

# Finite-size effects on the behavior of the susceptibility in van der Waals films bounded by strongly absorbing substrates

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We study critical point finite-size effects in the case of the susceptibility of a film in which interactions are characterized by a van der Waals-type power law tail. The geometry is appropriate to a slablike system with two bounding surfaces. Boundary conditions are consistent with surfaces that both prefer the same phase in the low temperature, or broken symmetry, state. We take into account both interactions within the system and interactions between the constituents of the system and the material surrounding it. Specific predictions are made with respect to the behavior of <sup>3</sup>He and <sup>4</sup>He films in the vicinity of their respective liquid-vapor critical points.

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## I. INTRODUCTION

Confinement to a finite volume introduces a variety of modifications to the behavior of a system in the vicinity of a phase transition. The existence of a single bounding surface leads to surface phase transitions [1–3], critical adsorption [1,2], wetting [4], and interface phenomena [5]. The requirement that the system is of finite extent in one or more directions generates effects associated with finite-size scaling theory [6–9], including shifts in critical points, dimensional crossover, rounding of phase transitions, and also to such phenomena as capillary condensation [10] and the interface delocalization phase transition [11,12].

In addition, the nature of the interaction within the system and between the system and the surrounding world influences leading and subleading thermodynamic behavior at and near a critical point [13–18].

In this paper we will discuss finite-size effects as they apply to the susceptibility of a film of a nonpolar fluid having a thickness  $L$  in which the intrinsic interaction  $J^l$  is of the van der Waals type, decaying with distance  $r$  between the molecules of the fluid as  $J^l \sim r^{-(d+\sigma)}$ . Here  $d$  is the dimensionality of the system while  $\sigma > 2$  is a parameter characterizing the decay of the interaction. The film is bounded by a substrate that interacts with the fluid with similar van der Waals type forces, i.e., of the type  $J^{l,s} \sim z^{-\sigma_s}$ , where  $z$  is the distance from the boundary of the system while  $\sigma_s > 2$  characterizes the decay of the fluid-substrate potential. For realistic fluids one has  $d = \sigma = \sigma_s = 3$ . The discussion in this paper will be quite general, but we will be principally interested in an Ising type model, which is commonly utilized to represent a nonpolar fluid.

As a specific application, we will estimate the parameters required for the prediction of the behavior of the finite-size susceptibility in the case of <sup>3</sup>He and <sup>4</sup>He films near their respective liquid-vapor critical points. We assume that the film is surrounded by gold surfaces. We will take into account both the van der Waals type interaction between the atoms of the <sup>3</sup>He (or <sup>4</sup>He) and the corresponding interaction between the Au atoms and <sup>3</sup>He (or <sup>4</sup>He) atoms.

According to general scaling arguments [2,19], the finite-size behavior of the susceptibility in a film of a fluid subject to (+,+) boundary conditions, i.e., conditions that strongly favor the liquid phase of the fluid over the gas phase is

$$\begin{aligned} \chi(t, h, L) - \chi_{\text{bulk}}(t, h) - L^{-1}[\chi_{\text{surface},1}(t, h) + \chi_{\text{surface},2}(t, h)] \\ = L^{\gamma/\nu} X(L/\xi_t, a_h h L^{\Delta/\nu}, b L^{2-\sigma-\eta}, h_{w,s} L^{(d+2-\eta)/2-\sigma_s}; a_\omega L^{-\omega}), \end{aligned} \quad (1.1)$$

where  $\chi_{\text{bulk}}(t, h)$  is the bulk susceptibility,  $\chi_{\text{surface},1}(t, h)$  and  $\chi_{\text{surface},2}(t, h)$  are the surface susceptibilities,  $\xi_t(T) = \xi_\infty(T \rightarrow T_c^+, h=0) \approx \xi_0^+ |t|^{-\nu}$  is the bulk correlation length,  $t = (T - T_c)/T_c$  is the reduced temperature,  $T_c$  is the bulk critical temperature,  $\xi_0^+$ ,  $a_h$ ,  $b$ ,  $h_{w,s}$ , and  $a_\omega$  are nonuniversal metric constants, while  $\nu$ ,  $\Delta$ ,  $\eta$ , and  $\omega$  are the universal critical exponents for the corresponding short-range system. For a schematic phase diagram in the  $(H, T)$  plane of the system see Fig. 1. Assuming  $\sigma > 2 - \eta$  and  $\sigma_s > (d + 2 - \eta)/2$ , one can expand (1.1), which leads to

$$\begin{aligned} \chi(t, h, L) \approx \chi_{\text{bulk}}(t, h) + L^{-1}[\chi_{\text{surface},1}(t, h) + \chi_{\text{surface},2}(t, h)] \\ + L^{\gamma/\nu} \{ X^{\text{sr}}(a_t L^{1/\nu}, a_h h L^{\Delta/\nu}; a_\omega L^{-\omega}) \\ + h_{w,s} L^{(d+2-\eta)/2-\sigma_s} X_{s,1}^{\text{lr}}(a_t L^{1/\nu}, a_h h L^{\Delta/\nu}) \\ + L^{-(\sigma_s-2+\eta)} [h_s^2 L^{-(\sigma_s-d)} X_{s,2}^{\text{lr}}(a_t L^{1/\nu}, a_h h L^{\Delta/\nu}) \\ + b L^{\sigma_s-\sigma} X_b^{\text{lr}}(a_t L^{1/\nu}, a_h h L^{\Delta/\nu})] \}, \end{aligned} \quad (1.2)$$

where  $X^{\text{sr}}$  is the (universal) scaling function characterizing the truly short-range system, while the remaining part in (1.2) describes the contributions due to the (subleading) long-range part of the interaction. While it is well established that  $X^{\text{sr}}$  tends to zero as  $\exp[-aL/\xi_\infty]$  with  $a$  a constant when  $L/\xi_\infty \gg 1$ , the functions  $X_{s,1}^{\text{lr}}$ ,  $X_{s,2}^{\text{lr}}$ , and  $X_b^{\text{lr}}$  are expected to decay only in a power-law-in- $L$  way.

Because of that, whenever  $L/\xi_\infty \gg 1$  the functions  $X_{s,1}^{\text{lr}}$ ,  $X_{s,2}^{\text{lr}}$ , and  $X_b^{\text{lr}}$  will determine the leading-in- $L$  finite-size contributions to the susceptibility of the system, and, therefore, the *leading* finite-size behavior of the susceptibility. Note that due to the lack of “+”  $\Leftrightarrow$  “−” symmetry in the surface

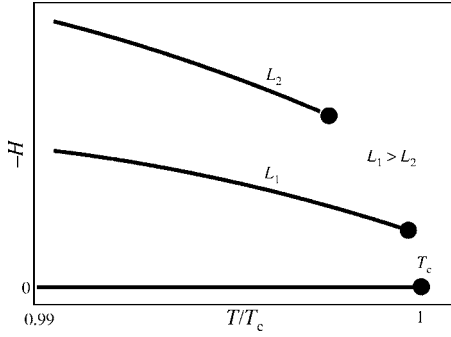


FIG. 1. A schematic  $(H, T)$  phase diagram near the critical point of a  $d$ -dimensional system with  $(+, +)$  boundary conditions [12,20]. The line  $H=0$ ,  $T < T_c$  represents the bulk phase coexistence line. (In the case of a fluid system the vertical  $-H$  axis then corresponds to the vapor side of the fluid-vapor coexistence curve.) The upper phase coexistence line is for a system with thickness  $L_2$ , while the lower one is for a system with thickness  $L_1$ , where  $L_1 > L_2$ . Away from the critical region the shift in the phase boundary is proportional to  $L^{-1}$ , while within it is proportional to  $L^{-\Delta/\nu}$ . As is shown, the lines of a first-order phase transition (with respect to the external bulk magnetic field) end at critical points of the  $(d-1)$ -dimensional system, the positions of which depend on  $L$ , on the amplitude of the (long-range) surface field, and on the presence or absence of long-range interactions between the spins of the system.

field given  $(+, +)$  boundary conditions, one finds in the susceptibility a term *linearly* proportional to  $h_{w,s}$  (in addition to the term proportional to  $h_{w,s}^2$ ).

With respect to their bulk critical behavior the nonpolar fluids around their liquid-vapor critical point belong to the Ising universality class. For the three-dimensional Ising model [21,22] one has  $\eta=0.034$ ,  $\gamma=1.2385$ ,  $\nu=0.631$ ,  $\alpha=0.103$ ,  $\beta=0.329$ ,  $\theta \equiv \omega\nu=0.53$ .

In the remainder of this paper we will consider only the case of identical substrates bounding the system. That is, we assume  $\chi_{\text{surface},1}(t, h) = \chi_{\text{surface},2}(t, h) \equiv \chi_{\text{surface}}(t, h)$  [23].

In the case of  $(+, +)$  boundary conditions the surface susceptibility is controlled by the extraordinary (or normal) surface universality class. One has

$$\chi_{\text{surface}}(t \rightarrow 0, h = 0) = \Gamma_{\text{surface}}^{\pm} |t|^{-\gamma_s}, \quad (1.3)$$

with  $\gamma_s = \gamma + \nu$  [1]. Thus, for the three-dimensional Ising universality class  $\gamma_s \approx 1.87$ . We are not aware of any study of explicit corrections to the behavior of this quantity due to van der Waals forces. It is clear that these forces do not suffice to change the surface universality class. That is, the critical exponents will remain the same as in the case of completely short-range interactions [2,19].

Let us now investigate in more detail the conditions under which the expansion in Eq. (1.1), leading to (1.2), can be justified. Some requirements, such as  $2 - \eta - \sigma < 0$ ,  $(d+2 - \eta)/2 - \sigma < 0$ , are obvious and normally are satisfied in any realistic system for which  $d = \sigma = 3$  and  $\eta \ll 1$  (i.e., for the 3d Ising model in which  $\eta = 0.034$  [21]). Important additional conditions arise, however, from the fact that we consider a *finite* system in which power law *long-range* surface fields

(i.e., substrate-fluid potentials) act. The influence of those long-range surface fields is felt everywhere in the finite system, the amplitude of the surface field being minimum at the center of the system. One can think of this smallest value as a type of a bulk field  $h$ , which has the effect of displacing the system from the position on the phase diagram on which its bulk field would otherwise place it. Taking into account contributions from both surfaces we obtain for the contribution of the long range surface field to an effective bulk symmetry-breaking field  $h_{b,s} = 2h_{w,s}[L/(2\xi_0^+)]^{-\sigma_s}$ . Since the bulk magnetic field scales as  $h[L/\xi_0^+]^{\Delta/\nu}$  one arrives at the criterion that in a film the finite-size contributions due to the long-range surface fields will be negligible in the critical region if

$$2|h_{w,s}|[L/(2\xi_0^+)]^{-\sigma}[L/\xi_0^+]^{\Delta/\nu} \ll 1, \quad (1.4)$$

i.e.,

$$2^{\sigma+1}|h_{w,s}|[L/\xi_0^+]^{\Delta/\nu-\sigma} \ll 1. \quad (1.5)$$

Note that  $h_{w,s} > 0$  corresponds to attractive walls, i.e., walls preferring the liquid phase of the fluid while  $h_{w,s} < 0$  corresponds to repulsive walls, i.e., to walls preferring the gas phase of the fluid. More detailed discussion on that point is presented in Appendix C, where we identify  $h_{w,s}$  in the framework of a mean-field type model. Using the relations between critical exponents it is easy to show that  $\Delta/\nu = (d+2-\eta)/2$ . Thus the relation (1.5) is consistent with the form (1.1). On the other hand,  $\Delta/\nu = d - \beta/\nu$  and, therefore,  $\Delta/\nu - \sigma = d - \sigma - \beta/\nu$ . By taking into account that for realistic systems  $d = \sigma$ , the condition (1.5) becomes

$$2^{\sigma+1}|h_{w,s}|[L/\xi_0^+]^{-\beta/\nu} \ll 1. \quad (1.6)$$

For most systems  $\xi_0^+$  is of the order of 3 Å. Taking the values of  $\beta$  and  $\nu$  to be appropriate to the 3d Ising model, we obtain in the case  $\sigma = 3$ ,

$$L \gg L_{\text{crit}} \equiv \xi_0^+(2^{\sigma+1}|h_{w,s}|)^{\nu/\beta} \approx 612|h_{w,s}|^{1.918} \text{ \AA}. \quad (1.7)$$

Later on in this article we will discuss the determination of the magnitude of  $|h_{w,s}|$  for the cases of  $^3\text{He}$  and  $^4\text{He}$  films bounded by Au surfaces. For the moment we note that in such systems  $|h_{w,s}| \approx 4$  (see Appendix C). The condition  $L \gg 9000$  Å must be met if finite-size effects due to the van der Waals interactions are to be negligible within the critical region of an  $^3\text{He}$  or  $^4\text{He}$  film. If  $L \sim 15\,000$  Å, which is experimentally realizable, then one expects van der Waals finite-size effects to play an essential role everywhere within the critical region. This implies that the value of the finite-size susceptibility at  $T_c$  will depend on  $L$  and on the choice of the bounding substrate (i.e., on the value of  $h_{w,s}$ ).

Away from  $T_c$  one expects [27,28]

$$\chi = \chi_{\text{bulk}} + \frac{1}{L}\chi_{\text{surface}} + \frac{1}{L^\sigma}\chi_{\text{Hamaker}} \cdots \quad (1.8)$$

Expressions similar to Eq. (1.2) have been shown to describe the finite-size behavior of the susceptibility in a fully finite system subject to periodic boundary conditions—in which case  $h_{w,s} \equiv 0$ —both in the instance of the exactly solvable spherical model [13,14,18] and via  $\varepsilon$ -expansion techniques (up to first order in  $\varepsilon$ ), in  $O(n)$  models [15].

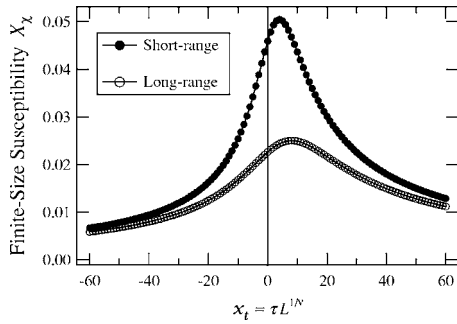


FIG. 2. A comparison between the behavior of the scaling functions of the susceptibility  $X_\chi(x_i)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *short range* and the same quantity for a fluid in which both interactions are *long range*. The thickness of the film is  $La$ , where  $L=3000$ , while  $a$  is the average distance between the molecules of the fluid. The scaling variable is  $x_i = \tau L^{1/\nu}$ , where  $\tau = 1 - T_c/T$  with  $T_c$  being the critical temperature of the corresponding short-or long-range system. The curves differ essentially from each other, in that they have different magnitudes at  $T_c$ . The maximum of the scaled susceptibility is also shifted.

Figure 2 displays the behavior of the susceptibility in a film in which the interactions are completely short range and of a film in which both the fluid-fluid and the fluid-substrate interactions are long range, the latter case corresponding to the actual experimental situation. We observe that the curves behave quantitatively differently in the two systems. At  $T_c$  and at coexistence, the susceptibility of the van der Waals type system is severely suppressed in comparison to that of the short-range system. As explained above and as we will see in more detail below, the magnitude of the maximum depends on the strength of the substrate-fluid coupling and is, therefore, *not* universal. Furthermore, there is a shift in the position of the maximum of the susceptibility. We expect that the curves shown here will resemble those obtained via experimental investigations.

In this article, we will explore the mechanisms underlying the similarity of the susceptibility in a fluid film near its bulk critical point to the susceptibilities plotted in Fig. 2. We investigate the behavior of the susceptibility as a function of the temperature, the external bulk magnetic field, the thickness of the film, and the strength of the fluid-substrate interaction.

The structure of the paper is as follows. First, in Sec. II we present a precise formulation of the model of interest along with the analytical expressions needed for its numerical treatment. The principal results for the behavior of the finite-size susceptibility are presented in Sec. III. Some technical details—including sums containing van der Waals type potentials—can be found in Appendix A. Appendix B contains a discussion of the role of the definition of  $L$  on the finite-size behavior of the susceptibility. It demonstrates that for  $L < L_{\text{crit}}$  the surface field plays a role of a quasirelevant variable allowing for which can significantly improve the scaling. An estimation of the parameters needed in order to apply the current results for the behavior of the susceptibility in  $^3\text{He}$  and  $^4\text{He}$  films is contained in Appendix C.

## II. THE MODEL

Perhaps the simplest model that captures the basic features of systems with van der Waals interactions is a modification of the one utilized by Fisher and Nakanishi in their mean-field investigation of short-range systems [30,31]. One starts with the following form of the functional for the free energy of the lattice system

$$\beta F = \sum_{\mathbf{r}} \left\{ \frac{1+m(\mathbf{r})}{2} \ln \left[ \frac{1+m(\mathbf{r})}{2} \right] + \frac{1-m(\mathbf{r})}{2} \ln \left[ \frac{1-m(\mathbf{r})}{2} \right] \right\} - \sum_{\mathbf{r}} h(\mathbf{r})m(\mathbf{r}) - \frac{1}{2} \sum_{\mathbf{r}, \mathbf{r}'} K(\mathbf{r}, \mathbf{r}')m(\mathbf{r})m(\mathbf{r}'), \quad (2.1)$$

where  $K(\mathbf{r}, \mathbf{r}') = \beta J'(\mathbf{r}, \mathbf{r}')$  is the nonlocal coupling between magnetic degrees of freedom,  $h(\mathbf{r})$  is an external magnetic field, and the magnetization  $m(\mathbf{r})$  is to be treated as a variational parameter. Note that in Eq. (2.1) the term in curly brackets corresponds to the entropic contributions, while the other terms are directly related to the interactions present in the system.

The variation of (2.1) with respect to  $m(\mathbf{r})$  leads to the following equation of state for our system:

$$m^*(\mathbf{r}) = \tanh \left[ \sum_{\mathbf{r}'} K(\mathbf{r}, \mathbf{r}')m^*(\mathbf{r}') + h(\mathbf{r}) \right]. \quad (2.2)$$

This equation can be solved numerically by applying the Newton-Kantorovich method. One is able to treat reasonably thick films, with  $L/a$  of the order of 3000 layers, corresponding to the experimental setup that we envisage as an example in our study. Its solution for a given geometry and external fields  $h(\mathbf{r})$  determine the order-parameter profile  $m^*(\mathbf{r})$  in the system.

We will be interested in a system with a *film* geometry. Then if  $\mathbf{r} = \{\mathbf{r}_{\parallel}, z\}$  and  $h(\mathbf{r}) \equiv h(\mathbf{r}_{\parallel}, z) = h(z)$  one has, because of the symmetry of the system,  $m(\mathbf{r}) \equiv m(\mathbf{r}_{\parallel}, z) = m(z)$ . The magnetization profile now depends only on the coordinate perpendicular to the plates bounding the van der Waals system. In this case, Eq. (2.2), which describes the behavior of the magnetization profile, becomes

$$m^*(z) = \tanh \left[ \beta \sum_{\mathbf{r}'} J(\mathbf{r} - \mathbf{r}')m^*(z') + h(z) \right], \quad (2.3)$$

where  $\mathbf{r}' = (\mathbf{r}'_{\parallel}, z')$ . Obviously, the above equation is equivalent to

$$m^*(z) = \tanh \left[ \beta \sum_{z'=0}^L \hat{\mathcal{J}}(z-z')m^*(z') + h(z) \right], \quad (2.4)$$

where

$$\hat{\mathcal{J}}(z) \equiv \sum_{\mathbf{r}'_{\parallel}} J(\mathbf{r}_{\parallel} - \mathbf{r}'_{\parallel}, z) = \sum_{\mathbf{r}_{\parallel}} J(\mathbf{r}_{\parallel}, z). \quad (2.5)$$

We will now assume that the fluid molecules occupy the region in space characterized by  $0 \leq z \leq L$  and that the layers

$z=0$  and  $z=L$  satisfy the (+,+) boundary conditions, i.e.,  $m(0)=m(L)\equiv 1$ . The number of layers containing spins that can fluctuate is, therefore,  $L-1$ .

Equation (2.4) is equivalent to

$$\operatorname{arctanh}[m^*(z)] = h(z) + \beta \sum_{z'} \hat{\mathcal{J}}(z-z') m^*(z'). \quad (2.6)$$

Taking the functional derivative of the both sides of Eq. (2.6) with respect to the field  $h(z^*)$  applied to the layer  $z^*$ , we obtain

$$\frac{G(z, z^*)}{1-m^2(z)} = \delta_{z, z^*} + \beta \sum_{z'} \hat{\mathcal{J}}(z-z') G(z', z^*), \quad (2.7)$$

where

$$G(z, z^*) \equiv \frac{\delta m(z)}{\delta h(z^*)} = \sum_{\mathbf{r}_{\parallel}} \langle S(\mathbf{0}, z) S(\mathbf{r}_{\parallel}, z^*) \rangle - \langle S(\mathbf{0}, z) \rangle \langle S(\mathbf{r}_{\parallel}, z^*) \rangle. \quad (2.8)$$

Equation (2.7) can be rewritten in the form

$$\sum_{z'} \left[ \frac{\delta_{z, z'}}{1-m^2(z')} - \beta \hat{\mathcal{J}}(z-z') \right] G(z', z^*) = \delta_{z, z^*}. \quad (2.9)$$

Now it is clear that the solution of the above equation with respect to  $G(z', z^*)$  is

$$G(z', z^*) = (\mathbf{R}^{-1})_{z', z^*}, \quad (2.10)$$

where  $\mathbf{R}^{-1}$  is the inverse matrix of the matrix  $\mathbf{R}$  with elements

$$R_{z, z'} = \frac{\delta_{z, z'}}{1-m^2(z')} - \beta \hat{\mathcal{J}}(z-z'). \quad (2.11)$$

One can define the ‘‘local’’ susceptibility

$$\chi(z) \equiv \sum_{z^*} G(z, z^*) = \sum_{\mathbf{r}_{\parallel}} \langle S(\mathbf{0}, z) S(\mathbf{r}_{\parallel}, z^*) \rangle - \langle S(\mathbf{0}, z) \rangle \langle S(\mathbf{r}_{\parallel}, z^*) \rangle. \quad (2.12)$$

Obviously,  $\chi \equiv \sum_z \chi(z)/(L+1)$  is the total susceptibility of the system per unit spin [see Eq. (2.12)]. Thus, one has

$$\chi(z) = \sum_{z^*} (\mathbf{R}^{-1})_{z, z^*}, \quad (2.13)$$

and

$$\chi = \frac{1}{L+1} \sum_{z, z^*} (\mathbf{R}^{-1})_{z, z^*}. \quad (2.14)$$

In Appendix A we demonstrate that the function  $\hat{\mathcal{J}}(z)$  can be written in the form

$$\hat{\mathcal{J}}(z) = J[c_{d-1} \delta(z) + c_{d-1}^m [\delta(z-1) + \delta(z+1)] + \mathcal{G}_d(z) \theta(z-2)], \quad (2.15)$$

where  $\delta(z)$  is the discrete delta function, while  $\theta(z)$  is the Heaviside function. Explicitly for  $d=\sigma=3$  one has (see Appendix A)

$$c_2 = \sum_{\mathbf{n} \in \mathbb{Z}^2} \frac{1}{1+|\mathbf{n}|^6} \approx 3.602, \quad (2.16)$$

$$\begin{aligned} c_2^{nm} = & -\frac{8}{3} \pi [(-1)^{1/3} K_0(\sqrt{2-2i\sqrt{3}\pi}) \\ & - (-1)^{2/3} K_0(\sqrt{2+2i\sqrt{3}\pi})] + \frac{\pi}{3} \left( \frac{\pi}{\sqrt{3}} - \ln 2 \right) \\ \approx & 1.183, \end{aligned} \quad (2.17)$$

and

$$\begin{aligned} \mathcal{G}_3(x) = & \frac{\pi}{3} \left[ \sqrt{3} \arctan \frac{\sqrt{3}}{2x^2-1} - \ln \left( 1 + \frac{1}{x^2} \right) \right. \\ & \left. + \frac{1}{2} \ln \left( 1 - \frac{1}{x^2} + \frac{1}{x^4} \right) \right]. \end{aligned} \quad (2.18)$$

The layer magnetic field  $h(z)$  is the only quantity in Eq. (2.6) the exact form of which still requires specification. In line with Eqs. (C6) and (C11) from Appendix C we take it to be of the form

$$h(z) = \frac{h_{w,s}}{(z+1)^{\sigma_s}} + \frac{h_{w,s}}{(L+1-z)^{\sigma_s}}, \quad 1 \leq z \leq L-1, \quad (2.19)$$

where  $h_{w,s}$  reflects the relative strength of the fluid-wall and fluid-fluid interactions [see Eqs. (C6), (C7), and (C12) below]. The above expression is consistent with the fact that the substrate occupies the region  $\mathbb{R}^{d-1} \times [L+1, \infty) \cup \mathbb{R}^{d-1} \times [-L+1, -\infty)$ . For  $^3\text{He}$  and  $^4\text{He}$  bounded by Au surfaces we show in Appendix C that  $h_{ws}=4$ . Note that (2.19) is derived for a system with  $\sigma=\sigma_s$ . According to (1.1) the finite-size effects due to the surface field  $h_{w,s}$  are controlled by  $h_{w,s} L^{(d+2-\eta)/2-\sigma_s}$ . For  $d=\sigma=\sigma_s=3$ , an Ising-like system, this leads to  $h_{w,s}/\sqrt{L}$ , where the value of  $\eta=0.034$  has been neglected, i.e.,  $\eta=0$  was used. Let us recall that within a mean-field treatment with respect to the critical behavior, the effective space dimension is  $d=4$  irrespective of the actual space dimension of the model under consideration. In order to have within the current mean-field model the same order of the finite-size effects due to  $h_{w,s}$  as in real systems we take in our model calculations  $\sigma_s=3.5$ . This value will be used in the remainder of the article whenever the substrate-fluid interaction is taken into account.

### III. NUMERICAL RESULTS AND FINITE-SIZE SCALING ANALYSIS

To determine the total susceptibility  $\chi(T, H|L, h_{w,s})$  and its ‘‘scaling function’’

$$X_{\chi} \equiv L^{-\gamma_{\chi}} \chi(T, H|L, h_{w,s}) \quad (3.1)$$

in a fluid film with thickness  $L$ , one has to solve Eq. (2.6) for  $1 \leq z \leq L-1$ , which allows one to construct the matrix  $\mathbf{R}$  with the use of Eq. (2.11). Finally, on the basis of Eq. (2.13)



one obtains the local susceptibility  $\chi(z)$ ,  $1 \leq z \leq L-1$ , and, summing, the total susceptibility. We recall that within the mean field treatment one has  $\beta = \nu = 1/2$ ,  $\gamma = 1$ ,  $\eta = 0$  and, for the extraordinary surface transition,  $\gamma_s = 3/2$  [1].

The analytic solution to the set of coupled nonlinear equations for the magnetization profile is, at present, known only for purely short-range, continuous, systems [32]. We review this solution in Sec. III A. Even in this case the finite-size susceptibility has to be determined numerically. The results are, again, presented in Sec. III A. Numerical methods appear to be unavoidable in order to solve the equations for the magnetization profile in the case of the long-range interactions of the van der Waals type. The results in this case will be discussed in Sec. III B.

### A. The model with purely short-range interactions for $H=0$

The equations to be solved in the continuum version of the purely short-range model of a mean-field Ising strip under  $(+, +)$  boundary conditions are

$$1 = \left[ 1 - \frac{\beta}{\beta_c} - \beta \frac{\partial^2}{\partial z^2} + m^2(z) \right] \chi(z), \quad (3.2)$$

$$0 = \left[ 1 - \frac{\beta}{\beta_c} - \beta \frac{\partial^2}{\partial z^2} + \frac{1}{3} m^2(z) \right] m(z). \quad (3.3)$$

Because conditions are identical at both bounding surfaces of the system, the solutions of the above equation satisfy  $m'(L/2) = 0$  and  $\chi'(L/2) = 0$ . The magnetization profile is known exactly [32]:

(i) when  $tL^2 \geq \pi^2$  [with  $t = (T - T_c)/T_c$ ]

$$m(z) = \frac{2K(k)}{L} \frac{dn(\zeta; k)}{sn(\zeta; k)}, \quad (3.4)$$

where

$$tL^2 = [2K(k)]^2(2k^2 - 1), \quad \zeta = [2K(k)/L]z, \quad (3.5)$$

and  $k^2 \geq 0$ .

(ii) when  $tL^2 \leq \pi^2$

$$m(z) = \frac{2K(k)}{L} \frac{1}{sn(\zeta; k)}, \quad (3.6)$$

where

$$tL^2 = -[2K(k)]^2(k^2 + 1), \quad \zeta = [2K(k)/L]z, \quad (3.7)$$

and  $k^2 \geq 0$ .

Here  $K(k)$  is the complete elliptic integral of the first kind,  $dn(\zeta; k)$  and  $sn(\zeta; k)$  are the Jacobian  $\Delta$  amplitude and the sine amplitude functions, respectively. The bulk critical point  $T = T_c$  corresponds to  $k^2 = 1/2$ . The above expressions are consistent with the following scaling form for the order parameter:

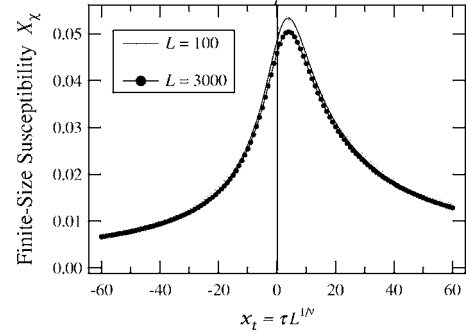


FIG. 3. The upper dotted line, for  $L=100$ , and the lower dotted line, for  $L=3000$ , illustrate the behavior of the scaling function of the susceptibility  $X_\chi(x_t)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *short range*. The scaling variable is  $x_t = (1 - T_c/T)L^{1/\nu}$ . Note that the maximum of the finite-size curves is at  $T > T_c$  which is due to the stabilizing effect of the  $(+, +)$  boundary conditions on the order parameter in the finite system. We observe that both curves differ at most around their maximal value. As it will be demonstrated in Fig. 4 the principal reason for this deviation is the improper choice of the value of the distance  $L$  between the plates.

$$m(z) = L^{-\beta/\nu} X_m\left(\frac{z}{L}, tL^{1/\nu}\right), \quad (3.8)$$

with  $\beta = \nu = 1/2$ .

The results from the finite-size scaling analysis of the behavior of the susceptibility for a system with short-range interactions are summarized in Figs. 3 and 4. Figure 3 compares the finite-size susceptibilities  $L^{-\gamma/\nu} \chi(T, h|L, h_{w,s})$  for short-range films with  $L=100$  and  $L=3000$  layers. Figure 4 presents the corresponding results for the ratio  $\chi(T, h|L, h_{w,s}=0)/\chi(T=T_c, h=0|L, h_{w,s}=0)$ . In both plots the scaling variable is  $x_t = (1 - T_c/T)L^{1/\nu}$ . The curves demonstrate a reasonably good scaling where the small deviations for  $L=100$  from the  $L=3000$  curve can be explained with the

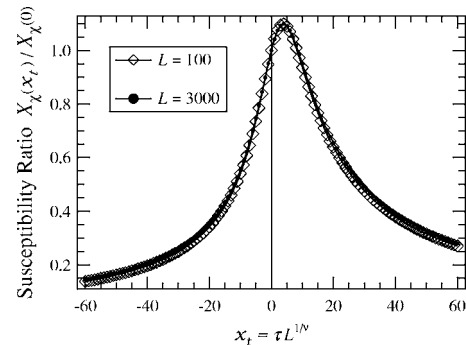


FIG. 4. The lines show the behavior of the scaling function of the *normalized* susceptibility  $X_\chi(x_t)/X_\chi(0)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *short range*. The curves are for  $L=100$  and for  $L=3000$ . The scaling variable is  $x_t = (1 - T_c/T)L^{1/\nu}$ . Both curves coincide perfectly well with each other. The main reason for the deviation of the curves in Fig. 3 is the improper choice of the length  $L$  (for a discussion see Appendix B).

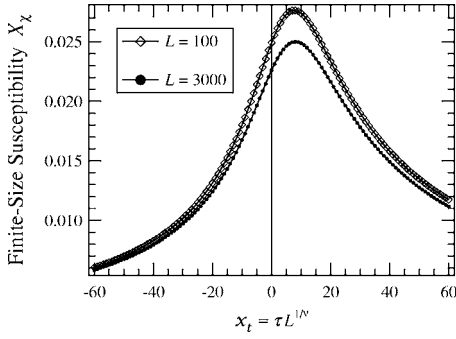


FIG. 5. The upper dotted line (for  $L=100$ ) and the lower dotted line (for  $L=3000$ ) show the behavior of the scaling function of the susceptibility  $X_\chi(x_t)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are of van der Waals type, i.e., are *long range*. The scaling variable is  $x_t=(1-T_c/T)L^{1/\nu}$ . We observe that both curves differ at most around their maximal value. The amplitude of the surface field for  $L=100$  is  $h_{w,s}=0.73$  while for  $L=3000$  it is  $h_{w,s}=4$  which ensures that the variable  $2\sigma_s+1|h_{w,s}|[L/\xi_0^+]^{\Delta/\nu-\sigma_s}=2^{4.5}|h_{w,s}|[L/\xi_0^+]^{-1/2}$  has the same value for both the cases.

ambiguousness in the definition of  $L$  (for a discussion see Appendix B), as well as with the corrections to scaling terms and the role of the background (nonuniversal terms). Note that the curves present the behavior of the *total* susceptibility and not only of its singular part.

## B. The model with van der Waals type interactions

We note that the critical temperature  $T_c$  depends on the presence or absence of long-range fluid-fluid interactions in the system. Let us denote by  $T_{c,lr}$  the critical temperature of the system with subleading long-range fluid-fluid interactions (from van der Waals type) and with  $T_{c,sr}$  the corresponding temperature for short-range fluid-fluid interactions. If  $K=\beta J^l$  then it is straightforward to show that  $K_{c,lr} \approx 0.161$ , while  $K_{c,sr} \approx 0.168$  in the framework of our model defined by Eq. (2.1).

The results from the finite-size scaling analysis of the behavior of the susceptibility for a system with long-range van der Waals type interactions are presented in Figs. 5–10. The scaling procedure is explained in detail in Appendix B.

### 1. The temperature dependence at $H=0$

Let us first consider the behavior of the finite-size susceptibility in the absence of an external magnetic field, which is equivalent to the behavior in a fluid system along the liquid-vapor coexistence line. Our results are presented in Figs. 5 and 6. One observes that the susceptibility possesses a maximum above the bulk critical temperature [which reflects that fact that the  $(+,+)$  boundary condition stabilize the long-range order at temperatures slightly above  $T_c$ ] and that this maximum is weaker than for the corresponding short-range system [see Fig. 3]. The scaling variable is  $x_t=(1-T_c/T)L^{1/\nu}$ . Note that the scaling functions decay much more

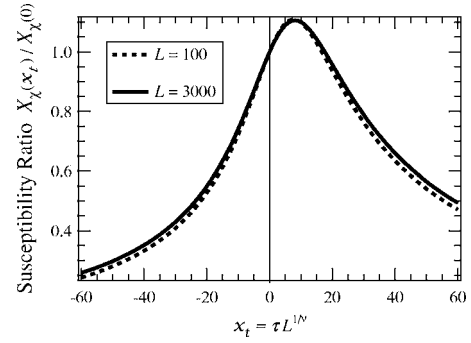


FIG. 6. The lines show the behavior of the scaling function of the *normalized* susceptibility  $X_\chi(x_t)/X_\chi(0)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *long range*. The curves are for  $L=100$  and for  $L=3000$ . The scaling variable is  $x_t=(1-T_c/T)L^{1/\nu}$ . We observe that both curves coincide perfectly well which each other only near the bulk critical point. The deviation of the curves from each other is due to the effect of the van der Waals interaction (compare with the short-range case) and increases with the increase of  $|x_t|$ . Note also that the scaling function decays much slower with  $|x_t|$  in comparison with the short-range case.

slowly as a function of  $|x_t|$  in comparison with the short-range case. The maximum of the short-range case is around  $x_t \approx 4$  while in the case of a van der Waals type system it is around  $x_t \approx 8$ . These results imply that, as expected, the long-range tails of the interactions help to stabilize the long-range order even a bit above the corresponding limit in  $T$  for the short-range system with  $(+,+)$  boundary conditions.

### 2. The temperature dependence of the susceptibility at $H \neq 0$

In this section we consider the behavior of the finite-size susceptibility for values of the external bulk magnetic field that support the vapor phase of the fluid. The results are presented in Fig. 7. Note that by changing the sign of  $H$  (by

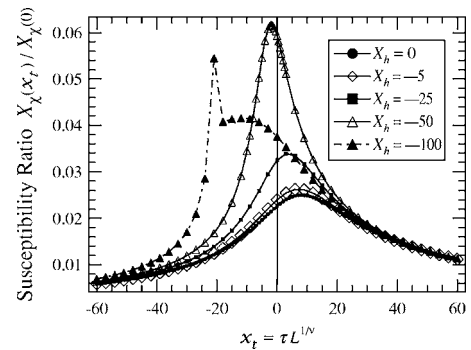


FIG. 7. The lines show the behavior of the scaling function of the susceptibility  $X_\chi(x_t, x_h)$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *long range*. The substrate-fluid potential is characterized by  $h_{w,s}=4$ , which corresponds to the situation of  $^3\text{He}$  or  $^4\text{He}$  films bounded by Au surfaces (see Appendix C). The curves are for  $L=3000$  and at  $x_h=0, -5, -25, -50, -100$ , where  $x_h=\beta H L^{\Delta/\nu}$ . The scaling variable is  $x_t=(1-T_c/T)L^{1/\nu}$ . The changed shape of the curve for  $x_h=-100$  signals that this curve is the precursor of a first-order phase transition.

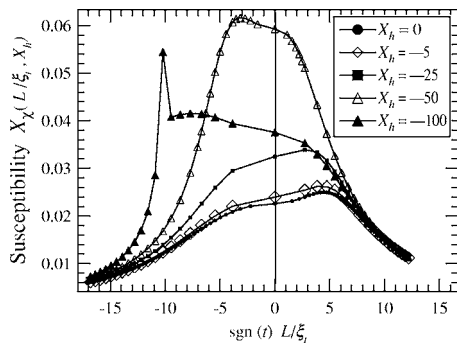


FIG. 8. The same as in Fig. 7 but the scaling function is presented as a function of  $L/\xi_t$  at several fixed values of  $x_h$ . We expect this curve to be a good approximation of the corresponding finite-size scaling function for a real three-dimensional experimental system of  ${}^3\text{He}$  or  ${}^4\text{He}$  films bounded by Au surfaces.

choosing negative values of  $x_h = \beta H L^{\Delta/\nu}$ ) one can show that the position of the maximum in the behavior of the susceptibility, which for  $H=0$  is at  $T > T_c$ , moves gradually toward  $T_c$  and for negative field with large enough magnitude can even be *below*  $T_c$ . In Fig. 8 we present the above results as a function of  $L/\xi_t$ . This resolves the question about the value of the nonuniversal metric factor in  $x_t$ . Note that then the shape of the curve and the position of its maximum shall be a reasonable approximation for the real experimental system of  ${}^3\text{He}$  or  ${}^4\text{He}$  films bounded by Au surfaces.

### 3. The field dependence of the susceptibility at $T \neq T_c$

Here we analyze the behavior of the finite-size susceptibility as a function of the field scaling variable  $x_h = \beta H L^{\Delta/\nu}$  for fixed values of the temperature close to the bulk critical temperature  $T_c$ . The results are presented in Fig. 9. The curves are for  $\tau = 0, 10^{-6}, 10^{-5}, 10^{-4}$ . Note that the behavior of the susceptibility possesses a peak that essentially differs from the corresponding background contribution only for

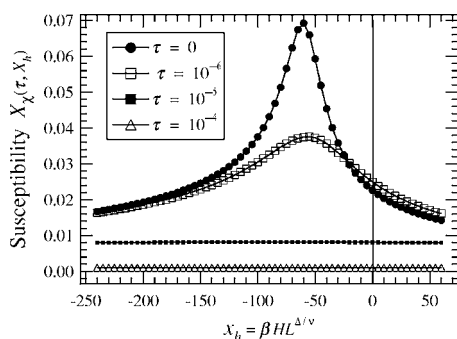


FIG. 9. The lines show the behavior of the scaling function of the susceptibility  $X_\chi(x_t, x_h)$  as a function of  $x_h$  at several fixed values of  $x_t$  for a fluid in which both the substrate-fluid and the fluid-fluid interactions are *long range*. The substrate-fluid potential is characterized by  $h_{w,s} = 4$ , which corresponds to the situation of  ${}^3\text{He}$  or  ${}^4\text{He}$  films bounded by Au surfaces (see Appendix C). The scaling variable is  $x_h = \beta H L^{\Delta/\nu}$ . The numerical calculations are performed for  $L = 3000$  layers.

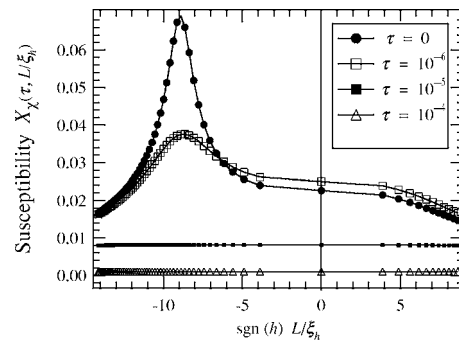


FIG. 10. The same as in Fig. 9 but the scaling function is presented as a function of  $L/\xi_h$  at several fixed values of  $\tau$ . We expect this curve to be a good approximation of the corresponding finite-size scaling function for a real three-dimensional experimental system of  ${}^3\text{He}$  or  ${}^4\text{He}$  films bounded by Au surfaces.

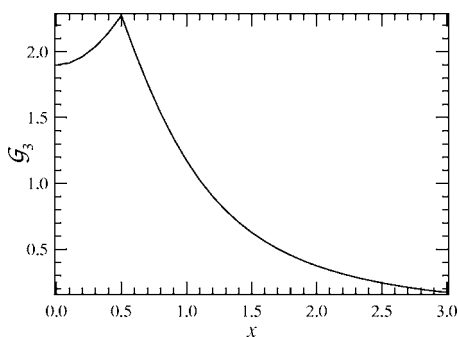
$|\tau| \lesssim 10^{-6}$ . In Fig. 10 we present the same results, this time as a function of  $L/\xi_h$ . This resolves the question about the value of the possible nonuniversal metric factor in  $x_h$ . Thus, the shape of the curve and the position of its maximum shall be a reasonable approximation for the real experimental system of  ${}^3\text{He}$  or  ${}^4\text{He}$  films bounded by Au surfaces.

## IV. CONCLUDING REMARKS AND DISCUSSION

In this article we investigated the behavior of the susceptibility in thin films with van der Waals type long-range interactions. Prominent examples of such systems are simple nonpolar fluids in thermodynamic equilibrium with their vapor, as well as binary fluid mixtures close to their demixing point. We have seen that despite the fact that this kind of interaction does not change the critical exponents of the system it nevertheless gives rise to a variety of finite-size effects that become dominant when  $L/\xi_\infty \gg 1$ . Furthermore, we have formulated a criterion regarding the conditions under which such effects also essentially modify the finite-size behavior of the susceptibility everywhere within the critical region. According to this criterion if the thickness  $L$  of the film is such that [see Eq. (1.7)]

$$L \lesssim L_{\text{crit}} = \xi_0^+ (16|h_{w,s}|)^{\nu/\beta}, \quad (4.1)$$

the effects due to the van der Waals interaction are essential and cannot be neglected. Here  $\xi_0^+$  is the amplitude of the bulk correlation length while the (dimensionless) factor  $h_{w,s}$  characterizes the strength of the fluid-substrate interaction  $\sim h_{w,s} z^{-\sigma}$ , where  $z$  is the distance from the substrate surface toward to the bulk of the fluid. In the case of  ${}^3\text{He}$  or  ${}^4\text{He}$  bounded by Au surfaces we find that at the corresponding critical point of both the fluids  $h_{w,s} \approx 4$  (see Appendix C). Then, for a three-dimensional Ising type system the direct evaluation yields the estimate  $L_{\text{crit}} \approx 9000 \text{ \AA}$ . A comparison when  $L/a = 3000$  layers (where  $a$  is the lattice constant) between the behavior of the finite-size susceptibility of a system with completely short-range interactions and one with long-range fluid-fluid and substrate-fluid interactions is given in Fig. 2. One observes a clear distinction between the curves

FIG. 11. The behavior of the  $\mathcal{G}_3$ -function as defined in (A9).

in the critical region. The calculations were performed using a mean-field type model which is described in detail in Sec. II. In order to determine the susceptibility one solves  $L/a = 3000$  coupled nonlinear equations; we make use of the Newton-Kantorovich method. We have chosen a film with this number of layers because it corresponds to a realistic experimental setup of  $^3\text{He}$  film between the Au electrodes of an experimental cell in which the smallest distance between the plates is  $1.5 \mu\text{m}$ ; the distance  $r_0$  between the atoms of  $^3\text{He}$  at its liquid-vapor critical point has been estimated to be  $r_0 \approx 4.9 \text{ \AA}$  (see Appendix C). For such a system the behavior of the susceptibility as a function of  $(1 - T_c/T)L^{1/\nu}$  for different values of the bulk field  $x_h = \beta H L^{\Delta/\nu}$  is shown in Fig. 7, while in Fig. 9 the susceptibility is plotted as a function of  $x_h$  for a few fixed values of  $\tau$ . The same data are shown in Figs. 8 and 10 as functions of  $L/\xi_t$  and  $L/\xi_h$ , respectively. We expect these curves to resemble the actual experimental data for  $^3\text{He}$  (or  $^4\text{He}$ ) film. One observes that for  $x_h = 0$ , the maximum of the susceptibility is *above* the bulk critical point. Furthermore, we note that when one is on the vapor side of the bulk phase diagram the maximum moves toward the bulk critical point with increasing distance from the coexistence curve in the phase diagram as a function of  $-x_h$  and that for  $-x_h$  large enough the maximum positions itself at a temperature less than  $T_c$ . Additionally, one observes that as a function of the scaling field variable ( $x_h$ , or  $y_h = L/\xi_h$ ) the susceptibility does not display an easily distinguishable maximum

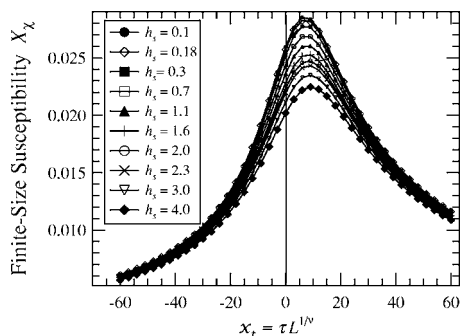


FIG. 12. The behavior of the finite-size susceptibility normalized per  $L^{\Delta/\nu}$  for different fixed values of  $h_{w,s}$  and for  $L=500$ . Within the mean-field approximation one has that  $\Delta/\nu=3$ . The values of  $h_{w,s}$  for which results are presented are  $h_{w,s}=0.1, 0.18, 0.3, 0.7, 1.1, 1.6, 2.0, 2.3, 3.0,$  and  $4.0$ . They model the role of different substrates that surround a given fluid film with thickness  $L$ .

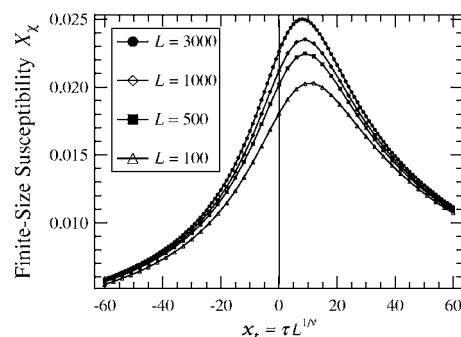


FIG. 13. The behavior of the finite-size susceptibility normalized per  $L^{\Delta/\nu}$  for different fixed values of  $L$  with the surface-field amplitude kept fixed at  $h_{w,s}=4$ . Systems with thickness  $L=3000, 1000, 500,$  and  $L=100$  are considered. The curves represent the behavior of the susceptibility of  $^3\text{He}$  and  $^4\text{He}$  films with different thickness when the surrounding surfaces are made of gold.

unless  $|\tau| \gtrsim 10^{-6}$ . The position of this maximum changes very slightly with  $t$  and is around  $\text{sign}(h)L/\xi_h \approx -8.7$  on the vapor side of the bulk phase diagram.

We stress that all of the above curves depend on the value of  $h_{w,s}$  and are, thus, nonuniversal. This implies that if  $h_{w,s}$  is kept fixed when  $L$  changes one will obtain different curves for the different  $L$ 's. The same will also be true when  $L$  is kept fixed but  $h_{w,s}$  changes. This is illustrated in Appendix B—see Figs. 11–13. Only when  $h_{w,s}/\sqrt{L}$  is kept fixed can a curve that does not depend on  $L$  nor on  $h_{w,s}$ , but just on their ratio, be obtained—see Fig. 14. In practice, one does not know the precise value of the system size  $L$ —an important issue for very thin film thicknesses (for more details see Appendix B). When this is also taken into account further improvement of the data collapse can be achieved as seen in Fig. 15, where the corresponding data for the susceptibility for fixed  $h_{w,s}/\sqrt{L}$  are normalized by its value at the bulk critical point. Definitely the above predictions are clearly experimentally verifiable. For a given fluid, one can either change the size  $L$  of the distance between the plates of the

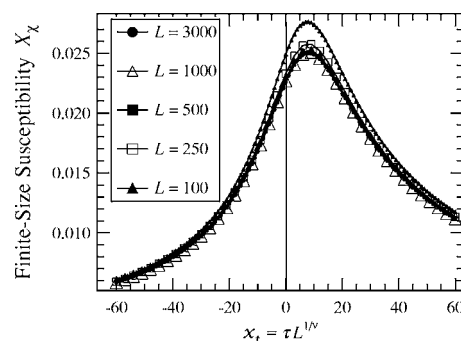


FIG. 14. The finite-size susceptibility for  $L=3000, L=1000, L=500, L=250, L=100$ . The amplitude of the surface magnetic field is rescaled in such a way that  $h_{w,s}/\sqrt{L}=\text{const}$  for all values of  $L$  and, as in the experimental realization,  $h_{w,s}=4$  for  $L=3000$ . One observes that practically all the curves for  $L \geq 250$  coincide with each other, i.e., the scaling is indeed valid. The curve with  $L=100$  differs from the others. Thus  $L=100$  is too small, and in this case the importance of  $\delta$  is demonstrated.



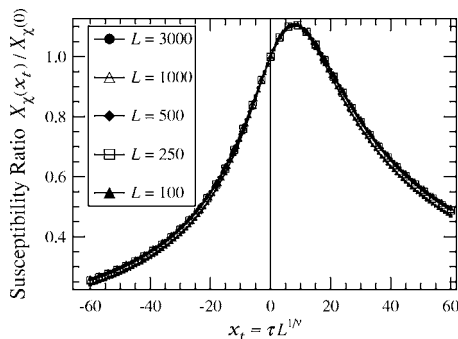


FIG. 15. The finite-size susceptibility for  $L=3000$ ,  $L=1000$ ,  $L=500$ ,  $L=250$ , and  $L=100$  normalized to its value at  $T=T_c$ . The amplitude of the surface magnetic field is rescaled in such a way that  $h_{w,s}/\sqrt{L}=\text{const}$  for all values of  $L$ .

experimental cell (i.e., the fluid film) or the corresponding substrate (i.e., the value of  $h_{w,s}$ ). The bigger the change in the new  $h_{w,s}$ , the bigger will be the deviation of the new curve of the finite-size susceptibility from the old one. Of course, this will be possible only if  $L \leq L_{\text{crit}}$ . When  $L \gg L_{\text{crit}}$  the universal behavior of the finite-size susceptibility in its standard form will prevail and the van der Waals interaction will only lead to small, probably experimentally negligible, corrections to the universal curve. Let us also note that when the experiment is performed for  $^3\text{He}$  or  $^4\text{He}$  around their liquid-vapor critical points according to our predictions one will obtain for any fixed  $L$ —even when  $L \leq L_{\text{crit}}$ —practically the same curve  $X_\chi$  for the finite-size susceptibility of both the fluids. For  $L \leq L_{\text{crit}}$  this will be simply due to the fact that  $h_{w,s} \approx 4$  for both the fluids (see Appendix C), while for  $L \gg L_{\text{crit}}$  that will be due to universality since near their liquid vapor critical points these fluids belong to the three-dimensional Ising universality class.

In the work described above, the effects of retardation on the van der Waals force have been neglected. These effects set in for distances  $r$  larger than  $160 \text{ \AA}$  between the He and Au atoms [33]. A possible concern is the influence of retardation on the system investigated in this paper. We have estimated that influence by performing numerical calculations in which an “extreme” retardation was imposed, in that the interaction potential was set to zero for separations  $r > 100$  layers. We discovered that the numerical consequence of retardation grows with increasing film thickness. At  $L=3000$  the difference between the calculation with the unretarded van der Waals force and the force with long-distance cutoff is 13.5% at  $T=T_c$ . This is an overestimate of the actual influence of retardation in experimental realizations. We note that retardation reduces the suppression of the susceptibility by the van der Waals interaction—see Fig. 2.

The numerical results reported above are obtained within a mean-field type model. If one goes beyond this and takes into account the influence of the fluctuations we do expect only quantitative changes in this behavior—all qualitative effects like the general shape of the curve of the finite-size susceptibility, including the relative positions [with respect to the bulk critical point ( $T=T_c, h=0$ )] of its maximum as a function of  $T, h$  and  $h_{w,s}$  will remain similar to the ones presented in Figs. 8 and 10. Of course, the values of the critical

exponents, as well as the precise position of the maximum will be influenced by the fluctuations. Finally, let us note that in the current study we did not take into account the influence of gravity on the behavior of the finite-size susceptibility. Because gravity leads to stratification of the density one expects an additional, more complicated  $z$  dependence of the local and, therefore, of the total susceptibility.

## ACKNOWLEDGMENTS

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## APPENDIX A: DERIVATION OF THE EQUATION FOR THE MAGNETIZATION PROFILE IN A VAN DER WAALS FILM

Here we derive an explicit form for the function  $\hat{\mathcal{J}}(z)$  for some basic cases of special physical interest. Namely we take  $J(\mathbf{r})$  to be of the “van der Waals form”

$$J(\mathbf{r}) = \frac{J}{1+r^{d+\sigma}}, \quad (\text{A1})$$

where  $r=|\mathbf{r}|$ , and  $d=\sigma=3$  for the “real” (nonretarded) van der Waals interaction.

Then one can further simplify the sum in the right-hand side of the above equation. Using the identity

$$\frac{1}{1+z^\alpha} = \int_0^\infty dt \exp(-zt) t^{\alpha-1} E_{\alpha,\alpha}(-t^\alpha), \quad (\text{A2})$$

where

$$E_{\alpha,\beta}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(\alpha k + \beta)}, \quad \alpha > 0, \quad (\text{A3})$$

are the Mittag-Leffler functions, the sum can be rewritten in the form

$$\sum_{\mathbf{r}'} J(\mathbf{r}-\mathbf{r}') m(z') = \sum_{z'=0}^L \hat{\mathcal{J}}_{d,\sigma}(z-z') m(z'), \quad (\text{A4})$$

where

$$\begin{aligned} \hat{\mathcal{J}}_{d,\sigma}(z) &= J \int_0^\infty dt t^{(d+\sigma)/2-1} E_{(d+\sigma)/2, (d+\sigma)/2}(-t^{(d+\sigma)/2}) \\ &\quad \times \left( \sum_{r_\parallel} e^{-r_\parallel^2} \right) e^{-tz^2}. \end{aligned} \quad (\text{A5})$$

The main advantage of the above form is that it factorizes the summation over the components of  $\mathbf{r}'_\parallel$ . With the help of the Poisson identity Eq. (A4) becomes

$$\begin{aligned} \sum_{\mathbf{r}'} J(\mathbf{r} - \mathbf{r}') m(z') &= J \left( \sum_{\mathbf{r}'_{\parallel}} \frac{1}{1 + \mathbf{r}'_{\parallel}{}^{d+\sigma}} \right) m(z) + J \int_0^{\infty} dt \left( \frac{\pi}{t} \right)^{(d-1)/2} t^{(d+\sigma/2)-1} E_{(d+\sigma)/2, (d+\sigma)/2}(-t^{(d+\sigma)/(2)}) \sum_{\substack{z'=0 \\ z \neq z'}}^L e^{-t(z-z')^2} m(z') \\ &+ J \int_0^{\infty} dt \left( \frac{\pi}{t} \right)^{(d-1)/2} t^{(d+\sigma)/2-1} E_{(d+\sigma)/2, (d+\sigma)/2}(-t^{(d+\sigma)/(2)}) \sum_{\substack{\mathbf{n} \in \mathbb{Z}^{d-1} \\ \mathbf{n} \neq 0}} e^{-\pi^2 \mathbf{n}^2 t} \sum_{\substack{z'=0 \\ z \neq z'}}^L e^{-t(z-z')^2} m(z'), \end{aligned} \quad (\text{A6})$$

where  $\mathbf{n} \in \mathbb{Z}^{d-1}$  is a  $(d-1)$ -dimensional vector with integer components, and all the lengths are measured in units of lattice spacings. 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 is equal to  $\exp(-2\pi |\mathbf{n}| |z-z'|)$ . Because of this exponential decay in the last row of the above equation we will take into account only the terms with  $|\mathbf{n}|=1$  and  $|z-z'|=1$  (the corresponding improvements that take into account  $\mathbf{n}=2, 3, \dots$  and  $|z-z'|=2, 3, \dots$  are obvious; as we will see even the contributions stemming from  $|\mathbf{n}|=1$  and  $|z-z'|=1$  are very small). It is clear that size dependent contributions that are due to the terms in the last row of (A6) will be exponentially small in  $L$ .

For  $d=\sigma=3$  the corresponding Mittag-Leffler function can be expressed in the following simple form

$$E_{3,3}(-t^3) = \frac{1}{3t^2} \left[ e^{-t} - 2e^{t/2} \cos\left(\frac{\pi}{3} + \frac{\sqrt{3}}{2}t\right) \right]. \quad (\text{A7})$$

Taking into account that, if  $x > 0$ ,

$$\pi \int_0^{\infty} t E_{3,3}(-t^3) e^{-tx} dt = \mathcal{G}_3(x), \quad (\text{A8})$$

where

$$\begin{aligned} \mathcal{G}_3(x) &= \frac{\pi}{3} \left[ \sqrt{3} \arctan \left| \frac{\sqrt{3}}{2x-1} \right| - \ln \left( 1 + \frac{1}{x} \right) \right. \\ &\quad \left. + \frac{1}{2} \ln \left( 1 - \frac{1}{x} + \frac{1}{x^2} \right) \right], \end{aligned} \quad (\text{A9})$$

we arrive at the following equation for the magnetization profile:

$$\begin{aligned} \operatorname{arctanh}[m^*(z)] &= h(z) + K \left\{ c_2 m^*(z) + c_2^{nm} [m^*(z+1) \right. \\ &\quad \left. + m^*(z-1)] + \sum_{\substack{z'=0 \\ |z'-z| \geq 2}}^L \mathcal{G}_3(|z-z'|^2) m^*(z') \right\}, \end{aligned} \quad (\text{A10})$$

where

$$c_2 = \sum_{\mathbf{n} \in \mathbb{Z}^2} \frac{1}{1 + |\mathbf{n}|^6} \approx 3.602, \quad (\text{A11})$$

and

$$\begin{aligned} c_2^{nm} &= -\frac{8}{3} \pi \int_0^{\infty} e^{-t/2 - \pi^2 t} \cos\left(\frac{\sqrt{3}}{2}t + \frac{\pi}{3}\right) + \mathcal{G}_3(1) \\ &= -\frac{8}{3} \pi [(-1)^{1/3} K_0(\sqrt{2-2i\sqrt{3}\pi}) - (-1)^{2/3} \\ &\quad \times K_0(\sqrt{2+2i\sqrt{3}\pi})] + \frac{\pi}{3} \left( \frac{\pi}{\sqrt{3}} - \ln 2 \right) \\ &\approx 0.009\,55 + 1.173\,54 \approx 1.183. \end{aligned} \quad (\text{A12})$$

As we see, the contribution due to the first part in Eq. (A12), and therefore the contributions due to the last row of Eq. (A6) are of the order of 1% in the constant  $c_2^{nm}$ . It is easy to verify that

$$\mathcal{G}(x) \approx \frac{\pi}{2} x^{-2} - \frac{\pi}{5} x^{-5} + \frac{\pi}{8} x^{-8} + O(x^{-11}), \quad x \rightarrow \infty. \quad (\text{A13})$$

Setting  $\mathcal{G} \equiv 0$  in Eq. (A10) one obtains an equation having a form that is familiar in the mean-field theory of short-range systems. Actually in our case the system in question has short-range interactions in the  $z$  direction and long-range ones within the planes perpendicular to  $z$ . The standard Ginzburg-Landau equation follows, for small  $m$ , after taking into account that  $\operatorname{arctanh}(m) \approx m + m^3/3 + O(m^5)$ . A continuum version of the equation follows from the replacement  $m(z-1) + m(z+1) \rightarrow 2m(z) + m''[z]$ . Obviously such a continuum version can also be constructed for the long-range system by adding the terms contributed by the function  $\mathcal{G}(x)$ , which is, in this case, a continuous function. Note that the function  $\mathcal{G}(x)$  is well defined everywhere for  $x \geq 0$  and not only for  $x \geq 1$  as we actually need it in the lattice formulation of the theory. Thus, in the continuum formulation of the theory the integration can be extended over the region  $z \in [0, L]$ . This does not change the long-range behavior of the magnetization profiles. In the continuum case the equation for the magnetization profile reads

$$m^*[z] + \frac{1}{3}(m^*[z])^3 = h[z] + K \left\{ c_2 m^*(z) + c_2^{nm} \left[ 2m^*[z] + \frac{d^2 m^*[z]}{dz^2} \right] + \int_0^L \mathcal{G}(|z-z'|^2) m^*(z') dz' \right\}. \quad (\text{A14})$$

## APPENDIX B: HOW TO SCALE

In the discussion up to now we have tacitly assumed that the value of  $L$  is precisely known. This is, however, not only an experimental problem—due to the roughness of the surface, the existence of impurities, dust, etc.—but also a theoretical problem that might play a role when  $L$  is not “large enough.” Let us make a brief comment about this issue. The definition of the size of the system is unambiguous only for systems with periodic boundary conditions. If  $N$  is the number of layers with independent degrees of freedom, then the size of the system is simply  $L=Na$ , where  $a$  is the distance between the layers. Any point in the system is equivalent to any other point. Therefore, any layer is equally suitable to be taken as the origin with respect to which one measures distance. However, how one proceeds for a system with  $(+,+)$  boundary conditions—when the first and the last layers have fixed degrees of freedom—is less clear. For consistency with periodic boundary conditions one can, of course, count the number of layers with independent degrees of freedom and let this, as in the case of periodic boundary conditions, be equal to  $N$ . Then the question is, shall we include in the total size of the system the half distance between the two outermost layers with independent degrees of freedom and the adjacent layers with the fixed degrees of freedom? A reasonable approach seems to be that at least half of these distances should be taken to belong to the system, i.e.,  $L=(N+1)a$ . This, of course, is not an unambiguous procedure. We have two layers with fixed degrees of freedom, which do not belong to the “substrate” surrounding the system that strongly prefers the ordered phase of the system in the case of  $(+,+)$  boundary conditions. Thus one has to somehow decide which portion of the bounding layers are to be counted within the system. Much more complicated is the case of systems with long-range interactions. Then any particle (atom or molecule) of the system interacts with any other one from the substrate. How then does one define the size of the system or the borderline between the substrate and the system? Let us denote by  $\hat{L}$  the “true” size of the system (which we do not know), and by  $L$  a reasonable approximation of that size [say, by taking, as above for the short-range case, the size to be  $L=(N+1)a$ ]. The last implies that  $\hat{L}=L+\delta$ , where  $\delta \ll \hat{L}$ . Figure 12 demonstrates the difficulties when studying the scaling in systems with subleading long-range interactions of the van der Waals type. The role of the long-range surface potentials, which are *irrelevant* in the renormalization group sense but for moderate values of  $L$ , i.e., for  $a \ll L \ll L_{\text{crit}}$  [see Eq. (1.7)], contribute to the *leading* behavior of the finite-size susceptibility is clearly seen. One can say that, for such values of  $L$ , the quantity  $x_s$  is a sort of

“dangerous” irrelevant variable—in the sense that, despite being irrelevant, one *cannot* neglect it when  $L < L_{\text{crit}}$ . We further note that the greatest deviation of the curves for different  $L$  from each other is around the maximum value of the scaling functions. The lack of the data collapse is due to the fact that  $x_s \sim h_{w,s}/\sqrt{L}$  is *not* the same for all the curves [see Eq. (1.7)]. Definitely similar spreading of the data for the finite-size susceptibility are to be observed if  $h_{w,s}$  is kept fixed while  $L$  changes—say  $h_{w,s}=4$  as in case of  $^3\text{He}$  or  $^4\text{He}$  confined by Au plates and—one considers  $L=3000, 1000, 500, 100$  (see Fig. 13). However, when  $x_s$  is kept fixed for the same values of  $L$  considered before, the data collapse improves greatly, as shown in Fig. 14. One observes that violations of scaling are now clearly detectable only for the smallest system size  $L=100$ . Let us now recall that when  $L$  is “large but small enough” the effect of  $\delta$ , i.e., of the fact that we do not know exactly the system size  $L$  is clearly evident. In the case of  $\chi$  one has  $\chi \approx \hat{L}^{\gamma/\nu} [1 + \delta(\gamma/\nu)\hat{L}^{-1} + O(\delta^2\hat{L}^{-2})] X_\chi(\hat{x}_t, \hat{x}_h | \hat{x}_s, \hat{x}_b, \hat{x}_\omega)$ , where  $\hat{x}_t = a_t \hat{L}^{1/\nu}$ ,  $\hat{x}_h = a_h h \hat{L}^{\Delta/\nu}$ ,  $x_s = h_{w,s} \hat{L}^{(d+2-\eta)/2-\sigma}$ ,  $\hat{x}_b = b \hat{L}^{2-\eta-\sigma}$ ,  $\hat{x}_\omega = a_\omega \hat{L}^{-\omega}$ . Note now that the expansion of the above expressions in terms of  $\hat{L}$  will yield all possible nonuniversal (proportional to  $\hat{L}^{-1}$ ) corrections to the leading finite-size behavior of the susceptibility with the greatest deviation of the curves for different  $\delta$  occurring near the maximum value of  $X_\chi$ . For the sake of precision let us also note that similar corrections will be produced if one takes into account the change from  $L$  to  $\hat{L}$  in the variables  $\hat{x}_t$ ,  $\hat{x}_h$ ,  $\hat{x}_s$ ,  $\hat{x}_b$ , and  $\hat{x}_\omega$ . Thus, only the leading finite-size behavior can be determined unambiguously. All corrections will depend on the definition of  $L$ , i.e., on  $\delta$ . There is, nevertheless, still something that one can do in order to check that the behavior of the susceptibility for  $L=100$  is simply due to the above explained unambiguity in the definition of  $L$ . Note, that if we normalize  $\chi$  to its value at a given point within the critical region—say to the value  $\chi_0$  at the bulk critical point ( $T=T_c$ ,  $H=0$ )—then, whatever the definition of  $L$  is, the *leading* behavior of the resulting quantity will *not* depend on this definition. Explicitly, we have

$$\frac{\chi}{\chi_0} \approx \frac{X_\chi(\hat{x}_t, \hat{x}_h | \hat{x}_s, \hat{x}_b, \hat{x}_\omega)}{X_\chi(0, 0 | \hat{x}_s, \hat{x}_b, \hat{x}_\omega)} + O(\hat{L}^{-1}). \quad (\text{B1})$$

The result from the application of the above procedure is shown in Fig. 15. We observe that all the curves, including  $L=100$ , now allow for data collapse and that only a small deviation of the curves from each other is observed for very large values of the scaling variable  $x_t$ , when the onset of the nonuniversal corrections to scaling due to the role of the fluid-fluid interaction (i.e., proportional to  $x_b$ ) is expected to set in. Thus, despite ignorance of the precise value of  $L$ , we are able to determine the leading finite-size behavior of the susceptibility.

## APPENDIX C: EVALUATION OF THE SCALING FIELD PARAMETERS FOR HELIUM

We imagine a simple model for helium ( $^3\text{He}$  or  $^4\text{He}$ ) in which atoms interact via a pair potential

$w^l(\mathbf{r}, \mathbf{r}') = -4J^l(\mathbf{r}, \mathbf{r}')$ . We assume that the fluid is bounded by a substrate whose particles interact with the helium 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  $\{p_i^s, p_j^l\}$ ,  $i \in \mathcal{S}$ ,  $j \in \mathcal{L}$  with  $\mathcal{L}$  and  $\mathcal{S}$  denoting the region occupied by the helium and substrate particles, respectively, the energy of the fluid is given by

$$\begin{aligned} \mathcal{E} &= \sum_{i \in \mathcal{S}, j \in \mathcal{L}} w_{i,j}^{l,s} p_i^s p_j^l + \frac{1}{2} \sum_{i,j \in \mathcal{L}} w_{i,j}^l p_i^l p_j^l \\ &= -4 \sum_{i \in \mathcal{S}, j \in \mathcal{L}} J_{i,j}^{l,s} p_i^s p_j^l - 2 \sum_{i,j \in \mathcal{L}} J_{i,j}^l p_i^l p_j^l, \end{aligned} \quad (C1)$$

where  $p_j^l \in \{0, 1\}$  and  $p_i^s \in \{0, 1\}$  denote the occupation numbers for the fluid and substrate particles, respectively. Since only the part  $\{p_j^l\}$  belonging to the fluid becomes critical around  $T_c$  and the fluctuations of the particles  $\{p_j^s\}$  belonging to the substrate are unimportant here, one can replace the latter ones by their mean-field values. If the fluid is in contact with a particle reservoir with a given (excess) chemical potential  $\mu$  and temperature  $T$ , the partition function for the liquid is

$$\begin{aligned} Z &= \sum_{\{p_j^l\}} \exp \left[ -\beta \left( \mathcal{E} - \mu \sum_{j \in \mathcal{L}} p_j^l \right) \right] \\ &= \sum_{\{p_j^l\}} \exp \left[ \beta \left( 4 \sum_{i \in \mathcal{S}, j \in \mathcal{L}} J_{i,j}^{l,s} \rho_i^s p_j^l + 2 \sum_{i,j \in \mathcal{L}} J_{i,j}^l p_i^l p_j^l + \mu \sum_{j \in \mathcal{L}} p_j^l \right) \right], \end{aligned} \quad (C2)$$

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

$$Z = \sum_{\{p_j^l\}} \exp \left[ \beta \sum_{j \in \mathcal{L}} \left( 4 \rho_s \sum_{i \in \mathcal{S}} J_{i,j}^{l,s} + \mu \right) p_j^l + 2 \beta \sum_{i,j \in \mathcal{L}} J_{i,j}^l p_i^l p_j^l \right]. \quad (C3)$$

By modeling the pair potentials as follows:

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

and

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

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

$$\begin{aligned} \sum_{i \in \mathcal{S}_{1/2}} J_{i,j}^{l,s} &= J^{l,s} \sum_{i \in \mathcal{S}_{1/2}} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|^{d+\sigma_s}} = J^{l,s} \sum_{r_1=0}^{\infty} \sum_{r_2=-\infty}^{\infty} \cdots \sum_{r_d=-\infty}^{\infty} \frac{1}{[(z_j + r_1)^2 + r_2^2 + r_3^2 + \cdots + r_d^2]^{(d+\sigma_s)/2}} \\ &\approx J^{l,s} \int_0^{\infty} dr_1 \int_{-\infty}^{\infty} dr_2 \cdots \int_{-\infty}^{\infty} dr_d \frac{1}{[(z_j + r_1)^2 + r_2^2 + r_3^2 + \cdots + r_d^2]^{(d+\sigma_s)/2}} \\ &= J^{l,s} \pi^{(d-1)/2} \frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\sigma_s \Gamma\left(\frac{d+\sigma_s}{2}\right)} z_j^{-\sigma_s}, \end{aligned} \quad (C4)$$

where  $z_j \geq 1$  characterizes the distance of the particle  $p_j$  from the boundary with the half space  $\mathcal{S}_{1/2}$  occupied by the substrate. We consider the fluid particles to be in the region  $0 \leq z \leq L$ , where  $L$  is the width of the film confined between the two surfaces. Therefore, the partition function is

$$Z = \sum_{\{p_j^l\}} \exp \left[ \beta \left( \sum_{j \in \mathcal{L}} \mu_j p_j^l + 2 \sum_{i,j \in \mathcal{L}} J_{i,j}^l p_i^l p_j^l \right) \right], \quad (C5)$$

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  $z_j + 1$ ,  $0 \leq z_j \leq L$ , 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 given by the superposition

$$V(z) = v_s [(z + 1)^{-\sigma_s} + (L + 1 - z)^{-\sigma_s}], \quad (C6)$$

with

$$v_s = -4 \pi^{(d-1)/2} \frac{\Gamma\left(\frac{1+\sigma_s}{2}\right)}{\sigma_s \Gamma\left(\frac{d+\sigma_s}{2}\right)} \rho_s J^{l,s}. \quad (C7)$$

In the current paper we choose such boundary conditions that  $\rho(0) = \rho(L) = 1$ , where  $\rho(z) = \langle p_j^l \rangle$ . This is known as (+,+) boundary conditions. The pressure  $p$  in the fluid as a function of  $\{\mu_j\}$  and  $T$  follows from  $\beta p = |\mathcal{L}|^{-1} \ln Z$ , where  $|\mathcal{L}|$  is the number of lattice sites in the region  $\mathcal{L}$ . The critical properties of this model can be directly derived from the known critical behavior of the corresponding magnetic system that one obtains under the transformation  $m_i = 2p_i - 1$ , where  $m_i \in \{-1, 1\}$ . One arrives at

$$\beta p = \frac{1}{2} \beta |\mathcal{L}|^{-1} \left[ \sum_{j \in \mathcal{L}} \mu_j + \sum_{i,j \in \mathcal{L}} J_{i,j}^l \right] - \beta f, \quad (C8)$$



where  $f$  is the free energy of the magnetic system

$$-\beta f = \ln \sum_{\{m\}} \exp \left[ \sum_{j \in \mathcal{L}} m_j h_j + \frac{1}{2} \sum_{i,j \in \mathcal{L}} K_{i,j} m_i m_j \right], \quad (\text{C9})$$

where

$$K_{i,j} = \beta J_{i,j}^l, \quad \text{and } h_j = \frac{1}{2} \beta \mu_j + \sum_{i \in \mathcal{L}} K_{i,j}. \quad (\text{C10})$$

The mean-field critical properties of the model (C9) are well known. The critical exponents are  $\beta = \nu = 1/2$ ,  $\gamma = 1$  and for the uniform system the critical point is at  $\{h=0, K_c^{-1} = \sum_i K_{i,j}\}$ . At the critical point  $\langle m_i \rangle_c = m_c = 0$ . Thus, for the fluid system we derive that the corresponding critical point is at  $\{K = K_c, \mu = \mu_c\}$ , where  $\mu_c = -2 \sum_{i \in \mathcal{Z}^d} J_{i,j}^l$ , while at this point  $\langle p_i \rangle_c = \rho_c = 1/2$ . With the help of  $\mu_c$  and  $\rho_c$  the corresponding expressions for  $h_j$  can be rewritten in the form

$$\begin{aligned} h_j &= \frac{\beta}{2} (\mu - \mu_c) - \frac{\beta}{2} \left( V_j + 4 \sum_{i \in \mathcal{S}} J_{i,j}^l \rho_c \right) \\ &= \frac{\beta}{2} (\mu - \mu_c) + \beta \frac{2\pi^{(d-1)/2}}{\sigma \Gamma\left(\frac{d+\sigma}{2}\right)} (J^{l,s} \rho_s - J^l \rho_c) \\ &\quad \times [(z_j + 1)^{-\sigma} + (L + 1 - z_j)^{-\sigma}]. \end{aligned} \quad (\text{C11})$$

From Eq. (C11) (see also [34]) one identifies that

$$h_{w,s} = 2\pi^{(d-1)/2} \frac{\Gamma\left(\frac{1+\sigma}{2}\right)}{\sigma \Gamma\left(\frac{d+\sigma}{2}\right)} \beta (\rho_s J^{l,s} - \rho_c J^l). \quad (\text{C12})$$

The equation of the magnetization profile (2.2) also directly follows from Eq. (C9). Denoting  $m_i^* = \langle m_i \rangle$  one obtains

$$m_i^* = \tanh \left[ \sum_j K_{i,j} m_j^* + h_j \right]. \quad (\text{C13})$$

Taking into account that  $\rho_c = 1/2$  one can rewrite  $m_i^*$  in the form  $m_i^* = 2\rho_i - 1 = (\rho_i - \rho_c)/\rho_c$  and, thus Eq. (C13) takes the form

$$\frac{\rho_i - \rho_c}{\rho_c} = \tanh \left[ \sum_j K_{i,j} \frac{\rho_j - \rho_c}{\rho_c} + h_j \right]. \quad (\text{C14})$$

In what follows we take the  ${}^3\text{He}$  or  ${}^4\text{He}$  atoms to be constrained by an Au substrate. Then, according to Refs. [35–37]  $v_s \approx -270 \text{ meV } \text{\AA}^3/r_0^3$ , where  $r_0$  is the distance between the helium atom and the Au surface. We will assume that  $r_0$  is the same as the distance between the  ${}^3\text{He}$  or  ${}^4\text{He}$  atoms (but being different for  ${}^3\text{He}$  and  ${}^4\text{He}$  cases, respectively). It is clear that  $r_0$  provides the scale of the length of the unit cell of the lattice on which we consider the fluid embedded. An estimation of  $r_0$  can be obtained from some general data for  ${}^3\text{He}$  or  ${}^4\text{He}$ . The critical density of  ${}^3\text{He}$  is  $\rho_c \approx 0.01375 \text{ mol/cm}^3 \approx 0.04145 \text{ g/cm}^3$  [38], while for  ${}^4\text{He}$  it is  $\rho_c \approx 0.017399 \text{ mol/cm}^3 \approx 0.0690 \text{ g/cm}^3$  [39,40], wherefrom one easily derives that at the critical point one has  $8.28 \times 10^{27}$  particles/ $\text{m}^3$  for  ${}^3\text{He}$  and

$1.38 \times 10^{28}$  particles/ $\text{m}^3$  for  ${}^4\text{He}$ . This leads to the conclusion that the space “allocated” for one particle is of the order of  $120.77 \text{ \AA}^3$  for  ${}^3\text{He}$  and of the order of  $72.55 \text{ \AA}^3$  for  ${}^4\text{He}$ , i.e., the size of one  ${}^3\text{He}$  atom at the critical point is of the order of  $4.9 \text{ \AA}$  while for  ${}^4\text{He}$  it is  $4.2 \text{ \AA}$ . Thus, for  $v_s$  one has  $v_s \approx -2.3 \text{ meV} \approx -3.68 \times 10^{-22} \text{ J}$  for  ${}^3\text{He}$  and  $v_s \approx -3.6 \text{ meV} \approx -5.82 \times 10^{-22} \text{ J}$  for  ${}^4\text{He}$ . For  $T$  near the critical temperature  $T_c = 3.3 \text{ K}$  of  ${}^3\text{He}$  [38] one has  $k_B T_c \approx 4.55 \times 10^{-23} \text{ J}$  and thus  $\beta \approx \beta_c \approx 2.2 \times 10^{22} \text{ J}^{-1}$  with  $\beta_c v_s \approx -8.1$ . For  ${}^4\text{He}$   $T_c = 5.2 \text{ K}$  [39,40] and therefore  $k_B T_c \approx 7.17 \times 10^{-23} \text{ J}$ ,  $\beta \approx \beta_c \approx 1.4 \times 10^{22} \text{ J}^{-1}$ , and  $\beta_c v_s \approx -8.1$ . Taking into account that the atomic weight of Au is  $196.97 u$ , whereas its density is  $19.3 \text{ g/cm}^3$  and having in mind that the atomic weight of  ${}^3\text{He}$  is  $3 u$  and that the atomic weight of  ${}^4\text{He}$  is  $4 u$  (where  $u = 1.6605 \times 10^{-27} \text{ kg}$  is the atomic mass unit), it is easy to verify that the number density of Au is  $7.1$  times larger than the number density of the  ${}^3\text{He}$  and  $5.7$  times larger than that of  ${}^4\text{He}$  at the critical point of the respective fluid. Since within the mean-field theory, the number density of both  ${}^3\text{He}$  and  ${}^4\text{He}$  at their respective bulk critical points is  $\rho = \rho_c = 1/2$ , we obtain that  $\rho_s \approx 3.55$  for  ${}^3\text{He}$  films and  $\rho_s \approx 2.85$  for  ${}^4\text{He}$  films. As an estimate of  $J^{l,s}$  one immediately derives from Eq. (C7) (for  $d = \sigma_s = 3$ ) the result that  $J^{l,s} \approx 4.95 \times 10^{-23} \text{ J}$  for  ${}^3\text{He}$  and that  $J^{l,s} \approx 9.75 \times 10^{-23} \text{ J}$  for  ${}^4\text{He}$ . Next, neglecting the contribution due to  $J^l$ , i.e., the interaction between the atoms of  ${}^3\text{He}$  and also between the atoms of  ${}^4\text{He}$ , one finds that  $h_{w,s} \approx -\frac{1}{2} \beta_c v_s \approx 4.05$  both for  ${}^3\text{He}$  and  ${}^4\text{He}$  films, i.e., the surface field is, indeed, relatively large and cannot be neglected.

Next, we justify the approximation made for  $J^l$ . Within the mean-field approximation we have  $\beta_c J^l = 0.160$ . Thus, from the experimentally known value of  $\beta_c$  we conclude that  $J^l \approx 7.3 \times 10^{-24} \text{ J}$  for  ${}^3\text{He}$  and  $J^l \approx 1.14 \times 10^{-23} \text{ J}$  for  ${}^4\text{He}$ . Note that these estimates are very close to those based on the general expectation that  $k_B T_c \sim J^l$ , which leads to  $J^l \sim 10^{-23} \text{ J}$ . Therefore,  $J^{l,s}/J^l \approx 6.6$  for  ${}^3\text{He}$  and  $J^{l,s}/J^l \approx 8.5$  for  ${}^4\text{He}$ , i.e., the interactions of the atoms of  ${}^3\text{He}$  and  ${}^4\text{He}$  with the Au substrate are much stronger than the interactions between themselves. If, nevertheless, one insists on taking these interactions into account a simple calculation shows that  $h_{w,s}$  changes from  $h_{w,s} = 4.05$  to  $h_{w,s} = 3.96$  for  ${}^3\text{He}$  and from  $h_{w,s} = 4.05$  to  $h_{w,s} = 3.97$  for  ${}^4\text{He}$ . Summarizing, one can conclude that the surface field has almost the same value for both the  ${}^3\text{He}$  and  ${}^4\text{He}$  films bounded by Au surfaces, and thus one can predict that the finite-size behavior of their finite-size susceptibilities for a given fixed  $L$  will be practically indistinguishable for both fluids.

We finish this appendix by briefly commenting on the correlation length amplitudes for the correlation lengths

$$\xi_i(T) \equiv \xi_{\infty}(T \rightarrow T_c^{\pm}, h = 0) \approx \xi_0^{\pm} |t|^{-\nu}$$

and

$$\xi_h(h) \equiv \xi_{\infty}(T_c, h \rightarrow 0) \approx \xi_{0,h} |h|^{-\nu/\Delta}.$$

One can show that in the case of a van der Waals fluid-fluid potential the amplitude  $\xi_0^{\pm}$  of the second moment correlation length is [34]

$$\xi_0^+ = \left[ \frac{\frac{1}{2d} \sum_{\mathbf{r}} \frac{r^2}{1+r^{d+\sigma}}}{\sum_{\mathbf{r}} \frac{1}{1+r^{d+\sigma}}} \right]^{1/2}. \quad (\text{C15})$$

Furthermore one has

$$\xi_0^- = \xi_0^+/\sqrt{2} \quad \text{and} \quad \xi_{0,h} = \xi_0^+/\sqrt[3]{3}. \quad (\text{C16})$$

The numerical evaluation of the sum (C15) for  $d=\sigma=3$  in the case of a simple cubic lattice then gives  $\xi_0^+=0.635 a$ . Taking into account that, as we derived above,  $a=4.9 \text{ \AA}$  for  ${}^3\text{He}$  and  $a=4.2 \text{ \AA}$  for  ${}^4\text{He}$  we obtain that  $\xi_0^+=3.11 \text{ \AA}$  for  ${}^3\text{He}$  and that  $\xi_0^+=2.67 \text{ \AA}$  for  ${}^4\text{He}$ . Of course the procedure used to

calculate the above numbers constitutes a very strong approximation and one shall not expect to reproduce the best known values of these quantities. Nevertheless, the comparison with the known data reported in the literature  $\xi_0^+=2.71 \text{ \AA}$  [26,41] for  ${}^3\text{He}$ , and  $\xi_0^+=2.0 \text{ \AA}$  [42] for  ${}^4\text{He}$ , shows that the above results are not too bad. One straightforward way to improve the above approximation is to consider the fluid imbedded not on a simple cubic but on a body centered cubic lattice which is probably ‘‘closer’’ to the reality since then the atoms are more closely packed. For such a lattice we obtain  $\xi_0^+=0.574 a$ , and thus  $\xi_0^+=2.811 \text{ \AA}$  for  ${}^3\text{He}$ , and  $\xi_0^+=2.409 \text{ \AA}$  for  ${}^4\text{He}$ . These results are indeed essentially close to the ones obtained by using much more elaborate methods [26,41,42].

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- [23] For the bulk susceptibility in the presence of van der Waals type interactions, one has [24]
- $$\chi_{\text{bulk}}(t, h) = \chi_{\text{bulk, sr}}(t, h) + \chi_{\text{bulk, lr}}(t, h),$$
- where [24–26]
- $$\chi_{\text{bulk, sr}}(t \rightarrow 0, h = 0) = \Gamma^\pm |t|^{-\gamma} [1 + \Gamma_1^\pm |t|^\theta + \Gamma_2^\pm |t|^{\theta_2} + \Gamma_{1,2}^\pm |t|^{\theta_2} + \Gamma_{\gamma, \alpha}^\pm |t|^{\gamma-\alpha} + \dots],$$
- and
- $$\chi_{\text{bulk, lr}}(t \rightarrow 0, h = 0) = \Gamma^\pm |t|^{-\gamma} [\Gamma_{\text{lr}}^\pm |t|^{\theta} (\ln |t|)^{-\sigma}].$$
- Here  $\theta_2 \approx 0.90$  [27] is the second Wegner exponent, while  $\theta_\sigma \equiv \nu(\sigma - 2 + \eta) \approx 0.65$  is the corresponding exponent due to the long-range tail of the van der Waals interaction. Note that  $\theta_\sigma$  is only slightly larger than the dominant Wegner term for the Ising universality class. Apart from the logarithmic corrections [of the predicted type  $\sim (\ln |t|)^\sigma$ ] the existence of such a correction to the scaling bulk term has been confirmed within the exactly solvable spherical model [13]. The logarithmic term ( $\sim \ln |t|$ ) has been observed, however, only for  $d + \sigma = 6$ . In [18], it has been demonstrated that such a term is a peculiarity of the model which is due to the degeneracy, within this model, of the exponents  $\omega = 4 - d$  and  $\omega_\sigma \equiv \theta_\sigma / \nu = \sigma - 2$  (when  $d + \sigma = 6$ ). Thus, for an Ising like system with subleading van der Waals type long-range interactions we expect that
- $$\chi_{\text{bulk, lr}}(t \rightarrow 0, h = 0) = \Gamma^\pm |t|^{-\gamma} [\Gamma_{\text{lr}}^\pm |t|^{\theta_\sigma}].$$
- As far as we are aware, no experimental verification of such type bulk correction to scaling has been reported in the available literature.
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- [28] In a fluid system the density is the quantity that couples via the van der Waals type interaction. The average local density is nonzero both below and above the critical point, whereas in a magnetic system  $m_0(T > T_c, H=0) = 0$ . Because of this, there exists a difference in the finite-size behavior of the fluid and the magnetic systems when  $T > T_c$ . One can argue that for a magnetic system in which  $T > T_c$  and  $h=0$  [29]

$$\chi = \chi_{\text{bulk}} + \frac{1}{L} \chi_{\text{surface}} + \frac{1}{L^{\sigma+1}} \tilde{\chi} + \dots$$

Eq. (1.8) is again valid below  $T_c$ .

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