Kelvin equation for bridging transitions

Alexandr Malijevský *
Research Group of Molecular and Mesoscopic Modelling, The Czech Academy of Sciences,
Institute of Chemical Process Fundamentals, 165 02 Prague, Czech Republic
and Department of Physical Chemistry, University of Chemical Technology, Prague, 166 28 Prague 6, Czech Republic

Martin Pospíšil
Department of Physical Chemistry, University of Chemical Technology Prague, Prague 6, 166 28, Czech Republic

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We study bridging transitions between a pair of nonplanar surfaces. We show that the transition can be described using a generalized Kelvin equation by mapping the system to a slit of finite length. The proposed equation is applied to analyze the asymptotic behavior of the growth of the bridging film, which occurs when the confining walls are gradually flattened. This phenomenon is characterized by a power-law divergence with geometry-dependent critical exponents that we determine for a wide class of walls' geometries. In particular, for a linear-wedge model, a covariance law revealing a relation between a geometric and Young's contact angle is presented. These predictions are shown to be fully in line with the numerical results obtained from a microscopic (classical) density functional theory.

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It is widely recognized that confining a fluid may dramatically change its phase behavior [1–3]. Perhaps the most familiar example of this is the phenomenon of capillary condensation, which refers to a shift of the liquid-gas phase boundary when a fluid is confined between two parallel walls a distance L apart [4–7]. According to the Kelvin equation, the condensation of the confined fluid occurs at a chemical potential μ, which is shifted from the saturation line $\mu_{\rm sat}(T)$ by an amount [8]

$$\delta\mu_{\rm cc}^{\rm slit}(L)=\frac{2\gamma\cos\theta}{L\Delta\rho}, \tag{1}$$

where γ is the liquid-gas surface tension, θ is Young's contact angle characterizing the wetting properties of the walls, and $\Delta\rho=\rho_l-\rho_g$ is a difference between the bulk liquid and gas number densities. Despite its simple form and macroscopic origin, the Kelvin equation is remarkably accurate even at the nanoscale, where we can expect that finite-size effects are particularly significant [9–11].

It is also well known that further and *qualitatively* new phenomena may occur if the planar symmetry of the confined system is broken [12–23]. In this case different wall shapes may induce new types of phase transition whose nature is steered by both thermodynamic and geometric parameters. For instance, the simple modification of making just one of the confining walls of finite extent H results in remarkably complex behavior from the interplay between two types of capillary condensation, meniscus depinning transitions and corner filling phase transitions, which are controlled by the aspect ratio $a=L/H$ [24]. Central to understanding this phenomena is a concept of an *edge contact angle* θ_e, proposed originally for the description of capillary condensation inside a finite slit [25]. Here θ_e is the angle at which the menisci, formed in the condensed state and pinned at the walls' edges, meet the walls. Simple geometric arguments then dictate that condensation in the finite slit occurs at the chemical potential $\mu_{\rm cc}^H=\mu_{\rm sat}-\delta\mu_{\rm cc}^H$, with [25]

$$\delta\mu_{\rm cc}^H=\frac{2\gamma\cos\theta_e}{D\Delta\rho}, \tag{2}$$

where H is the length of the walls and D is the width of the slit (intentionally distinguished from L for further purposes). Right at $\mu_{\rm cc}^H$, the edge contact angle is given implicitly by the equation

$$\cos\theta_e=\cos\theta-\frac{D}{2H}\left[\sin\theta_e+\left(\frac{\pi}{2}-\theta_e\right)\sec\theta_e\right], \tag{3}$$

from which it follows that $\theta_e\to\theta^+$ as $H\to\infty$.

In this paper we show that the concept of an edge contact angle can be advantageously used for the description of another type of condensation, this time induced by walls of arbitrary geometry and in the absence of pinning. To this end, consider a pair of symmetric walls, such that the local height of the "top" ("bottom") wall, relative to the horizontal plane $z=0$, is $z_w(x)>0$ $(-z_w(x))$, which we express as

$$z_w(x)=\frac{L}{2}+\psi(x). \tag{4}$$

Here $\psi(x)$ is assumed to be a differentiable function (except for $x=0$ where we allow for a possible kink) describing the shape of the walls that are of macroscopic extent along the remaining y axis. We will further assume that $\psi(x)$ is even and, without any loss of generality, has its global minimum at the origin. We note that these assumptions are not crucial and can be easily generalized, as will be discussed at the end.

If the contact angle of the walls is $\theta<\pi/2$ $(\theta>\pi/2)$, the system exhibits local condensation (evaporation), i.e. a *bridging transition*, near the origin when the chemical

*malijevsky@icpf.cas.cz

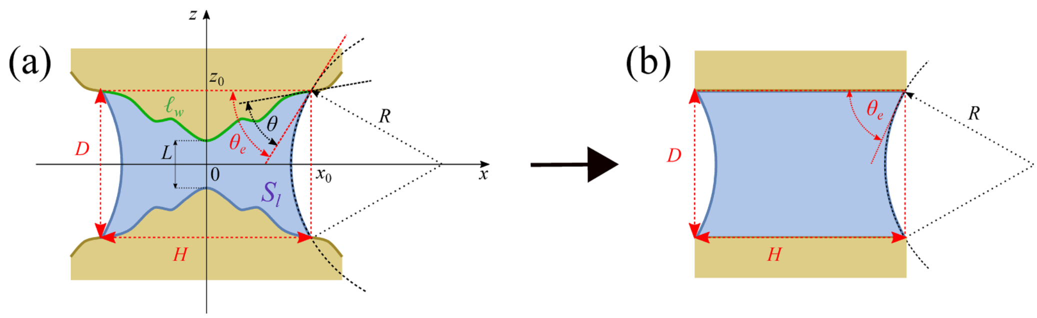

FIG. 1. (a) Schematic illustration of a locally condensed state induced by a pair of nonplanar walls. Macroscopically, the configuration is characterized by a presence of two symmetric menisci of Laplace radius $R = \gamma/(\delta\mu\Delta\rho)$ that connect the walls tangentially at the points $[\pm x_0, \pm z_0]$. The length of contact between the liquid (occupying the area S_l) and each surface is ℓ_w. To determine the location of the local condensation (bridging), the system can be mapped onto a model system corresponding to a finite planar slit (b) with the parameters $H = 2x_0$, $D = 2z_0$ and the edge contact angle satisfying $\tan\theta_e = z_w'(x_0)$.

potential $\mu_B = \mu_{\rm sat} - \delta\mu_B$, which can be determined by mapping the system to that of a finite slit, as illustrated in Fig. 1. In this way it follows that the condition for the bridging transition can be formally expressed in the same way as for condensation in a finite slit

$$\delta\mu_B = \frac{2\gamma\cos\theta_e}{D\Delta\rho} \tag{5}$$

in the following sense. Let $[x_0, z_0 \equiv z_w(x_0)]$ denote the point of contact between the meniscus and the wall (in the first quadrant). We now associate the bridged part of our system with a finite slit of length $H = 2x_0$ and width $D = 2z_0$, while the corresponding edge contact angle is determined by the slope of the wall tangent at x_0, $\theta_e = \tan^{-1}[z_w'(x_0)] + \theta$. At the bridging transition, the Laplace radius of the meniscus is $R = \gamma/(\delta\mu_B\Delta\rho)$, giving the geometric condition Eq. (5), valid for any bridged (locally condensed) state. The free energy balance between the unbridged and bridged states dictates that the value of θ_e corresponding to the bridging transition is given by

$$\bar{r}\cos\theta_e = r\cos\theta - \frac{D}{2H}\left[\sin\theta_e + \left(\frac{\pi}{2} - \theta_e\right)\sec\theta_e\right], \tag{6}$$

which extends Eq. (3) by introducing two dimensionless parameters: the "roughness" $r = \ell_w/H$ and its two-dimensional analog $\bar{r} = S/(HD)$. Here $\ell_w = 2\int_0^{x_0}\sqrt{1+[\psi'(x)]^2}\,dx$ is the liquid-wall contact length and $S = 4\int_0^{x_0} z_w(x)\,dx$ corresponds to the available volume between the confining walls, which consists of the portion occupied by liquid, $S_l = S - S_g$, and the portion filled by gas, $S_g = (\pi - 2\theta_e)R^2 - \sin\theta_e RD$ [see Fig. 1(a)]. We note that the bridging transition corresponds to local condensation provided the aspect ratio $D/H < \cos\theta^*$ where θ^* can be interpreted as the apparent contact angle given by Wenzel's law, $\cos\theta^* = r\cos\theta$ [26]. Similarly for $D/H > \cos\theta^*$, $\theta_e > \pi/2$ the bridging transition corresponds to a local evaporation (with bulk phase being a liquid).

At this point, we make several pertinent remarks regarding the applicability and limitations of Eq. (5). Specifically, in the derivation of the modified Kelvin equation we did not consider related interfacial phenomena, which under certain conditions may also occur. For instance, for walls possessing pockets or grooves, the individual walls may experience filling or unbending transitions below T_w accompanied by a jump in adsorption at the troughs [27,28]. Since this will effectively reduce both $\bar{r}$ and r, one may anticipate that the opposing effects in the change of both parameters may to some extent compensate; however, further numerical tests are needed. Above T_w, wetting layers will adsorb even at weakly corrugated walls, which will primarily affect the parameter $\bar{r}$ and shift the transition closer to saturation. This effect could be incorporated to Eq. (5) using the construction of Rascón and Parry [29], as demonstrated recently for sinusoidal walls [30]. Of course, packing effects, which are particularly significant near the surface of highly curved walls, may also affect the bridging scenario, as well as bulk critical phenomena, which would not allow for bridging transition if the walls' separation becomes comparable with the bulk correlation length. Here our main focus is on analyzing asymptotic behavior of bridging transitions for some simple, yet important model geometries utilizing the modified Kelvin equation and support the outcomes by comparing the analytic predictions with the numerical results using a more microscopic approach.

In the remaining part of our paper we illustrate the utility of the generalized Kelvin equation (5) emphasizing the connection between bridging and capillary condensation. We show that for a wide range of wall geometries, the local condensation between walls generates a critical phenomenon associated with the divergence of condensed film thickness, with geometrically dependent critical exponents, when the confining walls are flattened. Finally we test the analytic predictions on a microscopic level using a classical nonlocal density functional theory (DFT).

We illustrate the use of Kelvin's equation for bridging transitions between walls whose shape is described by the power law

$$\psi(x) = \alpha\frac{|x|^\nu}{L^{\nu-1}}, \tag{7}$$

with $\alpha, \nu > 0$, as originally suggested by Rascón and Parry [29] in their study of adsorption at a single wall. Hereafter, we will focus on the case of completely wet walls ($\theta = 0$), for which $\cos\theta_e = 1/\sqrt{1+\psi'^2(x_0)}$, where x_0 is given by Eq. (6). Clearly, it generally holds that $\delta\mu_B(L) < \delta\mu_{\rm cc}^{\rm slit}(L)$, but as the steepness parameter α tends to zero, so does the difference

$\Delta\mu = \mu_B - \mu_{cc}^{slit}$ according to the power law

$$\Delta\mu \sim \delta\mu_{cc}^{slit}(L)\alpha^{\beta_\alpha}, \quad \alpha \to 0, \tag{8}$$

where $\beta_\alpha = 1/(1+\nu)$. The process of the walls' flattening is accompanied by a growth of the bridging film thickness, with the asymptotic behavior

$$x_0 \sim L\alpha^{-\beta_\alpha}, \quad \alpha \to 0, \tag{9}$$

with a positive subdominant contribution of the order of $O(1)$. From the asymptotic behavior of $\Delta\mu$ and x_0 it follows that for steeper walls (large ν), the bridging transition occurs farther from μ_{cc}^{slit} and the growth of the bridging film is slower. In contrast to x_0, the subdominant correction to $\Delta\mu$ strongly depends on the walls geometry, and in particular on their curvature, as follows:

i. $\nu > 1$: For convex walls (positive curvature), the subdominant contribution to $\Delta\mu$ is of the order of $O(\alpha^{\frac{2}{\nu+1}})$ which is *positive*, meaning that the asymptotic result, Eq. (8), approaches the exact solution from below.

ii. $\nu < 1$: For concave walls (negative curvature), the subdominant contribution to $\Delta\mu$ is of the order of $O(\alpha^{\frac{2}{\nu+1}})$ which is *negative*, meaning that the asymptotic result, Eq. (8), approaches the exact solution from above.

iii. $\nu = 1$: In the marginal, linear case (zero curvature), the subdominant contribution to $\Delta\mu$ is only $O(\alpha^{\frac{4}{\nu+1}})$ and is positive.

The linear, double-wedge model, $\nu = 1$, turns out to be specific also for other reasons. First, it allows for the exact explicit solution of the Kelvin equation for any value of α, which can be expressed as

$$\frac{x_0}{L} = \frac{\xi\phi + \sqrt{2\xi(2\alpha+\phi)}}{2\xi(2-\alpha\phi)}, \tag{10}$$

where $\phi = \pi - 2\tan^{-1}\alpha$ and $\xi = \alpha + \alpha^3$. Second, there exists a *covariance law*

$$\delta\mu_B^\alpha(L;\theta = 0) = \delta\mu_{cc}^{slit}(\tilde{L};\theta = \tan^{-1}(\alpha)), \tag{11}$$

where

$$\tilde{L}(\alpha) = L + 2x_0\alpha. \tag{12}$$

For sufficiently small values of α, the parameter plays a role of a tilt angle (relative to horizontal) and the covariance law simplifies, such that

$$\tilde{L}(\alpha) \approx L(1 + \sqrt{\pi\alpha/2}), \tag{13}$$

relating a bridging transition induced by completely wet wedges of a tilt angle α and capillary condensation in infinite planar slit formed of partially wet walls with the contact angle $\theta = \alpha$.

The results (8) and (9) are rather general and applicable for a wide range of confinement models. This can be illustrated by considering a pair of walls of circular intersections of radius r with $\psi(x) = r - \sqrt{r^2 - x^2}$, corresponding to a pair of disks in two dimensions and to a pair of parallel cylinders in three dimensions. Here the large r analysis of the bridging transition leads to the results

$$\delta\mu_B = \delta\mu_{cc}^{slit}(L)\left[1 - c^2\left(\frac{L}{r}\right)^{\frac{1}{3}}\right], \quad r \gg L \tag{14}$$

and

$$x_0 = c(L^2 r)^{\frac{1}{3}}, \quad r \gg L, \tag{15}$$

with $c = (3\pi/16)^{1/3}$, which are consistent with Eqs. (8) and (9), respectively, for $\nu = 2$, as expected.

These macroscopic predictions have been tested by a microscopic classical density functional theory (DFT) [31].

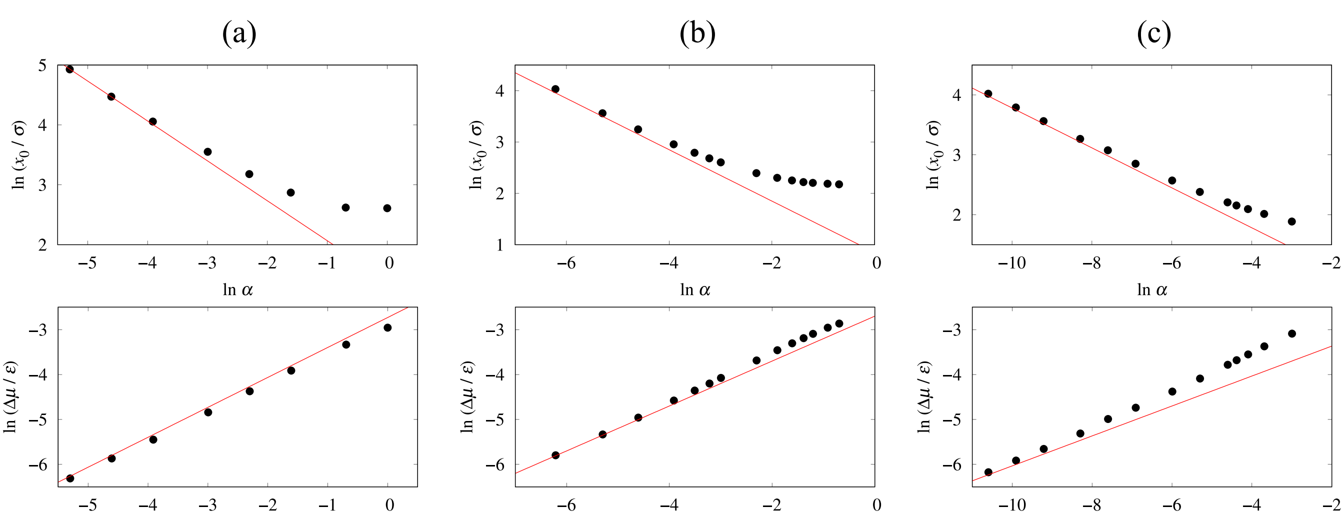

FIG. 2. Log-log plots showing the growth of the bridging films x_0 (upper panels) and the decrease of $\Delta\mu = \mu_B - \mu_{cc}^{slit}$ (lower panels) for the power-law-shaped walls given by Eq. (7) with (a) $\nu = 1/2$, (b) $\nu = 1$, and (c) $\nu = 2$ upon reducing the parameter α. The symbols represent the DFT results, and the straight lines have the slopes corresponding to the expected values of the critical exponent $\beta_\alpha = 1/(1+\nu)$. In all cases the minimum distance between the walls is $L = 10\,\sigma$.

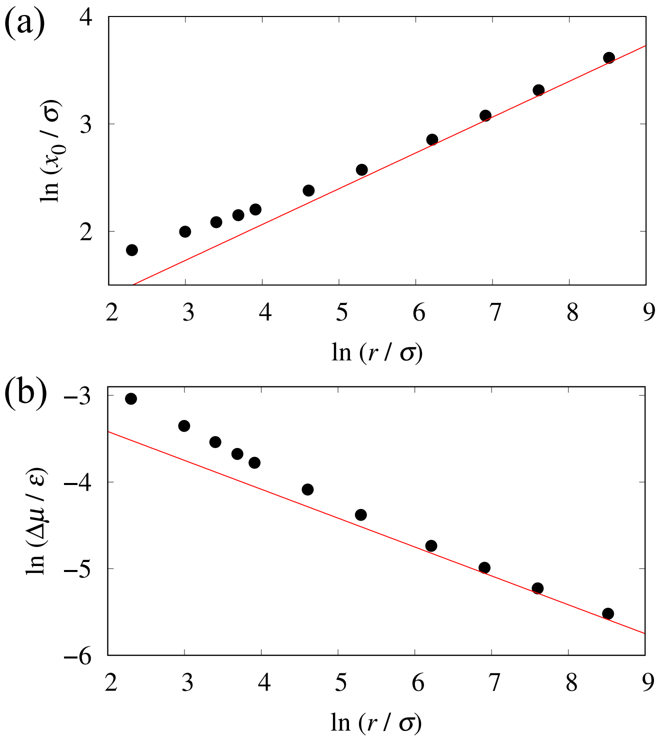

FIG. 3. Log-log plots showing DFT results for bridging transition between two parallel walls of circular cross section with a radius r separated by a distance $L = 10\,\sigma$. (a) Growth of the bridging film; (b) chemical potential offset in the chemical potential between bridging transition and capillary condensation $\mu_{\rm cc}^{\rm slit}(L)$ upon increasing r. Also shown are the expected asymptotic behavior as given by Eqs. (15) and (14), respectively.

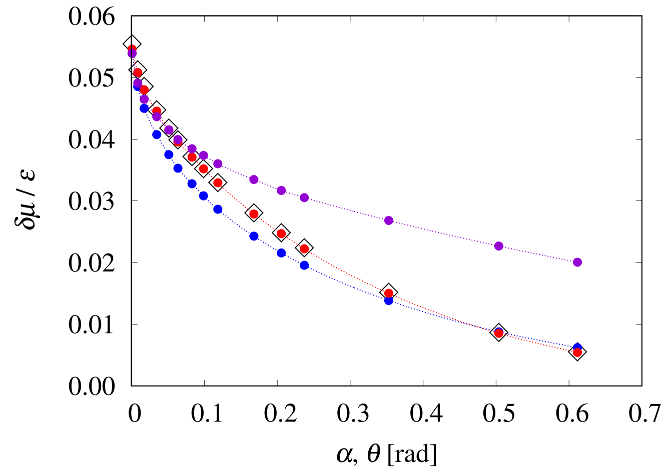

FIG. 4. DFT results showing a comparison between the location of bridging transition $\delta\mu_B^\alpha$ (squares) inside a double-wedge slit formed of completely wet walls ($\theta = 0$) with the tilt angle α and the closest distance $L = 10\,\sigma$ and capillary condensation $\delta\mu_{\rm cc}^{\rm slit}(\tilde{L})$ in a parallel infinite slit formed of partially wet walls with the contact angle $\theta = \alpha$. The effective slit width $\tilde{L}$ was determined by Eq. (12), with x_0 given by Eq. (10) (blue circles) and directly from DFT (red circles). Also shown are the DFT results for $\delta\mu_{\rm cc}^{\rm slit}(\tilde{L})$ with $\tilde{L}$ given by the asymptotic relation (13) (purple circles).

Within DFT, one minimizes the grand potential functional

$$\Omega[\rho] = \mathcal{F}[\rho] - \int [\mu - V(\mathbf{r})]\rho(\mathbf{r})\,dr, \qquad (16)$$

to determine the equilibrium density profile $\rho(\mathbf{r})$ of the fluid particles and the thermodynamic free energy of the system. Here $V(\mathbf{r})$ is the external potential arising from the confining walls and $\mathcal{F}[\rho]$ is the intrinsic free energy functional modeling the contribution from the fluid-fluid interactions. The latter is approximated by combining Rosenfeld's fundamental measure theory [32] describing accurately packing effects due to repulsive interactions, with a mean-field treatment of the attractive part of the interatomic interaction modeled by a truncated Lennard-Jones (LJ) potential whose parameters, σ and ε, are used as respective length and energy units. (For details regarding the DFT model see [30].)

In Fig. 2 we compare the predictions (8) and (9) with our DFT numerical results for square-root ($\nu = 1/2$), linear ($\nu = 1$), and parabolic ($\nu = 2$) wall geometries. In all cases, the DFT results for the growth of the bridging film thickness (as given by x_0) converge upon reducing the parameter α to the expected asymptotic behavior with the appropriate value of the critical exponent β_α. It is well seen that the growth of the film becomes slower as the exponent ν is increased and that the asymptotic lines are always approached from above, as expected. Also verified is the asymptotic rate of decline in $\Delta\mu$ characterizing the shift between the location of bridging transition and capillary condensation in the corresponding slit. Here, however, in line with the predictions, the manner in which the given asymptote is approached depends on the specific geometry, such that the convergence is from below for $\nu = 1/2$ but from above for $\nu = 2$, in which case the convergence is the slowest. Quantitatively similar to the latter case is the asymptotic behavior of bridging transitions between a pair of walls of a circular cross section of radius r. As demonstrated in Fig. 3, the DFT results exhibit the power laws predicted by Eqs. (14) and (15) for sufficiently large values of r, with both asymptotes being approached from above, as expected.

Finally, in Fig. 4 we test the covariance between bridging transition inside a double-wedge and capillary condensation in an infinite slit, as given by Eq. (11). To this end, we compared the DFT results for the location of bridging transition in the double-wedge formed of completely wet walls ($\theta = 0$) tilted by angle α relative to the horizontal, with DFT results for capillary condensation inside a slit formed of *partially* wet walls with the contact angle $\theta = \alpha$ and width $\tilde{L}$, which was determined (a) analytically, using Eqs. (10) and (12), (b) analytically, using the asymptotic relation (13), and (c) semianalytically, from Eq. (12) with x_0 determined from DFT density profiles for the double wedge. The comparison shows a very reasonable agreement for (a) and a perfect agreement for (c), while the asymptotic form for $\tilde{L}$ is shown to be accurate for $\alpha \lesssim 0.1$.

In summary, we have studied bridging transitions between two nonplanar surfaces. We have shown that the problem can be solved effectively by an appropriate mapping of the system to a much simpler one formed of a pair of parallel plates using the newly generalized Kelvin equation. The derivation of the equation extends the concept of the edge contact angle, which can be usefully utilized even for systems where no edges are present. In the second part of this paper, we studied the asymptotic behavior of bridging transitions and their relation to capillary condensation for a class of fundamental walls geometries. We have shown that gradual flattening of the confining walls leads to a critical phenomenon characterized by a diverging growth of the bridging film. Associated geometry-dependent critical exponents were determined and a covariance law revealing a relation between the geometric and Young's contact angle for wedgelike structures was found. All the analytical predictions have been verified by a microscopic density functional theory whose results not only support the anticipated asymptotic behavior of the bridging transitions but also the expected way at which the asymptotes are approached.

Natural extensions of this study include the analysis of bridging transitions between walls whose shape is described by a function which is not necessarily differentiable, i.e., include cusps. Here the solution of Eqs. (5) and (6) for x_0 (specifying the location of the bridging film boundary) must be compared with the one for a state pertinent to a meniscus pinned to a nearby edge to find a state of the global free-energy minimum; this requires solving the Kelvin-like equation but now for a fixed value of x_0 and unknown θ_e. Further but straightforward modifications are required for a description of bridging transitions between unlike walls. Of great interest would also be an analysis of an interplay between bridging and other confinement-induced phenomena leading to local condensation, such as wedge or groove filling. Finally, it would be desirable to extend the current study by considering surfaces possessing axial rather than translation symmetry and also to account for the effect of wetting layers adsorbed at the walls. We will attempt to address these tasks within our future work.

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