Wetting in a two-dimensional capped capillary. Part II: Three-phase coexistence.

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Abstract. In Part II of this study we consider two cases of three-phase coexistence. First, the capped capillary may allow for vapour, drop-like, and slab-like phases to coexist at the same values of temperature and chemical potential. Second, the slit pore forming the bulk of the capped capillary may allow for the coexistence between vapour, planar prewetting film and capillary-liquid. While the consideration of the former case allows us to summarise the phenomenology presented in Part I and to show that the transition line of wedge prewetting is shifted in capillary-like geometries by a constant value, depending on the capillary width, the careful examination of the latter case allows us to uncover a new phase transition in confined fluids, a continuous planar prewetting transition. A planar prewetting transition is known to be a distinctly first-order phenomenon, and typically taking place on the scale of several atomic diameters. A continuous prewetting transition, on the other hand, is scale invariant. Thus, apart from being of fundamental significance, this finding has potential for facilitating experimental detection as well as measurements of planar prewetting. Further, we provide proof for the existence of a tri-critical point of the three-phase coexistence line of the capped capillary while by considering a dynamic model of wetting we show how the relaxation of the system can be pinned by a metastable state. We present a full parametric study of our model system and support our findings with exhaustive examples of density profiles, adsorption and free energy isotherms, and full phase diagrams.

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1. Introduction

In Part I of this study we have shown how capping a one-dimensional (1D) slit pore, which results in a generically two-dimensional (2D) system, dramatically changes the phenomenology of wetting. The 2D system possesses the capillary wetting temperature, $T_{cw}$, which is the property of the pore and controls the order of capillary condensation (CC) at any given value of temperature. We have also shown the existence of capillary prewetting transition, where configurations of the pore filled with vapour coexist with those possessing a finite capillary-liquid slab. Finally, we have shown that wedge wetting can manifest itself in the capped capillary by the existence of a (metastable) fluid phase with drops in the capillary corners. The details of the density functional (DF) model, working equations and discussion of the numerical methodology can be found in Part I and we will be referring to them here when necessary. As the wetting behaviour is qualitatively the same, whether repulsions are treated with a non-local (weighted density approximation, WDA) or a local (local density approximation, LDA) functional, for computational convenience we adopt the latter approximation here.

To complete the description of phase behaviour of fluids confined in capped capillaries we focus on the (most general) case which exhibits two types of three-phase coexistence. First, the 1D capillary bulk, given by the associated slit pore, has three coexisting phases: vapour, capillary-liquid and planar thin film adsorbed on each wall. Second, the 2D capped capillary exhibits the coexistence of surface phases of vapour, capillary-liquid slab and capillary-liquid drops in the corners. The interplay of prewetting with continuous CC leads to the existence of a new type of phase transition – continuous prewetting. We proceed to addressing all details of three-phase coexistence and we shall also areas, where further research, preferably going beyond mean-field and including fluctuation effects, will be necessary.

Central to our discussion is figure 1, which shows the full phase diagram of the fluid in the capped capillary with the substrate parameters $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$ and width $H = 40$. The fluid is treated in LDA and the planar wetting temperature is $T_w = 0.755$. Note that the capillary in figure 1 differs from the one in figure 10 of Part I (with $H = 30$) only in the value of wall separation, $H$. The grey curves pertain to the phases inside the slit pore (capillary bulk, a 1D system), while the black curves correspond to the phases formed near the capping wall (capped capillary, a 2D system). Insets zoom on the triple points. All the phase transition lines are indexed and described in the caption of the figure. A solid line denotes transitions between stable phases, a dashed line denotes transitions between metastable phases. The regions of thermodynamic stability (but not metastability, spinodals are not shown) of a single phase are clearly labelled by text notes. Triple points are marked by filled circles. Critical points are marked by open circles. The dotted grey line 1 is the prewetting line of a single planar wall: the locus of phase transitions between vapour and a thin planar film. Regarding capillary bulk (slit pore), line 2 is the locus of phase transitions between vapour and capillary-liquid, line 3 – between vapour and thin film formed on each side.
Figure 1. Phase diagram of the capped capillary with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 40$; fluid treated in LDA, planar $T_w = 0.755$. The system exhibits all effects discussed in Part I. Grey color pertains to the capillary bulk (slit pore associated with the capped capillary), black color to the capped capillary. Regions where a single phase is thermodynamically stable are labelled by a text note. Each transition line is numbered and consists of two parts (except the planar prewetting line (1, grey, dotted)): solid part denotes a transition between thermodynamically stable phases, dashed part between metastable phases. Filled circles denote triple points. Open circles denote critical points. Insets zoom on the regions containing the triple points of the slit pore, $T_3^{slt} = 0.920$ and of the capped capillary, $T_3^{cc} = 0.865$. Note that the CC transition line consists of stable parts of lines 2 and 4, and capillary prewetting line of stable parts of lines 5 and 7.

List of transition lines by their labels, with a brief description of coexisting phases.

1: planar prewetting ($\Delta \mu_{pw}(T)$, vapour transforms to thin film), begins at $(T_w, 0) = (0.755, 0)$, ends at $(T_{pw}^c, \Delta \mu_{pw}^c) = (0.944, -4.72 \cdot 10^{-2})$,

2 and 4: CC ($\Delta \mu_{cc}(T)$, transition to capillary-liquid from vapour (line 2) and from thin film (line 4)), line 2 ends at $(0.929, -3.98 \cdot 10^{-2})$, line 4 begins at $(0.89, -4.45 \cdot 10^{-2})$, ends at $(T_{cc}^c, \Delta \mu_{cc}^c) = (0.994, -2.56 \cdot 10^{-2})$,

3: shifted planar prewetting ($\Delta \tilde{\mu}_{pw}(T)$, vapour to thin film in the associated slit pore), begins at $(0.848, -1.83 \cdot 10^{-2})$, ends at $(\tilde{T}_{pw}^c, \Delta \tilde{\mu}_{pw}^c) = (0.945, -4.89 \cdot 10^{-2})$,

5 and 7: capillary prewetting ($\Delta \mu_{cpw}(T)$, transition to capillary-liquid slab from vapour (line 5) and from drop phase (line 7)), line 5 begins at $(T_{cpw}, \Delta \mu_{cpw}) = (0.77, -3.33 \cdot 10^{-2})$ ($\Delta \mu_{cc} = 0.0086 \cdot 10^{-2}$), ends at $(0.873, -6.1 \cdot 10^{-2})$, line 7 begins at $(0.856, -5.65 \cdot 10^{-2})$, ends at $(\tilde{T}_{cpw}^c, \Delta \tilde{\mu}_{cpw}^c) = (0.93, -6.98)$,

6: shifted wedge prewetting ($\Delta \tilde{\mu}_{wpw}(T)$, vapour to drops in corners), begins at $(\tilde{T}_{wpw}, \Delta \tilde{\mu}_{wpw}) = (0.828, -3.68 \cdot 10^{-2})$ (point is on the CC line (line 2)), ends at $(\tilde{T}_{wpw}^c, \Delta \tilde{\mu}_{wpw}^c) = (0.885, -7.17 \cdot 10^{-2})$. 

2D capillary wetting
wall, line 4 – between thin film and capillary-liquid. Regarding the capped capillary, line 5 is the locus of transitions between vapour and configurations with capillary-liquid slab (capillary prewetting), line 6 – the locus of transitions between vapour and configurations with drops in corners (shifted wedge prewetting), line 7 – the locus of phase transitions between configurations with corner drops and a capillary-liquid slab.

To obtain the full phase diagram, we had to compute two triple points for three-phase coexistence inside the slit pore and the capped capillary. The condition for the coexistence of three fluid phases with density distributions $\rho_1, \rho_2, \rho_3$ can be expressed, similarly to the condition for the two-phase coexistence, given in equation (24) of Part I, by the requirement that each of the density profiles minimises the total free energy (equation (11) of Part I), and that the excess free energies of all three fluid configurations to be equal:

$$\left. \frac{\delta \Omega}{\delta \rho} \right|_{\rho_1} = \left. \frac{\delta \Omega}{\delta \rho} \right|_{\rho_2} = \left. \frac{\delta \Omega}{\delta \rho} \right|_{\rho_3} = 0$$

$$\Omega^{ex}[\rho_1] = \Omega^{ex}[\rho_2] = \Omega^{ex}[\rho_3],$$  \hspace{1cm} (1)

where, for a slit pore (1D system) $\Omega^{ex}[\rho^{slt}(y)] \equiv \Omega[\rho^{slt}(y)]$, see equation (2) of Part I, and in the case of the capped capillary (2D system), $\Omega^{ex}[\rho^{cpd}(x,y)]$ is given in equation (21) of Part I.

To locate the triple point, one has to solve the above system for the density profiles $\rho_1, \rho_2, \rho_3$ of the coexisting fluid configurations, as well as for the chemical potential, $\mu_3$, and the temperature $T_3$. An initial guess for $\mu_3$ and $T_3$ ($\mu_{3,0}$ and $T_{3,0}$) can be obtained by interpolating the three intersecting two-phase coexistence lines (which should intersect at a single point but due to computational error they will intersect at three points) and then use their mean as $\mu_{3,0}$ and $T_{3,0}$. As an initial guess for the densities one can then take the density profiles inside each of the three phases, which correspond to the data points on two-phase coexistence lines, closest to $\mu_{3,0}$ and $T_{3,0}$. So the strategy is similar to finding the point of two-phase coexistence, see equation (24) of Part I. Using arc-length continuation one can then trace the entire triple-line in the space of, e.g., parameters of the potential, $\varepsilon_w$ and $\sigma_w$, or wall separation, $H$, and search numerically for a tri-critical point. We leave the detailed numerical investigation of the triple, such as continuation with respect to the capillary width or substrate potential parameters, for future work.

The triple point splits each transition line passing through it into two branches: where the transition takes place between thermodynamically stable (solid line) and metastable (dashed line) fluid states. The stable branch of a transition line ends at a critical point (marked by open circles in figure 1). On the other hand, the end points of metastable branches of transition lines are not critical, they are associated with a metastable branch of the excess free energy $\Omega^{ex}(\Delta \mu)$ losing an intersection point with a stable branch. We investigate the mean-field signature of criticality in detail in section 2.

Considering the $\Delta \tilde{\mu}_{wpw}(T)$-lines in figure 10 of Part I and figure 1, we can, without the computation of the full wedge prewetting line, $\Delta \mu_{wpw}(T)$, prove, that confinement,
imposed by a second side wall of the capped capillary on the otherwise a wedge-shaped substrate, leads to the shift of the wedge prewetting transition by a unique and constant value, which is the same for the entire range of temperatures, where the wedge prewetting takes place. We are not aware of another study in the literature reporting the shift of wedge prewetting due to additional confinement of the fluid.

Using the DF approach with the arc-length continuation over the parameter $T$ (see equation (24) of Part I), we were able to calculate $\Delta \tilde{\mu}_{wpw} (T)$ transition lines of capillaries form figure 10 of Part I and figure 1 and obtain them as sets of data in the $T - \Delta \mu$ space. However, the arc-length continuation algorithm treats the continuation parameter as the unknown, thus there is no control over the particular values of $T$, at which a transition line is calculated. Thus each line was obtained at values of temperatures. Using spline-interpolation, we have computed both $\Delta \tilde{\mu}_{wpw} (T)$ transition lines from figure 10 of Part I and figure 1 at the set of 1000 points positioned equidistantly along the intersection of the temperature ranges, where both lines are found. The mean value of the difference between them along the $\Delta \mu$-axis was found to be $(0.16 \pm 0.01) \cdot 10^{-2}$.

Since the distance between both transition lines is constant (within the margin of rounding errors), there clearly exists a special $H$-dependence of the $\Delta \tilde{\mu}_{wpw} (T)$ transition line: at higher values of $H$ the $\Delta \tilde{\mu}_{wpw} (T)$-line spans a broader range of temperatures and shifts on the phase diagram entirely towards more negative chemical potentials. Obviously, as $H$ is increased, the capillary corners become more isolated and behave more like infinite wedges. At the same time, the CC behaves more like the bulk liquid – vapour coexistence (saturation): the $\Delta \mu_{cc} (T)$-line approaches bulk saturation ($\Delta \mu \equiv 0$), becomes more flat and also splits into transition lines forming the loci of vapour – capillary-liquid and thin film – capillary-liquid transitions (see, e.g., lines 2 and 4 in figure 1). A further increase in the value of the width $H$ of the capped capillary will obviously lead to $\Delta \tilde{\mu}_{wpw} (T)$-line spanning an even broader range of temperatures. In the limit $H \to \infty$, when the capped capillary becomes a right-angled wedge, that transition line runs tangent to bulk saturation (see, e.g., reference [1], where the wedge prewetting line, $\Delta \mu_{wpw} (T)$, is studied in detail), and the equivalence $\Delta \tilde{\mu}_{wpw} (T) \equiv \Delta \mu_{wpw} (T)$ takes place. We have thus shown, that there exists a unique, constant $H$-dependent shift of the entire $\Delta \mu_{wpw} (T)$-line in semi-infinite rectangular pores. Our conclusion is based on the observed constant shift between the two $\Delta \tilde{\mu}_{wpw} (T)$-lines of capillaries differing only in the value of wall separation. One can possibly obtain the analytic expression for the value of the shift, using thermodynamics methods, similar to those outlined in, e.g., references [2, 3]. We leave such a study for the future.

2. Vapour, drops and capillary-liquid slab

For confined fluids the dimensions of substrate geometry, e.g., the separation between the side walls, $H$, and the parameters of the substrate potential, $\varepsilon_w$, $\sigma_w$, act as thermodynamic fields controlling the phase behaviour of the fluid and have the same status as the bulk fields $T$ and $\mu$, see, e.g., the review [4]. We have illustrated this
Figure 2. Isothermal thermodynamic path at $T = 0.87$ ($T_{\text{slit}}^3 < T < T_{\text{ct}}^{\text{wpw}}$), $\Delta \mu_{\text{cc}} (T) = -3.89 \cdot 10^{-2}$. Capillary parameters are given in figure 1. As $\Delta \mu$ is increased, there are two stable consecutive first-order transitions: at $\Delta \mu_1 \equiv \Delta \mu_{\text{cpw}} (T) = -6.15 \cdot 10^{-2}$ and at $\Delta \mu_2 \equiv \Delta \mu_{\text{wpw}} (T) = -5.92 \cdot 10^{-2}$. (a) – (c) Representative density profiles of fluid configurations inside each of the three stable phases. Reference densities: $\rho_{\text{cc}}^{\text{vap}} = 0.06$, $\rho_{\text{cc}}^{\text{liq}} = 0.5$. (d) Excess free energy isotherm (unstable branches are not shown), which possesses three concave (stable) branches, defining the phases: vapour (dashed line, profile at $\Delta \mu = -6.39 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.39$ is shown in plot (a)), drop phase (solid grey line, profile at $\Delta \mu = -6 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.52$ is shown in plot (b)) and capillary-liquid slab phase (solid black line, profile at $\Delta \mu = -5.85 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.71$ is shown in plot (c)). Values of $(\Delta \mu, \Omega^{\text{ex}})$, corresponding to (a) – (c) are marked on (d) by open circles. See also figure 3 for the adsorption isotherm.

concept by, first showing how reducing the effective strength of the substrate potential (which can be measured by, e.g., the planar wetting temperature, $T_w$, so that a stronger substrate has a higher $T_w$) creates an additional (metastable) phase with capillary-liquid drops in the corners (see, e.g., Part I, where figure 2 has a single Van der Waals loop and figure 8 which has two Van der Waals loops). The system we investigate can serve as an illustration of the fact that $H$ is also an independent thermodynamic field. Increasing the wall separation of the capillary in figure 10 of Part I to get the capillary in figure 1, stabilizes the phase with corner drops, and results in the existence of two stable first-order phase transitions: from vapour to capillary-liquid drops (shifted wedge prewetting, $\Delta \tilde{\mu} (T)$, transition line 6 in figure 1) and then to a capillary-liquid slab (transition line 7). Also, all three phases can coexist at a triple point at $T = T_{\text{ct}}^{\text{wpw}}$.

When the shifted wedge prewetting transition is stable, there exist isothermal thermodynamic paths exhibiting two consecutive first-order phase transitions: shifted wedge prewetting and capillary prewetting. Consider, e.g., an isothermal path at $T = 0.87$, which vertically crosses the transition lines 6 and 7 on the phase diagram at
values of the disjoining chemical potential $\Delta \mu_1 \equiv \Delta \mu_{wpw} (T)$ and $\Delta \mu_2$, passing through the areas of stability of vapour, drop and slab phases, and ends at CC transition (line 2), at the value of disjoining chemical potential $\Delta \mu_{cc} (T)$. The typical density profiles inside each of the stable fluid phases are shown in figures 2(a) – 2(c). The isotherms of the path are presented in figure 2(d) (without the unstable branches) and figure 3.

At low values of chemical potential the system is represented in the phase diagram of figure 1 by a point below line 6, and the fluid inside the capped capillary is in a state of vapour, figure 2(a). Increasing $\Delta \mu$ isothermally corresponds to the point on the phase diagram moving vertically up, towards line 6. Crossing this line (at $\Delta \mu = \Delta \mu_1$) results in a discontinuous first-order phase transition (shifted wedge prewetting), which changes the structure of the fluid from vapour to the two capillary-liquid drops in the corners of the capillary (figure 2(b)). When the point representing the system on the phase diagram is in the region between lines 6 and 7, the configurations with capillary-liquid drops are stable. Increasing $\Delta \mu$ towards line 7 results in the slow growth of the drops, but when the system crosses line 7 (at $\Delta \mu = \Delta \mu_2$), there is a discontinuous transition to a state with a capillary-liquid slab formed at the capping wall (figure 2(c)). When the point of reference in the phase diagram is in the regions between lines 7 and 2, the slab phase is stable, and further isothermal increase of $\Delta \mu$ towards line 2 results in the slab growing into the capillary bulk, and the system undergoes the continuous CC at $\Delta \mu_{cc} (T)$.

Consider the excess free energy isotherm of the described thermodynamic route, figure 3(d). Each stable fluid phase is defined as the concave branch of $\Omega^{ex} (\Delta \mu)$-dependence. The branches are thus plotted with a dashed line for vapour, solid grey line for drop and solid black line for slab phases. At any given value of $\Delta \mu$ the system should select a state with the lowest value of the free energy, $\Omega^{ex}$. So, when the branches of $\Omega^{ex} (\Delta \mu)$ intersect, the system follows the minimal route along different branches, which results in two consecutive discontinuous first-order phase transitions in the fluid. In figure 2(c) the branches of $\Omega^{ex} (\Delta \mu)$ intersect at $\Delta \mu_1$ and $\Delta \mu_2$, and the system follows the path along the branches of $\Omega^{ex} (\Delta \mu)$ designated by open circles, which denote the values of $\Delta \mu$ and $\Omega^{ex}$ corresponding to the density profiles shown in figures 2(a) – 2(c). The points $(T, \Delta \mu_1)$ and $(T, \Delta \mu_2)$ thus belong to lines 6 and 7 on the phase diagram in figure 1.

We did not plot the unstable branches of the excess free energy, so as to avoid unnecessarily complicating the figure. Such states are more relevant for showing the continuity of an adsorption isotherm. Figure 3 shows the dependence $\Gamma (\Delta \mu)$, where the line specifications are the same as in figure 3(d) and unstable branches are plotted with a dotted line. For an isothermal thermodynamic route the chemical potential, $\Delta \mu$, is the control parameter, while the adsorption, $\Gamma (\Delta \mu)$, is the order parameter. A discontinuous phase transition thus corresponds to a jump in the value of adsorption, as the chemical potential is being increased. Finding the intersections of branches of the free energy is equivalent (due to the Gibbs rule, equation (22) of Part I) to an equal area construction on the $\Gamma (\Delta \mu)$-dependence. We have designated such constructions by solid
vertical lines at $\Delta \mu_1$ and $\Delta \mu_2$ in figure 3. Note that the two stable phase transitions correspond to the two different hysteresis loops on the adsorption isotherm, unlike, e.g., a single hysteresis loop in the case shown in figure 2(d) of Part I. The disjoining chemical potential of CC provides the vertical asymptote for the dependence $\Gamma(\Delta \mu)$: the point $(T, \Delta \mu_{cc})$ belongs to line 2 on the phase diagram, figure 1. The critical exponent for the divergence of the order parameter at CC has been obtained in reference [5] using an effective Hamiltonian formalism, and was confirmed in our previous study in reference [6] using the DF approach: $\Gamma \sim (\Delta \mu - \Delta \mu_{cc})^{-1/4}$.

The turning points of the $\Gamma(\Delta \mu)$-dependence – the spinodals – are very important for making predictions about the behaviour of an actual physical system, because in reality the system may remain in a particular phase as the control parameter is changed until the spinodal of the corresponding branch of free energy is crossed. Thus, a jump in adsorption can happen at a value of $\Delta \mu$ anywhere in the region, where the $\Gamma(\Delta \mu)$-dependence has more than a single value for the given value of the chemical potential. This leads to hysteresis in the fluid wetting behaviour: since the system can actually be found in metastable configurations, a route from vapour to CC may be taken through different states, than a route from CC to vapour. In section 5 we use a dynamic model to show how spinodals can pin the relaxation of the system to its equilibrium state.

As can be seen from the phase diagram in figure 1, the temperature region where
the three fluid phases can be stable is bounded from below by the triple point, at 
\[ T = T_{cpd}^3 = 0.865, \]
and from above – by the critical point of transition line 6, at 
\[ T = \tilde{T}_{wpw}^{cr} = 0.885. \]
In what follows of this section we examine in more detail these limiting cases.

Figure 4 depicts the isotherms and the density profiles of coexisting fluid
configurations corresponding to the thermodynamic route exactly at 
\[ T = T_{cpd}^3 = 0.865, \]
where vapour, drop and slab phases coexist. The three branches of the excess free energy,
\[ \Omega_{\text{ex}}(\Delta \mu), \]
defining the fluid phases, all cross at a single point (see figure 4(a)). The
transition values of the disjoining chemical potential are equal at this point: 
\[ \Delta \mu_1 = \Delta \mu_2 \]
(compare, e.g., figures 4(b), 2(d) and 3). The density profiles of the three coexisting
fluid configurations are plotted in figures 4(c) – 4(e). Note that the triple point exists in
the capillary with 
\[ H = 40, \]
does not exist in the capillary with identical substrate
potential, but with \( H = 30 \) (see phase diagrams in figure 10 of Part I and figure 1).
This happens, because a larger distance between the side walls allows for more isolation
of the capillary corners. As a consequence, wedge wetting manifests itself here as an
additional drop phase. The effect of higher isolation of capillary corners, leading to the
three-phase coexistence can also be achieved by reducing the effective strength of the
substrate potential (by that we mean, manipulating the substrate parameters in such a
way as to lower the value of its planar wetting temperature, \( T_w \)).

It is also quite interesting to consider the change in the triple temperature, as the
remaining thermodynamic fields, \( H \) and substrate parameters (\( \varepsilon_w \) and \( \sigma_w \)), are varied.
Obviously, increasing \( H \), or reducing the strength of the substrate will lead to higher
isolation of corners, and the triple point will remain. But reducing \( H \) or increasing the
substrate strength will lead to the appearance of the tri-critical point in the system,
where the three-phase coexistence terminates. The apparent existence of the tri-critical
point is again proven by the two examples, in figure 10 of Part I and in figure 1, where the
first one exhibits a triple-point, and the second one does not. We leave an investigation
of the triple-line for future studies.

Consider now the higher-temperature boundary of the region in the phase diagram,
where vapour, drop and slab phases can be stable at the same \( T \) (but different values
of \( \Delta \mu \)). It is set by the critical point of line 6, at temperature 
\[ \tilde{T}_{wpw}^{cr} = 0.885. \]
We contrast the behaviour of the fluid near that critical point with the behaviour near
the low-temperature end of line 6, at the temperature \( \tilde{T}_0 = 0.828, \) by considering two
isothermal routes. We also show how a mean-field DF approach is capable of capturing
a signature of the approach to criticality.

Figure 5 shows two free-energy isotherms: at \( T = 0.875 \lesssim \tilde{T}_{wpw} = 0.885 \) (the lower
isotherm, designated by an arrow, which also points to the area zoomed at on the inset)
and at \( T = 0.83 \gtrsim \tilde{T}_0 = 0.828 \) (the upper isotherm). Consider, first, the lower isotherm.
As can be seen from the inset, the vapour – drop transition is present and is stable, but
it is also clear (compare to, e.g. figure 2(d), which shows an isotherm at a relatively
lower temperature, \( T = 0.87 \)), that the branches of excess free energy, defining the
vapour and drop phases, tend to align and form a single branch, as \( T \to \tilde{T}_{wpw}^{cr} \). In the
Figure 4. Isothermal thermodynamic route at $T \equiv T_{cpd}^{3} = 0.865$. Vapour, drop and slab phases coexist at $\Delta \mu_{cpw}(T) = \Delta \mu_{wpw}(T) = -5.83 \cdot 10^{-2}$. Capillary parameters are given in figure 1. (a) and (b) Excess free energy and adsorption isotherms. Stable branches are defined as in figures 2(d) and 3. Dotted line denotes the unstable branches. Open circles mark values at three-phase coexistence: $\Omega_{ex}^{cr} = -5.29$, $\Gamma^{1} = 16.6$, $\Gamma^{2} = 65.8$, $\Gamma^{3} = 189.8$. Vertical line on (b) is at the transition value ($\Delta \mu = -5.83 \cdot 10^{-2}$), which can be obtained independently by two equal area constructions. (c) – (e) Density profiles of coexisting phases. Reference densities: $\rho_{cc}^{vap} = 0.06$, $\rho_{cc}^{liq} = 0.51$.

limit $T = \tilde{T}_{wpw}^{cr}$ the distinction between vapour and drop phases will be lost, as branches of excess free energy will join together and form one continuous branch of $\Omega_{ex}^{cr}(\Delta \mu)$, extending from $\mu = -\infty$. During an isothermal increase of the chemical potential at $T > \tilde{T}_{wpw}^{cr}$ the structure of the fluid changes continuously from vapour to a configuration with drops in the corners.

The structure of the upper isotherm in figure 5 is principally different. As is clear from the figure, the branch of excess free energy, which defines the drop phase (solid grey line), simply nearly loses the intersection point with the branch defining the vapour phase (dashed line). Generally, when lowering the temperature from $\tilde{T}_{wpw}^{cr}$ and computing consecutive isothermal thermodynamic routes, we observe that the branch of excess free energy, which defines the drop phase (solid grey line), moves up with respect to the one defining vapour (dashed line). The intersection is thus lost in the limit $T \equiv \tilde{T}_{0} = 0.828$ (compare with isotherms computed at higher $T$: see lower isotherm in figure 5 ($T = 0.875$), as well as isotherms in figures 2(d) ($T = 0.87$) and 4(a) ($T = 0.865$)). A concave branch of excess free energy, defining the drop phase can still be found on the isotherms at $T \lesssim \tilde{T}_{0}$, but it has no intersection with any other branches, thus even a metastable phase transition is lost. The vapour – drop transition line ($\Delta \mu_{wpw}(T)$, line 6 in figure 1, including its metastable part) can never cross the
Figure 5. Criticality of the shifted wedge prewetting. The figure shows two excess free energy isotherms at values of \( T \) near the ends of \( \Delta \mu_{wpw}(T) \)-line (line 6) from figure 1, each possessing two Van der Waals loops: of shifted wedge prewetting and of capillary prewetting. Each isotherm has three concave branches (connected by non-concave branches, plotted with dotted lines), defining the phases: vapour (dashed line), corner drops (solid grey) and capillary-liquid slab (solid black). Arrow points at the lower isotherm with the near-critical shifted wedge prewetting, at \( T_1 = 0.875 \lesssim \tilde{T}_{wpw}^{cr} = 0.885 \) (higher-\( T \) end of line 6 in figure 1), with transition at point \((\Delta \mu_{wpw}(T_1), \Omega^{ex}) = (-6.5 \cdot 10^{-2}, -5.62)\) (capillary prewetting is at point \((\Delta \mu_{cpw}(T_1), \Omega^{ex}) = (6 \cdot 10^{-2}, -5.87)\)). Inset zooms on the shifted wedge prewetting transition at \( \Delta \mu_{wpw}(T_1) \), which disappears in the limit \( T \to \tilde{T}_{wpw}^{cr} \), as the branches of excess free energy defining vapour and drop phases align and form a single branch defining vapour. The upper isotherms is at \( T_2 = 0.83 \gtrsim \tilde{T}_0 = 0.828 \) (lower-\( T \) end of line 6 in figure 1), with transition at point \((\Delta \mu_{wpw}(T_2), \Omega^{ex}) = (-4.7 \cdot 10^{-2}, -4.36)\) (capillary prewetting is at point \((\Delta \mu_{cpw}(T_2), \Omega^{ex}) = (-4.7 \cdot 10^{-2}, -4.36)\)). The shifted wedge prewetting transition disappears at \( T = \tilde{T}_0 \), because the branch of excess free energy defining drop phase losses intersection with the branch defining vapour. Thus, the temperature \( \tilde{T}_0 \) is not critical, whereas the temperature \( \tilde{T}_{wpw}^{cr} \) is critical.

CC line, because the density profiles \( \rho^{cpd}(x,y) \) with corner drops, can be solutions to the Euler-Lagrange equation (see equation (11) of Part I) only when the capillary bulk is filled with vapour, and such configurations are unstable above the CC line, where the bulk is filled with capillary-liquid.

The DF method, which we are using, is classical in the sense that it assumes the molecular positions to be fixed at their ensemble averages. The main limitation of such an approach is that the thermal fluctuations of particles around their equilibrium positions are completely neglected. As a result, the criticality, where such fluctuations play a dominant role, cannot be accounted for within a classical mean-field approach. However, as we have demonstrated, the analysis of Van der Waals loops allows us to
capture a signature of the approach to criticality, and that precisely is how we located the critical points on all presented phase diagrams (see, e.g., open circles in figure 1). Once a critical behaviour is known to exist, it can be studied with more appropriate methods, such as effective Hamiltonians and renormalisation group theory, see, e.g., [7, 8, 9, 10, 11]. We leave such studies for the critical points at $T = T_{cpw}^{cr}$ and $T = \tilde{T}_{wpw}^{cr}$ (e.g., end points of lines 6 and 7 in figure 1) for future research.

3. Three-phase coexistence in the slit pore

All the examples up to this point were restricted to cases where at a given temperature the capillary bulk (associated slit pore) can have at most two stable phases: vapour or capillary-liquid. We have shown that a transition between these phases changes dramatically, when the slit pore is capped by an additional wall and a capillary wetting temperature appears as a result. However, a slit pore can allow for the existence of a third phase, a thin film, which is a remnant of the prewetting on a single wall, see, e.g., [12]. In the next section we show, how such a complex behaviour of capillary bulk leads to a continuous prewetting transition in the capped capillary. Here we provide some background and briefly describe three-phase coexistence in the slit pore, using as an example the 1D slit pore whose full phase diagram is shown in figure 1 (solid and dashed grey lines). First, we briefly summarise the phenomenology of adsorption on a single wall and then describe the changes due to adding another wall to form a slit pore. Finally, we discuss the three-phase coexistence inside the capillary bulk and provide several representative examples associated with various isothermal thermodynamic routes near $T_{3}^{slt}$, figure 1.

Although wetting on a single wall and a slit pore is well understood, and has attracted considerable interest in the literature from the late 1980’s until the mid 1990’s (see, e.g., reviews in [13, 14, 15]), we believe it is appropriate and within the scope of the present study to provide a treatment of single-wall and slit-like substrates within our DF approach. Such treatment reveals the connections between the wetting scenarios of the 1D slit pore and 2D capped capillary, as well as providing the necessary background for studying the effect of capping a capillary, whose bulk can have multiple stable phases. In the existing literature numerical studies most relevant to the present section are, e.g., reference [16], where the three-phase coexistence in a slit pore is studied using a mean-field microscopic lattice-gas model of the fluid. The three phase coexistence is mentioned in references [17, 13]. The treatment of asymmetric slit-like substrates, using effective substrate potentials, as well as a non-local DF model, can be found in the recent work by Stewart and Evans [18].

In the case of a single planar wall immersed in vapour the bulk liquid – vapour transition has the option of becoming continuous (second-order), i.e., it can happen from the substrate surface. For example, in an isothermal approach to bulk saturation ($\Delta \mu \equiv 0$), at $T$ higher than the planar wetting temperature, $T_w$, the space above the wall is filled with liquid continuously, as the chemical potential approaches saturation.
The liquid – vapour transition is then preceded by prewetting, a first-order surface phase transition between the vapour and a thin (microscopic) film adsorbed on the substrate wall. Transition line 1 in figure 1 is the locus of prewetting transitions on the planar substrate – $\Delta \mu_{pw}(T)$. At values of $T$ below $T_w$, the liquid – vapour transition follows its bulk scenario (first-order): wall stays non-wet (non-zero contact angle), until the chemical potential reaches saturation, and the whole system abruptly transforms to a liquid state.

Confining a fluid which is in its vapour phase in a slit pore adds wall separation and parameters of the substrate potential to the set of bulk thermodynamic fields (temperature and chemical potential). The phenomenology of phase transition in the confined fluid maps to that in the bulk: the transition between vapour and capillary-liquid is of first order. But the denser coexisting phase (capillary-liquid) has lower density (far from the surfaces of both walls, where $\rho_{slt}(y)$ is nearly constant) than the density of the bulk liquid, coexisting with vapour at the same temperature. Moreover, the transition in the slit pore is essentially the shifted bulk liquid – vapour transition. This phenomenon is otherwise referred to as the Kelvin shift and was discussed earlier, in the Introduction. In the simplest macroscopic description, where all non-local fluid-substrate intermolecular effects are contained inside surface tensions, the vapour – capillary-liquid transition is given by equation (1) of Part I. The CC lines, which we present in this work (e.g., grey curves in figures 4, 9, 10 of Part I and in figure 1), describe the same phenomenon, but include all the fluid-fluid and fluid-substrate molecular interactions explicitly, in the model of the fluid free energy (equation (2) of Part I), which is equivalent to approximating the grand partition function.

A slit pore of any width, $H$, allows for the coexistence between vapour and capillary-liquid phases. Increasing $H$ leads to higher isolation of the walls and can result in the appearance of stable thin film adsorbed on both walls, coexisting with vapour, as it happens in the case of a single wall. An example of two slit pores, differing only in the values of wall separation, is provided by (see grey lines) figure 10 of Part I ($H = 30$: no thin film – capillary-liquid transition) and figure 1 ($H = 40$: stable thin film – capillary-liquid transition line appears, $\Delta \tilde{\mu}_{pw}(T)$, line 3). In the latter case, the three two-phase coexistence lines (2, 3 and 4) cross at a single point, at the slit triple temperature, $T_{slt}^3 = 0.92$, where all three phases (vapour, thin film and capillary-liquid) are stable and coexist.

The transition line where vapour coexists with a thin film on a single planar wall immersed in vapour (the planar prewetting line, $\Delta \mu_{pw}(T)$, line 1 in figure 1), is shifted in the slit pore entirely by a constant value and forms the transition line $\Delta \tilde{\mu}_{pw}(T)$ (line 3). An analytical relation between the shift of prewetting and the width of the capillary, $H$, can be obtained using standard field-theoretical thermodynamic methods, see, e.g., references [2, 3]. In the case presented on figure 1 the transition lines of planar prewetting, $\Delta \mu_{pw}(T)$ (line 1, figure 1), and of shifted planar prewetting in the slit pore, $\Delta \tilde{\mu}_{pw}(T)$ (line 3), were found by arc-length continuation of solutions to the equation (24) of Part I over the parameter $T$, and are thus given at different values
of temperature. Using spline interpolation, we have computed both transition lines at the set of 1000 equidistant points along the $T$-axis, between both ends of $\Delta \mu_{pw}(T)$-line (line 3), i.e. $T = 0.848$ and $T = 0.945 \equiv \tilde{T}_{pw}^c$. The calculated mean value for the shift of planar prewetting transition due to the presence of the second wall, forming the slit pore, along $\Delta \mu$-axis is found to be $(1.7 \pm 0.1) \cdot 10^{-3}$.

Due to the presence of the triple point, the transition to capillary-liquid takes place along lines 2 and 4 in figure 1, which together form the $\Delta \mu_{cc}(T)$-line, where capillary-liquid coexists with vapour (at $T < T_{3}^{st} = 0.92$, line 2) and thin film (at $T > T_{3}^{st} = 0.92$, line 4) phases. Figure 6 shows representative free energy isotherms, $\Omega(\Delta \mu)$, (unstable branches are not plotted) and coexisting density profiles (of only stable transitions) at temperatures below, at and above $T_{3}^{st}$. The dashed line, solid black line and grey
line in the plots of the isotherms and density profiles demarcate the vapour phase, the capillary-liquid phase, and the thin film phase, respectively. The density profiles plotted with a dotted line show the fluid configurations coexisting during planar prewetting on a single planar wall (the locus of phase transitions is $\Delta \mu_{pw}(T)$-line, line 1 in figure 1) at the same value of temperature.

When $T < T_{slt}^3$ (figures 6(a) and 6(b)) there is a single stable phase transition – between configurations of vapour and capillary-liquid. Figure 6(a) shows the complete branch of the free energy defining the thin film phase (solid grey line). It is bounded by its two turning points (spinodals). The branch defining the vapour phase (dashed line) extends from $\mu = -\infty$ up to its spinodal, whereas the capillary-liquid branch is bounded at higher values of $\Delta \mu$ by the bulk liquid – vapour coexistence ($\Delta \mu \equiv 0$). Increasing the temperature results in the thin film branch moving down relatively to the intersection of the vapour and capillary-liquid branches, as is clear from figures 6(c) and 6(e).

At $T = T_{slt}^3$ (figures 6(c) and 6(d)) the three branches of the free energy intersect at one point, at the value of disjoining chemical potential $\Delta \mu_3 \equiv \Delta \tilde{\mu}_{pw}(T_{slt}^3) = \Delta \mu_{cc}(T_{slt}^3)$. The triple point, $(\Delta \mu_3, T_{slt}^3)$, depends on the substrate parameters, $\varepsilon_w, \sigma_w$ and the capillary width, $H$. The dependence (triple-line) can be obtained numerically by using arc-length continuation applied to equation (1), with the parameter of interest. Finally, note that the density profiles of vapour and thin film phases in the slit pore (dashed and solid grey lines) are almost indistinguishable from those on a single planar wall (dotted lines).

At $T > T_{slt}^3$ (figures 6(e) and 6(f)) we find two stable transitions: vapour – thin film (at a lower value of $\Delta \mu$), and thin film – capillary-liquid (at a higher value of $\Delta \mu$). The density profiles of vapour in the slit pore and on the single wall are still very close. As for thin film profiles, the one on a single wall is closer to the one in the slit pore, which coexists with vapour, than the one coexisting with capillary-liquid.

A further increase in $T$ leads to the thin-film – vapour criticality at the value of shifted critical prewetting temperature, $T = \tilde{T}_{pw}^{cr}$. The density profiles become indistinguishable, with the corresponding phase branches of $\Omega(\Delta \mu)$ aligning. At a fixed $T > \tilde{T}_{pw}^{cr}$ the growth of the film adsorbed on each wall of the slit pore is continuous with $\Delta \mu$, until the first-order CC is reached and the entire pore is filled with capillary-liquid discontinuously.

4. Continuous prewetting

In the previous section we have demonstrated (in agreement with existing theory, e.g., references [13, 17]), that the prewetting of a single planar wall immersed in vapour, and the shifted prewetting of a slit pore immersed in vapour, are essentially equivalent phenomena. The transition line, which forms the locus of vapour and film coexistence in a slit pore, $\Delta \tilde{\mu}_{pw}(T)$, is shifted entirely from the prewetting line of the planar wall, $\Delta \mu_{pw}(T)$, by a well defined constant value related to the substrate parameters and pore width (see lines 1 and 3 in figure 4 and theory in, e.g., reference [2]). Also, the
calculated structure of the film phases formed in a slit and on a planar wall is nearly indistinguishable (see, e.g., figure 6). In this section we exploit this equivalence to demonstrate a case of continuous prewetting transition and highlight some important potential applications of this newly discovered phenomenon.

We focus on a capped capillary, whose bulk (the associated slit pore) allows for the coexistence between vapour and thin films adsorbed on the side walls. First, we show that the shifted prewetting transition becomes a continuous phenomenon in such systems, manifested by capillary-liquid fingers unbinding into the capillary bulk, as the chemical potential (pressure) is increased towards the value at shifted prewetting. Second, we show that an isothermal approach to CC goes through two consecutive stable continuous phase transitions. We are not aware of a previous study on continuous prewetting in a confined fluid. Below we also briefly discuss some obvious similarities to wetting of micro-steps (see, e.g., reference [19]). It is to be noted, however, that the fluids under consideration are confined and undergo saturation below the bulk liquid – vapour transition (due to Kelvin shift, e.g., equation (1) of Part I), unlike a step-shaped substrate immersed in vapour. Also, we expect the continuous prewetting in the capillary-like geometries to be much more accessible experimentally, than step wetting, because it requires much fewer conditions to be satisfied by the substrate in order to be observed. We elaborate on that at the end of the section.

Consider an isothermal thermodynamic route at $T = T_1$ in the interval $T_3^{sl} < T_1 < T_{pw}^{cr}$, where the pressure in the reservoir (or, equivalently, the disjoining chemical potential, $\Delta \mu$) is slowly increased from a low value, at which the fluid inside the capped capillary is in the vapour phase. In the phase diagram this corresponds to a path crossing vertically the transition lines $\Delta \mu_{pw}(T)$ and $\Delta \mu_{cc}(T)$ (lines 3 and 4 in figure 1). As we have seen in the previous section, an isothermal crossing of $\Delta \mu_{pw}(T)$-line corresponds to the phase transition in the capillary bulk, where vapour and thin film phases coexist (shifted prewetting transition, see, e.g., figures 6(b), 6(e)). One might intuitively expect that due to the presence of the capping wall this transition may happen continuously, analogously to the continuous CC (provided that the capping wall is sufficiently attractive). We indeed find it to be the case.

Figure 7 shows a representative set of adsorption and excess free energy isotherms, corresponding to the thermodynamic route at the temperature $T_1 = 0.93 > T_3^{sl}$. The region in $\Delta \mu$ is chosen in the vicinity of transitions in the capillary bulk. Figure 7(a) shows the adsorption isotherm which consists of two unconnected branches: the grey branch spans the interval of values of $\Delta \mu : -\infty \leq \Delta \mu \leq \Delta \mu_2$, and the black branch is limited to the interval $\Delta \mu : \Delta \mu_1 \leq \Delta \mu \leq \Delta \mu_3$. Figure 7(b) shows the free energy isotherm of the associated slit pore (capillary bulk), corresponding to the same thermodynamic route; unstable branches are not shown. In figure 7(b) the dashed, solid grey and solid black like denotes the branch of vapour, thin film and capillary-liquid, respectively. Figure 7(c) shows the excess free energy isotherm of the capped capillary, which consists of two unconnected branches. The numbered dotted vertical lines in each figure are drawn at the values of $\Delta \mu$, which denote: $1 - \Delta \mu_1$, the value of low-
Let us describe the way in which the two consecutive continuous phase transitions take place in the capped capillary, as the chemical potential of the containing reservoir pressure spinodal of the thin film phase inside the slit (the point \((T_1, \Delta \mu_1)\) is below, but near line 3 in the phase diagram), 2 – \(\Delta \mu_2 \equiv \Delta \mu_{\text{pw}}(T_1)\), the value of vapour – thin film coexistence in the capillary bulk (shifted prewetting transition: the point \((T_1, \Delta \mu_2)\) belongs to line 3 in the phase diagram), 3 – \(\Delta \mu_3 \equiv \Delta \mu_{\text{cc}}(T_1)\), the value of thin film – capillary-liquid coexistence in the capillary bulk (CC: the point \((T_1, \Delta \mu_3)\) belongs to line 4 in the phase diagram). The capillary bulk transitions from vapour to thin film and from thin film to capillary-liquid are both stable. In the capped capillary \(\Delta \mu_2\) and \(\Delta \mu_3\) provide vertical asymptotes for the diverging adsorption, \(\Gamma(\Delta \mu)\), plotted in figure 7(a). Several representative density profiles are shown in figure 8, where plots (a) – (c) correspond to \(\Delta \mu \rightarrow \Delta \mu_2\) and plots (d) – (f) correspond to \(\Delta \mu \rightarrow \Delta \mu_3\). The data values on the isotherms, corresponding to the presented density profiles are marked by filled (for profiles (b), (c)) and open (for profiles (d), (e)) circles in figures 7(a) – 7(c).

Let us describe the way in which the two consecutive continuous phase transitions take place in the capped capillary, as the chemical potential of the containing reservoir
is increased from a large negative value $\Delta \mu \sim -\infty$ (where the capped capillary is filled entirely with vapour) to the value $\Delta \mu = \Delta \mu_3$ (where the capped capillary is filled entirely with capillary-liquid), at the constant temperature $T_1 = 0.93$.

As $\Delta \mu$ is increased from a large negative value so that the point representing the system in the phase diagram, approaches and crosses the $\Delta \mu_{cpw} (T)$-line (line 7 in figure 1), the discontinuous (first-order) transition from the drop phase to capillary-liquid slab phase takes place at the value $\Delta \mu = \Delta \mu_{cpw} (T_1) = -7 \cdot 10^{-2}$ (this transition, manifested by a hysteresis S-loop in $\Gamma (\Delta \mu)$, is outside the range chosen for figure 7).

As $\Delta \mu$ is further increased, the point representing the system in the phase diagram approaches the shifted prewetting line, $\Delta \mu_{pw} (T)$ (line 3), and the density profiles begin to develop liquid-like fingers (see, e.g., figures 8(a) – 7(c)). The values of adsorption for the fluid configurations with fingers belong to the branch of $\Gamma (\Delta \mu)$, plotted in grey in figure 7(a). The values of the excess free energy belong to a strictly concave branch of $\Omega_{ex} (\Delta \mu)$ (grey curve in figure 7(c)), signifying that, first, the fluid states with liquid-like fingers are thermodynamically stable, i.e. observable, second, the configurations with liquid-like fingers form a fluid phase. As $\Delta \mu \rightarrow \Delta \mu_2 \equiv \Delta \mu_{pw} (T_1)$, the length of the fingers increases and diverges in the limit (see again the density profiles in figures 8(a) – 7(c)).

To understand the phase with liquid-like fingers, we have analysed vertical cross sections of various density profiles, $\rho^{pfd} (x, y)$, belonging to that phase. We chose two sets of values along the $x$-axis: $x_f$ – between the capping wall and the tips of the fingers, and $x_v$ – well inside capillary bulk, far away from the finger tips. We compared the slices $\rho (x_f, y)$ and $\rho (x_v, y)$ with the 1D density profiles of fluid configurations, coexisting inside the associated slit pore during the shifted prewetting transition at $\Delta \mu \equiv \Delta \mu_2 = \Delta \mu_{pw} (T_1)$: $\rho_{y,\text{film}} (y)$ and $\rho_{y,\text{vap}} (y)$. We have found that an equivalence similar to the one expressed by equation (27) of Part I, holds (within the margin of machine rounding error):

$$
\rho (x_f, y) \equiv \rho_{y,\text{film}} (y),
\rho (x_v, y) \equiv \rho_{y,\text{vap}} (y).
$$

(2)

The above relation proves, that the profiles with liquid-like fingers correspond to the continuous onset of the thin film phase, which is filling the capped capillary as $\Delta \mu \rightarrow \Delta \mu_2$, thus making shifted prewetting a continuous phase transition.

The order parameter of the continuous prewetting is again adsorption, $\Gamma (\Delta \mu)$, defined in equation (23) of Part I. While $\Delta \mu < \Delta \mu_2$, the bulk of the capped capillary is in the vapour phase (see figure 7(b)), and the development and growth of the denser phase from the capping wall leads to the divergence of the integral in equation (23) of Part I, so that $\Gamma \rightarrow \infty$, as $\Delta \mu \rightarrow \Delta \mu_2$. The value $\Delta \mu = \Delta \mu_2$ is the vertical asymptote for the branch of $\Gamma (\Delta \mu)$-dependence (grey line in figure 7(a)). The branch of the excess free energy, on the other hand, tends to a finite limit, as is typical in continuous phase transitions (grey line in figure 7(c)).

Increasing the control parameter, $\Delta \mu$, further above $\Delta \mu_2$ corresponds to a point,
Figure 8. Representative density profiles for an isothermal approach to CC at $T = 0.93$, which has two consecutive continuous transitions, see figure 7. Reference densities: $\rho_{cc}^{vap} = 0.09$, $\rho_{cc}^{liq} = 0.41$. (a) – (c) Density profiles of fluid states from the branch of the isotherm corresponding to continuous prewetting (figure 7, grey line). The values of $\Delta \mu$: $-4.4 \cdot 10^{-2}$, $-3.82 \cdot 10^{-2}$, $-3.80 \cdot 10^{-2}$; values of $\Gamma$: 55.4, 276.8, 527.9; values of $\Omega^{\text{ex}}$: -7.78, -12.73, -13.54. (d) – (f) Density profiles of continuous CC, which follows continuous prewetting (figure 7, black line). The values of $\Delta \mu$: $-8.3 \cdot 10^{-2}$, $-4.6 \cdot 10^{-2}$, $-4.37 \cdot 10^{-2}$; values of $\Gamma$: 193.6, 483.6, 898.1; values of $\Omega^{\text{ex}}$: -13.65, -14.96, -15.02. The values of adsorption and excess free energy are marked in figures 7(a), 7(c) by filled black circles for profiles (b), (c) and by open circles for profiles (d), (e).

representing the system in the phase diagram, advancing vertically between transition lines of shifted prewetting (line 3) and CC (line 4), towards CC. For values of $\Delta \mu$ in the interval $\Delta \mu_2 \leq \Delta \mu \leq \Delta \mu_3$ the associated slit pore is in the thin film phase (see figure 7(b)). All thermodynamically stable equilibrium fluid configurations in the capped capillary possess a thin film at both side walls.

As the value of $\Delta \mu$ is increased further, the meniscus starts to unbind from the capping wall into the capillary bulk (see density profiles in figures 8(d) – 8(f)). The analysis of vertical cross sections (similar to the one presented above) shows that the structure of the fluid between the capping wall of the capillary and the meniscus is identical to that of capillary-liquid coexisting with the thin film in the associated slit pore at $\Delta \mu = \Delta \mu_3$. The structure of the fluid far from the capping wall and the meniscus has, in turn, been found to be identical to the coexisting thin film phase. We also find the divergence of the order parameter: $\Gamma \to \infty$, as $\Delta \mu \to \Delta \mu_3$; the value $\Delta \mu = \Delta \mu_3$ provides the vertical asymptote for the $\Gamma (\Delta \mu)$-dependence (black curve in figure 7(a)). Since in this limit the excess free energy tends to a finite limit (black curve in figure 7(c)), the unbinding meniscus corresponds to the continuous CC.

We note that the density profiles, $\rho^{\text{pd}}(x,y)$, from the the Euler-Lagrange equation (equation (11) of Part I), can in fact be obtained for values of $\Delta \mu$ in the larger interval $\Delta \mu_1 \leq \Delta \mu \leq \Delta \mu_3$, which includes the metastable part of the thin film branch (the parts of black curves in figures 7(b) and 7(c) between $\Delta \mu_1$ and $\Delta \mu_2$). However, those states
are thermodynamically unstable, which follows immediately from the consideration of the \( \Gamma (\Delta \mu) \)-dependence (see black curve in figure 7(a)). The part of the \( \Gamma (\Delta \mu) \)-branch between \( \Delta \mu_1 \) and \( \Delta \mu_2 \) is non-monotonous, and, according to the Gibbs rule (see equation (22) of part I), the corresponding part of the excess free energy isotherm is not strictly concave. So, although the fluid configurations corresponding to this part of the isotherm solve the Euler-Lagrange equation, they do not minimise the free energy.

To summarise, we have shown that the planar prewetting transition can become a continuous (second-order) phenomenon in a capillary-like geometry, when the associated slit pore allows for the three-phase coexistence. Let us briefly highlight the potential ramifications of this finding.

One important consequence is that it allows one to take prewetting to an observable scale: the typical height of a thin film coexisting with vapour on a planar surface is several molecular diameters, and rather involved and specialised experimental techniques are required to even register an existence of prewetting, see, e.g., reviews in references [20, 21, 22, 23]. However, the same phenomenon in a capillary-like geometry corresponds to a singularity of an observable (the adsorption, \( \Gamma \)), rather than to a tiny jump in its value, thus registering a prewetting transition is simplified. Since the relation between planar prewetting on a wall and shifted prewetting in the slit-like geometry is clear (the value of the shift is constant for the entire transition line and can be established experimentally by, e.g., calibration), using capillary-like, rather than planar substrates can also simplify the measurement of microscopic prewetting transitions on various substrates.

The continuous prewetting is related to the phenomenon of step wetting, where a planar step of the height of several molecular diameters (the height should be that of the coexisting thin film), immersed in vapour, adsorbs liquid, showing a divergence of the meniscus as the prewetting pressure is approached (consider, e.g. [19]). We again expect the substrate in the form of a wide capped capillary to be more feasible to study experimentally than a microscopically high step. For one, the height of the step should be exactly equal to the height of the coexisting thin film (the value is very small: several molecular diameters). Using a capped capillary completely eliminates the need to implement such a highly precise microscopically patterned substrate: the continuous prewetting should be observable at any value of \( H > H_{cr}^3 \), where \( H_{cr}^3 \) is the tri-critical value for the appearance of the three-phase coexistence in a slit pore.

A further exploration of continuous prewetting would go beyond the scope of the present work dedicated to wetting in capped capillaries. Of particular interest would also be the study of critical exponents for the diverging thin film fingers, as well as for the growing meniscus at \( T > T_{slit}^3 \). Such investigation would allow us to establish Ising universality classes. Another important direction is accounting for fluctuations, which may prevent phase transitions from taking place in rather small systems at high temperatures. We note, however, that increasing the wall separation, \( H \), would reduce the fluctuation effects allowing, in principle, for the observation of the phenomena observed, which are not affected by increasing \( H \).
5. Slow relaxation

We have shown that reducing the attractive strength of the substrate potential (lowering $T_w$) gradually leads to the appearance of a metastable drop phase, which eventually stabilises for weaker substrates and even coexists with vapour and capillary-liquid slab phases: see, e.g., the upper isotherm in figure 5, where the concave branch of excess free energy, defining the (metastable) drop phase (grey line), is quite pronounced. We have restricted our consideration to fluids with vapour- and liquid-like densities, so the temperatures were chosen above the bulk triple point. At lower temperatures and/or weaker attractive substrates we expect more metastable branches of free energy to appear, due to effects of layering or freezing, see, e.g., [24]. In this section we use a dynamic model to show how the relaxation of the system is affected by metastability. In order to enhance the confinement effects of the substrate, we deviate from the definition of the external potential, given in equation (10) of Part I, and consider here a capped capillary formed from three 3-9 walls (see definition in equation (13) of Part I):

$$V(x, y) = V_{\varepsilon_w, \sigma_w}^{3-9}(x) + V_{\varepsilon_w, \sigma_w}^{3-9}(y) + V_{\varepsilon_w, \sigma_w}^{3-9}(H - y).$$

(3)

Using such a substrate potential leads to more pronounced hysteresis loops in the adsorption isotherms. Substrates of the type defined by equation (3) were studied in detail in our previous work in reference [6].

Under the standard assumptions of a local equilibrium [25] we use “model A” of the general dynamic universality class, describing the evolution of an open system in contact with the reservoir of particles, which keeps it at fixed values of $T$ and $\mu$ [26, 27]:

$$\frac{\partial \rho (\mathbf{r}, t)}{\partial t} = -\zeta \frac{\delta \Omega [\rho]}{\delta \rho (\mathbf{r}, t)},$$

(4)

where $\zeta$ defines time units as $(\zeta \varepsilon \sigma^3)^{-1}$. A particular value of $\zeta$ only affects the rate of relaxation to the equilibrium state without loss of generality [14]. We then set $\zeta \equiv 1$. The right hand side of equation (4) is equivalent to the left hand side of the Euler-Lagrange equation (see equation (11) of Part I). Thus, the stationary solutions to the integral-differential equation (4) form the extrema of fluid free energy and can be obtained independently by solving the Euler-Lagrange equation. More applications of model (4) within the DF framework can be found in, e.g., reference [28]. Details of numerical implementation of the implicit time-stepping scheme, which was used to solve equation (4), can be found in our previous work in reference [14]. A different model, incorporating the effects of hydrodynamic interactions has recently been proposed in references [29, 30].

In a dynamic setting, the adsorption isotherms act as bifurcation diagrams. Figure 9(a) shows the adsorption isotherm at $T = 0.8$ for the capillary with parameters $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 30$. The fluid is treated in LDA, the planar wetting temperature: $T_w = 0.755$. The system exhibits only a single first-order transition, namely the stable capillary prewetting transition at $\Delta \mu_{cpw}(T) = -4.95 \cdot 10^{-2}$, but there is also a metastable drop phase. Thermodynamically stable (and metastable) fluid states
Figure 9. Evolution of the density profiles in the capped capillary, whose substrate potential is defined in equation (3), with \( \varepsilon_w = 0.7, \sigma_w = 2, H_0 = 5, H = 30; \) at \( T = 0.8T_c, \zeta = 1. \) (a) Equilibrium adsorption isotherm (bifurcation curve). Solid line: stable/metastable equilibria, dashed line: unstable states, vertical dashed-dotted lines: routes of dynamic emptying, starting with the same initial density profile of capillary filled with capillary-liquid at CC (at \( \Delta \mu \equiv \Delta \mu_{cc}(T) = -4.65 \cdot 10^{-2} \)), passing at distances \( (\Delta \mu - \Delta \mu_1): 10^{-4}, 9 \cdot 10^{-3} \) and \( 14 \cdot 10^{-3} \) to the spinodal at \( (\Delta \mu_1, \Gamma_1) = (-0.091, 92.5) \). Inset: vertical dashed-dotted lines show routes of dynamic filling starting with same initial profile of capillary filled with vapour, passing close to metastable branch, at the distances \( (\Delta \mu_2 - \Delta \mu_2): 8 \cdot 10^{-5}, 4 \cdot 10^{-4}, 6 \cdot 10^{-4} \) to its right-most spinodal at \( (\Delta \mu_2, \Gamma_2) = (-0.041, 86.7) \). (b) Evolution \( \Gamma(t) \) for dynamic filling, note pinning to the metastable branch between \( (\Delta \mu_2, \Gamma_2) \) and \( (\Delta \mu_3, \Gamma_3) = 86.7. \) (c) Evolution \( \Gamma(t) \) for dynamic emptying; note the pinning to the spinodal at \( (\Delta \mu_1, \Gamma_1) \).

Form branches of the isotherm drawn with a solid line, the unstable branches are drawn with a dashed line. The system has three phases: vapour, corner drops and capillary-liquid slab. Their corresponding fluid configurations form concave branches of excess free energy. The capillary-liquid fills the entire capillary at \( \Delta \mu \equiv \Delta \mu_{cc}(T) = -4.65 \cdot 10^{-2} \).

Choosing a density configuration, which minimises \( \Omega[\rho_{\text{cpd}}(x, y)] \) at some value of \( \mu \equiv \mu_{\text{sat}} + \Delta \mu \) as an initial condition, and then using a different value in the equation (4), allows to study the relaxation of the system to a new equilibrium state. An independent calculation of equilibria (steady solutions of equation (4)) was used to control the convergence.

The resulting dynamics is most conveniently represented as evolution curves for \( \Gamma(t) \) (see figure 9). We consider several processes of dynamic capillary filling, where the initial condition belongs to the vapour phase, and in the final state \( (t \to \infty) \) the entire capillary is filled with capillary-liquid, figure 9(b). We also consider dynamic emptying, where the initial state of capillary-liquid relaxes to vapour, figure 9(c).

We find that the evolving system can spend considerable, albeit always finite, time in the vicinity of metastable states. Figure 9(b) illustrates the pinning to a whole branch.
Conclusion

In this two-part study we have investigated the phenomenon of capillary condensation. By applying a first-principles theory based on statistical mechanics, we have modelled a prototypical 2D system, namely a slit pore capped by an additional wall, and performed a full parametric study of the model to show how the additional spatial dimension in the confined fluid dramatically affects the nature of wetting. By manipulating the thermodynamic fields acting on the system, it is possible to switch its wetting behaviour between various mechanisms, or allow for several wetting mechanisms at the same time. The planar wetting temperature, $T_w$, serves as a convenient effective measure of the attractive strength exerted by the substrate on the fluid.

Our study further demonstrates, how computational access to isotherms and the concept of a Van der Waals loop can be used to analyse fluids in confinement. Until quite recently only a handful of studies presented adsorption isotherms, and even fewer presented complete phase diagrams of complex 2D systems. We have explored all possible wetting scenarios in a capped capillary, presented various phase diagrams, identifying every concave branch of free energy with a fluid phase and revealed the physics of the interplay between different wetting mechanisms. The numerical continuation technique makes calculations readily accessible, and we expect this methodology to have more applications in the mean-field DF calculations of fluids in a wide range of settings. We note also that a consistent analysis of thermodynamic stability of a given fluid configuration is impossible to carry out without access to a set of density profiles, which allows to analyse the convexity of the free energy. The arc-length continuation method allows for such analysis in a natural and consistent way, as we have demonstrated. Although the most technical details of continuation algorithms have been omitted, they are well documented in our previous work, in reference [14], in the form, which makes them readily accessible for application to DF problems.

Apart from the general phase behaviour, we have also discussed in detail the structure of coexisting fluid configurations, the excluded volume effects and criticality. We now summarise the main results of this two-part study noting that for the sake of clarity we also reiterate the main results of Part I:

- Capping a slit pore at one end by an additional wall leads to the **capillary wetting transition**. It is a discontinuous first-order phase transition characterised by the presence of the **capillary wetting temperature**, $T_{cw}$, which is a property of the pore and controls the order of CC. Capillary wetting can be manifested by, e.g., a continuous transition to CC at temperatures above $T_{cw}$, while below $T_{cw}$ CC remains abrupt (first-order).

- There exists a first-order **capillary prewetting** transition, which precedes a continuous CC. The capillary wetting transition can be viewed as the limiting case
of the capillary prewetting at $T = T_{cw}$. In the $T - \Delta \mu$ space the transition line of capillary prewetting runs tangentially to the condensation line of capillary bulk. Capillary prewetting possesses a critical point at the critical capillary prewetting temperature, $T_{cpw}^{cr}$, $T_{cw}$. However, we need to emphasise that the wetting on capped capillaries belongs to a different Ising universality class from that on a single planar wall. The critical exponents of an isothermal approach to capillary condensation above $T_{cw}$ can be found in references [6, 5].

- Wetting on wedge-shaped substrates immersed in vapour is dramatically affected by the addition of a third wall, which changes the geometry to a capped capillary. On the phase diagram of the fluid in the $T - \Delta \mu$ space the remnant of wedge prewetting (see, e.g., reference [1]) can form a transition line, which is translated relatively to the wedge prewetting line along the $\Delta \mu$-axis by a constant value. This has been referred to as the shifted wedge prewetting transition. The value of the shift depends on the width of the capillary and the parameters of the substrate forming it, with the mechanism of the shift being analogous to the shift of the bulk saturation inside a slit-like geometry (Kelvin shift). The relative value of the shift has been computed in one of the examples. We have also shown how the criticality associated with wedge prewetting affects the fluid configurations in the capillaries, whose phase diagram does not possess a transition line of the shifted wedge prewetting.

- We have confirmed the existence of a triple point, where all three near-wall phases (vapour, drops and capillary-liquid slab), which are separately associated with shifted wedge prewetting and capillary prewetting, can coexist. Moreover, we have shown, that a tri-critical point must also exist.

- The capillary bulk can exhibit a transition specific to a single planar wall, but shifted due to the presence of the additional wall – shifted planar prewetting. It is well understood and known to be of first order. We have found a continuous prewetting transition in capped capillaries, where the capillary bulk allows for shifted planar prewetting. In such systems the continuous CC is preceded by the continuous prewetting. In other words, the system has two consecutive continuous transitions, each associated with the divergence of adsorption. The adsorption isotherm of such capillaries consists of two unconnected diverging branches. We expect continuous prewetting to be easily accessible experimentally. It can potentially influence the experimental investigation of registering and measuring the characteristics of planar prewetting.

- The metastable fluid configurations have been found to affect the evolution of the system, pinning it to spinodals of the corresponding phase branches of the free energy.

We now briefly highlight directions where further research is in order. First, we note that in the presented density profiles the microscopic fluid configurations have well defined angles between the two-phase interface (level set at $(\rho_{vap}^{cc} + \rho_{liq}^{cc})/2$) and
the substrate see figures 2(d), 3, 5(a), 6(a), 8(c), 8(e) of part I and figures 2(b), (c), 4 (d), (e) and 8. The value of the angle is different from the contact angle at bulk liquid–vapour coexistence, which is often defined through Young’s equation. A deeper analytic exploration, possibly involving the concept of line tension would allow to better understand that effect.

Considering further the presented density profiles, we note that there should exist relations, connecting the values of the density profiles at contact with the substrate with the thermodynamic fields present in the system \((T, \mu, \varepsilon_w, \sigma_w, H)\). Such relations should exist for the contact at the corner apex \((\rho (x = 0, y = 0))\), as well as at each capillary wall \((\rho^{cpd} (x \equiv 0, y), \rho^{cpd} (x, y \equiv 0))\).

Regarding the described phenomenology of wetting, we emphasise again that we have not touched upon the universality of the reported phenomena. It is also of great interest to obtain the critical exponents for the various transitions we have presented, e.g., the power law describing \(\Delta \mu_{cpw} (T)\), as \(T \to T_{cw}\), the power law for the divergence of \(\Gamma (\Delta \mu)\) as \(\Delta \mu \to \Delta \tilde{\mu}_{pw} (T)\) in the case of the continuous prewetting transition. One might expect that the shifted wedge prewetting belongs to a different universality class than the wedge prewetting in the approach to bulk saturation, studied in, e.g., references [1, 31].

An analytic expression for the shift of the wedge prewetting in a capped capillary can be obtained following standard procedures, e.g., [4]. The three-phase coexistence between vapour, drop and capillary-liquid slab configurations requires additional investigation. We have only reported on the existence of the triple line (as function of parameter \(H\)), ending at the tri-critical point. The associated universality class remains to be established.

Further, there might be a first-order transition, preceding the continuous prewetting, similar to the way capillary prewetting precedes continuous condensation. A discovery of such a phase transition (or a proof that it does not exist) would then complete the picture of condensation in slit-like 2D geometries. Finally of interest would be how the various phase transitions are influenced by chemical and/or topographical wall heterogeneities which are known to have a substantial influence on wetting, e.g. [32, 33]. We hope to investigate these and related issues in future studies.

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