Interplay of critical Casimir and dispersion forces

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Using general scaling arguments combined with mean-field theory we investigate the critical ($T \simeq T_c$) and off-critical ($T \neq T_c$) behavior of the Casimir forces in fluid films of thickness L governed by dispersion forces and exposed to long-ranged substrate potentials which are taken to be equal on both sides of the film. We study the resulting effective force acting on the confining substrates as a function of T and of the chemical potential μ. We find that the total force is attractive both below and above T_c. If, however, the direct substrate-substrate contribution is subtracted, the force is repulsive everywhere except near the bulk critical point (T_c, μ_c), where critical density fluctuations arise, or except at low temperatures and $(L/a)(\beta\Delta\mu) = O(1)$, with $\Delta\mu = \mu - \mu_c < 0$ and a the characteristic distance between the molecules of the fluid, i.e., in the capillary condensation regime. While near the critical point the maximal amplitude of the attractive force if of order of L^{-d} in the capillary condensation regime the force is much stronger with maximal amplitude decaying as L^{-1}. In the latter regime we observe that the long-ranged tails of the fluid-fluid and the substrate-fluid interactions further increase that amplitude in comparison with systems with short-range interactions only. Although in the critical region the system under consideration asymptotically belongs to the Ising universality class with short-ranged forces, we find deviations from the standard finite-size scaling for $\xi \ln(\xi/\xi_0^{\pm}) \gg L$ even for $\xi, L \gg \xi_0^{\pm}$, where $\xi[t = (T - T_c)/T_c \to \pm 0, \Delta\mu = 0] = \xi_0^{\pm}|t|^{-\nu}$, is the bulk correlation length. In this regime the dominant finite-size contributions to the free energy and to the force stem from the long-ranged algebraically decaying tails of the interactions; they are not exponentially small in L, as it is the case there in systems governed by purely short-ranged interactions, but exhibit a power law decay in L. Essential deviations from the standard finite-size scaling behavior are observed also within the finite-size critical region $L/\xi = O(1)$ for films with thicknesses $L \lesssim L_{\mathrm{crit}}$, where $L_{\mathrm{crit}} = \xi_0^{\pm}(16|s|)^{\nu/\beta}$, with ν and β as the standard bulk critical exponents and with $s = O(1)$ as the dimensionless parameter that characterizes the relative strength of the long-ranged tail of the substrate fluid over the fluid-fluid interaction. We present the modified finite-size scaling pertinent for such a case and analyze in detail the finite-size behavior in this region. The standard finite-size scaling behavior is recovered only for $L \gg L_{\mathrm{crit}}$.

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I. INTRODUCTION

Since its first prediction in 1948 by Casimir [1], the effect named after him has raised significant theoretical and experimental interest and has been found to occur in numerous manifestations (see, e.g., Refs. [2–9]). Originally, Casimir considered vacuum fluctuations of the electromagnetic field between two parallel metal plates which restrict and modify the fluctuation spectrum leading to a dependence of the energy on the distance L between the plates. This so-called classical (actually, quantum mechanical) Casimir effect, which for decades had been considered as a theoretical curiosity, in recent years has turned into a subject of intensive research, not at least triggered by possible applications in micromechanical devices, and has been already verified with an impressive experimental accuracy [10–13]. Another manifestation of the Casimir effect, which has a significant impact towards a different scientific direction (see, e.g., Refs. [6,7,14–27]), is the so-called statistical-mechanical (thermodynamic) Casimir effect. In a fluid close to a continuous phase transition at a critical point T_c large fluctuations of the order parameter occur. If, as before, the fluid is confined by parallel plates at a distance L, and is in contact with a particle reservoir with a chemical potential μ, the grand canonical potential $\Omega_{ex}(T, \mu, L)$ of the fluid in excess to its bulk value $AL\omega_{\mathrm{bulk}}(T, \mu)$ depends on L so that one can define the effective force f between the plates per cross sectional area A and per $k_B T$ as

$$f(T, \mu, L) = -\beta \frac{\partial \omega_{ex}(T, \mu, L)}{\partial L}, \tag{1.1}$$

where $\beta = 1/(k_B T)$, $\omega_{ex}(T, \mu, L) = \bar{\omega}(T, \mu, L) - L\omega_{\mathrm{bulk}}(T, \mu) = \Omega_{ex}(T, \mu, L)/A$ is the excess grand canonical potential per cross sectional area A, $\Omega(T, \mu, L) = A\bar{\omega}(T, \mu, L)$ is the total grand canonical potential, and $\omega_{\mathrm{bulk}}(T, \mu)$ is the density of the bulk grand canonical potential. Besides temperature, chemical potential, and film thickness, the force also depends on which boundary conditions the surfaces impose on the system. The order near the surfaces can be either reduced or—which is the generic case for liquids confined by solid substrates—increased due to effective surface fields generated by the confinement. The latter case is known as $(+, +)$ boundary conditions (for a more precise definition see below). For this case the schematic phase diagram of a fluid film with thickness L is shown in Fig. 1.

One should keep in mind that the force $f(T, \mu, L)$ is a definition dependent quantity in the sense that it depends on

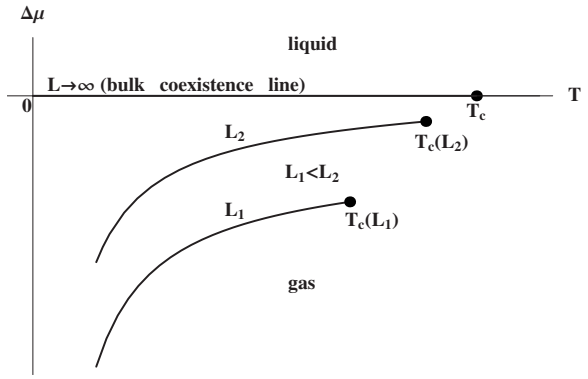

FIG. 1. The schematic phase diagram of a d-dimensional slab with $(+,+)$ boundary conditions for various thicknesses L and surfaces which prefer the liquid phase. The bent gas-liquid coexistence curves correspond to capillary condensation transitions for $L=L_1$ and $L=L_2$ with $L_1<L_2$ [compare Fig. 11(b)]. Away from the critical region the shift in the phase boundary relative to the bulk coexistence line $\Delta\mu=0$ is proportional to L^{-1}, while within the critical region it is proportional to $L^{-\Delta/\nu}$ where Δ and ν are the standard bulk critical exponents. The lines of first-order phase transition end at $(d-1)$-dimensional critical points $T_c(L_i)$ with coordinates $(T_{c,L_i},\Delta\mu_{c,L_i})$, $i=1,2$, the positions of which vary with L and depend on the presence and on the strengths of the fluid-fluid and the substrate-fluid interactions. For large L these points are located close to the bulk critical point T_c with coordinates $(T_c,\Delta\mu=0)$: $T_{c,L}-T_c\sim L^{-1/\nu}$ and $\Delta\mu_{c,L}\sim L^{-\Delta/\nu}$. Since the fluctuations in systems of reduced size are stronger, one typically has $T_{c,L_i}<T_c$; the fact that $\Delta\mu_{c,L_i}<0$ expresses the preferences of the identical walls.

how one defines the thickness of the film. A natural choice would be to take the distance between the planes defined by the positions of the nuclei of the top layer of each substrate. However, there are certainly other possible definitions, which will differ by a microscopic length. This implies that a quantitative comparison between experimental data and theory is only possible if the data are accompanied by a precise definition of what L is. Up to now seemingly there is no awareness of this issue yet.

Close to the critical point, the critical Casimir interactions are proportional to k_BT_c and therefore the interaction between the plates can become rather strong in a system with high T_c such as, e.g., in classical binary liquid mixtures. However, in such systems the direct dispersion forces between the fluid particles and between the fluid particles and the substrate particles also play an important role. The contributions of the dispersion forces to the total effective force can be distinguished from that of the critical Casimir forces by their temperature dependence, because the leading temperature dependence of the former does not exhibit a singularity. For this reason both in theoretical analyses and in interpretations of experimental data the contributions due to the dispersion forces are usually treated separately and, also for the critical region, are simply added as a regular background contribution to the total force (see, e.g., Refs. [17,18,22]).

The present investigation aims at studying in detail the actual interplay between the dispersion and the critical (fluctuation induced) forces in simple fluids bounded by strongly adsorbing identical walls.

The article is arranged as follows. In Sec. II we discuss the finite-size behavior of systems in which dispersion forces are present. There, in Sec. II B, we analyze the conditions under which their effect can be safely ignored as well as, in Sec. II C, how the Casimir force is affected when these conditions are not fulfilled. Section III presents the lattice gas model with van der Waals type long-ranged interactions which we investigate in the current study. In Sec. IV we present our results for the free energy and the force by focusing in Sec. IV A on our results for the force near criticality, while in Sec. IV B we discuss the behavior of the system off criticality, including the capillary condensation regime. Finally, in Sec. V we summarize our findings and comment on their experimental relevance. As far as possible we compare our results with previous findings for fluids governed by or exposed to dispersion forces. Important technical details are presented in Appendixes A–C.

II. FINITE-SIZE BEHAVIOR OF SYSTEMS WITH DISPERSION FORCES

A. Scaling with dispersion forces

In describing fluid systems near criticality one often resorts to the Ising model as a representative of the corresponding universality class, for which only nearest-neighbor interactions are considered. Instead, here we consider long-ranged pair interactions between the fluid particles decaying asymptotically $\sim J^l r^{-6}$ for distances r between each other and long-ranged substrate potentials $\sim J^{l,s} z^{-3}$ acting on fluid particles at a distance z from the flat surface of a semi-infinite substrate. (Here we do not embark into the extended microscopic description of confined binary fluid mixtures, which are expected to belong to the same universality class as the one-component fluids considered here explicitly.) Such systems also belong to the Ising universality class characterized by short-ranged forces [28]. This implies that the corresponding critical exponents and leading finite-size dependences are expected to be the same as for systems with short-ranged forces. The long-ranged part of the interactions leads to a regular contribution to the force, as considered and expected before, and in addition, as shown recently [21,29–31], to a serious modification of the finite-size behavior of its singular contribution. Indeed, in the case of d-dimensional systems, in which the interaction decays asymptotically with the distance $\sim r^{-d-\sigma}$ (with $\sigma>2$), the effective total force $f(T,\mu,L)$ between the plates can be cast [see Eq. (1.1)] into the form [21,25,32,33]

$$f(T,\mu,L) \simeq L^{-d} X[L/\xi_t, L/\xi_\mu, (L/\xi_0)^{-\omega_l} l, (L/\xi_0)^{-\omega_s} s, (L/\xi_0)^{-\omega} g_\omega] + \beta(\sigma-1) H_A(T,\mu) L^{-\sigma} \xi_0^{\sigma-d}. \quad (2.1)$$

Here X is the dimensionless, universal scaling function, ξ_t is the bulk correlation length $\xi(t\to\pm 0,\Delta\mu=0)=\xi_0^{\pm}|t|^{-\nu}$ at bulk coexistence $\mu=\mu_c$ and for $t=(T-T_c)/T_c\to\pm 0$, while $\xi_\mu(t=0,\Delta\mu\to 0)=\xi_{0,\mu}|\beta_c\Delta\mu|^{-\nu/\Delta}$ is the bulk correlation length at the critical temperature $T=T_c$ with $\beta_c=(k_BT_c)^{-1}$. For $T>T_c$ and $\Delta\mu=0$ one has $\xi_0=\xi_0^+$, while for $T<T_c$ and $\Delta\mu=0$ one has $\xi_0=\xi_0^-$ with the ratio ξ_0^+/ξ_0^- being universal. $\xi_{0,\mu}$ is the same for $\Delta\mu\to+0$ and $\Delta\mu\to-0$. The second term

in Eq. (2.1) stems from the free energy contribution $H_A L^{-(\sigma-1)}$, where $H_A(T,\mu)=A_t(T,\mu)+A_l(T,\mu)+A_{l,s}(T)$ with so-called Hamaker constants A_t, A_l, and $A_{l,s}$ (see below for more details). In addition, ω is the standard Wegner's correction-to-scaling exponent for short-ranged systems, while $\omega_l=\sigma-(2-\eta)$ and $\omega_s=\sigma-(d+2-\eta)/2$ are the correction to scaling exponents due to the long-ranged tails of the fluid-fluid and substrate-fluid interactions, respectively. Further L-dependent contributions to the force such as next-to-leading order contributions to the Hamaker terms or higher order corrections to scaling are neglected because they are smaller than those captured in Eq. (2.1). Here we consider a d-dimensional system characterized by an interaction given as the sum of a short-ranged and a long-ranged component with the latter decaying according to a power law $r^{-d-\sigma}$, with $2<\sigma<4$. We intend to vary the ratio λ of the strengths of the long-ranged and the short-ranged contributions. By varying λ we can quantitatively probe the importance of the long-ranged tails. One might envisage potential experiments in colloidal systems which allow for a dedicated tailoring of the form of the effective interactions between colloidal particles. We recall that, independent of λ, for $2<\sigma\leqslant 4$ the system still belongs to the corresponding short-ranged universality class, i.e., the critical exponents do not depend on σ. Such long-ranged interactions are called subleading long-ranged interactions [29,30]. In Eq. (2.1) η is the standard critical exponent characterizing the decay of the bulk two-point correlation function at the critical temperature, g_ω is the (dimensionless) scaling field associated with the Wegner-type corrections, while l and s are dimensionless nonuniversal coupling constants: l is proportional to the strength J^l of the long-ranged tail in the fluid-fluid interaction whereas s is proportional to the contrast between the substrate potential and the fluid-fluid interaction integrated over a half-space (see below). For the "genuine" nonretarded van der Waals interaction, which governs nonpolar fluids, one has $d=\sigma=3$ and thus $\omega_s>0$, $\omega_l>0$. We will further suppose that the positivity of ω_s and ω_l is fulfilled for all values of d and σ considered in the following. Accordingly, for L *large enough*, one can expand the scaling function X in Eq. (2.1):

$$f \simeq L^{-d}\{X^{\mathrm{sr}}[L/\xi_t,L/\xi_\mu]+(L/\xi_0)^{-\omega_s}sX_s^{\mathrm{lr}}[L/\xi_t,L/\xi_\mu] + (L/\xi_0)^{-\omega_\sigma}lX_l^{\mathrm{lr}}[L/\xi_t,L/\xi_\mu]+(L/\xi_0)^{-\omega}g_\omega X_\omega^{\mathrm{sr}}[L/\xi_t,L/\xi_\mu]\} + \beta(\sigma-1)H_A(T,\mu)L^{-\sigma}\xi_0^{\sigma-d}. \quad (2.2)$$

If Eq. (2.2) is valid the scaling function X^{sr}, which originates from the short-ranged interactions and describes the well-studied (short-ranged) critical behavior, provides the *leading* behavior of the force near the bulk critical point $(L/\xi_t=0,L/\xi_\mu=0)$. Here the notion "near the critical point" means $L/\xi_t=O(1)$ and $L/\xi_\mu=O(1)$, which defines the "critical region of the finite system." There X_ω^{sr}, X_l^{lr}, and X_s^{lr} represent only *corrections* to the leading L dependence. In particular, the value $X^{\mathrm{sr}}(0)=(d-1)\Delta_{a,b}$ is related to the Casimir amplitude $\Delta_{a,b}$, which depends only on the bulk universality class and the boundary conditions a,b at the two confining surfaces, i.e., the surface universality classes. There is considerable knowledge about the Casimir amplitudes, such as their exact values in $d=2$ [34–36] and in $d=3$ for the spherical model [16], ε-expansion results for $d=3$ [15,26], and mean-field values [17]. In the following we shall consider only the case of $(+,+)$ boundary conditions corresponding to strong equal surface fields acting at both surfaces, i.e., the case of strong adsorption of the fluid on the boundaries of the bounding substrate. While the scaling function X^{sr} decays exponentially for $L/\xi\gg 1$, in this regime the other scaling functions X_l^{lr} and X_s^{lr} in Eq. (2.2) decay according to a power law. For this reason these functions, which formally stem from corrections to scaling due to the subleading long-ranged tail in the fluid-fluid interaction and in the substrate potential, respectively, lead to *leading finite-size* contributions in the singular behavior of the force in the regime $L/\xi\gg 1$. In the case of *periodic* boundary condition—in which only the functions X_l^{lr} and X_ω^{sr} are present—the above statement has been verified for the spherical model [which, for periodic boundary conditions, represents the limit $n\to\infty$ of the $O(n)$ models]. We note that although the scaling function X_ω^{sr} characterizes the short-ranged universality class, the scaling field g_ω incorporates, in general, also contributions due to the long-ranged tails of the interaction. We refer the interested reader to Ref. [25] where explicit results about the above mentioned mixing of the corrections due to the long-ranged forces and the Wegner-type corrections have been reported. In the following we are only interested in the leading L-dependence of the force. Therefore we shall not discuss in further detail those contributions which are due to the corrections to scaling ruled by the Wegner exponent ω [37]; they produce corrections [38,39] both near the critical point, where they are of the order of $L^{-\omega}$, as well as away, where they decay exponentially.

B. Relevance-irrelevance criterion for the dispersion forces

We briefly comment on the conditions which justify an expansion of the type presented in Eq. (2.2). The requirements $2-\eta-\sigma<0$ and $(d+2-\eta)/2-\sigma<0$ are obvious and, as already mentioned, normally they are satisfied in any realistic system for which $d=\sigma=3$ and $\eta\ll 1$ [e.g., for the three-dimensional (3D) Ising model $\eta\simeq 0.034$ [37]]. One important additional condition arises (see Ref. [40]), however, from the fact that we consider not semi-infinite systems but systems which are finite in one dimension and thus exposed to power law *long-ranged* substrate-fluid potentials from both sides. Accordingly, these potentials act everywhere in the finite system; at the center of the film their sum is minimal but not zero. The effect of this value of the total external potential in the center can be interpreted as if the system has a nonzero effective bulk excess chemical potential $\Delta\mu_{\mathrm{eff}}$ despite the fact that the actual bulk system might be at bulk coexistence curve $\Delta\mu=0$. Taking into account the contributions from both surfaces in terms of the notations already introduced one has $\Delta\mu_{\mathrm{eff}}=2s[L/(2\xi_0)]^{-\sigma}$. Since the excess chemical potential scales as $\Delta\mu L^{\Delta/\nu}$ one finds that in a *film* the finite-size contributions due to the long-ranged substrate-fluid potentials will be negligible *in the critical region* if

$$2|s|[L/(2\xi_0)]^{-\sigma}[L/\xi_0]^{\Delta/\nu}\ll 1, \quad (2.3)$$

i.e.,

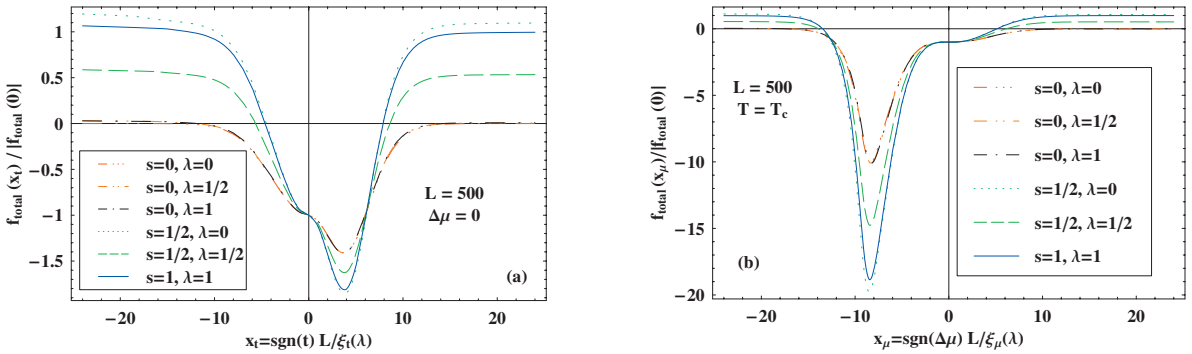

FIG. 2. (Color) (a) Temperature dependence at $\Delta\mu=0$ of the total Casimir force normalized by its value at the bulk critical point in a system with $L=500$ layers for different strengths λ and s of the long-ranged part of the fluid-fluid and fluid-substrate potentials, respectively; L and ξ_t are measured in units of the lattice constant of the lattice model. The total force depends significantly on the strengths of both potentials. Nonetheless it turns out that the critical part of the force exhibits universality and scaling behavior. For small L, however, important nonuniversal contributions due to the long-ranged parts of the aforementioned interactions emerge which cannot be neglected. Independent of the values of s and λ the force extremum always occurs at positive $t=(T-T_c)/T_c$, i.e., *above* the bulk critical temperature. This is due to the stabilizing effect of both the boundary conditions and of the long-ranged tails of the interactions on the order of the system so that the strongest fluctuations are expected to occur slightly above T_c and on the vapor side of the bulk coexistence curve. Since the Casimir force is generated by these fluctuations one expects and indeed observes that the force is strongest for such thermodynamic parameters. (b) Same as in (a) for the field dependence $\Delta\mu$ at $T=T_c$. The force extremum always occurs at negative values of $\Delta\mu$, i.e., on the gas side of the bulk coexistence curve.

$$2^{\sigma+1}|s|[L/\xi_0]^{\Delta/\nu-\sigma} \ll 1. \tag{2.4}$$

The sign of s is chosen such that $s>0(<0)$ corresponds to attractive (repulsive) walls, i.e., walls preferring the liquid (gas) phase of the fluid. A more detailed discussion of that point will be given below where we identify s within the framework of a mean-field model. Due to standard relations between critical exponents one has $\Delta/\nu=(d+2-\eta)/2$, so that relation (2.4) is consistent with Eq. (2.2). On the other hand due to $\Delta/\nu-\sigma=d-\sigma-\beta/\nu$ and with $d=\sigma$ for realistic systems the condition (2.4) turns into

$$2^{\sigma+1}|s|[L/\xi_0]^{-\beta/\nu} \ll 1. \tag{2.5}$$

With ξ_0 typically of the order of 3 Å, $\beta\simeq 0.329$, $\nu\simeq 0.631$ (3D Ising model), and for $\sigma=3$ one finds

$$L \gg L_{\mathrm{crit}} \equiv \xi_0(2^{\sigma+1}|s|)^{\nu/\beta} \simeq 612|s|^{1.918}\text{Å}. \tag{2.6}$$

Equation (2.6) represents a relevance-irrelevance criterion for van der Waals type substrate potentials in a film of thickness L: if $L \gg L_{\mathrm{crit}}$ the leading behavior of the force within the critical region will be that for a system with short-ranged interactions, while for thinner films $L \leqslant L_{\mathrm{crit}}$ the effects due to the van der Waals substrate potentials are expected to be relevant. Since s is typically not very small (see below), L_{crit} turns out to be surprisingly large. As discussed later for a variety of systems $|s| \in [1,2]$. However, for some systems such as ^{3}He or ^{4}He films near their bulk liquid-gas critical point and confined by Au substrate s can be as large as 4 [40]. Thus for most fluid systems, for which measurements of the Casimir force has been performed, L was much smaller than L_{crit}. We stress, however, that until now no Casimir force measurements for systems with $(+,+)$ boundary conditions near liquid-gas critical points have been reported. Therefore we are unable to confront our predictions explicitly with available experimental data.

Finally, we note that if for a particular choice of the fluid and of the surrounding substrate s happens to be small, also L_{crit}, as given by Eq. (2.6), will be small. Keeping in mind that in Ising-like three-dimensional systems (with $d=\sigma=3$ and $\eta\simeq 0.034$) the correction-to-scaling exponents $\omega\simeq 0.81$ [37], $\omega_l\simeq 1.03$, and $\omega_s\simeq 0.52$ are numerically not very different from each other, the determination of L_{crit} should in principle in this case take into account also the values of the scaling fields g_ω and l in addition to that one of s, i.e., Eq. (2.6) should be modified. However, in such a case an expansion of the type given in Eq. (2.2) will be valid for any reasonably large L with the contributions due to the Wegner type corrections as well as due to the long-ranged part of the interaction competing with each other and representing corrections to the leading behavior of the force which is given by the scaling function X^{sr}.

C. The behavior of the total Casimir force

Figure 2 presents the typical behavior of the total (including the contributions from the regular part of the free energy but neglecting the direct substrate-substrate interaction) Casimir force as a function of the temperature or the excess chemical potential, respectively. The force is normalized by its value at the bulk critical point. The precise meaning of the parameters s and λ, as well as the definition of the model within which the curves have been calculated, will be given below. Larger values of λ and s correspond to stronger long-ranged tails of the fluid-fluid and substrate-fluid interactions, respectively. The case $(\lambda=0, s=0)$ corresponds to truly short-ranged interactions. We expect these curves to resemble potential experimental data for the force occurring in nonpolar fluid films bounded by substrates which strongly prefer the

liquid phase of the fluid. (Experimentally, the contribution of the direct substrate-substrate interaction can be separated off by a control experiment with the fluid replaced by vacuum; therefore in the following we do not consider this direct contribution.) Despite the spread of the curves for different values of s and λ, it will turn out that a description in terms of scaling functions is possible if the data are suitably analyzed, provided that for a given value of s the film thickness L is sufficiently large [see Eq. (2.6)].

It is our aim to determine the leading L dependence of the Casimir force as a function of the temperature, the chemical potential, and of the parameters s and λ, and to clarify the relevance of these parameters for its behavior in a fluid film bounded by strongly adsorbing, identical walls. To this end and in view of the large parameter space, starting from a continuum density functional we describe the system in terms of a lattice gas model which is expected to capture the essential features of actual fluids as far as the critical behavior is concerned. For $L \gg L_{\mathrm{crit}}$ the terms entering into Eq. (2.2) are the most important ones [37–39], because for the systems under discussion here they provide the dominant singular finite-size behavior of the free energy and of other thermodynamic variables. Whenever $s \neq 0$, which is the generic or so-called normal case for actual fluids confined by solid substrates, the functions X^{sr} and X_s^{lr} will determine the leading critical finite-size behavior of the Casimir force. [We note that if the fluid film of interest is a wetting fluid on a solid substrate or an interfacial wetting film in binary liquid mixtures, one or two confining spectator phases are fluids, too. Apart from subtleties such as the occurrence of capillary waves at confining fluid interfaces, our present approach is expected to cover the important aspects also of these more complicated systems. The different preferences of the walls, however, lead to a situation which is not described by $(+,+)$ but by some type of $(+,-)$ boundary conditions and require, therefore, a separate consideration. The main qualitative difference is that the critical contribution of the force is then expected to be repulsive, and not attractive as for $(+,+)$ boundary conditions.] Due to the lack of the symmetry $s \to -s$ in the presence of $(+,+)$ boundary conditions, a term in the free energy, which is—to lowest order—linear in s, is indeed expected. So-called neutral walls, considered theoretically (see, e.g., Ref. [41] and references cited therein), correspond to $s=0$. In this special case X^{sr} and X_l^{lr} will determine the dominant finite-size behavior of the fluid system. For such a case X^{sr} and X_l^{lr} must be calculated for Dirichlet-Dirichlet boundary conditions. Recently a similar system of a fluid near a weakly attractive wall has been considered by Monte Carlo methods [42]; but in this study the interaction potential between the fluid particles has been truncated thereby rendering effectively a short-ranged potential. Finally, we emphasize again that for film thickness $L \leqslant L_{\mathrm{crit}}$ an expansion of the type given in Eq. (2.2) is not possible so that for these systems the van der Waals interaction will be important throughout the critical region, including the point $(T=T_c, \Delta\mu=0)$, i.e., in this case even the determination of the Casimir amplitudes is affected.

In the next section we present the model which we use to study the behavior of the Casimir force in systems with dispersion interactions.

III. THE MODEL

Within the density functional approach for inhomogeneous fluids, which in practice is mean-field-like in character, the grand canonical functional $\Omega[\rho(\mathbf{r})]$ of a fluid has to be minimized with respect to the local number density $\rho(\mathbf{r})$ [43,44] (in view of our focus on critical phenomena we refrain from using more sophisticated versions of density functionals):

$$\Omega[\rho(\mathbf{r})] = \int f_{\mathrm{HS}}(\rho(\mathbf{r})) + \frac{1}{2}\int\int \rho(\mathbf{r}) w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' + \int V(z)\rho(\mathbf{r}) d^3\mathbf{r} - \mu \int \rho(\mathbf{r}) d^3\mathbf{r}. \tag{3.1}$$

The fluid is confined between two parallel flat plates at a distance L which exert a substrate potential $V(z)$ with z as the normal distance from one wall. For an individual wall $V(z \to \infty) \sim z^{-\sigma}$ with $\sigma=3$ for a genuine van der Waals interaction; μ is the chemical potential and $f_{\mathrm{HS}}(\rho)$ is the bulk free energy density of a hard-sphere system acting as a reference system; $w(r)$ is the fluid potential which is suitably regularized at a molecular distance, i.e., it exhibits a negative, finite, plateau around $|\mathbf{r}|=0$ and tends to zero according to a power law for large values of $r=|\mathbf{r}|$. In Eq. (3.1) the integrals run over the slab volume.

In the spirit of focusing on the essential features of confined critical phenomena, one can further simplify the continuum functional in Eq. (3.1) by replacing it by its lattice version. This resembles the approach taken, e.g., by Fisher and Nakanishi [45,46] in their mean-field study of the same system but governed by short-ranged forces. The grand potential functional for this lattice gas system is

$$\Omega[\rho(\mathbf{r})] = k_B T \sum_{\mathbf{r}\in\mathcal{L}} \{\rho(\mathbf{r})\ln[\rho(\mathbf{r})] + [1-\rho(\mathbf{r})]\ln[1-\rho(\mathbf{r})]\} + \frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'\in\mathcal{L}} \rho(\mathbf{r}) w(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + \sum_{\mathbf{r}\in\mathcal{L}} [V(z)-\mu]\rho(\mathbf{r}), \tag{3.2}$$

where $\mathcal{L}$ is a simple cubic lattice in the region $0 \leqslant z \leqslant L$ occupied by the fluid. Here and in the following all length scales are taken in units of the lattice constant a of the order of a molecular diameter (and thus are dimensionless) so that the particle density $\rho(\mathbf{r})$ is dimensionless and varies within the range $[0,1]$. In Eq. (3.2) the terms in curly brackets correspond to the entropic contributions, while in an obvious way the other terms are directly related to the interactions present in the system.

The variation of Eq. (3.2) with respect to $\rho(\mathbf{r})$ leads to the equation of state for the equilibrium density $\rho^*(\mathbf{r})$

$$2\rho^*(\mathbf{r}) - 1 = \tanh\left(-\frac{\beta}{2}\sum_{\mathbf{r}'} w(\mathbf{r}-\mathbf{r}')\rho^*(\mathbf{r}') + \frac{\beta}{2}[\mu - V(z)]\right). \tag{3.3}$$

The advantage of this equation is that it lends itself to solving it numerically by iterative procedures. For a given geom-

etry and surface potential $V(z)$ the solution determines the equilibrium order-parameter profile $\rho^*(\mathbf{r})$ in the system. Inserting this profile into Eq. (3.2) renders the grand canonical potential of the system. In order to avoid the double sum in Eq. (3.2), which is inconvenient for the numerical treatment, from Eq. (3.3) one can easily derive the relation

$$k_B T \sum_{\mathbf{r}\in\mathcal{L}} \rho^*(\mathbf{r}) \operatorname{arctanh}[2\rho^*(\mathbf{r})-1] = \frac{1}{2}\sum_{\mathbf{r}\in\mathcal{L}} [\mu - V(z)]\rho^*(\mathbf{r}) - \frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'\in\mathcal{L}} w(\mathbf{r}-\mathbf{r}')\rho^*(\mathbf{r})\rho^*(\mathbf{r}'), \tag{3.4}$$

which yields for Eq. (3.2)

$$\Omega[\rho^*(\mathbf{r})] = \sum_{\mathbf{r}\in\mathcal{L}} \left(k_B T\{\rho^*(\mathbf{r})\ln[\rho^*(\mathbf{r})] + [1-\rho^*(\mathbf{r})]\ln[1-\rho^*(\mathbf{r})] - \rho^*(\mathbf{r})\operatorname{arctanh}[2\rho^*(\mathbf{r})-1]\} - \frac{1}{2}[\mu - V(z)]\rho^*(\mathbf{r}) \right). \tag{3.5}$$

Note that here $\rho^*(\mathbf{r})$ is no longer a free functional variable, with respect to which one has to minimize Eq. (3.5), but the solution of Eq. (3.3).

Denoting $\phi^*(\mathbf{r})=2\rho^*(\mathbf{r})-1$ and $\Delta\mu=\mu-\mu_c$, where $\mu_c=\frac{1}{2}\Sigma_{\mathbf{r}'} w(\mathbf{r}-\mathbf{r}')$, the equation of state (3.3) can be rewritten in the standard form

$$\phi^*(\mathbf{r}) = \tanh\left(\beta \sum_{\mathbf{r}'} J(\mathbf{r},\mathbf{r}')\phi^*(\mathbf{r}') + \frac{\beta}{2}[\Delta\mu - \Delta V(z)] \right), \tag{3.6}$$

where $J(\mathbf{r}-\mathbf{r}')=-w(\mathbf{r}-\mathbf{r}')/4$. The bulk properties of the model are well known (see, e.g., Refs. [47,48] and references therein). We recall that the order parameter ϕ^* of the system has a critical value $\phi^*=0$ which corresponds to $\rho_c=1/2$ so that $\phi^*=2(\rho^*-\rho_c)$. The bulk critical point of the model is given by $\{\beta=\beta_c=[\Sigma_{\mathbf{r}} J(\mathbf{r})]^{-1}, \mu=\mu_c=-2\Sigma_{\mathbf{r}} J(\mathbf{r})\}$ with the sum running over the whole lattice. Within the mean-field approximation the critical exponents for the order parameter and the compressibility are $\beta=1/2$ and $\gamma=1$, respectively. The *effective* surface potential $\Delta V(z)$ in Eq. (3.6) is given by [see Appendix A, in particular Eq. (A8) as an analog]

$$\Delta V(z) = \delta v_s[(z+1)^{-\sigma} + (L+1-z)^{-\sigma}], \tag{3.7}$$

$1\leqslant z\leqslant L-1$, where contributions of the order of $z^{-\sigma-1}$, $z^{-\sigma-2}$, etc. have been neglected,

$$\delta v_s = -4\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\sigma\Gamma\left(\frac{d+\sigma}{2}\right)}(\rho_s J^{l,s} - \rho_c J^l) \tag{3.8}$$

is a (T and μ independent) constant,

$$J(\mathbf{r}) \equiv J_{\mathrm{sr}}^l\{\delta(|\mathbf{r}|) + \delta(|\mathbf{r}|-1)\} + J^l/(1+|\mathbf{r}|^{d+\sigma})\theta(|\mathbf{r}|-1) \tag{3.9}$$

is a proper lattice version of $-w(\mathbf{r})/4$ as the interaction energy between the fluid particles, and

$$J^{l,s}(\mathbf{r}) \equiv J_{\mathrm{sr}}^{l,s}\delta(|\mathbf{r}|-1) + J^{l,s}/|\mathbf{r}|^{d+\sigma}\theta(|\mathbf{r}|-1) \tag{3.10}$$

is the one between a fluid particle and a substrate particle [here $\delta(x)$ is the discrete δ function [49] and $\theta(x)$ is the Heaviside step function with the convention $\theta(0)=0$]; ρ_s is the number density of the substrate particles in units of a^{-d}. Note that Eq. (3.9) incorporates the lattice version of the regularization of $J(\mathbf{r})$ at $\mathbf{r}=\mathbf{0}$ as implied by the original off-lattice density functional approach. Here we take into account on equal footing the two contributions to the effective interface potential [44] stemming from the missing fluid particles and from the substrate particles. From Eq. (3.6)–(3.10) one can identify the dimensionless coupling constant

$$s = -\frac{1}{2}\beta\delta v_s \tag{3.11}$$

[see Eq. (2.2); $s>0$ corresponds to walls preferring the liquid phase of the fluid]. The case $s=0$, which will be considered later, corresponds to $\rho_s J^{l,s}=\rho_c J^l$. Note that the effective potential δv_s is formed by the difference of the relative strength of the substrate-fluid interaction for a substrate with density ρ_s and that one of the fluid-fluid interaction for a fluid with a density ρ_c. In Eq. (3.7) the restriction $z\geqslant 1$ holds because we consider the layers closest to the substrate to be completely occupied by the liquid phase of the fluid (which implies that we consider the strong adsorption limit), i.e., $\rho(0)=\rho(L)=1$, which is achieved by taking the limit $J_{\mathrm{sr}}^{l,s}\to\infty$; therefore the actual values of $\Delta V(0)=\Delta V(L)$ will play no role. In order to preserve the monotonic behavior of $w(\mathbf{r})$ as a function of the distance r between the particles, in Eq. (3.9) we have to require that $J_{\mathrm{sr}}^l \geqslant J^l/(1+2^{(d+\sigma)/2})$.

In terms of ϕ the functional (3.2) turns into

$$\Omega[\phi(\mathbf{r})] = k_B T \sum_{\mathbf{r}\in\mathcal{L}} \left\{ \frac{1+\phi(\mathbf{r})}{2}\ln\left[\frac{1+\phi(\mathbf{r})}{2}\right] + \frac{1-\phi(\mathbf{r})}{2}\ln\left[\frac{1-\phi(\mathbf{r})}{2}\right] \right\} - \frac{1}{2}\sum_{\mathbf{r}\in\mathcal{L}} [\Delta\mu - \Delta V(z)]\phi(\mathbf{r}) - \frac{1}{2}\sum_{\mathbf{r},\mathbf{r}'\in\mathcal{L}} J(\mathbf{r},\mathbf{r}')\phi(\mathbf{r})\phi(\mathbf{r}') + \Omega_{\mathrm{reg}}, \tag{3.12}$$

where

$$\Omega_{\mathrm{reg}} = -\frac{1}{2}\sum_{\mathbf{r}\in\mathcal{L}}\left[\Delta\mu - \Delta V(z) - \sum_{\mathbf{r}'\in\mathcal{L}} J(\mathbf{r},\mathbf{r}')\right] \tag{3.13}$$

does not depend on ϕ and therefore is a regular background term which carries a L dependence and thus shows up in the force. An expression similar to the one in Eq. (3.5), which avoids the double sum and thus is more convenient for nu-

merical procedures, can also be obtained. With the identifications $\phi(\mathbf{r}) \leftrightarrow m(\mathbf{r})$ and $\frac{1}{2}[\Delta\mu - \Delta V(z)] \leftrightarrow h(z)$ one can rewrite the above expression for $\Omega[\phi(\mathbf{r})]$ as a functional $\Delta\Omega[m(\mathbf{r})] \equiv (\Omega - \Omega_{\mathrm{reg}})$, which describes a magnetic system at temperature T and in the presence of an external local and spatially varying magnetic field $h(z)$. In the remainder we shall use this mutual correspondence between the fluid and magnetic systems in order to make contact with existing theoretical results for any of them. We shall call the force calculated from using $\Omega[\phi(\mathbf{r})]$ the *total* Casimir force, while that part of the force calculated with the regular background term subtracted will be termed the *critical* Casimir force. This procedure corresponds to the analysis of experimental results if one subtracts from the value of the force measured around T_c the asymptote obtained by measuring this force well *above* T_c.

In accordance with Eq. (2.2), for the finite-size behavior of the excess grand canonical potential per unit area A of a liquid film in the case when both confining surfaces prefer strongly the liquid phase, one expects

$$\begin{aligned}\omega_{ex}(t,\mu,L|d,\sigma) &\simeq \sigma_{s,1}^{\mathrm{ns}} + \sigma_{s,2}^{\mathrm{ns}} + k_B T L^{-(d-1)} \\ &\times X_\Omega[L/\xi_t, (\beta\Delta\mu)(L/\xi_{0,\mu})^{\Delta/\nu}, (L/\xi_0)^{-\omega_l} l, (L/\xi_0)^{-\omega_s} s] \\ &+ [A_l(T,\mu) + A_{l,s}(T,\mu) + A_s(T)] L^{-(\sigma-1)}, \end{aligned} \tag{3.14}$$

where $\sigma_{s,1}^{\mathrm{ns}}$ and $\sigma_{s,2}^{\mathrm{ns}}$ are the nonsingular parts of the surface tensions at the surfaces 1 and 2, respectively (the singular parts are incorporated in X_Ω). Here

$$A_l(T,\mu) = -\frac{4\pi^{(d-1)/2}}{\sigma(\sigma-1)} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\Gamma\left(\frac{d+\sigma}{2}\right)} J^l \rho_b^2(T,\mu), \tag{3.15}$$

with ρ_b being the bulk fluid density at the given T and μ, represents that part of the Hamaker constant which is generated by the long-ranged part of the fluid-fluid interactions, i.e., the dispersion interaction [50,51], $A_s < 0$ is the part due to the direct long-ranged interactions between the two substrates, while $A_{l,s}(T) > 0$ is the corresponding term generated by the long-ranged tails of the substrate potentials acting on the fluid particles. According to Appendix A and with $J^{s,s}(\mathbf{r}-\mathbf{r}') = J^s/|\mathbf{r}-\mathbf{r}'|^{d+\sigma}$ for the interaction between substrate particles one has

$$A_s(T) = -\frac{4\pi^{(d-1)/2}}{\sigma(\sigma-1)} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\Gamma\left(\frac{d+\sigma}{2}\right)} J^s \rho_s^2(T), \tag{3.16}$$

and according to Appendix B 2

$$\begin{aligned} A_{l,s}(T,\mu) &= -2v_s \rho_b(T,\mu)/(\sigma-1) \\ &= \frac{8\pi^{(d-1)/2}}{\sigma(\sigma-1)} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\Gamma\left(\frac{d+\sigma}{2}\right)} J^{l,s} \rho_b(T,\mu) \rho_s(T) > 0, \end{aligned} \tag{3.17}$$

where (see Appendix A)

$$v_s = -4\pi^{(d-1)/2} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\sigma\Gamma\left(\frac{d+\sigma}{2}\right)} \rho_s J^{l,s}. \tag{3.18}$$

Note that $A_l < 0$ and $A_s < 0$, while $A_{l,s} > 0$, and that A_s is an analytic function of T. If both the fluid and the substrates are governed by van der Waals forces, the constants A_l, $A_{l,s}$, and A_s are not independent. As pointed out in Ref. [51] for such systems the parameters J^l, $J^{l,s}$, and J^s can be expressed in terms of the corresponding atomic polarizabilities α_l and α_s, i.e., $J^l \sim \alpha_l^2$, $J^s \sim \alpha_s^2$, and $J^{l,s} \sim \alpha_l \alpha_s$. (Note that this property implies that $J^l/\alpha_l^2 = J^s/\alpha_s^2 = J^{l,s}/\alpha_l\alpha_s$ is independent of the particular atomic or molecular species.) Therefore, one can write the sum of A_l, $A_{l,s}$, and A_s as a perfect square, i.e.,

$$\begin{aligned} A_l + A_{l,s} + A_s &= -\frac{4\pi^{(d-1)/2}}{\sigma(\sigma-1)} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\Gamma\left(\frac{d+\sigma}{2}\right)} \\ &\times [J^l \rho_b^2(T,\mu) - 2J^{l,s}\rho_b(T,\mu)\rho_s(T) + J^s \rho_s^2(T)] \\ &\sim -(\alpha_s \rho_s - \alpha_l \rho_b)^2 < 0, \end{aligned} \tag{3.19}$$

which leads to the conclusion, that for a Lennard-Jones fluid between two identical Lennard-Jones walls the effective dispersion interaction for the film is always attractive. Coating the substrate surfaces of the system with some additional material does not change this leading-order L dependence and therefore does not change the above property. This result is in full agreement with the Dzyaloshinskii-Lifshitz-Pitaevskii theory [52,53], which also predicts that the effective interaction between identical half-spaces separated by a thin film is always attractive [51,54].

The only quantity in Eq. (3.14), which still has to be identified for our model, is the value of the coupling constant l. According to Refs. [21,25,29]

$$l = v_\sigma / v_2, \tag{3.20}$$

where v_σ and v_2 are coefficients in the Fourier transform $\hat{J}(\mathbf{k}) = \Sigma_{\mathbf{r}} \exp(i\mathbf{k}\cdot\mathbf{r}) J(\mathbf{r})$ of the interaction $J(\mathbf{r})$ [see Eq. (3.9)]. One has [21,25,29,30,55] $\hat{J}(\mathbf{k}) = \hat{J}(\mathbf{0})[1 - v_2 k^2 + v_\sigma k^\sigma - v_4 k^4 + O(k^6)]$. It is easy to check that the short-ranged part $\hat{J}_{\mathrm{sr}}(\mathbf{k})$ of the Fourier transform of the interaction has the form $\hat{J}_{\mathrm{sr}}(\mathbf{k}) = J_{\mathrm{sr}}^l [1 + 2d - k^2 + O(k^4)] \equiv \hat{J}_{\mathrm{sr}}(\mathbf{0})[1 - v_2^{\mathrm{sr}} k^2 + O(k^4)]$, with $\hat{J}_{\mathrm{sr}}(\mathbf{0}) = (1+2d) J_{\mathrm{sr}}^l$ and $v_2^{\mathrm{sr}} = 1/(1+2d)$, while for the Fourier transform of the long-ranged part $\hat{J}_{\mathrm{lr}}(\mathbf{k}) = \hat{J}_{\mathrm{lr}}(\mathbf{0})[1 - v_2^{\mathrm{lr}} k^2$

$+v_\sigma^{\rm lr}k^\sigma - v_4^{\rm lr}k^4 + O(k^6)]$ an analytical expression in closed form can be obtained only for the product $\hat{J}_{\rm lr}(\mathbf{0})v_\sigma^{\rm lr}$:

$$\hat{J}(\mathbf{0})v_\sigma = \hat{J}_{\rm lr}(\mathbf{0})v_\sigma^{\rm lr} = J^l n(d,\sigma), \tag{3.21}$$

with

$$n(d,\sigma) = -\frac{\pi^{d/2+1}}{2^\sigma \sin(\pi\sigma/2)\Gamma[(d+\sigma)/2]\Gamma(1+\sigma/2)} > 0, \tag{3.22}$$

for $2<\sigma<4$. This leads to

$$l = \frac{\lambda n(d,\sigma)}{1+\lambda[\hat{J}_{\rm lr}^l(\mathbf{0})v_2^{\rm lr}]}, \tag{3.23}$$

with

$$\lambda = \frac{J^l}{J_{sr}^l}, \tag{3.24}$$

while $\hat{J}_{\rm lr}^l(\mathbf{0}) = \hat{J}_{\rm lr}(\mathbf{0})/J^l$ is the ground state energy $\hat{J}_{\rm lr}(\mathbf{0}) = J^l \Sigma_{\mathbf{r}}' 1/(1+|\mathbf{r}|^{d+\sigma})$, where $\mathbf{r}$ with $|\mathbf{r}|=0,1$ are omitted from the sum [see Eq. (3.9)], of a system with purely long-ranged interactions measured in units of J^l. Since both $\hat{J}_{\rm lr}(\mathbf{0})$ and $v_2^{\rm lr}$ depend also on the properties of the interaction at short distances it is clear that for the precise determination of the values of l the use of numerical methods is unavoidable. It can be shown that

$$\hat{J}_{\rm lr}^l(\mathbf{0})v_2^{\rm lr} = \frac{1}{2d}\sum_{\mathbf{r}} \frac{|\mathbf{r}|^2}{1+|\mathbf{r}|^{d+\sigma}}\theta(|\mathbf{r}|-1). \tag{3.25}$$

For the "genuine" van der Waals interaction $d=\sigma=3$ one has $n(3,3)=\pi^2/12\simeq 0.822$ and if the system is discretized in terms of a simple cubic lattice one has $\hat{J}_{\rm lr}^l(\mathbf{0})v_2^{\rm lr}\simeq 1.692$. In this case for $\lambda=0,1/2,1$, and 2 one has $l=0$, 0.222, 0.306, and 0.375, respectively. Note that for the Lennard-Jones (6,12) potential

$$w_{\rm LJ} = 4\varepsilon\left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^{6}\right], \tag{3.26}$$

the position of its minimum, which within our approach can reasonably be taken as the lattice spacing a, is at $a=\sqrt[6]{2}\,\sigma_0$. The value $-\varepsilon$ of its minimum corresponds to J_{sr}^l. Thus the leading, attractive part $-4\varepsilon(\sigma_0/r)^6$ of the long-ranged interaction equals $-2\varepsilon(a/r)^6$, which leads to the conclusion that for pure Lennard-Jones potentials $\lambda=2$.

We recall that for $L\gg L_{\rm crit}$, $\omega_s>0$, and $\omega_l>0$, in line with Eq. (3.14), the behavior of the Casimir force can be decomposed according to Eq. (2.2). The aim of the current study is to determine the leading finite-size behavior of the Casimir force in any region of the thermodynamic parameter space of the model. As stated in Sec. I, for any y, $X^{\rm sr}(x,y)$ decays exponentially for $|x|\to\infty$, while in that regime the other scaling functions $X_l^{\rm lr}$ and $X_s^{\rm lr}$ decay according to a power law. Based on the results of Refs. [21,29–31] one expects that the deviation from the leading short-ranged behavior sets for $L\gtrsim \xi\ln(\xi/\xi_0)$. For the scaling function $X_l^{\rm lr}$ one expects $X_l^{\rm lr}(x\to\infty,0)=X_1 x^{\eta-2}$, where X_1 is a universal constant.

Some information is also known about the asymptotic behavior of $X_s^{\rm lr}(x\to\infty,0)$ [56]. In Ref. [56] the authors have considered the behavior of the solvation force in a fluid with short-ranged forces (i.e., $J^l=0$) under the influence of long-ranged substrate potentials decaying at large distances z as $\delta v_s z^{-\sigma}$. In the case $A_l=A_s=A_{l,s}=0$ (i.e., for $T>T_c$ in a magnetic system in the absence of an external bulk magnetic field) they found numerically together with analytical mean-field arguments that the leading size dependence of the force f is of the order of $L^{-(\sigma+1)}$. If valid this would lead to $X_s^{\rm lr}(x\to\infty,0)=X_s x^{d/2-2+\eta/2}$. For a mean-field model with $d=4$ and $\eta=0$ this would imply $X_s^{\rm lr}(x\to\infty,0)=X_s$, i.e., this scaling function would tend to a constant away from the critical point (or vary $\sim\ln x$). Moreover, consistency with the structure of Eq. (2.2) imposes the temperature dependence $\sim t^{\beta-\nu}$ of the term $\propto L^{-(\sigma+1)}$. This differs from the result in Ref. [56], where the authors analyzed the system away from the scaling regime and purportedly reported that the corresponding term varies as $t^{-1}L^{-(\sigma+1)}$.

Finally, we finish this section by recalling that if $L\leqslant L_{\rm crit}$ (or if $\omega_s<0$ or $\omega_l<0$) an expansion of the type given in Eq. (2.2) is not possible. In that case the effects of the van der Waals interactions will be important everywhere in the critical region of the system, even at the bulk critical point.

IV. FINITE-SIZE BEHAVIOR OF FILM FREE ENERGIES AND OF THE CASIMIR FORCE

In this section we investigate the finite-size behavior of the total Casimir force within the full temperature range. Experimentally this force is accessible as the so-called solvation force. In Sec. IV A we focus on the critical behavior; the finite-size behavior off criticality is discussed in Sec. IV B. Before passing to a detailed analysis of the influence of the different parameters on the behavior of the force, we first provide a view on the *typical* behavior of the total force ($s=\lambda=1$) as a function of L/ξ_t at $\Delta\mu=0$ (i.e., at bulk coexistence) [see Fig. 3(a)], and as a function of L/ξ_μ at the critical temperature $T=T_c$ [see Fig. 3(b)]. The results are obtained within the model presented in the previous section choosing a film thickness $L=50$ layers. (Compare Fig. 2 for $L=500$; however, here the forces are not normalized by their value at T_c.) One observes that the force [neglecting the contributions from the direct substrate-substrate interaction so that the conclusion stated after Eq. (3.19) does not hold for $f_{\rm total}$ considered here] is always *repulsive* outside the critical region while within the critical region it becomes *attractive* due to the critical fluctuations of the density. One observes in both cases for $L/\xi>30$ (where ξ is either ξ_t or ξ_μ) that the contribution $\beta(\sigma-1)(A_l+A_{l,s})$ (indicated as "asymptote") provides a good approximation of the total force. Using Eqs. (3.15) and (3.17), and $\rho_c=1/2$, it can be shown that

$$\beta(\sigma-1)(A_l+A_{l,s}) = 4s\rho_b + \frac{4\pi^{d-1/2}}{\sigma}\frac{\Gamma\left[\frac{1+\sigma}{2}\right]}{\Gamma\left[\frac{d+\sigma}{2}\right]}\lambda K\rho_b(1-\rho_b), \tag{4.1}$$

where $K=\beta J_{\rm sr}^l$. Note that, if $s>0$ and $\lambda>0$, $\beta(\sigma-1)(A_l$

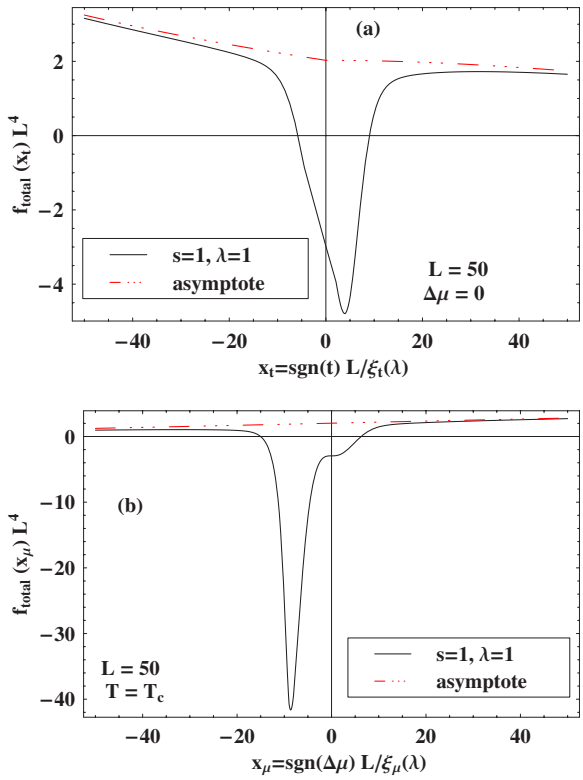

FIG. 3. (Color online) (a) The typical behavior of the total Casimir force (per area of the film cross section, in units of k_BT, and without the direct substrate-substrate interaction) at $\Delta\mu=0$ as a function of the temperature scaling variable in a system with substrate-fluid and fluid-fluid long-ranged interactions. One observes that outside the critical region the force is repulsive and becomes attractive only near the critical point of the system due to the critical fluctuation of the fluid density. (If the direct substrate-substrate interaction is added to f_{total}, the resulting force is attractive in the whole thermodynamic space.) The data correspond to $L=50$ and $s=\lambda=1$ [where $s=1$ for $T=T_c$, see Eq. (3.11)]. The asymptote [see Eqs. (3.15) and (3.17)] is given by $\beta(\sigma-1)(A_{l,s}+A_l)=4sK\rho_b+\lambda K\{4\pi^{d-1}\Gamma[(1+\sigma)/2]\}/\{\sigma\Gamma[(d+\sigma)/2]\}\rho_b(1-\rho_b)$, where in the present mean-field case $d=\sigma=4$, $K=\beta J^l_{\text{sr}}$, and for K_c see Eq. (4.6). Note that above the critical point $\rho_b=\rho_c=1/2$, while for $T<T_c$, ρ_b increases upon a decrease of the temperature. This leads to a clearly visible asymmetry in the asymptotic behavior of the force. (b) The same as in (a) but as function of the field scaling variable and at T_c. One again observes that everywhere outside the critical region the total force (without the direct substrate-substrate interaction) is repulsive and becomes attractive only near the critical point of the system due to the critical fluctuation of the fluid density.

$+A_{l,s})>0$, i.e., the force away from the critical region is *repulsive*.

In the following we analyze in detail the behavior of the force within the critical region and study its dependence on s, λ, and L.

A. Critical behavior

Within the present mean-field approach, one has $\beta=\nu=1/2$, $\eta=0$, and $\gamma=1$. Apart from logarithmic corrections, these mean-field values hold for $d=d_c=4$, provided the interactions governing the system are not too long ranged. Since for genuine van der Waals interactions $d=\sigma$, in the following we adopt $d=\sigma=4$, which leads to

$$f(t,\mu,L) \simeq L^{-4}\{X[L/\xi_t,(\beta\Delta\mu)(L/\xi_{0,\mu})^3,\ l(L/\xi_0)^{-2},s(L/\xi_0)^{-1}] + 3\beta[A_l(T,\mu)+A_{l,s}(T,\mu)+A_s(T)]\}. \tag{4.2}$$

Note that for $d=\sigma=4$, $\eta=0$ the requirements $\sigma>2-\eta$ and $\sigma>(d+2-\eta)/2$ for the irrelevance of the long-ranged van der Waals type contribution to the behavior of the force are fulfilled [57]. For the model considered here a direct estimate of L_{crit} yields $L_{\text{crit}}=32s$ (taking into account that here all distances are measured in units of the lattice spacing). Since $s=1$ is the largest value of s for which we shall provide numerical results, we conclude that for systems with $L\gg 32$ layers the van der Waals interaction is expected to give only corrections to scaling while for smaller L its effects will be important everywhere including the critical region of the system and will affect even the determination of the Casimir amplitude. Of course, the above estimate does not tell the exact meaning of "much larger than" 32, but we expect that a factor of 10 should put one onto the safe side. Thus the expectations is that for $L\gtrsim 300$ the van der Waals interaction will provide only corrections to scaling within the critical region. Our subsequent analysis will demonstrate that this expectation is indeed valid. We shall consider films with thicknesses $L=50$, 100, 500, and $L=1000$ layers. It will turn out that for $L=500$ and $L=1000$ the van der Waals effects are small, whereas for $L=50$ and $L=100$ it will turn out that they affect the behavior of the force for all values of the thermodynamic parameters.

In order to determine the scaling function X of the Casimir force one has to solve numerically Eq. (3.6) for $\phi^*(\mathbf{r})$ and to insert this solution into Eq. (3.5), where $\rho^*=(1+\phi^*)/2$. Due to the symmetry of the system one has $\phi^*(\mathbf{r})=\phi^*(z)$. We determine the force from the lattice version of Eq. (1.1) [see Eqs. (3.2) and (3.14)],

$$f(L,t|l,s)=-\frac{\beta}{2}[\omega_{ex}(L+1,t|l,s)-\omega_{ex}(L-1,t|l,s)]. \tag{4.3}$$

(There are alternative approximations of $\partial\omega_{ex}/\partial L$ which, however, yield the same leading behavior in L we are interested in.)

According to Appendix C, for $d=\sigma=4$ the equation for the order parameter reads [see Eq. (C15)]

$$\operatorname{arctanh}[\phi^*(z)]=\frac{1}{2}\beta[\Delta\mu-\Delta V(z)] + K\Big\{a_4\phi^*(z)+a_4^{nn}[\phi^*(z+1)+\phi^*(z-1)] + \lambda\sum_{\substack{z'=0\\ |z'-z|\geq 2}}^{L} g_4(|z-z'|)\phi^*(z')\Big\}, \tag{4.4}$$

where $K=\beta J_{sr}^{l}$, $\lambda=J^{l}/J_{sr}^{l}$ [Eq. (3.24)], and [see Eq. (C14)]

$$g_4(a)=\pi^{3/2}\int_0^\infty dt t^{3/2}E_{4,4}(-t^4)\exp[-ta^2]$$
$$=\frac{\pi^2}{2^{3/4}}\left\{[1+(\sqrt{2}a^2+1)^2]^{1/4}\left[\sin\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2+1]\right)\right.\right.$$
$$\left.-\cos\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2+1]\right)\right]$$
$$+[1+(\sqrt{2}a^2-1)^2]^{1/4}\left[\sin\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2-1]\right)\right.$$
$$\left.\left.+\cos\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2-1]\right)\right]\right\}. \quad (4.5)$$

In Eq. (4.4) $a_4=7+\lambda(c_4-4)$, $a_4^{nn}=1+\lambda(c_4^{nn}-1/2)$, where $c_4=4.900$ and $c_4^{nn}=1.028$ are constants evaluated in Eqs. (C17) and (C18), respectively. It is straightforward to show that the critical coupling of the *bulk* system is

$$K_c^{-1}(\lambda)=a_4(\lambda)+2a_4^{nn}(\lambda)+2\lambda\sum_{z\geq 2}g_4(z), \quad (4.6)$$

so that the bulk critical point coordinates are $[K=K_c(\lambda),\Delta\mu=0]$. Note that the position of the critical point depends on λ.

For $(+,+)$ boundary conditions one has $\rho(0)=\rho(L)\equiv 1$, or equivalently $\phi(0)=\phi(L)\equiv 1$. We have imposed the boundary conditions in such a way that the number of liquid layers with independent degrees of freedom is $L-1$. (We recall our remark in the Introduction that the Casimir force hinges on the definition of what is called the film thickness.) The function $g_4(a)$ accounts for the fluid-fluid long-ranged interaction. We note that in many analyses $g_4(a)$ is typically neglected; even in numerical treatments of van der Waals systems the range of the interaction between the fluid particles is often actually truncated rendering effectively a short-ranged potential. One can cast Eq. (4.4) also into a continuum form which is a close analog of the one usually derived from a Ginzburg-Landau-type Hamiltonian. The corresponding generalized Euler-Lagrange equation for the profile then reads [see Eq. (C20)]

$$\phi^*(z)+\frac{1}{3}(\phi^*(z))^3=\frac{1}{2}\beta[\Delta\mu-\Delta V(z)]$$
$$+K\left\{a_4\phi^*(z)+a_4^{nn}\left[2\phi^*(z)+\frac{d^2\phi^*(z)}{dz^2}\right]\right.$$
$$\left.+\int_0^L g_4(|z-z'|)\phi^*(z')dz'\right\}. \quad (4.7)$$

We start our evaluation of the Casimir force by first reproducing the analytically exactly available mean-field results for the force for $(+,+)$ boundary conditions. That serves also as a valuable check for the model we have described above.

For the following, Eq. (4.4) defines the model the finite-size behavior of which will be investigated in detail. In this model the long-ranged substrate fluid interaction is present via the substrate potentials ΔV, while the long-ranged fluid-fluid interaction is reflected by $\lambda\neq 0$. Accordingly, the fully short-ranged model corresponds then to $\Delta V=0$ and $\lambda=0$.

Before starting with the study of the influence of the different parts of the interaction on the behavior of the force we briefly comment on the universality of the scaling function X in Eq. (4.2) within mean-field theory.

1. Modified finite-size scaling for mean-field systems

Here we assume that L is large enough so that one is allowed to consider only the scaling fields which are relevant in renormalization-group sense. In this case, within non-mean-field theories hyperscaling and hyperuniversality are valid so that the finite-size behavior of the singular part of the grand canonical potential density $\beta\omega_s\equiv\beta\Omega_s/V$ near the bulk critical point of the system $(T=T_c,\ \mu=\mu_c)$ is given by [58]

$$\beta\omega_s(T,\mu,L)=L^{-d}X_{\bar{\omega}}\left(\frac{L}{\xi_t(\lambda)},\frac{L}{\xi_\mu(\lambda)}\right), \quad (4.8)$$

where $\xi_t\equiv\xi_\infty(T\to T_c^{\pm},\mu=\mu_c)=\xi_0^{\pm}(\lambda)|t|^{-\nu}$ and $\xi_\mu\equiv\xi_\infty(T=T_c,\mu\to\mu_c)=\xi_{0,\mu}(\lambda)|\beta_c\Delta\mu|^{-\nu/\Delta}$ are the second moment bulk correlation lengths. Here, as before, all lengths are measured in units of the lattice spacing a, $t=(T-T_c)/T_c$, $\Delta\mu=\mu-\mu_c$, and the parameter λ reflects the dependence of the bulk system on the long-ranged component of the fluid-fluid interaction. Note that there is no nonuniversal normalization factor in front of the universal scaling function $X_{\bar{\omega}}(x_t,x_\mu)$. Indeed, due to hyperuniversality $\lim_{T\to T_c^+}\beta\omega_s(T,\mu_c,\infty)\xi_t^d=Q$, where Q is a universal constant; this is consistent with the limit $L/\xi_t\to\infty$ of Eq. (4.8) with $\lim_{x\to\infty}X_{\bar{\omega}}(x,0)=Qx^d$.

Within mean-field theory hyperuniversality is lacking and generates a nonuniversal metric factor $A(\lambda)$, i.e.,

$$\beta\omega_s(T,\mu,L)=L^{-4}A(\lambda)X_{\bar{\omega}}^{\mathrm{MF}}\left(\frac{L}{\xi_t(\lambda)},\frac{L}{\xi_\mu(\lambda)}\right). \quad (4.9)$$

It is easy to check that within our model the bulk grand canonical potential density $\beta\omega_{s,\mathrm{bulk}}(T,\mu)$ of the system is a universal function of β/β_c and $\beta\Delta\mu$ in the sense that $\beta\omega_{s,\mathrm{bulk}}(T,\mu)$ is not proportional to any λ dependent term. Requiring this property to be compatible with Eq. (4.9) in the limit $L/\xi_t\to\infty$, it follows that $A(\lambda)$ has to be of the form $A(\lambda)=Q_{\mathrm{MF}}[\xi_0^+(\lambda)]^4$, where Q_{MF} is universal (i.e., independent of λ). Furthermore, one has $X_{\bar{\omega}}^{\mathrm{MF}}(x\to\infty,y)=x^4\tilde{X}_{\bar{\omega}}^{\mathrm{MF}}(x/y)$. Moreover, since $\beta\omega_{s,\mathrm{bulk}}(T,\mu)$ does not depend explicitly on λ it follows that the ratio ξ_t/ξ_μ does not depend on λ, which for our model can indeed be verified (see the following subsection). Thus Eq. (4.9) turns into the form

$$\beta\omega_s(T,\mu,L)=\left(\frac{L}{\xi_0^+(\lambda)}\right)^{-4}X_{\bar{\omega}}^{\mathrm{MF}}\left(\frac{L}{\xi_t(\lambda)},\frac{L}{\xi_\mu(\lambda)}\right), \quad (4.10)$$

where Q_{MF} has been incorporated into the scaling function $X_{\bar{\omega}}^{\mathrm{MF}}$. $X_{\bar{\omega}}^{\mathrm{MF}}$ is "universal," in the sense that it does not depend

on λ (neglecting the contributions due to the irrelevant scaling fields). Naturally, the ratio $\beta\omega_s(T,\mu)/\beta_c\omega_s(T_c,\mu_c)$ defines a scaling function that also does not depend explicitly on λ [see Eq. (4.9)], but this ratio does not offer the possibility to discuss the dependence of $\beta\omega_s(T,\mu)$ on other parameters of the model near the critical point because by construction at the critical point this ratio equals 1.

2. The Casimir force in systems with short-ranged interactions

For (+, +) boundary conditions and within mean-field theory the analytical form of the scaling function of the Casimir force in systems with short-ranged forces has been obtained in Ref. [17]. The corresponding result for $\Delta\mu=0$ is

$$\text{(i) } X^{\text{sr}}(y \geqslant 0) = -[2K(k)]^4 k^2(1-k^2), \tag{4.11a}$$

with $y=[2K(k)]^2(2k^2-1)$,

$$\text{(ii) } X^{\text{sr}}(0 \geqslant y \geqslant -\pi^2) = -4K^4(k), \tag{4.11b}$$

with $y=[2K(k)]^2(2k^2-1)$,

$$\text{(iii) } X^{\text{sr}}(y \leqslant -\pi^2) = -4K^4(k)(1-k^2)^2, \tag{4.11c}$$

with $y=-[2K(k)]^2(k^2+1)$, where $K(k)$ is the complete elliptic integral of the first kind, $0 \leqslant k < 1$. In Eq. (4.11) the scaling variable of $X^{\text{sr}}(y)$ is $y=tL^{1/\nu}=tL^2$ (here L is measured in units of a, i.e., in the scaling variable y L is dimensionless) and enters implicitly via $y=y(k)$ which can be inverted uniquely to $k=k(y)$ because y is a monotonic function of k. We note that $X^{\text{sr}}(y)$ is *analytic* for *all* values of y, because the film critical point $[T_c(L),\Delta\mu_c(L)]$ is located off coexistence at $\Delta\mu_c(L) \sim L^{-\Delta/\nu} \sim L^{-3}$ (see Fig. 1) [45,46]. Obviously one has $y \geqslant 0$ if $k \geqslant 1/\sqrt{2}$ (with $k=1/\sqrt{2}$ corresponding to the bulk critical point), $0 \geqslant y \geqslant -\pi^2$ if $1/\sqrt{2} \geqslant k \geqslant 0$ (with $k=0$ corresponding to the actual film critical point), and $y \leqslant -\pi^2$ if $-1 < k < 0$ (negative k describe the region below the bulk critical point).

In order to check universal aspects of our model and the reliability of our numerical procedures, for $\Delta\mu=0$ and T close to T_c in Fig. 4(a) we compare the results for $X^{sr}[x_t=\text{sgn}(t)L/\xi_t, x_\mu=\text{sgn}(\Delta\mu)L/\xi_\mu=0]$ obtained within the lattice model [Eq. (3.12) with $\Delta\mu=\Delta V=\Omega_{\text{reg}}=J'=0$] with the above analytical results of the continuum theory [17]. In addition, for $T=T_c$ and $\Delta\mu \neq 0$ in Fig. 4(b) we present the scaling function of the force $X^{sr}(x_t=0,x_\mu)$ as obtained within the lattice model in comparison with the numerical results of the continuum theory [22]. Here ξ_t is the bulk correlation length $\xi(t \to \pm 0, \Delta\mu=0)=\xi_0^{\pm}|t|^{-\nu}$, with $\nu=1/2$, while $\xi_\mu(t=0,\Delta\mu \to 0)=\xi_{0,\mu}|\Delta\mu|^{-\nu/\Delta}$ with $\nu/\Delta=1/3$. For the continuum model $\xi_0^+=a$, $\xi_0^-=a/\sqrt{2}$, and $\xi_{0,\mu}=a/\sqrt[3]{3}$ [22,59] (where a has been introduced as a length scale in order to achieve compatibility with the lattice model).

The Fourier transform $\tilde{g}(\mathbf{k})$ of the density-density correlation function

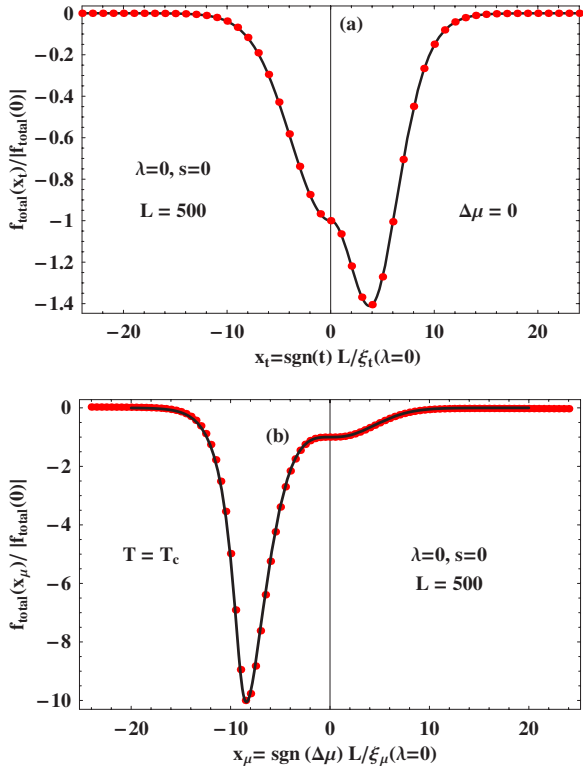

FIG. 4. (Color online) (a) Comparison for $\Delta\mu=0$ between the behavior of the total Casimir force in our mean-field lattice model with short-ranged interaction (dots) and the singular part of the force obtained within continuum mean-field Ginzburg-Landau theory [17] (full line). Both curves are normalized by their absolute values at the bulk critical point. This normalization is necessary because the Ginzburg-Landau theory predicts the force only up to a nonuniversal multiplicative factor. The lattice data have been calculated for $L=500$. Both curves overlap perfectly, which demonstrates that the corrections due to the corrections to scaling, regular contributions, and the existing arbitrariness in the definition of L can be safely ignored if L is of the order of 500 and the interaction is short ranged. Note that the minimum occurs above the critical point at $x_t=\text{sgn}(t)L/\xi_t \simeq 3.75$. (b) The same as in (a) for $T=T_c$ as a function of the field scaling variable $x_\mu=L/\xi_\mu$; the results for the singular part of the force within a continuum mean-field Ginzburg-Landau-type theory are from Ref. [22]. The minimum of the force occurs at $x_\mu \simeq -8.4$, i.e., on the vapor side of the bulk coexistence curve (with the walls preferring the liquid phase). The force minimum is about a factor 10 deeper than the force at T_c and ca. seven times deeper than the minimum along the temperature scan.

$$g(\mathbf{r}_1-\mathbf{r}_2) \equiv \langle\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)\rangle - \langle\rho(\mathbf{r}_1)\rangle\langle\rho(\mathbf{r}_2)\rangle = \frac{1}{4}[\langle\phi(\mathbf{r}_1)\phi(\mathbf{r}_2)\rangle - \langle\phi(\mathbf{r}_1)\rangle\langle\phi(\mathbf{r}_2)\rangle] \tag{4.12}$$

has the form

$$\tilde{g}(\mathbf{k}) = \frac{1}{[\rho(1-\rho)]^{-1} + \beta\tilde{w}(\mathbf{k})}. \tag{4.13}$$

From Eq. (4.12), using $-4\tilde{J}(\mathbf{k})=\tilde{w}(\mathbf{k})$ and the small k expansion of $\tilde{J}(\mathbf{k})$, one obtains for the second moment correlation

length ξ [compare with Eq. (6.9) in Ref. [59]]

$$\xi = \frac{\sqrt{v_2}}{\sqrt{\frac{\beta_c/\beta}{4\rho(1-\rho)} - 1}} = \frac{\sqrt{v_2}}{\sqrt{\frac{T/T_c}{1-\phi^2} - 1}}. \quad (4.14)$$

Solving the bulk equation $\phi = \tanh[\phi(\beta/\beta_c) + \beta\Delta\mu/2]$ for the order parameter one obtains from Eq. (4.14) that in the lattice system under consideration

$$\xi_0^+ = \sqrt{v_2}, \quad \xi_0^- = \xi_0^+/\sqrt{2}, \quad \xi_{0,\mu} = \sqrt{v_2}/\sqrt[3]{3}. \quad (4.15)$$

For a system with a fluid-fluid interaction given by Eq. (3.9) with $J^l=0$ (i.e., short-ranged interaction) and discretized on a cubic lattice one has $v_2 = 1/(1+2d)$, so that for $d=4$ one has $\sqrt{v_2} \simeq 1/3$. Figures 4(a) and 4(b) demonstrate that the normalized scaling functions as obtained within the continuum model and within the lattice model practically coincide once the amplitudes ξ_0 and $\xi_{0,\mu}$ for the two models are chosen as described above. Thus on the mean-field level the present lattice model is indeed suitable for investigating the Casimir force. We emphasize that at $T=T_c$ the minimum of the force does not occur at bulk coexistence $\mu=\mu_c$ but at a nonzero value $\Delta\mu$, determined for each L via $x_\mu \equiv \mathrm{sgn}(\Delta\mu) L/\xi_\mu \simeq -8.4$, i.e., on the gas side of the bulk coexistence curve (with the walls preferring the liquid phase). Similarly, if $\Delta\mu=0$ the minimum of the force is not at but above T_c, given by $x_t = \mathrm{sgn}(t) L/\xi_t \simeq 3.75$. We note that Fig. 4 actually provides a comparison between the behavior of the *total* Casimir force in a *lattice* model with short-ranged interaction with the *singular* part of the force obtained within *continuum* mean-field Ginzburg-Landau theory. If L is small enough the corrections to the universal behavior, which are due to the corrections to scaling, to regular contributions, and to the existing arbitrariness in the definition of L (see below as well as Appendix B in Ref. [40]), will become visible. For $L=50$ this is shown in Fig. 5. The role of L is visualized in Fig. 6. Since the Casimir force is a derivative of the excess free energy with respect to L it depends on the definition of L for a given system. In the current analysis this distance is taken to be the lattice spacing times the number of layers with independent degrees of freedom (which is $L-1$) plus two times half the distances between the outermost layers with frozen degrees of freedom and their adjacent inner layers, i.e., La.

3. The Casimir force in systems with van der Waals type interactions

In this subsection we analyze the effect of the range of the fluid-fluid and the substrate-fluid interactions on the behavior of the Casimir force, i.e., we consider systems in which either λ or s, or both, are nonzero. Note that $\lambda \neq 0$ implies $l \neq 0$ [see Eq. (3.23)]. To this end we first determine the bulk correlation length amplitudes ξ_0 and $\xi_{0,\mu}$ which depend on λ. Due to Eq. (4.15) this requires to calculate the Fourier coefficient v_2, for which we obtain

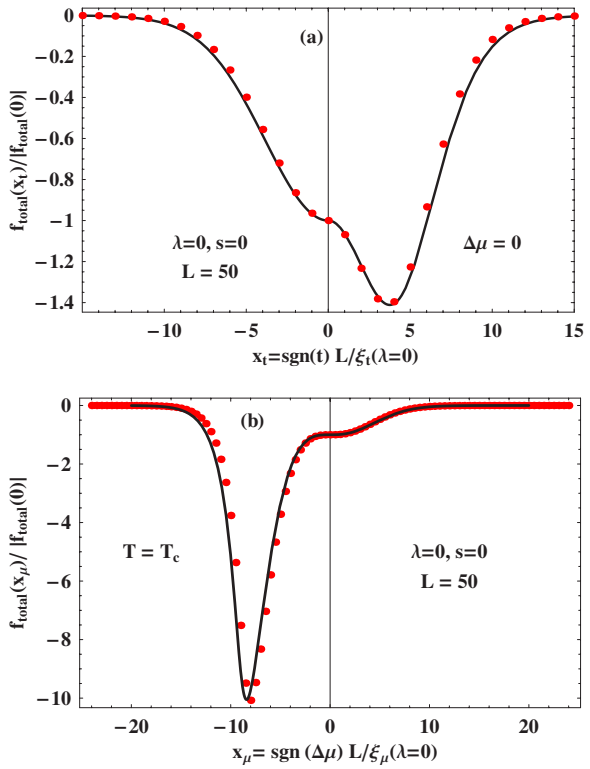

FIG. 5. (Color online) Comparison between the behavior of the total Casimir force normalized by its absolute value at the bulk critical point for a lattice model with short-ranged interactions for $L=50$ (dots) with the corresponding continuum Ginzburg-Landau result (full line). (a) For $\Delta\mu=0$ there are small differences between the two curves for $|\mathrm{sgn}(t) L/\xi_t| \gtrsim 5$ where corrections to scaling and the regular contributions start to show up. For $|\mathrm{sgn}(t) L/\xi_t| \gg 1$ both curves decay exponentially and therefore they cannot be distinguished for $|\mathrm{sgn}(t) L/\xi_t| \gtrsim 10$. (b) Same as (a) for $T=T_c$ and as function of $\Delta\mu$ in terms of the field scaling variable $x_\mu = L/\xi_\mu$. The deviations are largest around the minimum.

$$v_2 = \frac{1 + \frac{\lambda}{2d} \sum_{\mathbf{r}} \frac{|\mathbf{r}|^2}{1+|\mathbf{r}|^{d+\sigma}} \theta(|\mathbf{r}|-1)}{1 + 2d + \lambda \sum_{\mathbf{r}} \frac{1}{1+|\mathbf{r}|^{d+\sigma}} \theta(|\mathbf{r}|-1)}. \quad (4.16)$$

For $d=\sigma=4$ and for a hypercubic lattice a numerical evaluation yields

$$v_2 = \frac{1 + 0.829\lambda}{9 + 2.152\lambda}. \quad (4.17)$$

For $\lambda=0$, 1/2, 1, and 2 one thus obtains $\xi_0^+ = \sqrt{v_2} = 1/3$, 0.375, 0.405, and 0.447, respectively.

The corresponding numerical results for the behavior of the critical Casimir force f_{crit} are summarized in Figs. 7–10. (f_{crit} is that part of the total force f_{total} calculated with the regular background term subtracted; this procedure corresponds to the analysis of experimental results if one subtracts from the value of the force measured around T_c the asymptote obtained by measuring this force well *above* T_c.) While Figs. 7 and 8 deal with the temperature dependence of the

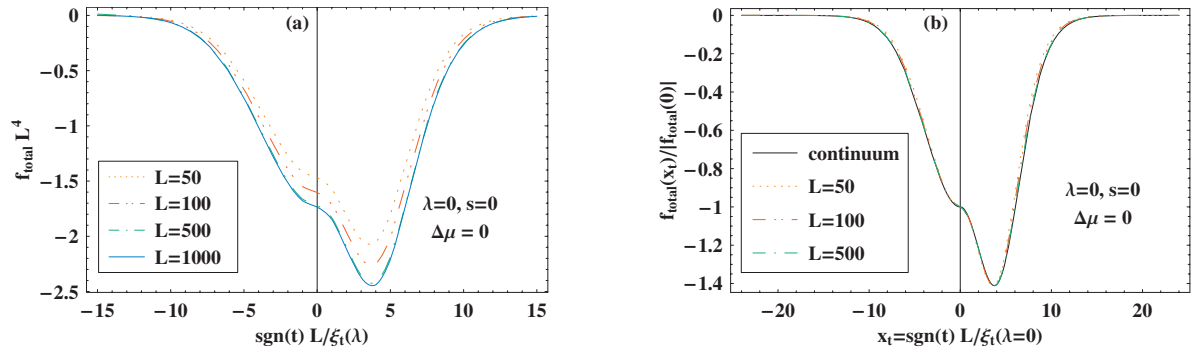

FIG. 6. (Color) Comparison between the behavior of the total unnormalized (a) and normalized (b) Casimir force in a lattice model with short-ranged interactions for different values of L. While in (a) the curves for $L=500$ and $L=1000$ practically coincide, which means that the nonuniversal corrections are negligible, the corrections become apparent for the film thicknesses $L=50$ and $L=100$. At the bulk critical point these corrections amount to 15% for $L=50$ and 8% for $L=100$. (b) If the curves from (a) are normalized by their values at the critical point they practically fall on top of each other and coincide with the continuum result. This occurs because the force is strongest at and near T_c and, by construction, the curves for different L are forced to coincide at $T=T_c$ thus shifting the possible deviations from each other towards large values of the scaling variable for which the force decays exponentially so that in that range all curves again coincide with each other.

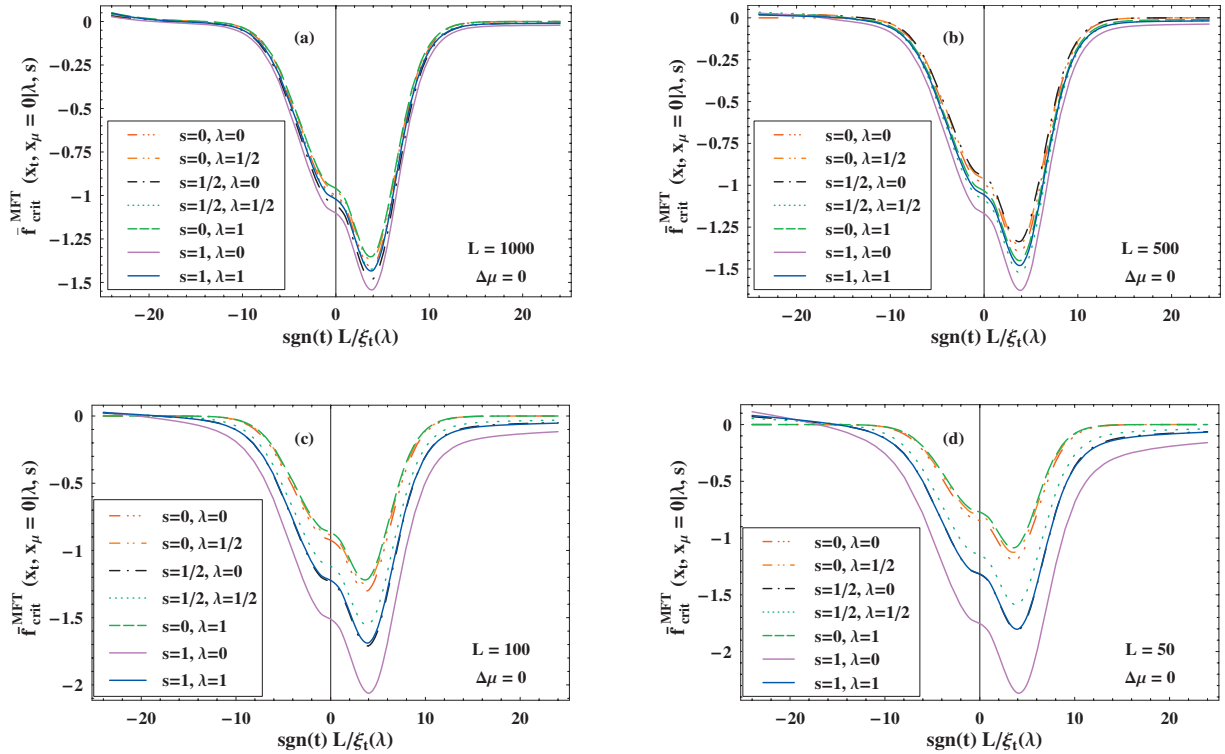

FIG. 7. (Color) Comparison between the behavior of the critical Casimir force normalized according to Eq. (4.19) for different values of L, λ, and s. The strength of the long-ranged fluid-fluid interaction is reflected by the value of λ (the larger λ the stronger is the long-ranged tail of the interaction in comparison with the short-ranged part [Eq. (3.24)]) and the strength of the long-ranged substrate-fluid interaction is reflected by the value of s (the larger s the stronger is the effective interaction with the substrate [Eqs. (3.8) and (3.11)]). We consider systems with $L=1000$ (a), 500 (b), 100 (c), and $L=50$ (d) layers. If L decreases one observes a more pronounced dependence on s and λ. While for $L=1000$ and $L=500$ all curves are very close to each other, they significantly deviate from each other for $L=100$ and $L=50$. For all L the maximal deviations with respect to the short-ranged case corresponding to $s=\lambda=0$ occur for $s=1,\lambda=0$ (which strengthens the force) and $s=0,\lambda=1$ (which weakens the force). As nonuniversal effects they depend on the absolute value of L. While for $L=1000$ the maximal deviation is (still) about 10%, for $L=50$ it reaches 100%. This profound dependence on the values of s and λ is most visible for $L=50$. Contrary to the situation for $L=1000$ and $L=500$, for $L=50$ none of the curves are even close to each other. The data show that the dependence on s is more sensitive than that on λ: changing the value of s leads to more pronounced deviations from the results for short-ranged forces than changing the value of λ. Furthermore, for smaller L the dependence on s is stronger and the curves vanish less rapidly for $x_t\to\infty$. We recall the asymmetry in the asymptotes of the total force for $x_t\to-\infty$ and $x_t\to\infty$ [see Fig. 3(a)]. In order to obtain its critical contribution the asymptote for $T>T_c$ was subtracted. For this reason one observes for $\bar{f}_{\rm crit}^{\rm MFT}$ a tendency to increase for $x_t\to-\infty$.

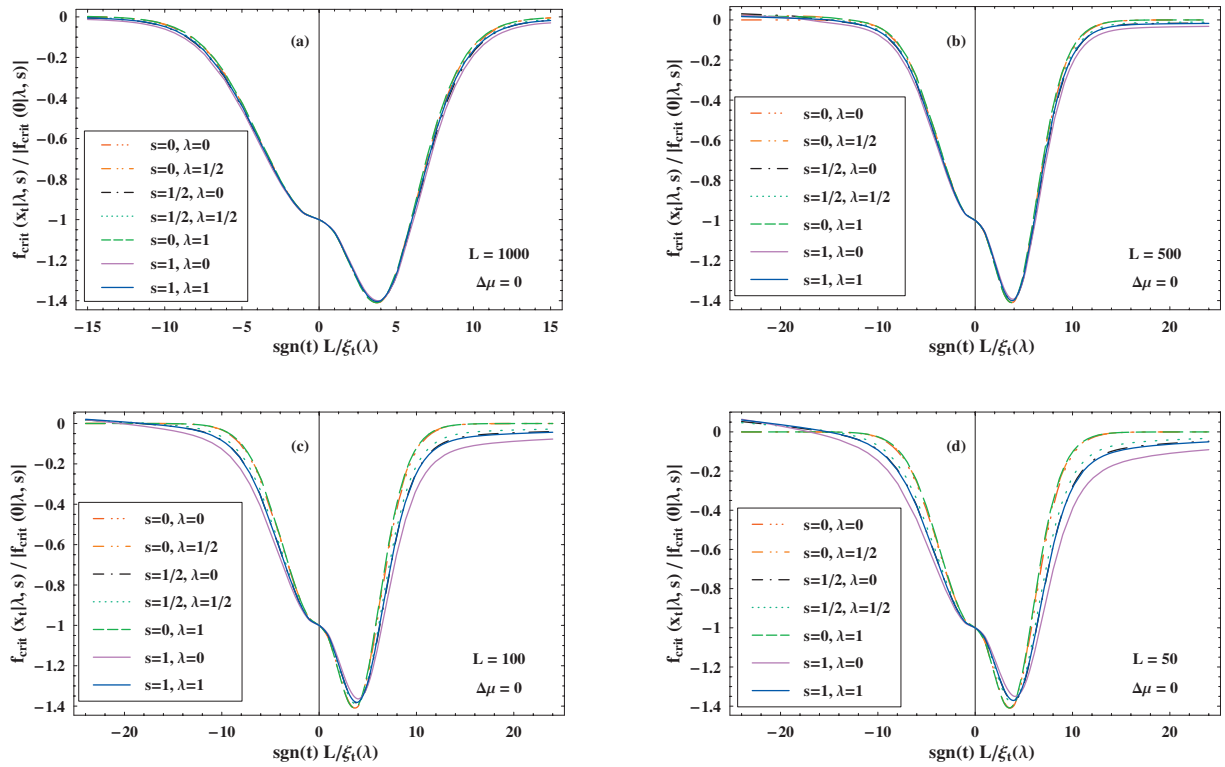

FIG. 8. (Color) Same data as in Fig. 7 but normalized by the value of the critical Casimir force at the bulk critical point. This normalization enforces coincidence of the curves at $x_t=0$. The figure demonstrates that this kind of normalization suppresses the visibility of the influence of the long-ranged interactions, which is actually rather strong for $L=50$ and $L=100$ (see Fig. 7). Nevertheless, for such values of L and large scaling arguments the data demonstrate the dominant character of the finite-size contributions to the force which are due to the van der Waals fluid-fluid (λ) and substrate-fluid interactions (s).

critical Casimir force at coexistence, Figs. 9 and 10 visualize the dependence on the excess chemical potential at $T=T_c$. In Figs. 8 and 10 the force is normalized by its value at the bulk critical point. This latter presentation does not allow one to compare the forces for different s and λ at the critical point, because there by construction this ratio equals 1 for all parameters. This partial lack of insight from this ratio can be overcome by choosing an alternative normalization, which keeps the dependence on λ and s even at the critical point:

$$\bar{f}_{\rm crit}(x_t,x_\mu|\lambda,s) = f_{\rm crit}(x_t,x_\mu|\lambda,s)/|f_{\rm crit}(0,0|\lambda=0,s=0)|. \tag{4.18}$$

Here $f_{\rm crit}(0,0|\lambda=0,s=0)$ is the leading asymptotic behavior $(d-1)\Delta_{+,+}L^{-d}$ of the critical Casimir force in a system with short-ranged forces. This can be inferred from experimental data of actual systems with dispersion forces by considering the limit $L \gg L_{\rm crit}$ [Eq. (2.6)] of the difference between the total Casimir force $f_{\rm total}$ and the regular background contribution [see Eq. (4.1) and the asymptote in Fig. 3] at the bulk critical point ($T=T_c$, $\Delta\mu=0$). In theoretical analyses $f_{\rm crit}(0,0|\lambda=0,s=0)$ can be determined directly by switching off the long-ranged parts of the interaction, i.e., by taking $\lambda=0$ and $s=0$ from the outset. As explained in Sec. IV A 1, within mean-field theory the right-hand side of Eq. (4.18) is not a ratio of *universal* scaling *functions* [Eq. (4.9)] as it is the case for the right-hand side of Eq. (4.18) beyond mean-field theory, i.e., for $d<4$. However, on the basis of the constructions in Sec. IV A 1 one can find a mean-field estimate for $\bar{f}_{\rm crit}(x_t,x_\mu|\lambda,s)$ in $d=3$ by determining, e.g., within our present mean-field approach,

$$\bar{f}_{\rm crit}^{\rm MFT}(x_t,x_\mu|\lambda,s) = \{[f_{\rm crit}(x_t,x_\mu|\lambda,s)/|f_{\rm crit}(0,0|\lambda=0,s=0)|] \times [\xi_0^+(\lambda=0)/\xi_0^+(\lambda)]^4\}_{\rm MFT}. \tag{4.19}$$

Figures 7 and 9 show the temperature and field dependence of $\bar{f}_{\rm crit}^{\rm MFT}$, respectively, for $L=1000$, 500, 100, and 50.

For decreasing values of L one observes that the dependence on s and λ becomes more pronounced. The maximum value of s we have considered is $s=1$. As stated in the beginning of Sec. IV A, in this case one expects that for $L>300$ the van der Waals interactions give rise only to corrections to the leading short-ranged behavior and that for thinner films there are significant deviations in the whole range of values of the scaling variables. These expectations are confirmed by Figs. 7 and 9. While for $L=1000$ and $L=500$ all curves are very close to each other they deviate from each other significantly for $L=100$ and $L=50$. Note that in all cases the force has a minimum *above* the critical point. The minimum is deepest for $s=1$, $\lambda=0$ and the force is weakest for $s=0$ and $\lambda=1$.

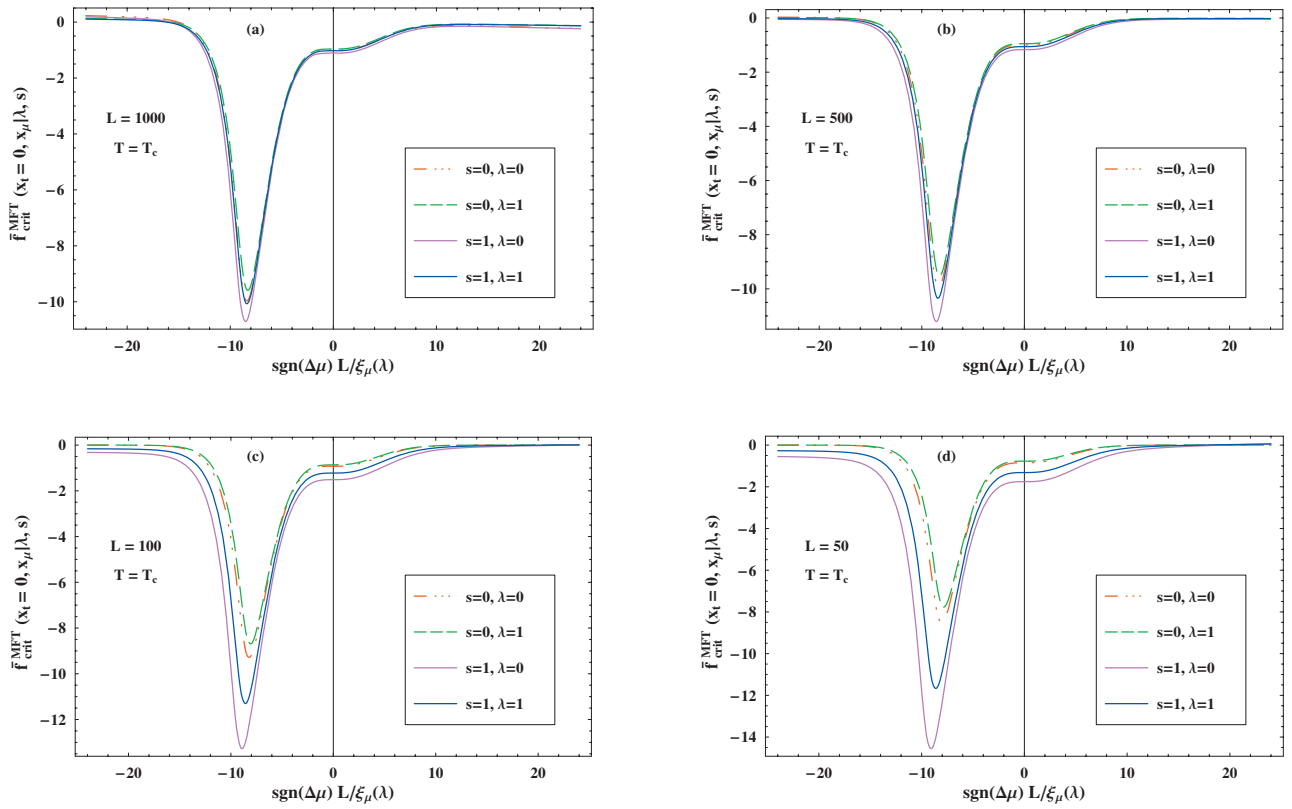

FIG. 9. (Color) Same as Fig. 7 as function of the field scaling variable $x_\mu = \mathrm{sgn}(\Delta\mu)L/\xi_\mu(\lambda)$ for $T=T_c$. The minimum of the force occurs for negative $\Delta\mu$, i.e., on the gas side of the bulk gas-liquid coexistence curve. The deepest minimum of the force occurs for $s=1$, $\lambda=0$. For $L=1000$ the force at the minimum is about 10 times stronger than the force at the critical point. If L decreases this minimum becomes even deeper; for $L=50$ the corresponding force is about 15 times stronger than at the critical point. The force is weakest for $s=0$, $\lambda=1$. Similar to Figs. 7 and 8 one again finds that the dependence on s is more sensitive than that on λ: changing the value of s leads to more pronounced deviations from the results for short-ranged forces than changing the value of λ. We recall the asymmetry in the asymptotes of the total force for $x_t \to -\infty$ and $x_t \to \infty$ [see Fig. 3(b)]. In order to obtain its critical contribution the asymptote for $T > T_c$ was subtracted.

Figures 8 and 10 show the same mean-field data as in Figs. 7 and 9, respectively, but now normalized by the actual values at the bulk critical point, i.e., $f_{\mathrm{crit}}(x_t, x_\mu|\lambda, s)/|f_{\mathrm{crit}}(0, 0|\lambda, s)|$. Whereas the coincidence of the curves at $x_t=0$ and $x_\mu=0$, respectively, is enforced by construction, for $L=50$ and $L=100$ there are significant differences for $|x_t| \gtrsim 10$, but barely affecting the minimum at $x_t \simeq 3.75$ (Fig. 8), and for $x_\mu < -4$ including the minimum at $x_\mu=-8.4$, but barely affecting the scaling regime $x_\mu \gtrsim 0$. The occurrence of the force minimum at *negative* values of x_μ, i.e., on the gas side of the bulk gas-liquid coexistence curve, can be understood by recalling that the Casimir force is a fluctuation induced force. The fluctuations are maximal at a small negative bulk field which is needed to neutralize the ordering effect (which suppresses the fluctuations) due to the substrate-fluid potential and thus of the $(+, +)$ boundary conditions. The ordering effect of the surface potentials can also be neutralized by increasing the temperature to values slightly above T_c. Therefore the magnitude of the force attains its maximum for $T=T_c$ at a negative value of x_μ and for $\Delta\mu=0$ at a positive value of x_t.

B. Finite-size behavior off criticality: Capillary condensation regime

To a certain extent Fig. 3 has already discussed some features of the force outside the critical region, where the total force is *repulsive*. Off criticality the force is well approximated by $\beta(\sigma-1)(A_l+A_{l,s})$ given by Eq. (4.1). The small deviations Δf of the force from its asymptotes (see Fig. 3) can be explained in terms of an effective finite-size contribution $\Delta\mu_L$ to the excess chemical potential $\Delta\mu$, which scales as $1/L$, i.e., the confined fluid at $\Delta\mu$ has approximately the properties of a bulk fluid at $\Delta\mu+\Delta\mu_L$ [60]. This implies $[\rho=(1+\phi)/2]$ that $\phi \simeq \phi_b(\Delta\mu+\Delta\mu_L) \simeq \phi_b(\Delta\mu) + \chi_b(\Delta\mu)\Delta\mu_L$, with the second term producing a contribution $\Delta f \sim 1/L$ relative to the leading first term. We recall that the total force discussed in Fig. 3 has turned out to be repulsive outside the critical region because it does not contain the contribution A_s from the direct substrate-substrate interaction. A_s carries only a weak and smooth temperature dependence via $\rho_s(T)$, which is not included in the degrees of freedom considered by the functional (3.2). If the contribution A_s is added to f_{total}, the resulting force is *attractive* [see

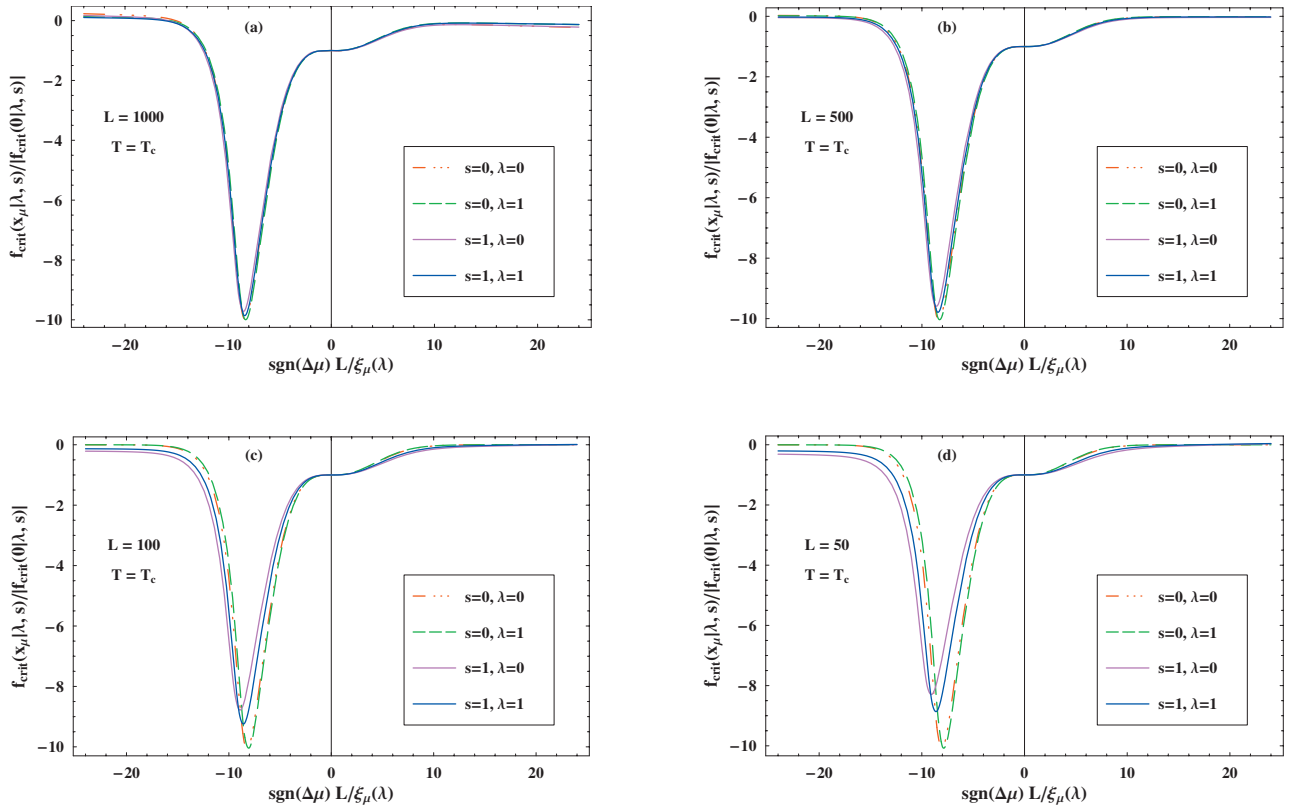

FIG. 10. (Color) Same data as in Fig. 9 but normalized by the value of the critical Casimir force at the bulk critical point. Whereas in Fig. 8 as a function of x_t, the deviations occur for $x_t \gtrsim 10$, here the deviations are most significant for $x_\mu \lesssim -4$, affecting in particular the minimum, but barely the scaling regime $x_\mu \gtrsim 0$. This is due to the fact that here the minimum of the force is rather deep (approximately 7 times deeper than the corresponding one in Fig. 8) so that the spread in the curves for $x_\mu \gtrsim 0$ is difficult to see, even for $L=50$, on the scale used in the plot.

Eq. (3.19)] throughout the whole thermodynamics space. Besides the critical regime there is, however, one additional region where the approximation of the force by $\beta(\sigma-1)(A_l + A_{l,s})$ is also not valid and where the force can be *attractive*, too, even if A_s is neglected.

This is the so-called capillary condensation regime, which will be discussed in the following. This capillary condensation regime occurs at low temperatures $T<T_c$ and for $L\Delta\mu = O(1)$ with $\Delta\mu<0$ if the walls prefer the liquid phase [22,61–63]. In accordance with Fig. 1 capillary condensation means that upon increasing the chemical potential in a film of thickness L there is a first-order phase transition between spatially inhomogeneous gaslike and liquidlike configurations at values $\Delta\mu_{\rm cap}<0$, i.e., before reaching the bulk gas-liquid coexistence curve $\Delta\mu=0$. The significant and interesting features of the force induced by capillary condensation are displayed in Figs. 11 and 12. For a film with $(+,+)$ boundary conditions, for $\Delta\mu<0$ with $|\Delta\mu|$ sufficiently small it is favorable for the system that $\phi\Delta\mu<0$, i.e., the equilibrium phase to be liquidlike. This means that ϕ is positive and thus follows the boundary conditions provided by the effective substrate potentials. If $\Delta\mu$ becomes more negative, at a given undersaturation $\Delta\mu=\Delta\mu_{\rm cap}(T,L)$ the sign of the order parameter changes abruptly to a negative value following the bulk field and forcing the appearance of two interfaces within the system. Accordingly, for large L the corresponding

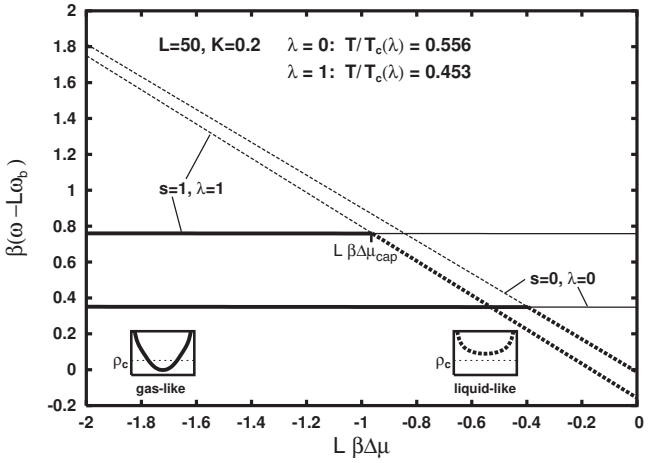

FIG. 11. Grand potential density in excess of the bulk contribution as function of $L\beta\Delta\mu$ for the two competing profile shapes (insets) in the capillary condensation regime for $(+,+)$ boundary conditions; $K=\beta J^l_{\rm sr}$. For $s=\lambda=0$ and $s=\lambda=1$ the curves intersect at $L\beta\Delta\mu_{cap}\approx -0.42$ and -0.95, respectively. The thermodynamically stable states correspond to the minimum branches of $\beta\omega$. They are presented by the thick parts of the lines. The thin parts of the lines indicate metastable states. The full lines correspond to gaslike states, the short-dashed lines to liquidlike states.

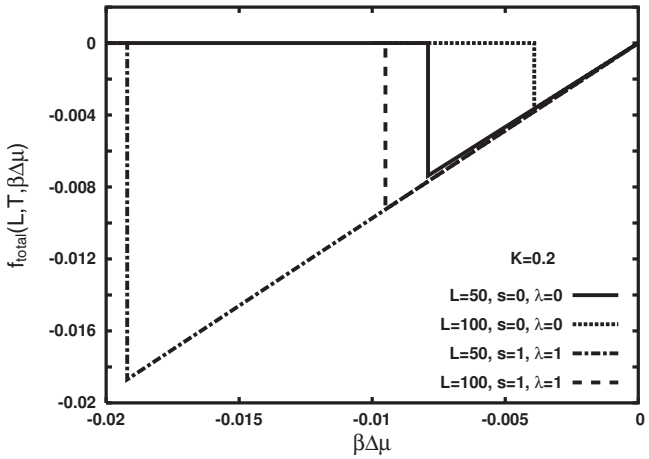

FIG. 12. Total force [obtained from Eq. (3.12)] per unit area and in units of β as a function of the chemical potential $\Delta\mu<0$ for $\beta|\Delta\mu|L=O(1)$ and $T<T_c$. The discontinuity of the force due to capillary condensation occurs at $\Delta\mu_{cap}(T,L)$. For $\Delta\mu>\Delta\mu_{cap}(T,L)$, with $\Delta\mu_{cap}\sim 1/L$, the leading behavior of the force is basically independent of L and is given by $2\phi_b\Delta\mu$. Note that the van der Waals contribution of the interaction strongly increases the maximal absolute value of the force. This occurs because both the long-ranged tails of the fluid-fluid (λ) as well as of the substrate-fluid (s) interactions promote the ordered state and increase the absolute value of $\Delta\mu_{cap}$ beyond which the coexistence of a reservoir of gas with a liquidlike film is no longer possible. In this plot $K=0.2$ corresponds to $T/T_c(\lambda)=0.556$ and 0.453 for $\lambda=0$ and $\lambda=1$, respectively. Both for $\Delta\mu<\Delta\mu_{cap}(T,L)$ and $\Delta\mu>0$ the leading behavior of the force is determined by the Hamaker term $\beta(\sigma-1)\times(A_l+A_{l,s})$ given by Eq. (4.1). In these regions the magnitude of the force is of the order of $L^{-\sigma}$ (i.e., L^{-4} within our model), while in the capillary condensed regime the maximal magnitude of the force is of the order of L^{-1}. For this reason on the present scales the curves for $\Delta\mu<\Delta\mu_{cap}(T,L)$ are not distinguishable.

contribution in Ω which is linearly proportional to $\Delta\mu$ changes by $2\phi_b\Delta\mu L$, thus leading to an L-independent change $2\phi_b\Delta\mu$ in the force. [This simple argument assumes that within this regime ($\Delta\mu\lesssim 0$, low T) in a large part of the film the order parameter profile $\phi(z)$ can be approximated by its bulk value ϕ_b.] Since the jump in the sign of ϕ occurs if the advantage of having ϕ_b with the same sign as $\Delta\mu$, i.e., $\phi_b\Delta\mu>0$ so that $\phi_b<0$, compensates the disadvantage of creating two surface free energy contributions in the system with a negative order parameter occurring inspite of $(+,+)$ boundary conditions, it is easy to understand that $\Delta\mu_{cap}\sim 1/L$. In Fig. 12 the total force is shown as the function of the chemical potential $\Delta\mu$. For $\Delta\mu>\Delta\mu_{cap}$, up to a leading order, it does not depend on L. As demonstrated numerically for large L, only the maximum absolute value of the force is L dependent, decreasing as $\sim 1/L$ due to the L dependence of $\Delta\mu_{cap}(T,L)$. Figures 11 and 12 present results for a system with short-ranged interactions ($s=\lambda=0$) and a system in which both the fluid-fluid and substrate-fluid interactions are long ranged ($s=\lambda=1$). It turns out that the behavior of the force in the considered (T,μ) region depends on s and λ mainly via the dependence of $\Delta\mu_{cap}$ on s and λ. This dependence is studied systematically in Fig. 13. It shows that

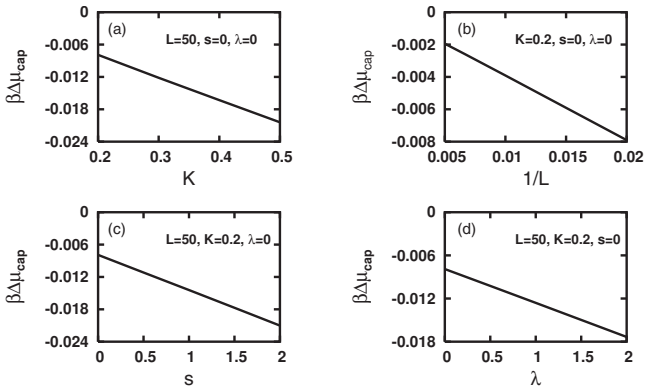

FIG. 13. The curves illustrate the loci $\Delta\mu_{cap}(T,L|\lambda,s)$ for capillary condensation leading to a jump of the Casimir force as a function of the coupling $K=J_{sr}^l/(k_BT)$ (a), the inverse linear size L (b), the relative strength of the surface-fluid potential s (c), and the strength of the van der Waals tail of the fluid-fluid interaction λ (d). All these dependences turn out to be linearly decreasing within the studied parameter range.

$\Delta\mu_{cap}$ depends linearly on K, L^{-1}, s, and λ. Furthermore, the maximal amplitude of the force also increases linearly if any of these parameters increases.

V. SUMMARY AND CONCLUDING REMARKS

In view of future experiments exploring the critical Casimir forces in classical one-or two-component fluids confined by parallel substrates with the same preference for their coexisting fluid phases we have analyzed the actual and generic interplay between the long-ranged fluctuation induced force and the long-ranged dispersion forces acting both between fluid molecules and between fluid and substrate molecules.

From general scaling arguments and explicit mean-field model calculations we have obtained the following main results:

(1) Based on general renormalization group arguments (Sec. II) we have established a relevance-irrelevance criterion (Sec. II B) for the importance of dispersion forces within the critical region of the system. It turns out that if the thickness L of the liquid film is much larger that L_{crit} [see Eq. (2.6)], within the critical region of the system the dispersion forces provide only corrections to the leading behavior of the force. However, outside the critical region, i.e., for temperatures $T\neq T_c$ or for undersaturations $\Delta\mu\neq 0$, the influence of the dispersion forces becomes important. This is of experimental importance because it is difficult to thermodynamically position the system right at the critical point. In the opposite case, i.e., for $L\lesssim L_{crit}$ the contribution of the van der Waals (dispersion) forces is always important and cannot be neglected even within the critical region of the system, including the bulk critical point. Within a mean-field-type model [Eqs. (3.1), (3.2), (3.6), (3.9), and (3.10)] we have studied the behavior of the force as a function of the strength of the long-ranged part of the fluid-fluid interaction, reflected by the parameter λ [Eq. (3.24)], on the strength of the long-ranged part of the effective substrate-fluid interaction, re-

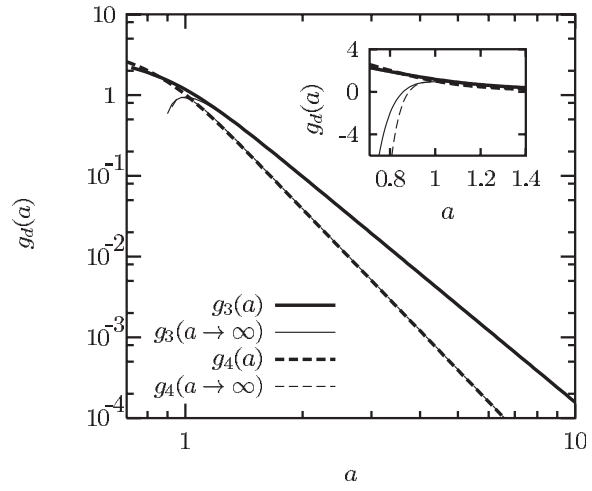

FIG. 14. The behavior of the function $g_d(a)$ and its asymptote for $d=\sigma=3$ and $d=\sigma=4$.

flected by the parameter s [Eq. (3.11)], on the thickness L of the film, and on the (relevant) temperature and chemical potential scaling fields. The interactions are taken to decay with the distance r between the fluid particles as $r^{-(d+\sigma)}$ and as $z^{-\sigma_s}$ for the distance z of a fluid particle from a single substrate. (Different from other theoretical model calculations we have taken the long-ranged tail of the fluid-fluid interaction fully into account, which amounts to respecting the fact that the function $g_d(a)$ [Eq. (4.5) and Fig. 14] is nonzero.) For a d-dimensional system we consider the case $\sigma > 2-\eta$ and $\sigma_s > (d+2-\eta)/2$, which guarantees that the long-ranged tails of the interactions change neither the bulk nor the surface universality classes [32,33]. The modified finite-size scaling, which is needed if one—as done here—compares within mean-field theory systems with different λ, is presented in Eq. (4.10). The results for the behavior of the force as a function of L/ξ_t and L/ξ_μ, where ξ_t and ξ_μ are the second-moment bulk correlation lengths for $\Delta\mu=0$ and at T_c, respectively, are summarized in Figs. 7–10. These explicit results confirm the relevance-irrelevance criterion mentioned above. The numerical results presented are for films with thicknesses $L=1000$, $L=500$, $L=100$, and $L=50$ layers in our simple cubic lattice model. We have varied λ and s between 0 (short-ranged model) and 1. Figures 7–10 show that for $L=1000$ and $L=500$ one observes universal scaling, i.e., independence on the values of s and λ, whereas this is lost for $L=100$ and $L=50$, which is in line with $L \lesssim L_{\mathrm{crit}}$. The comparison between Figs. 7 and 8 on one hand and Figs. 9 and 10 on the other hand shows which kind of analysis of the effects enhances or suppresses the visibility of the long-ranged forces. It turns out that L_{crit} is surprisingly large [see Eq. (2.6)], which enhances the importance of taking into account the dispersion forces for the interpretation of experimental data of critical Casimir forces in fluid systems.

(2) If all long-ranged interactions are taken into account—the fluid-fluid, the substrate-fluid, and the substrate-substrate one—for the case of $(+,+)$ boundary conditions studied here, we confirm explicitly within our model that the effective interaction between the substrates is attractive throughout the whole temperature range [see Eq. (3.19)]. The latter is described by three different Hamaker constants which account for the aforementioned interactions. If the direct substrate-substrate interaction is omitted (which amount to subtracting the force from the corresponding null experiment) the force is repulsive (see Figs. 2 and 3) except within the critical and the capillary condensation regime.

(3) For short-ranged systems, within the critical region our lattice model reassuringly reproduces the universal scaling function of the critical Casimir force as obtained from continuum field theory, provided L is sufficiently large (Sec. IV A 2 and Fig. 4). Surprisingly, even for short-ranged forces $(\lambda=s=0)$ $L=50$ and $L=100$ turn out to be too small in order to reach the universal scaling function given by the continuum field theory; $L=500$ and $L=1000$ are large enough in this respect (see Figs. 5 and 6).

(4) At low temperatures, $\Delta\mu<0$, and $L\Delta\mu=O(1)$, the force undergoes a jump as function of the excess chemical potential $\Delta\mu$ at a certain value $\Delta\mu_{\mathrm{cap}}<0$ caused by capillary condensation (see Figs. 1, 11, and 12). The position of the jump (Fig. 12) and its magnitude (Fig. 11) vary linearly as function of $1/T$, $1/L$, s, and λ (Fig. 13).

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APPENDIX A: DERIVATION OF THE EFFECTIVE HAMILTONIAN FOR A VAN DER WAALS SYSTEM CONFINED BETWEEN TWO PARALLEL PLATES

We consider a fluid composed of particles interacting via a pair potential $w^l(\mathbf{r}-\mathbf{r}')=-4J^l(\mathbf{r}-\mathbf{r}')$ and bounded by substrates whose particles interact with the liquid particles with a pair potential $w^{l,s}(\mathbf{r}-\mathbf{r}')=-4J^{l,s}(\mathbf{r}-\mathbf{r}')$. Within the lattice gas model for any given configuration $\mathcal{C}$ of particles $\{p_i^s, p_j^l\}$, $i\in\mathcal{S}$, $j\in\mathcal{L}$, where $\mathcal{L}$ and $\mathcal{S}$ denote the spatial region in a simple cubic lattice with lattice constant a occupied by the liquid and substrate particles, respectively, the energy of the fluid is given by

$$\mathcal{E} = \sum_{i\in\mathcal{S},j\in\mathcal{L}} w_{i,j}^{l,s} p_i^s p_j^l + \frac{1}{2}\sum_{i,j\in\mathcal{L}} w_{i,j}^l p_i^l p_j^l$$
$$= -4\sum_{i\in\mathcal{S},j\in\mathcal{L}} J_{i,j}^{l,s} p_i^s p_j^l - 2\sum_{i,j\in\mathcal{L}} J_{i,j}^l p_i^l p_j^l; \qquad \text{(A1)}$$

$p_j^l\in\{0,1\}$ and $p_i^s\in\{0,1\}$ denote the occupation numbers for the liquid and substrate particles, respectively. Since only the part $\{p_j^l\}$ corresponding to the fluid degrees of freedom exhibit criticality at T_c and the fluctuations of the substrate degrees of freedom $\{p_j^s\}$ are unimportant in this respect, one can replace the latter ones by their mean-field values. If the fluid is in contact with a particle reservoir at a given (excess) chemical potential μ and temperature T, the partition function for the liquid is

$$Z = \sum_{\{p_j^l\}} \exp\left[-\beta\left(\mathcal{E} - \mu \sum_{j\in\mathcal{L}} p_j^l\right)\right]$$
$$= \sum_{\{p_j^l\}} \exp\left[\beta\left(4 \sum_{i\in\mathcal{S}, j\in\mathcal{L}} J_{i,j}^{l,s}\rho_i^s p_j^l + 2\sum_{i,j\in\mathcal{L}} J_{i,j}^l p_i^l p_j^l + \mu\sum_{j\in\mathcal{L}} p_j^l\right)\right], \tag{A2}$$

where $\rho_i^s \equiv \langle p_i^s\rangle$. We assume that the solid substrate is only weakly influenced by the presence of its surface, so that $\rho_i^s = \rho_s = \text{const}$ in $\mathcal{S}$, which leads to

$$Z = \sum_{\{p_j^l\}} \exp\left[\beta\sum_{j\in\mathcal{L}}\left(4\rho_s\sum_{i\in\mathcal{S}} J_{i,j}^{l,s} + \mu\right)p_j^l + 2\beta\sum_{i,j\in\mathcal{L}} J_{i,j}^l p_i^l p_j^l\right]. \tag{A3}$$

Modeling the pair potentials as

$$J_{i,j}^l \equiv J_{\text{sr}}^l\{\delta(|\mathbf{r}_i - \mathbf{r}_j|) + \delta(|\mathbf{r}_i - \mathbf{r}_j| - 1)\} + J^l/(1 + |\mathbf{r}_i - \mathbf{r}_j|^{d+\sigma})\theta(|\mathbf{r}_i - \mathbf{r}_j| - 1), \tag{A4}$$

[note that $\theta(0)=0$ and $\delta(x)=1$ for $x=0$ and zero otherwise] and

$$J_{i,j}^{l,s} \equiv J_{\text{sr}}^{l,s}\delta(|\mathbf{r}_i - \mathbf{r}_j| - 1) + J^{l,s}/|\mathbf{r}_i - \mathbf{r}_j|^{d+\sigma_s}\theta(|\mathbf{r}_i - \mathbf{r}_j| - 1) \tag{A5}$$

one finds for $\Sigma_i J_{i,j}^{l,s}$:

$$\sum_i J_{i,j}^{l,s} - J_{\text{sr}}^{l,s}\delta(z_j) = J^{l,s}\sum_i \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^{d+\sigma_s}}$$
$$= J^{l,s}\sum_{r_1=0}^{\infty}\sum_{r_2=-\infty}^{\infty}\cdots\sum_{r_d=-\infty}^{\infty}\frac{1}{[(z_j+r_1)^2 + r_2^2 + r_3^2 + \cdots + r_d^2]^{(d+\sigma_s)/2}}$$
$$\simeq J^{l,s}\int_0^\infty dr_1\int_{-\infty}^{\infty} dr_2\cdots\int_{-\infty}^{\infty} dr_d\frac{1}{[(z_j+r_1)^2 + r_2^2 + r_3^2 + \cdots + r_d^2]^{(d+\sigma_s)/2}}$$
$$= J^{l,s}\int_0^\infty dr_1\int_0^\infty dr\frac{2\pi^{(d-1)/2}}{\Gamma\left(\frac{d-1}{2}\right)}\frac{r^{d-2}dr}{[(z_j+r_1)^2 + r^2]^{(d+\sigma_s)/2}}$$
$$= J^{l,s}\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\Gamma\left(\frac{d+\sigma_s}{2}\right)}\int_0^\infty dr_1(z_j+r_1)^{-\sigma_s-1}$$
$$= J^{l,s}\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\sigma_s\Gamma\left(\frac{d+\sigma_s}{2}\right)}z_j^{-\sigma_s}, \tag{A6}$$

where $z_j \geqslant 1$ characterizes the distance of the particle p_j from the boundary. We consider the fluid particles to be in the region $0 \leqslant z \leqslant L$, where L is the width of the film confined between the two surfaces. Therefore, the partition function is

$$Z = \sum_{\{p^l\}} \exp\left[\beta\left(\sum_{j\in\mathcal{L}}\mu_j p_j^l + 2\sum_{i,j\in\mathcal{L}} J_{i,j}^l p_i^l p_j^l\right)\right], \tag{A7}$$

i.e., the system is equivalent to one with a spatially varying chemical potential $\mu_j = \mu - V_j$ acting on a particle p_j at a distance z_j+1, $0 \leqslant z_j \leqslant L$, from the left boundary surface and at a distance $(L+1-z_j)$ from the right one where $V_j \equiv V(z_j)$ is the superposition

$$V(z) = -\rho_s J_{\text{sr}}^{l,s}[\delta(z) + \delta(L-z)] + v_s[(z+1)^{-\sigma_s} + (L+1-z)^{-\sigma_s}], \tag{A8}$$

where

$$v_s = -4\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\sigma_s\Gamma\left(\frac{d+\sigma_s}{2}\right)}\rho_s J^{l,s}. \tag{A9}$$

In the present study we choose $J_{\text{sr}}^{l,s}$ such that $\rho(0)=\rho(L)=1$, where $\rho(z)=\langle p_j^l\rangle$. This is implemented by taking $J_{\text{sr}}^{l,s}\to\infty$,

which is known as (+,+) boundary conditions applied to the system under consideration.

Note that in Eqs. (A6) and (A8) only the leading z dependence of the substrate potentials has been retained. We remark that there is some arbitrariness in what one calls the distance z. One might measure it from the last substrate layer or, say, from the midplane between the last substrate layer and the first liquid layer. These different choices as well as taking into account the actual discreteness of the substrate lattice in normal direction [see the second line in Eq. (A6)] lead to additional terms decaying as $z^{-\sigma_s-1}$, $z^{-\sigma_s-2}$, etc. In the following we do not consider such subdominant contributions.

One can easily determine the (leading) L-dependent contribution $\Delta\omega_{ex}^{(s,s)}$ in the excess grand canonical potential ω_{ex} which is generated by the direct interaction of the two substrate half-spaces a distance L apart. According to Eq. (A8), one has

$$\Delta\omega_{ex}^{(s,s)} = \sum_{z=L+1}^{\infty} \rho_s v_s z^{-\sigma_s}$$

$$\simeq -4\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\sigma_s\Gamma\left(\frac{d+\sigma_s}{2}\right)}\rho_s^2 J^s \int_{L+1}^{\infty} dz z^{-\sigma_s}$$

$$\simeq A_s(T)L^{-\sigma_s+1}, \tag{A10}$$

where A_s is given in Eq. (3.16). Also in this expression we have retained only the leading L-dependent part.

APPENDIX B: FINITE-SIZE BEHAVIOR OFF CRITICALITY

1. Finite-size contribution due to the long-ranged part of the fluid-fluid van der Waals interaction

Away from T_c the replacement of the fluctuating particle density by its mean value, which is inherent to the present mean-field approach, is a reliable approximation. This leads to the following finite-size contribution $\Delta\omega_{ex}^{(l)}$ to the excess grand canonical potential per area A that is due to the long-ranged tail of the fluid-fluid interaction $\hat{w}=-4J^l/(1+|\mathbf{r}|^{d+\sigma})\theta(|\mathbf{r}|-1)$:

$$\Delta\omega_{ex}^{(l)} \equiv \lim_{A\to\infty}\frac{1}{2A}\sum_{(\mathbf{r}_\parallel,z),(\mathbf{r}'_\parallel,z')\in\mathcal{L}} \hat{w}(\mathbf{r}_\parallel,z,\mathbf{r}'_\parallel,z')\rho(\mathbf{r}_\parallel,z)\rho(\mathbf{r}'_\parallel,z')$$

$$\simeq -2J^l\rho_b^2\sum_{\mathbf{r}_\parallel,z,z'}\frac{1}{1+[r_\parallel^2+(z-z')^2]^{(d+\sigma)/2}}$$

$$\simeq -4J^l\rho_b^2\frac{\pi^{(d-1)/2}}{\Gamma\left(\frac{d-1}{2}\right)}\sum_{z\neq z'}\int_0^{\infty}\frac{r^{d-2}dr}{[r^2+(z-z')^2]^{(d+\sigma)/2}}$$

$$\simeq -2J^l\rho_b^2\pi^{(d-1)/2}\frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\Gamma\left(\frac{d+\sigma}{2}\right)}\int_1^L dz\int_1^L dz'|z-z'|^{-(\sigma+1)}$$

$$\simeq A_l(T,\mu)L^{-\sigma+1}, \tag{B1}$$

where A_l is defined in Eq. (3.15) and the above integration over z has been performed under the restriction $|z-z'|\geqslant 1$, which mimics the regularization of $\hat{w}$ at $\mathbf{r}=\mathbf{r}'$. In all above steps in Eq. (B1) only the leading L-dependent terms, which are not part of the bulk or the surface contributions to the grand canonical potential, have been retained.

2. Finite-size contributions of the long-ranged tails of the substrate potentials for $T \ll T_c$

Away from T_c the leading order finite-size contribution to the grand canonical film potential due to the long-ranged tail of the substrate potential $V(z)\equiv\kappa J_{\mathrm{sr}}^{l,s}\delta(z-1)+v_s z^{-\sigma}$ of, say, the left wall is

$$\Delta\omega_{ex}^{(l,s)} \simeq \rho_b v_s\left(\sum_{z=1}^{L} z^{-\sigma_s}\right) \simeq \rho_b v_s\int_1^L dz z^{-\sigma_s} = -\frac{\rho_b v_s}{(\sigma_s-1)}L^{-\sigma_s+1}, \tag{B2}$$

where we have again retained only the leading L-dependent part.

Taking into account the contribution of the second surface, which renders a factor of 2 for the leading L-dependent part, we conclude that away from T_c the contribution of the tails of the substrate potentials to the behavior of the Casimir force is

$$\Delta f^{(l,s)} = -\beta\frac{\partial\Delta\omega_{ex}^{(l,s)}}{\partial L} = -2\beta\rho_b v_s L^{-\sigma_s} = \beta(\sigma_s-1)A_{l,s}, \tag{B3}$$

which is basically the result derived in Ref. [51] [see Eq. (6.11) therein] and is in full accordance with the findings of Ref. [56]. The constant $A_{l,s}$ is defined in Eq. (3.17).

APPENDIX C: ORDER PARAMETER PROFILE IN A FILM

Since in the present study the external potential $V(\mathbf{r})\equiv V(\mathbf{r}_\parallel,z)=V(z)$ depends only on the coordinate normal to the confining plates and there is no symmetry breaking in the lateral directions, the density profile also depends only on z so that Eq. (3.6) turns into the following equation for the order-parameter profile:

$$\phi^*(z) = \tanh\left(\beta\sum_{z'} J_l(z-z')\phi^*(z') + \frac{1}{2}\beta[\Delta\mu - \Delta V(z)]\right), \tag{C1}$$

where

$$J_l(z) \equiv \sum_{\mathbf{r}_\parallel'} J(\mathbf{r}_\parallel - \mathbf{r}_\parallel', z) = \sum_{\mathbf{r}_\parallel} J(\mathbf{r}_\parallel, z). \tag{C2}$$

Measuring distances in terms of the lattice spacing and taking the interaction of the form [see Eq. (3.9)]

$$J(\mathbf{r}) \equiv J^l_{\mathrm{sr}}[\delta(|\mathbf{r}|) + \delta(|\mathbf{r}|-1)] + \frac{J^l}{1+|\mathbf{r}|^{d+\sigma}}\theta(|\mathbf{r}|-1)$$
$$= (J^l_{\mathrm{sr}} - J^l)\delta(|\mathbf{r}|) + \left(J^l_{\mathrm{sr}} - \tfrac{1}{2}J^l\right)\delta(|\mathbf{r}|-1) + \frac{J^l}{1+|\mathbf{r}|^{d+\sigma}}, \tag{C3}$$

one can further simplify the sum on the right-hand side of Eq. (C1). Using the identity [64] (see also Ref. [7])

$$\frac{1}{1+y^\alpha} = \int_0^\infty dt \exp(-yt) t^{\alpha-1} E_{\alpha,\alpha}(-t^\alpha), \tag{C4}$$

where

$$E_{\alpha,\beta}(y) = \sum_{k=0}^{\infty} \frac{y^k}{\Gamma(\alpha k + \beta)}, \quad \alpha > 0, \tag{C5}$$

are the Mittag-Leffler functions, the sum over $\mathbf{r}_\parallel$ in Eq. (C2) can be rewritten as

$$J_l(z) = \left[(J^l_{\mathrm{sr}} - J^l) + 2(d-1)\left(J^l_{\mathrm{sr}} - \tfrac{1}{2}J^l\right)\right]\delta(z)$$
$$+ \left(J^l_{\mathrm{sr}} - \tfrac{1}{2}J^l\right)[\delta(z-1) + \delta(z+1)] + J^l_{d,\sigma}(z) \tag{C6}$$

with

$$J^l_{d,\sigma}(z) = J^l \int_0^\infty dt t^{(d+\sigma)/2-1} E_{d+\sigma/2,d+\sigma/2}(-t^{(d+\sigma)/2})$$
$$\times \left(\sum_{\mathbf{r}_\parallel} e^{-t\mathbf{r}_\parallel^2}\right) e^{-tz^2}. \tag{C7}$$

The main advantage of the above form is that it factorizes the summation over the components of $\mathbf{r}_\parallel$. Using the Poisson identity

$$\sum_{r=-\infty}^{\infty} e^{-tr^2} = \sqrt{\frac{\pi}{t}} \sum_{n=-\infty}^{\infty} e^{-\pi^2 n^2/t} \tag{C8}$$

one has

$$\sum_{z'=0}^{L} J^l_{d,\sigma}(z-z')\phi(z')$$
$$= J^l \left\{ c_d \phi(z) + \sum_{\substack{z'=0 \\ z\neq z'}}^{L} [g_{d,\sigma}(|z-z'|) + g^{nn}_{d,\sigma}(|z-z'|)]\phi(z') \right\}, \tag{C9}$$

where

$$c_d = \sum_{\mathbf{r}_\parallel} \frac{1}{1+\mathbf{r}_\parallel^{d+\sigma}} \tag{C10}$$

is a constant depending on d and σ. The function

$$g_{d,\sigma}(a) = \int_0^\infty dt \left(\frac{\pi}{t}\right)^{(d-1)/2} t^{d+\sigma/2-1} E_{d+\sigma/2,d+\sigma/2}(-t^{d+\sigma/2}) e^{-ta^2} \tag{C11}$$

reflects the contribution of the long-ranged van der Waals tails of the interaction, and the function

$$g^{nn}_{d,\sigma}(a) = \int_0^\infty dt \left(\frac{\pi}{t}\right)^{(d-1)/2} t^{d+\sigma/2-1}$$
$$\times E_{d+\sigma/2,d+\sigma/2}(-t^{d+\sigma/2}) \sum_{\substack{\mathbf{n}\in\mathbb{Z}^{d-1} \\ \mathbf{n}\neq\mathbf{0}}} e^{-\pi^2\mathbf{n}^2/t - ta^2} \tag{C12}$$

concerns mainly the coupling between neighboring sites in adjacent layers (see below). Here $\mathbf{n} \in \mathbb{Z}^{d-1}$ is a $(d-1)$-dimensional vector with integer components because all lengths are measured in units of the lattice spacing. It is easy to show that $\max_t \exp[-\pi^2\mathbf{n}^2/t + t(z-z')^2]$ is attained at $t = \pi|\mathbf{n}|/|z-z'|$ and equals $\exp(-2\pi|\mathbf{n}||z-z'|)$. Due to this exponential decay in the last term of Eq. (C9) one is able to take into account only the terms with $|\mathbf{n}|=1$ and $|z-z'|=1$, which amounts to the approximation $g^{n,n}_{d,\sigma}(a) \simeq g^{nn}_{d,\sigma}(\pm 1) \equiv \hat{c}^{nn}_{d,\sigma}$. It is straightforward to take into account additional, smaller terms corresponding to $|\mathbf{n}|=2,3,\ldots$ and $|z-z'|=2,3,\ldots$, but it turns out that already the contributions stemming from $|\mathbf{n}|=1$ and $|z-z'|=1$ are numerically very small. Thus the size dependent contributions due to the last term on the right-hand side of Eq. (C9) are exponentially small in L.

For $d=\sigma=4$ the corresponding Mittag-Leffler function can be expressed as

$$E_{4,4}(-t^4) = \frac{1}{\sqrt{2}t^3}\left[\cosh\left(\frac{t}{\sqrt{2}}\right)\sin\left(\frac{t}{\sqrt{2}}\right) - \cos\left(\frac{t}{\sqrt{2}}\right)\sinh\left(\frac{t}{\sqrt{2}}\right)\right]. \tag{C13}$$

For $a > 1/\sqrt[4]{2}$ this leads to the following representation of $g_4(a) \equiv g_{4,4}(a)$ [see Eq. (C11)]:

$$g_4(a) = \pi^{3/2} \int_0^\infty dt t^{3/2} E_{4,4}(-t^4)\exp[-ta^2]$$
$$= \frac{\pi^2}{2^{3/4}}\left\{[1+(\sqrt{2}a^2+1)^2]^{1/4}\left[\sin\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2+1]\right) - \cos\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2+1]\right)\right]\right.$$
$$\left. + [1+(\sqrt{2}a^2-1)^2]^{1/4}\left[\sin\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2-1]\right) + \cos\left(\frac{1}{2}\operatorname{arccot}[\sqrt{2}a^2-1]\right)\right]\right\} \tag{C14}$$

and the equation for the order parameter profile becomes

$$\operatorname{arctanh}[\phi^*(z)] = \frac{1}{2}\beta(\Delta\mu - \Delta V(z)) + K\Bigg\{ a_4\phi^*(z) + a_4^{nn}[\phi^*(z+1) + \phi^*(z-1)] + \lambda \sum_{\substack{z'=0 \\ |z'-z|\geqslant 2}}^{L} g_4(|z-z'|)\phi^*(z') \Bigg\}, \tag{C15}$$

where $K=\beta J_{\mathrm{sr}}^l$, and $\lambda = J^l/J_{\mathrm{sr}}^l$. In Eq. (C15) one has

$$a_4 = 7 + \lambda(c_4 - 4), \quad a_4^{nn} = 1 + \lambda\left(c_4^{nn} - \tfrac{1}{2}\right), \tag{C16}$$

where

$$c_4 = \sum_{\mathbf{n}\in\mathbb{Z}^3} \frac{1}{1+|\mathbf{n}|^8} \simeq 4.900 \tag{C17}$$

and

$$c_4^{nn} = g_4(1) + \hat{c}_{4,4}^{nn} \simeq 1.015 + 0.013 \approx 1.028. \tag{C18}$$

This shows that the contribution of $\hat{c}_4^{nn}$ to c_4^{nn} is ca. 1%.

For the asymptotic behavior one finds

$$g_4(a\to\infty) = \frac{\pi^2}{8}a^{-5} - \frac{33\pi^2}{1024}a^{-13} + O(a^{-21}). \tag{C19}$$

By setting $g_4 \equiv 0$, Eq. (C15) reduces to the well-known form of the mean-field theory for systems with short-ranged fluid-fluid forces. (Actually in our case setting $g_4\equiv 0$ corresponds to a system with short-ranged interactions in z direction and long-ranged ones within the planes perpendicular to z; only setting $\lambda=0$ or, equivalently, $J^l=0$ reduces the model to one with strictly short-ranged fluid-fluid interactions.) The standard Ginzburg-Landau equation follows from taking the expansion $\operatorname{arctanh}(\phi\to 0)=\phi+\phi^3/3+O(\phi^5)$. A continuum version of the equation follows from the replacement $\phi(z-1)+\phi(z+1)\to 2\phi(z)+\phi''(z)$. Obviously such a continuum version can be constructed also for a system with long-ranged forces by taking into account the function $g_4(a)$ (which then has to be considered as a function of a continuous variable). This exploits the fact that the function $g_4(a)$ is well defined for $a\geqslant 0$ [provided that for $0<a<1/\sqrt[4]{2}$ one takes the principal values of arccot to be in the interval $(0,\pi)$] and not only for $a\geqslant 1$, as actually needed for the lattice formulation of the theory. Therefore in the continuum formulation of the theory the integration can be extended to the full interval $z\in[0,L]$. This does not change the algebraic asymptotes of the density profiles. Thus in the continuum case the equation for the density profile in the presence of long-ranged interactions is an integrodifferential equation:

$$\phi^*(z) + \frac{1}{3}(\phi^*(z))^3 = \frac{1}{2}\beta[\Delta\mu - \Delta V(z)] + K\Bigg\{ a_4\phi^*(z) + a_4^{nn}\left[2\phi^*(z) + \frac{d^2\phi^*(z)}{dz^2}\right] + \lambda\int_0^L g_4(|z-z'|)\phi^*(z')dz'\Bigg\}. \tag{C20}$$

The behavior of the function $g_4(a)$ as well as its asymptote [Eq. (C19)] are shown in Fig. 14. Equation (C20) has to be augmented by the boundary conditions $\phi^*(z\to 0) = \phi^*(z\to L)=\infty$.

Note that, according to Eqs. (C15) [or Eq. (C20) in the continuum case] and (A8), the only *explicit* L dependence in the behavior of the order parameter profile enters via the asymptotes of the functions $V(z)$ and $g_4(|z|)$ for $|z|\gg 1$. They will then lead to contributions of the order of $L^{-\sigma}$ in the behavior of ρ away from T_c, i.e., there $\rho\simeq\rho_b+O(L^{-\sigma})$. The last result implies that the entropy term in Eq. (3.2) in this regime will produce contributions to ω_{ex} of the order of $L^{-\sigma}$. Such contributions can then be neglected in comparison with the ones described by A_l [see Eq. (B1)], A_s [see Eq. (A10)], and $A_{l,s}$ [see Eq. (B3)]. Obviously this argument is not specific for $d=4$ but is generally valid. Finally, we repeat that in the case $d=\sigma=3$ also an analytical expression for $g_3(z)$ can be derived [40]:

$$g_3(a) = \frac{\pi}{3}\left[\sqrt{3}\arctan\frac{\sqrt{3}}{2a^2-1} - \ln\left(1+\frac{1}{a^2}\right) + \frac{1}{2}\ln\left(1-\frac{1}{a^2}+\frac{1}{a^4}\right)\right]. \tag{C21}$$

The behavior of this function as well as its asymptote are also shown in Fig. 14.

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