

Density functional theory of long-range critical wetting

A. González and M. M. Telo da Gama

*Departamento de Física da Faculdade de Ciências e Centro de Física da Matéria Condensada da Universidade de Lisboa,
Avenida Professor Gama Pinto, 2, P-1649-003 Lisboa Codex, Portugal*

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The wetting properties of a fluid adsorbed at a solid substrate are studied by means of density functional theory. Explicit calculations of the substrate-liquid and substrate-gas density profiles are carried out and used to evaluate the asymptotic expansion for the interface potential of a system with long-range interactions. The range of validity of the asymptotic expansion is checked by comparing it with the interface potential obtained numerically through the constrained minimization of the density functional free energy. Depending on the parameters of the fluid-fluid and substrate-fluid interactions we find first-order or critical wetting transitions. In a limited range of parameters, the critical wetting transition is preceded by a first-order transition between a microscopic and a mesoscopic film, thus corroborating previous calculations and experiments for alkanes on brine. We find that the behavior of the alkanes on brine is not universal, since it requires fine-tuning of the fluid-fluid and substrate-fluid interactions. Finally, we investigate the influence of the short- and long-range forces on the location of the first-order transition. We find that for the models studied, the long-range forces cannot be treated perturbatively. Thus for this type of model it is not possible to separate the effects of short- and long-range forces as done in Landau theories, where the long-range forces are treated perturbatively.

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I. INTRODUCTION

Wetting and nonwetting are most commonly described in terms of a liquid droplet on a substrate, under conditions of liquid-gas coexistence. The three interfacial tensions are related by the (force balance) equation of Young [1,2]

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos(\theta), \quad (1)$$

where θ is the contact angle. Nonwetting occurs when $\theta \neq 0$. As the temperature is raised, the contact angle may vanish and the system is said to undergo a wetting transition, i.e., the interface between the substrate and the gas becomes macroscopic through the formation of a thick liquid layer [3]. This transition is of first or second order, as illustrated in a series of recent experiments [4].

A powerful method used in the study of wetting transitions is the interface potential $\omega(l)$, defined as the excess free energy per unit area of a substrate-gas interface with a wetting layer of thickness l , with respect to an infinite layer. For large l , the interface potential of a system with van der Waals forces tends to zero as

$$\omega(l) = \frac{a}{l^2}, \quad (2)$$

where a , the Hamaker constant, is proportional to the net van der Waals forces between the interfaces bounding the wetting film. Thus, for fluids with constant a critical wetting does not occur since the wetting transition is of first order if $a > 0$ and the interface is pinned if $a < 0$ [1,2].

The Hamaker constant, however, depends on the bulk polarizabilities in a subtle way [5] and

$$\omega(l) = \frac{a_2(T)}{l^2} + \frac{a_3}{l^3} + \dots \quad (3)$$

is a more realistic asymptotic potential and long-range critical wetting may occur when $a_2 \rightarrow 0^-$. Indeed, critical wetting driven by a vanishing Hamaker constant was predicted theoretically more than a decade ago [6,7] and was first observed for pentane on water recently [8].

Subsequent experiments, with hexane on brine [9], indicated that a first-order transition precedes the critical wetting transition observed at higher temperatures. At this first-order transition, a (microscopic) thin film coexists with a (mesoscopic) thick film at a temperature where a first-order wetting transition would occur in the absence of (weak) long-range interactions [9,10]. This sequence of transitions results from the competition of short- and long-range forces. When the temperature is raised, the balance of the long-range forces changes to favor wetting, and critical wetting occurs at the temperature where the Hamaker constant vanishes.

While a sequence of two transitions was predicted theoretically, in this context, for a particular model years ago [7], a systematic study based on an extension of Cahn's theory that includes weak long-range substrate-fluid interactions, appeared only recently [10]. The theory treats the long-range solid-fluid interactions as a perturbation of the free energy of a system with short-range interactions, and thus the question of separating the long- and short-range forces for a specific model remains open.

Density functional theory (DFT) has become one of the most useful microscopic approaches to inhomogeneous fluids and wetting phenomena [11]. The latest generation of DFTs is designed to describe (i) the bulk fluid equation of state (away from the bulk critical point), (ii) the liquid-gas interfacial structure, and (iii) the fluid's response to short-wavelength perturbations. These theories provide the means

to study the effects of short- and long-range interactions, in a nonperturbative fashion, for a given interaction model. DFTs neglect the effects of capillary waves, but these are irrelevant for long-range critical wetting in three dimensions [12].

In this paper we use a mean-field free energy functional [11] with a reference term given by the (nonlocal) fundamental-measures theory (FMT) [13]. In Sec. II we give a brief account of DFT and of the corresponding interface potential. In Sec. III we summarize the results of the asymptotic expansion of the interface potential derived in [12]. In Sec. IV details of the interactions and of the reference free energy functional are given, and in Sec. V we present our results. We finish with some comments and concluding remarks.

II. DENSITY FUNCTIONAL THEORY FOR WETTING: INTERFACE POTENTIAL

Density functional theory [11] was introduced in the study of inhomogeneous fluids more than 25 years ago [14] and was followed by the discovery of the prewetting transition [15], independently from Cahn's seminal work on wetting [3]. DFTs are still one of the most useful descriptions of wetting, although applications of the most sophisticated functionals to wetting problems are scarce. As we will discuss below this is due to the nontrivial effort required to implement numerical calculations with these density functionals, when the interfaces become mesoscopic. This is indeed what happens for the alkanes on brine, where a discontinuous transition from a microscopic to a mesoscopic film precedes the critical wetting transition. Here, we overcome this difficulty by combining direct (brute force) numerical minimization of the free energy functional, with the evaluation of the interface potential (for the same functional), using the analytic expansion derived in [12].

Since the application of DFT to wetting has come of age, we simply quote the main results. Consider an open, single-component, inhomogeneous system in the presence of an external potential $V_{\text{ext}}(\mathbf{r})$. It can be shown [11] that the grand potential of a fluid with pairwise interaction potential $v(r)$ at temperature T and chemical potential μ is the minimum of the functional

$$\Omega[\rho] = \mathcal{F}[\rho] + \int d\mathbf{r} [V_{\text{ext}}(\mathbf{r}) - \mu] \rho(\mathbf{r}), \quad (4)$$

where, for fixed $v(r)$, the intrinsic Helmholtz free energy \mathcal{F} is a unique functional of the density $\rho(\mathbf{r})$, i.e., it does not depend on the external potential.

The equilibrium profile is determined by minimizing Eq. (4), i.e.,

$$\frac{\delta\Omega[\rho]}{\delta\rho(\mathbf{r})} = 0. \quad (5)$$

Once the form of $\mathcal{F}[\rho]$ is known, Eq. (5) can be used to calculate the equilibrium structure of the system. Details of the numerical method used to solve this equation, for a particular form of \mathcal{F} to be described below, may be found in [16].

Let $v_\alpha(r) = v_{\text{ref}}(r) + \alpha[v(r) - v_{\text{ref}}(r)]$, with $\alpha \in [0, 1]$. Using the coupling constant algorithm [17], \mathcal{F} may be written as [11]

$$\mathcal{F}[\rho] = \mathcal{F}_{\text{ref}}[\rho] + \frac{1}{2} \int_0^1 d\alpha \int d\mathbf{r} d\mathbf{r}' \rho^{(2)}(\mathbf{r}, \mathbf{r}'; \alpha) v_\alpha(|\mathbf{r} - \mathbf{r}'|), \quad (6)$$

where $v_\alpha(r) = v(r) - v_{\text{ref}}(r)$ and $\mathcal{F}_{\text{ref}}[\rho]$ is the free energy functional of a system with pair potential $v_{\text{ref}}(r)$ and density $\rho(\mathbf{r})$. $\rho^{(2)}(\mathbf{r}, \mathbf{r}'; \alpha)$ is the pairwise density distribution function of a system at the same density $\rho(\mathbf{r})$ and where the particles interact via the pair potential $v_\alpha(r)$.

In three dimensions \mathcal{F} is known exactly for ideal gases only, although good approximations exist for fluids of hard spheres (HS). As in most applications we will take a fluid of HS as our reference system, but for the moment we do not need to specify \mathcal{F}_{ref} . If the remaining interactions v_α vary slowly on the scale of v_{ref} their contribution to \mathcal{F} may be treated at the mean-field level, i.e., the pairwise density distribution function is approximated by its (large r) asymptotic limit. Then the mean-field free energy functional is

$$\begin{aligned} \Omega[\rho] = & \mathcal{F}_{\text{ref}}[\rho] + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') v_\alpha(|\mathbf{r} - \mathbf{r}'|) \\ & + \int d\mathbf{r} [V_{\text{ext}}(\mathbf{r}) - \mu] \rho(\mathbf{r}). \end{aligned} \quad (7)$$

Equation (7) neglects the fluctuations that cause bulk properties to deviate from their classical behavior and capillary waves. The former are important in the critical region, close to the bulk critical point, while the latter are excited at low temperatures. However, in systems with long-range forces, capillary waves are irrelevant for wetting transitions in three bulk dimensions [1].

If we consider a fluid in contact with a (structureless) planar substrate, we can rewrite Eq. (7) as the sum of a bulk contribution, proportional to the volume of the fluid V , plus a surface contribution proportional to the area of the substrate A [12]

$$\Omega[\rho(z)] = V\Omega_b(\rho_b) + A\Omega_s[\rho(z)], \quad (8)$$

where subscripts b and s stand for bulk and surface, respectively, and $\rho(z)$ is the density profile that varies only in the direction perpendicular to the surface. If the density far from the substrate is that of the bulk fluid, ρ_b is a minimum of Ω_b (liquid or gas, with densities ρ_l and ρ_g , respectively) and the equilibrium states of the system are given by the minimum of the surface term Ω_s . At liquid-gas coexistence the surface term can be written as

$$\Omega_s(l) = \gamma_{sl} + \gamma_{lg} + \omega(l), \quad (9)$$

with γ_{sl} and γ_{lg} the substrate-liquid and liquid-gas interfacial tensions, and $\omega(l)$ the interface potential. In Eq. (9) we have replaced the functional dependence of Ω_s on $\rho(z)$, by a dependence on l , the thickness of the liquid layer adsorbed at the substrate. This thickness will be defined by $\rho(l) = (\rho_l + \rho_g)/2$, although other definitions are possible [12]. The extrema of $\omega(l)$ reproduce the stable (minima) and unstable

(maxima) thermodynamic states, but only the local minima have direct physical significance. In contrast to the equilibrium free energy, its nonequilibrium extension $\omega(l)$ is not uniquely defined. For a review see, e.g., [18].

It turns out that a particularly transparent analysis of wetting phenomena follows from the interface potential. This potential represents the substrate-gas interfacial tension, under the restriction that a liquid film with thickness l is present at the interface. The actual interfacial tension γ_{sg} and equilibrium thickness l_0 are obtained by minimizing $\omega(l)$. The interface potential may be found numerically by a constrained minimization of the free energy functional, at fixed l . In addition, at large l an analytical expansion for systems with long-range forces is available [12] and can be evaluated for the same free energy functional. The characteristic features of critical and complete wetting—for which l_0 diverges smoothly—are determined by the asymptotic behavior of $\omega(l)$, and this behavior is most easily described using the asymptotic expansion. The location of first-order transitions, however, requires the (constrained) numerical minimization of the free energy functional.

III. ASYMPTOTIC EXPANSION OF THE INTERFACE POTENTIAL

In the presence of long-range van der Waals forces between particles (fluid-fluid and substrate-fluid) the asymptotic form of $\omega(l)$ ($l \gg \xi$, where ξ is the fluid bulk correlation length) is given by [12]

$$\omega(l \rightarrow \infty) = - \sum_{i \geq 2} \frac{a_i}{l^i}, \quad (10)$$

where a_2 is proportional to the Hamaker constant [5].

Dietrich and Napiórkowski [12] derived analytic expressions for the coefficients a_i (up to $i=4$) in the framework of the mean-field functional described in the preceding section, and showed that they are given in terms of (a) the coefficients of the asymptotic expansions of the substrate-fluid and fluid-fluid interactions, and (b) the spatial moments of the equilibrium density profiles of the substrate-liquid and liquid-gas interfaces. Their approach takes into account the van der Waals tails of the interfaces and the (short-range) structure of the substrate-liquid and liquid-gas interfaces.

In the following we summarize their results. Assume that the substrate-fluid potential has the asymptotic expansion

$$V_{\text{ext}}(z \rightarrow \infty) = - \sum_{i=3}^{\infty} \frac{u_i}{z^i}, \quad (11)$$

and that the laterally averaged fluid-fluid potential, defined as

$$t(z) = \int_z^{\infty} dz' \int d\mathbf{r}_{\parallel} v[(\mathbf{r}_{\parallel}^2 + z'^2)^{1/2}], \quad (12)$$

has a similar expansion

$$t(z \rightarrow \infty) = - \sum_{i=3}^{\infty} \frac{t_i}{z^i}. \quad (13)$$

The first-order coefficient in Eq. (10) is found to be

$$a_2 = \frac{1}{2}(\rho_1 - \rho_g)(u_3 - \rho_1 t_3), \quad (14)$$

and depends on the leading coefficients of the long-range interactions (11) and (13) and on the coexisting liquid and gas densities. Equation (14) is exactly the same as the expression found in previous derivations, for pure Lennard-Jones systems, using simpler (sharp-kink) approximations for the interfacial structure (see, e.g., [1,2]). Note that although there is no explicit dependence of a_2 on the temperature, it does depend on T through the coexisting densities $\rho_l(T)$ and $\rho_g(T)$, and thus it may vanish at a temperature below the bulk critical temperature. In this case the next-to-leading term in Eq. (10) is required to be positive and has to be included.

Higher-order coefficients of the interface potential ($i \geq 3$) depend explicitly on the higher-order coefficients of the interactions and on the interfacial structure. The latter arises through the moments of the substrate-liquid and liquid-gas density profiles defined as [12]

$$d_{\text{sl}}^{(i)} = i \int_0^{\infty} dz z^{i-1} [1 - \rho_{\text{sl}}(z)/\rho_1] \quad (15)$$

and

$$d_{\text{lg}}^{(i)} = \frac{i}{\rho_1 - \rho_g} \int_{-\infty}^{\infty} dz z^{i-1} [\rho_{\text{lg}}(z) - \rho^{\text{sk}}(z)], \quad (16)$$

respectively. Here $\rho^{\text{sk}}(z)$ is the sharp-kink profile

$$\rho^{\text{sk}}(z) = \begin{cases} \rho_1, & z < l \\ \rho_g, & l < z, \end{cases} \quad (17)$$

where l is defined as in the preceding section. The moments are calculated by numerical integration of the substrate-liquid and liquid-gas density profiles, obtained by numerical minimization of the free energy functional (7).

The expressions for a_3 and a_4 obtained in this fashion differ from earlier results obtained using a sharp-kink approximation. For details see [12].

We use these asymptotic results to test the accuracy of the interface potential $\omega(l)$ obtained from the restricted minimization of the (same) free energy functional, at large l . Our numerical results for $\omega(l)$ are used, in turn, to test the range of validity of the asymptotic expansion (10).

IV. MODEL INTERACTIONS AND REFERENCE FREE ENERGY

It remains to specify the model interactions and the reference free energy functional. We have restricted ourselves to simple pair interactions with a minimum number of parameters. In order to allow for the possibility of long-range critical wetting, the fluid-fluid potential has the form

$$v(r) = v_{\text{HS}}(r) - \epsilon \left[v_7 \left(\frac{\sigma}{r} \right)^7 + v_6 \left(\frac{\sigma}{r} \right)^6 \right] \theta(r - \sigma), \quad (18)$$

where $\theta(r)$ is the usual Heaviside step function and $v_{\text{HS}}(r)$ is the HS potential

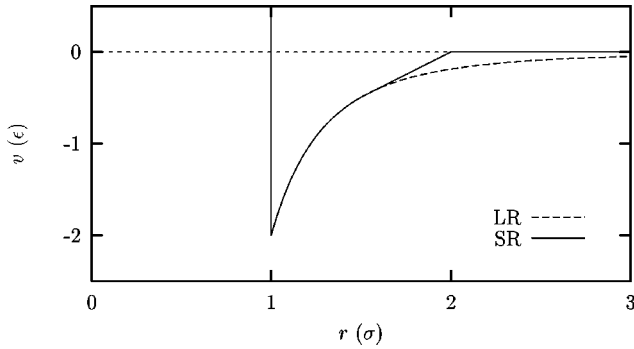


FIG. 1. Construction of the short-range (SR) fluid-fluid potential from its long-range (LR) counterpart, for $r_c = 2.0\sigma$. A similar procedure is applied to the substrate-fluid potential.

$$v_{\text{HS}}(r) = \begin{cases} \infty, & r < \sigma \\ 0, & \sigma < r, \end{cases} \quad (19)$$

where σ , the hard-sphere diameter, sets the unit of length, and ϵ the unit of energy. The usual reduced temperature $T^* = k_B T / \epsilon$ is therefore employed. We assume that the external (substrate-fluid) potential has a similar expansion

$$V_{\text{ext}}(z) = v_{\text{HS}}(z) - \epsilon \left[u_4 \left(\frac{\sigma}{z} \right)^4 + u_3 \left(\frac{\sigma}{z} \right)^3 \right] \theta(z - \sigma). \quad (20)$$

In order to investigate the competition between short- and long-range forces, invoked as the cause of the wetting behavior of alkanes on water, we constructed related short-range potentials by setting Eqs. (18) and (20) to zero at distances greater than r_c and z_c , respectively. To avoid numerical problems due to discontinuities, the short-range potentials are required to vanish at the cut off distance through a linear extrapolation of the corresponding long-range potentials (see Fig. 1). By contrast with Ref. [10], we do not assume that the short-range forces determine the location of the first-order wetting transition, while the long-range forces are responsible for the finite thickness of the wetting film and for the location of the critical wetting transition [10].

Consequently, we do not require (and indeed cannot define) a criterion for the cutoff distance as used in [10]. Indeed, we found (see Sec. V) that for the potentials considered in this work, and up to cutoff distances of various molecular diameters, significant differences are observed in the location of the first-order wetting transitions.

Finally, our choice of the fluid-fluid interactions, Eq. (18), renders the choice of reference system unique. We divide $v(r)$ into a reference, HS part $v_{\text{ref}}(r) = v_{\text{HS}}(r)$, and an attractive term

$$v_a(r) = v(\sigma) + [v(r) - v(\sigma)] \theta(r - \sigma). \quad (21)$$

A similar division is used for the (cutoff) short-range potentials.

There are several good approximations for the free energy functional of fluids of hard spheres. We choose to use for the reference free energy functional the (nonlocal) fundamental-measures theory of Rosenfeld [13], which is probably the best approximation available for nonuniform HS systems. The explicit form of \mathcal{F}_{ref} in FMT can be found in Ref. [13].

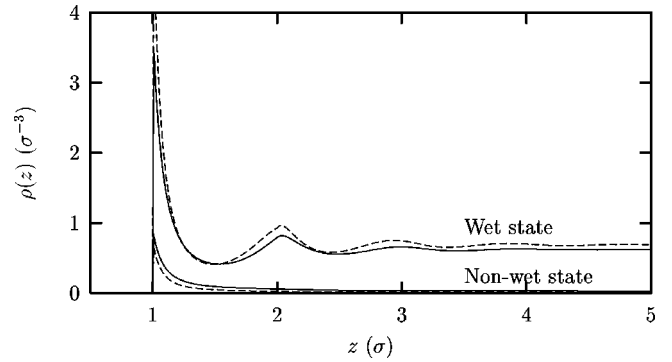


FIG. 2. Density profiles of the LR ($T^* = 1.0125$, solid line) and SR (cutoff at two molecular diameters, $T^* = 0.863$, dashed line) models with $u_4 = 2.7$, for the nonwet and wet states in coexistence at the first-order transition.

One of the strengths of the present work is that the wetting behavior of models characterized by well-defined interactions is analyzed in terms of a free energy functional that treats the short- and long-range models in the same fashion.

V. RESULTS

We have studied fluids with interactions specified by $v_7 = v_6 = 3/\pi = 0.955$, and solid substrates characterized by $2.5 \leq u_4 \leq 3.0$ and $u_3 = 0.3$. An infinite cutoff corresponds to systems with long-range interactions, while a finite cutoff characterizes the corresponding short-range system.

The interaction parameters were chosen in order to yield first-order and critical wetting transition temperatures at a reasonable distance from the bulk critical temperature. The structure at the first-order transition is illustrated in Fig. 2, where we plot the coexisting profiles for long- and short-range (LR and SR, respectively) systems, at a substrate characterized by $u_4 = 2.7$. The profiles are similar, although the density of the liquid adsorbed layer is higher for the SR model, resulting in a slightly more structured profile. The gas density is lower in the SR model. These differences are due to the lower transition temperature of the SR model [$T_{w,1}^*/T_c^* \approx 0.76$ for the long-range (LR) model and 0.67 for the SR model]. Interface potentials obtained for the LR system are plotted in Fig. 3, clearly indicating a first-order transition at $T^* \approx 1.0125$. On the other hand, the absence of re-

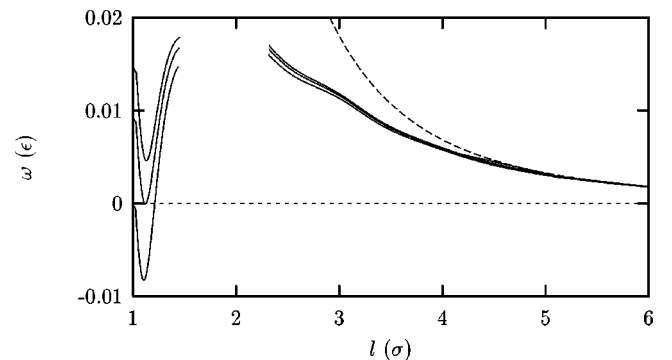


FIG. 3. Interface potentials $\omega(l)$ for an LR system with $u_4 = 2.7$ (solid lines). From top to bottom, $T^* = 1.020$, 1.0125, and 1.000. The dashed line shows the result of the asymptotic expansion [12] (up to fourth order) for $T^* = 1.020$.

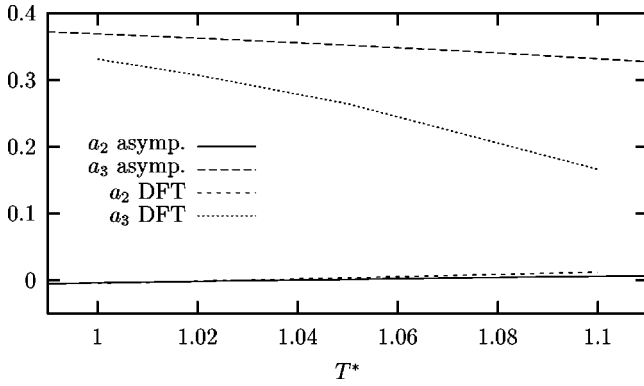


FIG. 4. Values of the coefficients a_i of $\omega(l)$, obtained from the asymptotic expansion of Ref. [12] and from the present approach.

sults for $1.5\sigma < l < 2.3\sigma$ is due to the fact that the states in this region are highly unstable, making it extremely difficult to obtain a sensible value of its energy.

The coefficients of the interface potential, a_i , are found by fitting the results for $\omega(l)$ (obtained through a constrained minimization of Ω_s) to the asymptotic form (10), in the range $10\sigma \leq l \leq 20\sigma$. The length of the meshes used in the numerical work is of the order of 300σ , but only results in a region of $\approx 20\sigma$ from the substrate have proven sufficiently accurate by comparison with the analytical results. This range of l is adequate for our purposes.

In Fig. 4 we compare the coefficients a_2 and a_3 obtained using the asymptotic method of Ref. [12] and the present approach. While the differences in a_2 are less than 1% (the critical-wetting temperature is $T_{w,c}^* \approx 1.04$ using the asymptotic method compared to $T_{w,c}^* \approx 1.03$ from the constrained numerical minimization), there are significant differences for the higher-order coefficients. These discrepancies result from a combination of limited numerical accuracy in the constrained minimization of Ω_s at large l , the interpolation used to calculate the coefficients, and the numerical evaluation of the moments of the density profiles, required to calculate the coefficients of the analytical expansion. These numerical procedures are very demanding since they involve differences of small numbers over a wide range of l .

The present approach, however, yields the interface potential in the vicinity of the substrate, and it is particularly accurate at and around its first minimum, which is beyond the range of the asymptotic approach ($i \leq 4$). This is illustrated in Fig. 3, where it is clear that, while the asymptotic result is accurate for $l > 5\sigma$, it cannot describe the structure of $\omega(l)$ at small l . In particular, it misses the first minimum and thus fails to describe the first-order transition between a thin and thick film that occurs in these systems.

As mentioned previously, both approaches yield a critical wetting transition for this LR system: the leading term of the expansion (10) changes from negative (preventing wetting) to positive (favoring wetting), while the next-to-leading term remains positive (favoring wetting). The critical wetting transition occurs at $T_{w,c}^* \approx 1.03$, thus following a first-order transition at $T_{w,1}^* \approx 1.0125$ (see Fig. 3). In Fig. 5 the thickness of the adsorbed liquid layer, calculated using the asymptotic expansion, plotted as a function of temperature, illustrates this sequence of transitions.

This behavior, however, is far from universal, as shown in

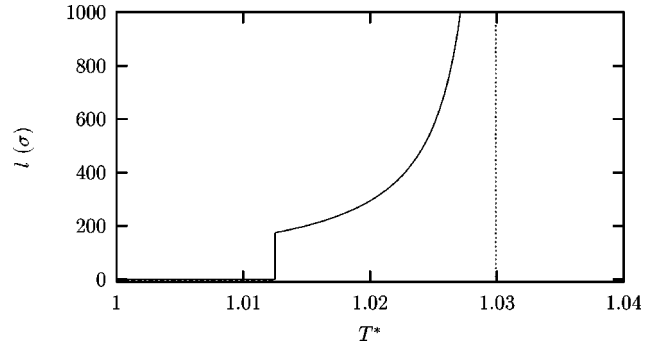


FIG. 5. Thickness of the adsorbed layer for an LR system with $u_4 = 2.7$ exhibiting a sequence of two transitions at $T^* = 1.0125$ and $T^* = 1.03$.

Table I. If the substrate is made slightly less attractive (by changing $u_4 = 2.7$ to 2.5) we find $T_{w,c}^* < T_{w,1}^*$ and thus critical wetting is prevented. Note that for this range of parameters, $T_{w,c}^*$ is almost constant, since a_2 depends explicitly only on u_3 [see Eq. (14) and below]. Table I also includes the (first-order) wetting temperatures for an SR ($r_c = z_c = 2\sigma$) model. The first-order wetting temperatures are significantly different for the LR and SR systems, although they appear to be related. For an SR model defined in this fashion, the LR forces have a nonperturbative effect on the structure of $\omega(l)$, at small l , and thus they affect the location of the first-order transition. We have repeated the calculation for an SR model with $r_c = z_c = 3\sigma$ (see Table I) and found that, even in this case, the LR transition temperature is not recovered. This means that there is no way of clearly separating the effects of short- and long-range forces, at least for the class of systems studied in this paper.

VI. CONCLUSIONS

We have investigated, by means of density functional theory, the influence of the short- and long-range forces on the location and nature of the wetting transition, for a fluid adsorbed at a solid substrate. To this end, we have calculated numerically the interface potential of the system, $\omega(l)$. In addition, we have calculated the substrate-liquid and liquid-gas density profiles, in order to evaluate the asymptotic expansion of the interface potential, $\omega(l)$, derived by Dietrich and Napiórkowski [12]. We found that both approaches agree for $l \geq 5\sigma$, but yield different results closer to the substrate. In particular, the asymptotic expansion fails to describe the first minimum of the interface potential obtained via DFT.

We have investigated the location and nature of the wetting transitions and found that a sequence of two transitions

TABLE I. Transition temperatures for LR and SR systems as a function of u_4 . Cutoff distances $r_c = z_c = 2\sigma$ and $r_c = z_c = 3\sigma$ for SR I and II, respectively.

u_4	$T_{w,c}^*$ LR	$T_{w,1}^*$ LR	$T_{w,1}^*$ SR I	$T_{w,1}^*$ SR II
2.5	1.060	1.100	0.97	
2.7	1.029	1.013	0.86	0.94
3.0	1.038	1.001	0.865	

may occur, as observed by Shahidzadeh *et al.* [9] for alkanes on brine. We checked that this behavior depends sensitively on the parameters of the substrate-fluid and fluid-fluid interactions. By changing slightly the substrate-fluid potential, the first-order wetting transition temperature increases above that of critical wetting and only first-order wetting occurs in the system, in agreement with earlier calculations based on a simpler free energy [19]. Those calculations also suggest that the sequence of two transitions, occurs only in a limited region of the interaction parameter space.

One of the aims of this work was the construction of a short-range counterpart of a microscopic long-range potential, capable of accounting for the first-order transition referred to above. This would justify the treatment of the long-range potential as a perturbation, responsible for the critical wetting transition only. We found that the cutoff procedure developed here cannot account for the location of the first-

order wetting transition, unless very large cutoffs are used. Thus, for this type of interaction, there is no way of clearly separating the short- and long-range forces. Further investigations, including a connection with the wetting of alkanes on water, are clearly required.

Finally, this implementation of an accurate DFT theory (combining brute force numerical minimization with the evaluation of the asymptotic interface potential) may be applied to other types of critical wetting, namely triple point wetting and complete wetting [1,2] where new experimental findings have been reported [20–22].

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