Wetting phenomena and the decay of correlations at fluid interfaces

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The physics of wetting in three dimensional systems with planar symmetry is revisited in order to explore the extreme sensitivity to microscopic interactions that underlies even thick film adsorption phenomena in $d = 3$. Beginning with short-ranged models of wetting by liquid at a wall-vapor interface, weighted density functional theory is used to obtain an accurate description of the mean-field interface potential along the entire saturated liquid branch. Well away from the bulk critical point, the long-range decay of this class of interface potentials is damped oscillatory rather than the generally assumed monotonic form. This result is best understood in the context of a recently published general theory of the asymptotic structure of liquids and their mixtures. The inescapable conclusion from mean-field theory is that over much of the saturated liquid curve, complete wetting is replaced by thick film pseudowetting associated with layering phenomena. However, oscillatory structure at microscopic wavelengths is strongly renormalized by the inclusion of capillary-wave fluctuations. To assess this aspect, the paper reviews the explicit linear renormalization group calculation of Chernov and Mikheev [Phys. Rev. Lett. **60**, 2488 (1988)]. One must distinguish between two cases: (i) pure wetting, where capillary-wave fluctuations renormalize the decay length of the damped oscillatory structure, and (ii) wetting in the presence of external capillary-wave damping (such as Earth's gravity), where the renormalization can dramatically reduce an oscillatory amplitude but cannot formally prevent the suppression of complete wetting. The second main aim of the paper is an attempt at a general survey of the plethora of length scales potentially relevant to thick film wetting phenomena in $d = 3$. A full description of short-ranged models of simple fluids is presented in terms of the behavior of monotonic and oscillatory decay lengths along the saturated liquid branch. Additional length scales of the same class arise from competition with exponentially decaying wall fields. Power-law interactions (dispersion forces) lead to a qualitatively different asymptotic regime. Notwithstanding the ultimate dominance of power-law structure at the longest range, moderately thick film wetting should still be influenced by short-ranged intermolecular forces, particularly in mean field. Finally, the equally crucial significance of asymptotic structure to wetting phenomena in liquid mixtures and in charged fluid systems is highlighted and attention drawn to recently published theories of the required asymptotic forms. In summary, the physics of wetting phenomena in three-dimensional systems is probably close to being fully understood, but the resulting picture for typical experimental systems is amazingly complex.

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I. INTRODUCTION

Wetting phenomena form a long established branch of physical chemistry [1]. Classically, one distinguishes cases in which a fluid wets (or spreads) at an interface (e.g., a solid-gas interface) from cases in which macroscopic drops of adsorbed phase are formed instead. Phenomenologically, this behavior is controlled by the surface tensions (surface excess free energies) of the various interfaces involved and even by the line tension of the three-phase contact region [2]. However, these systems are extremely sensitive to details of the intermolecular forces, in contrast to most bulk macroscopic phenomena, because the behavior is controlled by long-range fluid mediated interactions between weakly interacting interfaces. This fact has been well appreciated for some considerable time by Derjaguin and co-workers [3], but elsewhere the significance of microscopic details to wetting phenomena has only excited interest in the last decade and a half [4]. Here, I shall attempt a comprehensive classification of wetting phenomena based on the details of intermolecular

interactions, drawing on recent general theories of asymptotic correlations in liquids and their mixtures and on the linear renormalization group approach to incorporating interfacial fluctuations. In particular, three-dimensional wetting phenomena (both in models and reality) are revealed to form an amazingly complex universe, due to the existence of a plethora of relevant length scales, including some associated with oscillatory interactions.

From the point of view of interfacial physics, wetting phenomena arise whenever three distinct phases (of any class whatsoever) can come into mutual coexistence. Typically, this will arise because two phases are at or close to bulk two-phase coexistence, while the remaining phase is essentially a benign spectator (usually treated as a planar external field, or wall). Accordingly, one needs a minimum of three thermodynamic fields to discuss wetting phase behavior; namely, a substrate field (usually written h_1 or ϵ_w) and two bulk fields (say, T and μ, where T denotes temperature and μ the chemical potential). This phase diagram was first proposed in 1982 [5] and shows three important classes of interfacial

phase transitions believed to be appropriate to fluid wetting phenomena. These arise because the half-plane of bulk two-phase coexistence ($\mu = \mu_{cc}$, $T < T_c$) contains a curve of wetting phase transitions enclosing a region of partially wet wall-fluid interfaces. In this plane one can cross the wetting curve by varying ϵ_w or T to observe either a first-order wetting transition or continuous (critical) wetting; the point on the wetting transition curve where the order changes is a tricritical point. If instead one approaches the completely wet area from below (increasing the saturation of a wall-gas interface) then the adsorption isotherm will show a diverging adsorption in the limit of complete wetting (a second example of interfacial critical phenomena). If this path comes close to a first-order section of the wetting transition curve then one will also observe a thin-thick film transition, prior to complete wetting. The physics of these phenomena is usually understood by regarding them as interface delocalization processes [6].

In planar symmetry, the nature of wetting phase transitions is controlled by the underlying behavior of the interfacial free energy as a function of film thickness [usually written $V(\ell)$]. If $V(\ell)$ possesses a double well structure then the wetting transition is first order, with associated thin-thick transitions lying close to bulk two-phase coexistence. Otherwise, one observes so-called critical wetting. Such interface potentials are easily calculated in mean field from density functional theory. However, in dimension $d \leq 3$ one must also take into account the effect of capillary-wave (cw) fluctuations on the underlying potential. The important physical case of $d = 3$ is especially complex because, as discussed in detail in this paper, many relevant length scales can potentially alter the nature of an interface potential.

To understand wetting phenomena in the vicinity of wetting transitions one must consider cases in which thick films of adsorbed phase are present. In this case, the interfacial free energy is a subtle balance of the effects of the distant interfaces on one another. Apart from direct long-range external fields (whose effects are trivially understood and will only be briefly referred to below) such a pair of separating interfaces communicate via the long-range decay of their respective density profiles. Thus the thick film behavior of the interface potential is directly related to the asymptotic decay of inhomogeneous fluids.

Recent work by various groups has uncovered a general theory of medium-range and long-range correlations in liquids and their mixtures. In particular [7,8], beyond the range of external fields, the asymptotic decay of inhomogeneous density profiles into a bulk fluid is controlled by the bulk fluid direct correlation functions $c_{ij}(r)$ and hence possesses the same functional form as the bulk fluid total correlation functions $h_{ij}(r)$, linked to c_{ij} via the Ornstein-Zernike (OZ) equations. This also implies, through sum rule analyses or the use of wall-particle direct correlation functions $c_{wp}(z)$, precisely the same long-range behavior for a solvation force (mediated by the same fluid) or a disjoining pressure $[-\partial V(\ell)/\partial \ell]$ [9,10]. The most general approach to treating all these systems is therefore through a complex pole analysis of the common denominator that appears in the OZ equations, fol-

lowing Fourier transform. This approach is particularly enlightening for short-ranged models, where the common denominator implies a unique asymptotic form that is either a monotonic exponential decay or an exponentially damped oscillatory decay [10]. For mixtures there are in addition amplitude and phase relations that further simplify the physics [11,10], while in wall-fluid systems the amplitudes are of course dependent on the details of the external fields [8]. This approach is also directly applicable to charged fluid systems, due to the effects of electrostatic screening, where an especially rich pole structure arises [12,13]. The presence of power-law interactions (dispersion forces) greatly complicates the pole analysis, but one can make contact with previous approaches to the power-law decay of interfacial profiles [14] and in addition gain insight into the crossover to medium-range correlations controlled by repulsive interactions [15]. Finally, to include the effects of capillary-wave fluctuations on planar profiles in $d = 3$, one has recourse to linear renormalization group (LRG) theory [16,6].

To conserve on notation, hereinafter I shall focus on the case of wetting by pure liquid at a planar wall-gas interface. Close to saturation (bulk liquid-vapor coexistence), we must consider the possibility of a thick layer of adsorbed liquid that ends in an almost free liquid-vapor interface. The physics of this problem arises from the weak interference between the liquid tails of two virtually separate profiles; namely, a wall-liquid interface and a planar liquid-vapor interface. The general theory of asymptotic decay implies that both of these profiles decay into a given bulk liquid with the same functional form, that in turn defines the long-range behavior of the bulk liquid total correlation function [specifically, $rh(r)$]. For a finite-ranged model (Hamiltonian) one finds that pure exponential decay dominates asymptotic correlations for saturated liquids close to the critical temperature (T_c) but that elsewhere the asymptotic form is likely to show the familiar damped oscillatory behavior. Specifically, for mean-field models of simple fluids the crossover line in density-temperature space (ρ, T) where these two asymptotic forms possess the same exponential decay length, known as the Fisher-Widom (FW) [17] line, crosses the liquid-vapor coexistence curve at around $T/T_c \simeq 0.9$ [8,15]. At all temperatures below this point, the mean-field liquid-vapor profile (or saturated liquid radial distribution function) possesses an oscillatory liquid tail. The asymptotic decay of the wall-liquid profile shows exactly the same behavior, for a finite-ranged wall field. The amplitude of the tail decay is, however, dependent on the wall field [8,10]. Vapor tail decay is always monotonic because the FW line is constrained to lie above the mean-field liquid spinodal.

From [10] we can summarize the asymptotic behavior of short-ranged models as

$$\begin{aligned}
\delta\rho &\equiv \rho(z) - \rho_L \\
&= a\exp(-\alpha_0 z) + b\exp(-\alpha_0^{osc} z)\cos(\alpha_1 z - \theta) \\
&\quad + O(\delta\rho^2) ,
\end{aligned} \tag{1}$$

where positive z points away from an interface into bulk liquid (ρ_L), and the α_0, α_1 notation refers to simple poles

$q \equiv \pm\alpha_1 + i\alpha_0$ of $1/[1-\rho\hat{c}(q)]$ in the complex plane, with $\hat{c}$ denoting the three-dimensional (3D) Fourier transform of the bulk liquid direct correlation function. Clearly, $\alpha_1 \simeq 2\pi/\sigma$, to yield a wavelength close to σ, the repulsive-core diameter. The amplitudes a and b are defined by $\hat{c}'(q)$ and also, in the case of a wall-liquid profile, by the 1D Fourier transform of the wall-particle direct correlation function $\tilde{c}_{wp}(q)$ [10]. For simple models there is only one pole lying on the pure imaginary axis (α_0), while there exists an infinite number of separated oscillatory poles. In general, the next order oscillatory pole, with decay length $1/\alpha_0^{2osc}$ and wavelength roughly half that of the leading-order oscillatory pole, is well separated in terms of the decay length $(\alpha_0^{2osc} \gg \alpha_0^{osc})$ so that typically Eq. (1) is an accurate representation of the full profile beyond about the second minimum out from the interface. In any given case, to obtain the leading-order correction to the asymptotic form (relevant to the repulsive region of an attractive interface potential) one must consider $2\alpha_0$, $2\alpha_0^{osc}$, and α_0^{2osc}, as well as the non-dominant member of the α_0, α_0^{osc} pair.

Chernov and Mikheev [18] were the first to point out the significance of the damped oscillatory term in Eq. (1). Near the triple point the α_0^{osc} pole approaches the real axis so that oscillatory decay dominates the asymptotic form and the leading-order correction decays as $\exp(-2\alpha_0^{osc} z)$. Thus, in this region of phase space, wetting phenomena should be controlled by an interface potential whose long-range behavior is of the form of Eq. (1) with amplitude a set to zero. Since damped oscillatory decay would always yield a global minimum in the interface potential at some finite value of the film thickness, such a scenario could never yield true complete wetting (i.e., only thick pseudo wet films) and in approaches to pseudo wetting from off bulk two-phase coexistence one would often see layering transitions. This behavior is in marked contrast to earlier theories of complete and critical wetting, which were based instead on setting amplitude b to be zero [19,16]. However, in $d \leq 3$ one must also consider the effect of capillary-wave (cw) fluctuations on the mean-field interface potential. Chernov and Mikheev [18] argue that the oscillatory term is strongly renormalized because of the large value of α_1 (a high curvature contribution to the potential) and in fact use the linear renormalization group (LRG) theory of Fisher and Huse [16] to predict that sufficiently strong cw fluctuations would renormalize the value of α_0^{osc} so much that the oscillatory decay would cease to dominate the asymptotic form. In this case, they argue, the repulsive term in the interface potential would take over and an infinitely thick complete wetting film would form. At no stage do Chernov and Mikheev bother to include the α_0 term in their scenario. The main quantitative purpose of my paper is to reexamine this entire issue in detail, including specific calculations of the full interface potential appropriate to short-ranged models of simple fluids at weakly attractive walls and the thick film asymptotic behavior along the entire liquid-vapor coexistence curve.

Section II below uses the density functional theory approach of Tarazona and Evans [20], except that I use a more modern weighted density functional (WDA theory)

capable of an accurate representation of repulsive-core oscillatory packing, to calculate $V(\ell)$ appropriate to wetting above the FW line. The mean-field aspects of the predictions of Chernov and Mikheev are fully confirmed. In addition, the underlying physics concerning interference between damped oscillatory profile tails of weakly interacting interfaces is explicitly demonstrated. Section III reviews the LRG theory of fluctuating interfaces applied to oscillatory interface potentials and specific calculations are given using the WDA theory data. The contrast between the LRG conclusions of Chernov and Mikheev [18] and those of later authors [8] is seen to arise from the inclusion or exclusion of additional sources of capillary-wave damping. In particular, the significance of oscillatory interface potentials to real systems must be seriously taken into account under various conditions. The paper concludes (Sec. IV) with an extensive discussion that attempts an essentially complete classification of length scales that are potentially relevant to wetting phenomena in a wide variety of systems, both model and real. The entire saturated liquid curve of short-range models is surveyed, detailing the crossover between the low T regime of Chernov and Mikheev [18] and earlier theories appropriate to high T [19,16]. In addition, competition with external fields and the complications expected for charged fluids and systems with dispersion forces are discussed. The immediate relevance to wetting in fluid mixtures is also highlighted. In short, wetting phenomena in $d = 3$ are seen to belong to an amazingly complex universe of competing length scales. In particular, to predict physically relevant wetting behavior for any given system one must first undertake a very thorough examination of the underlying mean-field interface potential. Only then can the significance of capillary-wave phenomena be properly understood.

II. INTERFACE POTENTIAL IN MEAN FIELD

The description of damped oscillatory correlations in liquid state theory requires a careful treatment of repulsive-core interparticle interactions. In particular, van der Waals square-gradient theory, Landau theory, or any other local density functional treatment of an inhomogeneous fluid will always fail to yield oscillatory structure. From the point of view of the general theory of asymptotics [10], this arises because these crude treatments reduce the repulsive-core contribution to $c(r)$ to a δ function form (i.e., zero range). To describe a hard-core fluid radial distribution function or a wall-liquid interface profile, one requires a free energy functional that generates a realistic hard-core contribution to the bulk liquid direct correlation function. One solution is to use functionals of smoothed or weighted densities (hence the acronym WDA theory) with weight functions chosen to ensure a good representation of the hard sphere fluid $c(r)$. In mean field one usually treats the attractive correlations in the random phase approximation (RPA), which in fact, from comparisons with accurate bulk liquid integral equation theories [15], yields a direct correlation

function sufficient for our purposes in that it predicts a FW line that lies very close to accurate theory in the region of liquid-vapor coexistence (in terms of reduced variables). Close to solid states the details of $c(r)$ become more important [7], but the RPA treatment of attractive correlations appears to remain qualitatively correct. In this section I shall use the WDA theory due to Tarazona [21], as applied by van Swol and Henderson [22] to the model of square-well fluid adsorbed at a square-well wall. In terms of reduced variables $(T/T_c, \rho/\rho_c)$, this approach should represent a reasonable description of argonlike fluids adsorbed at weakly attractive substrates, apart from the absence of power-law dispersion forces (see Sec. IV) and the lack of capillary-wave broadening (taken into account in Sec. III). The exceptions to this are systems close enough to the liquid-vapor critical point to be controlled by bulk critical phenomena (not under discussion in this paper).

Evans et al. [8] have previously used the WDA theory referred to above to obtain liquid-vapor density profiles above the FW line, that clearly show damped oscillatory decay into bulk liquid. In particular, at $T/T_c = 0.64$ the amplitude of the largest oscillation of the liquid tail is a few percent of the saturated liquid density $(\rho_L \sigma^3 = 0.739$ where σ denotes the repulsive-core diameter), while the decay length $1/\alpha_0^{osc}$ is a little under 4σ. These parameters are appropriate for a detailed investigation of the asymptotic form of the mean-field interface potential, here using systems of length 40σ. Earlier work used smaller systems and thus failed to note the asymptotic details given below. Namely, this section repeats the wetting curve calculations of van Swol and Henderson [22], based on the Tarazona and Evans [20] procedure, but focuses on the thick film details at one specific temperature. I shall conclude that the first-order wetting transition curve obtained by van Swol and Henderson is in fact only a pseudowetting curve, at temperatures below the point where the FW line crosses the liquid-vapor coexistence curve $(T/T_c \simeq 0.90)$. For this mean-field model, critical wetting does not occur until even closer to the critical point (namely, above about $T/T_c = 0.93$).

The Tarazona and Evans route to obtaining $V(\ell)$ is to solve the density functional theory using a simple stable numerical method, such as Picard iteration, for a whole range of initial profiles at different values of ℓ. Given a sensible method of generating the initial profile (which should be a smooth splice between a wall-liquid interface and a liquid-vapor interface), a small number of iterations (here I use 40 iterations at a mixing parameter of 0.1) is sufficient to generate a reasonably converged adsorbed film profile and free energy, but at essentially the same value of ℓ as the starting profile. Typically, in Picard iteration, the amount of adsorbed film varies less than 0.05σ in such circumstances. Accordingly, one can generate a mean-field $V(\ell)$ curve whose shape or form is well characterized (provided of course one never mixes different numbers of iterations), although the absolute value of the surface free energy varies with the chosen iteration length or the numerical method. Note that only one value of ℓ corresponds to the true equilibrium state; the rest of $V(\ell)$ refers to mean-field metastable and unstable states in the

spirit of van der Waals. Despite the inevitable fuzziness to the physical reality of $V(\ell)$ it is precisely the quantity that appears in renormalization group (RG) theories of wetting. Namely, $V(\ell)$ is a bare interface potential defined by including correlations up to some arbitrarily chosen microscopic length. The Tarazona and Evans procedure is in effect a much higher quality approach to generating a bare potential than the usual crude matching criterion (which corresponds to no iterations at all and thus is highly dependent on the chosen method of splicing the two interfaces together to make the adsorbed film). For full details of the numerical procedures used the interested reader is referred to Ref. [22].

Figure 1 shows the interface potential at bulk liquid-vapor coexistence, in the region of a first-order pseudowetting transition, obtained from WDA theory of a square-well fluid at a square-well wall. More precisely, the plot shows the grand canonical potential of the wall-vapor interface as a function of the thickness (ℓ) of an adsorbed liquid film, as defined by the Tarazona and Evans procedure discussed above, in units of kT_c (k denotes Boltzmann's constant) per unit wall area (A). On this scale one can just begin to discern the damped oscillatory nature of the decay, as is appropriate to a state point lying above the FW line in phase space. Ignoring this aspect for the moment, Fig 1 is otherwise indicative of a standard first-order wetting transition. Namely, if one varies T (and ρ_L and ρ_V, to remain at bulk liquid-vapor coexistence) or equivalently the wall field ϵ_w (the method used here), the basic shape of the interface potential remains as plotted. The only important change is a shift in the relative depths of the two main minima (at $\ell \simeq 0$ corresponding to a dry wall and at $\ell = \infty$ corresponding to complete wetting). The value of ϵ_w used
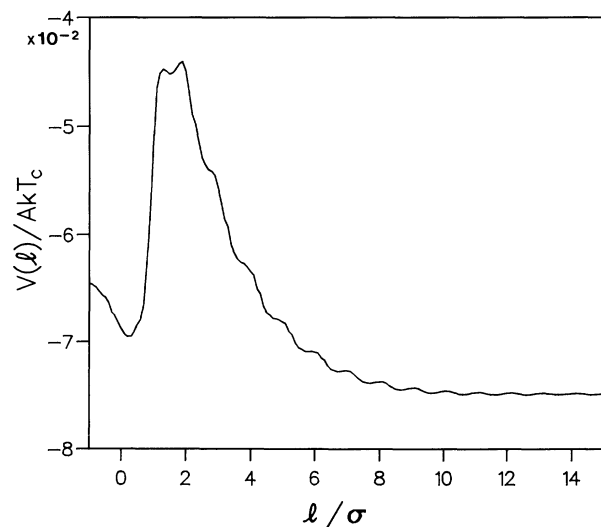

FIG. 1. The mean-field interface potential of a wall-vapor interface of square-well fluid adsorbed at a square-well wall, as a function of the thickness of the adsorbed liquid film. The temperature is at $T/T_c = 0.64$ which lies above the FW line (implying damped oscillatory decay) and the attractive wall field is $\epsilon_w = 1.81kT_c$ (which just favors infinitely thick films of liquid over a dry wall); see text.

to plot Fig. 1 lies just beyond the (pseudo)wetting transition point. At $\epsilon_w = 1.795kT_c$ one finds essentially the same curve except that now $V(0_+) = V(\infty)$, which in the absence of oscillatory decay would imply the presence of a first-order wetting transition from a thin adsorbed film to an infinitely thick film of liquid. At even lower values of ϵ_w the minimum at $\ell \simeq 0$ is the global minimum, which corresponds to partial wetting (in a macroscopic system partial wetting means that adsorbed liquid can only adsorb as drops surrounded by vapor, with a non-zero contact angle).

Fig. 2 shows the thick film region of Fig. 1, magnified by a factor of 40. The damped oscillatory decay of the interface potential (and hence its derivative, the disjoining pressure) is immediately apparent. These data also highlight the dramatic significance of the FW line mechanism to the existence of true complete wetting. For this system the global minimum lies at a film thickness of around 12σ or 13σ and regardless of how large one makes ϵ_w it is obvious that the global minimum of a damped oscillatory interface potential can never lie at infinite film thickness. Since in this model the wall field is strictly finite ranged, the oscillatory nature of the decay of $V(\ell)$ is independent of ϵ_w (but not the amplitude of the oscillations), the wavelength and decay length being determined purely by the bulk saturated liquid direct correlation function. In fact, the region $\ell > 20\sigma$ of Fig. 2 is readily fitted to the functional form Eq. (1), without the need for any pure exponential term [i.e. with amplitude a set to zero in Eq. (1)]. For this state point, the analytic asymptotic form, defined by $c(r)$ through the pole criteria $1 - \rho_L \hat{c}(q) = 0$ [8,10], has an inverse decay length of $\alpha_0^{osc} = 0.26/\sigma$ and wave number $\alpha_1 = 6.24/\sigma$. These values are fully consistent with fits to the density profile tails of isolated wall-liquid and liquid-vapor density profiles generated by WDA theory (the slight discrepancy with the values quoted in [8] being due to the small system size used in the earlier work). Similar fits

to the tail of the interface potential plotted in Fig. 2 are slightly less stable with respect to the value of α_0^{osc}. This is probably due to the nature of the Tarazona and Evans procedure; i.e., during the 40 Picard iterations allowed for minimization of the adsorbed film free energy, the value of ℓ becomes ill defined to around plus or minus a numerical grid size (0.05σ) [23]. Various fits averaged to a slightly higher value of α_0^{osc} (around $0.3/\sigma$), but the analytic asymptotic value is essentially equally applicable. In short, the numerical solution shown in Fig. 1 and Fig. 2 confirms that the interface potential decays with the same asymptotic form as the profile tails.

The general theory of asymptotics in short-ranged models yields a common profile form for the tails of all density profiles decaying into the same bulk liquid. In the region of phase space applicable to Fig. 1 and Fig. 2, this is a damped oscillatory decay with a wavelength and decay length determined by the bulk liquid direct correlation function [8]. Accordingly, above the FW line, the growth of a thick liquid film at a wall vapor interface (beyond the direct range of the wall field) involves the interference between two damped oscillatory profiles possessing identical wavelength and decay length. This mechanism ensures that the interface potential or its derivative, the disjoining pressure, possess precisely the same asymptotic form. Figure 3 shows two examples from the same system used to obtain Fig. 2. Case (a) corresponds to the global minimum in the interface potential (in this case, $\ell \simeq 13\sigma$), while case (b) is appropriate to the asymptotic region. The latter plot clearly illustrates the interference mechanism referred to above. Plot (a) shows that the global minimum in the free energy occurs at a film thickness at which the two profile tails are just beginning to
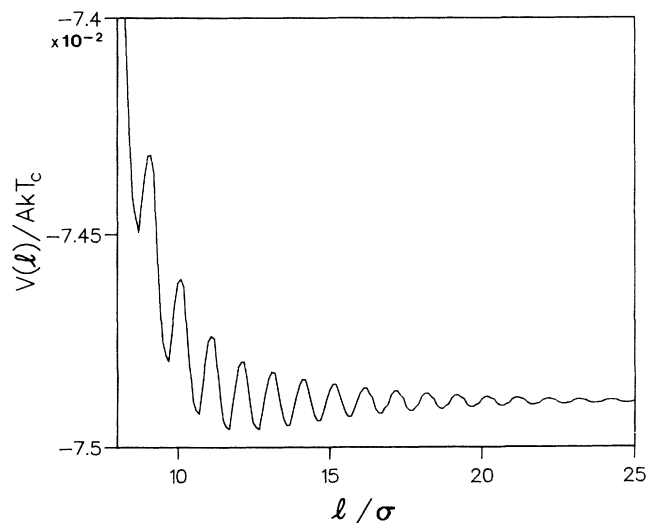

FIG. 2. The tail region of Fig. 1, magnified by a factor of 40 so as to show the nature of the global free energy minimum followed by damped oscillatory decay.
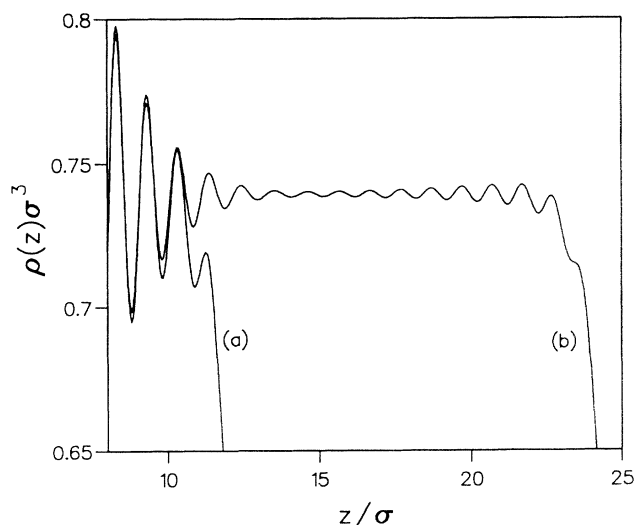

FIG. 3. Density profiles of liquid films adsorbed at a wall-vapor interface, corresponding to two values of the interface potential plotted in Fig. 1 and Fig. 2. The wall is situated at $z = 0$. Case (a) shows the far edge of the liquid film belonging to the global minimum in the free energy ($\ell = 12.7\sigma$); case (b) shows the "bulk" liquid region of a film profile belonging to the asymptotic form of the interface potential.

separate; i.e., when one can just discern the first oscillation belonging to the vapor-liquid profile.

III. cw BROADENING AND LRG THEORY

The surface of a nearly free liquid-vapor (or liquid-liquid) interface is constantly in motion, due to the presence of thermally excited capillary waves [24]. For short-ranged models in dimension $d \leq 3$, mean-field theory yields a very poor description of the cw broadening of a liquid-vapor profile [25]. This is because for such models $d = 3$ corresponds to an upper critical dimension, below which the tails of density profiles are dominated by universal capillary-wave correlations. Previous workers have developed a linear renormalization group approach, suitable for including the effects of cw broadening, in the special but physically relevant case of $d = 3$ [19,16]. Here, one renormalizes an interface Hamiltonian (or free energy) of the class

$$F_{cw} = \gamma \Delta A + V(\ell), \tag{2}$$

where $V(\ell)$ is a mean-field interface potential (as discussed in Sec. II above). The first term on the right side of Eq. (2) represents the restoring force (γ denotes surface tension) acting against the change in surface area (ΔA) resulting from capillary-wave fluctuations of the profile. Typically, one takes γ to be the surface tension of a free liquid-vapor interface, arguing that the dominant effect of capillary waves arises from the long wavelength limit [26]. I shall only explicitly consider approaches based on this assumption; however, it should be noted that recent work has concluded that the thickness dependence of the interfacial tension [$\gamma(\ell)$] cannot always be ignored because wetting phenomena can be influenced through next-to-leading-order contributions to the interface Hamiltonian such that capillary-wave effects persist even for $d > 3$ [27].

The LRG theory of Fisher and Huse [16] is equivalent to a Gaussian renormalization of the mean-field interface potential:

$$V_\tau(\ell) = \frac{1}{(2\pi)^{1/2}\xi_\perp(\tau)} \int_{-\infty}^{\infty} dz V(\ell + z) \exp\left(-\frac{z^2}{2\xi_\perp^2(\tau)}\right). \tag{3}$$

In $d = 3$ the capillary-wave broadening varies as the square root of the film thickness. Briefly (see, for example, the reviews [6,28]),

$$\xi_\perp^2(\tau) = \left(\frac{kT}{2\pi\gamma}\right)\tau, \tag{4}$$

where the appropriate value of τ (τ^*) is the length scale at which one can treat the renormalized potential with standard cw theory,

$$\xi_\parallel^2 \equiv \gamma A/[\partial^2 V_{\tau^*}(\ell)/\partial \ell^2]_{\ell=\bar{\ell}} \tag{5}$$

($\bar{\ell}$ denotes the film thickness at the potential minimum) and

$$\xi_\perp^2(\tau^*) = \frac{kT}{2\pi\gamma}\ln(\Lambda\xi_\parallel). \tag{6}$$

Thus $\tau^* = \ln(\Lambda\xi_\parallel)$, where Λ denotes a high wave number cw cutoff (usually assumed to be $\Lambda \simeq \sigma^{-1}$). Exactly the same Gaussian renormalization applies to the density profile or its derivative; i.e., replace $V(\ell + z)$ in Eq. (3) with the mean-field density profile $\rho_{MF}(\ell+z)$. The linear nature of the above RG theory arises in particular from the replacement of the lower limit in the integral of Eq. (3) with $-\infty$. This neglect of collisions with the repulsive wall potential is only valid if $\xi_\perp^2$ is sufficiently small; see below.

The LRG theory sketched above was first applied to purely monotonic potentials [Eq. (1) with $\alpha_0^{osc} > 2\alpha_0$], which yields first-order wetting and three classes of critical wetting phenomena [19,16]. Later, Chernov and Mikheev [18] considered the opposite case [Eq. (1) with $\alpha_0 > 2\alpha_0^{osc}$]. The general case follows from the one-dimensional Fourier transform of Eq. (3):

$$\tilde{V}_\tau(q) = \tilde{V}(q)\exp[-q^2\xi_\perp^2(\tau)/2]. \tag{7}$$

At first sight the asymptotic form of the interface potential cannot be affected by renormalization, apart from altering the amplitude of the profile tail, because the Gaussian factor in Eq. (7) cannot contribute to the pole structure. However, one must note from Eq. (4) that the amplitude goes to zero in the thick film limit, in the absence of any external cw damping such as gravity or finite wall area. The basic idea of Chernov and Mikheev is that a renormalized oscillatory interface potential can only remain dominant if the renormalization remains consistent with the curvature of the potential being controlled by the oscillation at the global minimum. In this regime one has $\alpha_1 \gg \alpha_0^{osc}$ and thus a dominant oscillation will greatly reduce the value of the correlation length in the plane of the interface; see Eq. (5). Explicitly, substituting the second term on the right side of Eq. (1) into Eq. (7), one has

$$\begin{aligned} V_\tau(\ell) &= V(\ell)\exp[-q^2\xi_\perp^2(\tau)/2] \\ &= a_V \exp(-\alpha_0^{osc}\ell)\exp(-\omega\tau) \\ &\quad \times \cos[\alpha_1\ell - \alpha_1\alpha_0^{osc}\xi_\perp^2(\tau) - \theta_V], \end{aligned} \tag{8}$$

where now q refers explicitly to the leading-order pole defined by the mean-field model, a_V and θ_V [in place of b and θ used in Eq. (1)] denote the mean-field oscillatory potential amplitude and phase, respectively, and following Chernov and Mikheev I have introduced the key renormalization parameter

$$\omega \equiv \frac{q_R^2 kT}{4\pi\gamma} \simeq \frac{\pi kT}{\gamma\sigma^2} \tag{9}$$

[$q_R^2 \equiv \alpha_1^2 - (\alpha_0^{osc})^2$]. Then, evaluating Eq. (5) and substituting $\Lambda\xi_\parallel = \exp(\tau^*)$, one has

$$\exp[(2 - \omega)\tau^*] \exp(-\alpha_0^{osc}\, \bar{\ell}) \simeq \frac{\gamma A \Lambda^2}{a_V \alpha_1^2}, \qquad (10)$$

which implies that $(2 - \omega)\tau^* = \alpha_0^{osc}\bar{\ell}$ to within a logarithmic constant. When this last result is substituted back into the renormalized potential, one finds that the effective decay length has been renormalized [18]:

$$V_{\tau^*}(\bar{\ell}) \sim \exp[-2\alpha_0^{osc}\, \bar{\ell}/(2 - \omega)]. \qquad (11)$$

Accordingly, only the weak capillary-wave regime $\omega < 1$ is consistent with an oscillatory interface potential. Otherwise, the effective inverse decay length $2\alpha_0^{osc}/(2 - \omega)$ is greater than $2\alpha_0^{osc}$ (which controls the repulsive part of the interface potential arising from $\delta\rho^2$ contributions [18]). Of course, the above scenario is only acceptable if $\omega < 2$, otherwise one is in a strong fluctuation regime and no oscillatory potential term should survive. In fact, the replacement of the lower limit of the integral in Eq. (3) is only acceptable in the linear regime $\xi_\perp^2 (\tau^*)\alpha_0^{osc} < \bar{\ell}$ which is just slightly more restrictive, given that $\alpha_1 \gg \alpha_0^{osc}$ as in Fig. 2. Apart from this latter detail (i.e., $\alpha_0^{osc} \neq 0$) the above discussion is identical to the LRG treatment of a surface roughening transition at $\omega = 2$ [6].

In the region of the triple point one will always be in the regime $2\alpha_0^{osc} < \alpha_0$ (see Sec. IV below), and so the Chernov and Mikheev scenario reviewed above should apply. The particular case treated in Sec. II has $\omega \simeq 5.4$ and so the mean-field prediction would not be relevant to thick wetting films. In fact, from Eq. (9) it follows that surface tensions appropriate to liquid metal systems are required before complete wetting is replaced by the oscillatory layering potentials predicted from mean-field theory. Exactly the same conclusion must hold for the density profile tails. That is, repeating the above LRG analysis, but with $V(\ell)$ replaced by $\rho(z')$, one finds the amplitude of an oscillatory profile tail is renormalized by the factor $\exp(-q_R^2\xi_\perp^2/2)$ with the phase shifted by $\alpha_1\alpha_0^{osc}\xi_\perp^2$. In which case, at a distance $\bar{\ell}$ from an interface the amplitude of an oscillatory tail is decaying as $\exp[-2\alpha_0^{osc}\bar{\ell}/(2 - \omega)]$. For thick film wetting, this implies that if $\omega > 1$ then the tails of the density profiles will interact at leading order via a repulsive $2\alpha_0^{osc}$ term rather than in an oscillatory fashion.

The above scenario of Chernov and Mikheev contrasts with the conclusions of Evans et al. [8]. The apparent conflict is due to the latter authors taking the view that in real systems one would expect $\xi_\perp^2$ to be controlled by external fields, due to the extremely weak logarithmic behavior of the pure wetting case, Eq. (6). For example, when capillary waves are damped by the presence of the earth's gravitational field g the maximum value of $\xi_\parallel^2$ is $\gamma/mg\Delta\rho$, where $m\Delta\rho$ is the change in mass density across the fluctuating interface. Similarly, if an experimental system was limited to a finite planar area A, then $\xi_\parallel^2$ would necessarily be restricted to remain below A^2. For example, taking as a typical value $\Lambda\xi_\parallel(\max) \simeq 10^7$, the cw damping would cease to reduce beyond about $\tau^* \simeq 16$. For the particular case discussed in Sec. II this translates into $\xi_\perp^2 < 4.4\sigma^2$. This suggests that the

LRG criterion $(\xi_\perp^2 \alpha_0^{osc} < \bar{\ell})$ is essentially always met in the presence of external cw damping (in $d = 3$); i.e., the central part of the liquid-vapor interface does not wander sufficiently to experience collisions with the repulsive wall potential. The presence of external damping is sufficient to prevent the renormalization of the oscillatory decay length discussed by Chernov and Mikheev. However, the Gaussian nature of the cw damping means that the amplitude of an oscillatory contribution is drastically reduced for values of $\xi_\perp/\sigma$ greater than about 0.3. For the example discussed above, the cw damping would prevent the damped oscillatory form from dominating the interface potential decay until films of many 100s of σ thick had formed, by which time the magnitude of the energy barrier separating the global minimum from complete wetting would be very small indeed. Nevertheless, the presence of external cw damping means that at sufficiently large $\bar{\ell}$ an underlying mean-field oscillatory interface potential must eventually win, since $\xi_\perp^2$ is finite, and so formally complete wetting is prevented for systems lying above the FW line in (ρ, T) space. In practice however, the Chernov and Mikheev criterion, $\omega < 1$, is likely to remain a good guide as to the likelihood of being able to observe the effects of a renormalized damped oscillatory potential. At the triple point of argonlike fluids $\omega \simeq 3$. The most favorable case would appear to be colloidal systems, since then α_1^2 should become extremely small (as the wavelength will now be determined by a large colloidal particle diameter) while γ should still be typical of ordinary fluids, implying $\omega \ll 1$.

To conclude this section, it is interesting to contrast the above scenario with the situation that would be found for complete drying at a wall-liquid interface. In short-ranged wall-fluid models complete drying is found at low values of ϵ_w, since if liquid molecules are significantly more attracted to each other than to the wall then at liquid-vapor coexistence it must become favorable for a thick (formally infinite) film of vapor to adsorb at the wall-liquid interface. The complete drying case is different to complete wetting over much of the liquid-vapor coexistence curve because the asymptotic forms of the liquid tail and the vapor tail differ. This arises because the FW line is constrained to lie above the mean-field liquid spinodal [8] and so the asymptotic behavior of a vapor tail of a liquid-vapor interface or a wall-vapor interface (or a bulk vapor radial distribution function) is always dominated by a monotonically decaying form. Thus, leaving aside the possible modification of the repulsive part of the interface potential by a damped oscillatory contribution, the case of complete drying in short-ranged models is precisely that envisaged in the early theories of wetting transitions [19,16]. Furthermore, the values of α_0 appropriate to a mean-field vapor tail are much higher than for a liquid tail (away from T_c) and so the renormalization of a drying film is much greater than for a wetting film; for the system discussed in Sec. II the value of ω defined by α_0^{vapor} is around 1.5, which is quite close to the strong fluctuation regime $\omega > 2$. A drying film also possesses the beneficial characteristic that the local structure induced by the wall is extremely weak, so that the interface potential is almost entirely determined by the

simple mean-field form renormalized by capillary waves. The fact that in this case essentially all medium-range and long-range correlations in the film are due to capillary waves has been successfully exploited in an extensive computer simulation study [29]. Unfortunately, there appears to be no documented report of an experimentally observed complete drying film, which may well be due to the ubiquitous presence of power-law dispersion interactions. As discussed in Sec. IV below, the presence of infinite-ranged power-law interactions qualitatively alters the asymptotic analysis. The pole on the imaginary axis (α_0) no longer exists and instead the longest-range correlations are controlled by singular behavior at the origin. Eventually, all density profiles and pair distribution functions must decay as a power law. However, for the theory of wetting or drying involving thick films, this situation is actually a bonus because in $d = 3$ power law tails are not renormalized [30] and so the mean-field interface potential is sufficient. In fact, a full solution can be written down for thick film continuous wetting phenomena in the presence of power-law interactions [31]. Since complete wetting films dominated by dispersion forces are well known classical phenomena [3], some authors have suggested that the absence of any experimental systems showing complete drying is due to fundamental asymmetries between the solid, liquid, and vapor polarizabilities that determine the attractive versus repulsive nature of the dispersion force contribution to an interface potential [32]. Finally, the issue of complete drying has been given a recent twist by a phenomenological argument that includes the effect of line tension at three-phase contact regions present in nonplanar symmetry [2]. Namely, regardless of the details of microscopic interactions, a positive line tension will act to reduce the wall-liquid surface area of any drop of liquid on a nearly dry surface. For sufficiently small drops this thermodynamic argument predicts a jump to zero contact [2].

IV. DISCUSSION

The theory of wetting phenomena is based on identifying an underlying mean-field interface potential, which is then subject to possible renormalization due to capillary-wave fluctuations. In $d = 3$, cw effects are marginal and wetting phenomena are subject to a plethora of non-universal length scales, arising from the details of the intermolecular interactions. In the case of thick wetting films, the interface potential is determined by the asymptotic form of weakly interacting density profile tails. Accordingly, a microscopic theory of wetting phenomena in three-dimensional systems must begin with a detailed investigation of the asymptotic behavior of interfacial profiles predicted by mean-field theory. Only after this stage does it make sense to consider the inclusion of cw fluctuations. However, the complexity of this basic initial step has proved daunting and to date no single group have attempted a general approach, choosing instead to just assume one possible class of physically relevant interface potentials. In this extended discussion I shall attempt a global survey of the many potentially relevant length

scales applicable to wetting phenomena. Apart from cw fluctuations, all of these length scales arise from the details of intermolecular forces. The unavoidable conclusion from this exercise is that everyday macroscopic wetting phenomena mask a truly amazing sensitivity to the details of microscopic interactions.

The behavior of the length scales controlling the asymptotic structure of simple finite-range models of fluids is given in Fig. 4. The curves show data defined by the direct correlation function of square-well fluid along the saturated branch of the liquid-vapor coexistence curve, with attractive interactions treated in the random phase approximation (the same WDA theory used in Sec. II). All the inverse decay lengths plotted are defined in Eq. (1), apart from α_0^{2osc} which refers to the leading-order correction to the asymptotic analysis beyond the leading-order poles (i.e., defined by the damped oscillatory pole possessing the second to largest decay length [10]). T_{tr} denotes the triple point temperature (which was only required here to an accuracy of about 10%). There are good reasons for supposing that Fig. 4 represents the general picture for almost all short-ranged models of simple fluids. In particular, (i) the FW line is constrained by the position of the mean-field liquid spinodal so that it will cross the saturated liquid curve (the point where $\alpha_0 = \alpha_0^{osc}$ in Fig. 4) at approximately the same point for all models whose liquid-vapor coexistence curves scale roughly with the same set of reduced variables (supported by a recent analysis using sophisticated liquid-state integral equation theory [15]), and (ii) simple models of liquids invariably yield an oscillatory pole that touches the real axis just beyond the melting line [7], and in any case it is inevitable that $\alpha_0^{osc}\sigma \ll 1$ at
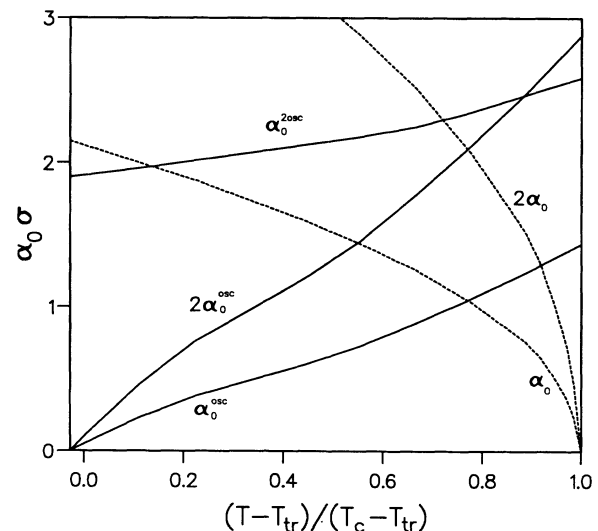
FIG. 4. The global behavior of inverse decay lengths controlling the mean-field asymptotic structure of short-ranged models of saturated liquid. Specific data were generated from the bulk fluid direct correlation function defined by the WDA theory discussed in Sec. II, but there are good reasons for believing that the qualitative picture is essentially universal. See text.

the triple point. The various classes of thick film wetting phenomena in mean-field models of short-ranged fluids can be read from Fig. 4 as follows. Repulsive contributions to an attractive interface potential will vary as $\delta\rho^2$, the $2\alpha_0$ and $2\alpha_0^{osc}$ curves. Note that α_0^{2osc} remains too high for it to be able to interfere here. The form of an attractive interface potential will be controlled in the thick film regime by whichever of the two inverse decay lengths α_0 and α_0^{osc} is the smallest. Thus, from Figure 4 the regime of Chernov and Mikheev (oscillatory interface potentials) holds from the triple point to beyond halfway to the critical point. The traditional theory of wetting phenomena, based on pure monotonically decaying potentials, is restricted to a fairly small region close to the critical point (where $2\alpha_0 < \alpha_0^{osc}$). In between these two isolated classes lie crossover regions where next-to-leading-order contributions need to be taken into consideration, namely, a regime at intermediate temperature where $\alpha_0^{osc} < \alpha_0 < 2\alpha_0^{osc}$, followed by a band of higher temperature states where $\alpha_0 < \alpha_0^{osc} < 2\alpha_0$. Whether or not these higher order terms contribute repulsive or attractive contributions to the interface potential might well be model dependent.

The clear message from Fig. 4 is that, over much of the saturated liquid curve, mean-field interface potentials of short-ranged models are oscillatory in the thick film regime. This oscillatory structure arises from repulsive intermolecular forces and has a wavelength close to the repulsive-core diameter. Such an interface potential is incompatible with complete wetting, since the global minimum must lie at finite $\bar{\ell}$. Instead, pseudo wetting films of $10\sigma - 20\sigma$ are implied. For slightly undersaturated systems, an oscillatory interface potential is associated with adsorption isotherms containing layering transitions that end at critical points with 2D universality [18].

When using LRG theory to incorporate the effects of thermally excited cw fluctuations, it is immediately apparent that oscillatory structure is markedly renormalized for $\xi_\perp > 0.3\sigma$. In particular, Gaussian smoothing of an oscillatory tail leads to a dramatically reduced oscillatory amplitude. In the absence of external sources of cw damping $\xi_\perp^2$ actually diverges with $\bar{\ell}$ (in $d = 3$). The resulting renormalization is then so severe that the decay length of an oscillatory tail is reduced [18]. For short-ranged models of argonlike fluids, the renormalization is strong enough to completely suppress damped oscillatory structure, while for systems with significantly weaker cw broadening ($\omega < 1$) LRG theory predicts a transition from pseudo wetting to complete wetting at a sufficiently high temperature. However, in $d = 3$ the presence of earth's gravity or finite wall area is sufficient to restrict the maximum value of $\xi_\perp$ to around 2σ, so that the damped oscillatory asymptotic form cannot formally be altered. Notwithstanding this formal result, for $\xi_\perp > 0.3\sigma$ the oscillatory amplitude is reduced so much that pseudo wetting films will be found at thicknesses of 100σ or more. In lower dimensional systems, the latter effect will be much more extreme and cw broadening is too strong to be treated by LRG theory [33].

So far we have only considered length scales arising

from cw fluctuations and short-ranged liquid correlations. Since the latter decay exponentially it is clear that the inverse decay length (λ) of an exponentially decaying wall field has precisely the same significance to wetting as the length scales plotted in Fig. 4. Accordingly, in such models the class of wetting alters whenever the value of λ is small enough to dominate the leading-order or second-order decay of the interface potential [34]. The effects of cw fluctuations on an interface potential dominated by an exponential wall field are directly analogous to the standard LRG theory of critical wetting [16,35]. Most recently, cw renormalization of the surface tension has also been considered [27].

The sensitivity of wetting phenomena to the details of microscopic interactions allows for a plethora of nonuniversal behavior. For example, various groups have considered cases where the interface potential contains a double attractive well structure [36], which obviously possess some features analogous to the case of oscillatory potentials. Experimentally, a wide variety of such *designer* wall-fluid systems are accessible via the technology known as self-assembled monolayer systems [37,38].

Although complicated by the plethora of potentially relevant length scales, the above scenario is straightforwardly applicable to short-ranged models of wetting phenomena. However, the situation in typical experimental systems is greatly complicated due to the ubiquitous presence of power-law dispersion forces. When power-law interactions [$\phi_p(r)$] are present the tails of a liquid-vapor interface must eventually decay as a power law, albeit with a very small amplitude proportional to $S(0) \equiv \rho kT\chi_T$ where χ_T denotes a bulk fluid isothermal compressibility [14]. In bulk fluids OZ theory implies $h(r) \to -S(0)^2\phi_p(r)/kT$ [39]. Wall-fluid interfaces can also be treated with OZ theory, via the introduction of wall-particle correlation functions [10]. One finds that $\tilde{c}_{wp}(0) \sim S(0)^{-1}$ so that the presence of a wall or another bulk phase increases the power-law amplitude by removing one factor of $S(0)$ [9]. The fluid mediated dispersion force contribution to solvation structure between two walls is therefore independent of $S(0)$ [9]. The single most important point regarding dispersion force effects is that in $d = 3$ capillary-wave fluctuations are too weak to renormalize power-law tails, even in the absence of external damping [30]. Accordingly, true critical wetting is described by mean-field theory and in fact an explicit general solution can be derived [31]. However, for all classes of wetting phenomena affected by intermediate-ranged structure one must continue to bear in mind the scenario obtained from short-ranged models.

A simultaneous treatment of power-law tails and intermediate-range structure is somewhat complicated because one cannot describe power-law correlations in terms of simple poles; rather one has to instead expand about the origin of the complex plane. As a consequence one loses the pole on the imaginary axis responsible for the α_0 monotonic decay in Eq. (1). In contrast, one still finds damped oscillatory poles more or less unaltered by the inclusion of dispersion forces [15]. Thus in mean-field models the intermediate-ranged structure of dense liquids is still dominated by damped oscillatory correlations. For

bulk liquid distribution functions and wall-liquid profiles, the crossover between oscillatory behavior and asymptotic power-law decay is controlled partly by the value of $S(0)$. Thus near the triple point one can only see the power-law decay at very long range (which for interface potentials means thick wetting films only) [15]. Accordingly, in mean-field models of experimental systems, Fig. 4 should be a good guide to the presence of layering transitions in moderately thick wetting films. Even the inclusion of cw fluctuations need not remove this latter conclusion [18]. However, since oscillatory structure is strongly renormalized by cw broadening whereas power-law tails are essentially unaffected, it follows that the region of phase space where damped oscillatory interface potentials play a role will be greatly reduced by the inclusion of cw effects whenever $\xi_\perp > 0.3\sigma$.

To conclude this survey, I shall note the equal significance of the above analysis to complex fluids, such as mixtures and charged fluids. The case of short-ranged models of fluid mixtures is a straightfoward generalization of the pure fluid analysis [10]. The pole analysis yields a unique asymptotic form for all pair distribution functions and wall-component density profiles; in particular, there is a single FW surface in phase space separating damped oscillatory asymptotic structure from monotonic decay [10]. Thus the number of relevant length scales does not grow out of hand. Although to date the equivalents of Fig. 4, appropriate to mean-field models of wetting at liquid-liquid, liquid-vapor, and wall-vapor interfaces of mixtures, have yet to be derived, there is no reason to expect damped oscillatory interface potentials to be any less dominant [40]. LRG theory of cw broadening is equally adaptable to all classes of fluid-fluid interfaces and very similar effects will arise from Gaussian smoothing as for a pure fluid liquid-vapor interface. Once again, the significance of cw fluctuations hinges on the size of $\xi_\perp$.

Pole analyses of asymptotic correlations in the restrictive primitive model of charged fluids (treated with the hypernetted-chain theory or the generalized mean spherical approximation) have recently been highlighted by various groups [13,12]. Furthermore, in Ref. [12] the authors have been able to justify a qualitative significance of their results to experimental systems of weakly asymmetric binary molten salts and electrolytes. The presence of charge neutrality (screening) reduces all correlations to the short-ranged model form given in Eq. (1). However, there are now two sets of simple poles that one must consider to map out the asymptotic behavior throughout phase space; namely, one set controlling long-range correlations in the charge density with another set arising from short-ranged interactions as in the simple fluid case. There are thus two important crossover lines in the phase space of charged fluids, signaling a change from monotonically decaying structure to damped oscillatory decay [12]. The equivalent of Fig. 4 therefore contains twice as many potentially relevant length scales. Wetting phenomena in electrochemical systems should therefore display remarkably rich behavior, directly interpretable in terms of microscopic length scales. Here one should note the ease of control one has over the sign and strength of electrode potentials (cf. ϵ_w).

To sum up, a proper theory of wetting phenomena must begin with a clear identification of all length scales that might possibly be relevant to an interface potential. This can be done by concentrating on the mean-field picture, noting that a careful treatment of repulsive force contributions is essential to obtain a proper description of damped oscillatory terms. For short-ranged models it is essential to understand the relative behavior of the α_0 and α_0^{osc} poles (Fig. 4), defined by the bulk liquid direct correlation function. The quality of an interface potential will be directly related to the quality of the bulk fluid direct correlation function belonging to a given theory. Furthermore, the oscillatory poles continue to play an important role even in the presence of power-law interactions. One must also consider length scales arising directly from the wall field. Then, in $d = 3$, one can use LRG theory to include the effects of cw fluctuations. The main conclusion here is that cw broadening of oscillatory structure is especially significant, although the presence of external damping protects the ultimate form of the asymptotic behavior. The implication of damped oscillatory interface potentials to the suppression of complete wetting phenomena is of particular note. The same general conclusions hold equally for wetting in fluid mixture systems. Finally, thanks to recent progress in describing the asymptotic structure of charged fluids, one could now extend the entire general theory of wetting to encompass electrochemical systems.

ACKNOWLEDGMENTS

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