bridging transition is pseudo–one dimensional and standard finite-size scaling arguments determine that this first-order transition is not precisely sharp but rounded on a scale set by $\exp(-\gamma LH/k_BT)$. This is largest for the bridging transition occurring near the triple point (since the aspect ratio $a = L/H$ is largest) but even for the smallest systems we have considered here this is negligibly small. For example, at low temperatures this implies that the transition from a gaslike to bridge state is rounded over the range $\Delta\mu/\mu_{sat} \approx \exp(-250)$. Fluctuation effects are most subtle for the condensation transition from a bridge phase to a liquidlike state. If the ends of the capillary are considered open then the transition can be viewed as the unbinding of the menisci from the edges of the patch to the ends of the capillary. Recall that at the condensation phase boundary $\theta_E = \theta$, so there is no macroscopic free-energy cost for translating the meniscus away from the edges of the patch. This allows for the possibility of a second order phase transition. However, more microscopically, there will always be local pinning of the menisci near the patch edges arising from intermolecular forces. If they are strong enough the menisci remain bound to the patch at $\mu = \mu_{CC}^-$ and the location of the menisci jump discontinuously, via a first-order transition to the ends of the capillary on the

crossing of the phase boundary. This is what we observe in the mean-field DFT. In principle, it is possible that thermal fluctuations in the position of menisci cause it to tunnel away from the patch edge so that its distance from the edge diverges continuously as μ is increased to μ_{CC}. This is directly analogous to condensation occurring in a capped capillary above the wetting temperature of the confining walls. However, since the line tension controlling the fluctuations of menisci (in the y direction) is large, of order γL, it is unlikely that such tunneling occurs and the menisci always remains pinned to the patch edges at μ_{CC}. This transition therefore also always remains first order and is accurately described by the classical DFT employed here.

In this Letter, we have examined the conditions under which bridging precedes capillary condensation in an idealized model of a heterogenous capillary slit. Using the standard Kelvin and a modified Kelvin equation, which allows correctly for the edge contact of the menisci in the bridge phase, we have derived a condition for the value of the aspect ratio L/H which leads to a triple point. Of particular interest is the existence of an upper universal value for the aspect ratio for a slit with maximum wetting contrast. This mesoscopic approach proves to be extraordinarily accurate even for molecularly narrow slits. Even for walls with single patches a number of extensions of our work are possible. For example, it would be interesting to consider how the stability of the bridge phase is affected when the contact angles of the patches on the two walls are different and also when the patches are sheared. This is a topic of future work.

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