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Analysis of the phase behaviour of a nano-confined Lennard-Jones fluid using a pseudo-spectral approach to classical density-functional models

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Declaration

I herewith certify that this dissertation is my own original work, and all the material which is not my own work has been properly acknowledged.

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Petr Yatsyshin

Abstract

Wetting phenomena provide a vivid manifestation of attractive intermolecular forces, putting to a test our microscopic picture of matter. Classical Density Functional (DF) theory is based on first principles of statistical mechanics and provides a way to account for various microscopic effects determining the behaviour of confined fluids.

In broad terms, the thesis consists of two parts, each expanding the existing body of knowledge in the respective field. In the first part a novel numerical methodology is developed, which allows one to solve any type of non-local integral or integral-differential equations typical of equilibrium and dynamic DF theories in one- and two-dimensional problems. The approach is based on pseudo-spectral collocation method and is demonstrated to be superior in speed and accuracy to existing commonly used approaches. Novel features include an integrating matrix operator, which is calculated outside of the non-linear solver loops and then used for fast evaluation of the non-local convolution-like terms with the highly accurate Clenshaw-Curtis quadrature, and a battery of techniques based on arc-length continuation providing a systematic and efficient way to compute density profiles, find surface phase transitions and obtain full phase diagrams.

The second part presents a DF study of an atomic fluid at given chemical potential and temperature spatially confined to a semi-infinite rectangular pore. Fluid-fluid and fluid-substrate interactions are with long-ranged Lennard-Jones forces. Far from the capping wall this prototypical two-dimensional system reduces to a one-dimensional slit pore. However, the broken translational symmetry dramatically changes the phenomenology of wetting from that of a slit pore. Detailed investigation reveals new phenomena related to the geometry. In particular, the existence of capillary wetting temperature, continuous capillary condensation transition, continuous planar prewetting transition, and more. Existence beyond mean-field is discussed briefly. Dynamic extension of the DF theory is used to study the relaxation of the system.

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To my dear grandfather Professor Mikhail Bezukh

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Introduction

The following thesis consists of three chapters and conclusion. The material is organised in such a way as to separate the two independent logical parts and allow for an easy cross-referencing of the material shared between them. Each chapter starts with an overview of recent and seminal works in the respective field. The scientific novelty is contained in second and third chapters, while the first chapter provides the platform for discussion.

The main purpose of the first chapter is to provide the working equations, as well as to clearly state their limits of applicability. It also provides an overview of seminal works, as well as latest developments in the field of Density Functional (DF) theories for confined classical fluids. The focus is towards single-component long-range interacting atomic fluids above bulk triple temperatures brought in contact with solid substrates. All other applications, such as colloids, fluids of charged particles, etc., as well as phenomena below the bulk triple point are omitted. Note that the aim is to provide an adequate snapshot of the modern state of the field, it is not to rediscover nor to collect in a single place the diverse well-known results. Thus whenever appropriate the reader is referred to published works.

The second chapter develops the numerical methodology. It starts with an overview and critique of existing widely used approaches. The newly proposed method is then systematically developed, starting from the discretisation by spectral collocation and proceeding to the details of the arc-length continuation technique. The material is used in the following chapter for the study of the capped capillary.

The third chapter contains a detailed and systematic description of wetting in a capped capillary. It starts by an overview of the relevant works in the field of wetting and proceeds to introduce the system and describe its behaviour.

The conclusion clearly summarises the novel results obtained by the author and contained in the second and third chapters and outlines the prospects of future research on the topic of the thesis.

For legal reasons I state here and repeat several times throughout the text that the material, the text and the figures in this manuscript are based on my dated preprints [6, 7, 8] and published papers [3, 5]. The other authors of the above preprints and published papers have been informed of this manuscript. I was also involved in the work in reference [9].

1 Density functional approaches to classical fluids

The main idea of DF approaches to classical fluids is that (in very general terms) they allow one to incorporate the fluid structure into the equation of state. In practice a DF approach is most useful for describing the structural inhomogeneities in fluids, such as those induced by the presence of a substrate. The connection to integral equation theories of bulk fluids can be made through correlation function hierarchies, which can be obtained by consecutively differentiating the free energy functional, see, e.g., the reviews by Evans in [10, 11]. A systematic development of the DF formalism can be found in fundamental reviews of the field, e.g., references [11, 12, 13]. In short, the DF theory is a formulation of statistical mechanics, where in order to come up with a particular set of governing equations one approximates directly the free energy, as a functional of the one-body density. By doing so one essentially loses track of the microscopic Hamiltonian, but a satisfactory description of interfacial phenomena can nevertheless be achieved, as we will see in the present chapter when constructing the DF approximation.

The free energy of the fluid in contact with the substrate consists of two main parts: the fluid-fluid and the fluid-substrate contributions. Within the generalised Van der Waals picture of soft matter (e.g., see seminal works [15, 16]), the fluid-fluid free energy should account for long-ranged attractive and short-ranged repulsive forces between fluid molecules. The fluid-substrate contribution is typically incorporated into the free energy by treating the substrate as an inert spectator phase and accounting for its effect upon the fluid by an appropriately chosen external potential. Moreover, there exist readily applicable prescriptions for various terms entering the “Van der Waals” expression for the free energy functional. If the latter is chosen carefully, one typically achieves a qualitatively sensible description of the system.

It seems that modern development of DF theories has two main directions. A more fundamental direction is the development of highly accurate approximations for repulsive (see section 1.1.2 for a detailed review) and attractive (see section 1.1.3) contributions to the fluid-fluid free energy functional for various types of model fluids. A more applied direction is trying to reproduce experimental or simulation results with highly customised DF approximations which include very fine effects (see section 1.1.5).

We will try to show with the case studies presented in this thesis, that there potentially exists a very fruitful third direction: using relatively simple and essentially *minimalistic* DF

approximations with the aim of performing full parametric studies (e.g., obtaining surface phase diagrams) and potentially discovering *qualitatively* new physical phenomena. Such approach follows the spirit of pioneering works of Ebner and Saam, where the first-order wall prewetting has been studied for the first time with a computationally tractable model [17]. The only requirement we have for the free energy functional is that it provides us with a qualitatively sensible picture of the system.

The author of the present work believes that parametric studies of simple model systems could potentially form a unique niche for DF theories, which in principle can not be challenged by other theoretical approaches. Let us provide a few argumentative examples. A powerful alternative approach to studying fluid structure is computer simulations, but they are typically very costly (especially when one is “shooting in the dark”, which is the essence of a full parametric study), and also have principal limitations, e.g., all interaction potentials are necessarily truncated. The DF calculations are significantly cheaper than simulations and can be implemented without truncating the tails of interaction potentials (see section (2.1.6)). Effective Hamiltonian approaches allow one to obtain elegant analytic results and account for thermal fluctuations, but they also introduce sets of (often restrictive) assumptions and simplifications, while DF theories are more in the *ab initio* spirit and do not assume the existence of interfaces, but obtain them as output, using only intermolecular potentials as input.

The main principle limitation of the DF theories is that they are mean-field, meaning that the effects of bulk critical fluctuations are omitted. Such fluctuations may lead to rounding (disappearance) of surface phase transitions or change the order of a transition [18]. DF theory also cannot account for capillary wave fluctuations, which may lead to broadening of interfaces in weak external fields. Nevertheless, one can still clearly define the limits of applicability for DF theories [11].

1.1 Free energy functional

Here we systematically construct the free energy functional used in chapter 3 for the study of wetting on flat substrates and in a capped capillary. At the same time we attempt to provide an adequate snapshot of the modern state of DF theories, as well as to highlight the fundamental seminal works. In all problems considered the amount of fluid is macroscopically large making the grand canonical ensemble a natural choice.

1.1.1 Splitting interactions

When the substrate is modelled as an inert spectator phase, a general expression for the fluid free energy functional in the grand canonical ensemble can be written in the following form

$$\Omega[\rho(\mathbf{r})] = F_{\text{in}}[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) V(\mathbf{r}) - \mu \int d\mathbf{r} \rho(\mathbf{r}), \quad (1.1)$$

where $F_{\text{in}}[\rho]$ is the intrinsic Helmholtz free energy functional determined by the molecular interactions in the fluid, $V(\mathbf{r})$ is the effective potential, describing the effect of the substrate upon the fluid particles, finally, μ is the chemical potential of the thermostat, which together with T (entering the expression for F_{in}) specifies the bulk thermodynamic fields in the problem. In the above expression the substrate remains unaffected by the fluid. This is a typical approach in wetting, however an alternative is suggested in, e.g., the work by Ustinov and Do [19], where a DF approximation is constructed, which allows the fluid to affect the substrate.

Atomic fluids with pairwise interactions are in general well described by generalized Van der Waals theories based on splitting repulsive and attractive fluid-fluid interactions [20, 14, 16, 15]. The corresponding approach within a DF formulation is to use a perturbation theory, where the reference system is the fluid with purely repulsive inter-particle interactions (e.g., a hard sphere fluid) and the attractions are imposed perturbatively [20, 14, 21]. One of the merits of using a perturbation approach (versus, e.g., a truncated functional Taylor expansion of $F_{\text{in}}[\rho]$ [21, 22]) is that the intrinsic free energy functional is naturally subdivided into the repulsive (F_{Rep}) and attractive (F_{Attr}) additive contributions:

$$F_{\text{in}}[\rho(\mathbf{r})] = \int d\mathbf{r} f_{\text{id}}(\rho(\mathbf{r})) + F_{\text{Rep}}[\rho(\mathbf{r})] + F_{\text{Attr}}[\rho(\mathbf{r})], \quad (1.2)$$

where the first term on the right hand side is the ideal entropic contribution, given exactly by $f_{\text{id}}(\rho) = k_{\text{B}} T \rho (\ln(\lambda^3 \rho) - 1)$, with k_{B} being the Boltzmann constant and λ being the thermal wavelength (the general framework of classical statistics is applicable when the quantum effects are negligible, i.e., the thermal wavelength is much smaller than the average spacing between the fluid particles [11, 23]). Modern development of DF theories is mostly focused on creating sophisticated approximations for the last two terms of (1.2). Recent treatments attempt to customise them for a particular fluid and/or phenomenon under consideration, see reviews from this decade in, e.g., references [24, 25, 26, 27].

A comment on the common in DF theories use of the chemical potential (instead of pressure) to specify the bulk thermodynamic point is in order. We note that it is frequently omitted in literature on DF theories, but is always implicit. In a bulk fluid in isothermal conditions, due to the equation of state, the pressure, P , is in a one-to-one correspondence with the chemical potential, μ . Thus, the thermodynamic point of the bulk fluid reservoir at a given value of T can be specified by prescribing a value of either P or μ . 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), but requires defining the space-dependent pressure tensor. The chemical potential, on the other hand, is still constant throughout the fluid, as can be seen from equation (1.1), and together with the constant temperature enters the set of thermodynamic fields describing an inhomogeneous fluid. Thus, the choice of μ over P as the parameter of the reservoir is more than just a convenience stemming from the form of equation (1.1).

1.1.2 Repulsive contribution to the free energy

A purely repulsive fluid consisting of hard molecules with spherical cores of diameter σ can be defined by the following pairwise inter-particle potential:

$$\varphi(r) = \begin{cases} 0, & \text{if } r < \sigma \\ \infty, & \text{otherwise} \end{cases}. \quad (1.3)$$

In the above expression the radial vector $\mathbf{r}$ can vary in three dimensions, thus (1.3) defines a fluid of hard spheres. If $\mathbf{r}$ is a two- or a one-dimensional vector, the potential in (1.3) would define a fluid of hard disks or hard rods respectively. In the present work we only consider the model hard sphere fluid. Note that applications in biology and colloidal science warranted the development of free energy functionals for fluids with non-spherical molecules. Consider, e.g., free energy functionals for three-dimensional fluids consisting of cubes [28], cylinders [29, 30], hexagons [31], platelets and rods [32]. The development of free energy functionals for fluids with various geometries of constituent particles is an active direction of development in modern DF theories.

Despite the seeming simplicity of the pairwise interactions given by (1.3), an exact free energy functional can be found only for the case of a one-dimensional fluid of hard rods. It has been obtained by Percus in the seminal work [33], from the analysis of the grand partition function. As for the fluid of hard spheres, the free energy functional, as well as the correlation structure and the thermodynamic equation of state can only be approximated, albeit to a very satisfactory degree. The study of hard sphere fluids (and their mixtures) is a broad subject on its own, and is quite active. A review of various approaches to the description of hard sphere fluids, as well as main results, can be found in recent dedicated book [34]. For the purposes of the present work it suffices to discuss one commonly used equation of state and several quite reliable approximations of increasing complexity for hard sphere free energy functionals.

Carnahan-Starling equation of state

The thermodynamic equation of state can be found by expanding the pressure P of the bulk fluid in powers of the number density ρ [20, 14]:

$$\frac{P}{\rho k_B T} = 1 + B_2 \rho + B_3 \rho^2 \dots + B_k \rho^{k-1} \dots, \quad (1.4)$$

where the *virial coefficients* are known analytically up to B_4 , and for higher powers of density they can be obtained from, e.g., simulations [34]. Considering the values of the virial coefficients, Carnahan and Starling noted in a seminal paper [35], that with a rather high accuracy ($\sim 10^{-2}$) the known virial coefficients of the hard sphere fluid can be approximated by a simple analytic expression, which also can be used to “guess” the higher-order coefficients and create a Padé approximant to the equation of state (1.4):

$$\frac{P}{\rho k_B T} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}, \quad (1.5)$$

where $\eta = \pi \sigma^3 \rho / 6$ is the *packing fraction*, which is given by the excluded volume of a sphere of diameter σ .

The Carnahan-Starling equation of state (1.5) is phenomenological in nature, but agrees with simulation results better than many theoretically consistent alternatives (such as, e.g., a Percus-Yevick equation of state, which follows from the specific closure to the Ornstein-Zernike equation, see, e.g., references [36, 34]). The added advantage of a simple analytic form of equation (1.5) makes it a popular choice in modern DF theories of single-component fluids [37], and we employ it in this work. Note, that the hard sphere fluid does not exhibit a liquid-vapour coexistence, but can freeze [34, 38].

We can obtain the excess over ideal free energy of the bulk hard sphere fluid from the equation of state, $P = P(\eta, T)$, using standard thermodynamics [20]:

$$F_{\text{hs}}(\rho, V, T) = \rho V k_B T \int_0^\eta \frac{dx}{x} \left(\frac{P(x, T)}{\rho k_B T} - 1 \right) \equiv \rho V \psi(\rho), \quad (1.6)$$

where V is the total volume occupied by the system of N particles and $\psi(\rho)$ is the *configurational part* of the free energy per particle. Note, that a DF approach is grand-canonical¹ and implies a *thermodynamic limit*: $N \rightarrow \infty$, $V \rightarrow \infty$, while $N/V \rightarrow \rho$, where ρ is the number density of the bulk fluid. Performing the integration in (1.6) we obtain the analytic

¹A rigorous canonical formulation of DF theory exists [39], but is rarely used in practice, mainly because an approximate canonical approach using a constrained minimization of (1.1) is satisfactorily accurate for large numbers of particles, see, e.g., references [40, 41].

expression for $\psi(\rho)$:

$$\psi(\rho) = k_B T \frac{\eta(4-3\eta)}{(1-\eta)^2}, \quad \eta = \pi\sigma^3\rho/6. \quad (1.7)$$

The expressions for the free energy (1.6) and (1.7) are defined and obtained for a bulk hard sphere fluid whose one-body density is: $\rho(\mathbf{r}) \equiv \rho$. In order to construct a DF approximation, where the density is spatially distributed (as would be if, e.g., a substrate is brought in contact with the fluid), one has to somehow generalize the function (1.7) to the *functional*. Below we describe three commonly used prescriptions of increasing complexity [3].

Local and weighted density functionals for hard spheres

The most straightforward way to turn the expression (1.6) into a functional is to simply allow for the $\mathbf{r}$ -dependence of the number density. This is commonly known as the Local Density Approximation (LDA) and was extensively used in earlier literature on DF theories [21]:

$$F_{\text{hs}}^{\text{LDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\rho(\mathbf{r})). \quad (1.8)$$

There exist extensive studies analysing the limits of applicability of the LDA hard sphere functional (see, e.g., references [11, 42, 43, 21]). The main shortcoming of the local functional (1.8) stems from the completely incorrect account for the correlation structure of the hard sphere fluid, where it leads to a spurious delta-like peak of the direct correlation function (the second functional derivative of free energy with respect to the density) [43].

Nevertheless, the use of LDA (1.8) is acceptable as $F_{\text{Rep}}[\rho]$ (see equations (1.1) and (1.2)) in the perturbative treatment of problems where repulsions between the fluid molecules are well balanced by attractions, such as, e.g., the case of a Lennard-Jones (LJ) fluid above the bulk triple point. Then the full direct correlation function of the fluid is determined at distances larger than σ by the attractive tail, which, in turn, may be duly captured by an appropriate attractive functional ($F_{\text{Attr}}[\rho]$ in equation (1.2)). The main advantage of the functional (1.8) is its computational simplicity. It is still being used as $F_{\text{Rep}}[\rho]$ in modern literature, mainly for parametric studies of systems where the phenomena of interest are determined by the attractive interparticle forces, e.g., a free or a nearly free interface between liquid-like and vapour-like phases of a LJ fluid [5, 3, 44, 45, 46].

One notorious shortcoming of using an LDA functional (1.8) as $F_{\text{Rep}}[\rho]$ in DF theories of confined fluids is that such treatment completely misses the oscillatory near-wall behaviour of the density profile of, e.g., a LJ fluid [3]. At low temperatures the near-wall oscillations grow in amplitude and their peaks become delta-like as freezing is approached. The term $(1-\eta)^{-2}$ in (1.7) obviously cannot allow the density minimizing $\Omega[\rho]$ to have high absolute values, hence, the peaks are not captured by DF theories using LDA repulsive functional

(1.8).² To remedy this shortcoming Nordholm et al. in [48] and later Tarazona and Evans in [49] advocated the use of a properly averaged density in the configurational part of the hard sphere free energy. The strategy of averaging the density ultimately gave rise to a battery of methods for constructing repulsive [50, 51, 52] and later also attractive [53, 54, 55, 56] functionals for simple fluids [57, 58, 59] and even mixtures [60]. It is commonly referred to as the Weighted Density Approximation (WDA) and requires an averaging procedure and a bulk equation of state as “input”. For a single-component hard sphere fluid we have the general form

$$F_{\text{hs}}^{\text{WDA}}[\rho] = \int d\mathbf{r} \rho(\mathbf{r}) \psi(\bar{\rho}(\mathbf{r})), \quad \bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r} + \mathbf{r}') W(\mathbf{r}'), \quad (1.9)$$

where the averaged density $\bar{\rho}(\mathbf{r})$ is defined with the help of the weight function $W(\mathbf{r})$. In this work we use a straightforward prescription due to Tarazona and Evans [49], where the density inserted into the configurational part of free energy is averaged over the volume of a single hard sphere of diameter σ :

$$\bar{\rho}(\mathbf{r}) = \frac{3}{4\pi\sigma^3} \int_{|\mathbf{r}-\mathbf{r}'| \leq \sigma} d\mathbf{r}' \rho(\mathbf{r}'), \quad (1.10)$$

or equivalently using (1.9), $W(\mathbf{r}) = 3/4\pi\sigma^3\Theta(\sigma - r)$, where $\Theta(x)$ is the Heaviside step function.

The use of the above averaging when constructing the fluid free energy functional with $F_{\text{Rep}}[\rho] \equiv F_{\text{hs}}^{\text{WDA}}[\rho]$ guarantees the direct correlation function obtained via the functional differentiation route would possess a step at the distance of one molecular diameter σ [49]. This, in turn, allows one to capture *qualitatively* the physics relevant to the excluded volume interactions between the fluid molecules (such as oscillations of density near walls). It is quite remarkable that the WDA functional based on equations (1.7), (1.9) and (1.10) allows one to uncover the freezing of a hard sphere fluid (where $F_{\text{in}} \equiv F_{\text{Rep}} \equiv F_{\text{hs}}^{\text{WDA}}$): this phenomenon is lost in an LDA treatment [38]. The main advantages of the Tarazona and Evans prescription are its relative computational simplicity, along with a qualitatively correct account of the excluded volume effects. In modern literature its use is restricted to works attempting to uncover the qualitatively new phenomena through, e.g., a full parametric study of the governing equations [3, 5, 61] or to check weather qualitative predictions stemming from macroscopic arguments still hold for nano-scale systems [62, 63]. Comparing the phenomenology obtained from WDA and LDA treatment of repulsions one can better understand the relative effect of attractive molecular interactions with respect to the repulsive interactions [7, 8].

²The reason given here for the inability of a DF theory with LDA for repulsions to describe near-wall structure in the fluid is “mathematical”. The “physical” reason is that the near-wall behaviour of the density is determined by the pair-correlation function of the fluid, which in any case is described incorrectly by an LDA hard sphere functional [43, 47].

In a later work [52] Tarazona developed a WDA functional for hard spheres, which reproduces (via a functional differentiation route) the three first terms of the virial expansion of the direct correlation function of a bulk hard sphere fluid following from the Percus-Yevick closure to the Ornstein-Zernike equation [14, 12]. The averaging expressed by (1.10) corresponds to the zero-order approximation of this more accurate WDA for hard spheres. Although the prescription outlined in [52] improves the quantitative agreement of DF theory with, e.g., simulation results, it comes at a price of a significantly increased computational complexity and also has a distinct ad hoc step, which involves eliminating one route of a quadratic equation from purely physical considerations. Nevertheless, the general strategy proposed by Tarazona in [52] found a fruitful application in constructing highly accurate attractive functionals.

Fundamental measure theory for hard spheres

The most influential approximation for $F_{\text{hs}}[\rho]$ has been proposed by Rosenfeld in the seminal paper [64] and termed the Fundamental Measure Theory (FMT). Some modifications of the original Rosenfeld's FMT are often used in modern literature to construct free energy functionals aimed at representing adsorption scenarios observed in simulations or experiments with real fluids (mostly in one-dimensional geometries, like a planar wall or a slit pore, due to high complexity of the governing equations), see, e.g., recent works [65, 66, 67]). There exists another active direction of research, mentioned earlier, which exploits certain ideas originally put forward by Rosenfeld in [64] and later developed by Tarazona and Rosenfeld in [68] for constructing free energy functionals for fluids with non-spherical constituent particles, e.g., references [28, 29, 30, 31, 32].

As was mentioned in [3], FMT prescriptions for $F_{\text{hs}}[\rho(\mathbf{r})]$ can be constructed by requiring that the hard sphere functional satisfies simultaneously a low density, or a low dimensional, limit together with an appropriate bulk thermodynamic condition, which can be given in the form of an equation of state [64, 69, 70]. The original FMT was constructed using the exact zero density limit of the hard sphere free energy functional and the scaled particle theory equation in the bulk, which is equivalent to the Percus-Yevick compressibility equation of state. A more accurate equation of state, namely that of Carnahan-Starling [35] has been incorporated into the FMT family of approximations for $F_{\text{hs}}[\rho(\mathbf{r})]$ by Tarazona in [71] for a single-component hard sphere fluid, and independently by Roth et al. in [69] for both a single-component fluid and an additive mixture of hard sphere fluids. A review of formalism and recent developments can be found in the recent paper by Roth [70] and the review by Tarazona et al. [47].

As discussed in reference [3], within the FMT proposed in [69] and nicknamed the White Bear version, which corresponds to the Carnahan-Starling equation of state in the bulk, the

expression for the hard sphere free energy functional is given in the form

$$F_{\text{hs}} = k_{\text{B}}T \int d\mathbf{r} \Phi(\{n_{\alpha}(\mathbf{r})\}), \quad (1.11)$$

where $\Phi(\{n_{\alpha}(\mathbf{r})\})$ is a function of the variables $n_{\alpha}(\mathbf{r})$ [64]:

$$\begin{aligned} \Phi(\{n_{\alpha}(\mathbf{r})\}) = & -n_0 \ln(1 - n_3) + \frac{n_1 n_2 - \mathbf{n}_1 \mathbf{n}_2}{1 - n_3} \\ & + (n_2^3 - 3n_2 \mathbf{n}_2 \mathbf{n}_2) \frac{n_3 + (1 - n_3)^2 \ln(1 - n_3)}{36\pi n_3^2 (1 - n_3)^2}. \end{aligned} \quad (1.12)$$

The weighted densities $n_{\alpha}(\mathbf{r})$, are obtained from the density, $\rho(\mathbf{r})$, by integrating with a corresponding weight:

$$n_{\alpha} = \int d\mathbf{r}' \rho(\mathbf{r} - \mathbf{r}') \omega_{\alpha}(\mathbf{r}'). \quad (1.13)$$

The weight functions are given by

$$\omega_0(\mathbf{r}) = \omega_2(\mathbf{r}) / \pi \sigma^2, \quad (1.14a)$$

$$\omega_1(\mathbf{r}) = \omega_2(\mathbf{r}) / 2\pi\sigma, \quad (1.14b)$$

$$\omega_2(\mathbf{r}) = \delta(\sigma/2 - r), \quad (1.14c)$$

$$\omega_3(\mathbf{r}) = \Theta(\sigma/2 - r), \quad (1.14d)$$

$$\boldsymbol{\omega}_1(\mathbf{r}) = \omega_2(\mathbf{r}) / 2\pi\sigma, \quad (1.14e)$$

$$\boldsymbol{\omega}_2(\mathbf{r}) = \delta(\sigma/2 - r) \mathbf{r}/r, \quad (1.14f)$$

where $\delta(\mathbf{r})$ is the Dirac's delta-function. The details on how an FMT functional can be implemented in various one-dimensional geometries can be found in the review paper by Roth [70].

A comparison of various approaches to the hard sphere functional illustrated by applications in the problems of wetting by a LJ fluid can be found in references [3, 72, 73]. In this work we will mainly use LDA and WDA prescriptions for $F_{\text{Rep}}[\rho]$ in the two-dimensional problems, however, in section 3.1.2 we will show by calculation that using an FMT functional is in fact excessive when one is interested in the qualitative phenomena, which are duly captured by the WDA and even an LDA functional in the range of vapour- and liquid-like bulk densities.

1.1.3 Attractive contribution to the free energy

Let us briefly discuss how one can construct the perturbative approximation (1.2) for the intrinsic free energy functional of a fluid consisting of identical isotropic particles with pairwise interactions given by $\varphi(\mathbf{r}_1, \mathbf{r}_2) \equiv \varphi(r_{12})$, where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. We assume that the fluid-

fluid potential can be split somehow into a reference part and a perturbation part: $\varphi(r_{12}) = \varphi_{\text{ref}}(r_{12}) + \varphi_{\text{pert}}(r_{12})$. Full details can be found in, e.g., the reviews by Evans in references [11, 12] or the seminal paper by Evans [21]. If the fluid particles interact with a pairwise potential $\varphi(r_{12})$, then the total potential energy of the fluid-fluid interactions for the fluid of N particles is given by:

$$U(\mathbf{r}_1, \mathbf{r}_2 \dots \mathbf{r}_N) \equiv \frac{1}{2} \sum_{i \neq j} \varphi(r_{ij}), \quad (1.15)$$

and the first-order functional derivative of the intrinsic free energy functional would generate the two-body density distribution:

$$\frac{\delta F_{\text{in}}[\rho(\mathbf{r})]}{\delta \varphi_{\text{Attr}}(\mathbf{r}_1, \mathbf{r}_2)} = \frac{1}{2} \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2). \quad (1.16)$$

The above equation (1.16) can be used to construct the perturbation DF approximation by considering a gradual “switching on” of the full interaction potential. First, select a path in the space of the pairwise potentials parametrised by the “charging” parameter $\alpha : 0 \leq \alpha \leq 1$ as follows

$$\varphi_{\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \varphi_{\text{ref}}(\mathbf{r}_1, \mathbf{r}_2) + \alpha \varphi_{\text{pert}}(\mathbf{r}_1, \mathbf{r}_2), \quad (1.17)$$

where the path invariance is guaranteed by the uniqueness of the functional $\Omega[\varphi]$. On functionally integrating equation (1.16) we obtain

$$F[\rho(\mathbf{r})] = F_{\text{ref}}[\rho(\mathbf{r})] + \frac{1}{2} \int_0^1 d\alpha \int d\mathbf{r}_1 \int d\mathbf{r}_2 \rho^{(2)}[\varphi_{\alpha}, \mathbf{r}_1, \mathbf{r}_2] \varphi_{\text{pert}}(\mathbf{r}_1, \mathbf{r}_2), \quad (1.18)$$

where F_{ref} is the free energy of the fluid with pairwise interaction potential $\varphi_{\text{ref}}(r_{12})$ and $\rho^{(2)}[\varphi_{\alpha}, \mathbf{r}_1, \mathbf{r}_2]$ is the two-body density of the fluid, where particles interact with the pairwise potential φ_{α} given by equation (1.17).³ Further approximations are required for $\rho^{(2)}[\varphi_{\alpha}, \mathbf{r}_1, \mathbf{r}_2]$. We will use in this work the simplest (and also the most popular in literature) Random Phase Approximation (RPA), which sets

$$\rho^{(2)}[\varphi_{\alpha}, \mathbf{r}_1, \mathbf{r}_2] = \rho(\mathbf{r}_1) \rho(\mathbf{r}_2). \quad (1.19)$$

In the case of simple atomic fluids the pairwise fluid-fluid potential can be conveniently split into the reference hard sphere part and the perturbative attractive part [15]: $\varphi = \varphi_{\text{hs}} + \varphi_{\text{Attr}}$, where φ_{hs} is given by equation (1.3) and the expression for φ_{Attr} requires specifying the intermolecular forces. Its choice is somewhat arbitrary and we will return to it further on. Using equations (1.18) and (1.19), we get the final expression for the intrinsic free energy of

³As noted in [21], we implicitly assumed the presence of an intermediate external potential whose field forces the density $\rho(\mathbf{r})$ to stay constant while the charging parameter is increased from 0 to 1. Mathematical details are investigated in references cited in [21].

the fluid:

$$F_{\text{in}}[\rho(\mathbf{r})] = F_{\text{hs}}[\rho(\mathbf{r})] + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \varphi_{\text{Attr}}(|\mathbf{r} - \mathbf{r}'|). \quad (1.20)$$

In order to understand the implication of RPA we take the second functional derivative of the intrinsic free energy functional (1.20) and obtain the direct correlation function [21]. With, e.g., the FMT approximation for $F_{\text{hs}}[\rho(\mathbf{r})]$ we would have in the limit of a uniform fluid:

$$\begin{aligned} c^{(2)}(r_{12}) &= -1/(k_{\text{B}}T) \frac{\delta^2 (F_{\text{in}}[\rho] - F_{\text{id}}[\rho])}{\delta \rho(\mathbf{r}_1) \delta \rho(\mathbf{r}_2)} \\ &\equiv c_{\text{PY}}^{(2)}(r_{12}) - 1/(k_{\text{B}}T) \varphi_{\text{Attr}}(r_{12}), \end{aligned} \quad (1.21)$$

where $c_{\text{PY}}^{(2)}(r)$ is the pair correlation function given by the Percus-Yevick closure to the uniform Ornstein-Zernike equation for the hard sphere fluid, see, e.g., reference [12] for details. Thus we see that the RPA perturbative functional (1.20) can correctly describe the packing effects caused by correlations due to repulsive forces and also captures the asymptotics of the pair-correlation function: $c^{(2)}(r_{12}) \sim 1/(k_{\text{B}}T) \varphi_{\text{Attr}}(r_{12})$ as $r_{12} \rightarrow \infty$.

Beyond RPA the two-body density can be approximated by the non-local expression containing only one-body densities:

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') \approx \rho(\mathbf{r}) \rho(\mathbf{r}') g([\rho], \mathbf{r}, \mathbf{r}'), \quad (1.22)$$

where $g([\rho], \mathbf{r}, \mathbf{r}')$, is the *pair correlation* function. In general it is non-local and has a functional dependence on the one-body density $\rho(\mathbf{r})$ in the bulk [20]. Its Fourier transform is called the *structure factor* and is directly measurable in fluids by light scattering techniques. This fact makes approximating $g([\rho], \mathbf{r}, \mathbf{r}')$ from assumptions about inter-particle potentials a very attractive subject for theoretical research. The general field is known as integral equation theories [74], and its main method is to create an approximate closure for the exact Ornstein-Zernike equation, which leads to a system of coupled integral equations, for the pair and direct correlation functions. Integral equation theories provide a very successful means of obtaining some parameters of bulk fluids, but unfortunately are unable to account for substrates. This shortcoming contributed to the motivation for creating the general DF theory in the late 1970's. The fact that the direct correlation function can be obtained via a functional differentiation route from the expression for the fluid free energy (see equation (1.21)) links closely the well developed subject of integral equation theories with a relatively newer subject of the DF theory.

One way in which modern DF theories (usually, the highly accurate ones, attempting to model particular experimental or simulation scenarios) make use of the results from integral equation theories is by aiming to “guess” prescriptions for F_{in} in (1.2), such that the direct

correlation function of a bulk fluid obtained from the DF approach via functional differentiation would resemble closely the (usually much more accurate) one obtained via a proper closure to the Ornstein-Zernike equation. This is typically achieved by constructing a WDA approximation in the spirit of earlier works by Tarazona and Evans [49, 52] discussed in the previous section, consider, e.g., references [54, 75, 76, 52]. With respect to using a WDA-type approximation in the attractive functional the perturbation theory route to the full free energy functional of the fluid $F_{\text{in}}[\rho]$ adds difficulty, because some correlations are accounted for in $F_{\text{Rep}}[\rho]$ (usually the short-ranged), and some in $F_{\text{Attr}}[\rho]$ (usually the long-ranged), so special care should be taken to avoid accounting for the same correlation effects twice.

In this work we are not modelling any particular experimental scenario, but aim to uncover new aspects of wetting phenomenology. We will follow a minimalistic approach and use well accepted approximations, which provide reliable qualitative description. In the range of vapour- and liquid-like bulk fluid densities such is given by the RPA functional (1.20), where we still need to provide the approximation for attractive interactions, which would yield an expression for $\varphi_{\text{Attr}}(\mathbf{r})$. Such general approach is quite popular in modern DF treatments of atomic fluids aimed at being general rather than precise, see, e.g., reviews [24, 11, 37, 27].

Lennard-Jones fluid

In atomic fluids like noble gases (Argon, Neon, Xenon, etc.) molecular interactions at long ranges are well approximated by London forces with a pairwise LJ potential [15]:

$$\varphi_{\varepsilon_0, \sigma_0}^{6-12}(r) = 4\varepsilon_0 \left[- \left(\frac{\sigma_0}{r} \right)^6 + \left(\frac{\sigma_0}{r} \right)^{12} \right], \quad (1.23)$$

where ε_0 and σ_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 (1.2) with the reference system being a fluid of purely repulsive hard spheres (1.3), often with a temperature-dependent diameter [77, 78]. The attractive perturbation is commonly expressed within the RPA for the attractive direct pair-correlation function (1.20). There exist two commonly used prescriptions for obtaining $\varphi_{\text{Attr}}(\mathbf{r})$ corresponding to the LJ potential (1.23). One is due to Weeks, Chandler and Anderson [79], the other is due to Barker and Henderson [78]. Both approaches have nearly equal status in modern DF literature [37] and lead to the same asymptotics of the attractive potential, which ultimately determines much of the physics of wetting [3, 7]. We will employ a slightly modified Barker and Henderson prescription. For numerical convenience we fix the molecular diameter of the reference hard sphere fluid and also set the low- r cutoff of the attractive tail to exactly one

hard sphere diameter:⁴

$$\varphi_{\text{Attr}}(r) = \begin{cases} 0, & r \leq \sigma \\ \varphi_{\epsilon, \sigma}^{6-12}, & r > \sigma \end{cases}, \quad (1.24)$$

where ϵ is an effective depth of the attractive potential well and σ is the diameter of the reference hard sphere fluid, see equation (1.23). The parameters of attractive potential σ and ϵ are commonly chosen as units of length and energy.

1.1.4 External contribution to the free energy

As is typical in the DF theories of wetting by fluids with vapour- and liquid-like bulk densities, we model the solid substrate as an inert spectator phase, accounting for its presence by an additive contribution to the total free energy functional (second term in equation (1.1)). A different model for the substrate, where it, in turn, can be affected by the fluid, has been adopted by Ustinov and Do in [19] for wetting in a cylinder.

In this work we consider a physically realistic case, where the fluid-substrate interactions are of the same nature as the fluid-fluid interactions, i.e., are governed at long distances by the pairwise LJ potential (1.23) with substrate-specific parameters $\epsilon_0 = \epsilon_w$, $\sigma_0 = \sigma_w$. At short distances the intermolecular potentials in general are very different from LJ [15, 80]. For fluid-fluid interactions this is accounted for by the perturbative DF approach which results in fluid-fluid potential being given by (1.24). In the case of the substrate one typically introduces a cutoff $H_0 \geq \sigma^{(i)}$ into the final expression obtained by integrating the LJ potential over the substrate volume [3]. Doing this has the added numerical benefit of avoiding the divergence of the external potential $V(\mathbf{r})$ at short distances from substrate walls, which otherwise leads to a super-exponential decay of the fluid density and requires special computational tricks to be resolved [3]. We discuss a zero cutoff in detail in section 3.1. Experimentally the cutoff H_0 can be controlled by coating the substrate with a layer of a foreign species [81].

Thus, in this work the total effective potential of the substrate acting on the fluid will be defined by integrating the LJ potential:

$$V(\mathbf{r}) = \rho_w \int_{\nu} d\mathbf{r}' \varphi_{\epsilon_w, \sigma_w}^{6-12}(|\mathbf{r} - \mathbf{r}'|), \quad (1.25)$$

where ρ_w is the effective density of the “substrate material” and ν is the volume occupied by the substrate, which includes the cutoff of the wall potential $\varphi_{\epsilon_w, \sigma_w}^{6-12}(r)$ at distance H_0 from the substrate wall. Note that there exist highly accurate ab initio models for the planar substrates of some alkali metals, [82, 83], which are often used in DF theories targeting quantitative description of experiments. The substrate potential (1.25), however, has in the

⁴The corrections introduced by using a temperature-dependent σ from [78] are marginal, so we fix it following the aforementioned minimalistic approach to the study of general wetting phenomenology. In section 1.1.5 we elaborate on the general limitations of the resulting governing equations.

case of a planar geometry the same asymptotic behaviour as the ab initio potentials, which makes it an adequate choice for qualitative investigations. Models for substrates similar to ours have been extensively used in older DF literature investigating wetting, most notably, in the seminal works of Ebner and Saam showing the existence of a first-order wetting transition on planar substrates [17, 84].

We consider three types of substrate geometry: a *planar wall* (the substrate fills a half-space and has a straight, planar border), a *slit pore* (two parallel planar walls separated by a finite distance), and a *capped capillary* (slit pore capped at one end by a planar wall). According to the theorem due to Mermin, see, e.g., reference [21], if a fluid is brought in contact with the first two types of substrates defined above, its one-body density would be one-dimensional (1D), while the third type of substrate would give rise to a two-dimensional (2D) density distribution. In the case of the planar wall coinciding with the $z - x$ plane, the expression for external potential of a homogeneous substrate can be *defined* as

$$V_0^{\text{wall}}(y) = \rho_w \int_{-\infty}^{\infty} dx' \int_{-\infty}^{\infty} dz' \int_{-\infty}^0 dy' \times \varphi_{\epsilon_w, \sigma_w}^{6-12} \left(\sqrt{x'^2 + (y - y')^2 + z'^2} \right), \quad (1.26)$$

where y is the distance in the lateral direction. Integrating allows us to define the power-law substrate potential for a coated planar wall:

$$V^{\text{wall}}(y) \equiv V_{\epsilon_w, \sigma_w}^{3-9}(H_0, y), \quad (1.27)$$

$$V_{\epsilon_w, \sigma_w}^{3-9}(H_0, y) = 4\pi\rho_w\epsilon_w\sigma_w^3 \left(-\frac{1}{6} \left(\frac{\sigma_w}{H_0 + y} \right)^3 + \frac{1}{45} \left(\frac{\sigma_w}{H_0 + y} \right)^9 \right), \quad (1.28)$$

where the cutoff $H_0 \geq 0$. If chosen to be non-zero H_0 prevents the divergence of $V_{\epsilon_w, \sigma_w}^{3-9}(H_0, y)$ as $y \rightarrow 0$. The case of an uncoated substrate is retrieved due to $V_0^{\text{wall}}(y) \equiv V_{\epsilon_w, \sigma_w}^{3-9}(H_0 = 0, y)$. In section 3.1 we will consider the implications of a zero and a finite cutoff.

The potential of the slit pore of width H , whose bottom wall coincides with the $z - x$ plane can be *defined* with the help of the planar wall as

$$V^{\text{slt}}(y) = V^{\text{wall}}(y) + V^{\text{wall}}(H - y). \quad (1.29)$$

The potential of the capped capillary can be *defined* by integrating the LJ potential (1.23)

over the external volume of a semi-infinite rectangular groove:⁵

$$V^{\text{cpd}}(x, y) = \rho_w \int_{-\infty}^{\infty} dz' \times \left(\int_{-\infty}^{\infty} dx' \times \left(\int_{-\infty}^{-H_0} dy' + \int_{H_0}^{+\infty} dy' \right) + \int_{-\infty}^{-H_0} dx' \int_{-H_0}^{H_0} dy' \right) \times \varphi_{\varepsilon_w, \sigma_w}^{6-12} \left(\sqrt{(x-x')^2 + (y-y')^2 + z'^2} \right). \quad (1.30)$$

We evaluate the above expression in part analytically, in part – numerically and will discuss in section 1.3.2, where we provide the governing equations.

1.1.5 Summary and comments

Approximations described above follow the generalized Van der Waals picture of atomic fluids, which is supported by existing observations [20, 14]. To summarise, in this thesis we will model fluids with long-ranged LJ (1.23) interactions using the grand free energy functional (1.1) based on the first-order perturbation theory expansion for the attractive part of the intrinsic free energy (1.2) and treating the substrate as an inert spectator phase. The reference system is the fluid of hard spheres and will be approximated either by LDA (1.8), WDA (1.9), (1.10) or White Bear FMT (1.11) – (1.14), which are all equivalent to using the Carnahan-Starling equation of state (1.5) in the bulk and correspond to an increasing accuracy in accounting for correlations. The perturbative attractive contribution to the free energy is expressed by the mean field functional (1.20) and is equivalent to the RPA for the bulk direct correlation function of a Van der Waals fluid. The split of attractive and repulsive LJ interactions follows the Barker-Henderson prescription (1.24), but the hard sphere diameter is fixed. The substrate exerts a long-ranged LJ potential on the fluid and is given by (1.27) – (1.30).

Such treatment is known 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, in order to get a quantitative agreement one must take special care. For example, the use of a hard sphere functional is not really optional if one wants to reproduce experimental or simulation results. Apart from the White Bear FMT discussed above, some authors use an equivalent, but formally different version due to Kierlik and Rosinberg [76] (e.g., [81, 85]). The RPA functional (1.20) captures the asymptotic tail of the “attractive” contribution to the direct correlation function of a uniform fluid, which suffices to capture the physics of wetting by liquid. In a more complete treatment, the hard sphere diameter, σ , 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 [86, 87, 88]. The attractive functional can go beyond RPA, which would require a non-local approximation for the pair correlation function. For example, there exist WDA approximations for the attractive

⁵One can imagine three semi-infinite chunks of identical material being brought together in a manner shown in figure 3.8.

functional, which provide it in the form similar to (1.9), with the analogues of $\psi(\bar{\rho})$ and the averaging procedure for $\bar{\rho}$ obtained using perturbation theory about a reference uniform Van der Waals fluid, e.g., [89], or by functional integration, starting from a reasonable analytic approximation to the bulk attractive direct correlation function [65, 90, 91]. The three-body attractive interactions can also contribute to the values of the observables, e.g., [92], which means that a term containing the three-body density and a corresponding (non-isotropic) interaction potential should be added to the expression (1.20). In approaches to wetting a highly accurate model for the substrate potential can use *ab initio* results [82, 83], and possibly account for the effect of the fluid upon the substrate, instead of modelling it as an inert phase [19].

Finally note that any DF approach is classical in the sense that fluctuations cannot be properly accounted for [11]. Any DF treatment breaks down in the approach to bulk criticality, where the correlation length becomes large and the behaviour of the fluid is dominated by long-ranged fluctuations. Note that there exists a square-gradient DF theory developed by Fisk and Widom [93], which can account for some effects resulting from the proximity to the bulk critical point. The functional used in this work is strictly mean-field, nevertheless, as we will show in section 3.3.1, it allows us to register a signature of critical behaviour in a confined fluid.

Arguably the main value of modern DF theories is, first, in their theoretical consistency, which allows one to use the inter-particle potentials as input and, by incrementally including finer effects, uncover the dominant physical processes contributing to the observed qualitative behaviour. Second, a detailed parametric investigation of governing equations allows one to find new phenomena, which may not yet be accessible experimentally or may not be anticipated. A historical example of the latter is provided, e.g., by the seminal work of Ebner and Saam [17] studying the first-order wall wetting. Finally, numerical investigations with the help of simple DF approximations can serve as guides to experimentalists and theoreticians (e.g., in the development of analytical approaches, like effective Hamiltonians).

1.2 Dynamic DF theories

The behaviour of non-equilibrated systems is much less understood than that of systems at equilibrium. A rigorous statistical theory for dynamic processes, which is able to account for molecular-level interactions, has not been developed yet. In large-scale systems one can get away with employing semi-phenomenological phase field models [94, 95]. However there is an active interest in modelling non-equilibrium systems by means of statistical mechanics. One way is provided by the DF formalism. In the absence of a rigorous result, it is generally agreed that if a statistical-mechanical system is not far from equilibrium [96], the expression for its free-energy functional $\Omega[\rho]$ (1.1) (with the corresponding approximation for $F_{\text{in}}[\rho]$) still holds

when a time-dependent one-body density, $\rho(\mathbf{r}, t)$, is substituted in place of its equilibrium counterpart $\rho(\mathbf{r})$. A detailed account of the dynamic DF formalism based on the above local equilibrium conjecture can be found in recent works [9, 97, 98, 99, 100, 101, 102].

Some successful applications of dynamic DF theories for Brownian particles, e.g., [9, 98, 103, 104, 105], where they seem to yield correct qualitative behaviour, suggest the applicability of dynamic DF approaches to diffusion problems. Several of the many recent attempts at developing dynamic DF theories include the works of Goddard et al. [9], where a model for relaxation in colloidal systems has been proposed, Rauscher [98], where advection has been incorporated into diffusive DF model, Marconi and Tarazona [103], where more inertial effects have been considered, Archer [100], where a model for atomic fluids including hydrodynamic interactions has been proposed. The general consensus in modern literature is that the DF formalism “crudely generalized” for dynamic systems (and we will employ this simplest specimen of dynamic DF theory) provides an adequate qualitative description of slow (diffusive) relaxation, while incorporating various viscous and hydrodynamic effects significantly complicates the resulting equations, but nevertheless seems to be the direction of the most active development of the modern dynamic DF theories [106, 107]. We proceed by outlining the two approaches which we will use to discuss some aspects of relaxational dynamics in section 3.4.

When a fluid is brought in contact with the substrate and the system is *isothermally* perturbed out of equilibrium, the first process contributing to the dynamics of its relaxation is a dissipative one, which can be described by the equation [94, 95, 8]:

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\zeta \frac{\delta \Omega[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r}, t)}, \quad (1.31)$$

where ζ determines the rate of relaxation to equilibrium.

The second mechanism contributing to the dynamics conserves mass and is associated with the diffusive flow. As follows from (1.1), for a system at equilibrium the chemical potential μ is constant. Out of equilibrium μ is both spatially- and time-dependent and its gradient can be viewed as an effective force acting on the fluid particles, and driving the system to equilibrium [3, 108, 21]. The flux of particles driven by this force is then given by $\mathbf{j}(\mathbf{r}, t) = -\gamma \rho(\mathbf{r}, t) \nabla \mu(\mathbf{r}, t)$, where we have introduced the positive mobility constant γ [108, 109], which is related to the diffusion coefficient, D , through $\gamma = D/k_B T$. The evolution of the fluid density is described by the continuity equation, namely $\partial \rho(\mathbf{r}, t) / \partial t = -\nabla \cdot \mathbf{j}(\mathbf{r}, t)$, which upon expressing $\mu(\mathbf{r}, t)$ with the help of (1.1) takes the form

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \gamma \nabla \cdot \left(\rho(\mathbf{r}, t) \nabla \left\{ \frac{\delta F_{\text{in}}[\rho(\mathbf{r}', t)]}{\delta \rho(\mathbf{r}, t)} + V(\mathbf{r}) \right\} \right), \quad (1.32)$$

otherwise known as the generalised diffusion equation [101, 96, 110, 111]. Quite notably, the equation (1.32) was postulated by Evans in the seminal work [21] on the applications of DF

theories to various problems in soft matter.

Adding the dissipative and the conservative contributions we can obtain the following equation for the time-dependent one-body density of the fluid:

$$\begin{aligned} \frac{\partial \rho(\mathbf{r}, t)}{\partial t} = & \gamma \nabla \left(\rho(\mathbf{r}, t) \nabla \left\{ \frac{\delta F_{\text{in}}[\rho(\mathbf{r}', \mathbf{t})]}{\delta \rho(\mathbf{r}, t)} + V(\mathbf{r}) \right\} \right) \\ & - \zeta \left(\frac{\delta F_{\text{in}}[\rho(\mathbf{r}', \mathbf{t})]}{\delta \rho(\mathbf{r}, t)} + V(\mathbf{r}) - \mu \right), \end{aligned} \quad (1.33)$$

where μ is the chemical potential attained by the system in the long time limit. A similar dynamic equation has been employed in the study of colloidal dewetting by Thiele et al. in [112]. We will consider several dynamic cases in section 3.4 and show that the rate at which the equilibrium state is attained by the system depends on the relative importance of dissipation to diffusion, which can be expressed by the ratio $\zeta \sigma^5 / \gamma$, see, e.g., the working equation (1.61) in the next section.

Note that the two models provided above have been known for a long time in phase field methodology and are otherwise referred to as model A (for the dissipative equation (1.31)) and model B (for the conservative equation (1.32)) of the general dynamic universality class [95, 94]. In this respect the DF theory offers a consistent “microscopic” way to approximate $\Omega[\rho]$ (and $F_{\text{in}}[\rho]$) starting from simple assumptions about fluid-fluid and fluid-substrate interactions. Furthermore, any stationary solution of equations (1.33), (1.31) or (1.32), $\rho(\mathbf{r}, t \rightarrow \infty)$, is equivalent to the one-body density, $\rho(\mathbf{r})$, minimizing the grand free energy (1.1). In this respect, turning to a dynamic formulation can be viewed as means to solving the problem of minimising $\Omega[\rho]$ in (1.1) [3].

1.3 Working equations

Here we provide equations for obtaining equilibrium and time-dependent fluid density profiles and for registering and studying the surface phase transitions. These equations will be used in section 2.1.7 as case studies for the proposed numerical methodology and in chapter 3 for the study of wetting in 1D and 2D substrates. Our main physical results [3, 5, 7, 8] are obtained using LDA and WDA prescriptions for $F_{\text{Rep}}[\rho]$ in (1.2). FMT is used in section 3.1.2 (in a 1D problem) for comparison between WDA and LDA, and in order to make the case that for the qualitative investigations of wetting by single-component atomic fluids the use of FMT may be excessive. Thus, the FMT functional (1.11) – (1.14) is of secondary importance for us and all working equations will be provided for the LDA (1.8) and WDA (1.9), (1.10) prescriptions for $F_{\text{Rep}}[\rho]$. Note that the working equations for 1D problems using an FMT repulsive functional are well known and can be found in, e.g., the reviews by Roth [70] and Tarazona et al. [47].

Both the LDA and WDA prescriptions for $F_{\text{Rep}}[\rho]$ can be written in the general form (1.9)

using a weight function $W(\mathbf{r})$:

$$W(\mathbf{r}) = \begin{cases} \frac{3}{4\pi\sigma^3} \Theta(\sigma - r) & \text{for WDA,} \\ \delta(\mathbf{r}) & \text{for LDA.} \end{cases} \quad (1.34)$$

1.3.1 Euler-Lagrange equation. Surface phase transitions.

When a substrate is brought in contact with a large reservoir containing fluid at some bulk chemical potential, μ , and temperature, T , and the system is equilibrated, the fluid density minimises the grand free energy functional $\Omega[\rho(\mathbf{r})]$ from (1.1):

$$\Omega[\rho(\mathbf{r})] = F_{\text{in}}[\rho(\mathbf{r})] + \int d\mathbf{r} \rho(\mathbf{r}) (V(\mathbf{r}) - \mu), \quad (1.35)$$

where using the approximations discussed in the previous chapter we can express the intrinsic free energy functional $F_{\text{in}}[\rho(\mathbf{r})]$ from (1.2) as

$$\begin{aligned} F_{\text{in}}[\rho(\mathbf{r})] = & k_{\text{B}}T \int d\mathbf{r} \rho(\mathbf{r}) (\ln \lambda^3 \rho(\mathbf{r}) - 1) + \int d\mathbf{r} \rho(\mathbf{r}) \psi(\bar{\rho}(\mathbf{r})) \\ & + \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \varphi_{\text{Attr}}(|\mathbf{r} - \mathbf{r}'|), \end{aligned} \quad (1.36)$$

where the first term is the ideal gas free energy, the second term is the repulsive free energy functional with $\psi(\rho)$ given by (1.7) and the averaged density, $\bar{\rho}(\mathbf{r})$, defined by (1.9) and (1.34), and the third term is the attractive free energy functional with $\varphi_{\text{Attr}}(r)$ given in (1.24), (1.23). The external potential $V(\mathbf{r})$ is given by either of the expressions in (1.27), (1.29) or (1.30) and defines the dimensionality of the fluid density $\rho(\mathbf{r})$. Integration in (1.35) and (1.36) is being carried out over the entire space occupied by the fluid.

In practice, in order to find the density, $\rho(\mathbf{r})$, one can either solve the Euler-Lagrange equation for the extrema of $\Omega[\rho]$ or use a dynamic formulation, e.g., the one given by equation (1.31), and go to sufficiently large times. We begin with the former, more conventional [37, 26] approach. The Euler-Lagrange equation for the minimization of $\Omega[\rho]$ in (1.35), (1.36) can be obtained by functional differentiation and has the following form

$$\begin{aligned} k_{\text{B}}T \ln \rho(\mathbf{r}) + \psi(\rho(\mathbf{r})) + \int d\mathbf{r}' \rho(\mathbf{r}') \psi'_{\rho}(\bar{\rho}(\mathbf{r}')) W(\mathbf{r} - \mathbf{r}') \\ + \int d\mathbf{r}' \rho(\mathbf{r}') \varphi_{\text{Attr}}(|\mathbf{r} - \mathbf{r}'|) + V(\mathbf{r}) - \mu = 0, \end{aligned} \quad (1.37)$$

where ψ'_{ρ} is the derivative of the configurational part of the hard sphere free energy (1.7) with respect to ρ . The first term is the entropic contribution, the second and third terms follow from the variation of the repulsive functional (1.9), the fourth term is from the variation of the attractive functional and the fifth term is the contribution to the constant chemical potential

due to the presence of the substrate.

Saturation

We will measure the values of chemical potential relative to that at the coexistence of bulk liquid and vapour (saturation). The density of the saturated vapour, ρ^{vap} , and liquid, ρ^{liq} , at a given T and the corresponding $\mu = \mu_{\text{sat}}(T)$ can be obtained in a standard way by considering the balance of chemical potentials ($\mu(\rho^{\text{vap}}) = \mu(\rho^{\text{liq}}) = \mu_{\text{sat}}$) and pressures ($P(\rho^{\text{vap}}) = P(\rho^{\text{liq}}) = P_{\text{sat}}$). The binodal can be obtained by setting $V(\mathbf{r}) \equiv 0$ and $\rho(\mathbf{r}) \equiv \rho = \text{const}$ in (1.35) and (1.37), and using the equilibrium thermodynamic relation $\Omega = -PV$:

$$\mu(\rho) = k_{\text{B}}T \ln \rho + \psi(\rho) + \rho\psi'_{\rho}(\rho) - \frac{32\pi}{9}\rho\sigma^3\varepsilon, \quad (1.38)$$

$$P(\rho) = P_{\text{hs}}(\rho) - \frac{16\pi}{9}\rho^2\sigma^3\varepsilon, \quad (1.39)$$

where ε and σ are the parameters of the attractive part of the fluid-fluid potential given in equations (1.23) and (1.24), and P_{hs} is the pressure of the hard sphere fluid given by the Carnahan-Starling equation (1.5). The last term in the $P(\rho)$ dependence is the integrated strength of the attractive potential (1.24). The coefficients before ρ and ρ^2 in the last terms of $\mu(\rho)$ and $P(\rho)$ respectively are specific to the Barker-Henderson split of the LJ potential. The bulk critical point of the model fluid (critical density, temperature and chemical potential) can be obtained from

$$\frac{\partial P(\rho)}{\partial \rho} = \frac{\partial^2 P(\rho)}{\partial \rho^2} = 0. \quad (1.40)$$

In this work we concern ourselves with wetting by liquid-like fluid phases, so the chemical potential will typically be taken at values below the bulk saturation, $\mu_{\text{sat}}(T)$. For some chosen value of the reservoir chemical potential, μ , a convenient T -invariant measure of its value is given by the *deviation* chemical potential $\Delta\mu$ defined for a given value of μ as:

$$\Delta\mu(T) = \mu - \mu_{\text{sat}}(T), \quad (1.41)$$

where for wetting by liquid-like phases one has $\Delta\mu \leq 0$.

System bulk and excess free energy

Far from the substrate walls the spatially distributed fluid density can become constant in one or more directions:

$$\lim_{r \rightarrow \infty} \rho(\mathbf{r}) = \rho_{\text{b}}(\tilde{\mathbf{r}}), \quad (1.42)$$

where the dimensionality of $\tilde{\mathbf{r}}$ is less than that of $\mathbf{r}$. For example, if the substrate forms a planar wall, $\rho(\mathbf{r}) \equiv \rho^{\text{wall}}(y)$, then far from it the density tends to the constant bulk value,

$\rho_b(\tilde{\mathbf{r}}) \equiv \rho_b = \text{const.}$ If the substrate forms a capped capillary,⁶ $\rho(\mathbf{r}) \equiv \rho^{\text{cpd}}(x, y)$, then the density far from the capping wall tends to that of a slit pore, $\rho_b(\tilde{\mathbf{r}}) \equiv \rho^{\text{slt}}(y)$. We will refer to this type of limits in general as the *system bulk* [7]. Note, that for the case of long-ranged fluid-fluid and fluid-substrate interactions the asymptotic behaviour of the fluid density in approaching the system bulk is affected by the parameters of attractive contributions of all interaction potentials and determines the mean-field critical exponents.⁷ We proceed to define the *excess* over bulk free energy as

$$\Omega^{\text{ex}}[\rho(\mathbf{r})] = \Omega[\rho(\mathbf{r})] - \Omega[\rho_b(\tilde{\mathbf{r}})], \quad (1.43)$$

and will use it extensively in the study of surface phase transitions. Note that the above definition is also applicable in the case of a free interface between two coexisting fluid phases.

The concept of excess free energy allows one to bridge the DF approach with, e.g., a macroscopic Young-Laplace-type description of interfaces in terms of surface tensions and contact angles. In this respect a DF theory arguably is as an *ab initio* approach, which yields surface tensions starting from assumptions about the inter-particle potentials. For example, in the case of a planar wall in contact with the saturated vapour, one can choose as ρ_b either of the values ρ^{vap} or ρ^{liq} . Then by definition of surface tension, e.g., book [113], and for the excess free energy taken per unit area, one would automatically get:

$$\sigma_{\text{wv}} = \Omega^{\text{ex}}[\rho(\mathbf{r})] \Big|_{\rho_b(\tilde{\mathbf{r}}) \equiv \rho^{\text{vap}}}, \quad \sigma_{\text{wl}} = \Omega^{\text{ex}}[\rho(\mathbf{r})] \Big|_{\rho_b(\tilde{\mathbf{r}}) \equiv \rho^{\text{liq}}}, \quad (1.44)$$

where σ_{wv} and σ_{wl} are the wall-vapour and wall-liquid surface tensions, respectively. Calculating the liquid-vapour surface tension, σ_{lv} , which is given analogously, by computing $\Omega^{\text{ex}}[\rho(\mathbf{r})]$ for a free interface, we can use the Young-Laplace equation to find the macroscopic contact angle at saturation, Θ :

$$\sigma_{\text{wv}} - \sigma_{\text{wl}} = \sigma_{\text{lv}} \cos \Theta. \quad (1.45)$$

Isotherms and surface phase coexistence

A single equilibrium density profile satisfying the Euler-Lagrange equation carries no information about the thermodynamic stability of the fluid state, since a particular solution to (1.37) might not minimise $\Omega[\rho(\mathbf{r})]$, but can correspond to, e.g., its saddle point in the phase space. In other words, finding a density profile by solving equation (1.37) does not guarantee, that the corresponding fluid state is physical. On the other hand, computing a family of solutions

⁶One can imagine three semi-infinite chunks of identical material being brought together in a manner shown in figure 3.8.

⁷In order to obtain the mean-field critical exponents one can do a sharp-kink [18] approximation for the density profile in the expression for the grand free energy functional (1.35), which will allow one to obtain the expression for the effective interface potential. The critical exponent is then determined by the minimum of the latter (see example in section 3.1). Formally the procedure is equivalent to determining the asymptotics of the density profile (see example in section 3.1.1).

parametrised by a thermodynamic field acting in the system (e.g., the chemical potential, μ) allows one to determine the stability of fluid configurations by finding the values of grand potential for each of the calculated density profiles. The resulting dependence of the fluid free energy on the thermodynamic field must be a concave function when the fluid is in a stable equilibrium [114]. Apart from answering the question about the thermodynamic stability of fluid states such an approach also allows us to register and study surface phase transitions.

In general the set of thermodynamic fields acting in confined microscopic systems typically includes the bulk fields (T and μ), the parameters of the interaction potentials (σ_w/σ , $\varepsilon_w/\varepsilon$, H_0/σ , where the parameters of fluid-fluid interactions are set as units), the parameters of geometry, e.g., H , in the case of a slit pore or a capped capillary. The excess free energy defined in (1.43) is, in general, a function of all the thermodynamic fields. It is also defined in such a way as to contain information about the effects specific only to the interfaces. In order to investigate the surface phase behaviour of the fluid one can fix all but one thermodynamic fields and study the behaviour of the characteristic level sets of Ω^{ex} . In our case a very convenient choice of such level set is an *isotherm*, $\Omega^{\text{ex}}(\mu)$, where all thermodynamic fields, but the chemical potential, are fixed. The thermodynamic density conjugate to μ is the Gibbs adsorption, Γ , related to $\Omega^{\text{ex}}(\mu)$ through the Gibbs equation [74]:

$$\Gamma = -\partial\Omega^{\text{ex}}/\partial\mu, \quad (1.46)$$

where the derivative is evaluated at a fixed value of T .

The difference $\Delta\Gamma \equiv \Gamma_2(\mu) - \Gamma_1(\mu)$, where Γ_1 and Γ_2 correspond to the coexisting fluid surface phases acts as a natural *order parameter* in the study of surface phase transitions in fluids, e.g., see references [18, 115]. A first-order transition is associated with a finite jump in $\Gamma(\mu)$, and a continuous transition – with its divergence. As mentioned above, for convenience, at any given value of T we will count the value of μ from bulk saturation, $\mu_{\text{sat}}(T)$, thus the *control parameter* is the deviation chemical potential, $\Delta\mu$, defined in (1.41). For the grand canonical ensemble in isothermal conditions there exists an exact sum rule, which relates adsorption to the fluid one-body density profile [116]:

$$\Gamma = \int d\mathbf{r} (\rho(\mathbf{r}) - \rho_b(\tilde{\mathbf{r}})), \quad (1.47)$$

where $\rho_b(\tilde{\mathbf{r}})$ is defined in (1.42) and integration is being carried out over the entire space occupied by the fluid.⁸ The above equation also suggests, that Γ can serve as a measure

⁸In cases, where the system bulk can exhibit a surface phase coexistence (e.g., in a capped capillary the associated slit pore can undergo prewetting) one should be careful to use the “right” coexisting phase as $\rho_b(\tilde{\mathbf{r}})$ in the region of metastability, and so one needs to keep track of the system bulk separately for each value of μ and T . Our numerical approach is based on a non-equidistant grid and thus allows us to have the discretisation mesh going far into the system bulk (typically the last point is $\sim 10^3\sigma$ from the wall whose adsorption is being investigated, see section 2.1.6), so when we calculate $\rho(\mathbf{r})$, we obtain the system bulk as well, and need not take special caution when computing Γ using equation (1.47).

for the amount of “excess over bulk” fluid, adsorbed on the substrate surfaces, hence the commonly used term – adsorption.

By using the numerical technique of arc-length continuation, which allows us to treat μ in the Euler-Lagrange equation (1.37) as a parameter, we can systematically compute sets of points on isotherms $\Omega^{\text{ex}}(\Delta\mu)$ and/or $\Gamma(\Delta\mu)$ for any given fixed T .⁹ Each data point corresponds to a solution of (1.37), i.e., a density profile. Computing the free energy isotherms allows us to identify thermodynamically stable density profiles, as such correspond to the data points on the concave branches of $\Omega^{\text{ex}}(\Delta\mu)$. The surface phase behaviour of the system can be investigated with the help of isotherms. First-order and continuous transitions correspond to Van der Waals loops (intersections of concave branches of $\Omega^{\text{ex}}(\Delta\mu)$), and divergences of $\Gamma(\Delta\mu)$, respectively. For a given value of T the Gibbs adsorption equation (1.46) provides a test for the calculation of isotherms $\Omega^{\text{ex}}(\Delta\mu)$ and $\Gamma(\Delta\mu)$ using definitions (1.43) and (1.47).

Given a set of points on an isotherm exhibiting a Van der Waals loop, we find the exact location of a first-order surface phase transition in the $\Omega - \mu$ plane and the coexisting density profiles, $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$, by solving a system of three equations: the two Euler-Lagrange equations for $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ (1.37), supplemented with the condition of equal grand free energies:

$$\begin{aligned} \frac{\delta\Omega}{\delta\rho}\Big|_{\rho_1(\mathbf{r})} &= \frac{\delta\Omega}{\delta\rho}\Big|_{\rho_2(\mathbf{r})} = 0 \\ \Omega^{\text{ex}}[\rho_1(\mathbf{r})] - \Omega^{\text{ex}}[\rho_2(\mathbf{r})] &= 0. \end{aligned} \quad (1.48)$$

A single system can exhibit various mechanism of wetting, leading to the possibility of coexistence between more than two fluid surface phases, e.g., a three-phase coexistence inside a slit pore between vapour, thick prewetting film, and capillary-liquid [117], or a three-phase coexistence inside a capped capillary between vapour, a surface phase of corner drops (remnant of wedge prefilling) and a surface phase of capillary-liquid slab [8, 5]. The condition for a three-phase coexistence of fluid configurations with density distributions $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$, $\rho_3(\mathbf{r})$ can be expressed, similarly to the condition for the two-phase coexistence in (1.48), by the requirement for each of the density profiles to minimise the total free energy, equation (1.37), and for the excess free energies of all three fluid configurations to be equal:

$$\begin{aligned} \frac{\delta\Omega}{\delta\rho}\Big|_{\rho_1(\mathbf{r})} &= \frac{\delta\Omega}{\delta\rho}\Big|_{\rho_2(\mathbf{r})} = \frac{\delta\Omega}{\delta\rho}\Big|_{\rho_3(\mathbf{r})} = 0 \\ \Omega^{\text{ex}}[\rho_1(\mathbf{r})] &= \Omega^{\text{ex}}[\rho_2(\mathbf{r})] = \Omega^{\text{ex}}[\rho_3(\mathbf{r})]. \end{aligned} \quad (1.49)$$

In order to find the triple point, one has to solve the above system for the density profiles $\rho_1(\mathbf{r})$, $\rho_2(\mathbf{r})$, $\rho_3(\mathbf{r})$ of the coexisting fluid configurations, as well as for the chemical potential, μ_3 , and the temperature T_3 .

⁹Details of the continuation algorithm are given in section 2.2.1.

In practice solving the equations (1.48) and (1.49) is quite involved: the associated discretised problem is quite stiff and one requires a very “nice” initial guess to solve it. Moreover, the number of unknowns entering the discretised equation (1.48) is two times larger than that in the Euler-Lagrange equation for a single density profile, and for the three-phase equilibrium expressed by (1.49) it is three times larger, which poses a significant computational challenge, especially for 2D problems. We provide details of the efficient and robust method for solving these equations in chapter 2.

Note that by applying the arc-length continuation to the system of equations (1.48) and treating T as the continuation parameter one can obtain the entire surface phase diagram in the $T - \mu$ plane, which completely describes the thermodynamic surface behaviour of the system. Applying arc-length continuation to (1.49) would allow one to trace the triple-line in the space of, e.g., the parameters of external potential, ε_w or σ_w , and search numerically for a tri-critical point.

1.3.2 Dimensionless form

Our working equation for all equilibrium problems is the Euler-Lagrange equation (1.37). For the dynamic problems we use either the dissipative model (1.31) or the combination of conservative and dissipative models (1.33). When the density of the fluid is constant in one or more directions, the integration along those directions can be carried out analytically reducing the dimensionality of the working equations by simplifying the expressions for $\varphi_{\text{Attr}}(\mathbf{r})$ in (1.24) and $W(\mathbf{r})$ in (1.34). In this section we will provide these simplified expressions for 1D and 2D problems. We choose the system of units given in Table 1.1, which leads, e.g., to the value of the bulk critical temperature $T_c = 1.006$.

Table 1.1: Units for equations in dimensionless form.

Unit	Measure
Length	σ
Energy	ε
Temperature	ε/k_B
Time	$\gamma^{-1}\sigma^2/\varepsilon$

1D problem

For the 1D problem of a planar wall or a slit pore immersed in vapour we have in the equations (1.37), (1.31) and (1.33):

$$\begin{aligned} \mathbf{r} &\equiv y \cdot \mathbf{e}_y, \\ V(\mathbf{r}) &\equiv V^{\text{wall}}(y) \text{ or } V(\mathbf{r}) \equiv V^{\text{slt}}(y), \end{aligned} \tag{1.50}$$

where the expressions for the external potentials are defined in (1.27) and (1.29). The 1D external potentials $V^{\text{wall}}(y)$ or $V^{\text{slt}}(y)$ give rise to the 1D density distributions

$$\rho(\mathbf{r}) \equiv \rho^{\text{wall}}(y) \text{ or } \rho(\mathbf{r}) \equiv \rho^{\text{slt}}(y), \quad (1.51)$$

respectively. Note that in the case of a slit pore the substrate potential $V^{\text{slt}}(y)$ from (1.29) can be viewed as the limit of the expression in equation (1.30) as $x \rightarrow \infty$.

The attractive potential in 1D problems, $\varphi_{\text{Attr}}(y) \equiv \int dz \int dx \varphi_{\text{Attr}}(\sqrt{x^2 + y^2 + z^2})$, is obtained by integrating equation (1.24):

$$\varphi_{\text{Attr}}(y) = \begin{cases} -\frac{6\pi}{5}, & \text{if } |y| \leq 1, \\ 4\pi \left(\frac{1}{5y^{10}} - \frac{1}{2y^4} \right), & \text{if } |y| > 1. \end{cases} \quad (1.52)$$

The weight function, $W(y) \equiv \int dz \int dx W(x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y + z \cdot \mathbf{e}_z)$, is obtained by integrating equation (1.34):

$$W(y) = \begin{cases} \frac{3}{4} (1 - y^2) \Theta(1 - y) & \text{for WDA,} \\ \delta(y) & \text{for LDA.} \end{cases} \quad (1.53)$$

2D problem

For the 2D problem of a capped capillary immersed in vapour we have in the equations (1.37), (1.31) and (1.33):

$$\begin{aligned} \mathbf{r} &\equiv x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y, \\ V(\mathbf{r}) &\equiv V^{\text{cpd}}(x, y), \end{aligned} \quad (1.54)$$

where the expression for the 2D external potentials is defined in (1.30) and gives rise to the 2D density distributions

$$\rho(\mathbf{r}) \equiv \rho^{\text{cpd}}(x, y). \quad (1.55)$$

The 2D reduction of expressions for $\varphi_{\text{Attr}}(\mathbf{r})$ in (1.24), $W(\mathbf{r})$ in (1.34), as well as the expression for the external potential $V^{\text{cpd}}(x, y)$ in (1.30) can be done analytically: the integrals over z can be obtained in a closed form. Unfortunately, some of the resulting expressions are quite complicated and lead to significant rounding errors if used in machine computations.¹⁰ For that reason we use a hybrid approach and evaluate some of the z -integrals entering these expression numerically.

¹⁰A good example is the expression for the interaction potential $\varphi_{\text{Attr}}(r)$ inside of the unit circle ($r < 1$), which can be found in, e.g., appendix B of reference [44]. We compute that part numerically, see equation (1.59).

First, let us integrate out z in the pairwise LJ potential in equation (1.23), and formally define the expression bearing a sense of the pairwise potential and useful, e.g., in the case of fluid density being constant in one direction $\varphi_{\varepsilon_0, \sigma_0}^{5-11}(r) \equiv \int dz \varphi_{\varepsilon_0, \sigma_0}^{6-12}(\sqrt{x^2 + y^2 + z^2})$:

$$\varphi_{\varepsilon_0, \sigma_0}^{5-11}(r) = \frac{3\pi\varepsilon_0\sigma_0}{2} \left[-\left(\frac{\sigma_0}{r}\right)^5 + \frac{21}{32}\left(\frac{\sigma_0}{r}\right)^{11} \right], \quad (1.56)$$

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

Now the expression for $V^{\text{cpd}}(x, y)$ can be written in the form:

$$V^{\text{cpd}}(x, y) = V^{\text{slt}}(y) + V^{\text{cap}}(x, y), \quad (1.57)$$

where $V^{\text{slt}}(y)$ is the potential of a slit pore given in (1.29) and $V^{\text{cap}}(x, y)$ accounts for the contribution due to the capping wall and is determined by integrating the fluid-substrate potential, $\varphi_{\varepsilon_w, \sigma_w}^{5-11}$ in (1.56) over the complement of the groove to the slit:¹¹

$$V^{\text{cap}}(x, y) = \int_{-\infty}^{-H_0} dx' \int_{-H_0}^{H+H_0} dy' \varphi_{\varepsilon_w, \sigma_w}^{5-11}(|\mathbf{r} - \mathbf{r}'|), \quad (1.58)$$

Any further analytic simplification of equation (1.58) leads to high numerical instabilities in the resulting expression, so we have preferred to compute $V^{\text{cap}}(x, y)$ in equation (1.58) numerically, using the Clenshaw-Curtis quadrature [3]. More details are provided in sections 2.1.3 and 2.1.5.

Consider now the attractive potential, which is defined in the 2D problem as $\varphi_{\text{Attr}}(r) \equiv \int dz \varphi_{\text{Attr}}(\sqrt{x^2 + y^2 + z^2})$. Integrating out z -coordinate in equation (1.24), we obtain

$$\varphi_{\text{Attr}}(x, y) = \begin{cases} 2 \int_{\sqrt{1-r^2}}^{\infty} dz \varphi_{1,1}^{6-12}(\sqrt{r^2 + z^2}), & \text{if } r \leq 1, \\ \varphi_{1,1}^{5-11}(r), & \text{if } r > 1. \end{cases} \quad (1.59)$$

The integral in the above expression can be taken analytically, the expression is given in, e.g., reference [44], but is again numerically very unstable and leads to high rounding errors when used in actual calculations. So a numerical Clenshaw-Curtis quadrature is again preferable for us in this work.

Finally, the 2D weight function, $W(x, y) \equiv \int dz W(x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y + z \cdot \mathbf{e}_z)$, is obtained

¹¹See, e.g., chunk 2 in figure 3.8.

from equation (1.34):

$$W(x, y) = \begin{cases} \frac{3\pi}{2} (1 - r^2) \Theta(1 - r) & \text{for WDA,} \\ \delta(\mathbf{r}) & \text{for LDA.} \end{cases} \quad (1.60)$$

Note that although we have defined the 2D pairwise potential, $\varphi_{\varepsilon_0, \sigma_0}^{5-11}$ (equation (1.56)), 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 $\mathbf{e}_z$. The fluid dimensionality remains identical to the three-dimensional hard sphere fluid described by the Carnahan-Starling equation of state (see equation (1.7)).

Dynamics

In the dynamic 1D and 2D problems with the governing equations (1.31) and (1.33) we will evaluate the spatial derivatives of all terms containing the intrinsic chemical potential, $\delta F_{\text{in}}[\rho]/\delta\rho$, numerically. The expression for $\delta F_{\text{in}}[\rho]/\delta\rho$ is given by the first four terms of the Euler-Lagrange equation (1.37).

In the case of a hybrid conservative-dissipative model the chosen unit of time amounts to rescaling the parameters γ and ζ from equation (1.33). For example, in the case of a 1D ($\mathbf{r} = z \cdot \mathbf{e}_z$) adsorption on a planar wall with a zero cutoff we are left with the equation (1.33) in the following form:

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial z} \left(\rho \frac{\partial}{\partial z} \left\{ \frac{\delta F_{\text{in}}}{\delta \rho} + V_0^{\text{wall}}(z) \right\} \right) - \kappa \left(\frac{\delta F_{\text{in}}}{\delta \rho} + V_0^{\text{wall}}(z) - \mu \right), \quad (1.61)$$

where $\rho \equiv \rho(z, t)$ and $\kappa = \sigma^5 \zeta / \gamma$ measures the relative importance of the dissipative and conservative terms.

2 Numerical methodology

The numerical approaches to solving the DF equations can be categorised, first, with respect to the method for evaluating the non-local integrals and second, with respect to the iterative procedure used for solving the resulting system of non-linear algebraic equations. A concise review of approaches prevailing in the modern literature can be found in the paper by Frink et al. [26]. In the case of dynamic DF problems one also needs to discretise the evaluation of spatial derivatives, and the result is a system of ordinary differential equations. Solving that system, in turn, requires one to choose an optimal scheme for marching in time.

The convolution-like form of non-local terms entering the DF equations prompts many authors to advocate a fast Fourier transform for their evaluation. Recent works include, e.g., references [118, 70]. The shortcomings are, first, that such methods often require grid points to be equidistant, which is wasteful in the regions, where density is nearly constant (e.g., far from the substrate walls and/or two-phase interfaces). Second, Fourier-based methods on non-periodic domains are equivalent to a higher order Simpson quadrature and possess an algebraic convergence rate with the number of discretization points. Finally, such methods often impose non-physical periodicities of the solution. We believe that integration in real space using a specialised quadrature is optimal, because when properly implemented such method is superior in accuracy and possesses a higher convergence rate than an approach based on stepping into the Fourier space. An exponentially converging Gauss quadrature was proposed by Frink and Salinger in [119], although its use was restricted to parts of the calculation domain, while a simple trapezoid rule was used for other parts, severely limiting the potential benefits of the spectral approach.

With respect to an iterative procedure for the spatially discretised 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 tends to be highly numerically unstable, often requires ad hoc modifications of consecutive iterations [70, 52]. 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 hysteresis due to a first-order transition) further ad hoc modifications drawing heavily on one's physical intuition might be necessary to customise the numerical method for a particular system, e.g., [118].

In the present work we develop a novel numerical approach for discretizing the DF equations based on the spectral collocation method [120, 121]. We obtain the density profile in the form

of a global rational interpolant [1] and for the first time present a recipe for constructing an *integrating operator*. Its entries are fixed for a given collocation grid, and it can be computed outside of the iteration loop for solving the discretised equations. This tremendously speeds up the evaluation of non-local terms inside the loop (such as that of Newton method), which is then done by a simple matrix-vector product. All integrals are computed in real space by a highly accurate Clenshaw-Curtis quadrature [2, 122], which according to the latest literature on numerical analysis is an optimal choice for smooth differentiable functions with respect to convergence rates, accuracy and numerical stability [123].

The problem is discretised on a non-uniform grid of collocation points. In spectral methods the set of collocation points is fixed by one's choice of the basis functions (Chebyshev polynomials in our case), but as has recently been shown by Tee and Trefethen in [1] and by Hale and Trefethen in [2], transplanting the collocation grid by a conformal map maintains the spectral accuracy in evaluating derivatives and integrals. We use several conformal maps from a unitary circle in the complex plane to control the distribution of the collocation points on the physical domain. Concentrating the grid points in the regions of the domain, where the solution is expected to exhibit steep gradients (near two-phase interfaces), while using a coarser mesh in the regions of regularly behaving or near-constant density (e.g., inside liquid or vapour phases) allows us to significantly reduce the number of unknowns in the discretised equations. Our proposed methodology typically uses a fraction of the number of grid points required by conventional methods to achieve the same accuracy (according to existing literature). The true power of our approach is unleashed in the application to 2D DF computations.

We further completely automate the numerical solution of DF equations for systems with and without surface phase transitions using a Newton iteration procedure in conjunction with an arc-length continuation technique [3]. A similar approach was first employed for DF calculations by Salinger and Frink in [124]. In general, the arc-length continuation technique can be used to systematically obtain a set of solutions to an algebraic equation, when a parameter is varied. Within a DF framework one is typically interested in obtaining multiple density profiles corresponding to a variable thermodynamic field, such as the chemical potential or temperature, as it would allow one to register a surface phase transition in the fluid. By treating the parameter as an unknown and supplementing the Euler-Lagrange equation (1.37) of the DF theory with a geometric constraint in the Euclidean vector space of the discretised problem we can systematically obtain all consistent solution-parameter combinations. For example, choosing the chemical potential (or the bulk fluid density) as the variable parameter, allows us to compute adsorption and free-energy isotherms (including their metastable and unstable branches) [5, 3, 124], while choosing temperature as variable would produce an isochore [125]. One can also systematically investigate the effects of changing a parameter inside the fluid-fluid or fluid-substrate potentials.

We believe that the Newton solver (and not a self-consistent approach) or its variation is the optimal numerical strategy for solving 1D and 2D DF problems. First, the convergence of the algorithm is in practice quite fast (our implementations typically converge in 2 – 3 iterations for both 1D and 2D problems). Second, the Newton algorithm conveniently doubles as the corrector step of the arc-length continuation scheme, which in turn *ensures* the numerical stability of the Newton algorithm. However, unlike, e.g., the Picard self-consistent method, the Newton method requires to find and invert the Jacobian matrix of the discretised problem 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 DF problems [118, 26, 119], where the number of unknowns would be significantly larger.

To summarise, we propose a novel methodology for any type of equilibrium and dynamic 1D and 2D DF problems. It possesses an exponential convergence rate allowing one to use a moderate number of grid points. Along with solving the Euler-Lagrange equations one automatically gets information about thermodynamic stability of solutions, as well as the overall phase behaviour of the system. The method is applicable to any type of local or non-local functional and quite flexible to be adapted to a particular substrate geometry. Implementation for 1D problems, along with convergence tests and examples is discussed in the publication [3]. However, the true computational power of the method is fully unveiled by performing 2D DF calculations [5]. In the present chapter we describe our method, provide working recipes and extensive examples.

2.1 Spatial discretisation

2.1.1 Spectral philosophy

Let us briefly go over the main ideas behind spectral methods, which are increasingly used in modern literature for, e.g., solving partial differential equations [120]. First, let us suppose that we know a function $f(x)$ defined on a (finite or infinite) interval $x \in [a, b]$. If $f(x)$ is finite everywhere in $[a, b]$ and sufficiently smooth, then given an orthonormal set of basis functions $\{\varphi(x)\}$ defined on the same interval, it is (usually) possible to express $f(x)$ in the form

$$f(x) = \sum_{n=0}^{\infty} a_n \varphi_n(x), \quad (2.1)$$

where the constants $\{a_n\}_{n=0}^N$ are called the *spectral coefficients*. As can be seen from the above expression, they define the function $f(x)$ as a vector in a vector space spanned by the basis functions.¹ Due to orthogonality, the value of each coefficient can be obtained by taking

¹The phraseology here is deliberately vague, as any definitive statement would require specifying the particular basis set, as well as imposing particular constraints on $f(x)$, such as, e.g., square-integrability or analyticity.

an “inner product” with the corresponding basis function:

$$a_n = (f, \varphi_n) \equiv \int_a^b dx \, \omega(x) f(x) \varphi_n(x), \quad (2.2)$$

where $\omega(x)$ is a non-negative weight function, corresponding to the basis set $\{\varphi_n\}$. The choice of a particular basis set depends on the properties of the function $f(x)$ and the interval $[a, b]$. For example, for periodic functions one typically uses Fourier series, for non-periodic functions on finite domains the optimal choice is usually Chebyshev or Legendre polynomials. If $[a, b]$ is infinite in one direction, an optimal choice might be to use Laguerre polynomials or a Chebyshev basis of rational functions. While for domains infinite in both directions the basis can be Hermite polynomials or sinc functions [120]. The practical advantage of using an expansion like (2.1) comes from truncating it at some index N :

$$f(x) = \sum_{n=0}^N a_n \varphi_n(x) + E_N^{\text{trunc}}(x), \quad (2.3)$$

where $E_N^{\text{trunc}}(x)$ is the error due to truncation. With the right choice of the basis set $\{\varphi_n\}$ and if the function $f(x)$ is sufficiently smooth, the truncation error decays exponentially fast with N :

$$\max_{x \in [a, b]} |E_N^{\text{trunc}}(x)| = O(e^{-\kappa N}), \quad (2.4)$$

where κ is called the spectral convergence rate. We will assess the convergence rate numerically for the method which we will develop.

Let us now suppose that the function $f(x)$ is an unknown solution to an (e.g., differential or integral) equation. Then representing it in the form of truncated series as in (2.3) and substituting into the equation allows one to reformulate the latter as a minimization problem for finding the spectral coefficients $\{a_n\}_{n=0}^N$. Such is the foundation of many very popular Galerkin-type approaches to solving differential equations [120], including the methods of spectral elements and finite elements. An additional benefit of using a truncated spectral expansion (2.3) is that the obtained approximate solution is known analytically. This fact not only allows one to easily manipulate the obtained solution, e.g., compute its values at various points inside the domain $[a, b]$, integrate or differentiate it, but also opens the door for theoretical analysis of the problem (in the cases when N is small, typically $N < 10$). A very good example of the latter is the field of quantum chemistry, where the wave functions of various complicated molecules are usually expressed as truncated expansions of simpler atomic wave functions.

For most applications the values of N are quite large (e.g., the problems we consider here may require to use $N \lesssim 10^2$ for 1D problems and $N \lesssim 10^4$ for 2D problems), and a direct

evaluation of spectral coefficients by computing the integrals in (2.2) (or similar integrals) is neither computationally efficient, nor is it straightforward to implement. For that reason most modern applications employ the pseudo-spectral philosophy, where instead of spectral coefficients one solves for the unknown values of the function on a fixed set of interpolation or *collocation* points inside the domain $[a, b]$. The pseudo-spectral collocation methods are based on the following idea. Given a truncated expansion of a sufficiently smooth function up to the order N (see equation (2.3)) on the set of polynomial basis functions, one can use an N -point Gauss quadrature on the same basis set to evaluate the spectral coefficients in (2.2):

$$a_n = \sum_{n=0}^N W_n \omega(x_n) f(x_n) \varphi(x_n) + E_N^{\text{Gauss}} \equiv \tilde{a}_n + E_N^{\text{Gauss}}, \quad (2.5)$$

where $\{x_n\}_{n=0}^N$ and $\{W_n\}_{n=0}^N$ are the Gauss abscissas and integration weights, which are typically known for a given basis set, E_N^{Gauss} is the error of Gaussian quadrature and $\tilde{a}_n$ is the approximate spectral coefficient when the error term is dropped. (For polynomial basis sets there usually are two choices of $\{x_n\}_{n=0}^N$, one always being the roots of highest degree polynomial in the expansion (2.3). The weights are the integrals of Cardinal functions used in Lagrangian interpolation on the set $\{x_n\}_{n=0}^N$ and are also usually known. For detail see, e.g., the book [120]). For polynomial basis sets the error due to truncation of the full spectral series (2.1) is of the same order as that due to evaluation of a spectral coefficient by the Gauss quadrature on the same basis set [120]:

$$\max_{x \in [a, b]} |E_N^{\text{trunc}}(x)| \sim E_N^{\text{Gauss}}. \quad (2.6)$$

Now the *approximate* spectral coefficients $\{\tilde{a}_n\}$ can be calculated all at once by a matrix-vector product, which follows from dropping the error term in (2.5) and rearranging the terms:

$$\tilde{\mathbf{a}}^{(N)} = \hat{M} \mathbf{f}^{(N)}, \quad M_{i,j} = \omega(x_j) \varphi_i(x_j) W_j, \quad (2.7)$$

where $\tilde{\mathbf{a}}^{(N)} = (\tilde{a}_1, \dots, \tilde{a}_N)^T$ is the N -vector of the approximate spectral coefficients, and $\mathbf{f}^{(N)} = (f_1, \dots, f_N)^T$ is the vector of function values at the abscissas of the Gauss quadrature: $f_n = f(x_n)$. Although the equation (2.7) is an approximation to the coefficients defined in (2.2), it is of the same order of accuracy as the truncation of the full series, and thus possesses an *exponential accuracy* as N is increased. One might argue, that although for each coefficient the error is of the same order as the truncation error in the spectral series, when the approximate coefficients are used to assemble the expression (2.3), the overall error will be higher due to summation. Rigorous numerical analysis shows that an N -point pseudo-spectral method is at least of the same accuracy as the $(N - 1)$ -point spectral method [120]. From now on we will drop the tilde and denote by $\{a_n\}$ the approximate spectral coefficients computed

with the Gauss quadrature. The abscissas of the Gauss quadrature $\{x_n\}$ corresponding to the basis set $\{\varphi_n\}$ will be called collocation points.

The fact that truncation error is the same as the error due to Gaussian quadrature is the reason why pseudo-spectral collocation methods have nearly completely taken over from the classical Galerkin-type spectral methods in the modern literature. Expression (2.7) is a concept: *any* mathematical operation on the expansion (2.3) can be expressed by a constant grid-dependent operator acting on the discrete data $\mathbf{f}$. One can immediately see the benefits of matrix representation, such as the one in equation (2.7): for a given basis set $\{\varphi_n(x)\}$ we can fix the Gaussian abscissas and *precompute* the operator $\hat{M}$. Then we can find the spectral coefficients of *any* function by a simple and fast matrix-vector product. For example, solving a non-linear differential equation typically involves an iteration procedure (such as a Newton method), where on every i -th step one has to obtain the spectral representation (2.3) for the updated approximation $f^{(i)}(x)$ to the solution. Then expressing mathematical operations like interpolation and differentiation by constant matrix operators is the key optimisation step of an algorithm aimed at reducing the calculation time.

Modern research into the theory of spectral methods has two main directions. A more fundamental one is looking to increase the accuracy of function representation on a given basis set by, e.g., using variable transformations to transplant the collocation points $\{x_n\}$. The second, more applied direction is looking for efficient and fast algorithms to compute matrix operators, such as $\hat{M}$ in equation (2.7): complex problems often require mesh-refinements (e.g., tracking a shock-wave), and operators depend on the collocation points $\{x_n\}$, so sometimes one must calculate them inside loops, which ends up being time-consuming. A review of spectral methods and problems one for which they can be employed can be found in recent books [121, 120]. An application driven overview is in reference [126].

We summarise the main benefits of applying spectral methodology in the following list:

- If implemented correctly spectral methods possess exponential accuracy with the number of discretization points.
- The implementation is memory-minimizing: a moderate number of grid points usually suffices to get acceptable accuracy. The grid sizes are typically a fraction of those in algebraically converging methods (like finite differences).
- Numerical solution is, in principle, accessible in an analytic form.
- Mathematical operations (like differentiation) are performed on the approximate solution exactly, and can be implemented by fast matrix-vector products.

The price one pays for the above benefits is that there is little control over the distribution of the collocation points $\{x_n\}$. Although in the final computer code the matrices are generally a lot smaller than with other methods, they are full and do not have any pattern which one

could take advantage of. In contrast, e.g., finite difference methods lead to sparse, diagonal matrices. Finally, extra care should be taken to ensure the numerical stability of the method.

2.1.2 Global interpolant

We start with the orthonormal basis set of Chebyshev polynomials. There are several reasons why we choose this set. Unlike most of the other polynomial basis sets, the Gauss quadrature abscissas forming the collocation grid, $\{x_n\}_{n=0}^N$, are known exactly and apart from being an optimal choice for Gauss quadrature possess many additional useful features (see Appendix 3.4.2). In the literature on numerical analysis research into spectral methods based on Chebyshev polynomials is quite active, with many recent results providing a high level of control over the distribution of the collocation grid on the physical domain through variable transformations. Finally, the method is quite flexible and can be configured to semi-infinite and infinite domains, so various problems can be addressed within the same general framework. The Chebyshev polynomials, $T_n(x)_{n=0}^\infty$, are defined for an argument in the interval $[-1, 1]$ as

$$T_n(\cos x) = \cos nx. \quad (2.8)$$

For the conventional Chebyshev pseudo-spectral method there are two sets of $N + 1$ collocation points on $[-1, 1]$ to choose from. The first is given by the roots of $T_{N+1}(x)$ and is referred to as the *Chebyshev points of the first kind* [127]. The second set is given by the roots of the first derivative of $T_{N+2}(x)$ and is sometimes referred to as the *Chebyshev points of the second kind*, or *Gauss-Lobatto points* [126, 127]. This second set always includes the end points of the interval, which is convenient for imposing boundary conditions, and so we will use those collocation points referring to them simply as *Chebyshev points*:

$$x_k = \cos \frac{k\pi}{N}, \quad k = 0, \dots, N. \quad (2.9)$$

Note that the most straightforward way to distribute the collocation points onto a finite physical domain $[a, b]$ is to map them linearly:

$$z_k = g(x_k), \quad g(x) = x(b - a)/2 + (b + a)/2, \quad (2.10)$$

where we introduce the convention denoting the physical spatial variable by z and the collocation points on the physical domain by z_k , while the spatial variable on the domain $[-1, 1]$ will be denoted by x and the Chebyshev points will be denoted by x_k . The key element of applying the method to a particular problem will be to choose the right map $z = g(x)$ for transplanting the Chebyshev points onto the physical domain and we provide a dedicated section below (see section 2.1.6). For now we assume that the domain of the physical problem $[a, b]$ is finite and that the collocation points are obtained by the transformation (2.10).

As follows from the previous section, in an $(N + 1)$ -point discretization scheme any function $f(z)$ will *implicitly* be represented as an $(N + 1)$ -degree polynomial

$$f(z) \equiv f(g(x)) \approx P_{N+1}(x) = \sum_{n=0}^N a_n T_n(x), \quad (2.11)$$

with $\{a_n\}$ being the Chebyshev coefficients and the above approximate relation being exact at the collocation points $z_k = g(x_k)$:

$$f(z_k) = P_{N+1}(x_k). \quad (2.12)$$

All the explicit operations will be performed on the data vector $\mathbf{f} = (f_0, \dots, f_N)^T$, where $f_k = f(z_k) \equiv f(g(x_k))$. The key to doing that is by accessing an analytical expression for $P_{N+1}(x)$ when creating the operator matrices, like the one in equation (2.7) from the previous section.

Since $P_{N+1}(x)$ is a polynomial, which interpolates the data $\mathbf{f}$, it is known to be *unique* [121], and any other polynomial interpolating the same data would be equivalent to the one in equation (2.11). Consider the expression

$$R_{N+1}(z) = \frac{\sum_{k=0}^N{}' \frac{(-1)^k}{z - z_k} f_k}{\sum_{k=0}^N{}' \frac{(-1)^k}{z - z_k}}, \quad (2.13)$$

where the primes indicate that the first and last terms in the sums are to be multiplied by $1/2$. The above expression is the *barycentric* form of the polynomial interpolating the data $\{f_k\}$ at linearly transformed Chebyshev points z_k [127]. It has many remarkable features. In the appendix to this chapter we derive the barycentric formula for an arbitrary set of interpolation nodes $\{z_k\}$, discuss its numerical stability and implementation challenges. We also explain why the barycentric form is preferable over, e.g., the well known Lagrangian form of the interpolating polynomial.

Important for applications is to know whether one can substitute the (possibly unknown) dependence $f(z)$ with its interpolant $R_{N+1}(z)$ and thus only be required to find the values of $f(z)$ at the set of collocation points to construct the expression (2.13). The well established answer is given by the following rigorous result, which is known to hold for Chebyshev points $\{x_k\}$ and linearly transplanted Chebyshev points $z_k = g(x_k)$ [121]. When $f(g(x))$ can be analytically continued in the complex plane to a function analytic inside an ellipse with foci at points $1 + 0 \cdot i$ and $-1 + 0 \cdot i$, and axis of lengths $2L$ and $2l$, then the following error estimate

holds [121]:

$$\max_{x \in [-1, 1]} |f(g(x)) - R_{N+1}(g(x))| \leq C(L + l)^{-N}, \quad (2.14)$$

where C is a positive constant.

Recently Tee and Trefethen [1] have proved a significantly less restrictive theorem, which establishes the above inequality for a *conformal* (possessing a non-zero first derivative) map of the Chebyshev points. When the collocation points $\{z_k\}$ are *not* linearly transplanted Chebyshev points, but are obtained under a conformal transformation, say $z_k = g_0(x_k)$, the global interpolant $R_{N+1}(z)$ in (2.13) is no longer a polynomial, but defines a *rational* function (ratio of polynomials), which still interpolates the data with the error cap provided by (2.14).

The challenge in constructing a conformal map $g_0(x)$ to transplant the Chebyshev points $\{x_k\}$ onto the physical domain, where they will form the collocation points $\{z_k\}$, is to ensure that such map *enlarges* the ellipse of analyticity of the underlying function $f(z) \equiv f(g(x)) \equiv f(g_0(x))$ (where $x \in [-1, 1]$), so that the rate of convergence of $R_N(z)$ to $f(z)$ is higher for $f(g_0(x))$ than for $f(g(x))$, where a simple linear transformation $g(x)$ is given in (2.10).

2.1.3 Clenshaw-Curtis quadrature

Summarizing the previous section we note that when the collocation grid of $N + 1$ points $\{z_k\}$ ($k = 0, \dots, N$) on the physical domain $[a, b]$ is given by a linear transformation (2.10), the barycentric form of the global interpolant (2.13) is equivalent to the Chebyshev spectral series (2.11) truncated at $n = N + 1$. When the grid on physical domain is obtained from the Chebyshev points via a conformal map, the global interpolant (2.13) is no longer a polynomial, but nevertheless maintains spectral accuracy in representing the underlying function $f(z)$, provided that the right map has been used. We aim to construct a numerical method, where all explicit manipulations will be done with the discrete set of data points $\mathbf{f} = (f_0, \dots, f_N)^T$, which in this section we assume to be known. However, implicitly we will be operating with high-accuracy expansion (2.11) and/or the global interpolant (2.13).

First we show how one obtains the value of the integral of the underlying function $f(z)$ over the domain $[a, b]$. Making a variable change we get

$$\int_a^b dz f(z) = \int_{-1}^1 dx f(g(x)) g'(x), \quad (2.15)$$

where the prime indicates the derivative of the map $z = g(x)$ used to transplant the domain $[-1, 1]$ and the Chebyshev points $\{x_k\}$ onto the physical domain $[a, b]$, where they form the collocation points $\{z_k\}$. Since the function $f(g(x)) g'(x)$ is defined on $[-1, 1]$, and we know its values at $N + 1$ Chebyshev points (obviously, we assume the map $g(x)$ to be known), we can *approximate* it as the truncated expansion in Chebyshev polynomials as in (2.11),

and then integrate it *exactly*. All we need to do is to obtain the Chebyshev coefficients $\{a_n\}$ (where $n = 0, \dots, N$) using the $N + 1$ data points $\mathbf{f} = (f_1, \dots, f_N)^T$, and then integrate the Chebyshev polynomials $T_n(x)$ analytically over $[-1, 1]$. One is finally left with an expression in the form:

$$\int_a^b dz f(z) \approx \sum_{n=0}^N \omega_n g'(x_n) f_n, \quad (2.16)$$

where $\{\omega_n\} = a_n \int_{-1}^1 dx T_n(x)$ ($n = 0, \dots, N$) are the *Clenshaw-Curtis weights*, which are known for the set of $N + 1$ Chebyshev nodes $\{x_k\}$ [121, 126]. The Chebyshev coefficients $\{a_n\}$ can (in principle) be obtained from the data vector $\mathbf{f}$ using the expression (2.7), but there exists a very efficient algorithm based on the fast Fourier transform, which allows one to obtain them in $O(N \log N)$ operations [126]. Integration of the Chebyshev polynomials $T_n(x)$ can be done analytically, see, e.g. the book [121]. We do not provide the explicit formulas for the weights $\{\omega_n\}$ here, as the form optimised for computations is quite complicated and can be found (along with the derivation) in, e.g., the paper by Waldvogel [122]. In the form readily implemented as MATLABTM computer code the Clenshaw-Curtis weights $\{\omega_n\}$ can be found in, e.g., the paper by Hale and Trefethen [2], p. 943. We note again that the only approximation in the above expression (2.16) comes from using the truncated spectral series in place of the function $f(g(x))g'(x)$, the integration of the truncated series being exact.

The described strategy for evaluating the integral is known as the Clenshaw-Curtis quadrature, see, e.g., references [2, 123, 121, 122], and it integrates *exactly* a polynomial of degree $N + 1$ defined on $z \in [a, b]$ by its values at the $N + 1$ linearly transplanted Chebyshev collocation points. Another route to a high-accuracy integration is to use the Gauss quadrature, which exactly integrates a polynomial of degree $2(N + 1)$ by optimizing not only the nodes (this is what we did above implicitly, because Chebyshev points are an optimal set of nodes for polynomial interpolation, see any book on numerical analysis and, e.g., the books [120, 121]), but also the integration weights (in the above case those were fixed by the choice of Chebyshev polynomials as the basis set). However, the Clenshaw-Curtis quadrature is *in fact* optimal for our purposes. First, the work to compute the Gauss quadrature would be $O(N^2)$ operations (see, e.g., references [121, 2]), which is quite a lot more than the $O(N \log N)$, especially in problems with non-local integral terms, where quadratures *have to enter the loops* of Newton method. Second, the gain in accuracy due to the Gauss quadrature is in fact quite elusive, as has recently been shown by Trefethen in [123]. Moreover, the recently published theorem due to Hale and Trefethen [2] establishes the exponential convergence (with N) of the N -point Clenshaw-Curtis quadrature (2.16) for smooth functions $f(x)$, provided that the collocation points on the physical domain $g(x_k) \equiv z_k$ are obtained by transplanting the Chebyshev points, $\{x_k\}$, with the conformal map $g(x)$.

2.1.4 Differentiating operator

Analogously to the integration strategy described above, the derivative, $f'(z)$, of the function $f(z)$ can in turn be approximated by taking the derivative of the expansion (2.11). Doing so and then computing the values at the collocation points would allow us to represent $f'(z)$ by the $(N+1)$ -th partial sum of the Chebyshev spectral series as well. Such is the approach of traditional spectral collocation methods, see, e.g., the application-oriented review by Weideman and Reddy [126] and the book by Boyd [120]. The main restriction of such approach is that the collocation points on the physical domain, $\{z_k\}$, have to be linearly transplanted (2.10) from the Chebyshev points in order for the error estimate (2.14) to hold.

We will follow a slightly different pass, which will allow us to better control the distribution of the collocation points on the physical domain. The idea is to directly differentiate the barycentric form of the interpolant (2.13). If the collocation points, $\{z_k\}$, are obtained by linear transformation of the Chebyshev points, $\{x_k\}$, the traditional spectral approach is retrieved. However, when the physical collocation points are obtained by mapping the Chebyshev points conformally, we will effectively be differentiating the rational function given by (2.13), which is known to exponentially accurately represent the smooth target function $f(z)$ [1, 127]. As has been shown recently by Tee and Trefethen, in the case of conformal mapping the derivative of (2.13), $R'_{N+1}(z)$, converges exponentially fast (error estimate is similar to (2.14)) to the derivative of the target function, $f'(z)$. The first and higher order derivatives of $R_{N+1}(z)$ can be obtained analytically and then expressed in the form of matrix operators (e.g., $\hat{D}^{(1)}$ and $\hat{D}^{(2)}$ for first- and second-order derivatives) multiplying the data vector, $\mathbf{f}$ [127, 1]:

$$\begin{aligned} f'(z) &\approx R'_{N+1}(z) = \hat{D}^{(1)}\mathbf{f} \equiv \mathbf{f}', \\ f''(z) &\approx R''_{N+1}(z) = \hat{D}^{(2)}\mathbf{f} \equiv \mathbf{f}'', \end{aligned} \tag{2.17}$$

where the expressions for the entries of $\hat{D}^{(k)} \equiv \{D_{ij}^{(k)}\}$ for any set of points $\{z_k\}$ are given in, e.g., reference [1]. Note, that the differentiation matrix for higher derivatives can be computed by raising the matrix for first derivative to a required power, however the computation of a power of a full matrix requires $O(N^3)$ operations, whereas using a recursive algorithm from [1] gets the same result in $O(N^2)$ operations. The recursive algorithm also results in less rounding error when computing the higher-order differentiation matrices.

2.1.5 Integrating operator

One of the main advantages of the collocation formulation of the spectral methodology, which has made the use of spectral methods widespread for solving differential equations is the concept of the differentiation matrix (2.17). In the last twenty or so years the rapidly growing machine power has made the manipulation of large full matrices readily accessible, which, in

turn, has stimulated a widespread interest in highly accurate spectral collocation methods. One of the active directions of modern research is increasing the efficiency of algorithmisation of spectral methods based on various sets of basis functions. In this section we develop an algorithm, which allows us to formulate the computation of a non-local integral expression containing the target function $f(z)$ as a matrix-vector product with the grid-dependent (but otherwise constant) matrix operator acting on the data $\mathbf{f}$. While the prescription is general and is readily applicable to any non-local problem (e.g., an integral equation), we will keep DF applications in mind [3].

Generally in DF computations one is interested in evaluating convolution-like integrals on the subinterval of the physical domain. In the most general case one is given the physical domain $[a, b]$ and needs to evaluate the non-local function of the form:

$$I(z) = \int_{A(z)}^{B(z)} Q(z - z') \rho(z') dz', \quad (2.18)$$

where the integral kernel, $Q(z)$, and the integration limits $A(z)$, $B(z)$, where obviously $[A(z), B(z)] \subset [a, b]$, are known functions. Given the global interpolant (2.13) to $\rho(z)$ represented by the data $\boldsymbol{\rho} = (\rho_0 \dots \rho_N)^T$ at the collocation points $\{z_k\}$, we are looking to find the discrete approximation to $I(z)$ at the same set of points, $(I(z_0) \dots I(z_N))^T \approx \mathbf{I}$, with $k = 0, \dots, N$. Moreover, we are looking to express it as a linear operator acting on the data $\boldsymbol{\rho}$:

$$\mathbf{I} = \hat{J} \boldsymbol{\rho}, \quad (2.19)$$

where $\hat{J} = \{J_{kj}\}$ is an $(N+1) \times (N+1)$ matrix.

Computing all $\{I(z_k)\}$ is equivalent to performing $N+1$ integrations, one for each of the collocation points $\{z_k\}$. For every such integral we can make a change of variable by transplanting $[-1, 1]$ onto the domain of integration, $[A(z_k), B(z_k)]$, with a conformal map $h_k(z)$ and thus obtaining an *intermediate* collocation mesh, $\{y_{kq}\}$, where

$$y_{kq} = h_k(x_q), \quad q = 0 \dots M, \quad k = 1 \dots N, \quad (2.20)$$

with M being the number of Chebyshev collocation points, $\{x_i\}$, transplanted from $[-1, 1]$ onto $[A(z_k), B(z_k)]$. Then we can apply the Clenshaw-Curtis quadrature to evaluate each integral.

While there may exist many suitable candidates for the maps $h_k(x)$ used to come up with the intermediate collocation mesh, $\{y_{kq}\}$, it turns out that the simple linear function (2.10)

leads to the overall performance being equivalent to using more sophisticated alternatives:²

$$z = h_k(x) = \frac{B_k - A_k}{2}x + \frac{A_k + B_k}{2}, \quad (2.21)$$

where z is the integration variable in (2.18), $A_k = A(z_k)$ and $B_k = B(z_k)$. Obviously, the number of intermediate points, M , used to compute the integrals $I(z_k)$ cannot affect the final size of the matrix operator, J , and one is tempted to choose a high value for M . However, practice has shown that the convergence of the overall scheme does not improve significantly beyond $M > 2N$, so we generally choose $M = 2N$.

A crucial step to algorithmisation is obtaining $\rho(y_{kq})$. In general, given the main collocation grid $\{z_k\}$ with the data $\{\rho_k\}$ and an intermediate collocation grid $\{\tilde{z}_k\}$, we can obtain the corresponding intermediate data $\{\tilde{\rho}_k\}$ by expressing the rational interpolant in equation (2.13) in the operator form:

$$\begin{aligned} \tilde{\rho} &= \hat{M}\rho, \\ M_{ij} &= \left(\sum_{p=0}^N \frac{(-1)^p}{\tilde{z}_i - z_p} \right)^{-1} \frac{(-1)^j}{\tilde{z}_i - z_j}. \end{aligned} \quad (2.22)$$

Rearranging the indices we eventually arrive at the expression for the entries of the integrating operator, J_{ij} , which depend *only* on the main collocation grid, $\{z_k\}$ [3]:

$$J_{ij} = \begin{cases} J'_{ij}/2, & \text{for } j = 1 \text{ and } j = N \\ J'_{ij}, & \text{otherwise} \end{cases}, \quad (2.23)$$

with

$$\begin{aligned} J'_{ij} &= \frac{(B_i - A_i)(-1)^j}{2} \sum_{q=0}^M \frac{\tilde{w}_q Q(z_i - y_{iq})}{y_{iq} - z_j} \\ &\quad \times \left(\sum_{m=0}^N \frac{(-1)^m}{y_{iq} - z_m} \right)^{-1}, \end{aligned} \quad (2.24)$$

where $\{\tilde{w}_q\}$ are the Clenshaw-Curtis weights corresponding to M Chebyshev points giving rise to the intermediate mesh.

As an example, we demonstrate how the integrating operator given in equation (2.23) may be used to calculate the attractive contribution to the intrinsic chemical potential given by the fourth term in the Euler-Lagrange equation (1.37), where $\mathbf{r} \equiv z \cdot \mathbf{e}_z$ and the potential

²Note that we are discussing the map used to transplant Chebyshev points and ultimately evaluate each of the integrals, $I(z_k)$ from (2.18), and *not* the map used to transplant the Chebyshev points to the physical domain to form the collocation grid $\{z_i\}$.

$\varphi_{\text{Attr}}(z)$ is given by (1.52). For a case, when fluid is confined to a pore and its density varies on the interval $[0, L]$ we can split the integral to account for the three smooth branches of $\varphi_{\text{Attr}}(z)$ [3]:

$$\begin{aligned} \int_0^L \varphi_{\text{Attr}}(z - z') \rho(z') dz' &= \int_{\max(0, z-1)}^{z-1} \phi_{\text{out}}(z - z') \rho(z') dz' \\ &+ \phi_{\text{in}} \int_{\max(0, z-1)}^{\min(z+1, L)} \rho(z') dz' + \int_{\min(z+1, L)}^L \phi_{\text{out}}(z - z') \rho(z') dz', \end{aligned} \quad (2.25)$$

where ϕ_{in} and $\phi_{\text{out}}(z)$ denote the constant “inner” ($|z| \leq 1$) and the smoothly decaying “outer” ($|z| \geq 1$) branches of $\varphi_{\text{Attr}}(z)$ in equation (1.52), respectively. Thus, the integrating operator for the discrete version of (2.25) is essentially the sum of the three integration matrices constructed for each of its three constitutive terms, by using the general expression (2.23). In a similar manner any 1D convolution-type integral may be conveniently cast as a matrix operating on the discrete values of $\rho(z)$.

Extension to two dimensions

Consider a function $f(x, y)$ depending on two variables. We discretise the domain $[-1; 1] \times [-1; 1]$ with $N_x + 1$ Chebyshev points in x and $N_y + 1$ Chebyshev points in y , which we then map conformally onto the physical domain. The natural generalization of (2.13) gives for the 2D global interpolant:

$$R_{N+1}(x, y) = \frac{\sum_{i=0}^{N_x} \sum_{j=0}^{N_y} \frac{\omega_i^x}{x - x_i} f_{ij} \frac{\omega_j^y}{y - y_j}}{\sum_{i=0}^{N_x} \sum_{j=0}^{N_y} \frac{\omega_i^x \omega_j^y}{(x - x_i)(y - y_j)}}, \quad (2.26)$$

where the element f_{ij} of the matrix $\hat{f}_{N_x \times N_y}$ corresponds to data at the point (x_i, y_j) of the Chebyshev grid.

At the core of obtaining the integrating operator is the expression for the interpolating operator. In the 1D case it is given by (2.22). In the 2D case the generalisation is obtained as follows. Given the new collocation grid $\left\{ \{\tilde{x}_i\}_{i=0}^N; \{\tilde{y}_i\}_{i=0}^M \right\}$, non-intersecting with the base grid $\left\{ \{x_i\}_{i=0}^{N_x}; \{y_i\}_{i=0}^{N_y} \right\}$, we can find the data $\hat{f}_{N \times M}$ by a matrix product:

$$\hat{f} = \hat{M}_x \hat{f} \hat{M}_y, \quad (2.27)$$

$$\tilde{f}_{ij} = \sum_{p=0}^{N_x} \sum_{q=0}^{N_y} \frac{\frac{\omega_p^x}{\tilde{x}_i - x_p}}{\sum_{s=0}^{N_x} \frac{\omega_s^x}{\tilde{x}_i - x_s}} f_{pq} \frac{\frac{\omega_q^y}{\tilde{y}_j - y_q}}{\sum_{s=0}^{N_y} \frac{\omega_s^y}{\tilde{y}_j - y_s}}, \quad (2.28)$$

where the matrices $\hat{M}_x$ and $\hat{M}_y$ are the 1D interpolation operators (2.22) on the collocation grids $\{x_i\}_{i=0}^{N_x}$ and $\{y_i\}_{i=0}^{N_y}$ independently. The integrating operator is then easily implemented directly on a machine, using the steps described above for the 1D case. Even though the computations necessary to construct the integration matrices become rather involved, a significant advantage is that such calculations need to be done only once and the matrices can be stored and reused for other calculations in the same geometry, such as obtaining isotherms and surface phase diagrams. Moreover, the aforementioned exponential accuracy is even more important in a 2D geometry, as it allows one to obtain very accurate results with only a moderate number of grid points.

2.1.6 Collocation points on physical domain

The exponential accuracy (2.14) of an N -point discretisation scheme is preserved under *any* conformal transformation $z = g_0(x)$ of the domain $[-1, 1]$ containing N Chebyshev points $\{x_k\}$ (2.9) to the physical domain $[a, b]$, where they form the set of collocation points $\{z_k\}$. However, the rate of convergence with N depends on the size of the ellipse of analyticity of the underlying target function $f(z) \equiv f(g(x))$ (see expression for the error (2.14)). Therefore, the map should be chosen in such a way as to enlarge the ellipse of analyticity, thus increasing the accuracy of the N -point scheme. In practice this corresponds to selecting such a map $z = g_0(x)$ that the parts of the domain $[a, b]$ containing steep gradients of the target function $f(z)$ would contain sufficiently many collocation points, $\{z_k\}$. Note that the actual number of points is in practice much smaller than with non-spectral discretisation methods.

In our case the target function is the density, $\rho(z)$, and it is unknown. Hence, we use physical intuition to select a proper map which would position the collocation points densely in the region of *expected* steep gradients. One such region is near the substrate walls, where the density oscillates, due to repulsive excluded volume interactions between the fluid particles. Depending on the value of the temperature, the liquid-vapour interface may or may not require many collocation points to be resolved. Strictly speaking, each problem warrants an *a priori* consideration of which map to use to get the set of collocation points.

First consider a finite domain $[a, b]$, where $a, b < \infty$. The linear map (2.10) concentrates the collocation points very densely at the ends of the domain and is generally not a good choice. For example in DF problems like a slit pore the oscillations of the wall-fluid interface can extend deep into the volume of the pore and will not be properly described. For a finite domain a generally good choice is to use the truncated Taylor expansion for

$$g(x) = \frac{1}{\sin(x)}, \quad (2.29)$$

renormalised in such a way as to have $g(-1) = a$ and $g(1) = b$. The above transformation serves to counteract the high density of the Chebyshev points near the ends of $[-1, 1]$. Due

to the divergence of (2.29) at $z = \pm 1$, one has to use a low-order Taylor expansion. Such a map has been proposed by Hale and Trefethen in [2] and called the “sausage” map, because it transplants an ellipse with foci ± 1 in the complex plane to an oval-like domain. For example, truncating the Taylor expansion of (2.29) at the ninth order and renormalising to have $g(\pm 1) = \pm 1$, one gets [2]:

$$g_s(x) = \frac{1}{53089} (40320z + 6720z^3 + 3024z^5 + 1800z^7 + 1225z^9). \quad (2.30)$$

A transplantation to any finite physical domain is done by applying the composition of the above map with the linear map in (2.10). We have used the above map for discretising along y -axis the capped capillaries studied in chapter 3.

For very low temperatures, where the fluid develops delta-like solidification peaks, one can use a specialised map developed by Hale and Tee in [2], which transplants a unit circle in the complex plane to a rectangular domain with multiple vertical slits. In practice one has to prescribe a set of abscissas in $[-1, 1]$ and the corresponding set of densities for the collocation points, which will be concentrated around the abscissas. Given the number N of Chebyshev points $\{x_k\}$, one can use the algorithm proposed by Hale and Tee to solve for the transplanted points $\{\tilde{x}_k\}$, and then one can transplant them linearly onto the physical domain using (2.10). In our case the use of Clenshaw-Curtis quadrature requires us to also know the values of the first derivative of the map at each collocation point. Since the map is given *at* the set of Chebyshev points, the values of derivative can be obtained numerically with spectral accuracy using the differentiation operator (2.17). In this thesis we have no recourse to the map with multiple slits, but it was used by the author of the thesis to obtain the equilibrium and dynamic density distributions of hard rods in the collaborative project [9].

As an example of the kind of control that we have over the distribution of the collocation points, figures 2.1 and 2.2 show three sets of $N = 10$ and $N = 20$ collocation points illustrating the two maps discussed above. Open circles show Chebyshev points, grey filled circles show the collocation points transplanted with the sausage map (2.30) [1], filled black circles show the points transplanted using the map of Hale and Tee [2] with two abscissas located at -0.7 and 0.2 (designated by vertical lines). Although a casual consideration does not seem to reveal much difference between the Chebyshev points and the collocation points obtained using the sausage map, the depletion of Chebyshev points in the centre of the domain (with respect to the sausage collocation points) is quite significant. In the case of discretising a slit pore (and the capped capillary, along y -axis), using linearly transplanted Chebyshev points results in a very low convergence rate and requires about ten times larger values of N to resolve the density at temperatures above the bulk triple point, than it does when the sausage map (2.30) is used.

Consider now the case where the physical interval $[a, b]$ is possibly infinite in one direction.

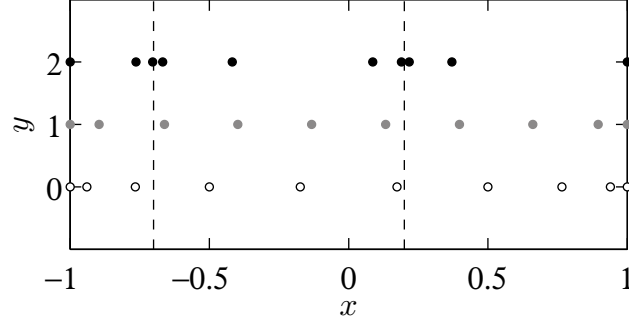


Figure 2.1: Three sets of $N = 10$ collocation points. Open circles: Chebyshev points; filled grey circles: collocation points obtained by transplanting the Chebyshev points with sausage map, (2.30) [1]; filled black circles: collocation points obtained by transplanting the Chebyshev points with Hale and Tee map [2] with two concentration abscissas at $x = -0.7$ and $x = 0.2$, designated by vertical lines.

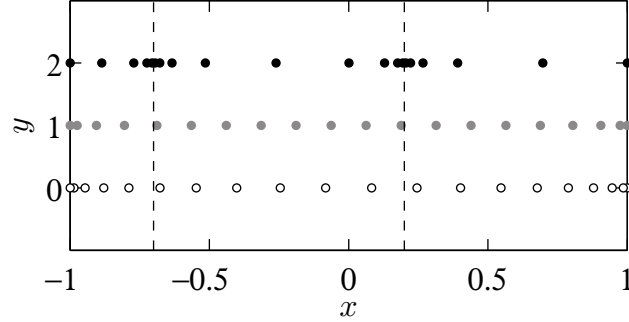


Figure 2.2: Same as figure 2.1 but for $N = 20$ points.

A typical problem requiring discretisation on such domain is fluid in contact with a single planar wall. In that case the steepest gradient of the density is expected in the vicinity of the minimum of $V^{\text{wall}}(z)$ (see expression in (1.27)), at $z_0 = (2/5)^{\frac{1}{6}} \sigma_w \approx 0.94\sigma_w$, where the density profile attains its global maximum. The density maximum is accompanied by a sequence of oscillations which become more pronounced for strongly attractive substrates and/or lower temperatures, inducing in the limit a freezing or a layering transition, when the fluid exhibits a solid-like, long-ranged ordering.

Therefore, in order to adequately capture the oscillations of the profile, the collocation grid should be dense in the near-wall region of the physical domain. For such cases we obtain the collocation points on the physical domain, $z \in [0, L]$ by mapping N Chebyshev points, $x \in [-1, 1]$, using the map

$$g_h(x) = \frac{p(1+x)}{1-x+2p/L}, \quad (2.31)$$

where p is an empirically chosen parameter, so that $1 < p \ll L$. With this transformation, about half of the Chebyshev points are mapped to the interval $[0, p]$; the other half are mapped

to $[p, L]$. This allows us to avoid the wasteful concentration of the collocation points in the bulk of the system, where the fluid density varies slowly. The parameter p is typically calibrated by a few trial calculations so that the near-wall oscillations of the density profile fall within $[0, p]$. However, the results of calculations are not sensitive to p , which only affects the convergence rate (the axis of the analyticity ellipse in (2.14)). It is important to emphasise that at the liquid-vapor interface $\rho(z)$ does not vary as steeply as the profile near the wall (at least in the range of vapour-like bulk densities) and the way the collocation points are distributed with (2.31) is usually sufficient to resolve the transition of $\rho(z)$ to the bulk vapour-like value.

One can also take the limit $L \rightarrow \infty$ in (2.31), essentially considering the whole physical domain $[0, \infty)$. In that case one would *automatically* include the boundary condition of contact with the system bulk, which in the case of a planar wall immersed in vapour is expressed by the bulk equation (1.38). We use the map (2.31) for the study of wetting on single planar wall and to discretise the capped capillary along the x -axis. In the latter case setting $L \rightarrow \infty$ allows us to automatically incorporate the boundary condition of contact with the associated slit pore (capillary bulk).

2.1.7 Convergence tests. Newton method

In this section we illustrate the proposed discretisation scheme by computing several density profiles and obtaining numerically the convergence rates expressed by the accuracy estimate in (2.14). After the equilibrium equation (1.37), is discretised, one is left with the set of N non-linear algebraic equations. While most authors use a self-consistent type of approach (like Picard iterations, see, e.g., a recent review by Roth [70]), we advocate using a predictor-corrector scheme, like the standard Newton algorithm, see, e.g., book [128]. Although it requires inverting the Jacobian matrix, Newton typically converges in very few iterations, it is very stable numerically, so long as one has access to the analytic expression for the Jacobian (and we do), and provided that the initial guess is not very bad (we will ensure the optimal initial guess by using continuation). A Picard method, on the other hand, typically requires hundreds of iterations for the same problems and tends to be numerically unstable, requiring one to have recourse to ad hoc ways of ensuring convergence (e.g., weighted averaging over several consecutive iterations to come up with an initial point for the next one [70]). However the main advantage of using a Newton scheme in DF problems comes from the natural way to incorporate the arc-length continuation algorithm (see next section), which serves to adjust the initial guess, thus making Newton-based numerical scheme decisively superior to a self-consistent one (at least for 1D and 2D DF computations, as the extremely large number of unknowns may shift optimality back to Picard-type scheme in three-dimensional problems, see the recent work by Knepley et al. [118]).

The implementation of non-local terms by matrix operators facilitates the calculation of the Jacobian whose entries are evaluated analytically, which is known to accelerate the con-

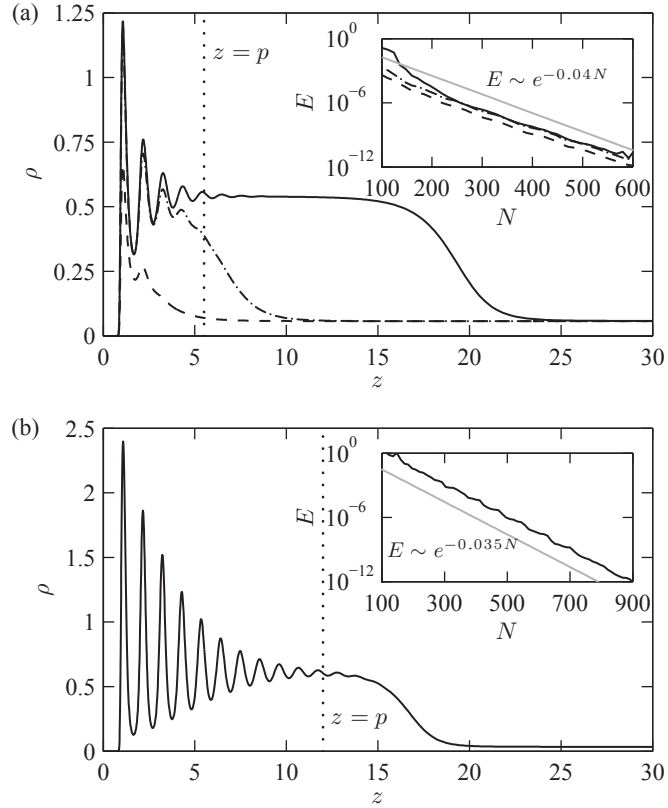


Figure 2.3: Demonstration of the exponential convergence for the numerical scheme. The profiles are calculated using WDA. (a) Dashed and dash-dotted curves are density profiles of fluid states coexisting during the prewetting transition ($\Delta\mu_0 = -0.008$), whereas the profile plotted by the solid line corresponds to a thick film ($\Delta\mu \approx -10^{-4}$) at the same temperature. $T = 0.85$, $\varepsilon_w = 0.4$, with $L \rightarrow \infty$ and $p = 5.5$, see (2.31). (b) Highly structured profile of a fluid adsorbed on a strongly attractive substrate at $T = 0.85T_{\text{crit}}$, $\Delta\mu \approx -10^{-3}$, $\varepsilon_w = 0.5$, with $L \rightarrow \infty$ and $p = 12$. The vertical dotted lines in (a) and (b) demarcate the $z = p$ line, dividing the computational domain so that half of the collocation points lie in $[0, p]$. The insets show the corresponding decay of the error, $E(N)$ (2.32), together with the corresponding convergence rates obtained by least-squares fitting (grey lines).

vergence of the Newton algorithm compared to the Jacobian obtained by finite differences [129]. In the computations presented below we used $N = 300$ grid points. For a domain of length, e.g., 80 molecular diameters (this is where 90% of collocation points were concentrated, because we have used the map (2.31) with $L \rightarrow \infty$) this corresponds to an average of less than 4 collocation points per molecular diameter, which is to be contrasted with the average of 20 mesh points per molecular diameter for non-spectral methods, e.g. references [72, 73, 47, 70]. The Newton scheme converged in less than 4 iterations (that seems to be the average number for all calculations, including 2D) for the chosen tolerance of 10^{-10} for the target function.

We present a few representative density profiles demonstrating the exponential convergence of the scheme [3]. Figure 2.3(a) shows the two coexisting density profiles, which correspond to a prewetting transition, as well as a density profile of a thicker film, whose bulk density is close to that of the saturated vapour. The near-wall oscillations are present due to the non-local repulsive part of the WDA free-energy functional, see section (1.3). The inset on figure 2.3(a) demonstrates the exponential rate of convergence with the number N of discretization points. Considering the profile calculated using $N = 1000$ collocation points as a reference one, we define the error, $E(N)$, for the profile calculation with $N < 1000$ as:

$$E(N) = \sqrt{\sum_{k=1}^{1000} [R_N(\chi_k) - R_{1000}(\chi_k)]^2}, \quad (2.32)$$

where $R_{N+1}(x)$ is defined in (2.13) and is evaluated at $\chi_k = L(k-1)/999$.

Figure 2.3(b) shows a profile for an extreme case of a fluid at low temperature whose chemical potential is close to coexistence, together with the error, $E(N)$ (2.32), plotted in the inset. The density profile is highly structured near the wall, but our calculation method still converges exponentially fast and is capable of achieving an accuracy of 10^{-5} with $N = 300$ grid points.

2.2 Continuation

Apart from obtaining the structure of the fluid at fixed values of parameters entering the Euler-Lagrange equation (1.37), it is often necessary to trace the change of some measure of a profile with one or more parameters (T , μ , strengths and ranges of potentials, etc.), thus obtaining a complete surface phase diagram. A common DF-related example is the calculation of an adsorption isotherm of vapour in contact with the wall as the chemical potential approaches bulk saturation. The measure of the profile is then adsorption, Γ , defined in equation (1.47), which is being traced with the parameter, μ . Moreover, given an isotherm, $\Gamma(\mu)$, one typically is interested in the value μ_0 , at which the surface phase transition occurs. When such value is found (e.g., by a Maxwell equal area construction), one can ask about how it would change with the temperature, or any of the other parameters entering the initial equations for the fluid density. Simply changing the parameter in the equation and then running it through the numerical solver does not always work, since, e.g., there can be several solutions at a given value of the parameter (metastable states) or no solutions at all. The first case is realised anywhere between the spinodals of a hysteresis-type isotherm, while the second one is exactly the case of the spinodal. Thus, many authors resort to ad hoc techniques. In the case of an adsorption isotherm one can be incrementing the value of Γ , rather than μ along the unstable parts of the isotherm between the spinodals and solving a constrained Euler-Lagrange equation, or solving along $\mu \rightarrow \mu_{\text{coex}}$ until the first spinodal,

and then $\mu_{\text{coex}}^- = \mu \rightarrow 0$ until the the second spinodal [72, 73]. Both methods require control during execution, as well as being problem-specific.

As we will see, the problem of tracing the surface phase transition is equivalent to the one of tracing the isotherm, but is formulated in a different function space. The arc-length continuation, which was first introduced into DF calculations by Frink and Salinger [124] also allows one to find exactly and trace spinodals, triple points and even critical points. All this can be done in a regular, systematic way requiring no control during execution, as well as no additional customisation for different problems. For example, in this work tracing the capillary condensation curves and the surface phase diagrams presented in section 3 was done by the same algorithm and virtually using the same machine code as tracing an adsorption isotherm. Furthermore, one can carry out the analysis of thermodynamic stability of a given fluid configuration by computing a set of profiles and analysing the convexity of the free energy as a function of the continuation parameter. We will be using this approach extensively in chapter 3.

Finally, the use of arc-length continuation technique in many cases allows one to obtain the density profile at the parameter values of interest. In the example with the planar liquid adsorption, it is obvious that far from the two-phase coexistence (at large negative values of $\Delta\mu$) the density profile is almost a straight line, having everywhere (except in a tiny near-wall region) the value of the bulk vapour density. Any kind of iterative scheme would easily yield a solution to the Euler-Lagrange equation (1.37) using constant bulk density as the initial guess. However, as saturation is approached the profile gains oscillatory structure near the wall, also forming a plateau at the value of saturated liquid density, while decaying to the bulk vapour density further away from the wall. An iterative scheme would require a very good initial guess to converge to the solution in that case. Attempting to find such a profile directly many authors resort to ad hoc techniques mixing different iterations, e.g., references [70, 52], or even simplifying the problem by looking for the solution in the form of an analytic function defined by a set of parameters, e.g., seminal works [17, 84] and sometimes the sharp-kink approximation [18].³ On the other hand, using the continuation technique one can simply continue the solution obtained far from saturation along the chemical potential, thus guaranteeing the best possible initial guess for the iterative procedure on each successive continuation step. If only the highly structured density profile at some given value $\mu_1 \sim \mu_{\text{sat}}$ is required, the continuation is terminated in the vicinity of $\mu \approx \mu_1$, then the resulting solution is used as an initial guess at $\mu = \mu_1$. Thus, the continuation technique also offers a compromise to simplifying the physical problem or controlling meticulously each iteration step and relying on physical intuition. That compromise has the appealing form of a systematic approach, completely automated and not requiring the attention of the user during execution.

³Although the importance and value of the sharp-kink approximation is in yielding analytic results from the DF approach.

2.2.1 Formalism

Below we provide the geometric considerations underlying the numerical technique for obtaining a set of solutions to problems with a free parameter [3]. The rigorous mathematical details of the methodology are outlined in the books by Krauskopf [130] and Allgower [128]. Some aspects of implementation can be found in the manual [4]. The technique is general, and applicable to any set of discretised equations. The notation used throughout this section is independent of the notation outside of it.

A DF approach comes down to an integral equation for the density. The parameter could be, e.g., the chemical potential, μ . After the governing equation (1.37) is discretised in space with an N -point scheme, it becomes an algebraic equation of the form $\mathbf{F}(\mathbf{x}) = \mathbf{0}$. Here the vector-valued function $\mathbf{F} : \mathbb{R}^{N+1} \rightarrow \mathbb{R}^N$ represents the discretised equation, while the elements of vector $\mathbf{x} \in \mathbb{R}^{N+1}$, $\mathbf{x} = [\mathbf{y}, \mu]$ contain the discretised solution, $\mathbf{y} \in \mathbb{R}^N$, as well as the corresponding value of the parameter, μ , which for now we assume being fixed. We also assume that we can solve the algebraic equation at some value of parameter, so that we have a starting point $\mathbf{x}_0$ in the $(N + 1)$ -dimensional space: $\mathbf{F}(\mathbf{x}_0) = \mathbf{0}$. Now we want to find all possible vectors $\mathbf{x} = [\mathbf{y}, \mu]$, consistent with the equation, by essentially treating μ as an unknown. The N -dimensional vector-function $\mathbf{F}(\mathbf{x}) \equiv [F_1(\mathbf{x}), \dots, F_N(\mathbf{x})]$ has to be supplemented with an additional component $F_{N+1}(\mathbf{x})$, such that $[F_1(\mathbf{x}), \dots, F_{N+1}(\mathbf{x})] = \mathbf{0}$ would form a set of $N + 1$ equations for the same number of the unknowns.

To derive that additional constraint let us consider the problem in geometric terms. In the space $\mathbb{R}^{N+1}$ each component $F_i(\mathbf{x}) = 0$ forms a hyper-surface. The locus of N such hyper-surfaces intersecting in $\mathbb{R}^{N+1}$ (the number of hyper-surfaces is one less than the number of dimensions) forms a $(N + 1)$ -dimensional space curve. Given the point $\mathbf{x}_0 \equiv [\mathbf{y}_0, \mu_0]$ on that curve, we are looking to parametrise it in the form $\mathbf{x}(l)$, or, equivalently, to find a systematic way of obtaining a sequence of its points in $\mathbb{R}^{N+1}$. Note that when the parameter, μ , is fixed at its initial value μ_0 , the equation $\mathbf{F}(\mathbf{y}, \mu_0) = \mathbf{0}$ can be viewed as the intersection of N hyper-surfaces in $\mathbb{R}^N$ (the number of hyper-surfaces is equal to the number of dimensions), with its locus being a single point – the solution $\mathbf{y} \in \mathbb{R}^N$.

The vector $\boldsymbol{\tau}_0$ tangent to the curve $\mathbf{x}(l)$ at the point $\mathbf{x}_0$ spans the null-space of the Jacobian matrix of dimensions $N \times (N + 1)$ evaluated at the point $\mathbf{x}_0$, $F_x(\mathbf{x}_0) = \partial \mathbf{F} / \partial \mathbf{x}|_{\mathbf{x}_0}$. In order to obtain the next point on the curve $\mathbf{x}(l)$, we use a predictor-corrector scheme, where we first displace the starting point by a distance ds along the tangent (the step of the predictor):

$$\mathbf{X}^0 = \mathbf{x}_0 + ds \boldsymbol{\tau}_0. \quad (2.33)$$

Second, we apply the Newton method to the following set of $N + 1$ equations to solve for $\mathbf{x}$

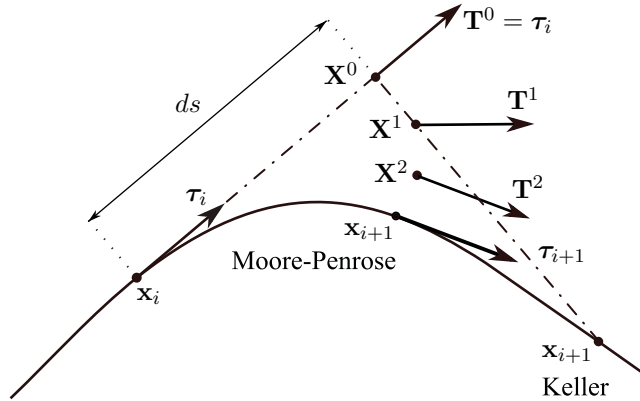


Figure 2.4: Schematic representation of the Moore-Penrose and Keller continuation algorithms [3, 4].

(the step of the corrector):

$$\mathbf{F}(\mathbf{x}) = \mathbf{0}, \quad (2.34a)$$

$$F_{N+1}(\mathbf{x}) \equiv (\mathbf{x} - \mathbf{X}^0) \cdot \boldsymbol{\tau}^* = 0, \quad (2.34b)$$

where the dot denotes the inner product, and the star denotes a transposed vector. The superscript 0 marks the 0-th Newton iteration step.

Geometrically the above equations correspond to the problem in $\mathbb{R}^{N+1}$ of finding the intersection of the curve defined by N intersecting hypersurfaces ($\mathbf{F}(\mathbf{x}) = 0$) with the hyperplane defined by its normal vector, $\boldsymbol{\tau}$, and the starting point $\mathbf{X}^0$.

The choice $\boldsymbol{\tau} = \boldsymbol{\tau}_0$ in equation (2.34b), followed by Newton iterations to find $\mathbf{x}$ corresponds to the so-called *Keller arclength continuation method* [130]. On completion of the corrector step, when the subsequent point $\mathbf{x} = \mathbf{x}_1$ on the curve is obtained, the new tangent vector $\boldsymbol{\tau}_1$ has to be found as the vector spanning the null space of $F_x(\mathbf{x}_1)$.

There is a slightly different method developed originally for systems of differential equations, the so-called *Moore-Penrose arc-length continuation* algorithm [4], where the vector $\boldsymbol{\tau}$ in equation (2.34b) is defined as the tangent vector to the curve $\mathbf{x}(l)$ at the subsequent point $\mathbf{x}$, rather than the starting point. Geometrically such choice of $\boldsymbol{\tau}$ corresponds to the requirement for $\mathbf{x}$ to be the closest point on the curve $\mathbf{x}(l)$ to $\mathbf{X}^0$. Unlike the Keller scheme, one has to be solving simultaneously for $\boldsymbol{\tau}$, as well as for $\mathbf{x}$, but that extra work is comparable to the work required to find the null space of the Jacobian in the Keller method. The advantage of using Moore-Penrose over Keller is that the estimate obtained for $\boldsymbol{\tau}$ is expected to be more accurate. The convergence of both methods is illustrated schematically in figure 2.4 for the process of finding the point $\mathbf{x}_{i+1}$ starting from $\mathbf{x}_i$.

Below we provide the Newton algorithm for Moore-Penrose continuation, i.e., for solving equations (2.34) for $\{\mathbf{x}, \boldsymbol{\tau}\}$, starting with $\{\mathbf{X}^0, \mathbf{T}^0\}$, and iterating over $\{\mathbf{X}^k, \mathbf{T}^k\}$ until the

norm of the right hand side in equations (2.34) becomes less than the required tolerance: [4, 3]

$$\mathbf{X}^{k+1} = \mathbf{X}^k - H_{\mathbf{x}}^{-1}(\mathbf{X}^k, \mathbf{T}^k) H(\mathbf{X}^k, \mathbf{T}^k), \quad (2.35)$$

$$\mathbf{T}^{k+1} = \mathbf{T}^k - H_{\mathbf{x}}^{-1}(\mathbf{X}^k, \mathbf{T}^k) R(\mathbf{X}^k, \mathbf{T}^k), \quad (2.36)$$

where

$$H(\mathbf{X}, \mathbf{V}) = \begin{pmatrix} F(\mathbf{X}) \\ 0 \end{pmatrix}, \quad (2.37)$$

$$H_{\mathbf{x}}(\mathbf{X}, \mathbf{T}) = \begin{pmatrix} F_{\mathbf{x}}(\mathbf{X}) \\ \mathbf{T}^* \end{pmatrix}, \quad (2.38)$$

$$R(\mathbf{X}, \mathbf{T}) = \begin{pmatrix} F_{\mathbf{x}}(\mathbf{X}) \mathbf{T} \\ 0 \end{pmatrix}. \quad (2.39)$$

All the isotherms and phase diagrams presented in this work have been obtained using the arc-length technique described in this section. Extensive examples on the application of the methodology developed in this chapter are provided in chapter 3, including the practical recipes for calculating the wetting isotherms (section 3.2.1) and full surface phase diagrams (section 3.2.2).

Let us provide here a short example illustrating the application of the numerical continuation technique. Consider a substrate, which in three dimensions forms a square channel, infinite along z . The temperature is fixed at $T = 0.7$, the values of the substrate parameters for the potential defined in (1.25) are $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$ and side length 30, the repulsive functional is approximated using LDA. The channel is assumed connected to the reservoir of fluid at its ends, at $z \rightarrow \pm\infty$. The fluid density can thus vary along x and y and the density distribution $\rho(x, y)$ can be obtained using (1.37) with $\mathbf{r} = \mathbf{x} \cdot \mathbf{e}_x + \mathbf{y} \cdot \mathbf{e}_y$. Picking the chemical potential μ as the parameter we continue a solution obtained at a high negative value of $\Delta\mu$ in the direction of increasing μ , which corresponds to computing an adsorption isotherm. For every value of μ we use the obtained density profile to calculate the excess grand potential $\Omega^{\text{ex}}[\rho]$ defined in equation (1.43). Thus we are obtaining the free energy isotherm $\Omega^{\text{ex}}(\Delta\mu)$. It is plotted in figure 2.5. The full black and grey lines denote concave and non-concave branches of $\Omega^{\text{ex}}(\Delta\mu)$, respectively.

Since the excess free energy of thermodynamically stable configurations is a strictly concave function of thermodynamic fields in the system [74] (in our case it is μ), we immediately can conclude that all the solutions to the Euler-Lagrange equation, whose respective values of the excess free energy belong to the grey lines in figure 2.5, are unstable, and their density profiles do not minimise the free energy functional $\Omega[\rho(\mathbf{r})]$. For illustration we have provided a selection of several unstable density profiles in figure 2.6. Arguably, one can study the relaxation from such states using dynamic formulation of DF theory. We discuss unstable

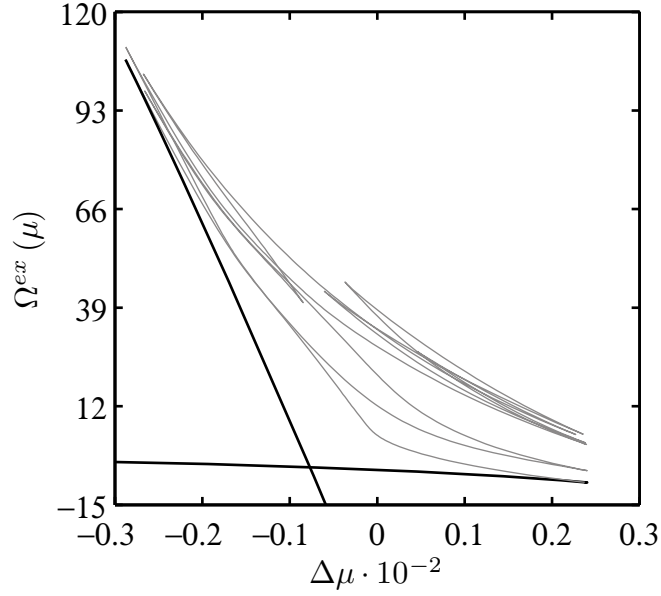


Figure 2.5: Grand potential isotherm at $T = 0.7$ inside a square pore. The substrate is given by (1.25) with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$. Black line: concave branches of free energy. Grey line: non-concave branches of free energy.

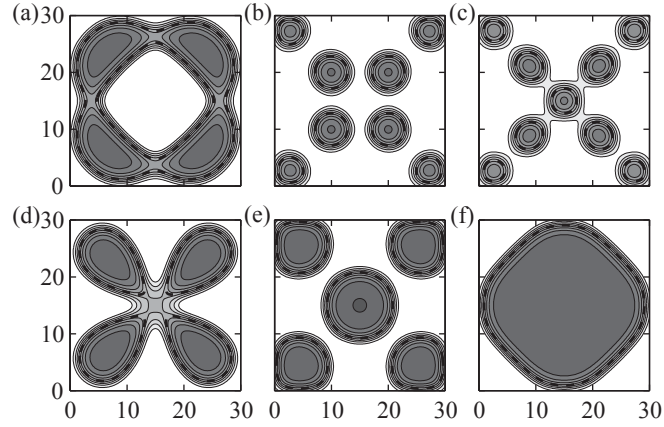


Figure 2.6: Several density distribution inside the square pore whose grand potential isotherm is given in figure 2.5 and whose respective values of $\Omega[\rho(x, y)]$ belong to the non-concave (grey) branches of free energy. Thus, the distributions shown are not thermodynamically stable.

configurations in more detail in section 3.4.

The two concave branches (black lines in figure 2.5) intersect at a single point, which corresponds to capillary condensation inside the square pore.

3 Wetting

The origins of the modern field of wetting are often associated with the seminal works of Cahn [134] and Ebner and Saam [17] which explore a class of phase transitions caused by the non-uniformity of fluids on the microscale: the surface phase transitions. An earlier study developing the statistical thermodynamics for wetting transitions using the concept of disjoining pressure belongs to Frumkin and Derjaguin, see references [135] and [136] and references [6-8] therein, but remained largely unknown in the western literature. The field has seen a rapid growth 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 [137, 138, 139].

Wetting of substrates with complicated geometries is a very rapidly developing modern direction of research, which is being pursued with various theoretical and experimental methods. Investigations of wetting on nano-structured and patterned substrates are interesting from a fundamental statistical physics perspective, as confined fluid surfaces may exhibit various kinds of first-order and continuous transitions [140, 23, 141, 142, 143, 144, 145]. 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 surface phase rule (1.46), to various transitions and metastable states. Capillary phenomena associated with nano-confinement provide a vivid manifestation of attractive intermolecular forces, putting to a test our microscopic picture of matter [16]. Current applied interest in chemical engineering includes microfluidics [146, 147], design of nano-scale chemical reactors [148, 149] and biomimetic surfaces [150] or surfaces with variable wetting properties [151].

One should be very careful when dealing with fluid interfaces at the nano-scale, where the non-uniformity of fluid plays an important role. A satisfactory model for non-uniform fluids 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 DF theories, and simulations [21, 20, 14, 25].

DF theory in particular allows one to obtain detailed information about the structure of

the fluid, but all DF approximations are mainly restricted to numerical studies (although, a sharp-kink approach developed by Dietrich in [18] can yield analytical results) and also cannot account for all 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, see, e.g., references [152, 153, 154, 155, 156]. However, unlike DF theories, effective Hamiltonians cannot provide details of the microscopic fluid structure as they a priori assume the existence of interfaces, often of a particular shape. The limitations of this approach have been discussed in reference [18].

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 chapter 1. Starting from reasonable assumptions about the nature of fluid-fluid and fluid-substrate forces it allows one to obtain consistently all the characteristics of an adsorption process, such as surface tensions, contact angles, interfaces, etc. Sophisticated DF theories offer a computationally inexpensive alternative to molecular dynamic simulations, and often allow one to reproduce experimental results. Recent developments include the studies of adsorption of Argon, Neon and Xenon on planar substrates of various compositions, see references [65, 66, 157, 81]. 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 [3], they have a principal advantage over simulations and may allow one to obtain mean-field critical exponents [5, 158]. At the same time, the relatively low cost of DF calculations allows one to explore the parameter space of governing equations, obtaining complete phase diagrams and possibly uncovering qualitatively new phenomena.

The main novel results presented in this chapter concern the surface phase behaviour of a fluid confined to a capped capillary, which is a prototypical 2D pore. We will contrast the phenomenology of capillary wetting with that of wetting on a planar wall, in a slit pore and in a right-angled wedge, and show how the dimensionality of the substrate dramatically affects the behaviour of the confined fluid. The presented material is based on the published papers by Yatsyshin, Savva and Kalliadasis regarding adsorption on a planar wall [3] and in a capped capillary [5] (also consider the dated preprint by the same authors [6]), and recent preprints by the same authors on the same topics [7, 8].

3.1 Planar wall

Wetting on a single wall is well understood, as it had been attracting considerable interest in the literature from the late 1980's until the mid 1990's (see, e.g., reviews in [159, 160, 11, 161, 162]). In the present section we will provide a treatment using a DF framework detailed in

chapter 1. Understanding wetting on a planar wall forms the context for the study of wetting in geometrically modified substrates. Thus, present section is important for the discussion of the main novel results of the thesis, such as continuous capillary condensation in section 3.2.1 and continuous prewetting in section 3.3.3.

Consider a planar substrate in contact with a fluid. One important property of such system is wetting temperature, T_w . When the substrate is brought in contact with saturated vapour at temperature $T > T_w$, it will be entirely covered by liquid. On the other hand at $T < T_w$ there will only be a mesoscopic liquid film adsorbed on the substrate wall. With respect to the behaviour in the approach to T_w , there can be two distinct scenarios. If we choose a starting thermodynamic point at saturation and at $T < T_w$ and then quasi-statically approach the value T_w following a thermodynamic route along the bulk coexistence line, then either the thickness of initially adsorbed thin film will jump discontinuously to infinity at $T = T_w$ (first-order wetting transition) or it will continuously diverge at that point (continuous or second-order wetting transition). The order of the wetting transition is controlled by the complicated interplay of fluid-fluid and fluid-substrate forces and has been a subject of detailed investigations by theoreticians and experimentalists for many years [163, 18, 139]. We restrict our attention exclusively to substrates exhibiting a first-order wetting transition, as off saturation such substrates can also allow for the coexistence of mesoscopic surface fluid phases whose investigation is significantly simplified by using our methodology from chapter 1 for unconstrained solution of the DF equations.

When brought in contact with undersaturated vapour, planar substrates exhibiting a first-order wetting transition can allow for the coexistence of mesoscopic liquid films adsorbed on the wall (planar prewetting transition). This effect was first found for LJ fluids in contact with planar walls by Ebner and Saam [17]. More specifically, let us suppose we have fixed a value $T > T_w$ and $\mu < \mu_{\text{sat}}$ ($\Delta\mu < 0$, see equation (1.41)) and begin to increase μ quasi-statically at constant T . The adsorption, $\Gamma(\mu)$ (see equation (1.47)), may undergo a finite jump (first order surface phase transition) at some value $\Delta\mu \equiv \Delta\mu_{\text{pw}}(T)$. Further increase of $\Delta\mu$ towards saturation, would lead to the adsorption growing continuously and diverging (complete wetting transition): $\Gamma(\mu) \rightarrow \infty$ as $\mu \rightarrow \mu_{\text{sat}}$. Note, that the magnitude of the prewetting jump in adsorption increases with lowering the temperature and diverges in the limit: $\Delta\mu_{\text{pw}}(T) \rightarrow \infty$ as $T \rightarrow T_w$.

A schematic surface phase diagram of the first-order wetting substrate in contact with undersaturated vapour is presented in figure 3.1. Any isothermal thermodynamic route at T such that $T_w \leq T \leq T_{\text{pw}}^{\text{cr}}$ would exhibit a first-order transition between thin and thick mesoscopic films. The loci of these transitions form the prewetting line. In the following section we will apply various DF approximations to computing the prewetting lines and discuss in detail the structure of density profiles. In what remains of this section we will briefly describe some aspects of the surface phase diagram below using notions of effective

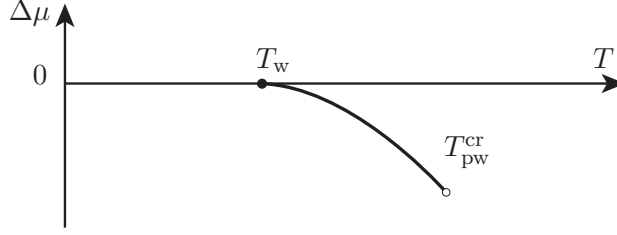


Figure 3.1: Schematic surface phase diagram of the planar substrate with a first-order wetting transition in contact with undersaturated vapour. The values of $\Delta\mu$ are counted from saturation. The prewetting line, $\Delta\mu_{\text{pw}}(T)$, where mesoscopic thin and thick films coexist, runs tangent to saturation at the substrate wetting temperature T_w . The approach follows the law $\Delta\mu_{\text{pw}}(T) \sim (T - T_w)^{3/2}$ as $T \rightarrow T_w$. The prewetting line ends at the critical prewetting temperature, where the coexisting films become indistinguishable. The critical point belongs to the 2D Ising universality class.

interface potential and surface thermodynamics.

Diverging adsorption during complete wetting

In order to establish the asymptotic behaviour of the diverging adsorption $\Gamma(\mu)$ in the limit $\mu \rightarrow \mu_{\text{sat}}$ we involve some ideas behind the development of interfacial potentials. First, note that the effective height of the adsorbed film, h , is simply proportional to adsorption. The former can be defined, e.g., by renormalising the adsorption with the density of the saturated liquid, ρ^{liq} , which in turn can be obtained by solving the algebraic equations for the binodal (1.38) and (1.39):

$$h(\mu) = \Gamma(\mu) / \rho^{\text{liq}}(T). \quad (3.1)$$

In the case of the planar wall the density profile depends on a single coordinate: $\rho(\mathbf{r}) \equiv \rho(y)$. Assuming that for thick adsorbed films the fine details of fluid structure (such as, e.g., the near-wall oscillations of the density or the steepness of the liquid-vapour interface) are not very important, we can think of parametrising the density profile of the liquid film of thickness h adsorbed on the wall as a sharp-kink [18]:

$$\rho_{\text{sk}}(y) = \rho^{\text{liq}}\Theta(h - y) + \rho^{\text{vap}}\Theta(y - h), \quad (3.2)$$

where ρ^{vap} and ρ^{liq} are the densities of saturated liquid and vapour and $\Theta(x)$ is the step-function. Upon substituting the above parametrisation into the expression for the full grand free energy $\Omega[\rho(y)]$ (equation (1.35)), we can in turn parametrise it as $\Omega(h, T, \mu)$. The equilibrium height of the liquid film would then correspond to the minimum of $\Omega(h, T, \mu)$ with respect to h and can in principle be obtained from an algebraic equation. The details of the procedure of substituting $\rho_{\text{sk}}(y)$ into $\Omega[\rho(y)]$, balancing and identifying various terms

can be found in, e.g., the paper by Dietrich and Napirowsky [164] or the review by Dietrich [18]. The result important for us is that the final expression for $\Omega(h, T, \mu)$ has the following general form, which apart from being rigorously obtained is quite intuitive. We have per unit area:

$$\Omega(h, T, \mu) = -h\Delta\mu (\rho^{\text{liq}} - \rho^{\text{vap}}) + \sigma_{\text{wl}}(T) + \sigma_{\text{lv}}(T) + \omega(h, T), \quad (3.3)$$

where σ_{wl} is the wall-liquid surface tension (see equation (1.44)), σ_{lv} is the liquid-vapour surface tension and $\omega(h, T)$ is the effective potential of wall-interface interactions.

The first term on the right-hand side of equation (3.3) is the bulk contribution equal to the work necessary to replace a slab of vapour of infinite area and height h with a slab of liquid of the same height. It depends linearly on h . From the first law of thermodynamics we have for the work per unit area:

$$\delta W = (P_v - P_l) h = -h\Delta\mu (\rho^{\text{liq}} - \rho^{\text{vap}}), \quad (3.4)$$

where P_v is the pressure in the slab of vapour and P_l is that in the slab of liquid. Near saturation we can approximate them as $P_v \approx P_{\text{sat}} + \rho^{\text{vap}}\Delta\mu$ and $P_l \approx P_{\text{sat}} + \rho^{\text{liq}}\Delta\mu$, which accounts for the second equality in the above equation and the first term in equation (3.3). Note that δW does not enter the expression for the excess over the bulk (surface) grand free energy $\Omega^{\text{ex}}[\rho]$ defined in equation (1.42). The second and third terms in the analytic expression for $\Omega(h, t, \mu)$ correspond to the energy per unit area of the two interfaces of the liquid film: with the wall and with the bulk vapour respectively. Naturally, these energies cannot depend on h . The last term is the excess free energy per unit area of the adsorbed liquid film. Its decay rate would determine the asymptotic of adsorption during complete wetting [165, 18]:

$$\omega(h, T) \sim \frac{a_2}{l^2}, \quad (3.5)$$

where $a_2 \equiv a_2(T)$ is the Hamaker constant. That $\omega(h, T)$ has the above asymptotic can be readily seen from the expressions (1.35) and (1.36) for the total grand free energy $\Omega[\rho]$ under the sharp-kink approximation $\rho \equiv \rho_{\text{sk}}$ given in equation (3.2). The potential of fluid-substrate interactions decays far from the wall as $V(y) \sim 1/y^3$ (see equation (1.28)), the potential of the attractive fluid-fluid interactions decays as $\varphi_{\text{Attr}}(y) \sim 1/y^4$ (see equation (1.52)). On substituting the sharp-kink expression for the density profile one has to integrate from h to infinity once the term with the fluid-substrate potential and twice the term with the fluid-fluid potential, which amounts to the power l^{-2} in the effective potential in equation (3.5).

Given the asymptotic of the effective potential expressed by equation (3.5) and using the condition of minimal grand free energy as a function of the film thickness, $\partial\Omega(h, T, \mu)/\partial h = 0$, we have after differentiating equation (3.3):

$$\Delta\mu \sim \frac{2a_2}{(\rho^{\text{liq}} - \rho^{\text{vap}}) h^3}, \quad (3.6)$$

which amounts to the following law for the divergence of film thickness (or, equivalently, the adsorption, see equation (3.1)) during the complete wetting:

$$\Gamma \sim (\Delta\mu)^{-1/3}. \quad (3.7)$$

We can use the above result to show why the transition line of planar prewetting, $\Delta\mu_{\text{pw}}(T)$, indeed runs tangent to the saturation line as depicted in the schematic figure 3.1, and we can also establish the asymptotic of its decay to zero as $T \rightarrow T_w$. In order to do this we will involve some concepts from surface thermodynamics detailed in, e.g., the papers by Evans and Marconi [166, 117], and the reviews [161, 113].

Surface Clausius-Clapeyron equation. Prewetting line near saturation. Criticality

The first law of thermodynamics for the differential of the total energy of a fluid with an interface has the following form:

$$dE = TdS - pdV + \mu dN + \sigma dA, \quad (3.8)$$

where V is the volume of the fluid, S is the total entropy, N - the total amount of particles, σ is the work necessary to increase the interfacial area by one unit of square. Defining the grand potential in the usual way as $\Omega = E - TS - \mu N$ and using the extensiveness of the total energy, we get the formula for the grand potential of a fluid with an interface

$$\Omega = -PV + \sigma A, \quad (3.9)$$

and its differential

$$d\Omega = -pdV - SdT - Nd\mu + \sigma dA. \quad (3.10)$$

In agreement with the system bulk introduced for inhomogeneous systems in section 1.3, one can formulate equivalent thermodynamic definitions of bulk and excess (surface) contributions to the total amount of particles, energy, entropy, etc. For example, splitting the bulk and surface contributions to the total number of particles in the system, we can define $N = N_b + N_s$, where (see, e.g., the review by Schick in [161])

$$N_s = A \lim_{V, A \rightarrow \infty} \left(N - V \lim_{V \rightarrow \infty} \frac{N}{V} \right) / A \equiv A\Gamma, \quad (3.11)$$

where the agreement with adsorption defined using inhomogeneous density $\rho(\mathbf{r})$ in equation (1.47) is obvious for the case of the planar wall.

Splitting grand potential and entropy into bulk and surface (excess) contributions we have:

$$\begin{aligned} N &= N_b + \Gamma A, \\ \Omega &= \Omega_b + \Omega^{\text{ex}}, \\ S &= S_b + sA. \end{aligned} \tag{3.12}$$

Finally, recalling the differential of the bulk part of the grand potential [14]:

$$d\Omega_b = -pdV - S_b dT - N_b d\mu, \tag{3.13}$$

we have from equations (3.10), (3.12) and (3.13) for the differential of excess grand potential [166]:

$$d\Omega^{\text{ex}} = -sAdT - \Gamma Ad\mu + \sigma dA, \tag{3.14}$$

which also proves the Gibbs sum rule expressed by equation (1.46).

Now for the two films coexisting during prewetting (thin and thick films) and thus forming the two surface phases we have the equality of two grand potentials with the differentials of the surface parts given in (3.14) ($d\Omega_1^{\text{ex}} = d\Omega_2^{\text{ex}}$). Fixing the area, we obtain the surface Clausius-Clapeyron equation:

$$(s_1 - s_2) dT + (\Gamma_1 - \Gamma_2) d\mu = 0, \tag{3.15}$$

where the indexa 1 and 2 denote respectively the thin and thick films coexisting during prewetting. The above equation provides the slope of the coexistence curve $\Delta\mu_{\text{pw}}(T)$. We can now integrate over temperature from T_w to some $T > T_w$ and use the asymptote for the divergence of the film thickness of the thick coexisting film in the approach to saturation given by equation (3.7). For the thick coexisting film with adsorption Γ_2 it takes the form $\Gamma_2 \sim (\Delta\mu_{\text{pw}})^{-1/3}$, while Γ_1 is finite in the limit $T \rightarrow T_w$, due to wetting transition being of first order. Using equations (3.15) and (3.7) we get

$$\begin{aligned} \Delta\mu_{\text{pw}} &= 1/(\Gamma_2 - \Gamma_1) \int_{T_w}^T (s_1 - s_2) dT \\ &\sim \Delta\mu_{\text{pw}}^{1/3} (T - T_w). \end{aligned} \tag{3.16}$$

The above is equivalent to

$$\Delta\mu_{\text{pw}} \sim (T - T_w)^{3/2}, \tag{3.17}$$

which shows that, first, the prewetting line runs tangent to saturation and, second, the asymptote of its decay near wetting temperature is 3/2 [167, 168].

The critical prewetting point (at $T = T_{\text{pw}}^{\text{cr}}$) belongs to the two dimensional Ising univer-

salinity class because the film thickness remains finite at the critical prewetting point, and the correlation length may diverge in two directions parallel to the interface. The order parameter vanishing at this point is the difference in adsorption of the prewetting films $\Delta\Gamma = (\Gamma_2 - \Gamma_1)$, see, e.g., the work by Evans and Parry [160] and references therein. It follows that during an approach to the prewetting critical point along the prewetting line the order parameter vanishes as $\Delta\Gamma \sim (T_{\text{pw}}^{\text{cr}} - T)^{1/2}$ in mean field, and as $\Delta\Gamma \sim (T_{\text{pw}}^{\text{cr}} - T)^{1/8}$ beyond mean field.

3.1.1 Asymptotic analysis of the DF equations

Using a DF approach to study planar adsorption we look for the one-dimensional density profile, $\rho(\mathbf{r}) \equiv \rho(z)$, by solving the Euler-Lagrange equation (1.37), where $\mathbf{r} \equiv z \cdot \mathbf{e}_z$. As has been discussed in section 1.1.4, the external potential of a homogeneous substrate is given by the expression in (1.26) and forms a particular case of a pre-plated substrate given in (1.27), whose potential has a cutoff at a distance $H_0 \geq 0$ from the wall. We note again that the form of the Euler-Lagrange equation (1.37) for the fluid density remains the same in every geometry, and it is only the dimensionality of $\mathbf{r}$ that changes, along with the expressions for the attractive potential, φ_{Attr} , given in (1.52) and the averaging weight, W , given in (1.53). All details associated with $\mathbf{r}$ varying in one dimension are discussed in section 1.3.2.

Far from the substrate wall (we will consider the expression (1.26) with a zero cutoff, but the asymptotic behaviour of the density $\rho(z)$ at large z is not affected by a non-zero cutoff) the fluid density should asymptotically approach its constant bulk value, ρ_b , due to the decay of the wall potential with z . Since the integration in the repulsive contribution to the chemical potential (second and third terms of equation (1.37)) is done over a finite volume (because the weight function is essentially a step), the asymptotic behaviour of $\rho(z)$ is determined by the attractive contribution (fourth term of (1.37)) and the wall potential. In one dimension, using the expression (1.52) for $\varphi_{\text{Attr}}(z)$ we have:

$$\begin{aligned} \int_{\substack{\mathbf{r}=z \cdot \mathbf{e}_z, \\ z \in [0, \infty]}} d\mathbf{r}' \rho(\mathbf{r}') \varphi_{\text{Attr}}(|\mathbf{r} - \mathbf{r}'|) &\equiv A \int_0^\infty \varphi_{\text{Attr}}(z - z') \rho(z') dz' \\ &= c + O\left(\frac{1}{z^3}\right), \end{aligned} \quad (3.18)$$

where A is the area of the wall and c is some constant. Since for large z the leading term of the wall potential in (1.26) (and in (1.27)) is also $O(1/z^3)$, it follows that as $z \rightarrow \infty$:

$$\rho(z) = \rho_b + \frac{\alpha}{z^3} + O\left(\frac{1}{z^4}\right), \quad (3.19)$$

where α is a constant to be determined. More discussion of the asymptotic behaviour of density profiles in 1D geometries may be found in a recent work by Yatsyshin et al. [3] and

a more detailed study by Barker and Henderson [169]. By substituting the expression (3.19) into the Euler-Lagrange equation (1.37), expanding asymptotically and matching orders of z , we can obtain two algebraic equations for the parameters in the asymptotic expansion (3.19). More specifically, from the $O(z^0)$ terms we obtain a nonlinear equation for the density in the bulk, ρ_b , which is equivalent to the expression for the bulk chemical potential (1.38). By matching the $O(z^{-3})$ terms of the Euler-Lagrange equation (1.37), we obtain an expression for the rate of decay of the fluid density into the bulk, α [3]:

$$\alpha = \frac{2\pi (\rho_b - \varepsilon_w \rho_w \sigma_w^6)}{3} \left(\frac{d\mu}{d\rho} \Big|_{\rho_b} \right)^{-1}, \quad (3.20)$$

where ε_w and ρ_w are the strength parameter of the LJ substrate potential and the effective density of the substrate material, respectively (see, e.g., expression (1.25)), and $d\mu/d\rho$ is the derivative of the chemical potential (which in dimensional form is given by equation (1.38)) with respect to ρ .¹

One way to make use of the asymptotic decay of $\rho(z)$ in (3.19) is by formulating the problem numerically on a finite but sufficiently large domain, e.g., $[0, L]$ with $L \gg 1$. Then the attractive contribution to the chemical potential (fourth term in the Euler-Lagrange equation (1.37)) can be split into two integrals: from 0 to L and from L to infinity providing a high level of control over accuracy, while at the same time avoiding the unnecessary discretization of the density at very large distances from the wall [3]:

$$\begin{aligned} 1/A \int_{\substack{\mathbf{r}=z\mathbf{e}_z, \\ z \in [0, \infty]}} d\mathbf{r}' \rho(\mathbf{r}') \varphi_{\text{Attr}}(|\mathbf{r} - \mathbf{r}'|) &\approx \int_0^L \varphi(z - z') \rho(z') dz' \\ &+ \int_L^\infty \varphi(z - z') \left(\rho_b + \frac{\alpha}{z'^3} \right) dz' + O\left(\frac{1}{L^4}\right). \end{aligned} \quad (3.22)$$

Figure 3.2 with logarithmic axes shows the asymptotic behaviour at $z \gg 1$ of two density profiles (solid line) coexisting at a prewetting transition at $T = 0.85$ and $\Delta\mu = -0.008$ on a substrate with a zero cutoff and the values of other parameters $\varepsilon_w = 0.4$, $\sigma_w = 1.25$, $\rho_w = 1$. The calculation is done using WDA for repulsive interactions (one can see some structure in the profiles near the wall, at $z = 0$). The profiles are both computed on a finite domain $[0, L]$ with $L = 80$ and using the expression (3.22). Note how closely the profiles follow their asymptotic (dashed line) given in (3.19). For values of $\Delta\mu$ closer to saturation one would have to use a larger value of L (or an map to a semi-infinite domain g_h (2.31), where $L \rightarrow \infty$)

¹Note, that all expressions are written in dimensionless units, according to the Table 1.1. Equation (3.20) has the following dimensional form

$$\alpha = \frac{2\pi (\varepsilon \rho_b \sigma^6 - \varepsilon_w \rho_w \sigma_w^6)}{3} \left(\frac{d\mu}{d\rho} \Big|_{\rho_b} \right)^{-1}. \quad (3.21)$$

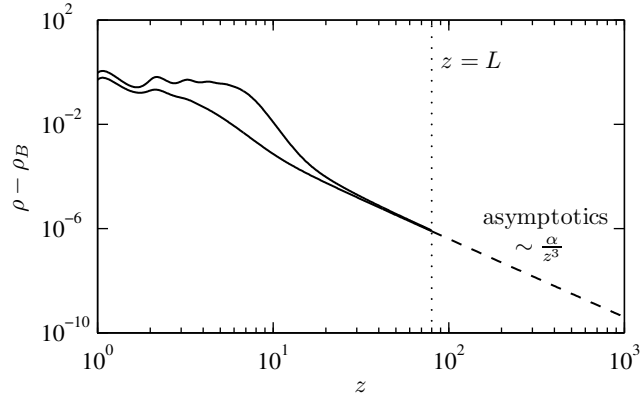


Figure 3.2: Asymptotic behaviour at $z \gg 1$ of two density profiles coexisting at a planar prewetting transition [3]. Solid line shows $(\rho(z) - \rho_b)$, dashed line shows the asymptotic tail α/z^3 with $\alpha \approx 0.4$. The vertical dotted line demarcates the end of the computational domain at $z = L = 80$, where $\rho(L) - (\rho_b + \alpha/L^3) \sim 10^{-7}$.

due to the liquid-vapour interface unbinding into the bulk of the fluid.

Now consider the case of $z \rightarrow 0$. Then the wall potential with a zero cutoff given by $V_0^{\text{wall}}(z)$ from (1.26) diverges as $O(-1/z^9)$. All the terms of the Euler-Lagrange equation (1.37), depending on the density non-locally remain finite as $z \rightarrow 0$, and one is left with balancing the ideal contribution, $\sim \ln \rho(z)$, with the diverging wall potential, $V_0^{\text{wall}}(z) \sim O(-1/z^9)$. This amounts to a super-exponential decay of the density near the wall, i.e., $\rho \propto \exp(-1/z^9)$ as $z \rightarrow 0$. The difficulties in the discretisation of a density with such behaviour are surmounted by using a change of variable, $\rho(z) = f(z) \exp(-V_0^{\text{wall}}(z)/T)$, where after substitution into the Euler-Lagrange equation (1.37) $f(z)$ would have a finite limit at the wall.

3.1.2 DF approach. LDA, WDA and FMT for repulsions

We will again present the phenomenology of wall wetting but this time it is obtained using DF the approach. Everywhere throughout this section the substrate potential is given by (1.27) and (1.28) with zero cut-off: $H_0 = 0$. More details and other approaches to planar wetting (including experiments) can be found in, e.g., the reviews [139, 160, 11, 18]. According to the schematic surface phase diagram in figure 3.1, when the wetting transition is of first order, an isothermal approach to saturation ($\Delta\mu \rightarrow 0$) may be preceded by prewetting. Then the adsorption isotherm $\Gamma(\Delta\mu)$ or, equivalently, the film height $h(\Delta\mu)$ defined in equation (3.1) possesses a Van der Waals hysteresis loop. Computing fluid configuration by solving the Euler-Lagrange equation is complicated due to the fact that there exist multiple solutions between the turning points (spinodals) of the isotherms. Near a spinodal the number of Newton iterations required to converge to a solution is strongly dependent on the initial guess and may result in many Newton iterations or in no convergence at all. Employing arc-length continuation described in detail in section 2.2.1 guarantees an optimal initial guess

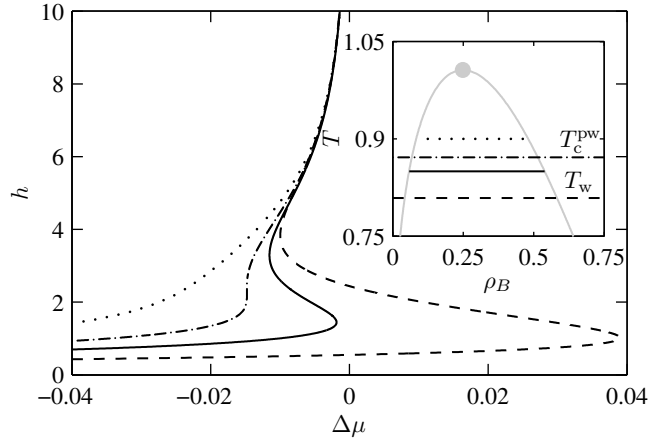


Figure 3.3: Wetting isotherms calculated using WDA with $\varepsilon_w = 0.4$, $\sigma_w = 1.25$, $\rho_w = 1$ showing approach to saturation at different temperatures. Wall wetting temperature is at $T_w = 0.81$; isotherm at T_w is plotted with a dashed line. Critical prewetting temperature is at $T_{pw}^{cr} = 0.87$, with critical prewetting at $\Delta\mu_0 = -0.015$; isotherm at T_{pw}^{cr} is plotted with a dashed-dotted line. Solid curve: isotherm with a prewetting transition at $T = 0.85$, $\Delta\mu_0 = -0.008$, followed by complete wetting at $\Delta\mu = 0$. Dotted curve: isotherm at $T = 0.9 > T_{pw}^{cr}$. Inset shows the binodal; values of temperatures corresponding to the isotherms are designated by horizontal lines of the same style [3].

for every Newton iteration. We note again that the main idea of the method is to treat the (independent) parameter μ in the Euler-Lagrange equation as an unknown and close the system of equations with an additional geometric constraint. This approach allows us to determine systematically all possible states without relying on one's physical insight to come up with a “nice” initial guess as was used to be done in some earlier studies, e.g., [170, 171, 72].

Figure 3.3 shows representative isotherms summarising the wetting scenarios. The calculation is done using WDA for repulsions, the substrate parameters are $\varepsilon_w = 0.4$, $\sigma_w = 1.25$, $\rho_w = 1$. The calculated wetting temperature is $T_w = 0.81$, and the critical prewetting temperature is $T_{pw}^{cr} = 0.87$. The inset in the figure shows the bulk binodal, which is obtained with the help of continuation over T of the solutions to the dimensionless equations (1.38) and (1.39) (without continuation it is not straightforward to solve the system near T_c). The values of temperature corresponding to the isotherms on the main plot are designated by horizontal lines of the same style on the binodal. At $T < T_w$ the observed equilibrium film thickness $h(\Delta\mu)$ does not exceed several molecular diameters, even for bulk pressures approaching saturation. This is the partial wetting regime, and it corresponds to a non-zero contact angle, Θ , see, e.g., (1.45) [139, 18]. At $T = T_w$ (dashed curve) the contact angle vanishes, $\Theta = 0$, and the Maxwell equal area construction (equivalent due to the Gibbs rule (1.46) to finding the intersecting branches of $\Omega^{ex}(\mu)$) yields the transition at $\Delta\mu = 0$, so at $T = T_w$ a microscopic

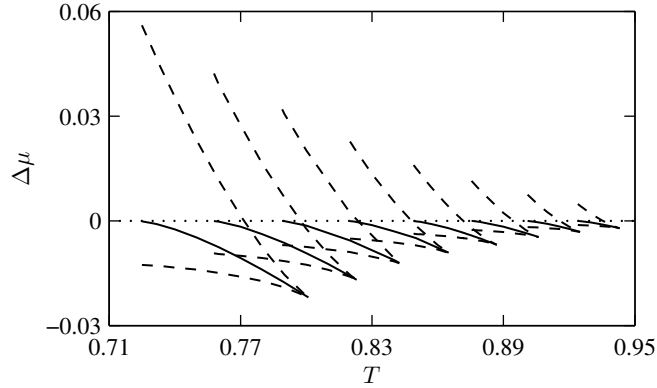


Figure 3.4: Prewetting lines (full line) with spinodals (dashed line) for several values of ε_w (other wall parameters are fixed), increasing from left to right, calculated using FMT. For a fixed ε_w points on each prewetting line form the locus of $(\Delta\mu_0, T)$, and points on its spinodals form the locus of the turning points of the isotherms. The parameter ε_w takes the values (right to left): 0.35, 0.36, 0.38, 0.4, 0.42, 0.44, 0.46, 0.48 [3].

film coexists with an infinitely thick film.

For temperatures in the range $T_w < T < T_{pw}^{cr}$ thin and thick mesoscopic films can coexist (see full curve in figure 3.3). This is the prewetting regime, and the observed film thickness changes discontinuously when the deviation chemical potential crosses the coexistence value, $\Delta\mu_0$, obtainable by, e.g., the equal area construction. As $T \rightarrow T_{pw}^{cr}$ from below, the area given in the Maxwell construction vanishes as the critical prewetting temperature is approached (the critical prewetting isotherm is plotted with a dashed-dotted curve in figure 3.3). For temperatures at $T > T_{pw}^{cr}$, the observed film thickness grows continuously with $\Delta\mu \rightarrow 0$, up until saturation, where it fills the entire space *continuously* (see dotted curve in figure 3.3). The critical point of prewetting belongs to the 2D Ising universality class and exists beyond mean-field.

Due to the effects of molecular packing the density profiles have pronounced oscillations in the near-wall region, which are typically localised within a few molecular diameters from the wall. At low temperatures the fluid can form a highly structured, solid-like (rather than liquid-like) film in the vicinity of the wall and the wetting isotherms would become step-like. In that case as $\Delta\mu \rightarrow 0$ the fluid undergoes a succession of first-order transitions, each with its own range of temperatures where a jump in coverage occurs. Such wetting regime is known as the layering transition, see, e.g., [172, 171, 11, 18].

Now we contrast the LDA prescription for the reference hard sphere functional with those given by WDA and FMT. As noted in chapter 1, LDA can be classified as the simplest model for the hard sphere fluid which can account for the spatial dependence of the number density. In the early literature DF theories based on the LDA for repulsions were quite popular, see, e.g., [173, 43, 42]. The analysis of the structure factor suggested that the liquid-vapour

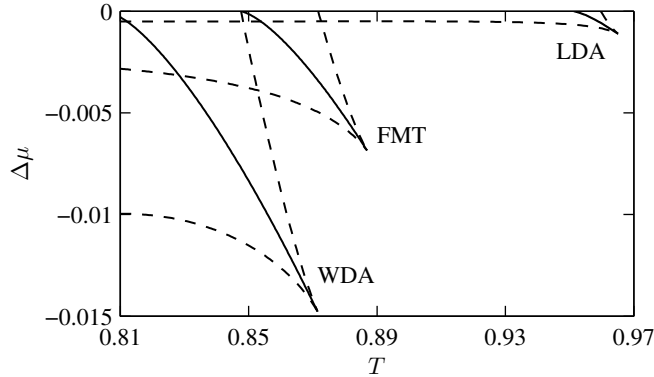


Figure 3.5: Prewetting lines (full line) with spinodals (dashed line) for $\varepsilon_w = 0.4$ calculated using (left to right) WDA, FMT and LDA [3].

interface can be described. The version of WDA in (1.9) and (1.10) can, in turn, be classified as the simplest model which can account not only for the spatial dependence of the fluid number density, but also for the correlations within the hard sphere fluid, e.g., [49, 42]. A systematic comparative study of various WDA prescriptions for the hard sphere functional in the application to the problems of planar liquid adsorption can be found in, e.g., [73, 72].

The most sophisticated approximations for the repulsive part of the fluid free energy functional belong to the FMT family, see chapter 1. The distinct feature of an FMT approximation is that the hard sphere functional is constructed as a local function of the weighted densities, see equations (1.11) – (1.14), which are themselves non-local weighted averages of the density. Such choice of variables is dictated by the geometric qualities of non-penetrable hard bodies and is invariant with respect to the dimensionality of the fluid and even the shape of its constituent molecules. With an FMT approximation the correlation structure of the hard sphere fluid usually compares very well with simulation results, e.g., [174].

The technical difficulties involved in the practical implementation of FMT functionals, where it is necessary to compute several weighted densities (see equations (1.14)), force some authors to use simpler approximations, like WDA or even LDA, especially when dealing with higher-dimensional problems, e.g., [5, 7, 8, 44, 45]. The use of numerical methodology developed in chapter 2 facilitates calculation. As an illustration we have calculated the prewetting lines for various values of the substrate strength parameter ε_w using the White Bear FMT [69] in the repulsive part of the free energy functional, see equations (1.11) – (1.14). As was noted in section 1.3, the working equations for the case of a planar substrate can be found in, e.g., the review paper by Roth [70] and the review by Tarazona and co-workers [47]. The calculation of a prewetting line can be done by applying arc-length continuation to the condition of two-phase coexistence expressed by equation (1.48). It can also be done by computing a set of prewetting isotherms for varying values of T and applying an equal area construction to each isotherm to find the corresponding transition values of the chemical potential, $\Delta\mu_0$, which together with T form the prewetting line.

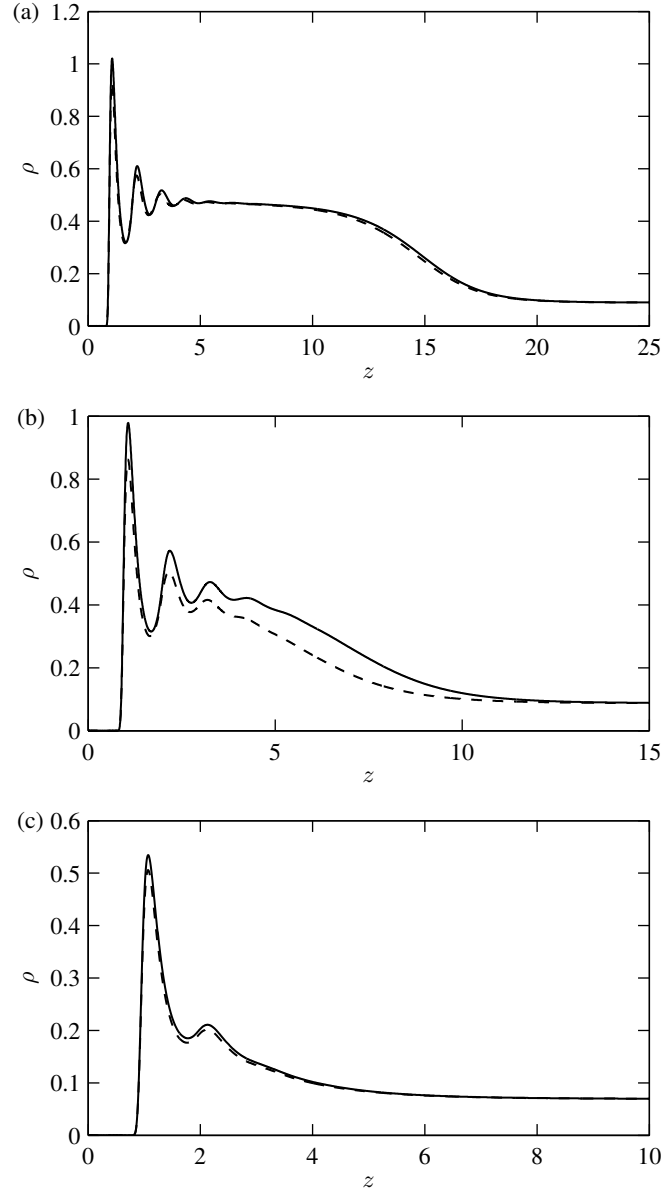


Figure 3.6: Comparison of density profiles calculated using WDA (solid curves) and FMT (dashed curves), with $\varepsilon_w = 0.4$, $T = 0.91$ [3]. (a) Thick adsorbed film, $\Delta\mu = -10^{-3}$. (b) Thinner adsorbed film, $\Delta\mu = -10^{-2}$. (c) No film is adsorbed, $\Delta\mu = -10^{-1}$.

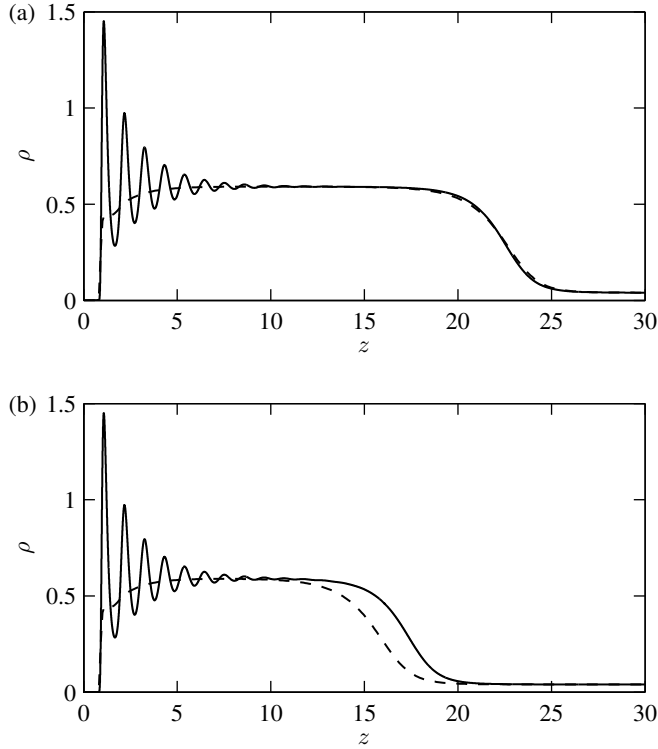


Figure 3.7: Wetting profiles calculated using WDA (solid line) and LDA (dashed line), with $\varepsilon_w = 0.4$, $T = 0.8$. (a) Thick adsorbed film, $\Delta\mu \approx -10^{-4}$. (b) Thin adsorbed film, $\Delta\mu \approx -10^{-3}$ [3]. Note that according to the surface phase diagram in figure 3.5 the films are thermodynamically metastable ($T < T_w$ for both LDA and WDA treatment). The thermodynamics, however, is not important to us in the present comparison of the profile structure. Choosing a low value of temperature allows us to showcase the near-wall density oscillations.

Figure 3.4 shows a sequence of prewetting lines together with their spinodals plotted in the $T - \Delta\mu$ plane, each corresponding to a different value of the substrate strength parameter, ε_w (see equations (1.27)). Given ε_w , each prewetting line is defined for $T_w < T < T_{pw}^{cr}$ and, together with its spinodals, it divides the $T - \Delta\mu$ half-plane ($\Delta\mu < 0$) into regions corresponding to the thermodynamic stability of films of various thickness. For weaker substrate potentials the prewetting lines shift towards the critical temperature and the range $T_w < T < T_{pw}^{cr}$ decreases.

For a given strength of the substrate potential, DFTs using different approximations for the hard sphere part of the free energy functional normally predict markedly different wetting behaviour, as can be seen from figure 3.5, which shows the prewetting lines calculated using LDA, WDA and FMT. Due to the different values of T_w and T_{pw}^{cr} , a direct comparison between the density profiles obtained from WDA and FMT is appropriate for temperatures above the T_{pw}^{cr} obtained from both approximations. A comparison between the WDA and the White Bear FMT approximation is given in figure 3.6 for the case where both predict complete wetting.

As can be seen, the WDA possesses a qualitative agreement with the more sophisticated FMT approximation for the interfaces between liquid and vapor, and between wall and liquid film, for values of μ “quite near” (e.g., Fig. 3.6, (a)) and “quite far” (e.g., Fig. 3.6, (c)) from saturation. The reason for the agreement in the case of complete wetting is, of course, the fact that for high values of temperature the profiles are not very structured near the wall, and WDA turns out to be a sufficiently good approximation. The density profiles calculated at the “intermediate” values of the deviation chemical potential, where the wetting isotherm “bends”, typically reveal a disagreement between the calculations using WDA and FMT (e.g., figure 3.6, (b)). As the value of T is increased further, the agreement between WDA and FMT would persist for larger intervals of μ , the respective isotherms corresponding to either approximation would be “closer” to each other on the $\Delta\mu - h$ plane. On the other hand, for lower temperatures the effects of packing become more important, and the density profiles obtained using FMT and WDA differ significantly.

It is very interesting to see how well a functional using LDA for repulsions can describe a thick film, i.e., the liquid-vapour interface portion of the profile. Figure 3.7 shows density profiles calculated using WDA (solid line) and LDA (dashed line) for repulsions. The value of temperature is chosen so that within both approximations the wall is non-wet, i.e., the value of T is below the T_w predicted by both approximations. Consequently, the liquid films are metastable, which is not of principle importance for us in comparing the profile structure. The value of chemical potential is chosen close to saturation to reduce the effects of the wall. The liquid-vapour interfaces match for rather thick profiles as $\Delta\mu \rightarrow 0$ (see figure 3.7(a)), since then they are essentially free from the effects of the wall. For larger $\Delta\mu$, see figure 3.7(b), the effects of the near-wall layering in the fluid alter the liquid-vapour interface of the profiles calculated using the WDA as compared to those obtained from the LDA. This result confirms the earlier analysis, see, e.g., the work by Tarazona and Evans in reference [43], and illustrates the limits of applicability of DF approximations treating repulsions locally. In general our results indicate that as long as one is not particularly interested in the near-wall structure of the adsorbed fluid, using LDA for repulsions in the free energy functional allows one to retrieve an adequate qualitative description of interfaces between liquid-like and vapour-like fluid surface phases.

3.2 Capped capillary

We turn to the study of the surface phase behaviour of a LJ fluid confined in a prototypical two-dimensional pore [7, 8]. We will show how the dimensionality of the problem dramatically affects the phenomenology of wetting by contrasting wetting on a planar wall, a slit pore, a capped capillary and a right-angled wedge. First, consider a slit pore formed by two parallel planar walls of infinite area, which are separated by the distance H . When the pore is

immersed in a large reservoir filled with vapour at pressure P below saturation, it can exhibit a two-phase coexistence between the configurations of the pore being filled with vapour and with capillary-liquid, see, e.g., references [175, 176]. Let us first consider this coexistence invoking only the concepts from surface thermodynamics which we discussed earlier in section 3.1.

The grand potential of the slit pore filled with vapour is given by the sum of the bulk and surface terms, see equation (3.9):

$$\Omega_1 = -PHA + 2\sigma_{\text{wv}}A, \quad (3.23)$$

where due to the presence of two walls we have the coefficient 2 in front of the wall-vapour surface tension. The grand potential of the pore filled with liquid is given analogously, but with the pressure being that at saturation (otherwise liquid cannot be formed, since $P < P_{\text{sat}}$):

$$\Omega_2 = -P_{\text{sat}}HA + 2\sigma_{\text{wl}}A. \quad (3.24)$$

At coexistence we have $\Omega_1 = \Omega_2$, so equating the two expressions from above we obtain finally:

$$P = P_{\text{sat}} - \frac{2(\sigma_{\text{wv}} - \sigma_{\text{wl}})}{H}. \quad (3.25)$$

The transition taking place at the value given by the above expression can be used to define the fluid surface phase – capillary-liquid, which can be viewed as the surface phase coexisting with vapour in the pore. The first-order transition between these surface phases, which we will call capillary condensation (CC), is essentially the shifted bulk saturation (as is immediately clear by, e.g., considering the limit $H \rightarrow \infty$) and the equation (3.25) is otherwise referred to as the Kelvin equation.

The Kelvin equation (3.25) can be expressed in terms of the shift of chemical potential in the same way as it was done previously in equation (3.4) for pressures near saturation. Using also the Young-Laplace equation (1.45) for the contact angle at saturation, Θ , we have the following expression for the shift of the transition chemical potential:

$$\mu = \mu_{\text{sat}} - \frac{2\sigma_{\text{lv}} \cos \Theta}{H(\rho^{\text{liq}} - \rho^{\text{vap}})} \equiv \mu_{\text{sat}} + \Delta\mu_{\text{cc}}(T), \quad (3.26)$$

where ρ^{liq} and ρ^{vap} denote as usual the liquid and vapour densities at bulk saturation, σ_{vl} is the vapour-liquid surface tension and by $\Delta\mu_{\text{cc}}(T)$ we define the transition line of CC. As we will see in later chapters from a fully microscopic calculation of the CC line, the Kelvin equation allows one to capture some of its very important features. First, note that $\Delta\mu_{\text{cc}}(T)$ crosses the saturation line at the temperature T_0 , where the contact angle is $\pi/2$. The value $\Delta\mu_{\text{cc}}(T)$ decreases for T increasing from T_0 defined as $\Theta(T_0) = \pi/2$ to T_{w} (where $\cos \Theta \rightarrow 1$).

On the other hand, for high temperatures the value $\Delta\mu_{cc}(T)$ should be increasing due to $\sigma_{lv}(\rho^{\text{liq}} - \rho^{\text{vap}})^{-1}$ vanishing in the approach to bulk criticality. This competition should lead to the CC line possessing a minimum in the T - $\Delta\mu$ plane near the planar wetting temperature T_w . More details and discussion can be found in the review by Dietrich [18] (page 158). Our fully microscopic calculations presented in later sections shows the presence of the minimum on the CC line near T_w .

Although for higher T the value $\Delta\mu_{cc}(T)$ decreases, it does not reach zero due to the critical point being shifted in the slit pore of the finite width H . The critical point of CC transition belongs to the 2D Ising universality class [160]. For a given wall separation the shift of CC critical temperature, $T_c(H)$, from the bulk critical temperature, T_c , is controlled by the 3D bulk correlation length exponent $\nu = 1/2$ (beyond mean field $\nu \approx 0.63$) [177, 178]:

$$T_c(H) = T_c - H^{-1/\nu}. \quad (3.27)$$

Now consider a *capped capillary*, namely a slit pore closed at one end by a third wall, as shown in figure 3.8. On the one hand, one expects CC to be of first order, since the capped capillary reduces to a slit pore as $x \rightarrow \infty$. On the other hand, the capping wall may provide sufficient free 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 ($P \rightarrow P_v^-$), the meniscus should unbind continuously into the “capillary bulk” ($x \rightarrow \infty$), 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 [152] and independently numerically in reference [5], for the case of dispersive fluid-fluid and fluid-substrate interactions. An isotherm of drying (reservoir filled with liquid, and $P \rightarrow P_v^+$) for a capillary with purely repulsive hard walls and a fluid with short-ranged, square well, fluid-fluid potential is considered by Roth and Parry in [158]. A recent paper by Malihevsky [179] discusses the possibility of hysteresis behaviour during complete wetting of a capped capillary with dispersive fluid-fluid and fluid-substrate interactions using mean-field DF approach. Another illuminating recent work of Rascon and co-workers [177] considers the order of the surface phase transition in the capped capillary and contains theoretical as well as experimental results.

We begin by investigating in section 3.2.1 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. This leads us to discover a *capillary wetting* transition, which using a mean-field approach is found to be preceded by the *capillary prewetting* transition. We also show how the mean-field phenomenology of wetting in a capped capillary maps to that of wetting on a single planar wall. In sections 3.2.3 and 3.3.1 we examine the interplay between wetting in a capped capillary and in a right-angled wedge (capillary corner), which leads to a three-phase coexistence. We

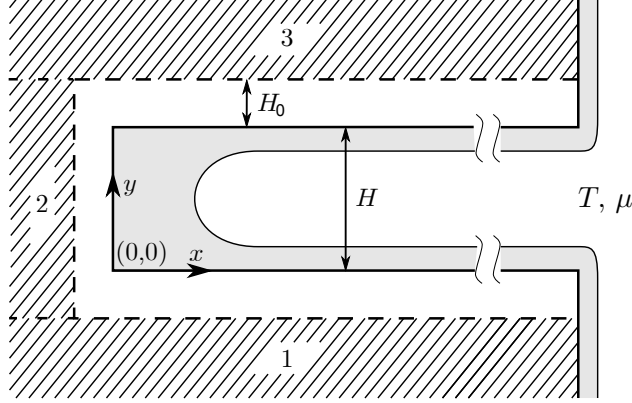


Figure 3.8: Sketch of adsorption in the capped capillary of width H opening into a reservoir of particles on the right at bulk temperature T and chemical potential μ . The grey area denotes an adsorbed capillary-liquid. The hatched areas denote parts of the substrate with parameters of pairwise LJ fluid-substrate interactions ε_w , σ_w . The substrate potential has a cutoff $H_0 \geq \sigma_w$. The directions of the two axis x and y and the origin $(0,0)$ are also shown. Tildes denote the infinitely long separation of the capping wall on the left from the channel opening into the reservoir on the right.

proceed to consider the case where capillary bulk (the slit pore) exhibits a three-phase coexistence, which leads us to the discovery of a *continuous shifted planar prewetting* transition. The text is based on the dated preprints by Yatsyshin, Savva and Kalliadasis [6, 7, 8] and published papers by the same authors [3, 5]. The fluid-fluid and fluid-wall interactions are dispersive, making a possible close “real-world” analogue, e.g., noble gas in contact with an alkali metal [157, 67].

We provide representative examples from the detailed numerical study of the parameter space of the DF theory equations. Considering several examples of capped capillaries with various substrate parameters we argue in terms of complete surface phase diagrams in the $T - \Delta\mu$ space together with wetting isotherms of excess free energy, $\Omega^{\text{ex}}(\Delta\mu)$, and adsorption, $\Gamma(\Delta\mu)$. The deviation chemical potential, $\Delta\mu$, is given as the difference of the applied chemical potential, μ , from the saturation chemical potential at bulk liquid – vapour coexistence, μ_{sat} , see equation (1.41).

The density profiles of fluid inside the capped capillary, $\rho(x, y) \equiv \rho^{\text{cpd}}(x, y)$, are obtained from the Euler-Lagrange equation (1.37), where $\mathbf{r} = x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y$, the external potential, $V^{\text{cpd}}(x, y)$, is defined by (1.30), and all the details of transforming to the 2D geometry are discussed in section 1.3.2. The expression for the excess free energy defined in (1.43) takes for the capped capillary the following form:

$$\Omega^{\text{ex}} = \Omega \left[\rho^{\text{cpd}}(x, y) \right] - \Omega \left[\rho^{\text{slt}}(y) \right], \quad (3.28)$$

where $\rho^{\text{slt}}(y)$ is the density inside the slit pore, to which the capped capillary reduces infinitely far from the capping wall, and which thus forms its bulk, see also discussion in section (1.3.1). The adsorption is defined following the expression in (1.47) as

$$\Gamma = \int dx dy \left(\rho^{\text{cpd}}(x, y) - \rho^{\text{slt}}(y) \right). \quad (3.29)$$

The choice of particular values for the parameters of the substrate (ε_w , σ_w and H_0) was affected (without loss of generality) by numerical convenience and a restriction that the wetting transition on the planar substrate with the same parameters is first-order. We tried to select substrate potentials with relatively high planar wetting temperatures 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.

3.2.1 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 the planar substrate exhibits prewetting. We further set the chemical potential, $\mu = \mu_{\text{sat}} + \Delta\mu$, in equation (1.37) 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 for the Euler-Lagrange equation (1.37), where the initial guess is taken to be that of the vapour inside a slit pore, at the same chemical potential and temperature: $\rho_{N_{xy}}^{\text{cpd},0}(x, y) \equiv \rho^{\text{slt}}(y)$. After obtaining the solution $\rho_{N_{xy}}^{\text{cpd}}(x, y)$, given on the spatial grid by the set of data points ρ_{ij} , we perturb the vector $[\mu, \rho_{ij}]$ and, adding to the equation (1.37) 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 μ , also by the Newton method. The described tactics is the essence of the arc-length continuation technique detailed in section 2.2.1, which allows us to systematically obtain consecutive solutions to (1.37) at values of $\Delta\mu$ increasing towards CC, i.e., a wetting isotherm. The details of implementing arc-length continuation, along with a discussion of various geometrical constraints, are also covered, e.g., by Yatsyshin et al. in [3] and by Salinger and Frink in [124, 180]. 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 (μ). 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, $\Delta\mu_{cc}(T)$, the length of the slab increases and diverges in the limit $\Delta\mu \rightarrow \Delta\mu_{cc}$. Examination of the fluid structure (a detailed discussion is postponed until section 3.2.3) 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 3.9. A typical Van der Waals loop in the excess free energy dependence, $\Omega^{\text{ex}}(\Delta\mu)$, in figure 3.9(a) indicates that a first-order 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 3.9(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 surface phase rule, equation (1.46).

The adsorption diverges as $\Delta\mu \rightarrow \Delta\mu_{cc}(T)$ indicating that CC in a capped capillary is a continuous phenomenon. The critical exponent for the diverging height of the liquid slab was first obtained analytically by Parry et al. in [152]:

$$\Gamma \sim (\mu_{cc} - \mu)^{-1/4}. \quad (3.30)$$

The value of the exponent can be inferred following the same line of arguments as for the planar wall, see section 3.1 and equations (3.5) and (3.7). The divergence of the meniscus height (which is proportional to the adsorption) is determined by the leading power of the decaying effective interface potential.

In the case of the capped capillary the full external potential acting on the fluid is given by equation (1.30), and after separating the y -dependent external potential of a slit pore (see equation (1.57)), the x -dependent part is expressed by $V^{\text{cap}}(x, y)$ in equation (1.58), which is equivalent to the external potential acting on the fluid from the infinite rectangular slab of substrate material capping the slit pore to form the capillary (see chunk 2 in figure 3.8). It follows from equations (1.58) and (1.56) that $V^{\text{cap}}(x, y) \sim 1/x^4$ as $x \rightarrow \infty$. We then employ the sharp-kink approximation for the slab of capillary liquid of length h adsorbed on the capping wall and insert it into the expression for $\Omega[\rho]$ in equation (1.35). Integrating over the volume of vapour we would have to integrate $V^{\text{cap}}(x, y)$ over x from h to infinity to get the effective interface potential $\omega_{\text{cpd}}(h)$ (see also discussion in section 3.1). Thus, to leading power it would decay with h as [152, 181]

$$\omega_{\text{cpd}}(h) \sim \frac{1}{h^3}. \quad (3.31)$$

The total effective potential, $V_{\text{cpd}}(h)$, includes the capillary bulk energy contribution corresponding to the work necessary to replace a slab of vapour with a slab of capillary-liquid

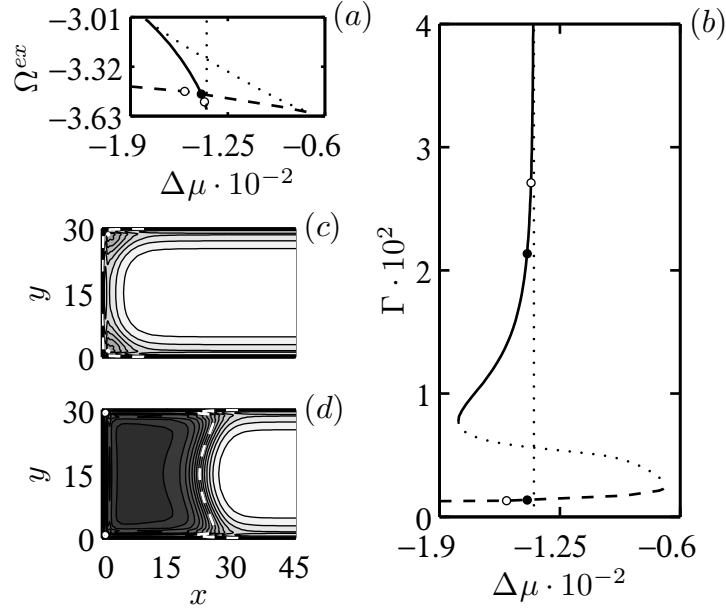


Figure 3.9: Capillary prewetting transition at $T = 0.93$, $\Delta\mu_{cpw}(T) = -1.43 \cdot 10^{-2}$ in the capped capillary with $H = 30$, $\varepsilon_w = 0.85$, $\sigma_w = 1.35$, $H_0 = 2.2$; fluid treated in WDA, planar $T_w = 0.927$. CC of the associated slit pore (capillary bulk) is at $\Delta\mu_{cc}(T) = -1.39 \cdot 10^{-2}$. (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 surface phases, coexisting at $\Delta\mu_{cpw}$: 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 $\Delta\mu = \Delta\mu_{cc}$, indicated by vertical dotted line). Capillary prewetting is marked by the filled circle at $\Delta\mu_{cpw}$ and $\Omega^{ex}(\Delta\mu_{cpw}) = -3.49$. Open circles show the two continuation data points, whose corresponding density profiles were used as initial guess in equation (1.48). (b) Adsorption isotherm. Line styles and open circles are defined as in plot (a). Note that $\Delta\mu = \Delta\mu_{cc}$ 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 $\rho_{cc}^{vap}(T) = 0.1$ (white), and $\rho_{cc}^{liq}(T) = 0.43$ (dark grey). The white dashed line indicates interface between vapour and capillary-liquid.

($\sim (\mu - \mu_{cc}) h$):

$$V_{cpd}(h) \sim (\mu - \mu_{cc}) h + \frac{A}{h^3}. \quad (3.32)$$

The condition of the above being minimised by the equilibrium height of the meniscus h gives rise to the value of exponent in equation (3.30).

We now return to the discussion of the first-order transition taking place near the capping wall. The coexisting density profiles are shown in figures 3.9(c) and 3.9(d). For illustration purposes, throughout the manuscript filled contours of 2D density profiles are coloured in

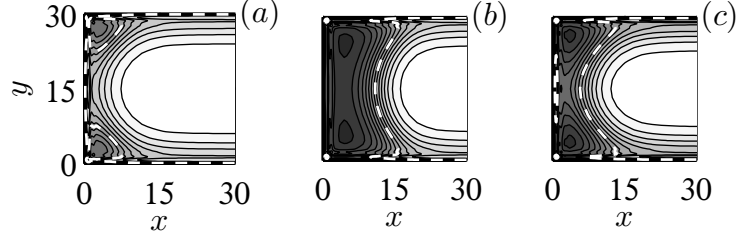


Figure 3.10: Density profiles coexisting during capillary prewetting at different values of T in the capillary of figure 3.9. (a) and (b) $T = 0.95$, $\Delta\mu_{cc}(T) = -1.4 \cdot 10^{-2}$, $\Delta\mu_{cpw}(T) = -1.7 \cdot 10^{-2}$, reference densities: $\rho_{cc}^{\text{vap}} = 0.11$, $\rho_{cc}^{\text{liq}} = 0.40$. The isotherms have a single Van der Waals loop and look similar to those in figure 3.9 (a), (b). However, the coexisting density profile (a) from the vapour branch of $\Omega^{\text{ex}}(\Delta\mu)$ has a different topology: it shows corner drops. (c) Density profile at the critical capillary prewetting point, at $T_{cpw}^{\text{cr}} = 0.963$, $\Delta\mu_{cpw}^{\text{cr}} \equiv \Delta\mu_{cpw}(T_{cpw}^{\text{cr}}) = -1.9 \cdot 10^{-2}$ (see figure 3.11); $\Delta\mu_{cc}(T_{cpw}^{\text{cr}}) = -1.4 \cdot 10^{-2}$, $\rho_{cc}^{\text{vap}} = 0.13$, $\rho_{cc}^{\text{liq}} = 0.37$.

shades of grey between bulk vapour-like and bulk liquid-like densities at CC, at the given temperature, $\rho_{cc}^{\text{vap}} \equiv \rho_{cc}^{\text{vap}}(\Delta\mu_{cc}(T), T)$ (white) and $\rho_{cc}^{\text{liq}} \equiv \rho_{cc}^{\text{liq}}(\Delta\mu_{cc}(T), T)$ (dark grey), respectively. The values of ρ_{cc}^{vap} and ρ_{cc}^{liq} can be obtained for the given temperature T by solving the bulk equation (1.38) at the value of μ corresponding to the CC at the same temperature. The value of μ at CC is, in turn, obtained by solving the DF equations for the slit pore associated with the capped capillary (in practice for each type of substrate the surface phase diagram of capillary bulk (associated slit pore), $\Delta\mu = \Delta\mu_{cc}(T)$, had been computed, and particular values of $\Delta\mu_{cc}(T)$ were then obtained by interpolating the vapour – capillary-liquid transition line). We further define the sharp liquid – vapour interface (dashed white line) by the Gibbs dividing surface, forming the level set at the value $(\rho_{cc}^{\text{vap}} + \rho_{cc}^{\text{liq}})/2$.

For the purposes of all subsequent discussions we note again (see also section 1.3) that within the DF treatment a thermodynamically stable surface phase of the fluid can be identified with a concave branch of the grand potential (or its excess contribution, Ω^{ex}), as a function of the control parameter ($\Delta\mu$). When the fluid can have multiple surface phases, its free energy has multiple concave branches. The transition value of the control parameter, where two (or more) fluid surface 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, $\mu = \mu_{\text{sat}} + \Delta\mu$. We consider isothermal thermodynamic routes (T is fixed), which singles out the only control parameter – μ . In what follows we will identify completely a concave branch of the excess free energy as a function of the chemical potential, $\Omega^{\text{ex}}(\Delta\mu)$, with the concept of a fluid surface phase.

We will discuss the structure of 2D density profiles, $\rho^{\text{cpd}}(x, y)$, in detail in section 3.2.3, 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 calculated coexisting profiles are quite representative of the two fluid surface phases corresponding to the intersecting stable branches of $\Omega^{\text{ex}}(\Delta\mu)$, figure 3.9(a). We will refer to them as *vapour* (dashed line, typical profiles are shown in figures 3.9(c) and 3.10(a)) and *capillary-liquid slab* (solid line, typical profiles are shown in figures 3.9(d) and 3.10(b)). As will be made clear in section 3.2.2 from the consideration of the full surface phase diagram, this first-order transition is indicative of a new surface phase transition, first-order capillary wetting, in the same way as, e.g., the wall prewetting is indicative of the first-order wall wetting (see section 3.1). We therefore refer to the transition discussed as *capillary prewetting*.

For wide capillaries, where the corners are sufficiently isolated, one might expect a mechanism of wetting related to the filling of the 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 show distinct droplet-like structures with sharp interfaces. An example is given in figures 3.10(a) and 3.10(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 3.9 (only two concave branches). The development of drops in the corners occurs continuously from the vapour phase (at low $\Delta\mu$ the density profiles are of the type shown in figure 3.10(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 3.2.3, there can be an additional first-order transition associated with drop formation in capillary corners. It exists only within a mean-field level of treatment and is related to wedge prefilling (see, e.g., the paper by Rejmer et al. in reference [182]). Finally, we note that a further increase of T leads to mean-field criticality of the capillary prewetting transition and the calculated coexisting density profiles become indistinguishable, see figure 3.10(c). We will return to the mean-field DF description of critical points in the later section 3.3.1. However, we note that beyond mean-field the critical point of capillary prewetting with the density profile shown in figure 3.10(c) does not exist [177, 182], as it belongs to the 1D Ising universality class.

3.2.2 Phase diagram

To systematise the first-order surface phase transitions in the capped capillary, we obtain the complete surface phase diagram, where we plot the deviation chemical potential of the transitions versus the transition temperature. Thus, one wetting isotherm (e.g., figure 3.9) possibly corresponds to one point on the line forming the locus of surface phase transitions in the $T - \Delta\mu$ space (we will refer to them as *transition lines*). The surface phase diagram of the capped capillary from the previous section is presented in figure 3.11 and consists of two transition lines. The CC line of the associated slit pore (capillary bulk) $\Delta\mu_{\text{cc}}(T)$ (grey),

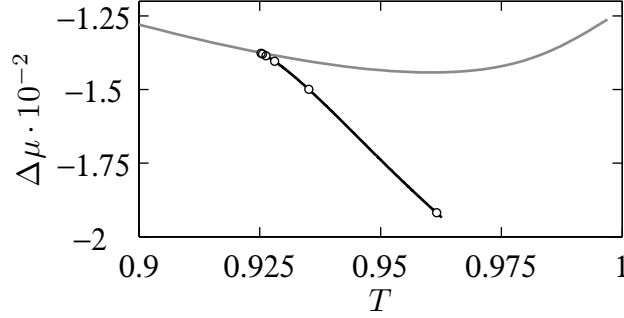


Figure 3.11: Full surface phase diagram of wetting in the capped capillary with $H = 30$ from figure 3.9. The CC line of capillary bulk (associated slit pore), $\Delta\mu_{cc}(T)$, is plotted in grey. It ends at the CC critical point, $(T_{cc}^{cr}, \Delta\mu_{cc}^{cr}) \equiv (0.996, -1.26 \cdot 10^{-2})$. 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 the 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 3.12.

forms in the case of the capped capillary the locus of continuous transitions corresponding to the diverging adsorption (see figure 3.9(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 3.9(a)).

Each point on a transition line corresponds to the two coexisting density profiles ρ_1 and ρ_2 , and the chemical potential of the transition μ , which enter equation (1.48) as unknowns. For the $\Delta\mu_{cc}(T)$ -line: $\rho_1 \equiv \rho_1^{slt}(y)$ and $\rho_2 \equiv \rho_2^{slt}(y)$ are the coexisting vapour and capillary-liquid density profiles inside the slit pore (where CC is of first order) and $\Omega^{ex} \equiv \Omega[\rho_y]$, as defined by equation (1.35) in the space of 1D fluid configurations, $\rho(\mathbf{r}) \equiv \rho^{slt}(y)$. Each point on $\Delta\mu_{cpw}(T)$ -line, in turn, satisfies the same equation, where $\rho_1 \equiv \rho_1^{cpd}(x, y)$ and $\rho_2 \equiv \rho_2^{cpd}(x, y)$ are the 2D density configurations coexisting inside the capped capillary during the first-order vapour – slab transition, and Ω^{ex} is defined by equation (3.28).

In practice, to find a solution to equation (1.48) by, e.g., a Newton's method, one needs to provide an initial guess of the coexisting density profiles and the transition chemical potential. Equation (1.48) is highly non-linear and 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 (1.48) at a given temperature, one can, e.g., compute a free energy isotherm at that temperature (e.g., figure 3.9(a)), find by interpolation the approximate intersection point of its branches, which would provide the initial guess for μ . The two density profiles, corresponding to the data points on the excess free energy isotherm and belonging to vapour and slab branches, closest to the intersection, can provide the initial guess for ρ_1 and ρ_2 . In the example from figure 3.9, the data points giving rise to the initial guess for equation (1.48) 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 the 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 (1.48) on T parametrises the set of first-order surface 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 one 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 (1.48), where T is treated as the parameter, see section 2.2.1 for details of the algorithm. 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 tracing with μ an easily obtainable density vapour profile). The danger of tracing a particular surface phase transition with T is that one obtains only line of that particular transition; the approach is oblivious to the possible presence of other first-order transitions occurring at the same T , but possibly at a different μ , which can be revealed by a Van der Waals loop on the isotherm. Therefore, after computing the surface phase diagram by tracing each transition line individually with arc-length continuation, we selectively compute several isotherms from the considered range of temperatures – to make sure, that there are no unaccounted surface phase transition in that range.

Let us consider the surface phase diagram from figure 3.11 in more detail. The CC transition line, $\Delta\mu_{cc}(T)$ (grey), forms the full surface 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 in the surface 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 Kelvin equation (3.26). Note the minimum of $\Delta\mu_{cc}(T)$ in the vicinity of the planar wetting temperature $T_w = 0.927$, which was predicted by the Kelvin equation (see discussion following equation (3.26)).

The capped capillary reduces to its associated slit pore as $x \rightarrow \infty$, thus CC is the *bulk transition* for the capped capillary. Let consider in detail the $\Delta\mu_{cpw}(T)$ -line extending into the bulk vapour segment of the full surface phase diagram and show that it indeed run tangent to the CC line. Writing again the surface Clausius-Clapeyron equation for the slope of the coexistence curve between large and small capillary-liquid slabs (3.15), which was derived from first principles of thermodynamics in section 3.1, we have in complete analogy with the

discussion of equations (3.16) and (3.17):

$$(s_1 - s_2) dT + (\Gamma_1 - \Gamma_2) d\mu = 0, \quad (3.33)$$

where the indexa 1 and 2 denote the small and large capillary-liquid slabs coexisting during capillary prewetting and $d\mu$ is counted from $\mu_{cc}(T)$. For the large coexisting meniscus with adsorption Γ_2 we have the asymptote near CC (see equation (3.30)) $\Gamma_2 \sim (\Delta\mu_{cc} - \Delta\mu_{cpw})^{-1/4}$, while Γ_1 of the smaller coexisting slab is finite in the limit $T \rightarrow T_{cw}$. Integrating the above over temperature from T_{cw} to some $T > T_{cw}$, we have

$$\begin{aligned} \Delta\mu_{cc} - \Delta\mu_{cpw} &= 1/(\Gamma_2 - \Gamma_1) \int_{T_{cw}}^T (s_1 - s_2) dT \\ &\sim (\Delta\mu_{cc} - \Delta\mu_{cpw})^{1/4} (T - T_w). \end{aligned} \quad (3.34)$$

Thus the capillary prewetting line is indeed tangent to the CC line and approaches it with the exponent 4/3:

$$\Delta\mu_{cc} - \Delta\mu_{cpw} \sim (T - T_{cw})^{4/3}, \quad (3.35)$$

as $T \rightarrow T_{cw}$.

Returning to our DF calculation consider figure 3.12(a), which shows the liquid – vapour interfaces (menisci) of the fluid configurations with capillary-liquid slabs, coexisting during capillary prewetting with vapour configurations. On the $\Delta\mu_{cpw}(T)$ -line in figure 3.11, the respective transitions are marked by open circles. As the value of T is lowered quasi-statically, the meniscus of the coexisting slab configurations unbinds into the capillary bulk. In the surface phase diagram such fluid configurations fall on the $\Delta\mu_{cpw}(T)$ -line, where it approaches the $\Delta\mu_{cc}(T)$ -line. We can define the measure of the “meniscus height”, i.e., the distance from the capping wall to the liquid meniscus as:²

$$L_m = \Gamma / (H\rho_{cc}^{\text{liq}}). \quad (3.36)$$

As it is clear from figure 3.12(b), where we plot L_m for the configurations in figure 3.12(a) as a function of T , the menisci heights of coexisting slab configurations diverge along the $\Delta\mu_{cpw}(T)$ -line, as it approaches the CC line. There clearly exists a *limiting* value of temperature, $T = T_{cw}$, such that $L_m \rightarrow \infty$ as $T \rightarrow T_{cw}$ and the entire capillary is filled with capillary-liquid. Moreover, according to the equations (3.30) and (3.35), the divergence of slab length follows the law

$$L_m \sim (T - T_{cw})^{-1/3}, \quad (3.37)$$

as $T \rightarrow T_{cw}$.

²See also, e.g., the definition of the effective height of film adsorbed on a planar wall in equation (3.1).

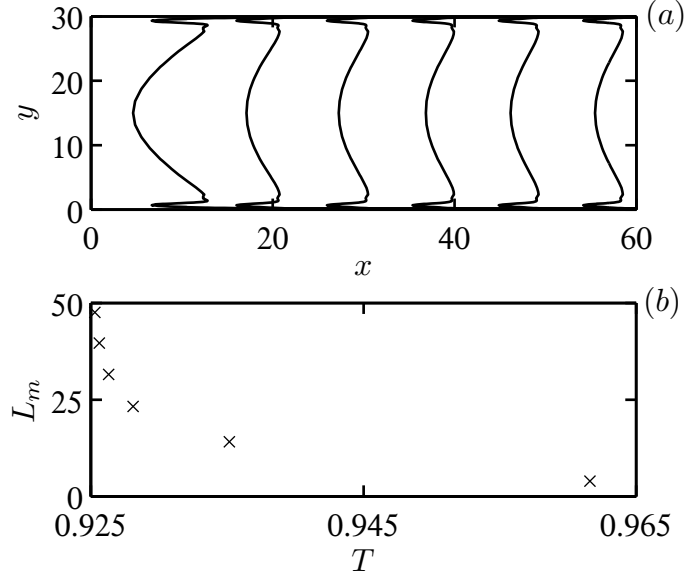


Figure 3.12: A set of fluid configurations coexisting during capillary prewetting. (a) Liquid menisci of configurations inside the capped capillary with parameters given in the caption of figure 3.9, coexisting with vapour configurations during capillary prewetting transitions at values of T (right to 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 surface phase diagram, figure 3.11. (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 $T \rightarrow T_{cw} \approx 0.925$.

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 $(T_{cw}, \Delta\mu_{cpw}(T_{cw}))$ in the surface phase diagram belongs to *both* transition lines, namely $\Delta\mu_{cc}(T_{cw}) = \Delta\mu_{cpw}(T_{cw})$. Thus, the $\Delta\mu_{cpw}(T_{cw})$ -line approaches the $\Delta\mu_{cc}(T_{cw})$ as $T \rightarrow T_{cw}$, and has a single common point with it at $T = T_{cw}$. In other words, our DF calculation reproduces the fact that $\Delta\mu_{cpw}(T_{cw})$ -line runs tangent to the CC line.

The phenomenology of wetting in 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 $\Delta\mu_{cpw}(T)$ -line acts as the wall prewetting line, see section 3.1. 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* [6, 5]. Note that in the discussion of our numerical results the existence of capillary wetting temperature follows from the observed divergence of the coexisting slab configurations, as the CC transition line is approached along the capillary prewetting line. In our DF approach T_{cw}

is associated with an infinitely long coexisting capillary-liquid slab, but the actual calculations are always restricted to a finite domain. For every calculated surface phase diagram we provide the value of the accuracy, Δ_{cw} , for the calculated capillary wetting temperature, $\bar{T}_{\text{cw}} \approx T_{\text{cw}}$, which we define as the distance of the last computed point on $\Delta\mu_{\text{cw}}$ -line to $\Delta\mu_{\text{cc}}$ -line along the $\Delta\mu$ -axis.

$$\Delta_{\text{cw}} \equiv |\Delta\mu_{\text{cpw}}(\bar{T}_{\text{cw}}) - \Delta\mu_{\text{cc}}(\bar{T}_{\text{cw}})|. \quad (3.38)$$

Let us summarise the mean-field phenomenology inferred with the help of DF calculations. Capillary wetting temperature separates two types of CC. For isothermal thermodynamic routes to CC at $T < T_{\text{cw}}$ the surface phase with a finite capillary-liquid slab is metastable. CC then is of first order, and the 2D capped capillary pore behaves in the same way as a 1D slit pore. On the other hand, at $T > T_{\text{cw}}$ CC is a continuous transition. The capillary-liquid slab grows continuously into the capillary bulk as, e.g., $\mu \rightarrow \mu_{\text{cc}}$ isothermally. If the capillary prewetting line is crossed (see figure 3.11), CC is preceded by the first-order surface phase transition between fluid vapour and a capillary-liquid slab of finite length (e.g., figure 3.9). Hence, in our mean-field treatment an isothermal approach to CC at $T = T_{\text{cw}}$ can be viewed as the limiting case of capillary prewetting, where the coexisting slab is of infinite length: $L_{\text{m}} \rightarrow \infty$. The higher-temperature end of the capillary prewetting line at $T = T_{\text{cpw}}^{\text{cr}}$ is a critical point: the coexisting mean-field configurations become structurally indistinguishable and the branches of free energy defining vapour and slab surface phases align to form a single branch in the limit $T \rightarrow T_{\text{cpw}}^{\text{cr}}$. The critical prewetting density profile for the capped capillary considered in this section is shown in figure 3.10(c).

Beyond mean-field the critical point of capillary prewetting does not exist, as it belongs to the 1D Ising universality class: for configurations near the capping wall the correlation length along the interface between capillary-liquid and vapour can diverge only along a single direction. A recent study by Rascon and co-workers [177] revealed that beyond mean-field the capillary prewetting transition is rounded by fluctuation, but the transition at T_{w} survives. For $T \rightarrow T_{\text{cw}}$ the capillary wetting transition is continuous due to strong fluctuation effects, which also reduce the mean-field value of T_{w} .

3.2.3 Fluid structure, connection to wedge wetting

Here we explore in more detail the microscopic surface phases formed near the capping wall. First, we describe in detail the fluid structure, second, we come back to the question from the previous section about whether the mechanism of corner wetting can 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 3.10(a)), but the formation of such configurations happened continuously and was not associated with a separate concave branch of excess free energy. Let us consider a capillary with a stronger substrate potential (lower planar T_{w}): $\varepsilon_{\text{w}} = 0.85$, $\sigma_{\text{w}} = 1.5$, $H_0 = 2.8$, $H = 30$. The fluid is treated in WDA, the

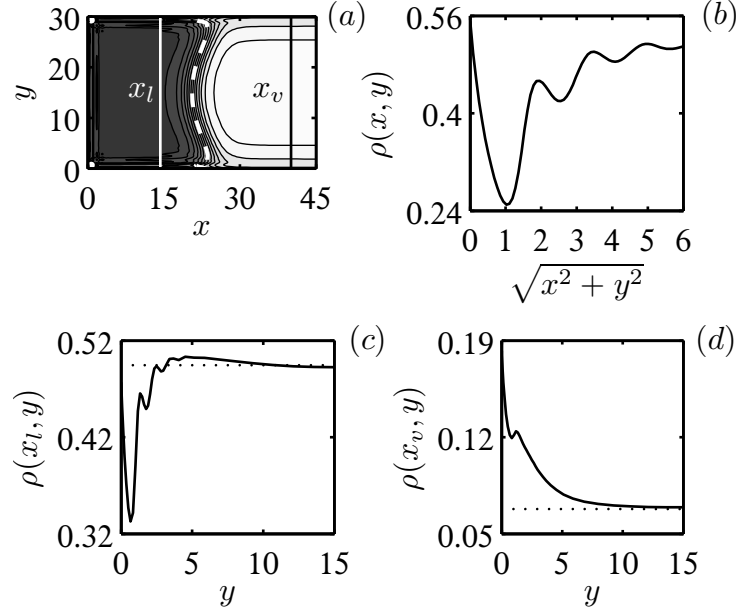


Figure 3.13: (a) Density profile of the coexisting capillary-liquid slab configuration at $T = 0.88$, $\Delta\mu_{cpw}(T) = -2.4 \cdot 10^{-2}$ in the capillary with $H = 30$, $\varepsilon_w = 0.85$, $\sigma_w = 1.5$, $H_0 = 2.8$; the fluid is treated in WDA, planar $T_w = 0.868$. Vertical lines show 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 $\rho_{cc}^{liq} = 0.5$ and $\rho_{cc}^{vap} = 0.07$.

planar wetting temperature: $T_w = 0.868$. The capillary wetting temperature is $T_{cw} = 0.87$, with the accuracy $\Delta_{cw} = 0.006 \cdot 10^{-2}$.

Structure of adsorbate

We discuss the fluid structure for 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_{cw} – for the slab surface phase to be thermodynamically stable. We chose the value $T = 0.88$, just above T_{cw} . All the 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 without loss of generality we have fixed (see section 1.3 and table 1.1). The WDA treatment of the repulsive fluid free energy developed from the analysis of the molecular fluid-fluid correlations [49] treats the repulsions non-locally and captures this excluded volume effect in the microscopic fluid structure.

Figure 3.13 shows the density profile (figure 3.13(a)) and three representative cross sections: along the corner bisector (figure 3.13(b)), well inside capillary-liquid (at x_1 , figure 3.13(c)) and vapour (at x_v , figure 3.13(d)). The values x_1 and x_v are marked on the density profile by white and black vertical lines. Considering the slice along the corner bisector in figure 3.13(b), we note pronounced oscillations with maxima set approximately one hard sphere diameter apart, with amplitude rapidly (exponentially, [74]) decaying away from the apex of the corner. The same is true about the slice inside capillary-liquid in figure 3.13(c). Even along a slice inside vapour one can see a single oscillation, figure 3.13(d).

The horizontal dotted lines in figures 3.13(c) and 3.13(d) mark the values of ρ_{cc}^{liq} and ρ_{cc}^{vap} . The slices presented uncover further the physics of an isothermal slab growth as $\mu \rightarrow \mu_{cc}$ and illustrate the reasoning behind our choice of the reference values ρ_{cc}^{vap} and ρ_{cc}^{liq} to scale plotted data. As can be seen from the figures, the density slices inside each surface phase, $\rho(x_1, y)$ and $\rho(x_v, y)$, tend to their corresponding reference values, ρ_{cc}^{liq} and ρ_{cc}^{vap} , with $y \rightarrow H/2$. Moreover, our computations show that, generally, the density cross sections taken well inside the vapour and slab surface phases are *identical* (within the margin of machine rounding errors) 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 :

$$\begin{aligned}\rho(x_1, y) &\equiv \rho_{y,\text{liq}}(y), \\ \rho(x_v, y) &\equiv \rho_{y,\text{vap}}(y).\end{aligned}\tag{3.39}$$

The latter result is very important for the proposed analogy in the phenomenology of wetting in 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., figure 3.6, figure 3.7 and reference [3]. 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 in a capped capillary, the role of the bulk is played by the fluid surface phase of the associated slit pore. Increasing μ at $T > T_{cw}$ leads to the formation of the liquid-like slab, whose length diverges in the limit of the continuous CC, as $\mu \rightarrow \mu_{cc}$. The equivalence expressed by equations (3.39) 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 similar to that of planar wetting. Note, however, that the critical exponents characterising wetting in a capped

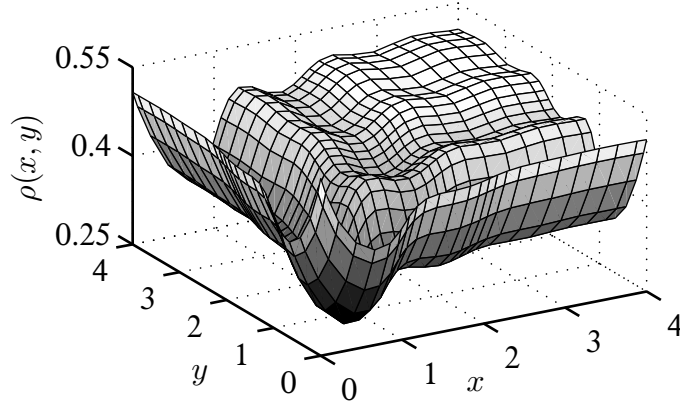


Figure 3.14: Surface plot of the density profile from figure 3.13(a) in the near-corner region showing the oscillations of fluid density caused by non-local excluded volume interactions.

capillary are different from those of planar wetting, see references [152, 177]. For example, in the case of the planar wall $\Gamma \sim \Delta\mu^{-1/3}$ as $\Delta\mu \rightarrow 0$, while in the case of the capped capillary $\Gamma \sim (\mu_{cc}-\mu)^{-1/4}$ as $\mu \rightarrow \mu_{cc}$. We return to critical exponents in more detail in section 3.2.4.

The spatially heterogeneous near-corner fluid structure is best visualised with a surface plot of $\rho^{\text{cpd}}(x, y)$ and is presented in figure 3.14. Considering it in more detail, we note that the density oscillations are primarily localised 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 3.13(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., [183]. 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 μ , as was done, e.g., by Henderson in [184] for open wedges immersed in liquid.

Relation to wetting in wedges

A careful investigation of the fluid surface phase behaviour reveals that apart from the capillary prewetting, an additional first-order surface 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

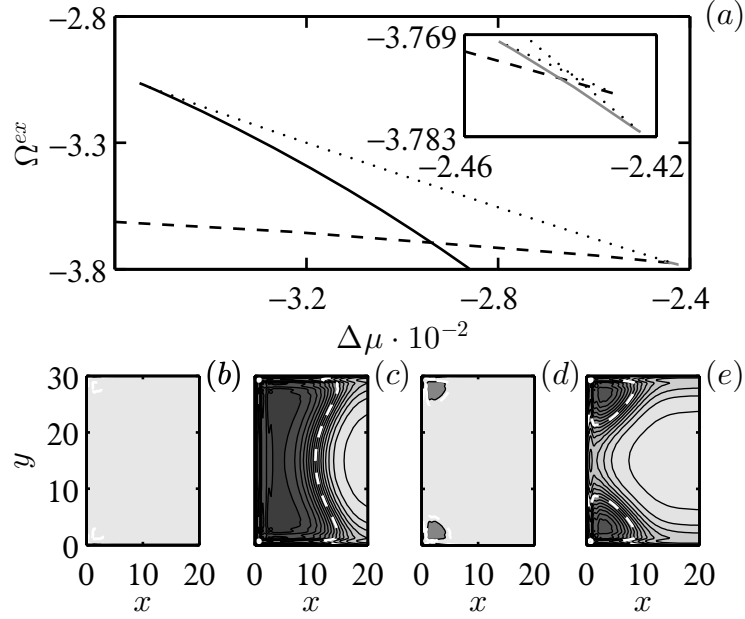


Figure 3.15: Isothermal adsorption in capillary from figure 3.13 at $T = 0.906$; $\Delta\mu_{cc}(T) = -2.4 \cdot 10^{-2}$, reference densities: $\rho_{cc}^{\text{vap}} = 0.08$, $\rho_{cc}^{\text{liq}} = 0.46$. (a) Excess free energy isotherm. It possesses three concave branches (connected by non-concave branches, dotted line), which define three surface phases: vapour (dashed), capillary-liquid (solid black) and drops (solid grey, see inset). There are two consecutive surface phase transitions (revealed by intersections of concave branches): capillary prewetting, at $\Delta\mu_{cpw} = -2.94 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -3.70$, and (metastable, see inset) shifted wedge prefilling, at $\Delta\tilde{\mu}_{wpw} = -2.44 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -3.77$. (b) and (c) Coexisting profiles at capillary prewetting. (d) and (e) Coexisting profiles at (metastable) shifted wedge prefilling.

free energy isotherm is shown in figure 3.15(a) and has three concave branches, which define the surface phases of vapour (dashed line), capillary-liquid slab (black solid line) and corner drops (grey solid line, see inset). The isotherm exhibits two Van der Waals loops, that of capillary prewetting (where the dashed branch crosses the solid black one), and that of the additional (metastable) surface phase transition (where the dashed branch crosses the solid grey branch, magnified on the inset). The density profiles of the two consecutive transitions are shown in figures 3.15(b) – 3.15(e). Note that the vapour configuration coexisting with the capillary-liquid slab (figure 3.15(b)), possesses a level set at $(\rho_{cc}^{\text{vap}} + \rho_{cc}^{\text{liq}})/2$, noticeable in the capillary corners. The existence of that level set here is due to the excluded volume effects and the resulting near-wall density oscillations, unlike, e.g., the configurations with corner drops on plots (d) and (e), which coexist during the first-order transition, see inset of figure 3.15(a).

The full surface phase diagram of the capped capillary is shown in figure 3.16. The grey curve is the CC transition line ($\Delta\mu_{cc}(T)$), the black curves are the capillary prewetting tran-

sition 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 3.15(a), taking place between vapour and drop surface phases. We will denote it $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line. In our example it is bounded at the lower- T end, at $T_0 = 0.905$, and at the higher- T end at $T \equiv \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.908$).

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 surface phase diagram in figure 3.11 we have $T_{\text{cw}}^{\text{cr}} - \bar{T}_{\text{cw}} \approx 0.374$, while for the one in figure 3.16 we have $T_{\text{cw}}^{\text{cr}} - \bar{T}_{\text{cw}} \approx 0.737$. The effect can be attributed to the relatively stronger 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 stronger substrate. For the capillary in figure 3.11 we have $T_{\text{w}} = 0.927$, while for the capillary in figure 3.16 the value is lower: $T_{\text{w}} = 0.868$. In planar wetting a stronger attracting substrate also has a more pronounced prewetting transition line, as is demonstrated by, e.g., figure 3.4.

Regarding the $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line we note that its higher-temperature end at $T = \tilde{T}_{\text{wpw}}^{\text{cr}}$ is a mean-field critical point. Computing various free energy isotherms for $T \rightarrow (\tilde{T}_{\text{wpw}}^{\text{cr}})^-$ we find, that the concave branch defining the drop surface phase tends to align with the branch defining the vapour surface phase (see, e.g., dashed and solid grey lines in figure 3.15(a)) and forms a single branch in the above limit. The density profiles of fluid configurations coexisting along the $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -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 $T \lesssim \tilde{T}_0$ the excess free energy isotherms still possess three concave branches, with the branch defining the drop surface 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 3.10(a) and 3.10(b)). Although the nature of the phenomenon was unclear, the relation to wetting in a wedge was prompted by the fluid structure. On the other hand, we have established that a surface phase diagram of the capped capillary can possess a separate transition line, $\Delta\tilde{\mu}_{\text{wpw}}(T)$, forming the locus of first-order transitions between fluid configurations with corner drops. We also found, that the $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line ends at a critical temperature, $\tilde{T}_{\text{wpw}}^{\text{cr}}$, above which the formation of corner drops happens continuously with increasing $\Delta\mu$ at a fixed T . So, by considering again the continuous formation of the corner drops in the capillary from the previous section (figure 3.10(a)), we see that somehow the effect of criticality at $\tilde{T}_{\text{wpw}}^{\text{cr}}$ is still present, even though the transition line (which should end at $T = \tilde{T}_{\text{wpw}}^{\text{cr}}$) is not found on the full surface phase diagram (figure 3.11). Such an effect is only possible, if the transition to configurations with corner drops (given in the case of figure 3.16 by the $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line) is not related to the capped capillary, but exists independently. Based on these arguments, we now can relate the transition line $\Delta\tilde{\mu}_{\text{wpw}}(T)$ to wedge prefilling (whose transition line we would denote

$\Delta\mu_{\text{wpw}}(T)$), which is studied in, e.g., the work by Rejmer et al. in reference [182].

Since the capped capillary exhibits features specific to adsorption on right-angled wedges, let us briefly discuss wetting on a 2D wedge starting from the macroscopic thermodynamic picture and proceeding to finer features due to surface effects and fluctuations. The Kelvin shift expressed by equation (3.25) is equivalent to the expression for the additional (positive) pressure in the phase situated on the concave side of the curved meniscus between liquid and vapour:

$$\Delta P = \sigma/R, \quad (3.40)$$

where R is the radius of curvature of the meniscus [113].

Consider a wedge in contact with undersaturated bulk vapour whose chemical potential is close to saturation, so that in principle thermodynamically there may be a metastable liquid phase with the same chemical potential. The pressure inside such liquid phase is *lower* than the pressure of the stable vapour at the same chemical potential. It follows from equation (3.40) then, that there can only be a macroscopic amount of (metastable) liquid at the apex of the wedge, when it is situated on the convex side of the meniscus which it forms with the bulk vapour (so that the bulk vapour, which has a higher pressure, is on the concave side of the meniscus). This provides a restriction on the contact angle, Θ , which has to be less or equal to the angle which a line orthogonal to the bisector of the wedge makes with each of its sides (such line forms a limiting case between a concave and a convex shape of the liquid-vapour meniscus when liquid is adsorbed in the wedge apex):

$$\Theta(T) \leq \pi/2 - \alpha/2, \quad (3.41)$$

where α is the opening angle of the wedge [185]. If we now approach saturation isothermally, it follows that the above condition defines the range of temperatures, where the wedge can be wet by liquid at saturation. The upper limit on Θ defines the filling temperature of the wedge T_f (it is always less than the planar T_w , where $\Theta(T_w) = 0$) as $\Theta(T_f) = \pi/2 - \alpha/2$. For the right-angled wedge, which we are dealing with in the case of a capped capillary this transforms to

$$\Theta(T_f) = \pi/4. \quad (3.42)$$

A microscopic mean-field approach to wetting on 2D wedges shows that a complete wedge filling may be preceded off coexistence and above T_f by first-order transitions between fluid configurations with drops of different sizes formed at the apex. The line of such transitions runs tangent to bulk saturation at T_f and possess a critical point [182]. Beyond mean-field such “prefilling” transition is rounded by fluctuations, and its critical point does not exist, because it belongs to the 1D Ising universality class (since the transition happens near the apex, the correlation length parallel to the interface can diverge only in one direction). On the other hand, the transition at saturation is genuine and can be first-order or continuous

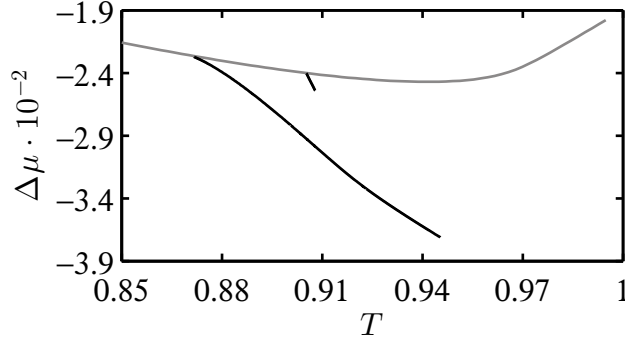


Figure 3.16: Surface phase diagram of the capped capillary from figure 3.13. Solid grey curve: CC-line, ending at $(T_{cc}^{cr}, \Delta\mu_{cc}(T_{cc}^{cr})) = (0.995, -1.97 \cdot 10^{-2})$. Solid black lines: capillary prewetting, $\Delta\mu_{cpw}(T)$, which is tangent to CC at $(T_{cw}, \Delta\mu_{cpw}(T_{cw})) = (0.871, -2.23 \cdot 10^{-2})$, $\Delta_{cw} = 0.0065 \cdot 10^{-2}$, and ends at $(T_{cpw}^{cr}, \Delta\mu_{cpw}(T_{cpw}^{cr})) = (0.945, -3.7 \cdot 10^{-2})$, and shifted wedge prefilling, $\Delta\tilde{\mu}_{wpw}(T)$, which is bounded by $(\tilde{T}_0, \Delta\mu_{cpw}(\tilde{T}_0)) = (0.905, -2.4 \cdot 10^{-2})$ and $(\tilde{T}_{wpw}^{cr}, \Delta\mu_{cpw}(\tilde{T}_{wpw}^{cr})) = (0.908, -2.5 \cdot 10^{-2})$. The lower- T end of shifted wedge prefilling belongs to the CC line.

[186, 155].

Our analysis is based on the mean-field approach, so naturally we come across remnants of wedge prefilling. In section 3.3.1 we show, how our mean-field DF treatment leads to the wedge prefilling line, $\Delta\mu_{wpw}(T)$, being shifted in the capped capillary due to confinement, analogously to how the wall prewetting is shifted in a slit pore [117] (the shifted wall prewetting, just like normal prewetting is a genuine transition and exists beyond mean-field [160]). In the case of the capped capillary discussed in section 3.2.1 (see the surface phase diagram in figure 3.11), the coexisting fluid configurations from figures 3.10(a) and 3.10(b) are supercritical with respect to the shifted wedge prefilling. We expect that either the $\Delta\mu_{wpw}(T)$ -line ends above the $\Delta\mu_{cc}(T)$ -line, or the shift of the $\Delta\mu_{wpw}(T)$ -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, one could compute the full wedge prefilling line, and then study how it is influenced by the addition of a third wall (the second side wall of the capped capillary) at various distances H , and computing the surface phase diagrams of the resulting capped capillaries of varying heights. Such investigation, however, has a quite limited applicability, because beyond the mean-field treatment wedge prefilling is rounded by fluctuations.

Finally, we note that the lower-temperature end of the shifted wedge prefilling line (at $\tilde{T}_0$) does not have to coincide with the CC line, as can be seen from, e.g., figure 3.17, which shows the full surface 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

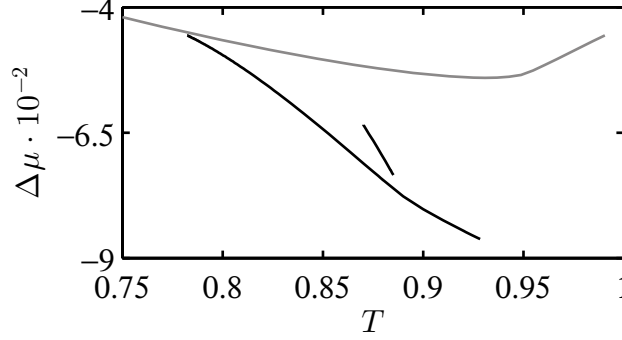


Figure 3.17: Surface phase diagram of the capped capillary with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 30$; fluid treated in LDA, planar $T_w = 0.755$. Solid grey curve: CC-line, ending at $(T_{cc}^{cr}, \Delta\mu_{cc}(T_{cc}^{cr})) = (0.99, -4.56 \cdot 10^{-2})$. Solid black lines: capillary 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 $(T_{cpw}^{cr}, \Delta\mu_{cpw}(T_{cpw}^{cr})) = (0.928, -8.62 \cdot 10^{-2})$, and shifted wedge prefilling, $\Delta\tilde{\mu}_{wpw}(T)$, which is bound by $(\tilde{T}_0, \Delta\mu_{cpw}(\tilde{T}_0)) = (0.87, -6.33 \cdot 10^{-2})$ and $(\tilde{T}_{wpw}^{cr}, \Delta\mu_{cpw}(\tilde{T}_{wpw}^{cr})) = (0.885, -7.34 \cdot 10^{-2})$. Note that lower- T end of shifted wedge prefilling line does not lie on the CC transition line, unlike, e.g., figure 3.16.

system is similar to the one studied by Yatsyshin et al. [5].

3.2.4 A different substrate potential. Critical exponent

One advantage of using a DF approach is that one is not really restricted in the choice of the external potential, and deviating from an intuitively appealing form (1.25) does not entail any additional complications in constructing a DF approximation. Within this subsection we will consider several systems, where the external potential, $V(x, y)$, entering the Euler-Lagrange equation (1.37) is not given by (1.30), (which follows from the definition in (1.25)), but is a combination of three 3-9 potentials from (1.28) [5]:

$$\begin{aligned} V(x, y) &= V_{\varepsilon_w, \sigma_w}^{3-9}(H_0, y) + V_{\varepsilon_w, \sigma_w}^{3-9}(H_0, x) + V_{\varepsilon_w, \sigma_w}^{3-9}(H_0, H - y) \\ &\equiv V^B(y) + V^L(x) + V^T(H - y), \end{aligned} \quad (3.43)$$

where the superscript stands for bottom, left and top walls of the capillary, respectively. For simplicity we fix in this section the value of the capillary width: $H = 30$, and two of the three wall parameters: $\sigma_w = 2$, $H_0 = 5$. We also use the LDA repulsive functional in this section. The examples we present will differ in the values of the strength parameters of the walls, $\varepsilon_w^{(i)}$, which we will provide together with the wetting temperatures, $T_w^{(i)}$, and macroscopic contact angles at saturation, $\Theta^{(i)}$ (see definition in (1.45)), for each $V^{(i)}$ in the equation (3.43).

The model for substrate potential (3.43) was chosen for computational convenience, as well

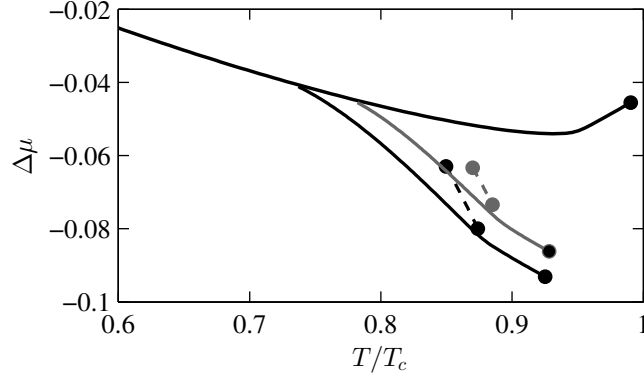


Figure 3.18: Surface phase diagram of the capped capillary from figure 3.17 recomputed using external potential (3.43) with all parameters being the same. Fluid treated in LDA. Black lines show the capillary prewetting transition and the remnant of wedge prefilling computed using substrate potential (3.43). Grey curves reproduce transition lines from figure 3.17.

as to present several non-symmetric examples in a straightforward way. Note that the physics of the external field comes down to the effect of long-ranged pairwise London forces acting between the fluid and the substrate particles, and is inherent in the prescription given by (3.43) as much as in the one given by (1.30). Moreover, the entire spectrum of phenomena discussed should not be restricted to *any* particular model for the substrate, so long as it arises from the dispersive pairwise forces.

First let us show that the mean-field phenomenology described in the previous section is not altered due to a different choice of the substrate. Setting the three walls to have equal values of the strength parameters: $\varepsilon_w^{(i)} = 0.7$, we calculate the full surface phase diagram and contrast it with the one shown in figure 3.17 obtained with the same value, $\varepsilon_w = 0.7$, but using substrate potential (1.30). As can be seen from figure 3.18, the entire surface phase diagram with potential (3.43) (black lines) appears shifted and stretched with respect to the one obtained with the potential (1.30) (grey lines); obviously, the CC transition line is the same in both cases and is plotted with black line.

Next in figure 3.19 we provide several examples, which demonstrate that the topology of the density profiles coexisting during capillary prewetting can vary quite significantly, when the symmetry of the substrate potential is broken, as is shown in figure 3.8. The parameters of the substrate potential (3.43) are given in the caption of the figure for each pair of the coexisting density profiles.

Exponent of slab growth

Consider now the *complete wetting* of the capillary as $\Delta\mu \rightarrow \Delta\mu_{cc}$ isothermally, above T_{cw} . Using an effective Hamiltonian model Parry et al. [152] have obtained the critical exponent

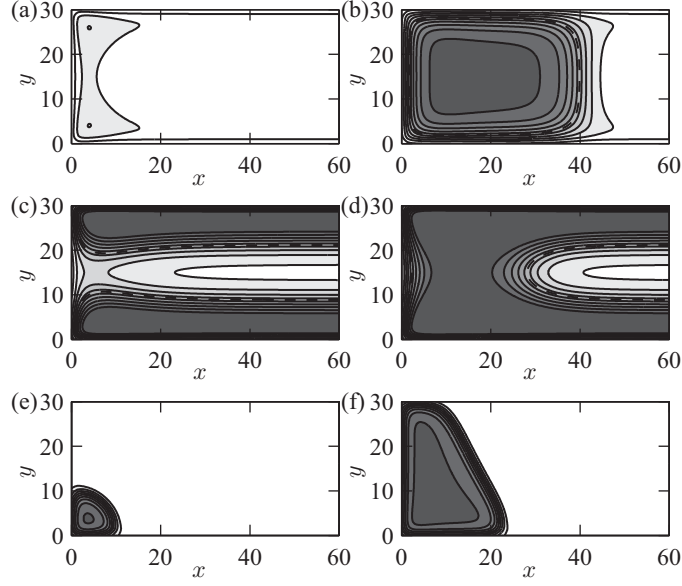


Figure 3.19: Density profiles in non-symmetric capped capillaries coexisting during capillary prewetting [5]. The fluid-substrate potential is given by (3.43). Dashed line is the interface between capillary-liquid and vapour defined as usual, $(\rho_{cc}^{\text{vap}} + \rho_{cc}^{\text{liq}})/2$, see section 3.2.1.

- (a) and (b): $T = 0.95$, $\Delta\mu_{cc} = -8.4 \cdot 10^{-3}$, $\Delta\mu_{cpw} = -9 \cdot 10^{-3}$, $\varepsilon_w^{\text{B}, \text{L}, \text{T}} = .3$, $T_w^{\text{B}, \text{L}, \text{T}} = .96$, $\Theta^{\text{B}, \text{L}, \text{T}} = 31.2^\circ$;
(c) and (d): $T = 0.96$, $\Delta\mu_{cc} = -.058$, $\Delta\mu_{cpw} = -.06$, $\varepsilon_w^{\text{B}, \text{T}} = .8$, $\varepsilon_w^{\text{L}} = .3$, $T_w^{\text{B}, \text{T}} = .71$, $T_w^{\text{L}} = .96$, $\Theta^{\text{B}, \text{L}, \text{T}} = 0$;
(e) and (f): $T = 0.72$, $\Delta\mu_{cc} = -.018$, $\Delta\mu_{cpw} = -.032$, $\varepsilon_w^{\text{B}, \text{L}} = .8$, $\varepsilon_w^{\text{T}} = .3$, $T_w^{\text{B}, \text{L}} = .71$, $T_w^{\text{T}} = .96$, $\Theta^{\text{B}, \text{L}} = 0$, $\Theta^{\text{T}} = 109.25^\circ$.

for the diverging length of the liquid slab. Our DF approach does not impose the existence of an interface; rather the interface is obtained as “output”, using only intermolecular potentials on “input”. This allows us to directly calculate the adsorption, defined in (3.29), which is the natural order parameter in the system, since it is conjugate to the chemical potential, see the Gibbs rule (1.46).

To capture properly the asymptote of the smooth decay of $\rho(x, y)$ into the capillary bulk, which ultimately determines the critical exponent, we used a non-uniform grid, sufficiently dense in the interval $x \leq 100\sigma$ to resolve the liquid-vapour interface, while imposing the boundary condition of contact with the slit pore at $x \sim 10^4$ [5]. The calculations were carried out for a range of temperatures and substrate strength parameters, without truncating the tails of the interaction potentials, $\varphi_{\text{Attr}}(r)$ in (1.59) and $V(x, y)$ in (3.43). Figure 3.20 summarises our results, which seem to agree well with the analytical work of Parry et al. [152], where the asymptote $-1/4$ for the diverging adsorption has been obtained (also see equation (3.30)).

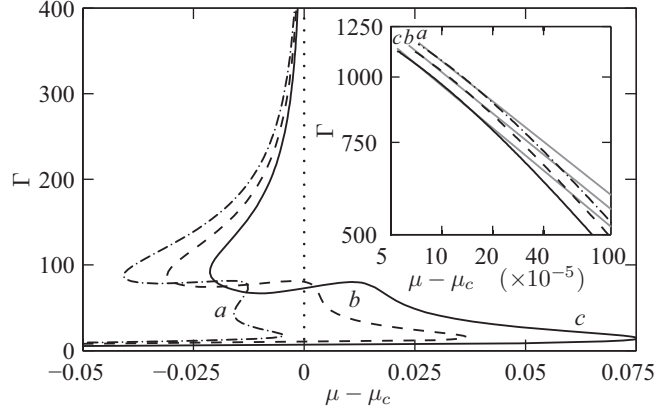


Figure 3.20: Adsorption isotherms at $T = .85$, $\Delta\mu \rightarrow \Delta\mu_{cc}$ of symmetric capped capillaries whose fluid-substrate potential is given by (3.43) [5]. Inset: Estimated critical exponents (black) with a guide to eye (grey): $\Gamma \sim (\mu_{cc} - \mu)^{-1/4}$ [5].
 a : $\varepsilon_w^{B, L, T} = .7$, $T_w^{B, L, T} = .76$, $\Theta^{B, L, T} = 0$, $\Gamma \sim (\mu_{cc} - \mu)^{-.256}$,
 b : $\varepsilon_w^{B, L, T} = .6$, $T_w^{B, L, T} = .82$, $\Theta^{B, L, T} = 0$, $\Gamma \sim (\mu_{cc} - \mu)^{-.262}$,
 c : $\varepsilon_w^{B, L, T} = .5$, $T_w^{B, L, T} = .87$, $\Theta^{B, L, T} = 26.8^\circ$, $\Gamma \sim (\mu_{cc} - \mu)^{-.269}$.

Note that the critical exponent for the complete wetting of the capped capillary (3.30) should not be confused with that for the critical wetting of a two- and three-dimensional wedge obtained by Parry et al. [155, 154] and other authors in, e.g., references [182, 187], as in those cases (analogously to the case of a single planar wall) the shift in chemical potential is counted from saturation: $\Delta\mu = \mu - \mu_{sat}$. The physics of these systems (all of them being considered as bulk complete wetting is approached: $\mu \rightarrow \mu_{sat}$) is, strictly speaking, different from that of the capped capillary, which undergoes complete filling (the CC transition) off of the bulk coexistence, at $\Delta\mu_{cc}$.

3.3 Three-phase coexistence

We complete our description of the surface phase behaviour of LJ fluids confined to capped capillaries by presenting the case of a capillary, which exhibits two types of three-phase coexistence. First, there is the coexistence between the surface phases of vapour, slab and corner drops at the capping wall. Note, however, that those transitions are rounded by fluctuations beyond mean-field. Second, the 1D capillary bulk given by the associated slit pore can have three coexisting surface phases: vapour, capillary-liquid and thick prewetting film adsorbed on each side wall. The interplay of planar prewetting and continuous CC leads to the existence of a new type of surface phase transition – continuous planar prewetting, which should exist beyond the mean-field level of treatment.

Central to the discussion of this section is figure 3.21, which shows the full surface phase diagram of the fluid in the capped capillary with the substrate parameters $\varepsilon_w = 0.7$, $\sigma_w = 2$,

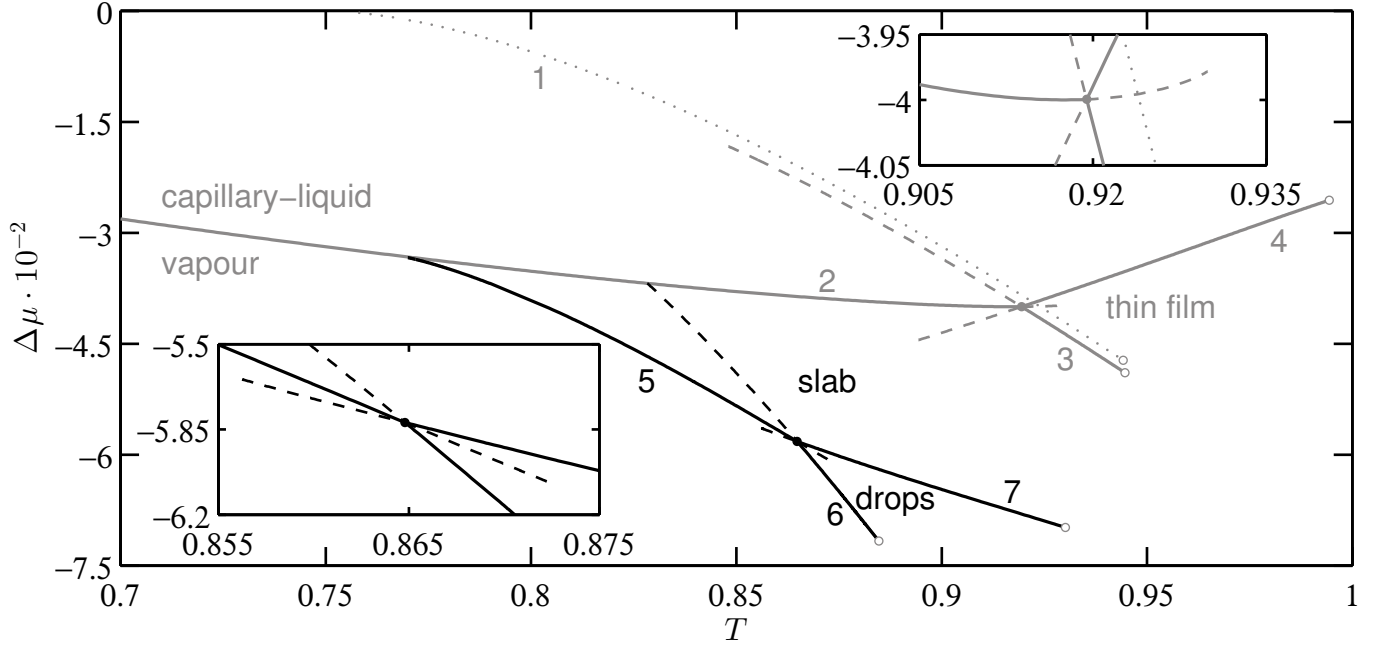


Figure 3.21: Surface phase diagram of the capped capillary with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 40$; fluid treated in LDA, planar $T_w = 0.755$. Grey colour pertains to the capillary bulk (slit pore associated with the capped capillary), black colour – to the capped capillary. Regions where a single surface phase is thermodynamically stable are labelled by a text note. Each transition line is numbered and consists of two parts (except for the planar prewetting line (1, grey, dotted)): solid and dashed, which denote transitions between thermodynamically stable and metastable surface phases, respectively. Filled circles denote triple points. Open circles denote critical points. Insets zoom on the regions containing the triple points of the slit pore, $T_3^{\text{slt}} = 0.920$ and of the capped capillary, $T_3^{\text{cpd}} = 0.865$, respectively. Note that CC transition line consists of stable parts of lines 2 and 4, and capillary prewetting line – of stable parts of lines 5 and 7. Following is the list of transition lines by their labels, with a brief description of coexisting surface phases:

- 1: planar prewetting ($\Delta\mu_{\text{pw}}(T)$, vapour transforms to thick prewetting film), begins at $(T_w, 0) = (0.755, 0)$, ends at $(T_{\text{pw}}^{\text{cr}}, \Delta\mu_{\text{pw}}^{\text{cr}}) = (0.944, -4.72 \cdot 10^{-2})$,
- 2 and 4: CC ($\Delta\mu_{\text{cc}}(T)$, transition to capillary-liquid from vapour (line 2) and from thick prewetting film (line 4)), line 2 ends at $(0.929, -3.98 \cdot 10^{-2})$, line 4 begins at $(0.89, -4.45 \cdot 10^{-2})$, ends at $(T_{\text{cc}}^{\text{cr}}, \Delta\mu_{\text{cc}}^{\text{cr}}) = (0.994, -2.56 \cdot 10^{-2})$,
- 3: shifted planar prewetting ($\Delta\tilde{\mu}_{\text{pw}}(T)$, vapour to thick prewetting film in the associated slit pore), begins at $(0.848, -1.83 \cdot 10^{-2})$, ends at $(\tilde{T}_{\text{pw}}^{\text{cr}}, \Delta\tilde{\mu}_{\text{pw}}^{\text{cr}}) = (0.945, -4.89 \cdot 10^{-2})$,
- 5 and 7: capillary prewetting ($\Delta\mu_{\text{cpw}}(T)$, transition to capillary-liquid slab from vapour (line 5) and from drop surface phases (line 7)), line 5 begins at $(T_{\text{cw}}, \Delta\mu_{\text{cw}}) = (0.77, -3.33 \cdot 10^{-2})$ ($\Delta\mu_{\text{cc}} = 0.0086 \cdot 10^{-2}$), ends at $(0.873, -6.1 \cdot 10^{-2})$, line 7 begins at $(0.856, -5.65 \cdot 10^{-2})$, ends at $(\tilde{T}_{\text{cpw}}^{\text{cr}}, \Delta\tilde{\mu}_{\text{cpw}}^{\text{cr}}) = (0.93, -6.98)$,
- 6: shifted wedge prefilling ($\Delta\tilde{\mu}_{\text{wpw}}(T)$, vapour to drops in corners), begins at $(\tilde{T}_0, \Delta\tilde{\mu}_0) = (0.828, -3.68 \cdot 10^{-2})$ (point is on the CC line (line 2)), ends at $(\tilde{T}_{\text{wpw}}^{\text{cr}}, \Delta\tilde{\mu}_{\text{wpw}}^{\text{cr}}) = (0.885, -7.17 \cdot 10^{-2})$.

$H_0 = 5$ and width $H = 40$. The fluid is treated in LDA with the fluid-substrate potential given by equations (1.30) and (1.23), the planar wetting temperature: $T_w = 0.755$. Note that capillary in figure 3.21 differs from the one in figure 3.17 (with $H = 30$) only in the value of wall separation, H . The grey curves pertain to the surface phases inside the slit pore (capillary bulk, a 1D system), while the black curves correspond to the surface phases formed near the capping wall (capped capillary, a 2D system). Insets zoom on the triple points. All the transition lines are indexed and described in the caption of the figure. Solid and dashed lines denote transitions between stable and metastable surface phases respectively. The regions of thermodynamic stability (but not metastability: spinodals are not shown) of a single surface phase are labelled by the text notes. Triple points are marked by filled circles. Critical points are marked by open circles. The dotted grey line 1 is the prewetting line of a single planar wall (see section 3.1): the locus of transitions between vapour and thick prewetting film. Regarding capillary bulk (slit pore), line 2 is the locus of transitions between vapour and capillary-liquid, line 3 – between vapour and thick prewetting film on the side walls, line 4 – between thick prewetting film and capillary-liquid. Regarding the capped capillary, line 5 is the locus of transitions between vapour and configurations with capillary-liquid slab (capillary prewetting), line 6 – the locus of transitions between vapour and configurations with corner drops (shifted wedge prefilling), line 7 – the locus of transitions between configurations with corner drops and a capillary-liquid slab.

The full surface phase diagram possesses two triple points corresponding to three-phase coexistence inside the slit pore and the capped capillary. In order to locate the triple point we solve the system of equations given in (1.49) for the coexisting density profiles $\rho_1(x, y)$, $\rho_2(x, y)$, $\rho_3(x, y)$, chemical potential, μ_3 , and temperature T_3 . An initial guess for μ_3 and T_3 ($\mu_{3,0}$ and $T_{3,0}$) can be obtained by interpolating the three intersecting lines of two-phase coexistence to find three intersection points (due to computational errors, it will not be a single point), and then using their mean as $\mu_{3,0}$ and $T_{3,0}$. As an initial guess for the densities one can then take the density profiles inside each of the three surface phases corresponding to the data points on the two-phase coexistence lines closest to $\mu_{3,0}$ and $T_{3,0}$. So the overall strategy is similar to finding the point of two-phase coexistence, see equation (1.48) and discussion in section 3.2.2. Applying arc-length continuation may then allow one to trace the triple-line in the space of, e.g., the parameters of the potential ε_w and/or σ_w .

The triple point splits each transition line passing through it into two parts, the one where the transition takes place between thermodynamically stable surface phases (solid lines on figure 3.21) and the one where the transition is between thermodynamically metastable surface phases (dashed line on figure 3.21). Stable parts end in critical points (marked by open circles in figure 3.21). The end points of metastable parts of transition lines are not critical in the same sense, as they are associated with the metastable branch of the excess free energy $\Omega^{\text{ex}}(\Delta\mu)$ losing its intersection point with the stable branch. We provide more detail on the

mean-field signature of criticality at the end of the next section.

Considering the $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -lines in figures 3.17 ($H = 30$) and 3.21 ($H = 40$) we can, without computing the full wedge prefilling line $\Delta\mu_{\text{wpw}}(T)$, show that the confinement imposed by the second side wall of the capped capillary leads to the shift of the mean-field wedge prefilling line. Using arc-length continuation over T (see equation (1.48)), we can obtain $\Delta\tilde{\mu}_{\text{wpw}}(T)$ transition lines as sets of data in the $T - \Delta\mu$ space. With the help of spline-interpolation we compute both $\Delta\tilde{\mu}_{\text{wpw}}(T)$ transition lines from figures 3.17 and 3.21 at a set of 1000 points positioned equidistantly along the intersection of the temperature ranges where both lines are found. The mean value of the difference between them along the $\Delta\mu$ -axis is found to be $(0.16 \pm 0.01) \cdot 10^{-2}$, thus showing the fact that $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line is shifted in a capillary due to finite H .

Finally, let us discuss what happens to the surface phase diagram from figure 3.21 in the limits of large and small slit separations H . In the limit of large H both the capillary prewetting (line 5) and the side wall prewetting (line 3) must tend to the prewetting line of a single (capping) wall (line 1). Similarly, in the limit of large H the capillary prewetting (line 5) must tend to the prefilling of a single right-angled wedge (line 6). Thus, the crossing of these lines shown in the surface phase diagram forms a special case, but is not representative of the large H behaviour: in the limit of large H lines 5, 6 and 3 align with line 1. Conversely, at small H only the CC (transition line 2) exists.

3.3.1 Three surface phases near the capping wall

Here we discuss the isotherm at $T = T_3^{\text{cpd}}$ passing through the point of coexistence between vapour, corner drops and slab surface phases. Note that the transition discussed is rounded by fluctuations beyond the mean-field level of treatment. For confined fluids the wall separation H and the parameters of the substrate potential ε_w and σ_w are thermodynamic variables and have the same status as the bulk variables T and μ , see, e.g. the review by Henderson in reference [74]. We have seen how increasing the effective strength of the substrate potential leads to the existence of the (metastable) surface phase of corner drops (see, e.g., figure 3.9 with a single Van der Waals loop and figure 3.15 with two Van der Waals loops). A further increase in the wall separation (see, e.g., capillaries, in figures 3.17 and 3.21) stabilises the drop surface phase and leads to shifted wedge prefilling (transition line 6 in figure 3.21) and the coexistence of all three surface phases.

When the shifted wedge prefilling is stable, there must exist thermodynamic routes with two consecutive first-order transitions corresponding to shifted wedge prefilling and capillary prewetting. Consider, e.g., the isotherm at $T = 0.87$, which vertically crosses lines 6 and 7 in the surface phase diagram at the values $\Delta\mu_1 \equiv \Delta\tilde{\mu}_{\text{wpw}}(T)$ and $\Delta\mu_2$ respectively, thus passing through the areas of stability of vapour, drop and slab surface phases, and ends at CC (line 2). The typical density profiles of each of the stable surface phases are shown in figures

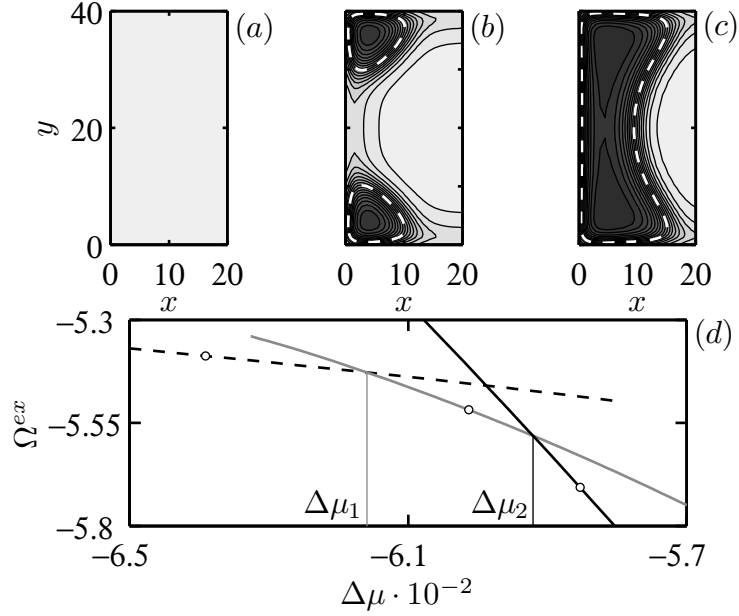


Figure 3.22: Isothermal thermodynamic route at $T = 0.87$ ($T_3^{\text{slt}} < T < \tilde{T}_{\text{wpw}}^{\text{cr}}$), $\Delta\mu_{\text{cc}}(T) = -3.89 \cdot 10^{-2}$. Capillary parameters are given in figure 3.21. As $\Delta\mu$ is increased, there are two stable consecutive first-order transitions: at $\Delta\mu_1 \equiv \Delta\mu_{\text{cpw}}(T) = -6.15 \cdot 10^{-2}$ and at $\Delta\mu_2 \equiv \Delta\tilde{\mu}_{\text{wpw}}(T) = -5.92 \cdot 10^{-2}$. (a) – (c) Representative density profiles of fluid configurations inside each of the three stable surface phases. Reference densities: $\rho_{\text{cc}}^{\text{vap}} = 0.06$, $\rho_{\text{cc}}^{\text{liq}} = 0.5$. (d) Excess free energy isotherm (unstable branches are not shown), which possesses three concave (stable) branches defining the surface phases of vapour (dashed line, profile at $\Delta\mu = -6.39 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.39$ is shown in plot (a)), corner drops (solid grey line, profile at $\Delta\mu = -6 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.52$ is shown in plot (b)) and capillary-liquid slab (solid black line, profile at $\Delta\mu = -5.85 \cdot 10^{-2}$, $\Omega^{\text{ex}} = -5.71$ is shown in plot (c)). Values of $(\Delta\mu, \Omega^{\text{ex}})$, corresponding to (a) – (c) are marked on (d) by open circles. See also figure 3.23 for the adsorption isotherm.

3.22(a) – 3.22(c). The excess free energy isotherm (without the unstable branches) and the adsorption isotherm (unstable branches plotted with dotted line; dotted vertical line denotes CC) are presented in figures 3.22(d) and 3.23. The branches of vapour, corner drops and slab are plotted in each isotherm with dashed, solid grey, and solid black lines respectively. Open circles (left to right) correspond to the density profiles of each surface phase shown in figures 3.22(a) – 3.22(c), respectively. The points $(T, \Delta\mu_1)$ and $(T, \Delta\mu_2)$ belong to lines 6 and 7 in the surface phase diagram in figure 3.21.

At low values of $\Delta\mu$ the thermodynamic point representing the system in the surface phase diagram is situated below line 6, thus the capillary is filled with vapour (figure 3.22(a)). A quasi-static isothermal increase of $\Delta\mu$ corresponds to the point advancing vertically towards line 6. Upon crossing line 6 (at $\Delta\mu = \Delta\mu_1$) the system undergoes the shifted wedge prefilling and two drops in the capillary corners form discontinuously (figure 3.22(b)). When the system

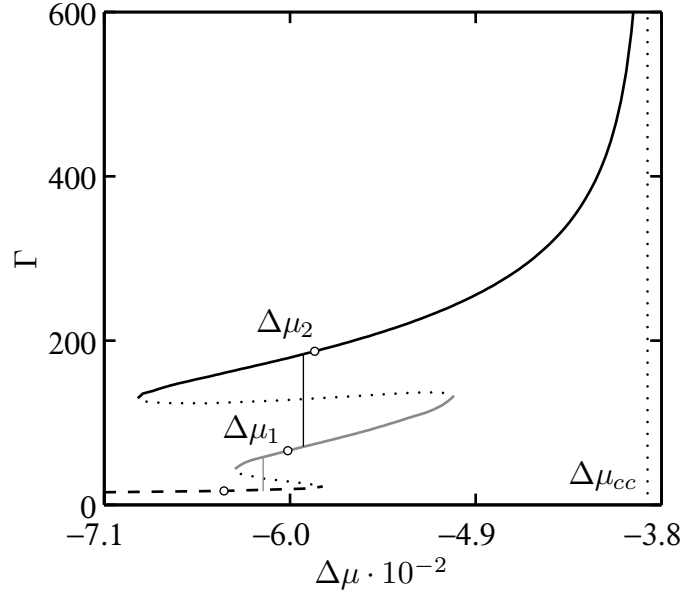


Figure 3.23: Adsorption isotherm at $T = 0.87$. Line styles and open circles are defined as in figure 3.22(d); dotted branches denote thermodynamically unstable states. Dotted vertical line is drawn at $\Delta\mu_{cc}(T) = -3.89 \cdot 10^{-2}$ and forms the vertical asymptote for $\Gamma(\Delta\mu)$. The two Van der Waals loops give rise to the transition values $\Delta\mu_1$ (shifted wedge prefilling, adsorption jumps from $\Gamma_1^1 = 16.7$ to $\Gamma_1^2 = 58$) and $\Delta\mu_2$ (capillary prewetting, adsorption jumps from $\Gamma_2^1 = 70.7$ to $\Gamma_2^2 = 183.3$).

is in the region between lines 6 and 7, the drops are stable. The quasi-static advancing towards capillary prewetting (line 7) is associated with the growth of the drops, which upon crossing line 7 (at $\Delta\mu = \Delta\mu_2$) transform discontinuously into the slab surface phase (figure 3.22(c)). When the system is found in the region of the surface phase diagram between lines 7 and 2, the slab is stable. Further increase of $\Delta\mu$ proceeds with the growth of the slab and subsequent continuous CC as line 2 is approached.

The phenomenology becomes rather transparent after looking at the excess free energy and adsorption isotherms in figures 3.22(d) and 3.23. At any given value of $\Delta\mu$ the system selects a state with the lowest value of Ω^{ex} . Thus, the intersections of branches of $\Omega^{\text{ex}}(\Delta\mu)$ at $\Delta\mu_1$ and $\Delta\mu_2$ signify the two consecutive first-order transitions. On the adsorption isotherm the transitions correspond to the two Van der Waals hysteresis loops of $\Gamma(\Delta\mu)$, and the values $\Delta\mu_1$ and $\Delta\mu_2$ can be obtained by the equal area construction (see Gibbs equation (1.46)).

In mean-field theories the turning points of, e.g., isotherms – the spinodals – are important for making predictions about the behaviour of an actual physical system. Due to metastability, the system may persist in its current phase as $\Delta\mu$ is being varied quasi-statically inside the region between the spinodals, where the free energy has more than a single value for a given value of $\Delta\mu$. This leads to the hysteresis in the fluid wetting behaviour: a quasi-static route

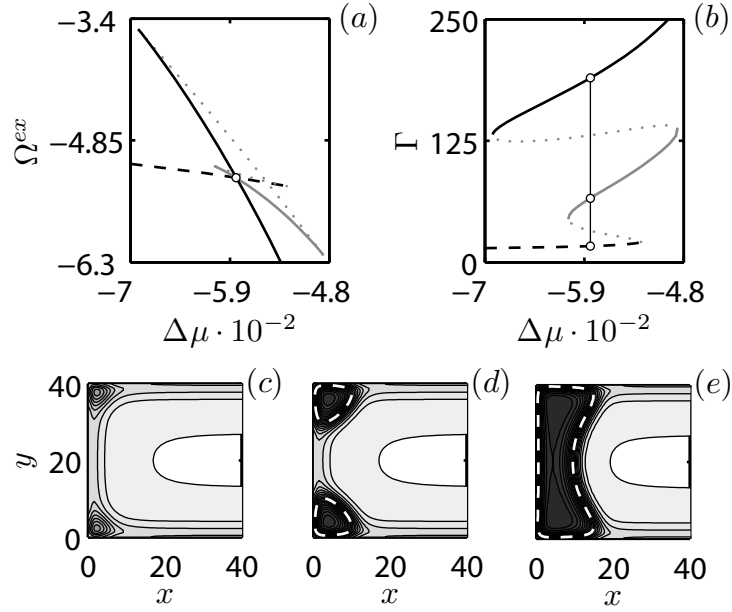


Figure 3.24: Isothermal thermodynamic route at $T \equiv T_3^{\text{cpd}} = 0.865$. Vapour, drop and slab surface phases coexisting at $\Delta\mu_{\text{cpw}}(T) = \Delta\tilde{\mu}_{\text{wpw}}(T) = -5.83 \cdot 10^{-2}$. Capillary parameters are given in figure 3.21. (a) and (b) Excess free energy and adsorption isotherms. Stable branches are defined as in figure 3.22(d). Unstable branches are plotted with the dotted line. Open circles mark values at three-phase coexistence: $\Omega^{ex} = -5.29$, $\Gamma^1 = 16.6$, $\Gamma^2 = 65.8$, $\Gamma^3 = 189.8$. Vertical line on (b) is at the transition value ($\Delta\mu = -5.83 \cdot 10^{-2}$). (c) – (e) Density profiles of coexisting surface phases. Reference densities: $\rho_{\text{cc}}^{\text{vap}} = 0.06$, $\rho_{\text{cc}}^{\text{liq}} = 0.51$.

from vapour to CC may be taken through different states than a quasi-static route from CC to vapour. In section 3.4 we use a dynamic model to show how spinodals can pin the relaxation of the system.

As can be seen from the surface phase diagram in figure 3.21, the temperature region where the three fluid surface phases can be stable is bounded from below by the triple point, at $T \equiv T_3^{\text{cpd}} = 0.865$, and from above – by the critical point of transition line 6, at $T \equiv \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.885$. In what follows we examine in more detail these limiting cases. Figure 3.24 shows the isotherms (figures 3.24(a), (b)) and the coexisting density profiles at $T \equiv T_3^{\text{cpd}} = 0.865$ (figures 3.24(c) – (e)), where vapour, drop and slab surface phases coexist. The three branches of the excess free energy $\Omega^{\text{ex}}(\Delta\mu)$ all cross at a single point. Relatively to the previously discussed case, we have now $\Delta\mu_1 = \Delta\mu_2$. The wall separation H effects the vapour-drop transition, for example, the transition is stable and the triple point exists in the capillary with $H = 40$ (figure 3.21), but does not exist in the capillary with the same substrate potential but with $H = 30$ (figure 3.17). This happens because a larger distance between the side walls allows for more isolation of the capillary corners.

Consider now the higher-temperature boundary of the region in the surface phase diagram,

where vapour, drop and slab surface phases can be stable at the same T . It is set by the critical point of line 6, at $T = \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.885$. In order to show how a mean-field DF approach is capable of capturing the signature of criticality, we contrast the surface phase behaviour near $\tilde{T}_{\text{wpw}}^{\text{cr}}$ with that near the low-temperature end of line 6, at $T = \tilde{T}_0 = 0.828$. Figure 3.25 shows two free-energy isotherms: at $T = 0.875 \lesssim \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.885$ (the lower isotherm, designated by an arrow pointing at the area zoomed at on the inset) and at $T = 0.83 \gtrsim \tilde{T}_0 = 0.828$ (the upper isotherm). As can be seen from the inset, there is a stable vapour – drop transition on the lower isotherm. It is also quite clear (compare, e.g., to figure 3.22(d) where the isotherm is at a relatively lower temperature, $T = 0.87$), that the branches of excess free energy defining the vapour and drop surface phases tend to align and form a single branch as $T \rightarrow \tilde{T}_{\text{wpw}}^{\text{cr}}$ from below. In the limit the distinction between vapour and drop surface phases is lost, there is a single continuous branch of Ω^{ex} extending from $\mu = -\infty$. During an isothermal increase of $\Delta\mu$ at $T > \tilde{T}_{\text{wpw}}^{\text{cr}}$ the structure of the fluid changes continuously from vapour to configurations with drops in the corners.

The structure of the upper isotherm in figure 3.25 is principally different. As is clear from the figure, the branch of Ω^{ex} defining the drop surface phase (solid grey line) loses its intersection point with the branch defining the vapour surface phase (dashed line). None of the branches align in the limit $T \rightarrow T_0$ from above. Computing sets of isotherms at T decreasing from $\tilde{T}_{\text{wpw}}^{\text{cr}}$, we note that the branches of Ω^{ex} defining the drop surface phase (solid grey line), “move up” with respect to those defining vapour (dashed line). The intersection is thus lost in the limit $T \equiv \tilde{T}_0 = 0.828$ (compare with isotherms computed at relatively higher values of T , e.g., the lower isotherm in figure 3.25 ($T = 0.875$), and isotherms in figures 3.22(d) ($T = 0.87$) and 3.24(a) ($T = 0.865$)). Distinct concave branches of Ω^{ex} defining the metastable drop surface phase can still be found on the isotherms at $T \lesssim \tilde{T}_0$, but they have no intersections with any other branches.

We see that the mean-field DF theory allows one to find potential critical points. The tactics of finding limiting-case isotherms described above was used to locate the critical points on all the surface phase diagrams presented. Of-course, once a potential critical point is obtained, it should be properly examined using appropriate methods, which can probe beyond the mean-field level of description [188, 187, 189, 144, 181].

3.3.2 Three phases in the capillary bulk

All the examples up to this point were restricted to cases where at a given temperature the capillary bulk can have at most two stable surface phases, either vapour or capillary-liquid, which transform in a first-order or a continuous CC. In the present section we consider a case of three-phase coexistence in the slit pore providing a platform for the discussion of continuous prewetting transition in the next section. In the existing literature a numerical study most relevant to the present section is, e.g., the work of Bruno et al. [190], where the three-phase

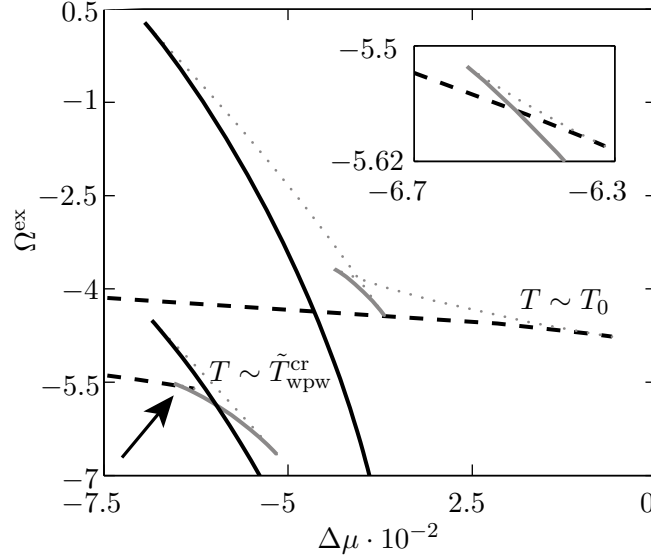


Figure 3.25: Mean-field signature of criticality in the shifted wedge prefilling. Showing two excess free energy isotherms at values of T near the ends of $\Delta\tilde{\mu}_{\text{wpw}}(T)$ -line (line 6) from figure 3.21, each possessing two Van der Waals loops, that of shifted wedge prefilling, and of capillary prewetting. Each isotherm has three concave branches (connected by non-concave branches, plotted with dotted lines), defining the surface phases of vapour (dashed line), corner drops (solid grey) and capillary-liquid slab (solid black). Arrow points at the lower isotherm with the near-critical shifted wedge prefilling, at $T_1 = 0.875 \lesssim \tilde{T}_{\text{wpw}}^{\text{cr}} = 0.885$ (higher- T end of line 6 in figure 3.21), with transition at point $(\Delta\tilde{\mu}_{\text{wpw}}(T_1), \Omega^{\text{ex}}) = (-6.5 \cdot 10^{-2}, -5.5)$ (capillary prewetting is at point $(\Delta\mu_{\text{cpw}}(T_1), \Omega^{\text{ex}}) = (6 \cdot 10^{-2}, -5.87)$). Inset zooms on the shifted wedge prefilling transition at $\Delta\tilde{\mu}_{\text{wpw}}(T_1)$, which disappears in the limit $T \rightarrow \tilde{T}_{\text{wpw}}^{\text{cr}}$, where the branches of Ω^{ex} defining vapour and drop surface phases align forming a single vapour branch. The upper isotherms is at $T_2 = 0.83 \gtrsim \tilde{T}_0 = 0.828$ (lower- T end of line 6 in figure 3.21), with the transition at point $(\Delta\tilde{\mu}_{\text{wpw}}(T_2), \Omega^{\text{ex}}) = (-4.7 \cdot 10^{-2}, -4.36)$ (capillary prewetting is at point $(\Delta\mu_{\text{cpw}}(T_2), \Omega^{\text{ex}}) = (-4.7 \cdot 10^{-2}, -4.36)$). The shifted wedge prefilling transition disappears at $T = \tilde{T}_0$ because the branch of Ω^{ex} defining the drop surface phase loses its intersection with the branch defining vapour.

coexistence in a slit pore is investigated with a mean-field microscopic lattice-gas model. The three-phase coexistence is treated using a DF theory by Evans and Marconi in reference [117] and by Evans and Parry in reference [160]. The treatment of asymmetric slit-like substrates using effective substrate potentials, as well as a DF theory, can be found in the recent work by Stewart and Evans [191].

Increasing the wall separation leads to higher isolation of the walls and may allow for stable prewetting transition (see section 3.1). As an example consider the grey lines in figures 3.17 ($H = 30$, no prewetting) and 3.21 ($H = 40$, where line 3, $\Delta\tilde{\mu}_{\text{pw}}(T)$, forms the locus of

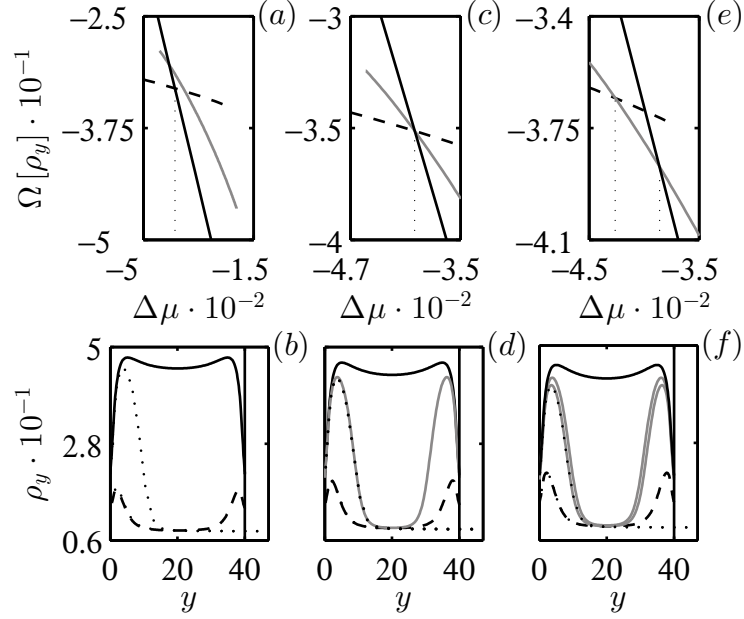


Figure 3.26: Stable transitions during adsorption in the slit pore near its triple temperature, $T_3^{\text{slt}} = 0.92$ (the full surface phase diagram forms the part of figure 3.21 plotted with full grey lines). (a) and (b) $T = 0.910 < T_3^{\text{slt}}$, coexisting surface phases are vapour and capillary-liquid, at $\Delta\mu = -4 \cdot 10^{-2}$, $\Omega[\rho^{\text{slt}}] = -3.3 \cdot 10^{-1}$. (c) and (d) $T = 0.920 \equiv T_3^{\text{slt}}$, coexisting surface phases are vapour, thick prewetting film, and capillary-liquid, at $\Delta\mu = -4 \cdot 10^{-2}$, $\Omega[\rho^{\text{slt}}] = -3.5 \cdot 10^{-1}$. (e) and (f) $T = 0.927 > T_3^{\text{slt}}$, the coexistence is between vapour and thick prewetting film, at $\Delta\mu = -4.3 \cdot 10^{-2}$, $\Omega[\rho^{\text{slt}}] = -3.7 \cdot 10^{-1}$, and between thick prewetting film and capillary-liquid, at $\Delta\mu = -9 \cdot 10^{-2}$, $\Omega[\rho^{\text{slt}}] = -3.9 \cdot 10^{-1}$. Note, that we do not distinguish between surface phases of vapour and thin prewetting film, referring to both as vapour. In (a), (c) and (e) unstable branches of Ω are not plotted, dotted vertical lines mark values of $\Delta\mu$ corresponding to stable transitions. Branches of Ω -isotherms are plotted with different line styles to distinguish between vapour (dashed black), capillary-liquid (solid black) and thick prewetting film (solid grey) surface phases. On (b), (d), (f) the coexisting density profiles are plotted with the same line styles as the branches of Ω defining respective surface phases. Black vertical lines mark the position of the second side wall of the slit pore, the first side wall being at $y = 0$. The dotted density profiles correspond to planar prewetting (at the same value of T as the respective transition in the pore), which takes place at (b) $\Delta\mu = -3.5 \cdot 10^{-2}$, (d) $\Delta\mu = -3.8 \cdot 10^{-2}$, and (f) $\Delta\mu = -4.1 \cdot 10^{-2}$.

transitions between thick prewetting film and capillary-liquid). In the latter case the three two-phase coexistence lines (2, 3 and 4) cross at a single point, at the slit triple temperature $T_3^{\text{slt}} = 0.92$, where all three surface phases (vapour, thick prewetting film and capillary-liquid) are stable and coexist.

The planar prewetting line, $\Delta\mu_{\text{pw}}(T)$ (line 1 in figure 3.21), is shifted in the slit pore along

the $\Delta\mu$ -axis by a constant value $(1.7 \pm 0.1) \cdot 10^{-3}$ and thus forms the transition line of shifted planar prewetting, $\Delta\tilde{\mu}_{\text{pw}}(T)$ (line 3). Note that the critical point of shifted prewetting in a slit pore is genuine and is found beyond mean-field [117]. An analytic relation between the shift of prewetting and the width of the capillary was obtained by Evans and Marconi [166]. Due to the presence of the triple point the transition to capillary-liquid takes place along lines 2 and 4, which together form the $\Delta\mu_{\text{cc}}(T)$ -line, where capillary-liquid coexists with vapour (at $T < T_3^{\text{slt}} = 0.92$, line 2) and with thick prewetting film (at $T > T_3^{\text{slt}}$, line 4), respectively. Figures 3.26(a), (c) and (e) show representative free energy isotherms, $\Omega(\Delta\mu)$, (unstable branches are not plotted) at temperatures below, at and above T_3^{slt} , respectively. The respective coexisting density profiles for stable transitions are shown in figures 3.26(b), (d) and (f). On the plots of isotherms and density profiles the surface phases of vapour, capillary-liquid and thick prewetting film are denoted by dashed, solid black and grey lines respectively. The density profiles plotted with dotted line correspond to single wall prewetting (transition line 1 in figure 3.21) at the same temperature as the transitions in the slit pore. Dotted vertical lines on (a), (c) and (e) designate the values of $\Delta\mu$ at the transition; full vertical line on (b), (d) and (f) designate the second wall of the slit pore, the first wall being at zero.

When $T < T_3^{\text{slt}}$ (figures 3.26(a) and 3.26(b)) there is a single stable surface phase transition between vapour and capillary-liquid. Figure 3.26(a) shows the complete metastable branch of $\Omega(\Delta\mu)$ defining the surface phase of thick prewetting film (solid grey line). It is bounded by its two turning points (spinodals). The branch defining vapour (dashed line) extends from $\mu = -\infty$ up to its spinodal, whereas the capillary-liquid branch is bounded at higher values of $\Delta\mu$ by the bulk saturation ($\Delta\mu \equiv 0$). Increasing the temperature results in the film branch “moving down” relatively to the intersection of the vapour and capillary-liquid branches, see, e.g., figures 3.26(c) and 3.26(e).

At $T = T_3^{\text{slt}}$ (figures 3.26(c) and 3.26(d)) the three branches of $\Omega(\Delta\mu)$ intersect at one point, at $\Delta\mu_3 \equiv \Delta\tilde{\mu}_{\text{pw}}(T_3^{\text{slt}}) = \Delta\mu_{\text{cc}}(T_3^{\text{slt}})$. Using arc-length continuation for equation (1.49) one can obtain the full triple-line as a function of, e.g., parameters of the substrate potential ε_w and/or σ_w . Note that the density profiles inside vapour and thick prewetting film in the pore (dashed and solid grey lines) are almost indistinguishable from those on a single planar wall (dotted lines).

At $T > T_3^{\text{slt}}$ (figures 3.26(e) and 3.26(f)) we find two consecutive stable transitions: shifted prewetting (at a lower value of $\Delta\mu$), and CC (at a higher value of $\Delta\mu$). The density profiles of vapour in the slit pore and on the single wall are still very much alike. We do not distinguish between vapour and thin prewetting film. As for the profiles of thick prewetting film, the one on a single wall is closer to the one in the slit pore, which coexists with vapour, than the one coexisting with capillary-liquid.

A further increase in T leads to criticality of shifted prewetting at $\tilde{T}_{\text{pw}}^{\text{cr}}$, which belongs

to the 2D Ising universality class and exists beyond mean-field. Within our mean-field DF treatment we note that the density profiles of coexisting states become indistinguishable and the respective branches of $\Omega(\Delta\mu)$ align forming a single branch. At a fixed $T > \tilde{T}_{\text{pw}}^{\text{cr}}$ the growth of adsorbed film is continuous with $\Delta\mu$ up until the first-order CC.

3.3.3 Continuous planar prewetting

In the previous section we have seen (in agreement with the existing theory, e.g., references [160, 176, 117]), that the prewetting of a single planar wall and the shifted prewetting of a slit pore are essentially equivalent phenomena. The transition line of wall prewetting, $\Delta\mu_{\text{pw}}(T)$, is shifted in a slit pore and forms the transition line $\Delta\tilde{\mu}_{\text{pw}}(T)$. Given the substrate parameters, the value of the shift is determined by the pore width. In this section we show how capping the slit pore results in the planar prewetting becoming a continuous surface phase transition manifested by capillary-liquid fingers unbinding into the capillary bulk, as $\Delta\mu \rightarrow \Delta\tilde{\mu}_{\text{pw}}(T)$ isothermally. This is a qualitatively new phenomenon and has not been reported in literature. Moreover, the critical point of continuous prewetting belongs to the 2D Ising universality class and thus the transition is genuine and should be observable beyond mean field.

Consider again the surface phase diagram presented in figure 3.21 and an isothermal thermodynamic route at $T = T_1$ in the interval $T_3^{\text{slt}} < T_1 < \tilde{T}_{\text{pw}}^{\text{cr}}$ across the transition lines $\Delta\tilde{\mu}_{\text{pw}}(T)$ and $\Delta\mu_{\text{cc}}(T)$ (lines 3 and 4 in figure 3.21). An isothermal crossing of $\Delta\tilde{\mu}_{\text{pw}}(T)$ -line corresponds to the shifted prewetting of the capillary side walls (see, e.g., figures 3.26(b), 3.26(e)) and one might intuitively expect that this transition may happen continuously via a nucleation of the new surface phase on the capping wall, just like the continuous CC is nucleated from a capillary-liquid slab adsorbed on the capping wall at $\mu < \mu_{\text{cc}}$. We indeed find this to be the case in our system.

Figure 3.27 shows a representative adsorption and excess free energy isotherms corresponding to the thermodynamic route at $T_1 = 0.93 > T_3^{\text{slt}}$ on the surface phase diagram (see figure 3.21). The region in $\Delta\mu$ is chosen near $\Delta\tilde{\mu}_{\text{pw}}(T_1) \equiv \Delta\mu_2$ and $\Delta\mu_{\text{cc}}(T_1) \equiv \Delta\mu_3$. These values are marked by the dashed vertical lines in each of the sub-figures, along with the value $\Delta\mu_1$ of the spinodal of the shifted prewetting in the associated slit pore. Thus, on the surface phase diagram the point $(T_1, \Delta\mu_1)$ is below, but near line 3, the point $(T_1, \Delta\mu_2)$ belongs to line 3, and the point $(T_1, \Delta\mu_3)$ belongs to line 4. Several representative density profiles are shown in figure 3.28, where plots (a) – (c) correspond to $\Delta\mu \rightarrow \Delta\mu_2$ and plots (d) – (f) correspond to $\Delta\mu \rightarrow \Delta\mu_3$. The data values on the isotherms, corresponding to the presented density profiles are marked by filled (for profiles (b), (c)) and open (for profiles (d), (e)) circles in figures 3.27(a) – 3.27(c), thus, e.g., the grey curves on figures 3.27 (a) and (c) correspond to the fluid states possessing “fingers”.

The adsorption isotherm (figure 3.27(a)) consists of two unconnected branches: the grey branch spans the interval of values of $\Delta\mu : -\infty \leq \Delta\mu \leq \Delta\mu_2$, and the black branch is

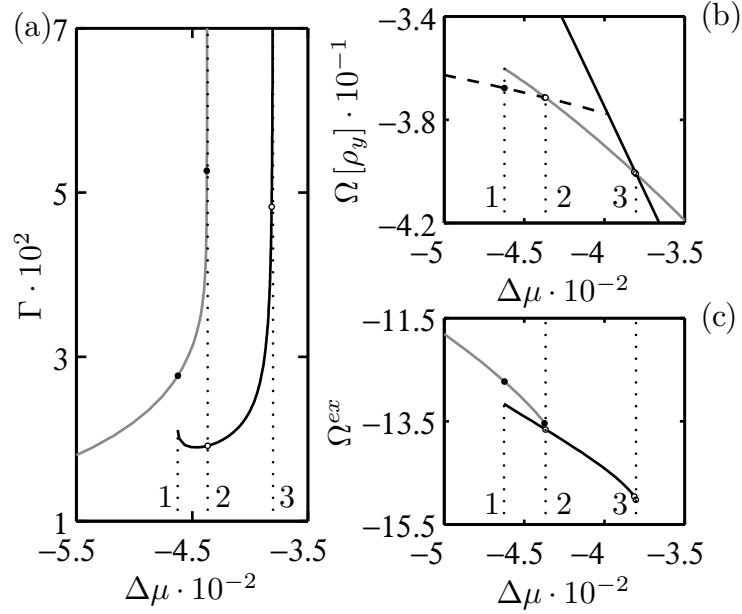


Figure 3.27: Isothermal thermodynamic route at $T = 0.93$, across transition lines 3 ($\Delta\tilde{\mu}_{pw}(T)$, shifted prewetting) and 4 ($\Delta\mu_{cc}(T)$, CC) in figure 3.21. There are two consecutive continuous transitions: continuous prewetting at $\Delta\mu_2 \equiv \Delta\tilde{\mu}_{pw}(T) = -4.37 \cdot 10^{-2}$, followed by continuous CC at $\Delta\mu_3 \equiv \Delta\tilde{\mu}_{cc}(T) = -3.8 \cdot 10^{-2}$. (a) Adsorption isotherm of the capped capillary consisting of two diverging branches of continuous prewetting (grey) and continuous CC (black). (b) Free energy isotherm of associated slit pore (capillary bulk), where (similarly to figure 3.26) black dashed, solid grey, and solid black lines denote vapour, thick prewetting film and capillary-liquid surface phases respectively. (c) Excess free energy isotherm of the capped capillary; branches defined as in (a). Continuous prewetting and continuous CC occur at $\Omega^{ex} \approx -13.55$ and $\Omega^{ex} \approx -15.03$ respectively. On (a) – (c) the vertical dotted lines are drawn at $\Delta\mu_1 = -4.6 \cdot 10^{-2}$ (spinodal of thick prewetting film), $\Delta\mu_2$ and $\Delta\mu_3$. Representative density profiles are plotted in figure 3.28 and marked on isotherms by black circles for profiles (b) – (c) and open circles for profiles (e) – (f).

limited to the interval $\Delta\mu : \Delta\mu_1 \leq \Delta\mu \leq \Delta\mu_3$. The values $\Delta\mu_2$ and $\Delta\mu_3$ provide vertical asymptotes for the diverging branches of adsorption. Figure 3.27(b) shows the free energy isotherm of the associated slit pore (capillary bulk), corresponding to the same thermodynamic route; unstable branches are not shown. In figure 3.27(b) the dashed, solid grey and solid black branches denote respectively the surface phases of vapour, thick prewetting film and capillary-liquid in the associated slit pore. The capillary bulk transitions from vapour to thick prewetting film and from the thick prewetting film to capillary-liquid are both stable. Figure 3.27(c) shows the excess free energy isotherm of the capped capillary corresponding to the adsorption isotherm in figure 3.27(a).

Let us describe the way in which the two consecutive continuous surface phase transitions

take place in the capped capillary as the chemical potential of the reservoir is increased from a large negative value $\Delta\mu \sim -\infty$ (where the capillary is filled entirely with vapour) to the value $\Delta\mu = \Delta\mu_3$ (where it is filled entirely with capillary-liquid), at the constant temperature $T_1 = 0.93$. As $\Delta\mu$ is increased from a large negative value, so that the point representing the system in the surface phase diagram approaches and crosses the $\Delta\mu_{\text{cpw}}(T)$ -line (line 7 in figure 3.21), there is a first-order transition between the corner drops and the capillary-liquid slab at the value $\Delta\mu = \Delta\mu_{\text{cpw}}(T_1) = -7 \cdot 10^{-2}$ (this transition, manifested by a hysteresis S-loop in $\Gamma(\Delta\mu)$, is outside the range chosen for figures 3.27(a), (c)).

As $\Delta\mu$ is increased towards $\Delta\tilde{\mu}_{\text{pw}}(T_1) \equiv \Delta\mu_2$, the density profiles begin to develop fingers (see, e.g., figures 3.28(a) – 3.28(c)). The values of adsorption for the fluid configurations with fingers belong to the branch of $\Gamma(\Delta\mu)$, plotted in grey in figure 3.27(a). The values of the excess free energy belong to a concave branch of $\Omega^{\text{ex}}(\Delta\mu)$ (grey curve in figure 3.27(c)), thus the fluid states with fingers are thermodynamically stable and form a surface phase. As $\Delta\mu \rightarrow \Delta\mu_2 \equiv \Delta\tilde{\mu}_{\text{pw}}(T_1)$, the “length” of the fingers increases and diverges in the limit (see again the density profiles in figures 3.28(a) – 3.27(c)).

Investigating the structure of the new surface phase we consider vertical cross sections of various density profiles choosing two sets of values along the x -axis: x_f – between the capping wall and the “tips” of the fingers, and x_v – well inside capillary bulk, far away from the finger “tips”. The purpose is to compare the slices $\rho(x_f, y)$ and $\rho(x_v, y)$ with the 1D density profiles of fluid configurations coexisting inside the associated slit pore during the shifted prewetting transition at $\Delta\mu \equiv \Delta\mu_2 = \Delta\tilde{\mu}_{\text{pw}}(T_1)$: $\rho_{y,\text{film}}(y)$ and $\rho_{y,\text{vap}}(y)$. We find that an equivalence similar to the one expressed by equation (3.39), holds (within the margin of machine rounding error):

$$\begin{aligned}\rho(x_f, y) &\equiv \rho_{y,\text{film}}(y), \\ \rho(x_v, y) &\equiv \rho_{y,\text{vap}}(y).\end{aligned}\tag{3.44}$$

The above relation proves that the profiles with fingers correspond to the *continuous* onset of the surface phase of thick prewetting film, which is filling the capped capillary as $\Delta\mu \rightarrow \Delta\mu_2$.

Now we can find the mean-field exponent of the divergence. First, we employ the same considerations as those leading to the expression (3.31) for the binding potential of the meniscus, and obtain the similar expression for the binding potential of the finger of length l :

$$\omega_{\text{fin}}(l) \sim \frac{1}{l^3},\tag{3.45}$$

as $l \rightarrow \infty$. The total effective potential, $V_{\text{fin}}(l)$, includes apart from ω_{fin} the energy contribution from the capillary bulk, which is straightforward to obtain due to the computationally

established equivalence of the fingers with the thick prewetting film (in equation (3.44)):

$$V_{\text{fin}}(l) \sim (\tilde{\mu}_{\text{pw}} - \mu) l + \frac{A}{l^3}. \quad (3.46)$$

The condition of the above being minimised by the equilibrium length of the fingers, l , gives rise to the exponent of the diverging length of the fingers:

$$l \sim (\tilde{\mu}_{\text{pw}} - \mu)^{-1/4}, \quad (3.47)$$

as $\mu \rightarrow \tilde{\mu}_{\text{pw}}$ from below.

The adsorption, $\Gamma(\Delta\mu)$, is defined in equation (3.29). For $\Delta\mu < \Delta\mu_2$, the bulk of the capped capillary is in the vapour (see figure 3.27(b)), and the development and growth of the fingers from the capping wall leads to the divergence of the integral in equation (3.29), so that $\Gamma \rightarrow \infty$, as $\Delta\mu \rightarrow \Delta\mu_2$. The value $\Delta\mu = \Delta\mu_2$ is the vertical asymptote for the branch of $\Gamma(\Delta\mu)$ -dependence (grey line in figure 3.27(a)). The branch of the excess free energy tends to a finite limit (grey line in figure 3.27(c)). For values of $\Delta\mu$ above $\Delta\mu_2$ the thermodynamic point representing the system in the surface phase diagram is found between the transition lines of the shifted prewetting (line 3) and CC (line 4). Thus, for values of $\Delta\mu$ in the interval $\Delta\mu_2 \leq \Delta\mu \leq \Delta\mu_3$ the associated slit pore possess a stable thick prewetting film on the side walls (see figure 3.27(b)) and according to the definition of Γ in equation (3.29), its value is again finite (for $\Delta\mu < \Delta\mu_3$), since the bulk surface phase with profile $\rho^{\text{slt}}(y)$ is no longer vapour, but is a thick prewetting film.

As the value of $\Delta\mu$ is increased above $\Delta\mu_2$, and towards $\Delta\mu_3$, the meniscus starts to unbind from the capping wall into the capillary bulk (see density profiles in figures 3.28(d) – 3.28(f)). We observe a case of continuous CC. The analysis of vertical cross sections shows that the structure of the fluid between the capping wall of the capillary and the meniscus is identical to that of capillary-liquid coexisting with the thick prewetting film in the associated slit pore at $\Delta\mu = \Delta\mu_3$. The structure of the fluid far from the capping wall and the meniscus is identical (within machine error margins) to the coexisting thick prewetting film surface phase. As $\Delta\mu \rightarrow \Delta\mu_3$, $\Gamma(\Delta\mu) \rightarrow \infty$, so that the value $\Delta\mu_3$ is the vertical asymptote of the respective branch of adsorption (see black curve in figure 3.27(a)). The excess free energy tends to a finite limit (black curve in figure 3.27(c)).

Note that additional density profiles, $\rho^{\text{cpd}}(x, y)$, solving the Euler-Lagrange equation (1.37), can be obtained for values of $\Delta\mu$ in the interval $\Delta\mu_1 \leq \Delta\mu \leq \Delta\mu_2$, where the thick prewetting film is metastable in the capillary bulk (see the part of black curve in figure 3.27(a) and the part of grey curve (corresponding capillary bulk) in figure 3.27(b) between $\Delta\mu_1$ and $\Delta\mu_2$). However, those states are thermodynamically unstable, which follows immediately from the consideration of the $\Gamma(\Delta\mu)$ -dependence (see black curve in figure 3.27(a)). The part of the $\Gamma(\Delta\mu)$ -branch between $\Delta\mu_1$ and $\Delta\mu_2$ is non-monotonous, and, according to the Gibbs

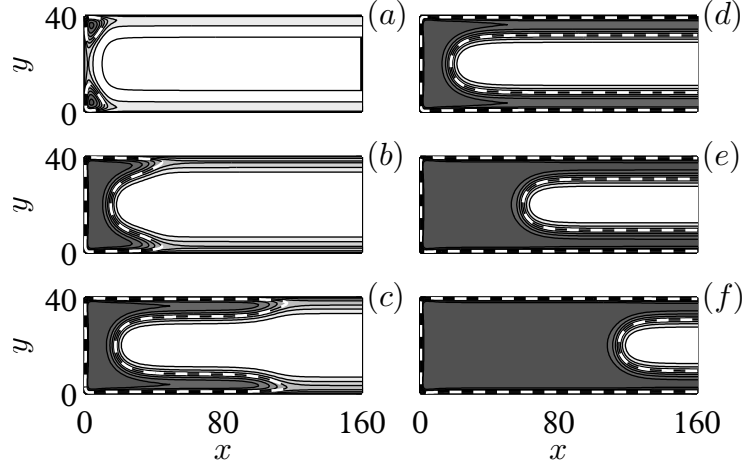


Figure 3.28: Representative density profiles for an isothermal approach to CC at $T = 0.93$, which has two consecutive continuous transitions, see figure 3.27. Reference densities: $\rho_{cc}^{\text{vap}} = 0.09$, $\rho_{cc}^{\text{liq}} = 0.41$. (a) – (c) Density profiles of fluid states from the branch of the isotherm corresponding to continuous prewetting (figure 3.27, grey line). The values of $\Delta\mu$: $-8.3 \cdot 10^{-2}$, $-4.6 \cdot 10^{-2}$, $-4.37 \cdot 10^{-2}$; values of Γ : 193.6, 483.6, 898.1; values of Ω^{ex} : -13.65, -14.96, -15.02. (d) – (f) Density profiles of continuous CC, which follows continuous prewetting (figure 3.27, black line). The values of $\Delta\mu$: $-4.4 \cdot 10^{-2}$, $-3.82 \cdot 10^{-2}$, $-3.80 \cdot 10^{-2}$; values of Γ : 55.4, 276.8, 527.9; values of Ω^{ex} : -7.78, -12.73, -13.54; The values of adsorption and excess free energy are marked in figures 3.27(a), 3.27(c) by filled black circles for profiles (b), (c) and by open circles for profiles (d), (e).

rule (see equation (1.46)), the corresponding part of the excess free energy isotherm is not everywhere concave. So, although the fluid configurations corresponding to that part of the isotherm solve the Euler-Lagrange equation (1.37), they do not minimise the free energy. We note again that a consistent DF analysis of the thermodynamic stability of a given fluid configuration obtained by solving the Euler-Lagrange equation is *impossible* to carry out without access to a *set* of density profiles, which allows one to analyse the convexity of the free energy. The arc-length continuation method from section 2.2.1 allows for such analysis in a natural and consistent way, as we have just shown.

To summarise, we have shown that the planar prewetting transition can become continuous (second-order) in a capillary-like geometry, when the associated slit pore allows for the three-phase coexistence. Beyond mean-field the diverging fingers allow for the correlation length parallel to the interface to diverge in two dimensions, thus the continuous prewetting corresponds to the 2D Ising universality class and is a genuine, observable surface phase transition. Moreover, the competition between CC and continuous prewetting at the slit pore triple point, at $T = T_3^{\text{slt}}$, is specific to the geometry of the capped capillary and poses an interesting scaling problem, which may be treated using renormalisation group methods. Finally, we note that continuous prewetting should be observed in wedges immersed in vapour

when the chemical potential of the reservoir is increased towards that of prewetting of the wedge walls. The continuous prewetting is related to the phenomenon of step wetting, where a planar step of the height of several molecular diameters (the height should be that of the coexisting thick prewetting film), immersed in vapour, adsorbs liquid, showing a divergence of the meniscus as the prewetting chemical potential is approached [175].

One important ramification of the existence of continuous prewetting in geometrically modified substrates is that it may allow one to take prewetting to an observable scale: at temperatures above T_w the typical height of a thick prewetting film coexisting with vapour (it is equivalent to the thin prewetting film) on a planar surface is several molecular diameters, so rather involved and specialised experimental techniques are required to register prewetting, see, e.g., reviews in references [192, 172, 193, 139]. However, the same phenomenon in a modified geometry (capillary- or wedge-like) corresponds to a singularity of the observable (Γ), rather than to a tiny jump in its value, thus at least registering a prewetting transition should be simplified.

Further investigation of continuous prewetting beyond a mean-field forms one of the most important planned directions of future work.

3.4 Dynamics of wetting

In this section we consider slow relaxational dynamics of an adsorbed LJ fluid, which arguably can be qualitatively described by a dissipative or a hybrid dissipative-conservative model, as was discussed in section 1.2. The equation for the dissipative model is given in (1.31) and for the hybrid model – in (1.33). As usual, for the case of a 1D density distribution, $\rho(\mathbf{r}, t) \equiv \rho(z, t)$, we insert into the equations $\mathbf{r} = z \cdot \mathbf{e}_z$, and for the 2D distribution, $\rho(\mathbf{r}, t) \equiv \rho(x, y, t)$, we insert $\mathbf{r} = x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y$. We note again that the models we employ are phenomenological, but nevertheless well established. The most active direction in the development of dynamic statistical approaches is accounting for various viscous and hydrodynamic interactions, see, e.g., a recent work by Goddard et al. [9].

The process of relaxation can be triggered, e.g., by switching off an initially present external field. The dissipative model (1.31) ensures that the bulk value of the chemical potential remains equal to μ at all times and is usually applied to open systems, see, e.g., a recent work by Thiele et al. [112] and a fundamental treatise by Langer [95]. We employ the dynamic formulation of DF to investigate, first, the stability of equilibrium fluid density distributions, $\rho(\mathbf{r})$, with respect to small perturbations. We also identify the relative effects of dissipative and conservative processes on the evolution of the system. Second, we study the rate for relaxation of various initial conditions to the respective states which provide extrema to $\Omega[\rho(\mathbf{r})]$. We show how “proximity” to stable or metastable equilibria can pin the evolution of the system. We also show how the dynamics of wetting can be systematised in terms of

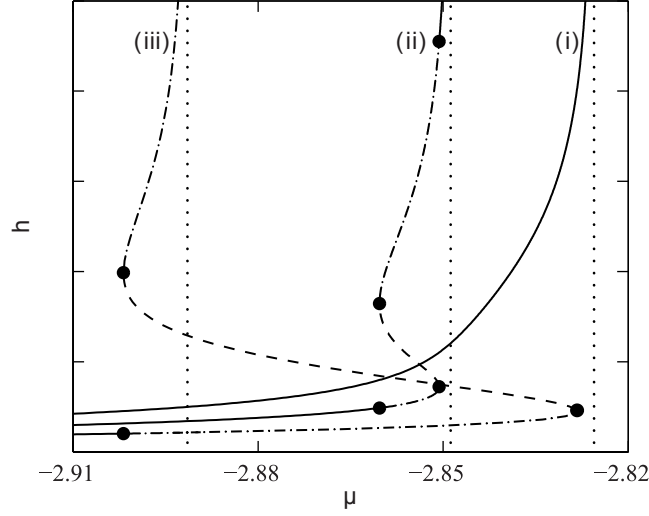


Figure 3.29: Adsorption isotherms calculated using WDA, with $\varepsilon_w = 0.4$, $\sigma_w = 1.25$, $T_w = 0.81$, $T_{pw}^{cr} = 0.87$. The solid, dash-dotted and dashed branches correspond to stable, metastable and unstable equilibria respectively. (i) complete wetting at $T = 0.9 > T_{pw}^{cr}$, (ii) prewetting at $T_w < T = 0.85 < T_{pw}^{cr}$, (iii) partial wetting at $T = 0.79 < T_w$. The coexistence values of chemical potentials for each temperature are shown by the vertical asymptotes of the isotherms (denoted by dotted lines). Filled circles are added for clarity, to mark the points where the isotherm branches change stability [3].

adsorption isotherms, which can be interpreted as bifurcation curves.

3.4.1 Planar wall

Consider adsorption on a planar wall described in section 3.1.2. Here we use a wall with a zero cutoff ($H_0 = 0$ in (1.27)), so its potential is given by (1.26). The parameters of the planar wall potential are fixed throughout this section to $\varepsilon_w = 0.4$, $\sigma_w = 1.25$, $\rho_w = 1$. We use WDA in the repulsive part of the DF functional, which leads to the value of the wetting temperature $T_w = 0.81$ and the value of the critical prewetting temperature $T_{pw}^{cr} = 0.87$. In hysteresis isotherms (those possessing a Van der Waals loop) one can identify thermodynamically stable, metastable and unstable branches. Figure 3.29 shows the stability of the three types of adsorption isotherms rescaled (similarly to section 3.1.2) to amount to an observable film thickness, h , see equation (3.1). Full, dashed-dotted and dashed lines denote stable, metastable and unstable branches. Isotherm (i) is at $T > T_{pw}^{cr}$, isotherm (ii) is at $T_w < T < T_{pw}^{cr}$, isotherm (iii) is at $T < T_w$.

As also discussed in [3], every point on an isotherm corresponds to a density profile which apart from minimizing the free energy, $\Omega[\rho(\mathbf{r})]$, provides a stationary solution to the dynamic equations (1.31) and (1.33). The characteristic feature of a stable branch is that when the associated density profiles are perturbed and allowed to relax, they will always return back

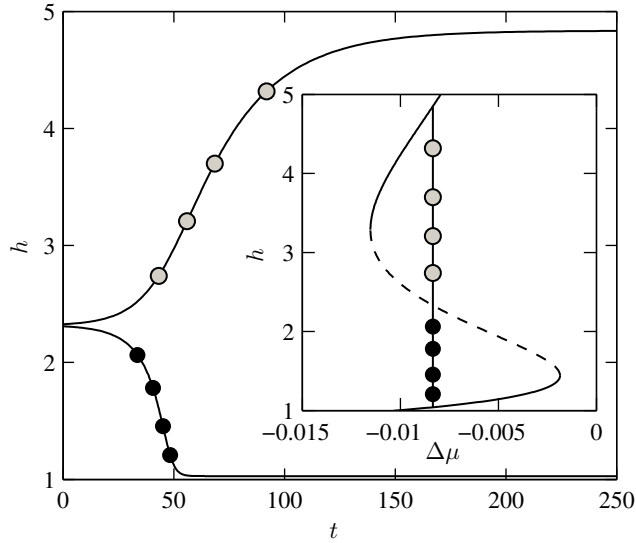


Figure 3.30: Evolution of film thickness, $h(t)$, corresponding to an unstable branch of a hysteresis isotherm at $T = 0.85$ (curve (ii) in figure 3.29), $\Delta\mu = -0.8 \cdot 10^{-2}$, $\kappa = 0.5$ [3]. Perturbed unstable equilibrium states evolve to either of the two metastable states, depending on the sign of the small perturbation in (3.49). The filled black and grey circles correspond to the snapshots of the evolving density profiles, $\rho(z, t)$, shown in figures 3.31(a) and 3.31(b), respectively. The inset shows the position of time-dependent film thickness on the adsorption isotherm.

to the respective stable stationary states. A density profile associated with a point on a metastable branch possesses a basin of attraction in the phase space of solutions to (1.31) or (1.33), and only initial conditions $\rho(z, t=0)$ within that basin eventually relax to the respective metastable state. In comparison, the basin of attraction of a stable density profile covers the whole phase space. An unstable state cannot be reached through a dynamic process, and hence cannot be observed. Any infinitesimal perturbation imposed on an unstable density profile will force it to evolve to a metastable equilibrium state. For a given value of the chemical potential the dynamic equations (1.61) can have a single stable stationary solution or up to two metastable ones, always accompanied by an unstable stationary solution.

The process of complete wetting (curve (i) in figure 3.29) gives rise to an entirely stable isotherm. Any hysteresis-type isotherm (curves (ii) and (iii)) possesses two metastable branches. In our numerical experiments we solved the equation (1.33) given in a non-dimensional form in (1.61), imposing at all values of time, t , a boundary condition of vanishing flux: at the wall and in the bulk of the fluid. For the planar wall the boundary conditions have the form [3]:

$$\left(\frac{\partial}{\partial z} \frac{\delta F_{\text{in}}}{\delta \rho} + V_0^{\text{wall}} \right)_{z=0, \infty} = 0. \quad (3.48)$$

For marching in time we used the `ode15s` function in MATLABTM, which is based on an implicit scheme with backward differentiation formulas and adaptive time stepping [194]. For

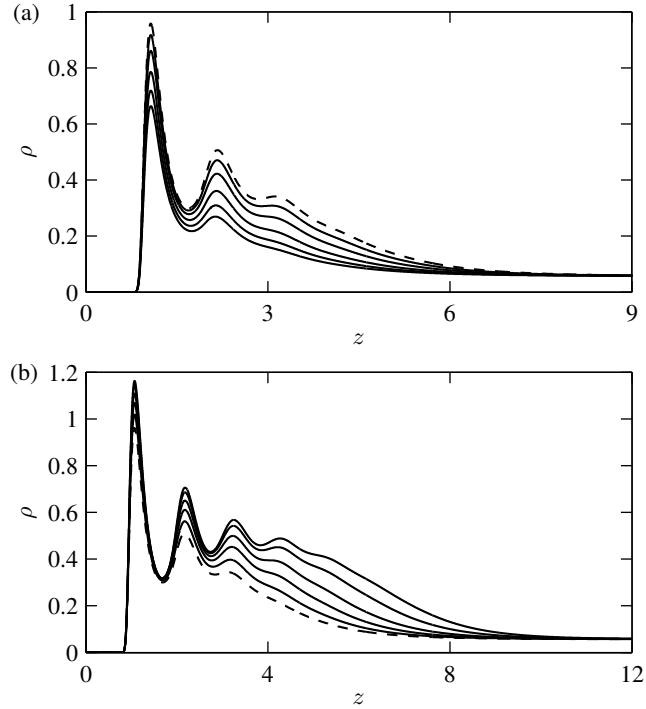


Figure 3.31: Snapshots of time-dependent density profiles corresponding to the evolution of the film thickness from figure 3.30 [3]. Dashed curves correspond to the initial density distributions obtained by imposing a small perturbation to an unstable profile, see equation (3.49). (a) Dynamic drying (from top to bottom) at times $t = 33, 40, 45$ and 48 . (b) Dynamic wetting (from bottom to top) at times $t = 43, 56, 69$ and 91 .

our calculations, we typically used 200 to 300 mesh points with a relative tolerance of 10^{-8} for each time step, which typically required less than 10 minutes on a standard 64-bit desktop computer.

To study the dynamics near the unstable branch of the isotherm we constructed initial density profiles, $\rho(z, t = 0)$, by solving the Euler-Lagrange equation with an additional small external field $\tilde{\delta}(z)$:

$$\frac{\delta F_{\text{in}}[\rho]}{\delta \rho} + V_0^{\text{wall}}(z) + \tilde{\delta}(z) - \mu = 0, \quad (3.49)$$

where $\tilde{\delta}(z)$ is an arbitrary, localised function with $|\tilde{\delta}(z)| \ll 1$ and $\tilde{\delta}(z) \rightarrow 0$ as $z \rightarrow \infty$. Equation (3.49) allows us to obtain density profiles that are arbitrarily close to an equilibrium profile associated with a point on the unstable branch of the isotherm.

When the system relaxes to equilibrium, the evolution depends on the sign of the disturbance in equation (3.49) (see figure 3.30). The initial profiles chosen for $\tilde{\delta}(z) > 0$ evolve to thicker profiles ($h(t)$ evolves to the upper metastable branch of the isotherm, see inset on figure 3.30). On the other hand, for $\tilde{\delta}(z) < 0$ the profiles tend to recede (film thickness evolves to the lower branch of the isotherm). In the phase space of stationary solutions of

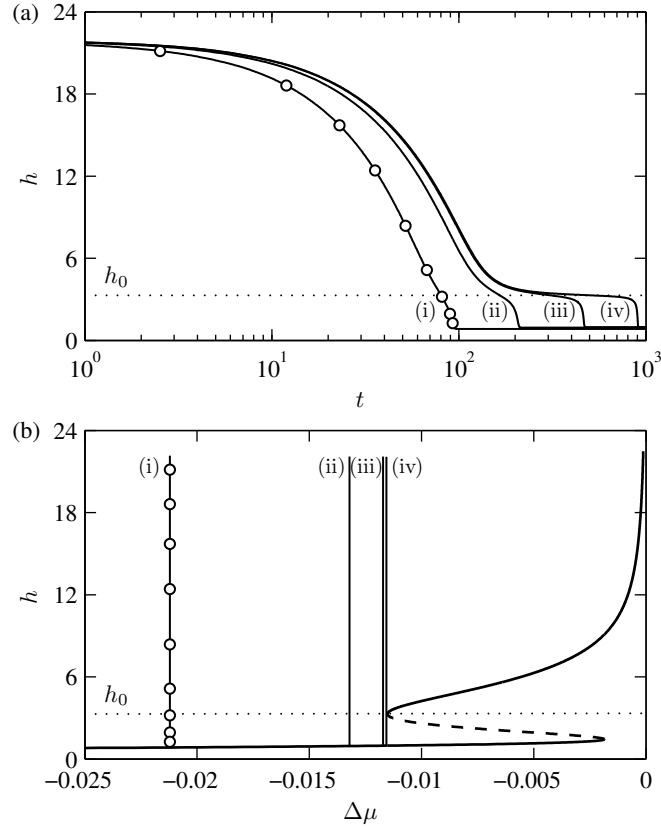


Figure 3.32: Dynamic drying of thick films at $T = 0.85$ and $\kappa = 1$ [3]. The values of deviation chemical potential are $\Delta\mu = -2.1, -1.3, -1.17, -1.16 \cdot 10^{-2}$ for curves (i) – (iv), respectively. (a) Temporal evolution of film thickness. (b) Position of curves (i)–(iv) on the adsorption isotherm. Open circles correspond to the snapshots of time-dependent density profile in figure 3.33. Note that as $\Delta\mu$ approaches the left spinodal of the isotherm, the evolution of the film thickness, $h(t)$, slows down near the value at the spinodal point, $h_0 = 3.3$.

dynamic equation (1.61), choosing this two types of initial conditions corresponds to a small perturbation of the unstable fluid state in the “direction” of either of the metastable equilibrium states. We can also see from the figure that drying happens faster than wetting, which is probably due to the initial condition of drying being closer to the respective metastable branch of the isotherm (see, for example, the inset of figure 3.30). Figure 3.31 depicts a few selected snapshots of the time-dependent density profile.

Consider now relaxation of a liquid film from a large, possibly macroscopic, value of the thickness to a much lower, microscopic value. This kind of dynamic drying can be triggered, e.g., by instantly lowering the temperature or pressure of a nearly saturated fluid. In practice the initial density profile can be formed by choosing an equilibrium profile at a value of μ different from the one used in the dynamic equation (1.61). Several representative examples are presented in figure 3.32, with density profiles at various times shown in figure 3.33.

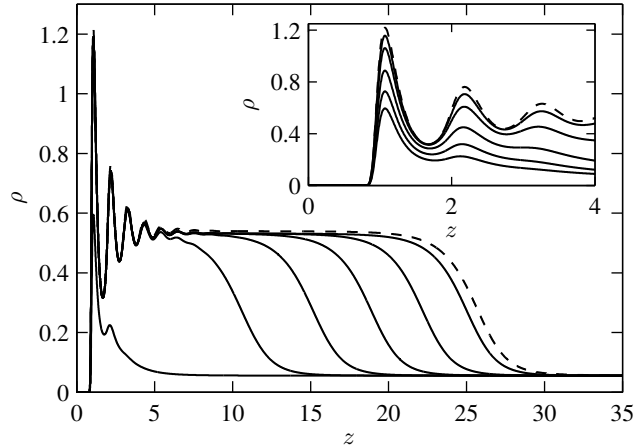


Figure 3.33: Snapshots of the time-dependent density profile in a dynamic drying process (see curve (i) in figure 3.32). The dashed line corresponds to the initial density profile, whereas the solid lines show the density profiles (from right to left) at intermediate times $t = 2.5, 12, 23, 35.5, 52$. This is continued onto the inset zooming into the near-wall region for times $t = 52, 67, 81, 89.5, 92.5$. The evolution of the fluid-wall interface begins much later than the liquid-vapor interface starts to recede – at $t > 52$ [3].

When we choose μ to be closer to the spinodal point of the isotherm, the film thickness takes more time to equilibrate (see curves (i)–(iv) in figure 3.32(a)), exhibiting in the extreme case a nearly steady behaviour when the height of the film, $h(t)$, reaches that of the spinodal point, h_0 (see, e.g., curve (iv) in figure 3.32(a)). This behaviour is a dynamic manifestation of the presence of hysteresis in the equilibrium isotherm. In principle, it is possible to choose such a values of μ that the film thickness would stay in the vicinity of h_0 for any given finite amount of time. However, as $t \rightarrow \infty$, the film would eventually relax to the stationary value on the isotherm (see figure 3.33 for an example of evolving density profiles).

The attraction to stable (or metastable) solutions becomes rather extreme during dynamic wetting when the system is near total saturation and $\Delta\mu \rightarrow 0^-$. Similarly to the previously considered case of drying, we can trigger a relaxation process by, e.g., instantaneously changing the temperature and the bulk pressure of an equilibrated fluid partially wetting the substrate. In the resulting dynamic process of wetting the system appears to be attracted not just to a single stable solution, as in the above case of drying near a spinodal point, but to the whole set of stable equilibria with similar values of μ . Depending on the proximity of the chemical potential to saturation, the evolution to the final state can take arbitrarily long times, as shown in figure 3.34. On the other hand, for intermediate values of μ which are sufficiently far from both the spinodal and saturation points, relaxation occurs over the shortest period of time (see, e.g., curves corresponding to the evolution towards h_2 in figure 3.34).

Finally, we consider the relative effect of conservative and dissipative processes in the equation (1.61), which is controlled by the parameter κ . Since, strictly speaking, the system

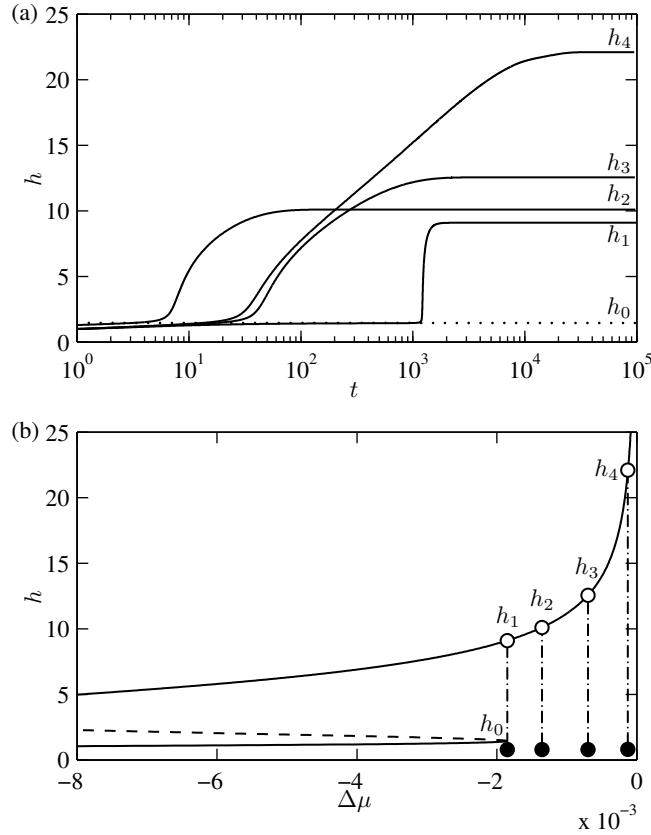


Figure 3.34: Relaxation of film thickness to a larger value, $T = 0.85$, $\kappa = 1$ [3]. Filled and open circles denote the initial and final thicknesses for each dynamic process, respectively. The final thicknesses, h_1 – h_4 , correspond to $\Delta\mu = -1.85, -1.35, -0.12, -0.7 \cdot 10^{-3}$, respectively. (a) Temporal evolution of film thickness $h(t)$. (b) Position of time-dependent film thickness on the adsorption isotherm. The process of evolution to h_1 is slowed down by the presence of the spinodal point at $h_0 = 3.3$. At $\Delta\mu = -0.7 \cdot 10^{-3}$ the process of evolution to h_4 is rather slow due to proximity to saturation.

equilibrates in an infinite amount of time, we have to introduce some kind of a measure for the proximity to equilibrium, in order to analyse the effect of κ . We define an “equilibration time”, t_{eq} , as the time required for the adsorbed film to achieve 90% of its equilibrium thickness. Our computations show that t_{eq} is inversely proportional to κ , with the coefficient of proportionality depending on the initial condition (see figure 3.35 for a representative result).

3.4.2 Capped capillary

Considering the 2D problem, we will, as usual, set in all equations $\mathbf{r} = x \cdot \mathbf{e}_x + y \cdot \mathbf{e}_y$. In section 3.2.3 we have shown that increasing the attractive strength of the substrate potential (lowering T_w) gradually leads to the appearance of a metastable drop surface phase, which

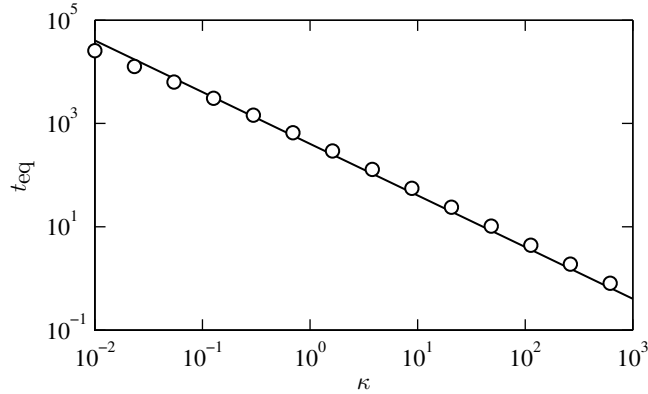


Figure 3.35: The effect of relative rate parameter, κ , see equation (1.61), on the equilibration time, t_{eq} , for evolution processes corresponding to curve (iii) in figure 3.32(b). The plot shows the computed values of t_{eq} (open circles) as a function of κ , together with the least squares fit: $t_{eq} = 403/\kappa$ (solid line) [3].

eventually stabilises for stronger substrates and even coexists with vapour and capillary-liquid slab surface phases: see, e.g., the upper isotherm in figure 3.25, where the concave branch of excess free energy, defining the (metastable) drop surface phase (grey line), is quite pronounced. In this thesis we considered fluids with vapour- and liquid-like densities and the temperatures were chosen above the bulk triple point. At lower temperatures and/or stronger attractive substrates one might expect more metastable branches of free energy to appear, due to effects of layering or freezing, see, e.g., [171]. In this section we show how the relaxation of the fluid confined in the capped capillary is affected by metastability. In order to enhance the confinement effects of the substrate, we choose the external potential in the form given in equation (3.43), as it leads to more pronounced hysteresis loops in the adsorption isotherms. It is clear from the study of dynamic planar wetting presented in the previous section that when the hybrid conservative-dissipative model (1.33) is used to describe an open system, the evolution is dominated by the dissipative term, so we will restrict our consideration of 2D dynamics to the dissipative model given by equation (1.31), where a particular value of ζ only affects the rate of relaxation to the equilibrium state, without loss of generality [3], see figure 3.35. We then set $\zeta \equiv 1$.

We note again, that the right hand side of the dissipative equation (1.31) is equivalent to the left hand side of the Euler-Lagrange equation (1.37). Thus, the stationary solutions to the integral-differential equation (1.31) form the extrema of fluid free energy and can be obtained independently by solving the Euler-Lagrange equation. As we have also seen above, in a dynamic setting, the adsorption isotherms act as bifurcation diagrams. Figure 3.36(a) shows the adsorption isotherm at $T = 0.8$ for the capillary with parameters $\varepsilon_w^{(i)} = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 30$. The fluid is treated in LDA, the planar wetting temperature: $T_w = 0.755$. The system exhibits only a single stable first-order transition – capillary prewetting at $\Delta\mu_{cpw}(T) = -4.95 \cdot 10^{-2}$, but there is also a metastable drop surface phase. Thermo-

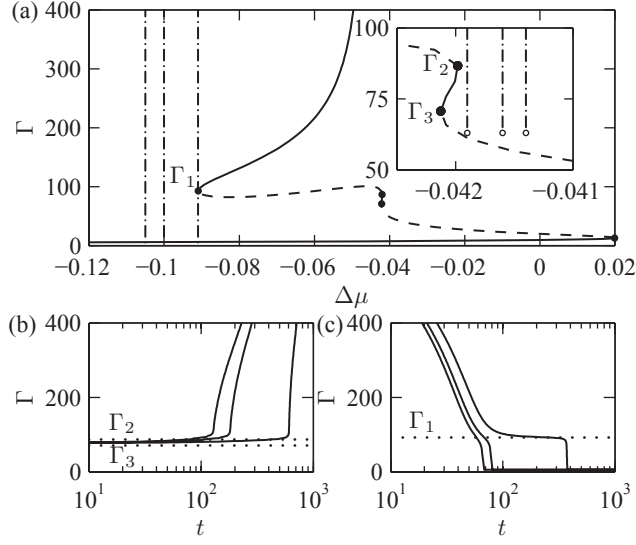


Figure 3.36: Evolution of the density profiles in the capped capillary, whose substrate potential is defined in equation (3.43), with $\varepsilon_w = 0.7$, $\sigma_w = 2$, $H_0 = 5$, $H = 30$; at $T = 0.8$, $\zeta = 1$.

(a) Equilibrium adsorption isotherm (bifurcation curve). Solid line: stable/metastable equilibria, dashed line: unstable states, vertical dashed-dotted lines: routes of dynamic emptying, all starting with the same initial density profile of capillary filled with capillary-liquid at CC (at $\Delta\mu \equiv \Delta\mu_{cc}(T) = -4.65 \cdot 10^{-2}$), passing at distances $(\Delta\mu - \Delta\mu_1)$: 10^{-4} , $9 \cdot 10^{-3}$ and $14 \cdot 10^{-3}$ to the spinodal at $(\Delta\mu_1, \Gamma_1) = (-0.091, 92.5)$.

Inset: vertical dashed-dotted lines show routes of dynamic filling, all starting with same initial profile of capillary filled with vapour, passing close to metastable branch, at the distances $(\Delta\mu - \Delta\mu_2)$: $8 \cdot 10^{-5}$, $4 \cdot 10^{-4}$, $6 \cdot 10^{-4}$ to its right-most spinodal at $(\Delta\mu_2, \Gamma_2) = (-0.041, 86.7)$.

(b) Evolution $\Gamma(t)$ for dynamic filling, note pinning to the metastable branch between $(\Delta\mu_2, \Gamma_2)$ and $(\Delta\mu_3, \Gamma_3) = 86.7$.

(c) Evolution $\Gamma(t)$ for dynamic emptying; note the pinning to the spinodal at $(\Delta\mu_1, \Gamma_1)$.

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

Choosing a density configuration, which minimises $\Omega[\rho^{\text{cpd}}(x, y)]$ at some value of $\mu \equiv \mu_{\text{sat}} + \Delta\mu$ as an initial condition, and then using a different value in the equation (1.31), allows us to study the relaxation of the system to a new equilibrium state. An independent calculation of equilibria (steady solutions of equation (1.31)) was used to control the convergence.

The resulting dynamic behaviour is most conveniently represented with the help of evolution

curves for $\Gamma(t)$ (see figure 3.36). We consider several processes of dynamic capillary filling. Initial condition is the capillary filled with vapour, and the final state ($t \rightarrow \infty$) is the capillary filled with capillary-liquid, figure 3.36(b). We also consider dynamic emptying, where the initial state of capillary-liquid relaxes to vapour, see figure 3.36(c).

Analogously to the 1D case we find that the evolving 2D system can spend considerable, albeit always finite, time in the vicinity of metastable states. Figure 3.36(b) illustrates the pinning to a whole branch of metastable states, while figure 3.36(c) shows pinning to a single metastable state – the spinodal of the capillary prewetting.

Conclusion

In conclusion I summarise my main results. In broad terms, there are two themes in this thesis. The first is the new approach for performing large-scale equilibrium and dynamic DF calculations and full parametric studies of model systems. The second is the new surface phase transformations and dynamic relaxation phenomena, which were found in the 2D capillary by employing the developed approach. Special notes are made regarding the existence of surface phase transitions beyond the mean-field level of treatment.

New numerical methodology

I have developed, implemented and tested a novel highly efficient numerical method for solving the integral and integral-differential equations of the DF theory and its dynamic extension in one and two dimensions. The method is based on the highly accurate discretisation scheme which implements Galerkin-type spectral ideas with a global interpolant obtained by collocation. The approach is built upon the latest progressive results in the fields of numerical analysis and applied mathematics. Namely, the use of various conformal maps to transplant the collocation points onto the physical domain allows one to control the density of the grid without sacrificing the exponential accuracy of the pseudo-spectral representation. The latter amounts to creating a set of global rational functions exponentially converging to the target function as the number of discretisation points is increased.

Spectral methods become increasingly popular in the modern world of large-scale calculations. The number of dedicated works in the latest numerical literature is rapidly increasing. With exponentially growing machine power such methods begin to offer serious competition to the more traditional approaches based on finite elements and finite differences, and I believe have a good chance of superseding them in the future. If properly implemented, spectral schemes are significantly more accurate and efficient. One of the main practical advantages of using the collocation form of a spectral approach is that it allows one to express differentiation in the form of a matrix operator which one multiplies with the data vector in order to differentiate the spectral approximation.

In this thesis I have offered an extension of the matrix formulation to equations containing non-local integral terms and proposed an integrating operator to calculate the convolution-like terms of DF equations via a fast matrix-vector product. This significantly speeds up the calculation. In a more general setting the developed approach can be used to discretise any type of a non-local integral term with a piecewise smooth kernel and/or a functional dependence in the limits of integration. The integrating operator can be reduced to an interpolating operator, which in turn is useful, e.g., in multi-grid iterative techniques to facilitate and speed-up the transformation to a new grid. The fact that the calculation of the integrating operator is completely independent from the equation to be solved allows one to pre-compute it, store it separately from the solution during the solving procedure, and also re-use it for any other problem discretised on the same collocation grid. I emphasise here that the pre-computing step allows us to speed-up significantly the solving procedure, e.g., many of the 2D DF calculations presented were done on a laptop computer, with the calculation of a single density profile taking on the order of a minute, and that of an isotherm – on the order of an hour.

The proposed numerical methodology in its present form is applicable to any 1D and 2D DF problems, with any type of free energy functional, so long as the geometry of the problem can be mapped to a rectangle (possibly with infinite borders). A straightforward extension to a class of three-dimensional DF calculations can be done, e.g., using a sharp-kink parametrisation of the profile. As I have demonstrated, the method enables one to use a moderate number of mesh points to discretise the problem, while maintaining a high accuracy of function representation. After discretisation, the integral equations of equilibrium problems and the partial differential equations of the dynamic problems are reduced respectively to the algebraic and ordinary differential equations for the data vector. I argue that, at least for 1D and 2D problems, using a Newton predictor-corrector iterative procedure to solve the algebraic equations of the equilibrium problem or perform the implicit time-stepping in the dynamic problems is superior in convergence and more reliable than a self-consistent type of procedure (e.g., Picard iterations). Moreover, the Newton method does not require any special customisation for particular problems, nor any manual control over iterations (again, unlike some of the Picard schemes commonly employed in modern DF literature). Furthermore, using a predictor-corrector scheme allows us to apply easily the arc-length continuation technique, which is being widely used in the latest literature on dynamical systems. Independently from the few existing works, I have adapted, implemented and tested the arc-length continuation technique for integral equations. In large 2D problems it is also quite important to supplement the algorithm with a suitable dynamic step-size control.

In this thesis I applied the arc-length continuation to address two typical 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 most important step in practice

is to obtain a starting point for continuation. Typically, one can consider some limiting value of the continuation parameter, where the solution to the equation is “well-behaved”, meaning that one does not have to cook up a special initial guess for the Newton iterations to converge to a solution. For example, the calculation of a free energy or an adsorption isotherm is best started from a low value of the chemical potential, where the fluid is in the vapour phase and thus the walls have little effect on its density profile. In that case a simple initial guess, e.g., $\rho^{\text{cpd}}(x, y) \equiv \rho_{\text{cc}}^{\text{vap}}$ suffices. On the other hand, the computation of a line of surface phase transitions 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. Note that, as we have seen, a consistent analysis of thermodynamic stability of a given fluid configuration is impossible to carry out without access to a set of density profiles, which allows one to analyse the convexity of the branches of free energy. Thus computing a set of density profiles (and not just a single profile) is a necessary part of the mean-field analysis of the thermodynamic behaviour of the system.

To summarise, in this thesis I have demonstrated how using a pseudo-spectral discretisation and an arc-length continuation for the DF equations essentially amounts to a complete toolbox for the efficient, systematic and reliable investigation of the phase behaviour of statistical-mechanical systems within a mean field treatment. Applying the proposed method allows one (after choosing a suitable approximation for the free energy functional) to follow a set of essentially standard steps to obtain the full picture of the system’s surface phase behaviour. The prescriptions given are applicable to any DF problem and are free from ad hoc steps. I expect that the arc-length continuation will dramatically affect the entire field of DF calculations in the near-future. The overall proposed numerical methodology shows faster convergence, higher reliability and requires less customisation in applications to various DF problems than all conventional numerical strategies known to me from the existing literature on DF computations.

Wetting in a capped capillary

By applying the DF theory, which is based on the first principles of statistical mechanics, I have modelled a prototypical 2D fluid system, namely a rectangular capillary, which can be obtained by, e.g., capping a slit pore at one end by an additional wall. I have performed a full parametric study of the model and demonstrated how the additional spatial dimension in the confined fluid dramatically affects the nature of wetting. By manipulating the thermodynamic fields acting on the system, it is possible to switch its wetting behaviour between various wetting mechanisms. Although being fundamental, the results obtained offer principal ways to control wetting in geometrically modified substrates, which is important in, e.g., nanofluidics and design of lab-on-chip devices.

Until quite recently only a handful of studies presented adsorption isotherms, and even

fewer presented complete surface phase diagrams of complex 2D systems. I have explored various wetting scenarios in a capped capillary formed from a substrate which in the case of a planar geometry exhibits first-order wetting. Identifying the concave branches of $\Omega(\mu)$ with fluid surface phases allowed us to construct full mean-field surface phase diagrams, which in turn have revealed the interplay between different wetting mechanisms in the system. Apart from the general surface phase behaviour, we have also discussed in detail the structure of coexisting fluid configurations, the excluded volume effects and some aspects of criticality. My main results regarding the DF study of the capped capillary are summarised by the following list.

- Capping a slit pore at one end adds one spatial dimension to the system, which leads to the existence of the *capillary wetting transition*. It is a discontinuous first-order surface phase transition characterised by the presence of the *capillary wetting temperature*, T_{cw} , which is a property of the pore and allows one to control the order of isothermal CC.
- At temperatures higher than T_{cw} , CC is continuous and is manifested by the slab of capillary-liquid nucleated at the capping wall and filling the pore as $\mu \rightarrow \mu_{cc}$ from below, quasi-statically. The adsorption in that limit diverges as $\Gamma \sim (\mu_{cc} - \mu)^{-1/4}$. Below T_{cw} configurations with capillary-liquid slabs are metastable and CC is a first-order surface phase transition. In a 1D slit pore CC is always of first order, so the existence of continuous CC in the case of a 2D capillary is a direct consequence of the additional spatial dimension. The continuous CC exists beyond mean-field [152].
- Within mean-field, there exists a first-order *capillary prewetting* transition, which precedes the continuous CC. The capillary wetting transition can be viewed as the limiting case of the capillary prewetting at $T = T_{cw}$. In the $T - \mu$ plane the transition line of capillary prewetting runs tangentially to the CC line: $(\mu_{cc} - \mu_{cpw}) \sim (T - T_{cw})^{4/3}$ as $T \rightarrow T_{cw}$ from above. Capillary prewetting possesses in mean-field a critical point at the *critical capillary prewetting temperature*, T_{cpw}^{cr} . Beyond mean-field the critical point does not exist as it belongs to the 1D Ising universality class. The capillary prewetting transition is rounded by fluctuations.
- Within mean-field, wetting in 2D wedge-shaped substrates immersed in vapour is affected by the addition of a third wall, which changes the geometry to a rectangular capped capillary. On the surface phase diagram of the fluid in the $T - \mu$ plane the remnant of wedge prefilling can form a transition line, which is translated relatively to the wedge prefilling line along the μ -axis by a constant value. This is referred to as the *shifted wedge prefilling* transition. Given the substrate parameters, the value of the shift is determined by the width of the capillary. Beyond mean-field the critical point of wedge prefilling does not exist as it belongs to the 1D Ising universality class. The wedge prefilling and shifted wedge prefilling transitions are thus rounded by fluctuations.

- Within mean-field a triple point has been found where three fluid surface phases (vapour, corner drops and capillary-liquid slab) can coexist near the capillary capping wall.
- *Continuous planar prewetting* transition has been discovered. It is well known that the individual walls of a slit pore (the bulk of the capped capillary) can exhibit planar prewetting at $\mu = \tilde{\mu}_{\text{pw}}$, which is shifted from the prewetting of a single planar wall (at $\mu = \mu_{\text{pw}}$) by a constant value related to the pore width. In the 2D capillary the shifted planar prewetting becomes continuous and is manifested by the liquid-like fingers (whose height is that of the thick prewetting film) nucleated at the capping wall and unbinding into the capillary bulk as $\mu \rightarrow \tilde{\mu}_{\text{pw}}$ from below quasi-statically. The adsorption in that limit is found to diverge as $\Gamma \sim (\tilde{\mu}_{\text{pw}} - \mu)^{-1/4}$. The same transition should occur in wedge-shaped substrates immersed in vapour as $\mu \rightarrow \mu_{\text{pw}}$. In the capped capillaries continuous planar prewetting precedes the continuous CC. Thus, the system has two consecutive continuous transitions, each associated with the divergence of adsorption with the exponent $-1/4$. The critical point of continuous prewetting belongs to the 2D Ising universality class, thus the transition is genuine and exists beyond mean-field. It is likely that continuous prewetting is accessible experimentally. It also may influence the experimental investigations of planar prewetting transitions.
- Metastable states have been found to affect the dynamic behaviour of the fluid. In particular, the relaxation times become very large near the spinodals of grand free energy.

Based on the results presented in the thesis, there are several studies planned for the future. As for the numerical methodology, I plan to extend it to more complicated 2D domains, which cannot easily be mapped onto a rectangle with possibly infinite borders. Such extension would allow one to study wetting of various corrugated substrates. I also plan to implement an algorithm of dynamic grid-refinement, which may allow one to further reduce the number of collocation points, as well as being useful in treating complicated dynamic DF problems with moving interfaces.

As for the future work based on the presented study of the capped capillary, first of all, a detailed investigation of continuous planar prewetting is in order and planned for. Such study will include wedge-shaped substrates, an attempt will also be made to go beyond the mean-field level of description and consider the effects of fluctuations.

Another possible study may concern the details of the microscopic fluid structure near the walls. Note that the interfaces (see, e.g., figures 3.9(d), 3.10, 3.12(a), 3.13(a), 3.15(c), 3.15(e), 3.22(b), 3.22(c), 3.24(d), 3.24(e) and 3.28) possess quite well defined angles at the three-phase contact line. The values of these contact angles are determined by the microscopic fluid-fluid and fluid-substrate interactions. Note that such a contact angle is different from the Young-Laplace contact angle, which is defined for the fluid in contact with a planar wall at bulk

saturation. A deeper investigation, possibly involving the concept of line tension, may lead to a better understanding of the characteristics of microscopically defined contact angles.

Appendix: Barycentric formula and its benefits

The problem of interpolating a function $f(x)$ given on the computational domain on the set of $N+1$ nodes $\{x_k\}$, $k = 0 \dots N$ by the data $\{f_k\}$ is treated in virtually every book on applied mathematics. In our case, we want to use interpolation to discretise and solve numerically an integral or an integral-differential equation for the function $f(x)$, so we are looking to use interpolation to transform such equation into a set of algebraic equations for the data $\{f_k\}$. In contrast, much of the interpolation theory has been historically devoted to tabulating various analytic functions for practical computations, and is hardly used in modern practises, where re-computing a function is cheaper than storing the tables of that function. We will assume a finite computational domain for now; in section 2.1.6 it is shown how to deal with infinite domains.

The problem we are addressing consists of two sub-problems. First, we need to have a convenient interpolation formula, which would be numerically stable, computable in a small number of floating point operations (multiplications and additions), and allowing one to easily extend the number of nodes from N to $N_1 > N$, with a small additional effort. Second, since we are not restricted to any particular set $\{x_k\}$, we want to use that freedom to optimise the accuracy of function representation, and choose “the best” set of N interpolation nodes. For example, it is very well known, that the efficiency of polynomial interpolation is higher when the grid points are clustered near the ends of the domain, while a uniform distribution of the nodes leads to numerical instability when interpolating by polynomials of high degree [131].

Let $P_N(x)$ be the polynomial interpolant of degree N . Such polynomial is know to be unique [121], and its most famous representation is called the Lagrange form:

$$P_N(x) = \sum_{k=0}^n \frac{\prod_{j=0, j \neq k}^n (x - x_j)}{\prod_{j=0, j \neq k}^n (x_k - x_j)} f_k. \quad (3.50)$$

Unfortunately, the above expression is not very convenient on practice, so we modify its form. Introducing a polynomial $q(x) = \prod_{j=0, j \neq k}^n (x - x_j)$, we can rewrite equation (3.50) as

$$P_N(x) = q(x) \sum_{k=0}^n \frac{f_k}{(x - x_k) q'(x_k)}, \quad (3.51)$$

where $q'(x)$ denotes the derivative of $q(x)$.

Applying equation (3.51) to interpolate a function $f(x) \equiv 1$, we get the following equiva-

lence:

$$1 \equiv q(x) \sum_{k=0}^n \frac{1}{(x - x_k) q'(x_k)}. \quad (3.52)$$

Finally, dividing equation (3.51) by equation (3.52), we arrive at the *barycentric formula* for the polynomial interpolant [127]:

$$P_N(x) = \frac{\sum_{k=0}^n \frac{w_k}{x - x_k} f_k}{\sum_{k=0}^n \frac{w_k}{x - x_k}}, \quad (3.53)$$

where the *barycentric weights* $w_k \equiv 1/q'(x_k)$, $k = 1 \dots n$, are defined as

$$w_k = \frac{1}{\prod_{j=0, j \neq k}^n (x_k - x_j)}. \quad (3.54)$$

Comparing the two equivalent expressions (equations (3.50) and (3.53)) for the interpolating polynomial of degree N , we note the obvious advantages for using the barycentric form over the standard Lagrange form in practical calculations. First, the expression (3.50) requires $O(N^2)$ floating point operations to compute, where in the case of expression (3.53) one only needs to precompute the weights in $O(N^2)$ operations, while the actual computation of the interpolant takes $O(N)$ operations. In a numerical scheme, where interpolation is used inside a loop (e.g., a Newton iterative algorithm), the advantage is obvious, since the weights $\{w_k\}$ can be precomputed outside of the loop, stored in memory and reused throughout the loop, thus making execution faster by a factor of N operations. If the weights in (3.53) are computed for a given domain, say $[-1, 1]$, linearly mapping to any other finite domain, say $[a, b]$, corresponds to multiplying the expression for weights (3.54) by the factor $2^N / (b - a)^{-n}$, which cancels out in the barycentric formula (3.53). Thus without loss of generality we can restrict our attention to the model computational interval $[-1, 1]$. Extending the interpolation grid by adding a node x_{N+1} requires in the case of Lagrange formula (3.50) a recalculation of the whole interpolant from scratch (performing $O(N^2)$ operations), whereas barycentric form only requires updating the weights in $O(N)$ operations. Finally, the barycentric form is numerically stable unlike the classical Lagrange form, meaning that small changes in the values of the nodes typically do not result in large changes in the values of the interpolant. More details and discussion can be found in the review paper by Berrut and Trefethen in reference [127].

Note, that the barycentric form of the interpolant, unlike its Lagrange form, is not ensured against division by zero. While for points x exactly equal to the grid nodes this can be taken care of by using an exception in the computer code, the real question of numerical stability is associated with a case $x \rightarrow x_k$, where the corresponding value $w_k / (x - x_k)$ tends to infinity: will interpolation at point $x \approx x_k$ be associated with a large rounding error? A simplified

and short answer is that it will not, because the inaccuracies associated with subtracting large numbers appear in such cases in both the numerator and the denominator of (3.53) and “cancel out”. A rigorous treatment of numerical stability of equation (3.53) can be found in references [132, 133].

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