Wetting in a two-dimensional capped capillary. Part I: Wetting temperature and capillary prewetting.

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Abstract. In this two-part study we investigate the phase behaviour of a fluid spatially confined in a semi-infinite rectangular pore formed by three orthogonal walls and connected to a reservoir maintaining constant values of pressure and temperature in the fluid. Far from the capping wall this prototypical two-dimensional system reduces to a one-dimensional slit pore. However, the broken translational symmetry leads to a wetting behavior strikingly different from that of a slit pore. Using a realistic model of an atomic fluid with long-ranged Lennard-Jones fluid-fluid and fluid-substrate interactions, we present for the first time detailed computations of full phase diagrams of two-dimensional capped capillaries. Our analysis is based on the statistical mechanics of fluids, in particular density functional theory. We show the existence of capillary wetting temperature, which is a property of the pore, and relatively to the fluid temperature determines whether capillary condensation is a first-order or a continuous phase transition. We also report for the first time a first-order capillary wetting transition, which can be preceded by a first-order capillary prewetting. A full parametric study is undertaken and we support our findings with exhaustive examples of density profiles, adsorption and free energy isotherms, as well as full phase diagrams.

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1. Introduction

The origins of the field of wetting are often associated with the seminal works of Cahn [1] and Ebner and Saam [2], where a new class of phase transitions caused by the non-uniformity of fluids in the microscale had been envisaged and studied for the first time. Since then, the field has seen a rapid growth, especially over the last two decades or so, with a multitude of experimental and theoretical studies which have clearly defined wetting as an outstanding cross-disciplinary field driving and building upon progress in statistical physics, simulations and even hydrodynamics and quantum mechanics [3, 4, 5].

The usual macroscopic description of fluid interfaces based on surface tensions becomes rather limited at the nano-scale where the fluid is non-uniform [6]. In fact a satisfactory model for the fluid and associated phenomena such as wetting and surface phase transitions at the nano-scale should account for the molecular interactions in the system. Popular theoretical approaches for such phenomena include phenomenological Landau or Van der Waals theories, interfacial Hamiltonians, rigorous statistical mechanical approaches, such as mean field lattice models and density functional (DF) theories, and simulations [7, 8, 9, 10].

DF theory in particular allows one to obtain detailed information about the structure of the fluid, but all DF models are mainly restricted to numerical studies and also cannot account for the fluctuation effects. Models based on effective Hamiltonians, on the other hand, are often amenable to analytic investigations, and may include the effects of thermal fluctuations in the system. When coupled with a renormalization technique, such models can offer a powerful tool for obtaining rigorous results, such as critical exponents and universality classes, see, e.g. references [11, 12, 13, 14, 15]. However, unlike DF models, effective Hamiltonians cannot provide details of the microscopic fluid structure as they a priori assume the existence of interfaces, often a particular shape. The limitations of this approach have been discussed in reference [16].

In the present study we employ a microscopic mean field DF approach. The details of the formalism, limits of applicability, as well as references to rigorous proofs can be found in the reviews of Wu [10] and Evans [17]. Starting from reasonable assumptions about the nature of fluid-fluid and fluid-substrate forces one can obtain theoretically consistently all the characteristics of an adsorption process, such as surface tensions, contact angles, interfaces, etc. Sophisticated DF models offer a computationally inexpensive alternative to molecular dynamic simulations, and often allow to reproduce experimental results. Recent developments include the studies of adsorption of Argon, Neon and Xenon on planar substrates of various compositions, see references [18, 19, 20, 21]. DF theories also provide a convenient bridge between the nano- (molecular simulation) and micro- (experimentally accessible) scales. Since DF calculations can be implemented without truncating the tails of interaction potentials [22], they have a principal advantage over simulations and also provide a way to verify analytically predicted critical exponents [23, 24]. At the same time, the relatively low
cost of DF calculations allows to explore the parameter space of models, obtaining complete phase diagrams and possibly uncovering qualitatively new phenomena.

A DF model approximates the additive free energy of the fluid, which consists of two main parts: the fluid-fluid and the fluid-substrate contributions. The fluid-fluid free energy should account for long-ranged attractive and short-ranged repulsive forces between fluid molecules. The fluid-substrate interactions are typically modelled by considering the substrate as an inert spectator phase and accounting for its effect on the fluid by an appropriately chosen external potential, which enters the expression for the free energy.

Finally, DF models can be extended to dynamic systems, using e.g. models A or B of the general dynamic universality classes [25], which allows to capture the characteristics of the system as it relaxes slowly to its equilibrium, see e.g. references [26, 27, 28, 29].

In the present study we consider the phase behaviour of a fluid confined in a prototypical two-dimensional (2D) pore. We show how the dimensionality of the problem dramatically affects the phenomenology of wetting. Investigations of wetting on nanostructured substrates are interesting from a fundamental statistical physics perspective, as confined fluid surfaces may exhibit various kinds of first-order and continuous phase transitions [30, 31]. Exciting new phenomena are mainly determined by the interplay of various length and energy scales in the system, e.g., ranges and strengths of fluid-fluid and fluid-substrate potentials, characteristic dimensions of confining geometries, and even particle sizes. These parameters may act as thermodynamic fields and lead, according to the Gibbs phase rule, to a multitude of phase transitions and metastable states. Capillary phenomena associated with nano-confinement provide a vivid manifestation of attractive molecular forces, putting to a test our microscopic picture of matter [32]. Active applied interest in chemical engineering includes microfluidics [33, 34], design of nano-scale chemical reactors [35, 36] and biomimetic surfaces [37] or surfaces with variable wetting properties [38].

Consider a slit pore formed by two parallel planar walls of infinite area, which are separated by a distance \( H \). When the system is immersed in a large reservoir filled with vapour at pressure \( P \) (the temperature is assumed fixed), simple thermodynamic considerations of the energy necessary to form two wall-fluid interfaces lead to the possibility of two-phase coexistence within the pore: between vapour and capillary-liquid phases (see, e.g., [39]). The transition between these phases is in fact the shifted bulk liquid – vapour transition (saturation). It is a first-order phenomenon, where the pore becomes filled with a denser phase (capillary-liquid) discontinuously, if the pressure in the reservoir becomes equal to \( P_v \), defined by the Kelvin equation:

\[
P_v = P_t - \frac{2\sigma_{lv} \cos \Theta}{H} + \ldots,
\]

where \( P_t \) is the pressure at bulk saturation, \( \sigma_{lv} \) is the liquid – vapour surface tension and \( \Theta \) is the macroscopic contact angle at bulk coexistence. The above expression neglects various microscopic effects, the most important being the competition between fluid-fluid and fluid-wall forces, which can be accounted for by, e.g., an effective interfacial
potential [16], or, more consistently, within a DF approach [40]. A detailed description of surface thermodynamics associated with this prototypical case of confinement can be found in, e.g., reference [41].

Now consider a capped capillary, namely a slit pore closed at one end by a third wall, as shown in figure 1. On one hand, one expects the transition to a state, where the pore becomes filled with capillary-liquid from vapour – capillary condensation (CC) – to be of first order, since the capped capillary reduces to a slit pore as $x \to \infty$. On the other hand, the capping wall may provide sufficient energy for the fluid inside the pore to form a liquid meniscus even when $P < P_v$. In the latter case, as the pressure in the reservoir is increased towards CC ($P \to P_{v+}$), the meniscus should unbind continuously into the “capillary bulk” ($x \to \infty$), making CC a continuous (second-order) phenomenon. The critical exponent for the diverging length of the liquid slab, formed at the capping wall has been obtained analytically in reference [11] and was confirmed numerically in reference [23], for the case of dispersive fluid-fluid and fluid-substrate interactions. An isotherm of drying (reservoir filled with liquid, and $P \to P_{v+}$) for a capillary with purely hard walls and a fluid with short-ranged square well fluid-fluid potential is considered by Roth and Parry in [24].

Here we investigate the reasons behind the existence of two different regimes of CC in a capped capillary pore: a continuous regime, when the filling is happening “from the surfaces”, and an abrupt one, when CC happens from capillary bulk. The fluid-fluid and fluid-wall interactions are dispersive, making the closest physical analogue Argon in contact with solid carbon dioxide. We use a fully microscopic DF approach and provide density profiles, adsorption isotherms and full phase diagrams.
2. Free energy functional

The equilibrium states of a statistical mechanical system correspond to the minima of its free energy as a function of all parameters describing these states (e.g., thermodynamic variables pressure, temperature and molar volume for bulk fluids). In confined fluids, where structural inhomogeneities on a micro-scale contribute significantly to the behaviour of the system, the fluid structure itself constitutes such a “parameter” and has to enter the expression for the free energy. Starting from a model for the molecular interactions in the system, it is possible to construct an expression for the free energy in the form of a functional of the one-body fluid density $\rho(r)$. In the present study we utilise an application of DF theories to the general case of confined atomic fluids, whose microscopic structure is well described by generalized Van der Waals theories [32, 9].

When a substrate is brought in contact with a large reservoir containing the fluid at some bulk pressure and temperature and the system is equilibrated, the fluid density minimizes the grand free energy functional $\Omega[\rho(r)]$:

$$
\Omega[\rho(r)] = F_{\text{in}}[\rho(r)] + \int d\mathbf{r} \rho(\mathbf{r}) V(\mathbf{r}) - \mu \int d\mathbf{r} \rho(\mathbf{r}),
$$

(2)

where $F_{\text{in}}[\rho]$ is the intrinsic free energy, determined by the molecular interactions in a free fluid, $V(\mathbf{r})$ is the effective potential, describing the effect of the substrate upon the fluid (in our case the substrate is modelled as an inert spectator phase, which cannot be affected by the fluid), and finally, $\mu$ is the chemical potential of the thermostat, which together with $T$ (which enters the expression for $F_{\text{in}}$) specifies the bulk thermodynamic fields in the problem.

A comment is in order at this point, frequently omitted in the DF literature. In a bulk fluid in isothermal conditions, due to the equation of state, the pressure, $P = P_v$, is in one-to-one correspondence with the chemical potential, $\mu$. Thus, the thermodynamic point of the bulk fluid at a given value of $T$ can be specified by prescribing a value of either $P_v$ or $\mu$. However, when the fluid is brought in contact with the substrate, it becomes inhomogeneous and the interfacial stress can no longer be described by a scalar parameter ($P_v$), but requires defining a space-dependant pressure tensor. The chemical potential, on the other hand, is still constant throughout the fluid, as can be seen from equation (2), and together with the constant temperature enters the set of thermodynamic fields describing an inhomogeneous fluid. Thus, the common in DF models choice of $\mu$ over $P_v$ as the parameter of the reservoir is more than just a convenience stemming from the form of equation (2).

2.1. Model for the fluid

In atomic fluids, molecular interactions at long ranges are well approximated by London forces with a pairwise Lennard-Jones (LJ) potential [42]:

$$
\varphi^{6-12}_{\epsilon_0, \sigma_0}(r) = 4\epsilon_0 \left[ -\frac{\sigma_0^6}{r^6} + \frac{\sigma_0^{12}}{r^{12}} \right],
$$

(3)
where $\varepsilon_0$ and $\sigma_0$ are measures of the strength and range of the potential, respectively. The short-ranged interactions and correlations are dominated by repulsions, facilitating the use of a perturbation scheme with the reference system being a fluid of purely repulsive hard spheres, along with the random phase approximation for the attractive direct pair-correlation function [17]:

$$F_{\text{in}}[\rho(r)] = \int d\mathbf{r} \left( f_{\text{id}}(\rho(\mathbf{r})) + F_{\text{hs}}[\rho(\mathbf{r})] \right) + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \varphi_{\text{attr}}(|\mathbf{r} - \mathbf{r}'|),$$  \hspace{1cm} (4)

where $f_{\text{id}}(\rho) = k_B T \rho (\ln \rho - 1)$ is the free energy of the ideal gas with the Boltzmann factor, $k_B$, and the thermal wavelength, $\lambda$, $F_{\text{hs}}[\rho]$ is the free energy of a purely repulsive hard sphere fluid, and $\varphi_{\text{attr}}(r)$ is the effective potential describing molecular attractions. Using the Barker and Henderson prescription, we have [43]

$$\varphi_{\text{attr}}(r) = \begin{cases} 0, & r \leq \sigma \\ \varepsilon, & r > \sigma \end{cases},$$ \hspace{1cm} (5)

where $\varepsilon$ is an effective depth of the attractive well and $\sigma$ is the diameter of the reference hard sphere fluid.

For the hard sphere fluid we take the configurational part of the free energy corresponding to the semi-phenomenological Carnahan-Starling equation of state [44]:

$$\psi(\rho) = k_B T \eta \frac{(4 - 3\eta)}{(1 - \eta)^2}, \quad \eta = \pi \sigma^3 \rho / 6.$$ \hspace{1cm} (6)

The hard sphere free energy in the second term of equation (4) can then be written as

$$F_{\text{hs}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\bar{\rho}(\mathbf{r})), \hspace{1cm} (7)$$

where $\bar{\rho}$ is a spatially averaged fluid density, which corresponds to a weighted density approximation (WDA) and accounts for the non-local correlations in the hard sphere fluid leading, e.g., to the oscillatory near-substrate structure of the density profile. In this work we will use a prescription for averaging due to Tarazona and Evans [45], which reproduces at distance $\sigma$ the step of the direct correlation function of the hard sphere fluid, thus capturing the leading-order excluded-volume effect [46]:

$$\bar{\rho}(\mathbf{r}) = \frac{3}{4\pi \sigma^3} \int_{|\mathbf{r} - \mathbf{r}'| \leq \sigma} d\mathbf{r}' \rho(\mathbf{r}').$$ \hspace{1cm} (8)

Alternatively, one can use a local density approximation (LDA) [47], by setting

$$\bar{\rho}(\mathbf{r}) \equiv \rho(\mathbf{r}).$$ \hspace{1cm} (9)

Using LDA is less demanding computationally, which becomes important when investigating numerically the parameter space of the model. Comparing the results obtained from WDA and LDA one can understand the relative effect of attractive molecular interactions with respect to the repulsive interactions.
2.2. Model for the substrate

We consider a physically realistic case, where the interactions between the fluid and solid particles are of the same nature as the fluid-fluid interactions, i.e. governed at long distances by the dispersive London forces with the pairwise LJ potential, given in equation (3), with substrate-specific parameters \( \varepsilon_0 = \varepsilon_w, \sigma_0 = \sigma_w \). It is known that in wetting (unlike dewetting) the end-effects are negligible [48], which allows us to model the wetting on a capped capillary of a large length by considering a semi-infinite pore, figure 1. As is typical in the DF theories of fluids with vapour- and liquid-like densities, we model the solid substrate as an inert spectator phase, accounting for its presence by an additive external potential (second term in equation (2)). A different model for the substrate, where it, in turn, can be affected by the fluid, has been adopted by Ustinov and Do in [49] for wetting on a cylinder.

The external potential due to the substrate acting on the fluid is obtained by integrating the LJ potential over the volume of the substrate. For the capped capillary we assume that three semi-infinite pieces of material have been brought together in a manner shown in figure 1. Since the intermolecular potential at short distances is very different from LJ [42, 50], we introduce a cutoff, \( H_0 \geq \sigma_i \), separating the substrate from the fluid. This has the added numerical benefit of avoiding the divergence of the external potential at short distances, which leads to a super-exponential decay of the fluid density near the walls and requires special computational tricks to be resolved [22]. Experimentally a cutoff can be implemented by coating the substrate with a layer of a foreign species [21].

By integrating the pairwise LJ potential, equation (3), over the volume of the substrate of constant density \( \rho_w \), we arrive at the expression for the potential \( V(x, y) \) exerted on the fluid by the three walls of the capillary (see chunks 1 – 3 in figure 1):

\[
V(x, y) = \rho_w \int_{-\infty}^{\infty} dz' \times \left( \int_{-\infty}^{\infty} dx' \times \left( \int_{-H_0}^{H_0} dy' + \int_{H_0}^{+\infty} dy' \right) + \int_{-\infty}^{-H_0} dx' \int_{-H_0}^{H_0} dy' \right) \\
\times \varphi_{\varepsilon_w, \sigma_w}^{6-12}\left( \sqrt{(x - x')^2 + (y - y')^2 + z'^2} \right). \tag{10}
\]

2.3. Comments

The approximations giving rise to our free energy functional (equations (2), together with (4) – (10)) follow the generalized Van der Waals picture of atomic fluids, which is supported by existing observations [8, 9]. The model is able to capture the dominant physical effects determining the qualitative behaviour of the system in the range of liquid-like and vapour-like fluid densities. However, obtaining quantitative information for a particular system would require a more detailed model.

For example, there exist more sophisticated hard sphere functionals, e.g. [51, 52], which accurately describe the full repulsive direct correlation function for a wide range
of temperatures. However, the excluded volume effects do not play a significant role in the process of wetting [22, 40, 47], as is also demonstrated with calculations in the following sections.

The attractive functional (last term in equation (4)) captures the asymptotic tail of the “attractive” contribution to the direct correlation function of a bulk fluid, which along with a non-local treatment of the density, suffices to capture the physics of wetting by vapour or liquid [9]. In a more complete treatment, the hard sphere diameter, $\sigma$, should be made weakly temperature-dependent, but in the absence of a unified approach, the choice of a particular prescription depends on the range of temperatures [53, 54, 55]. The attractive functional can have the same non-local form as the repulsive one (equation (7)), with the analogues of $\psi(\bar{\rho})$ and the averaging procedure for $\bar{\rho}$ obtained using perturbation theory around a reference uniform bulk fluid, e.g. [56], or by functional integration, starting from a reasonable analytic approximation to the bulk attractive direct correlation function [18, 57, 58]. Finally, the three-body attractive interactions can also contribute to the values of quantities that can be observed experimentally, such as adsorption, e.g. reference [59].

An optimal model for the substrate potential can use \textit{ab initio} results [60, 61], and possibly account for the effect of the fluid on the substrate, instead of modelling it as an inert phase [49].

In the apparent absence of a generally accepted approach, which would allow to retrieve observed values and resolve the specific peculiarities of a given system, the main value of DF models is, first, in their theoretical consistency, which allows us to use the inter-particle potentials as input and, by incrementally including finer effects, to uncover the dominant physical processes contributing to the observed qualitative behaviour. Second, a detailed parametric investigation of DF models allows us to uncover new phenomena, which may not yet be accessible experimentally (as was the case with first- and second- order wall wetting during their discovery in reference [2]). Finally, DF investigations serve as guides to both experimentalists and theoreticians (e.g., in the development of analytical approaches, like effective Hamiltonians).

3. Working equations

Given the reservoir parameters $T$ and $\mu$, the Euler-Lagrange equation for the minimization of $\Omega[\rho]$ defined in equation (2), has the form

$$T \ln \rho (r) + \psi (\rho (r)) + \int d r' \rho (r') \psi'_{\rho} (\bar{\rho} (r')) W (r - r')$$

$$+ \int d r' \rho (r') \varphi_{\text{attr}} (|r - r'|) + V (r) - \mu = 0,$$

where the integration is carried out over the entire volume occupied by the fluid ($0 \leq x \leq \infty$, $0 \leq y \leq H$, figure 1), $\psi'_{\rho}$ is the derivative of the configurational hard sphere free energy (equation (6)) with respect to the density and $W(r)$ is the weight
function defining $\bar{\rho}$ in equations (8), (9) through volume integrals with step- and delta-functions:

$$W(r) = \begin{cases} 
\frac{3}{4\pi\sigma^3} \Theta(\sigma - r) & \text{for WDA,} \\
\delta(r) & \text{for LDA.}
\end{cases}$$

(12)

When the density of the fluid is constant in one or more directions, the integration along those directions can be carried out analytically in equation (11), reducing its dimensionality by simplifying the expressions for $\varphi_{\text{attr}}$ (equation (5)) and $W$ (equation (12)). To study the phase behaviour of the fluid in the capped capillary, we need to be able to find the densities in the capillary and in the slit pore, to which it reduces to as $x \to \infty$ (thus the slit pore forms the capillary bulk). The former corresponds to a two-dimensional, and the latter – to a one-dimensional (1D) reduction of the general equation (11). The expressions for both geometries are given in the following subsections. From now on we set the parameters of fluid-fluid interactions $\varepsilon$ and $\sigma$ to be units of energy and length.

3.1. 1D problem

For the 1D problem of the slit pore immersed in vapour we have in equation (11):

$$r \equiv y \cdot e_y, \quad \rho(r) \equiv \rho_{\text{slt}}(y).$$

The substrate potential, $V(r) \equiv V_{\text{slt}}(y)$, is defined as the limit of the expression in equation (10) as $x \to \infty$:

$$V_{\varepsilon_w,\sigma_w}^{\text{slt}}(y) = V_{\varepsilon_w,\sigma_w}^{3-9}(y) + V_{\varepsilon_w,\sigma_w}^{3-9}(H - y),$$

$$V_{\varepsilon_w,\sigma_w}^{3-9}(x) \equiv 4\pi\varepsilon_w\rho_w\sigma_w^3 \left( -\frac{1}{6} \left(\frac{\sigma_w}{x}\right)^3 + \frac{1}{45} \left(\frac{\sigma_w}{x}\right)^9 \right).$$

(13)

The attractive potential, $\varphi_{\text{attr}}(y) \equiv \int dz \int dx \ \varphi_{\text{attr}}(\sqrt{x^2 + y^2 + z^2})$, is obtained by integrating equation (5):

$$\varphi_{\text{attr}}(y) = \begin{cases} 
\frac{-6\pi}{5}, & \text{if } |y| \leq 1, \\
4\pi \left( \frac{1}{5y^{10}} - \frac{1}{2y^4} \right), & \text{if } |y| > 1.
\end{cases}$$

(14)

The weight function, $W(y) \equiv \int dz \int dx \ W(x \cdot e_x + y \cdot e_y + z \cdot e_z)$, is obtained by integrating equation (12):

$$W(y) = \begin{cases} 
\frac{3}{4} (1 - y^2) \Theta(1 - y) & \text{for WDA,} \\
\delta(y) & \text{for LDA.}
\end{cases}$$

(15)

3.2. 2D problem

For the 2D problem of the capped capillary immersed in vapour we have in equation (11): $r \equiv x \cdot e_x + y \cdot e_y, \quad \rho(r) \equiv \rho_{\text{cpd}}(x, y)$ and the substrate potential $V(r) \equiv V_{\text{cpd}}(x, y)$
is defined in equation (10). The 2D reduction of equation (11) can be done analytically: the integrals over $z$ can be obtained in a closed form. Unfortunately, some of the resulting expressions are very complicated and lead to significant rounding errors if used in computations. For that reason we use a hybrid approach and evaluate some of the $z$-integrals in equation (11) numerically.

First, let us integrate out $z$ in the pairwise LJ potential in equation (3), and formally define an expression that resembles the 2D case where the fluid density is constant in one direction, $\varphi_{5-11}^{\varepsilon_0,\sigma_0}(r) \equiv \int dz \varphi_{6-12}^{\varepsilon_0,\sigma_0}\left(\sqrt{x^2 + y^2 + z^2}\right)$:

$$\varphi_{5-11}^{\varepsilon_0,\sigma_0}(r) = \frac{3\pi \varepsilon_0 \sigma_0}{2} \left[-\left(\frac{\sigma_0}{r}\right)^5 + \frac{21}{32}\left(\frac{\sigma_0}{r}\right)^{11}\right],$$

(16)

where (as everywhere for the 2D problem) $r = \sqrt{x^2 + y^2}$.

Now the expression for $V(x,y)$ can be written in the form:

$$V^{\text{cpd}}(x,y) = V^{\text{slt}}(y) + V^{\text{cap}}(x,y),$$

(17)

where $V^{\text{slt}}(y)$ is the potential of a slit pore (equation (13)) and $V^{\text{cap}}(x,y)$ accounts for the contribution due to the capping wall and is determined by integrating the fluid-substrate potential, $\varphi_{5-11}^{\varepsilon_w,\sigma_w}$ (see equation (16)), over chunk 2 in figure 1:

$$V^{\text{cap}}(x,y) = \int_{-\infty}^{-H_0} dx' \int_{-H_0}^{H+H_0} dy' \varphi_{5-11}^{\varepsilon_w,\sigma_w}\left(|r - r'|\right),$$

(18)

Any further analytic simplification of equation (18) leads to high numerical instabilities in the resulting expression, so we have preferred to compute $V^{\text{cap}}(x,y)$ in equation (18) numerically, using the Clenshaw-Curtis quadrature [22].

Consider now the attractive potential defined in the 2D problem as $\varphi_{\text{attr}}(r) \equiv \int dz \varphi_{\text{attr}}\left(\sqrt{x^2 + y^2 + z^2}\right)$. Integrating out $z$-coordinate in equation (5), we obtain

$$\varphi_{\text{attr}}(x,y) = \begin{cases} 2 \int_{\sqrt{1-r^2}}^{\infty} dz \varphi_{1,1}^{6-12}\left(\sqrt{r^2 + z^2}\right), & \text{if } r \leq 1, \\ \varphi_{1,1}^{5-11}(r), & \text{if } r > 1. \end{cases}$$

(19)

Noteworthy is that the integral in (19) can be done analytically [62], but the resulting expression is again unstable numerically, leading to high rounding errors, when used in actual calculations. So a numerical quadrature is preferable.

Finally, the 2D weight function, $W(x,y) \equiv \int dz W(x \cdot e_x + y \cdot e_y + z \cdot e_z)$, is obtained from equation (12):

$$W(x,y) = \begin{cases} \frac{3\pi}{2} (1 - r^2) \Theta (1 - r) & \text{for WDA,} \\ \delta (r) & \text{for LDA.} \end{cases}$$

(20)

Note that although we have defined the 2D pairwise potential, $\varphi_{5-11}^{\varepsilon_0,\sigma_0}$ (equation (16)), its use in our expressions is justified by formally changing the orders of integration and...
reflects a simple fact that the fluid density is constant along direction $e_z$. The fluid dimensionality remains identical to the three-dimensional hard sphere fluid described by the Carnahan-Starling equation of state (see equation (6)).

3.3. Numerical strategy

The numerical approaches to solving equation (11) can be categorized, first, with respect to the method for evaluating the non-local integrals and second, with respect to the iterative method for solving the discretized equation (63).

The convolution-like form of non-local terms prompts many authors to advocate a fast Fourier transform. Recent works include, e.g., references [64, 65]. The shortcomings are, first, that such methods often require equidistant grid points, which is not necessary in the regions where density is nearly constant. Second, Fourier-based methods on non-periodic domains are equivalent to a higher order Simpson quadrature and possess an algebraic convergence rate. Finally, such methods often impose non-physical periodicities of solution. We believe that the use of a specialized quadrature in real space is preferable. A combination of a Gauss quadrature and an algebraically converging trapezoid rule was proposed in reference [66].

In the present work we use a novel numerical approach based on the Chebyshev pseudo spectral collocation method [67, 68]. The problem is discretized on a non-uniform grid of collocation points, with the solution obtained in the form of a rational interpolant [69]. Using conformal maps from a unitary circle in the complex plane, we can control the distribution of the collocation points on the calculation domain concentrating them in the regions, where the solution exhibits steep gradients (near walls, near liquid – vapour interface) and using a moderate number of points in the regions of regularly behaving or near-constant density (inside liquid/vapour phases).

We evaluate all integral terms in real space by a highly accurate Clenshaw-Curtis quadrature [70, 71], which in the latest numerical analysis literature has been found to be an optimal choice with respect to convergence rates, accuracy and stability [72].

Our numerical method possesses an exponential convergence rate, while at the same time allowing to use a moderate number of collocation points. The interested reader is referred to our earlier work [22], where all the details of implementation, along with convergence tests and examples are provided.

In the present study we extend the method used in reference [22], which could only deal with 1D problems, by utilising the appropriate interpolant on a tensor product grid and constructing integration matrices for 2D geometries that can be mapped to a square. Even though the computations necessary to construct the integration matrices become rather involved, a significant advantage is that such calculation needs to be done only once and the matrix can be stored and reused for other calculations in the same geometry, such as for obtaining isotherms and phase diagrams. Moreover, the aforementioned exponential accuracy is even more important in a 2D geometry, as it allows us to obtain very accurate results with only a moderate number of grid points.
With respect to an iterative procedure for the spatially discretized problem, the numerical methods for DF calculations mostly use self-consistent Picard iterations. The tradition of that approach goes back to the earliest works in the 1970s. The method is highly numerically unstable, often requires ad hoc modifications of consecutive iterations. Furthermore, the convergence is typically achieved after hundreds or thousands of iterations, and in the case of multiple existing solutions (e.g., when the system undergoes a first-order phase transition) further ad hoc modifications drawing heavily on one’s physical intuition might be necessary to customize the numerical method for a particular system, e.g. [64].

We completely automate the numerical solution of DF equations for systems with and without phase transitions using a Newton iteration procedure in conjunction with an arc-length continuation technique [22]. Such approach was first used for DF calculations by Salinger and Frink in [73]. In our implementation the convergence is typically achieved in 2 – 3 iteration steps, and we believe the Newton solver or its variation to be an optimal strategy for 1D and 2D problems. However, unlike Piccard, the Newton method requires to find and invert the Jacobian matrix on every iteration, which may shift optimality back to a variation of a self-consistent approach (they typically do not require expensive matrix inversions) in three-dimensional problems [63, 66].

In general, the arc-length continuation technique can be used to obtain sets of solutions to equation (11) corresponding to a variable parameter (typically, a thermodynamic field acting in the system). By treating the parameter as an unknown and supplementing (11) the procedure with a geometrical constraint in the space of the discretized problem, one can systematically obtain all the possible solution-parameter combinations consistent with the equation (11). For example, choosing the chemical potential (or the bulk density) as the variable parameter, allows us to obtain adsorption isotherms [73], while choosing temperature would produce an isochore, e.g. [74]. One can also study the dependence of density on the parameters of the fluid-fluid or fluid-wall potentials [73, 22].

3.4. Isotherms and phase diagrams

A single density profile carries no information about the thermodynamic stability of the fluid state, since a particular solution of equation (11) might not minimise $\Omega [\rho (r)]$, but can correspond to its saddle point in the phase space. So finding a density profile by solving equation (11) does not guarantee, that the corresponding fluid state is physical. On the other hand, computing a family of solutions parametrised by a thermodynamic field allows to determine the stability of fluid configurations by finding $\Omega [\rho]$ for each of the calculated density profiles. The resulting dependence of the fluid free energy on the thermodynamic field is a concave function, when the fluid is in a stable equilibrium [75]. We will be using such an approach extensively in this work [76]. Apart from determining the thermodynamic stability of fluid states it allows to locate phase transitions.

For a fluid configuration inside the capped capillary we define the free energy
excessive over capillary bulk as

\[ \Omega^{\text{ex}} = \Omega \left[ \rho^{\text{cpd}} (x, y) \right] - \Omega \left[ \rho^{\text{slt}} (y) \right], \tag{21} \]

where the value, given by equation (2), is computed for the solutions to (11) on the functional spaces of 2D and 1D density profiles, respectively. The excess free energy is thus a function of thermodynamic fields acting in the system and carries information about effects specific only to the 2D confinement of the fluid. Thermodynamically stable fluid states belong to its concave branches in the space of all fields acting in the system \cite{76}. In order to reveal the phase behaviour of the fluid we obtain characteristic level sets of \( \Omega^{\text{ex}} \) – the isotherms.

The set of thermodynamic fields in our problem consists of the parameters of the pairwise fluid-substrate potential, the width of the capillary and the bulk fields \( T \) and \( \mu \). While we will reveal the effects of all relevant fields on the phase behaviour of the system, for convenience and consistency we will be considering various isothermal thermodynamic routes at fixed values of substrate parameters. Thus, the thermodynamic variable allowed to change is \( \mu \). Note that in a macroscopic description by equation (1), \( P_l \) and \( P_v \) are in one-to-one correspondence with \( \mu \), due to the bulk equation of state.

The thermodynamic density conjugate to \( \mu \) is adsorption, \( \Gamma \), related to \( \Omega^{\text{ex}} \) through the Gibbs equation \cite{76}:

\[ \Gamma = -\partial \Omega^{\text{ex}}/\partial \mu, \tag{22} \]

where the derivative is evaluated at a fixed value of \( T \). In our study \( \Gamma \) acts as a natural order parameter. A first-order surface phase transition is associated with a finite jump in \( \Gamma \), and a continuous surface phase transition – with the divergence of \( \Gamma \) as a function of one of the thermodynamic fields. At any given value of \( T \) we count the value of \( \mu \) from bulk saturation, \( \mu_{\text{sat}} (T) \), thus the control parameter is the disjoining chemical potential, \( \Delta \mu \), defined as \( \Delta \mu = \mu - \mu_{\text{sat}} \).

For the grand canonical ensemble in isothermal conditions there exists an exact sum rule, which relates adsorption to the fluid one-body density profile \cite{77}:

\[ \Gamma = \int dx \ dy \left( \rho^{\text{cpd}} (x, y) - \rho^{\text{slt}} (y) \right). \tag{23} \]

The above equation also suggests, that \( \Gamma \) is a convenient measure for the amount of “excess over bulk” fluid, adsorbed on the substrate surface (in our case – the capping wall and corners), hence the commonly used term – adsorption.

By using arc-length continuation for equation (11), treating \( \mu \) as the continuation parameter, we compute sets of points on an isotherm \( \Omega^{\text{ex}} (\Delta \mu) \). Each data point on the isotherm corresponds to a density profile. Computing free energy isotherms allows us to identify thermodynamically stable density profiles, as they correspond to the data points on the concave branches of \( \Omega^{\text{ex}} (\Delta \mu) \). It also allows us to detect phase transitions: a first-order transition is manifested by a Van der Waals loop (the intersection of concave branches), and a continuous phase transition – by a finite limit of the free
energy isotherm and a divergence of the adsorption isotherm. For every value of $T$ we additionally make sure that our calculation of the isotherms $\Omega_{ex} (\Delta \mu)$ and $\Gamma (\Delta \mu)$ is correct by computing $\Gamma (\Delta \mu)$ from equation (23) and comparing it versus the values obtained independently from the Gibbs equation (22), which relates adsorption and free energy isotherms.

Given a set of points on an isotherm exhibiting a Van der Waals loop, we find the exact location of the first-order phase transition in the $\Omega - \mu$ plane and the coexisting density profiles, $\rho_1$ and $\rho_2$, by solving a system of three equations: the two Euler-Lagrange equations for $\rho_1$ and $\rho_2$, supplemented with the condition of equal grand free energies:

$$\frac{\delta \Omega}{\delta \rho} \bigg|_{\rho_1} = \frac{\delta \Omega}{\delta \rho} \bigg|_{\rho_2} = 0$$

$$\Omega_{ex} [\rho_1] - \Omega_{ex} [\rho_2] = 0,$$  

(24)

where for the capped capillary we use the excess free energy $\Omega_{ex} [\rho] \equiv \Omega_{ex} [\rho_{cpd} (x, y)]$ defined in equation (21), and for the slit pore (capillary bulk) – the full grand free energy given by equation [2], i.e $\Omega_{ex} [\rho] \equiv \Omega [\rho_{slt} (y)]$. We use the data from the isotherm to select an initial guess for solving equation (24). Normally we chose the two density profiles, whose corresponding free energies belong to the intersecting branches of $\Omega_{ex} (\Delta \mu)$ and lie close to the intersection point in the $\Omega - \mu$ plane.

By applying the arc-length continuation to the system of equations (24) and treating $T$ as the continuation parameter we can obtain the phase diagram in the $T - \mu$ plane, thus completely describing the thermodynamic phase behaviour of the system. In what follows we discuss the calculations of isotherms and full phase diagrams in detail in the following section.

4. Physics of wetting on a capped capillary

In this section we present a number of representative calculations taken from a detailed numerical study of the parameter space and discuss the possible adsorption scenarios and surface phase transitions occurring in the system. More specifically, we consider several examples of capped capillaries with various substrate parameters and argue in terms of complete phase diagrams in the $T - \Delta \mu$ space together with wetting isotherms of excess free energy, $\Omega_{ex} (\Delta \mu)$, and adsorption, $\Gamma (\Delta \mu)$. The disjoining chemical potential, $\Delta \mu$, is given as the difference of the applied chemical potential, $\mu$, from the saturation chemical potential at bulk liquid – vapour coexistence, $\mu_{sat}$.

We note that the choice of particular values for parameters in the governing equations was affected (without loss of generality) by numerical convenience. For example, we tried to select substrate potentials with relatively high planar wetting temperatures, $T_w$, to avoid layering transitions [16, 78], and also for the liquid – vapour interfaces to be sufficiently smooth and resolvable on a moderately dense mesh. Obviously, the generality of our conclusions is not impaired by such considerations.
4.1. Capillary prewetting

Consider a capillary with width $H = 30$ and a substrate defined by $\varepsilon_w = 0.85$, $\sigma_w = 1.35$ and $H_0 = 2.2$. The fluid is treated within WDA. For the case of a planar wall in contact with vapour we find the wetting temperature to be $T_w = 0.927$. We start the investigation of the capped capillary by setting $T = 0.93$, a more or less arbitrarily chosen value in the region where a planar substrate wall exhibits prewetting. We further set the chemical potential, $\mu = \mu_{\text{sat}} + \Delta \mu$, in equation (11) to a rather low value ($\Delta \mu = -5$), so that the fluid is well inside the bulk vapour phase, and thus almost unaffected by the presence of the substrate. This facilitates the convergence of Newton’s scheme, where the initial guess is taken to be that of the vapour inside a slit pore, at the same chemical potential and temperature: $\rho_{\text{cpd}}^{\text{slit}}(y) \equiv \rho_{\text{cp}}^{\text{slit}}(y)$. After obtaining the solution $\rho_{\text{cp}}^{\text{slit}}(x,y)$, given on the spatial grid by the set of data points $\rho_{ij}$, we perturb the vector $[\mu, \rho_{ij}]$ and, adding to the equation (11) a geometric constraint of continuity in the $(N_{xy} + 1)$-space, we solve the resulting system of equations for the next density profile and the corresponding $\mu$, also by the Newton method. The described tactics is the essence of the arc-length continuation technique, which allows us to systematically obtain consecutive solutions to (11) at values of $\Delta \mu$ increasing towards CC, i.e. a wetting isotherm. The details of implementation, along with a discussion of various geometrical constraints, are covered in our previous work [22]. The main practical benefit is that the algorithm serves to adjust each obtained solution to provide an optimal initial guess for finding the next one, at a different value of the parameter ($\mu$). The continuation must be initiated from a starting point – a solution at some known value of the parameter, which is why we start from a simple vapour profile far from coexistence.

We observe that at higher values of $\Delta \mu$ a liquid-like slab starts to form near the capping wall. As the chemical potential approaches its value at CC, $\Delta \mu_{\text{cc}}(T)$, the length of the slab increases and diverges in the limit $\Delta \mu \to \Delta \mu_{\text{cc}}$. Examination of the fluid structure (details are given in section 4.3) reveals, that the liquid-like phase forming the slab is identical to capillary-liquid, while the vapour-like phase filling the capillary bulk is identical to the vapour, where both the vapour and capillary-liquid are taken at CC. The behaviour of the fluid is best understood in terms of isotherms shown in figure 2. A typical Van der Waals loop in the excess free energy dependence, $\Omega^{\text{ex}}(\Delta \mu)$, in figure 2(a) indicates that a first-order phase transition occurs at $\Delta \mu = \Delta \mu_{\text{cpw}}(T)$ (marked by a filled circle), where the concave branches of excess free energy cross. The adsorption isotherm, $\Gamma(\Delta \mu)$, presented in figure 2(b) possesses a characteristic hysteresis behaviour, with the equal area construction giving the same value for $\Delta \mu_{\text{cpw}}$, as the intersection of branches of $\Omega^{\text{ex}}(\Delta \mu)$, thus providing a test for our numerical implementation via an exact Gibbs phase rule, equation (22). The adsorption diverges as $\Delta \mu \to \Delta \mu_{\text{cc}}(T)$ indicating that CC in a capped capillary is a continuous phenomenon. The critical exponents for the diverging height of the liquid slab were obtained analytically by Parry et al in [11] and numerically in our previous work in [23].

The coexisting density profiles are shown in figures 2(c) and 2(d). For illustration
Figure 2. Capillary prewetting transition at $T = 0.93$, $\Delta \mu_{\text{cpw}} (T) = -1.43 \cdot 10^{-2}$ in the capped capillary with $H = 30$, $\varepsilon_w = 0.85$, $\sigma_w = 1.35$, $H_0 = 2.2$; fluid treated in WDA, planar $T_w = 0.927$. CC of the associated slit pore (capillary bulk) is at $\Delta \mu_{\text{cc}} (T) = -1.39 \cdot 10^{-2}$. (a) Excess free energy isotherm. It has two concave branches connected by a non-concave branch (dotted line). The concave branches define two thermodynamically stable phases, coexisting at $\Delta \mu_{\text{cpw}}$: vapour (dashed line, branch extends from $\Delta \mu = -\infty$, up to its spinodal at $\Delta \mu = -0.68 \cdot 10^{-2}$) and capillary-liquid slab (solid line, branch extends from its spinodal at $\Delta \mu = -1.80 \cdot 10^{-2}$ up to $\Delta \mu = \Delta \mu_{\text{cc}}$, indicated by vertical dotted line). Capillary prewetting is marked by the filled circle at $\Delta \mu_{\text{cpw}}$ and $\Omega_{\text{ex}} (\Delta \mu_{\text{cpw}}) = -3.49$. Open circles show the two continuation data points, whose corresponding density profiles were used as initial guess in equation [(12)]. (b) Adsorption isotherm. Line styles and open circles are defined as in plot (a). Note that $\Delta \mu = \Delta \mu_{\text{cc}}$ is the vertical asymptote for $\Gamma (\Delta \mu)$. Capillary prewetting corresponds to the jump of adsorption from $\Gamma_1 = 14$ to $\Gamma_2 = 214$, marked by filled circles. (c), (d) Coexisting density profiles. Data rescaled between $\rho_{\text{vap}}^\text{bulk} (T) = 0.1$ (white), and $\rho_{\text{liq}}^\text{bulk} (T) = 0.43$ (dark grey). The white dashed line indicates interface between vapour and capillary-liquid.

purposes, throughout the manuscript filled contours of 2D density profiles are coloured in shades of gray between bulk vapour-like and bulk liquid-like densities at CC, at the given temperature, $\rho_{\text{cc}}^\text{vap} \equiv \rho_{\text{cc}}^\text{vap} (\Delta \mu_{\text{cc}} (T), T)$ (white) and $\rho_{\text{cc}}^\text{liq} \equiv \rho_{\text{cc}}^\text{liq} (\Delta \mu_{\text{cc}} (T), T)$ (dark grey), respectively. The values of $\rho_{\text{cc}}^\text{vap}$ and $\rho_{\text{cc}}^\text{liq}$ are obtained by assuming a uniform density distribution and solving equation (11) in the absence of the wall potential ($V (r) \equiv 0$, $\rho (r) \equiv \rho = \text{const}$). We define the sharp liquid – vapour interface (dashed white line) by the Gibbs dividing surface, forming the level set at the value $(\rho_{\text{cc}}^\text{vap} + \rho_{\text{cc}}^\text{liq}) / 2$.

For the purposes of all following discussions we note that a thermodynamically stable fluid phase can be identified with a concave branch of the free energy (or excess free energy), as a function of the control parameter. When a system can be in multiple phases, its free energy has multiple concave branches. The transition value of the control
Figure 3. Density profiles coexisting during capillary prewetting at different values of $T$ in the capillary of figure 2. (a) and (b) $T = 0.95$, $\Delta \mu_{cc}(T) = -1.4 \cdot 10^{-2}$, $\Delta \mu_{cpw}(T) = -1.7 \cdot 10^{-2}$, reference densities: $\rho_{cc}^{vap} = 0.11$, $\rho_{cc}^{liq} = 0.40$. The isotherms have a single Van der Waals loop and look similar to those in figure 2 (a), (b). However, the coexisting density profile (a) from the vapour branch of $\Omega^{ex}(\Delta \mu)$ has a different topology: it shows corner drops. (c) Density profile at the critical capillary prewetting point, at $T_{cr}^{cpw} = 0.963$, $\Delta \mu_{cpw}^{cr} = \Delta \mu_{cpw}(T_{cr}^{cpw}) = -1.9 \cdot 10^{-2}$ (see figure 4); $\Delta \mu_{cc}(T_{cr}^{cpw}) = -1.4 \cdot 10^{-2}$, $\rho_{cc}^{vap} = 0.13$, $\rho_{cc}^{liq} = 0.37$.

parameter, where two (or more) fluid phases coexist, is then defined as the abscissa of the point where the two (or more) concave branches of free energy intersect. We consider capillaries immersed in a large reservoir, where the state of the (bulk) fluid can be controlled. Bulk fluid states are defined by the temperature, $T$, and chemical potential, $\mu = \mu_{sat} + \Delta \mu$. We consider isothermal thermodynamic routes ($T$ is fixed), so the only control parameter is $\mu$. In what follows we will identify completely a concave branch of the excess free energy as a function of the chemical potential, $\Omega^{ex}(\Delta \mu)$, with the concept of a fluid phase.

We will discuss the structure of 2D density profiles, $\rho^{cpd}(x, y)$, in detail in section 4.3, where we consider an example of the density distribution possessing pronounced excluded volume effects. For now we note that for the chosen value of $T$, the obtained coexisting profiles are quite representative of the two fluid surface phases corresponding to the intersecting stable branches of $\Omega^{ex}(\Delta \mu)$, figure 2(a). We will refer to them as vapour (dashed line, typical profiles are shown in figures 2(c) and 3(a)) and capillary-liquid slab (solid line, typical profiles are shown in figures 2(d) and 3(b)). As will be made clear in section 4.2 from the consideration of the full phase diagram, this first-order phase transition is indicative of a new capillary bulk phase transition in the same way as, e.g., the wall prewetting (coexistence between two microscopic liquid films on the surface of a planar wall) is indicative of first-order wall wetting [16]. We therefore refer to the described phase transition as capillary prewetting.

For wide capillaries, where the corners are sufficiently isolated, one might expect a mechanism of wetting related to the filling of corners. Indeed, at higher temperatures the fluid configurations from the vapour branch of the excess free energy become denser in the near-corner regions as $\Delta \mu$ is increased and can even exhibit distinct droplet-like structures with sharp interfaces. An example is given in figures 3(a) and 3(b), where at $T = 0.95$ the coexisting density configurations are those of two drops in the corners and a capillary-liquid slab. However, the excess free energy and adsorption isotherms
look qualitatively similar to those shown in figure 2 (only two concave branches). The development of drops in the corners happens continuously from the vapour phase (at low $\Delta \mu$ the density profiles are of type shown in figure 3(a)), and we cannot associate it with a surface phase transition here, as there is no additional Van der Waals loop on the wetting isotherm. However, as we will show in section 4.3, there can be an additional first-order phase transition associated with drop formation in capillary corners, and it is related to wedge prewetting (see, e.g., [79]). Finally, we note that a further increase of $T$ leads to criticality of the capillary prewetting transition and the calculated coexisting density profiles become indistinguishable, see figure 3(c). We will return to this point in much more detail in part II.

4.2. Phase diagram

To systematise the study of the first-order phase transitions between near-wall fluid configurations and the continuous transitions to CC, we obtain the complete phase diagram of the capped capillary, where we plot the disjoining chemical potential of the transitions versus the transition temperature. Thus, one wetting isotherm (e.g., figure 2) possibly corresponds to one point on the line forming the locus of phase transitions in the $T - \Delta \mu$ space (we will refer to them as transition lines). The phase diagram of the capped capillary we considered above is presented in figure 4 and consists of two transition lines. The CC transition line of the associated slit pore (capillary bulk), $\Delta \mu_{cc}(T)$ (grey), forms in the case of the capped capillary the locus of continuous transitions corresponding to the diverging adsorption (see figure 2(b)). The transition line of capillary prewetting, $\Delta \mu_{cpw}(T)$ (black), forms the locus of the crossing branches of $\Omega^{ex}(\Delta \mu)$ (see figure 2(a)).

Each point on a transition line corresponds to the two coexisting density profiles $\rho_1$, $\rho_2$ and the chemical potential of the transition $\mu$, which enter equation (24) as unknowns. For the $\Delta \mu_{cc}(T)$-line: $\rho_1 \equiv \rho_{1l}^{slit}(y)$ and $\rho_2 \equiv \rho_{2l}^{slit}(y)$ are the coexisting vapour and capillary-liquid density profiles inside the slit pore (where CC is a first-order transition) and $\Omega^{ex} \equiv \Omega[\rho_y]$, as defined by equation (2) in the space of 1D fluid configurations, $\rho(r) \equiv \rho_{l}^{slit}(y)$. Each point on $\Delta \mu_{cpw}(T)$-line, in turn, satisfies the same equation, where $\rho_1 \equiv \rho_{1l}^{cpd}(x, y)$ and $\rho_2 \equiv \rho_{2l}^{cpd}(x, y)$ are the 2D density configurations coexisting inside the capped capillary during the first-order vapour – slab transition, and $\Omega^{ex}$ is defined by equation (21).

In practice, to find a solution to equation (24) by, e.g., Newton’s method, one needs to provide an initial guess of the coexisting density profiles and the transition chemical potential. Equation (24) is highly non-linear, non-local, involving integrations over the entire calculation domain, which makes it quite unstable numerically, and a poor initial guess results in non-convergence. To find a good initial guess to solve equation (24) at a given temperature, one should compute a free energy isotherm at that temperature (e.g., figure 2(a)), find by interpolation the approximate intersection point of its branches, which would provide the initial guess for $\mu$. The two density profiles, corresponding to
Figure 4. Full phase diagram of wetting on the capped capillary from figure 2. The CC transition line of capillary bulk (associated slit pore), $\Delta \mu_{cc}(T)$, is plotted in grey. It ends at the CC critical point, $(T_{cc}^{cr}, \Delta \mu_{cc}^{cr}) \equiv (0.996, -1.26 \cdot 10^{-2})$. The transition line of capillary prewetting, $\Delta \mu_{cpw}(T)$, is plotted in black and is tangential to the CC transition line at $(T_{cw}, \Delta \mu_{cw}) \equiv (0.925, -1.38 \cdot 10^{-2})$, calculated with accuracy $\Delta_{cw} = 0.0016 \cdot 10^{-2}$ (see main text). The transition line $\Delta \mu_{cpw}(T)$ ends at the capillary prewetting critical point: $(T_{cpw}^{cr}, \Delta \mu_{cpw}^{cr}) \equiv (0.963, -1.93 \cdot 10^{-2})$. The open circles on $\Delta \mu_{cpw}(T)$ denote the capillary prewetting transitions, whose coexisting slab profiles are plotted in figure 5.

The data points on the excess free energy isotherm and belonging to its vapour and slab branches, closest to the intersection, can provide the initial guess for $\rho_1$ and $\rho_2$. In the example from figure 2, the data points giving rise to the initial guess for equation (24) are marked by open circles on the isotherms. In the case of non-convergence the calculation of the isotherm should be refined to provide more data points near the intersection of its branches and thus a better initial guess. After convergence of the numerical scheme one obtains a single point on a transition line. The rest of the transition line is best found by arc-length continuation, using the obtained solution as the starting point.

The dependence of equation (24) on $T$ parametrizes the set of first-order phase transitions as a one-dimensional curve in the space spanned by the two coexisting profiles and the transition chemical potential. Adding a geometric constraint of curve continuity allows to trace the whole set, starting from a single point (defined by the two coexisting profiles and the transition chemical potential) by, e.g., applying the arc-length continuation to the discretised equation (24), where $T$ is treated as the parameter. The practical value of this approach is quite significant: although any wetting isotherm gives rise to no more than a single point on each of the transition lines, we do not need to compute sets of isotherms in order to obtain those transition lines, but can instead systematically trace each line with temperature in the same manner as we obtained the isotherms (by “tracking” with $\mu$ an easily obtainable density profile in the vapour phase). The danger of tracking a particular phase transition with $T$ is that one obtains the transition line of that transition only; the approach is oblivious to the possible presence of other first-order phase transitions happening at the same $T$, but possibly at a different $\mu$, which can only be revealed by a Van der Waals loop on an isotherm. Therefore, after computing the phase diagram by tracing each transition
Figure 5. Liquid menisci of configurations inside the capped capillary with parameters given in the caption of figure 2, coexisting with vapour configurations during capillary prewetting transitions at values of $T$ (right to left): 0.9253, 0.9256, 0.9263, 0.9281, 0.9352, 0.9616. The transitions at these values of $T$ are marked by open circles on the full phase diagram, figure 4. (b) Menisci heights, $L_m$, for configurations shown in (a) as a function of temperature. As $T$ is lowered along the transition line, the length of coexisting capillary-liquid slab increases and diverges in the limit $T 	o T_w \approx 0.925$.

Let us consider the phase diagram from figure 4 in more detail. The CC transition line, $\Delta \mu_{cc}(T)$ (grey), forms the full phase diagram of the slit pore associated with the capped capillary. It separates the configurations of the capillary filled entirely with vapour (below the CC line on the phase diagram) from those filled entirely with capillary-liquid (above the CC line), and is obtained from a fully microscopic approach, where the only model input is the pairwise fluid-fluid and fluid-substrate inter-molecular interactions (unlike the empirical equation (1), which provides a macroscopic model of the same phenomenon).

The capped capillary reduces to its associated slit pore as $x \to \infty$, thus the fluid in the slit forms the bulk of the capped capillary, and CC is the bulk transition. The $\Delta \mu_{cpw}(T)$-line, which extends into the bulk vapour segment of the phase diagram is one of our main findings and we examine it in more detail. First, we show that it does run tangent to the CC line. Second, we show that the point of contact is associated with a new type of phase transition happening in the capillary bulk, due to the presence of the capping wall.

Figure 5(a) shows the liquid – vapour interfaces (menisci) of the fluid configurations with capillary-liquid slabs, coexisting during capillary prewetting with vapour
configurations. On the $\Delta \mu_{\text{cpw}} (T)$-line in figure 4, the respective transitions are marked by open circles. As the value of $T$ is lowered, the meniscus of a coexisting slab configuration unbinds into the capillary bulk. On the phase diagram such fluid configurations fall on the $\Delta \mu_{\text{cpw}} (T)$-line, where it approaches the $\Delta \mu_{\text{cc}} (T)$-line. We can define the measure of the “meniscus height”, i.e. the distance from the capping wall to the liquid meniscus as

$$L_m = \Gamma / \left( H \rho^\text{liq}_{\text{cc}} \right).$$

(25)

As it is clear from figure 5(b), where we plot $L_m$ for the configurations in figure 5(a) as a function of $T$, the menisci heights of coexisting slab configurations diverge along the $\Delta \mu_{\text{cpw}} (T)$-line, as it approaches the CC line. There clearly exists a limiting value of temperature, $T = T_{cw}$, such that $L_m \to \infty$ as $T \to T_{cw}$ and the entire capillary is filled with capillary-liquid. Thus, for an isothermal thermodynamic route to CC at $T = T_{cw}$, the configuration where the capillary is filled entirely with vapour coexists with the configuration possessing a capillary-liquid slab of an infinite length (i.e., the capillary is filled entirely with capillary-liquid), which is only possible if the point $(T_{cw}, \Delta \mu_{\text{cpw}} (T_{cw}))$ on the phase diagram belongs to both transition lines, namely $\Delta \mu_{\text{cc}} (T_{cw}) = \Delta \mu_{\text{cpw}} (T_{cw})$. Thus, the $\Delta \mu_{\text{cpw}} (T_{cw})$-line approaches the $\Delta \mu_{\text{cc}} (T_{cw})$ as $T \to T_{cw}$, and has a single common point with it at $T = T_{cw}$. In other words, $\Delta \mu_{\text{cpw}} (T_{cw})$-line runs tangent to the CC line.

The phenomenology of wetting on the capped capillary, thus, maps to that of a fluid in contact with a planar wall and undergoing a first-order wetting transition: the CC line acts as saturation line, and the $\Delta \mu_{\text{cpw}} (T)$-line acts as the wall prewetting line, see, e.g., [22]. Following the analogy with planar wetting, we have termed the vapour–slab transition as capillary prewetting, while the value $T = T_{cw}$ is termed capillary wetting temperature. Note that our observation for the existence of capillary wetting temperature relies on the observed divergence of the coexisting slab configurations, as the CC transition line is approached along the capillary prewetting line. The presence of the capillary wetting temperature has been confirmed with numerous calculations performed over a broad range of parameters and appears to be the feature of the 2D geometry.

While the capillary wetting temperature, $T_{cw}$, is associated with an infinite capillary-liquid slab, for practical purposes the calculations are always restricted to a finite domain. In the case of planar wetting, one has access to mean-field critical exponents near the planar wetting temperature, $T_w$, which can be obtained from thermodynamics [80, 81], and used to extrapolate the calculation data and find the wetting temperature of a particular substrate with an almost experimental precision, see, e.g., [82, 83]. In our case such analytic results are obviously unavailable, and we entirely rely on the computations. For every calculated phase diagram we provide the value of the accuracy, $\Delta_{cw}$, for the calculated capillary wetting temperature, $T_{cw} \approx T_{cw}$, which we define as

$$\Delta_{cw} \equiv \left| \Delta \mu_{\text{cpw}} (T_{cw}) - \Delta \mu_{\text{cc}} (T_{cw}) \right|.$$

(26)
The capillary wetting temperature separates the two types of CC. For isothermal thermodynamic routes to CC at $T < T_{cw}$ the phase, where fluid configurations possess a finite capillary-liquid slab, is metastable. CC then happens discontinuously from the capillary bulk as a first-order transition, and the 2D capped capillary does not exhibit any principal difference to a 1D slit pore. On the other hand, at $T > T_{cw}$ the CC is a continuous transition: it happens from the capping wall. The capillary-liquid slab grows continuously into the capillary bulk, as, e.g., $\mu \to \mu_{cc}$ isothermally. If the capillary prewetting line is crossed (see figure 4), the CC is preceded by the first-order transition between fluid configurations with vapour and a capillary-liquid slab of finite length (e.g., figure 2). Hence, an isothermal approach to CC at $T = T_{cw}$ can be viewed as the limiting case of capillary prewetting, where the coexisting slab is of infinite length: $L_m \to \infty$. The discovery of $T_{cw}$ is of fundamental importance. Even though the capillary prewetting transition may be influenced by thermal fluctuations, which in the DF methodology are left unaccounted for, the presence of prewetting would be revealed by the two distinct types isothermal CC in the capillary bulk, namely first-order versus continuous, depending on whether $T$ is below or above $T_{cw}$. This should be observable experimentally and is impervious to thermal fluctuations.

The higher-temperature end of the capillary prewetting line at $T = T_{cpw}^{cr}$ is a critical point. Our mean-field DF approach reveals the signature of criticality: the coexisting configurations become structurally indistinguishable and the branches of free energy defining vapour and slab phases align to form a single branch in the limit $T \to T_{cpw}^{cr}$. The critical prewetting density profile for the capped capillary we have considered in this section is shown in figure 3(c).

4.3. Fluid structure, connection to wedge wetting

Here we explore deeper the microscopic surface phases formed near the capping wall. First, we describe in detail the fluid structure, second, we come back to the question which was left open in the previous section: can the mechanism of corner wetting be intensified to possibly form a separate surface phase? So far we have observed some structural resemblance to wedge wetting (e.g., the profile with corner drops in figure 3(c)), but the formation of such configurations happened continuously and was not associated with a dedicated concave branch of excess free energy. Since we focus now on the microscopic details of fluid structure, a comment on the role of fluctuations in the system is in order. For capillaries, where the difference between the capillary wetting temperature, $T_{w}$, and prewetting critical temperature, $T_{cpw}^{cr}$, is large, one can arguably select a value of $T : T_{cpw} < T < T_{cpw}^{cr}$ to be sufficiently low, so that the effects of interface fluctuations would be comparable to those on a planar interface and will not distort significantly the fluid structure.

We proceed to examining a capillary with a weaker substrate potential (lower planar $T_{w}$): $\varepsilon_w = 0.85$, $\sigma_w = 1.5$, $H_0 = 2.8$, $H = 30$. The fluid is treated in WDA, the planar wetting temperature being $T_w = 0.868$. The capillary wetting temperature is $T_{cw} = 0.87,$
Figure 6. (a) Density profile of the coexisting capillary-liquid slab configuration at $T = 0.88, \Delta \mu_{\text{cpw}}(T) = -2.4 \cdot 10^{-2}$ in the capillary with $H = 30, \varepsilon_w = 0.85, \sigma_w = 1.5, H_0 = 2.8$; the fluid is treated in WDA, planar $T_w = 0.868$. Vertical lines show the position of slices inside the capillary-liquid, at $x_l = 14$, and inside the vapour, at $x_v = 40$. (b) Slice along a bisector. (c), (d) Slices inside capillary-liquid and vapour at $x_l, x_v$ (due to symmetry, shown for $0 \leq y \leq H/2$), dotted horizontal lines are at $\rho_{\text{liq}}^{\text{cc}} = 0.5$ and $\rho_{\text{vap}}^{\text{cc}} = 0.07$.

We discuss the fluid structure on the example of the density profile with the capillary-liquid slab. For illustration purposes we would like the temperature to be low, so that the fluid density has a pronounced structure, but, at the same time, it should be above $T_{\text{cw}}$ – for the slab phase to be thermodynamically stable. We chose the value $T = 0.88$, just above $T_{\text{cw}}$. All analysis below holds for any slab-like configuration (even metastable) with $L_m$ larger than the near-wall region, where the density oscillates. For example, in the case of our chosen substrate potential the meniscus height should satisfy $L_m > 5$.

Generally, the presence of the substrate walls causes oscillations of the fluid density in the near wall region. The effect is due to the competition between the attraction of fluid molecules to the wall (which is strongest in the vicinity of the wall) and the very strong repulsions between the fluid molecules at short distances. The latter effect is, in turn, due to an overlap in electron orbitals and the Pauli exclusion principle, and is included into classical fluid models by prescribing the particles to have rigid finite-sized cores – hard spheres of (strictly speaking) temperature-dependent diameter, which, for reasons given in the introduction, we set to unity ($\sigma \equiv 1$), without loss of generality. The WDA DF approximation to the fluid free energy, developed from the analysis of the molecular fluid-fluid correlations [45], treats the repulsions non-locally and captures
this excluded volume effect in the microscopic fluid structure.

Figure 6 shows the density profile (figure 6(a)) and three representative cross sections: along the corner bisector (figure 6(b)), well inside capillary-liquid (at $x_l$, figure 6(c)) and vapour (at $x_v$, figure 6(d)). The values $x_l$ and $x_v$ are marked on the density profile by white and black vertical lines. Considering the slice along the corner bisector in figure 6(b), we note pronounced oscillations, set approximately one hard sphere diameter apart, with amplitude rapidly (exponentially, [76]) decaying away from the apex of the corner. The same is true about the slice inside capillary-liquid in figure 6(c). Even along a slice inside vapour one can see a single oscillation, figure 6(d).

The horizontal dotted lines in figures 6(c) and 6(d) mark the values of $\rho_{\text{liq}}^{\text{cc}}$ and $\rho_{\text{vap}}^{\text{cc}}$.

The presented slices further uncover the physics of an isothermal slab growth as $\mu \to \mu_{\text{cc}}$ and illustrate the reasoning behind our choice of the reference values $\rho_{\text{vap}}^{\text{cc}}$ and $\rho_{\text{liq}}^{\text{cc}}$ for scaling the plotted data. As can be seen from the figures, the density slices inside each phase, $\rho (x, y)$ and $\rho (x, y)$, tend to their corresponding reference values, $\rho_{\text{liq}}^{\text{cc}}$ and $\rho_{\text{vap}}^{\text{cc}}$, with $y \to \infty$. Moreover, our multiple computations show that, generally, the density cross sections taken well inside the vapour and slab phases are exactly identical (within the margin of machine rounding error) to the 1D density profiles, $\rho_{y,\text{liq}} (y)$ and $\rho_{y,\text{vap}} (y)$, of fluid configurations coexisting during CC in the associated slit pore, at the same $T$:

$$\rho (x_l, y) \equiv \rho_{y,\text{liq}} (y),$$
$$\rho (x_v, y) \equiv \rho_{y,\text{vap}} (y).$$

(27)

The latter result is very important for our proposed analogy in the phenomenology of wetting on a capped capillary and on a planar wall. In planar wetting at $T > T_{w}$, when the nearly saturated fluid ($\mu \lesssim \mu_{\text{sat}}$) is brought in contact with the planar substrate wall, its density profile exhibits a characteristic plateau of nearly constant liquid-like density at the wall, see, e.g., reference [22]. The nearly constant value at the plateau is exactly the density of the liquid at saturation ($\mu = \mu_{\text{sat}}$), at the same $T$. For wetting on a capped capillary, the role of the bulk is played by the fluid phase in the associated slit pore. Increasing $\mu$ at $T > T_{cw}$ leads to the formation of the liquid-like slab, whose length diverges in the limit of the continuous CC, as $\mu \to \mu_{\text{cc}}$. The equivalence expressed by equations (27) proves, that the slab is formed from nothing else, but the capillary-liquid, which coexists with vapour during CC in the slit pore, associated with the capped capillary. Thus, CC is indeed the bulk transition for the capped capillary and the phenomenology is identical to that of planar wetting. Note, however, that wetting on a capped capillary belongs to a different Ising universality class, than planar wetting, see [23, 11]. The different universality class entails, e.g., that as bulk coexistence is approached in both systems, the divergence of adsorption in the case of a planar wall and the capped capillary follows different power laws: for the case of the planar wall $\Gamma \sim \Delta \mu^{-1/3}$, while in the case of the capped capillary $\Gamma \sim (\mu - \mu_{\text{cc}})^{-1/4}$.

Finally, we note that a slice inside vapour (considered up to the half of capillary width), $\rho (x_v, y)$, figure 6(c), is also exactly identical to the density profile of a fluid (vapour) at the same $T$ and $\mu$ in contact with a single planar wall. In other words,
"vapour" configurations inside a capped capillary, a slit pore, and in contact with a planar wall are all identical, which is why the respective phase is everywhere referred to simply as vapour, in contrast to, e.g., capillary-liquid phase, where the density plateau in a slit pore is different from that at a planar wall.

The spatially heterogeneous near-corner fluid structure is best visualized with a surface plot of $\rho_{\text{cpd}}(x,y)$ and is presented in figure 7. Considering it in more detail, we note that the density oscillations are primarily localized near the apex of the corner and decay rapidly into the capillary bulk. The absolute maximum of the density is reached exactly at the corner apex, followed by its absolute minimum positioned on the corner bisector (see also figure 6(b)). In the presented example the capillary is quite wide, its side walls are far apart, so the presented part of the $\rho_{\text{cpd}}(x,y)$ surface looks symmetric about the bisector and resembles the fluid density distribution inside a symmetric wedge, e.g., [84]. However, in a narrower capillary that seeming near-corner symmetry would be broken by the influence of the second side wall, whose total effect would result from the combination of molecular repulsions due to the increased geometrical confinement of the fluid and attractions to the wall. By following standard steps, it is possible to obtain exact sum rules, linking the values of the 2D density, $\rho_{\text{cpd}}(x,y)$, at contact with the capping wall, the side walls, and even the corner apex, with the bulk thermodynamic variables $T$ and $\mu$, as it was done, e.g. in references [85, 86] for open wedges immersed in liquid.

A careful investigation of the fluid phase behaviour reveals that besides the capillary prewetting, an additional first-order phase transition can occur, which involves fluid configurations possessing drops in the corners. For the chosen substrate parameters this transition takes place only between metastable fluid configurations. A representative excess free energy isotherm is shown in figure 8(a) and has three concave branches, which define the fluid phases of vapour (dashed line), capillary-liquid slab (black solid line) and corner drops (grey solid line, see inset). The isotherm exhibits two Van...
Figure 8. Isothermal adsorption in capillary from figure 6 at $T = 0.906$; $\Delta \mu_\text{cc} (T) = -2.4 \cdot 10^{-2}$, reference densities: $\rho_\text{cc}^{\text{vap}} = 0.08$, $\rho_\text{cc}^{\text{liq}} = 0.46$. (a) Excess free energy isotherm. It possesses three concave branches (connected by non-concave branches, dotted line), which define three fluid phases: vapour (dashed), capillary-liquid (solid black) and drops (solid grey, see inset). There are two consecutive phase transitions (revealed by intersections of concave branches): capillary prewetting, at $\Delta \mu_{\text{cpw}} = -2.94 \cdot 10^{-2}$, $\Omega_\text{ex} = -3.70$, and (metastable, see inset) shifted wedge prewetting, at $\Delta \tilde{\mu}_{\text{wpw}} = -2.44 \cdot 10^{-2}$, $\Omega_\text{ex} = -3.77$. (b) and (c) Coexisting profiles at capillary prewetting. (d) and (e) Coexisting profiles at (metastable) shifted wedge prewetting.

The full phase diagram of the capped capillary is shown in figure 9. The grey curve is the CC transition line ($\Delta \mu_\text{cc} (T)$), the black curves are the capillary prewetting transition line ($\Delta \mu_{\text{cpw}} (T)$), it is tangential to $\Delta \mu_\text{cc} (T)$ and the locus of (metastable) transitions of the type shown in the inset of figure 8(a), taking place between vapour and drop phases. We will denote it as $\Delta \tilde{\mu}_{\text{wpw}} (T)$-line. In our example it is bounded at the lower-$T$ end, at $T_0 = 0.87$, and at the higher-$T$ end at $T \equiv \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.885$.

First, note that the capillary wetting temperature is lower and the capillary prewetting spans a broader temperature range, than in the example from the previous section: for the phase diagram in figure 4 we have $T_{\text{cw}}^{\text{cr}} - T_{\text{cw}} = 0.374$, while for the one in
We have $T_{cw}^c - \bar{T}_{cw} = 0.737$. The effect can be attributed to the relatively weaker attracting substrate. We use the value of planar wetting temperature, $T_w$, as an effective measure of the substrate attractive strength, with a lower $T_w$ corresponding to a weaker substrate. For the capillary in figure 4 we have $T_w = 0.927$, while for the capillary in figure 9 the value is lower: $T_w = 0.868$. In planar wetting a weaker attracting substrate also has a more pronounced prewetting transition line, as shown in, e.g., reference [22].

Regarding the $\Delta \tilde{\mu}_{wpw}(T)$-line we note that its higher-temperature end at $T = \tilde{T}_{wpw}^c$ is a critical point. Computing various free energy isotherms for $T \rightarrow \left( \tilde{T}_{wpw}^c \right)^-$ we find, that the concave branch defining the drop phase tends to align with the branch defining the vapour phase (see, e.g., dashed and solid grey lines in figure 8(a)) and forms a single branch in the above limit. The density profiles of fluid configurations coexisting along the $\Delta \tilde{\mu}_{wpw}(T)$-line become identical in the same limit. On the other hand, the lower-temperature end of the transition line at $T = \tilde{T}_0$ does not possess the above signature of criticality: at $T \lesssim \tilde{T}_0$ excess free energy isotherms still possess three concave branches, with the branch defining the drop phase being entirely metastable, without an intersection with the vapour branch.

In the previous section we have noted the existence of fluid configurations possessing corner drops (see coexisting profiles in figures 3(a) and 3(b)). Although the nature of the phenomenon was unclear, the relation to wetting on a wedge was prompted by the fluid structure. On the other hand, we have established that a phase diagram of the capped capillary can possess a separate transition line, $\Delta \tilde{\mu}_{wpw}(T)$, forming the locus of first-order transitions between fluid configurations with corner drops. We also found, that the $\Delta \tilde{\mu}_{wpw}(T)$-line ends at a critical temperature, $\tilde{T}_{wpw}^c$, above which the formation of corner drops happens continuously with increasing $\Delta \tilde{\mu}$ at a fixed $T$. So, by considering again the continuous formation of the corner drops in the capillary from the previous section (figures 3(a) and 3(b)), we see that somehow the effect of criticality at $\tilde{T}_{wpw}^c$ is still present, even though the transition line (which should end at $T = \tilde{T}_{wpw}^c$) is not found on the full phase diagram (figure 4). Such effect is only possible, if the transition to configurations with corner drops (given in the case of figure 3 by the $\Delta \tilde{\mu}_{wpw}(T)$-line) is not related to the capped capillary, but exists independently. Based on these arguments, we now can relate the transition line $\Delta \tilde{\mu}_{wpw}(T)$ to the wedge prewetting (whose transition line we would denote $\Delta \mu_{wpw}(T)$), which is studied in detail in, e.g., reference [79].

In Part II of this study we will show, that the entire wedge prewetting line, $\Delta \mu_{wpw}(T)$, and its critical temperature, $T_{wpw}^c$, are shifted in the capped capillary due to confinement, analogously to how bulk coexistence is shifted in a slit pore due to the Kelvin effect, see equation (1). In the case of the capped capillary discussed in section 4.1 (phase diagram in figure 4), the coexisting fluid configurations from figures 3(a) and 3(b) are supercritical with respect to the shifted wedge prewetting. We expect, that either the $\Delta \mu_{wpw}(T)$-line ends above the $\Delta \mu_{cc}(T)$-line, or the shift of $\Delta \mu_{wpw}(T)$-line, due to the second side wall of the capillary, does not allow for $\Delta \tilde{\mu}(T)$-line to form.
To better understand the interplay between wedge and capillary wetting through the DF-type simulation, one can compute the full wedge prewetting line, and then study, how that line is influenced, by adding a third wall (second side wall of the capped capillary) at various distances $H$, and computing the phase diagrams of the resulting capped capillaries of varying heights. Such an exploration, however, goes beyond the scope of the present study dedicated to the study of capped capillaries.

Finally, we note that the lower-temperature end of the shifted wedge prewetting line (at $T_0$) does not have to coincide with the CC line, as can be see from, e.g., figure 10, which shows the full phase diagram of the capped capillary with parameters $\varepsilon_w = 0.7, \sigma_w = 2, H_0 = 5, H = 30$; fluid is treated in LDA, planar wetting temperature: $T_w = 0.755$. The system is similar to the one we have studied in reference [23].

5. Summary

Our study of wetting phenomena in capped capillaries is based on statistical mechanics, in particular non-local interactions in the fluid were taken into account explicitly through the use of DF formulation for the fluid free energy. We employed two DF approximations for the fluid free energy: one treating repulsions non-locally (WDA) and one treating them locally (LDA). The fact, that both approximations treat attractions in a non-local fashion and lead to essentially the same wetting behaviour of the fluid (above the bulk triple point, in the range of liquid- and vapour-like densities), shows that the presented physics of wetting is controlled by the long-ranged attractive forces acting in the fluid, see, e.g., figures 9 and 10.

We have implemented an arc-length continuation technique to address two very important problems of mean-field analyses of physical systems, namely the computation
of an isotherm (adsorption and free energy), and the computation of a phase diagram. The methodology is readily applicable to other fluid settings while the most important step in its practical implementation is obtaining a starting point. Typically, one can consider some limiting value of the continuation parameter, where the equation is numerically well-behaved, i.e., one does not have to come up with an initial guess for the Newton iterations to converge to a solution. An example is provided in the calculation of free-energy or an adsorption isotherm, where the continuation is initiated from a low value of the parameter, $\mu$, hence the system is in the vapour phase, and almost unaffected by the substrate. The Newton algorithm converges fast and a simple initial guess $\rho_{cpd}(x,y) \equiv \rho_{vap}^{cc}$ suffices. On the other hand, the computation of a phase line involves the analysis of an approximate isotherm to get a starting point, but the value of the continuation parameter ($T$) need not correspond to any special limiting case of the problem.

For the study of the fluid phase behaviour we have adopted a method, where we identify the fluid phase with a concave branch of the excess free energy in the space of thermodynamic fields. A first-order phase transition then is given by the intersection of concave branches. The order parameter for the transitions we presented is the adsorption: a first-order transition is associated with a finite jump in its value, while a continuous transition – with its divergence. Our results can be summarised as follows:

- We have shown the existence of the capillary wetting temperature, $T_{cw}$, which is the intrinsic property of the 2D pore, in the same sense as the wetting temperature, $T_{cw}$, is the property of the 1D planar substrate. It controls the order of the phase transition in capillary bulk: at $T < T_{cw}$ CC is of first order (as it is in a slit pore), while at $T > T_{cw}$ it is a continuous phase transition associated with the diverging

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**Figure 10.** Phase diagram of the capped capillary with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 30$; fluid treated in LDA, planar $T_w = 0.755$. Solid grey curve: CC-line, ending at $(T_{cc}^{cr}, \Delta\mu_{cc}(T_{cc}^{cr})) = (0.99, -4.56 \cdot 10^{-2})$. Solid black lines: capillary prewetting, $\Delta\mu_{cpw}(T)$, which is tangent to CC at $(T_{cw}, \Delta\mu_{cpw}(T_{cw})) = (0.78, -4.6 \cdot 10^{-2})$, $\Delta_{cw} = 0.06 \cdot 10^{-2}$, and ends at $(T_{cw}^{cr}, \Delta\mu_{cpw}(T_{cw}^{cr})) = (0.928, -8.62 \cdot 10^{-2})$, and shifted wedge prewetting, $\Delta\tilde{\mu}_{wpw}(T)$, which is bound by $(\tilde{T}_0, \Delta\mu_{cpw}(\tilde{T}_0)) = (0.87, -6.33 \cdot 10^{-2})$ and $(\tilde{T}_{cw}^{cr}, \Delta\mu_{cpw}(\tilde{T}_{cw}^{cr})) = (0.885, -7.34 \cdot 10^{-2})$. Note that lower-$T$ end of shifted wedge prewetting line does not lie on the CC transition line, unlike, e.g., figure 9.
slab of capillary-liquid formed at the capping wall. Obtaining the capillary wetting temperature requires one to solve a set of 2D Euler-Lagrange equations in the space of density profiles $\rho(x,y)$ for various values of temperature and chemical potential.

- We have shown the existence of the first-order capillary prewetting transition, where the vapour coexists with a capillary-liquid slab of a finite length formed at the capping wall. The CC at $T = T_{cw}$ can be viewed as the limiting case of capillary prewetting. The typical phase diagram of the capped capillary, thus, consists of the phase diagram of the slit pore, which acts as capillary bulk, and the transition line of capillary prewetting, which is the consequence of 2D confinement of the fluid.

- The remnant of wetting on wedge-like substrates is manifested in capped capillaries by a (metastable) fluid phase with drops in the capillary corners. In Part II we shall demonstrate, that in the capped capillary the wedge prewetting is shifted, due to confinement by the additional side wall.

- The fluid has been found to possess a highly oscillatory structure in the corners. The oscillations are due to the excluded volume effects and decay rapidly away from the apices.

We expect our findings to stimulate further theoretical research of microscopic pores as well as experimental investigations. In Part II we explore deeply the complicated interplay between different mechanisms of 2D wetting. We consider an example of the system, which exhibits two types of three-phase coexistence: first, the capped capillary allows for stable vapour, drop and capillary-liquid slab phases, second, the capillary bulk allows for stable phases of vapour, planar prewetting film and capillary-liquid. We also identify potentially fruitful areas for future investigation, which are prompted by our results presented in both parts.

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References

[1] J. W. Cahn. Critical point wetting. *J. Chem. Phys.*, 66:3667, 1977.
[2] C. Ebner and W. F. Saam. New phase-transition phenomena in thin Argon films. *Phys. Rev. Lett.*, 38:1486–1489, 1977.
[3] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley. Wetting and spreading. *Rev. Mod. Phys.*, 81:739, 2009.
[4] T. M. Squires and S. Quake. Microfluidics: Fluid physics at the nanoliter scale. *Rev. Mod. Phys.*, 77:977, 2005.
[5] D. Bonn and D. Ross. Wetting transitions. *Rep. Prog. Phys.*, 64:1085 – 1163, 2001.
[6] F. Dutka, M. Napliorkowski, and S. Dietrich. Mesoscopic analysis of Gibbs’ criterion for sessile nanodroplets on trapezoidal substrates. *J. Chem. Phys.*, 136(,):064702, 2012.
2D capillary wetting

[7] R. Evans. The nature of the liquid-vapour interface and other topics in the statistical mechanics of non-uniform, classical fluids. *Adv. Phys.*, 28:143–200, 1979.

[8] M. Plischke and B. Bergeisen. *Equilibrium Statistical Physics*. World Scientific Publishing Co. Pte. Ltd., 2006.

[9] J. Hansen and I. McDonald. *Theory Of Simple Liquids*. Academic Press, 1976.

[10] J. Wu. Density functional theory for chemical engineering: From capillarity to soft materials. *AIChE J.*, 52:1169, 2006.

[11] A. O. Parry, C. Rascon, N. B. Wilding, and R. Evans. Condensation in a capped capillary is a continuous critical phenomenon. *Phys. Rev. Lett.*, 98:226101, 2007.

[12] M. Tasynkevich and S. Dietrich. Complete wetting of nanosculptured substrates. *Phys. Rev. Lett.*, 97:106102, 2006.

[13] A. O. Parry and C. Rascon. Critical effects at 3D wedge wetting. *Phys. Rev. Lett.*, 85:345, 2000.

[14] A. O. Parry, C. Rascon, and A. J. Wood. Universality for 2D wedge wetting. *Phys. Rev. Lett.*, 83:5535, 1999.

[15] J. L. Cardy and P. Nightingale. Finite-size analysis of first-order phase transitions: Discrete and continuous symmetries. *Phys. Rev. B*, 27:4256, 1983.

[16] S. Dietrich. *Phase Transitions and Critical Phenomena*, chapter 1. Wetting Phenomena, pages 2 – 219. Academic Press, 1988.

[17] R. Evans. *Lecture Notes, 3rd Warsaw School of Statistical Physics*, chapter Density Functional Theory for Inhomogeneous Fluids I: Simple Fluids in Equilibrium. Lecture Notes, 3rd Warsaw School of Statistical Physics, 2009.

[18] M. Zeng, J. Mi, and C. Zhong. Boundary of prewetting transition of Ar on a Li surface. *Phys. Rev. B*, 82:125452, 2010.

[19] Y. Yu, Y. Li, and Y. Zheng. Thin-thick film transitions on a planar solid surface: A density functional study. *Chin. Phys. Lett.*, 27:037101, 2010.

[20] S. A. Sartarelli and L. Szybisz. Adsorption of Ar on planar surfaces studied with a density functional theory. *Phys. Rev. E*, 80:052602, 2009.

[21] F. Ancilotto and F. Toigo. First-order wetting transitions of neon on solid CO$_2$ from density functional calculations. *J. Chem. Phys.*, 112:4768, 2000.

[22] P. Yatsyshin, N. Savva, and S. Kalliadasis. Spectral methods for the equations of classical density-functional theory: Relaxation dynamics of microscopic films. *J. Chem. Phys.*, 136:124113, 2012.

[23] P. Yatsyshin, N. Savva, and S. Kalliadasis. Geometry-induced phase transition in fluids: Capillary prewetting. *Phys. Rev. E*, 87:020402(R), 2013.

[24] R. Roth and A. O. Parry. Drying in a capped capillary. *Mol. Phys.*, 109:1159, 2011.

[25] P. Hohenberg and B. I. Halperin. Theory of dynamic critical phenomena. *Rev. Mod. Phys.*, 49:435, 1977.

[26] B. Goddard, A. Nold, N. Savva, G. A. Pavliotis, and S. Kalliadasis. General dynamical density functional theory for classical fluids. *Phys. Rev. Lett.*, 109:120603, 2012.

[27] B. Goddard, A. Nold, N. Savva, P. Yatsyshin, and S. Kalliadasis. Unification of dynamic density functional theory for colloidal fluids to include inertia and hydrodynamic interactions: derivation and numerical experiments. *J. Phys.: Condens. Matter*, 25:035101, 2013.

[28] A. Archer and R. Evans. Dynamical density functional theory and its application to spinodal decomposition. *J. Chem. Phys.*, 121(9):4246–4254, September 2004.

[29] U. M. B. Marconi and P. Tarazona. Dynamic density functional theory of fluids. *J. Phys.: Condens. Matter*, 12:A413 – A418, 2000.

[30] K. Binder. Modelling of wetting in restricted geometries. *Annu. Rev. Mater. Res.*, 38:123 – 142, 2008.

[31] S. Herminghaus, M. Brinkman, and R. Seeman. Wetting and dewetting of complex surface geometries. *Annu. Rev. Mater. Res.*, 38:101, 2008.

[32] D. Chandler, J. D. Weeks, and H. C. Anderson. Van der Waals picture of liquids, solids, and phase transformations. *Science*, 220:787, 1983.
2D capillary wetting

[33] M. Rauscher and S. Dietrich. Wetting phenomena in nanofluidics. *Annu. Rev. Mater. Res.*, 38:143, 2008.

[34] H. Craighead. Future lab-on-a-chip technologies for interrogating individual molecules. *Nature*, 442:387, 2006.

[35] Kawase M. Gerlach, I. and K. Miura. In-situ preparation of supported precious metal and metal oxide nanoparticles by nanoreactor flash pyrolysis. *Microporous and Mesoporous Materials*, 122:79, 2009.

[36] A. Calvo, B. Yameen, F. J. Williams, J. A. A. A. Soler-Illia, and A. Azzaroni. Communication mesoporous films and polymer brushes helping each other to modulate ionic transport in nanoconfined environments. An interesting example of synergism in functional hybrid assemblies. *J. Am. Chem. Soc.*, 131:10866, 2009.

[37] Z. Gou and W. Liu. Biomimic from the superhydrophobic plant leaves in nature: Binary structure and unitary structure. *Plant Sci.*, 172:1103, 2007.

[38] N. R. Bernardino and S. Dietrich. Complete wetting of elastically responsive substrates. *Phys. Rev. E*, 85:051603, 2012.

[39] W. F. Saam. Wetting, capillary condensation and more. *J. Low Temp. Phys.*, 157:77 – 90, 2009.

[40] R. Evans. Fluids adsorbed in narrow pores: phase equilibria and structure. *J. Phys. Condens. Matter*, 2:8989 – 9007, 1990.

[41] R. Evans and U. M. B. Marconi. Phase equilibria and solvation forces for fluids confined between parallel walls. *J. Chem. Phys.*, 86:7138, 1987.

[42] J. A. Barker and D. Henderson. What is “liquid”? understanding the states of matter. *Rev. of Mod. Phys.*, 48(4):587–671, 1976.

[43] J. A. Barker and D. Henderson. Perturbation theory and equation of state for fluids. II. A successful theory of liquids. *J. Chem. Phys.*, 47:4714–4721, 1967.

[44] N. F. Carnahan and K. E. Starling. Equation of state for nonattracting rigid spheres. *J. Chem. Phys.*, 51:635–636, 1969.

[45] P. Tarazona and R. Evans. A simple density functional theory for inhomogeneous liquids, wetting by gas at a solid-liquid interface. *Mol. Phys.*, 52:847–857, 1984.

[46] P. Tarazona. A density functional theory of melting. *Mol. Phys.*, 52:81–96, 1984.

[47] P. Tarazona, U. M. B. Marconi, and R. Evans. Phase equilibria of fluid interfaces and confined fluids. non-local versus local density functionals. *Mol. Phys.*, 60:573–595, 1987.

[48] A. Papadopoulou, F. v. Swol, and U. M. B. Marconi. Pore-end effects on adsorption hysteresis in cylindrical and slitlike pores. *J. Chem. Phys.*, 97:6942, 1992.

[49] E.A. Ustinov and D. D. Do. Modeling of adsorption in finite cylindrical pores by means of density functional theory. *Adsorption*, 11:455 – 477, 2005.

[50] I. Ispolatov and B. Widom. Unified approach to prewetting and wetting phase transitions. *Physica A*, 279:203–212, 2000.

[51] P. Tarazona and Y. Rosenfeld. From zero-dimension cavities to free-energy functionals for hard disks and hard spheres. *Phys. Rev. E*, 55:R4873, 1997.

[52] R. Roth, R. Evans, A. Lang, and G. Kahl. Fundamental measure theory for hard-sphere mixtures revisited: the white bear version. *J. Phys.: Condens. Matter*, 14:12063–12078, 2002.

[53] J.P.R.B. Walton and N. Quirke. Modelling the phase behaviour of a fluid within a pore. *Chem. Phys. Lett.*, 129:382, 1986.

[54] R. L. Cotterman, B. J. Schwarz, and J. M. Prausnitz. Molecular thermodynamics for fluids at low and high densities. part 1: Pure fluids containing small or large molecules. *AIChE J*, 32:1787, 1986.

[55] B. Q. Lu, R. Evans, and M. M. Telo da Gama. The form of the density profile at a liquid-gas interface. *Mol. Phys.*, 55:1319, 1985.

[56] J. K. Lee, J. A. Barker, and G. M. Pound. Surface structure and surface tension: Perturbation theory and monte carlo calculation. *J. Chem. Phys.*, 60:1976, 1974.

[57] M. B. Sweatman. Weighted density functional theory for simple fluids: Supercritical adsorption
of a lennard-jones fluid in an ideal slit pore. *Phys. Rev. E*, 63:031102–1 – 031102–9, 2001.

[58] E. Thiele. Equation of state for hard spheres. *J. Chem. Phys.*, 39:474, 1963.

[59] J. A. Barker, R. A. Fisher, and R. O. Watts. Liquid argon: Monte carlo and molecular dynamics calculations. *Mol. Phys.*, 21:657, 1971.

[60] A. Chizmeshya, M. W. Cole, and Z. Zaremba. Weak binding potentials and wetting transitions. *J. Low Temp. Phys.*, 110:677–684, 1998.

[61] P. J. Marshall, M. M. Szczesniak, J. Sadlej, G. Chalasinski, M. A. Horst, and C. J. Jameson. *Ab initio* study of van der waals interaction of CO$_2$ with Ar. *J. Chem. Phys.*, 104:6569, 1996.

[62] A. Pereira and S. Kalliadasis. Equilibrium gas-liquid-solid contact angle from density-functional theory. *J. Fluid Mech.*, 692:53 – 77, 2012.

[63] L. G. D. Frink, A. G. Salinger, M. P. Sears, Weinhold J. D., and A. L. Frischknecht. Numerical challenges in the application of density functional theory to biology and nanotechnology. *J.Phys.: Condens. Matter*, 14:12167–12187, 2002.

[64] M. G. Knepley, D. A. Karpeev, S. Davidovits, R. S. Eisenberg, and D. Gillespie. An efficient algorithm for classical density functional theory in three dimensions: Ionic solutions. *J. Chem. Phys.*, 132:124101, 2010.

[65] R. Roth. Fundamental measure theory for hard-sphere mixtures: a review. *J. Phys.: Condens. Matter*, 22:063102, 2010.

[66] L. G. D. Frink and A. G Salinger. Two- and three-dimensional nonlocal density functional theory for inhomogeneous fluids. *J. Comp. Phys.*, 159:407 – 424, 2000.

[67] J. P. Boyd. *Chebyshev and Fourier Spectral Methods*. Dover Publications, Inc., 2001.

[68] L. N. Trefethen. *Spectral Methods in MATLAB*. SIAM, 2000.

[69] T. W. Tee and L. N. Trefethen. A rational spectral collocation method with adaptively transplanted chebyshev grid points. *SIAM Journal of Scientific Computing*, 28(5):1798–1811, 2006.

[70] N. Hale and L. N. Trefethen. New quadrature formulas from conformal maps. *SIAM J. Numer. Anal.*, 46(2):930–948, 2008.

[71] J. Waldvogel. Fast construction of the Fejér and Clenshaw-Curtis quadrature rules. *BIT Num. Math.*, 43:001 – 018, 2003.

[72] L. N. Trefethen. Is gauss quadrature better than clenshawcurtis? *SIAM Review*, 50:67 – 87, 2008.

[73] A. G. Salinger and L. J. D. Frink. Rapid analysis of phase behavior with density functional theory. I. Novel numerical methods. *J. Chem. Phys.*, 118(16):7457–7465, 2003.

[74] M. M. Telo da Gama and U. M. B. Marconi. Crossover between complete wetting and critical adsorption. *Physica A*, 171:69–79, 1991.

[75] R. B. Griffiths and J. C. Wheeler. Critical points in multicomponent systems. *Phys. Rev. A*, 2:1047, 1970.

[76] D. Henderson. *Fundamentals of Inhomogeneous Fluids*. Dekker, New York, 1992.

[77] F. v. Swol and D. Henderson. Wetting at a fluid-wall interface. Computer simulation and exact statistical sum rules. *J. Chem. Soc., Pharaday Trans. 2*, 82:1685, 1986.

[78] P.C. Ball and R. Evans. Structure and adsorption at gas-solid interfaces: Layering transitions from a continuum theory. *J. Chem. Phys.*, 89:4412 – 4423, 1988.

[79] K. Rejmer, S. Dietrich, and M. Napiorkowski. Filling transition for a wedge. *Phys. Rev. E*, 60:4027 – 4042, 1999.

[80] W. F. Saam, J. Treiner, E. Cheng, and M. W. Cole. Helium wetting and prewetting phenomena at finite temperatures. *J. Low Temp. Phys.*, 89:637, 1992.

[81] E. H. Hauge and M. Schick. Continuous and first-order wetting transition from the van der waals theory of fluids. *Phys. Rev. B*, 27:4288, 1983.

[82] S. A. Sartarelli, L. Szybisz, and I. Urrutia. Adsorption of Ne on alkali surfaces studied with a density functional theory. *Phys. Rev. E*, 79:011603, 2009.

[83] E. Cheng, G. Mistura, H. C. Lee, M. H. W. Chan, M. W. Cole, C. Carraro, W. F. Saam, and F. Toigo. Wettin transitions of liquid hydrogen films. *Phys. Rev. Lett.*, 70:1854, 1993.
[84] P. Bryk, R. Roth, M. Schoen, and S. Dietrich. Depletion potentials near geometrically structured substrates. *Europhys. Lett.*, 63:233, 2003.

[85] J. R. Henderson. Interfacial statistical geometry: Fluids adsorbed in wedges and at edges. *J. Chem. Phys.*, 120:1535, 2003.

[86] D. Henderson. Interfacial statistical geometry: Fluids adsorbed in wedges and at edges. *J. Chem. Phys.*, 210:1535, 2004.