

Solvation Forces in Near-Critical Fluids. Ising Model Results*

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Recent developments in the statistical theory of simple fluids in a film geometry near bulk criticality is reviewed. We summarize results obtained by exact or approximate, but very accurate methods within Ising model. Particular attention is paid to the properties of the measurable solvation force and its relation to the structure of the confined system, in the Ising model given by magnetization profiles. Relevance of the reviewed results for various physical systems is briefly discussed.

Key words: confined fluids, critical phenomena, Ising model

I. INTRODUCTION

Simple fluids or binary fluid mixtures near criticality belong to the universality class of the Ising model. If one exploits the mapping between a fluid and the Ising model, then all the universal properties of a fluid, such as critical exponents or scaling functions for various quantities, can be calculated within this very simple model. The Onsager exact solution of the two dimensional ($d = 2$) Ising model allowed to verify general predictions of the theory of critical phenomena by explicit results. However, this solution is limited to $d = 2$ and to the case of vanishing bulk magnetic field H [1]. Other approaches, such as series expansions or Monte Carlo simulations, can account for the bulk magnetic field and higher dimension but they are not always accurate enough to infer reliable conjectures [2,3].

In the last few years a considerable progress has been made in developing a technique of approximate but very accurate calculations in $d = 2$ Ising model with an external field. The density-matrix renormalization-group (DMRG) technique [4] is based on the transfer-matrix approach and provides a very efficient algorithm for construction of the *effective* transfer matrices for large systems; the effective transfer matrix is then diagonalized numerically. DMRG method was originally introduced to study the ground state of quantum spin chains [5] and then was extended to study equilibrium properties of two-dimensional classical lattices [6]. Comparisons with the exact solutions show that for the case of vanishing bulk magnetic field this

* Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

method is very accurate in a wide range of temperatures, also near the bulk critical temperature T_c [7,8]. In principle the DMRG method should work equally well in the presence of an arbitrary external field. Therefore, only recently the verification of predictions of the theory of critical phenomena for two-dimensional systems in the presence of a bulk field became possible. Despite the limitation to two dimensions the DMRG results provide a valuable insight into the structure of the scaling functions.

Whereas for the bulk system the theory of critical phenomena is very well established, the theory of confined fluids near bulk criticality is far from being complete. As follows from the finite-size scaling theory [9], the confinement results in shifting and/or rounding of the bulk critical point. On the other hand, the presence of a surface leads to spatial variations of the order parameter, which entails new surface critical exponents; the theory of surface critical phenomena predicts fundamentally different surface universality classes depending on the type of a surface [10]. The near-critical properties of a particular confined system follow from combined effects of the finite size and specific walls-fluid interactions. The main difficulties for the theory arise from the fact that these combined effects lead to many new phenomena, which in turn may influence each other. For example, in the case of strongly adsorbing walls the phenomenon of capillary condensation takes place away from the bulk coexistence [11] (in the Ising model, which is equivalent to the lattice-gas model of a fluid, capillary condensation takes place for nonvanishing magnetic field). On the other hand, near the bulk critical point, the Casimir effect arises [12]. The properties of the confined fluid for temperatures between the bulk critical temperature and the critical temperature associated with the capillary condensation are very special. The fluid is simultaneously in a critical region of two different critical points, located close to each other and the capillary condensation can influence the Casimir effect significantly. It is more difficult to develop a theory of crossover phenomena, since it is not clear a priori which degrees of freedom are irrelevant, and typically it is not justified to make simplifying assumptions as in the bulk theories. In the case of no reliable general predictions, the role of accurate results obtained in a model system is invaluable. Only recently, thanks to the finite-size version of the DMRG method applied to the $d = 2$ Ising model in a strip geometry with arbitrary surface and bulk magnetic fields, a significant progress has been made in understanding the confined near-critical fluids. We stress that properties of confined fluids are of a broad interest; fluids in porous media are important for various applications. Also there is a need to understand the rich variety of phenomena observed experimentally for fluids adsorbed in porous solids as Vycor, silica gels or carbon powders. For physics of colloids there is also a fundamental issue of how a fluid confined between two colloid particles influences the effective force between them.

In this review we summarize the recent results for the confined near-critical fluids obtained within the $d = 2$ Ising model in a strip geometry. Emphasis is placed on the effective force between the confining walls (the excess pressure induced by the confinement), as this quantity can be measured in real fluids using the atomic force

microscope (AFM) or the surface force apparatus (SFA) [13]. Recent results show the rich variation of the fluid-mediated part of the excess pressure, called the solvation force, when the thermodynamical variables are shifted away from the critical point either in temperature [14], or in magnetic field [15], or in both, the temperature and the magnetic field [16]. We compare all the cases studied so far and try to draw general conclusions concerning the relation between the strength of the solvation force and the structure of the confined fluid. The expected behavior in $d = 3$ and the possible relevance of these results for the experiment and for the behavior of systems other than simple fluids is mentioned briefly.

II. THERMODYNAMICS FOR A CONFINED FLUID

Consider a confined simple fluid, which is in contact with a reservoir at fixed chemical potential μ and temperature T (Fig. 1). In addition to the bulk term, the grand thermodynamical potential of confined fluid has an extra contribution, due to the presence of the confining walls of a surface area A a distance L apart:

$$\Omega = -pV + \Omega_{exc} \quad (1)$$

In the above p is the bulk pressure and V is the volume occupied by the fluid. For a slit geometry an increment in the grand potential is given by

$$d\Omega = -SdT - Nd\mu - pdV + 2\sigma dA - fAdL \quad (2)$$

where σ is the wall-fluid surface tension, and fA is the force, which has to be applied externally to keep the walls at the distance L . The presence of two extra thermodynamic fields A and L leads to many new phenomena [11]. We concentrate on two effects relevant for our study: the phenomenon of capillary condensation and the excess pressure in the confined fluid.

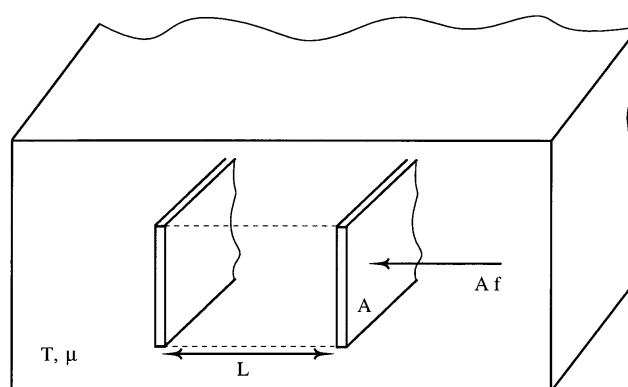


Figure 1. System of two substrates of surface area A , repelling with the force Af .

A. Capillary condensation: Consider a simple fluid in a gas phase, close to the bulk coexistence with the liquid, confined between two strongly adsorbing walls. For sufficiently large L , the last term in (2) can be neglected. If the liquid phase is metastable in the bulk and the walls are strongly adsorbing, then $\omega_b^l > \omega_b^g$, whereas $\sigma^l < \sigma^g$. Here ω_b^i is the bulk Ω per unit volume and the superscripts l, g refer to the liquid and the gas phase respectively. For sufficiently small L , such that

$$L \leq \frac{2(\sigma^g - \sigma^l)}{\omega_b^l - \omega_b^g} \quad (3)$$

$\Omega^l \leq \Omega^g$, *i.e.*, the dense phase becomes stable and the dilute phase becomes metastable between the strongly adsorbing walls. The first-order transition in the confined fluid is termed capillary condensation and is described by the Kelvin equation, following directly from (3) within standard thermodynamics

$$\Delta\mu_{co} = \frac{2(\sigma^g - \sigma^l)}{L(\rho^l - \rho^g)} \quad (4)$$

$\Delta\mu_{co}$ is the chemical potential deviation from the value corresponding to the bulk phase-coexistence and ρ^l, ρ^g are the bulk densities of the respective coexisting phases. Since for different temperatures T the parameters assume different values, $\Delta\mu_{co}$ depends on temperature. The capillary condensation line terminates at the (capillary condensation) critical point (μ_{cL}, T_{cL}) , whose position on the (μ, T) phase space depends on L and on the wall-fluid interaction [17].

B. Solvation force: As already mentioned above, finite-size contributions to the grand thermodynamic potential of a fluid, confined between two parallel walls separated by a distance L , give rise to a force per unit area, f , between the walls; it can be expressed as a pressure difference [11]:

$$f = -(1/A) \left(\frac{\partial \Omega}{\partial L} \right)_{\mu, T, A} - p \quad (5)$$

where p is the pressure of the bulk fluid in the reservoir. Clearly, $f(L) \rightarrow 0$ when $L \rightarrow \infty$. The excess pressure $f(L)$ has two contributions: a force arising from a direct interactions between the material of two confining walls and the indirect force associated with the fluid-fluid and wall-fluid interactions. The latter, called the solvation force, depends on the thermodynamic state of a fluid, *i.e.* on (μ, T) . $f(L)$ can be measured directly with the AFM or the SFA, although the geometry used in these techniques is not that of parallel walls. A suitably adapted AFM can measure the force between a silica surface mounted on the cantilever tip of the AFM and a flat surface of a sample im-

mersed in a fluid [18]. The SFA measures the solvation force for a liquid contained between crossed mica cylinders [13]. Both techniques provide high force and spatial resolutions.

Solvation force is relevant for fluid phase equilibria in confined systems, therefore, its features have been studied intensively, both theoretically, mostly in mean-field (lattice or Landau or density functional theory) and experimentally, since early eighties [11]. It has been found that for simple fluids, confined by identical walls, the solvation force is attractive for large separations, *i.e.*, $f_{solv}(L) < 0$ for large L . $f_{solv}(L)$ decays exponentially for $L \rightarrow \infty$. At small wall separations $f_{solv}(L)$ can oscillate, reflecting the same packing effects, which give rise to highly structured density profiles. Solvation force is also a good order parameter; it jumps at the first-order capillary condensation phase transition [17]. At fixed large L and fixed temperature, below the capillary condensation critical temperature T_{cL} , $f_{solv}(L)$ should change abruptly from values appropriate to a “gas” phase, f_{solv}^g , to a value appropriate to a dense “liquid” phase, f_{solv}^l . Macroscopic arguments, valid for wide slits, lead to the following approximations for the force in both phases [17]:

$$f_{solv}^l(\mu, L) \approx -\Delta\mu(\rho_l - \rho_g) \quad (6)$$

and

$$f_{solv}^g(\mu, L) \approx 0 \quad (7)$$

These approximations imply the jump

$$\Delta f_{solv} \equiv f_{solv}^l - f_{solv}^g \sim -\Delta\mu_{co}(\rho_l - \rho_g) \quad (8)$$

Criticality in a confined system is associated with vanishing of Δf_{solv} . The Kelvin equation (4) implies that the magnitude of the jump should decrease in the same fashion as the interfacial tension as T increases at fixed L :

$$\Delta f_{solv} \approx -2\sigma(T)/L \quad (9)$$

where $\sigma(T)$ is the interfacial tension between coexisting “gas” and “liquid” phases. At the capillary condensation critical point f_{solv} exhibits a singular behavior, *i.e.*, $(\partial f_{solv}/\partial L)_{\mu, T}$ and $(\partial^2 f_{solv}/\partial L^2)_{\mu, T}$ diverge at (μ_{cL}, T_{cL}) .

More recently, the properties of the solvation force near *bulk* criticality received a lot of attention in connection with the, so called, Casimir effect. The finite-size scaling theory predicts that at the bulk critical point of a fluid the solvation force becomes long-ranged as a result of critical fluctuations [19], a phenomenon which is a direct ana-

log of the well-known Casimir effect in electromagnetism [20]. The existence of the long-ranged critical Casimir force should be common to all systems, characterized by fluctuating quantities with external constraints [12]. As yet, there has been no direct, unambiguous experimental verification of the critical Casimir effect in fluids [12], although recent experiments do provide indirect evidence for its existence [21]. One of the difficulties is that the predicted leading power law decay of the Casimir force at bulk criticality

$$f_{\text{solv}}(L) \sim k_B T_c A_{12} (d-1) L^{-d} \quad \text{as} \quad L \rightarrow \infty \quad (10)$$

is for (bulk) spatial dimension $d=3$, of the same form as the force arising from dispersion forces. Moreover, in many systems the amplitude may be much smaller than the corresponding Hamaker constant [12,22]. The Casimir amplitude, A_{12} , is a universal number for fixed boundary conditions, *i.e.* for particular type of the walls. However, its value depends on the surface universality classes of the confining walls [12]. In this review we will be concerned with two surface universality classes [10]: the ordinary and the normal transition. In the first case, the surface suppresses the order parameter with the result that the system undergoes a second-order phase transition in the presence of a disordered phase at the surface. The normal transition is the most relevant for experiments on pure fluids or for binary mixtures, and occurs when the surface orders as a result of an external field. A considerable amount of effort has been spent to calculate the value of the Casimir amplitude for different boundary conditions [12,22] not only because A_{12} is a universal number that governs the asymptotic ($L \rightarrow \infty$) behavior of the solvation force, but also due to the common belief that the solvation force in critical fluids is the strongest at the critical point. Indeed, since the bulk fluctuations in fluids are of the largest extent at the critical point, one may expect that the effect of the external constraints, such as the confining walls should be the largest exactly at the critical point and moreover it should be independent of the kind of the external walls. However, explicit results obtained in the Ising model show that the solvation force is much stronger, in some cases two orders of magnitude, for states which lie slightly *off bulk criticality*, as we discuss in detail below.

III. FINITE-SIZE SCALING HYPOTHESIS

Consider a fluid confined in a slit of a width L and subject to the surface fields. The density profile can be described as a function of the distance from the left wall, $\rho(z/L)$, with the distance defined as a fraction of the whole width, $0 \leq z/L \leq 1$. When L is increased to L_1 at the same thermodynamic state, the shape of the density profile $\rho(z/L_1)$ is different. It is because in general there are other important length scales, describing the shape of the profile. For example, near the wall the density varies on the length scale of the bulk correlation length $\xi_b(T, \mu)$. The correlation length shows the distance from the wall up to which the density of a fluid is influenced by the wall. It is

because the presence of the wall may be viewed as a perturbation of the fluid, which extends up to distances $\sim \xi_b$. Far from the critical point $\xi_b(T, \mu)$ is of a molecular size. For sufficiently wide slits, the shape of the density profile near each wall is the same on the molecular length scale for various widths of the slit. However, when $L \rightarrow L_1$, then for the same fraction of the film width the density in the two films is different. In the critical region, the bulk correlation length increases on approaching the critical point and at the critical point diverges. Again, if the shape of the density profile near each wall is determined by the bulk correlation length, changing the film width without changing $\xi_b(T, \mu)$ leads to a different shape of the profile $\rho(z/L_1)$. Suppose now that together with the change $L \rightarrow L_1$ we simultaneously change all the relevant length scales, such that the ratios between them and the width of the film remain the same. For example, $\xi_b(T, \mu) \rightarrow \xi_b(T_1, \mu_1)$ such that $L/\xi_b(T, \mu) = L_1/\xi_b(T_1, \mu_1)$. This is possible in the critical region, where the molecular length scale, fixed once and for ever, is irrelevant. The remaining length scales, particularly the bulk correlation length, depend on the thermodynamical state which can be varied. When all the relevant length scales are simultaneously increased by the same factor, then for $z/L = z_1/L_1$ we obtain $\rho(z/L)/\rho(z_1/L_1) = \text{const}$. This is because the whole system is uniformly expanded. The magnitude of the density changes when the thermodynamic state is varied, therefore, the whole profile is rescaled under the uniform increase of all the length scales.

The above scaling hypothesis [1] leads to a prediction that the density profile is proportional to a scaling function, with the distance measured in either length scale, for example L or ξ_b . The remaining arguments of the scaling function are the ratios of the chosen length scale and the other relevant length scales. Hence, the scaling function describes in fact a whole family of the density profiles for various ratios of the relevant length scales. The proportionality constant is determined by the thermodynamical state and relates the magnitude of the density in the slit to the bulk density. Similar scaling occurs for other physical quantities. The relevant length scales are associated with all the scaling fields relevant for the critical behavior. We define the relevant length scales and write the formal expressions following from the scaling hypothesis after defining the Ising model.

IV. ISING MODEL IN A FILM GEOMETRY

In simple fluids or in binary fluid mixtures the tendency for ordering at the boundary layers is decreased due to the missing neighbors beyond the boundary of the fluid. At the same time, the walls of the container interact directly with the fluid and this interaction can be modeled by surface fields, which in different systems can be of different strength and range. The theory of bulk critical phenomena [1] says, that all the microscopic length scales are irrelevant for the universal critical behavior. The only relevant length scale is the (macroscopic) bulk correlation length. Accordingly, a simple fluid in a slit in a critical region can be described by the lattice-gas model in a film geometry with strictly short-range interactions and the interactions between the

walls and the molecules of the system can be modeled by strictly short range (“contact”) interactions.

The lattice gas model can be mapped onto the Ising ferromagnet, when the site occupied by the particle is mapped onto spin up and the empty site onto spin down. The lattice consists of L parallel lattice layers at spacing $a \equiv 1$, so that the distance between the layers is $\mathcal{N} = La$. Each layer has A sites, labeled i, j, \dots , and at each site there is an Ising spin variable taking the value $\sigma_i = \pm 1$. We assume only nearest-neighbor interactions of strength J and a Hamiltonian of the form:

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - H \sum_i \sigma_i - H_1 \sum_i^{(1)} \sigma_i - H_L \sum_i^{(L)} \sigma_i \quad (11)$$

where the first sum runs over all nearest-neighbor pairs of sites, while the last two sums run respectively over the first and the L -th layer. H is a bulk field and H_1 and H_L are the surface fields. We assume that both surface fields lead to preferential adsorption of the positively magnetized bulk phase on the inner surfaces of the film (*i.e.* $H_1 = H_L > 0$) and that the bulk field favors the opposite *i.e.* negatively magnetized bulk phase. We take $H_1 = H_L = h_1 J$, with $h_1 > 0$. The film has the finite width \mathcal{N} , but we will take the two-dimensional thermodynamic limit $A \rightarrow \infty$. If one approximates the fluid by a lattice gas model then the equivalence between lattice gas and the Ising model follows as usual: the bulk magnetic field H of the former is proportional to the deviation of the chemical potential from the bulk phase boundary $\mu_c(T)$ in the latter *i.e.* $H \sim \mu - \mu_c(T)$. The lattice-gas model analog of the density in the fluid is related to the magnetization by $\rho = (m + 1)/2$.

A. Criticality in films: According to the scaling hypothesis, near criticality various physical quantities should obey scaling [1,23]. In the Ising system the scaling fields, describing the deviation from the bulk criticality are: the reduced deviation from the critical temperature $\tau = (T - T_c)/T_c$ and the bulk magnetic field H . In the presence of a wall there is an additional field, namely the surface field H_1 . H_1 describes the crossover between the ordinary $H_1 = 0$ and the normal $H_1 \rightarrow \infty$ transitions, related to the nonadsorbing and to the strongly adsorbing walls respectively. The length scales related to the above scaling fields are: $l_\tau \propto \tau^{-\nu}$, $l_H \propto H^{-\nu/\Delta}$ and $l_1 \propto H_1^{-\nu/\Delta_1}$, where ν , Δ and Δ_1 are the critical indices [10]. The bulk correlation length ξ_b reduces to l_τ in the case of $H = 0$, and to l_H in the case of $\tau = 0$. The remaining length scale, l_1 , describes the distance from the wall up to which the system responds linearly to a weak surface field H_1 at bulk criticality. Although at the critical point the system no longer responds linearly to the external field, the boundary layer remains paramagnetic for $H_1 \rightarrow 0$. This is due to the missing neighbors, which cause the effective interaction per spin at the boundary layer weaker than in the bulk. The paramagnetic phase at the boundary layer does not abruptly change into the critical system in the subsequent layers, but rather extends smoothly to the distance $\sim l_1$ from the wall [24].

In confined systems the finite size L becomes another relevant length scale. The combined effect of L and l_1 modifies the bulk critical behavior. For the Ising film, that is of infinite extent in $d - 1$ dimensions parallel to the walls, true criticality can occur provided $d - 1 \geq 2$ – the lower critical dimension of the corresponding bulk system. Criticality for finite L lies in the universality class of the bulk $d - 1$ system. The location of the critical point in the (T, H) phase space depends on the type of surfaces.

(a) $H_1 = H_L = 0$. In films with free boundaries the Ising symmetry dictates two-phase coexistence to be at $H = 0$. For $d \geq 3$ and large but finite L , a line of coexistence ends at the critical temperature $T_c(L) < T_c$. Finite-size scaling [9] predicts the following expression for the shift of the critical temperature:

$$(T_c(L, H_1) - T_c)/T_c \approx -L^{-1/\nu} X_c(H_1 L^{\Delta_1/\nu}) \quad (12)$$

where the scaling function $X_c(w)$ reduces to the amplitude $X_c(0)$ for $H_1 = 0$.

(b) $H_1 = H_L > 0$. In this case the phenomenon similar to the capillary condensation takes place, when the bulk magnetic field $H < 0$ favours negatively magnetized phase, whereas the surface fields H_1, H_L favour the positively magnetized phase. The “capillary condensation” of the positively magnetized phase in the film is described by the analog of the Kelvin equation (4):

$$-H_{co}(T) \approx \sigma(T)/Lm^*(T) \quad (13)$$

where $\sigma(T)$ is the interfacial tension between the coexisting (+) and (–) phases and $m^*(T) > 0$ is the bulk spontaneous magnetization. The presence of thick wetting films of + spin in the (–) phase gives rise to non-trivial corrections, which shift the condensation line to larger values of $|H|$ [27], nevertheless the Kelvin equation does predict the correct qualitative behavior of the condensation line at low temperatures. The two phase coexistence ends in a (capillary) critical point (H_{cL}, T_{cL}) . $T_{cL}(H_1)$ lies below the temperature of the bulk critical point T_c . The expression for the temperature shift is given by (12) and the similar form holds for $\Delta H_c \equiv H_c(L, H_1)$ [25]:

$$\Delta H_c \approx -L^{-\Delta/\nu} Y_c(H_1 L^{\Delta_1/\nu}) \quad (14)$$

In $d = 2$ Ising films the situation is similar. Although there can be no true phase transition for finite L , *i.e.*, nonanalytic behavior of the free energy, specific heat, *etc.* is rounded forming maxima, there is still a line of sharp (very weakly rounded) first-order transitions [26,28]. The rounding in H or in T is expected to be proportional to $L^{-3/2} \exp(-L\sigma/k_B T)$, where σ is the surface tension between coexisting bulk phases [29]. The pseudocoexistence field $H_{co}(L)$ can be identified with the maximum $H_0(T)$ of the free energy $f(H)$ at fixed L, T , and H_1 [16,28]; $H_0(T)$ calculated for $L = 200$

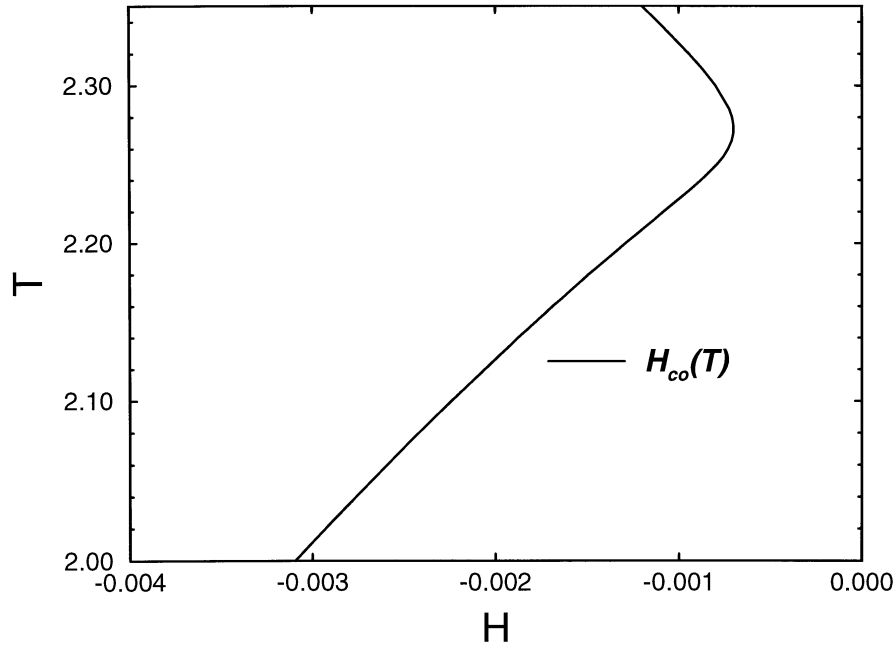


Figure 2. Pseudocoexistence line $H_{co}(T)$ (solid line) for the $d = 2$ Ising strip of width $L = 200$, surface fields $H_1 = H_2 = 10$ (normal transition).

and $H_1 = 10$ in [16] is shown in Fig. 2. Determining the pseudocritical temperature needs additional criteria, since the line $H_0(T)$ continues above T_c .

B. Finite-size scaling in the $d = 2$ Ising film: (a) Magnetization profiles. The magnetization profile in the $d = 2$ Ising film is defined as

$$m(z) \approx m_l \equiv \langle \sigma_l \rangle, \quad z \approx la \equiv l \quad (15)$$

where σ_l denotes a typical spin in the l th row (with $l = 1, 2, \dots, L$) corresponding to a perpendicular distance z ($0 \leq z \leq L$) from the first wall. The magnetization profile can be written in two equivalent scaling forms, each form suitable in different thermodynamic conditions:

$$m(z; L, \tau, H, H_1) \approx |\tau|^\beta M_\tau^\pm \left(\frac{z}{L}; R_\tau, R_H, R_{H_1} \right) \quad (16)$$

$$m(z; L, \tau, H, H_1) \approx |H|^{\beta/\Delta} M_H^\pm \left(\frac{z}{L}; R_\tau, R_H, R_{H_1} \right) \quad (17)$$

where

$$R_\tau = L|\tau|^\nu, \quad R_H = L|H|^{v/\Delta}, \quad R_{H_1} = L|H_1|^{v/\Delta_1} \quad (18)$$

are ratios between the width of the film and the length scales associated with τ , H and H_1 respectively. M_τ^\pm and M_H^\pm are universal scaling functions for the positive and the negative values of the scaling fields τ and H respectively. Their form is the same in any system belonging to the Ising universality class up to the nonuniversal metric factors. For $\tau \neq 0, H \neq 0$, either form of the scaling is appropriate. The (16) is suitable for $\tau \neq 0, H = 0$, whereas, the other one, (17) – for $\tau = 0, H \neq 0$. At criticality, $\tau = H = 0$, only two length scales, L and l_1 remain, and the scaling takes either one of the two forms

$$m(z; L, \tau = 0, H = 0, H_1) = z^{-\beta/\nu} \mathcal{M}_c \left(\frac{z}{L}; R_{H_1} \right) \quad (19)$$

or equivalently

$$m(z; L, \tau = 0, H = 0, H_1) = L^{-\beta/\nu} \mathcal{N}_c \left(\frac{z}{L}; R_{H_1} \right) \quad (20)$$

where \mathcal{M}_c and \mathcal{N}_c are universal scaling functions.

(b) Solvation force. The free energy per site of the $d = 2$ Ising film with two surface fields $H_1 = H_L$ can be written for large L as

$$f(L, T, H, H_1) = f_b + 2f_w/L + f^*(L)/L \quad (21)$$

where f_b is the bulk free energy, f_w is the L -independent surface contribution from each wall, and f^* is the finite-size correction to the free energy. The latter vanishes for $L \rightarrow \infty$. Such a term gives rise to the generalized force, which is analogous to the solvation force (5) between the plates in confined fluids [11]

$$f_{solv} = -(\partial f^*/\partial L)_{H, T, H_1} \quad (22)$$

From the general theory of critical finite-size scaling [9] it follows that the solvation force should scale

$$f_{solv} \approx L^{-2} F(R_\tau, R_H, R_{H_1}) \quad (23)$$

At fixed points $\tau = 0, H = 0$ and $R_{H_1} = 0$ or $R_{H_1} = \infty$ the scaling function F reduces to $F(0, 0, 0) = \mathcal{A}_{00} k_B T_c (d-1)$ or $F(0, 0, \infty) = \mathcal{A}_\infty k_B T_c (d-1)$, where \mathcal{A}_{00} and \mathcal{A}_∞ are universal Casimir amplitudes. Within the scaling hypothesis it is not possible to determine the shape of the scaling function for finite τ, H, H_1 . The renormalization group theory

also does not allow for finding the scaling functions with sufficient accuracy. The reliable results for the universal scaling function $F(R_\tau, R_H, R_{H_1})$ could only be obtained from exact solutions, which are mainly restricted to two-dimensional systems at vanishing bulk field, or by very accurate, approximate method. The available results in the $d = 2$ systems will be described in the next section.

V. RESULTS FROM THE EXACT AND THE DMRG METHOD CALCULATIONS

Existing results for the Casimir amplitudes and for the scaling function of the solvation force show that these quantities crucially depend on the surface universality classes of the confining walls. For the Ising model in two dimensions there exist only two surface universality classes (a) the ordinary transition $H_1 = 0$, and (b) the normal transition $H_1 \neq 0$, since the boundary is one-dimensional. Thus, for identical walls there are two possibilities: (a) nonadsorbing walls $H_1 = H_L = 0$ and (b) adsorbing walls $H_1 = H_L \neq 0$.

A. Nonadsorbing walls: (a) Temperature dependence of the solvation force at $H = 0$. In the case of free boundary conditions, $H_1 = H_L = 0$ (ordinary transition) and in vanishing bulk field $H = 0$, *i.e.*, when a fluid is at the critical density or a binary liquid mixture is at the critical composition, f_{solv} as a function of temperature attains a pronounced minimum *below* the bulk critical temperature T_c . This behavior was concluded from the fact that for free boundaries the scaling function of the solvation force at vanishing bulk magnetic field satisfies [14].

$$F_{00}(-R_\tau) = F_{++}(R_\tau) \quad (24)$$

where $F_{00}(R_\tau) \equiv F(R_\tau, 0, 0)$ and where $F_{++}(R_\tau) \equiv F(R_\tau, 0, \infty)$ is the scaling function for strips with fixed boundary conditions (+/+) (normal transition). It follows that in $d = 2$ the Casimir amplitude for free boundary conditions is the same as for (+/+). These amplitudes were calculated exactly using conformal invariance [30]: $\mathcal{A}_{00} = \mathcal{A}_{++} \equiv \mathcal{A}_\infty = -\pi/48$. At the minimum the amplitude of the scaling function is about 6.6 times the Casimir value. The minimum of F_{00} occurs at $R_\tau = -1.26$, *i.e.*, when the bulk correlation length $\xi_b \equiv \xi(H = 0, \tau) \equiv \mathcal{A}_\tau l_\tau$ becomes comparable to the half of the film width $L \sim 2.23\xi_b$. The result that the minimum of the solvation force lies below T_c was explained by the fact that in a film with free boundaries the critical point is shifted to $T_{cL} < T_c$. Thus, it might be expected that the minimum of $F_{00}(R_\tau)$ should be located at $H = 0$ and near $T = T_{cL}$ rather than at T_c [14]. In $d = 2$ films there is no true criticality but the minimum should lie near the pseudocritical point, which is also shifted below T_c .

(b) Bulk field dependence of the solvation force at $T = T_c$. The renormalization group theory predicts that near the critical point the “magnetic” scaling field $l_H \propto H^{\nu/\Delta}$ is equivalent to the “temperature” scaling field $l_\tau \propto \tau^{-\nu}$. Therefore, the behavior of the solvation force as a function of H at $T = T_c$ should be analogous to the behavior of f_{solv} as a function of the temperature at $H = 0$. The results of the DMRG calculations con-

firmed this expectation [15]. $f_{solv}(H)$ attains a pronounced minimum at some small value $H_{min} < 0$ (see Fig. 3). A new feature is the evenness of the scaling function $F_{00}(R_H) \equiv F(0, R_H, 0)$, which is expected from the symmetry properties of the Ising film with free boundaries. This means that the solvation force has a second, symmetric minimum located at $H_{min} > 0$. Locations of the extrema of the solvation force is consistent with the case (a), *i.e.*, the minima occur when $R_H \approx 1.12$, *i.e.*, when $L \approx 2.88\xi_b$, but now the bulk correlation length is of “magnetic” origin, *i.e.*, $\xi_b \equiv \xi(H, \tau = 0) \equiv \mathcal{A}_H l_H$. The extremum of $f_{solv}(H)$ as a function of the field H at $T = T_c$ is weaker than the extremum of the function $f_{solv}(T)$ at $H = 0$; the value of $F_{00}(R_H)/k_B T_c$ at the minimum is approximately 3.8 times the Casimir amplitude. It is instructive to observe how the shape of magnetization profiles changes with H . For very weak H , such that $R_H \ll 1$, magnetization profiles are almost flat, with a slight difference between the value of magnetization at the surface and in the middle part of the film. Also for stronger H , such that $R_H \gg 1$, the profiles are flat in the whole film, except from very narrow regions close to the walls (see Fig. 4). For these values of H the solvation force is small and the scaling function $F_{00}(R_H)$ is nearly constant. The rapid change of $F_{00}(R_H)$ takes place when $R_H \sim 1$ and is associated with profiles which are highly nonuniform across the whole film.

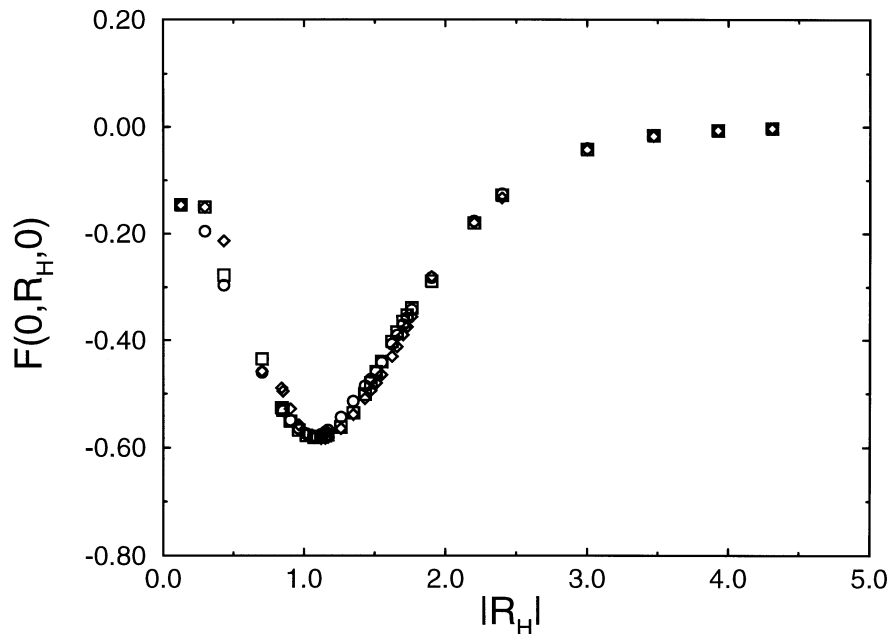


Figure 3. Scaling function of the solvation force $F(0, R_H, 0)$ calculated for 2D Ising films at $T = T_c$, surface fields $H_1 = H_L = 0$ and several widths $L = 100$ (circles), 124 (squares), 150 (diamonds).

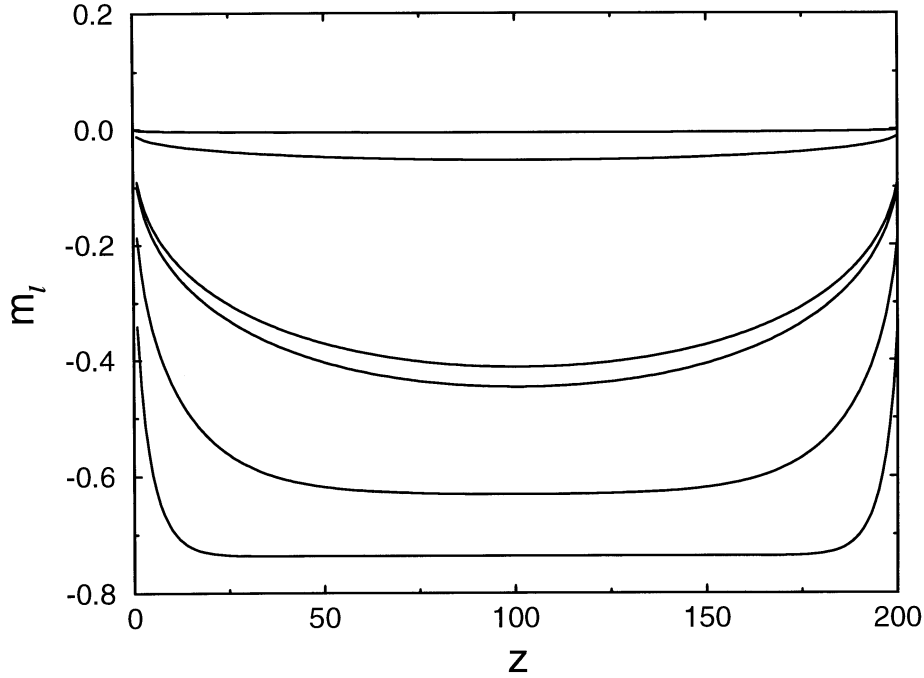


Figure 4. Magnetization profiles m_l for the 2D Ising film of width $L = 200$ at $T = T_c$, $H_1 = H_L = 0$ and several values of the bulk field: the top profile corresponds to $H = -10^{-6}$, then subsequently from the next to the top to the bottom profile: $H = -10^{-5}$, -1.1×10^{-4} , -1.3×10^{-4} , -0.001 , -0.01 . H is in units of the coupling constant J , z is in units of the lattice constant, magnetization is dimensionless.

B. Adsorbing walls: (a) Temperature dependence of the solvation force at $H = 0$.

For Ising films with $H_1 = H_L > 0$ in vanishing bulk field $H = 0$, the extremum of the solvation force as a function of temperature is shifted from T_c , similarly to the case of free boundaries. However, for adsorbing walls the minimum of f_{solv} at T_{min} lies above the bulk critical temperature T_c (see (24)). In $d = 2$ f_{solv} and its scaling function were determined by Evans and Stecki [14] for strips with fixed boundary conditions (+/+) imposed on the spins in the surface layers. (+/+) boundary conditions translates into $H_1 = H_L = J$ and corresponds to strongly adsorbing walls, *i.e.* to the normal transition fixed point. Using an exact formulae of Au-Yang and Fisher [25] for the free energy of the Ising strip with two surface fields, $H_1 H_L > 0$, the authors derived analytic expressions for f_{solv} and its scaling function and found that the minimum of the scaling function $F_{++}(R_\tau) \equiv F(R_\tau, 0, \infty)$ occurs when $R_\tau = 1.26$. The amplitude at this extremum is, like in the case of free boundaries, about 6.6 times the Casimir value. Sufficiently far below T_c , $f_{solv}^{(++)}$ decays as $\exp(-L/\xi_b)$ as $L \rightarrow \infty$, in agreement with mean-field predictions [17]. For $R_H \lesssim -1$ and $R_H \gtrsim 6$ the scaling function is almost zero. We can observe the same relation between the shape of the magnetization profile and the behavior of the solvation force as in the case of the nonadsorbing walls, *i.e.*, the mini-

mum of $F_{++}(R_\tau)$ is associated with highly nonuniform profiles. Although Evans and Stecki did not calculate profiles for their system, in [31] magnetization profiles for Ising film with slightly weaker surface fields $H_1 = H_L = 0.8 J$ at $H = 0$ were presented for different temperatures above T_c . For this film of the width $L = 100$ the scaling variables R_τ around the minimum of $F_{++}(R_\tau)$ correspond to τ between 0.001 and 0.04 and hence to the most nonuniform profiles.

(b) Bulk field dependence of the solvation force at $T = T_c$. For $d = 2$ Ising films the scaling function of f_{solv} at $T = T_c$ and nonzero H was obtained using the DMRG method by Drzewiński and co-authors [15]. The $f_{solv}(H)$ was found to be negative (attractive force) for all considered H (Fig. 5). The bulk field dependence of the solvation force at $T = T_c$ is similar to the temperature dependence at $H = 0$, *i.e.*, f_{solv} has a minimum at some $H_{min} < 0$. Due to the symmetry breaking boundary conditions, there is only one minimum. The striking feature is that the strength of the force at H_{min} is very much larger than that at the bulk critical point. The minimum of the scaling function of the solvation force $F(0, R_H, \infty)$ is located at $R_H \approx 3.2$. At this minimum $F(0, R_H, \infty)/k_B T_c$ is approximately 100 times the Casimir amplitude A_{++} ! This result is opposite to the result found for nonadsorbing walls, whereby the extremum of $f_{solv}(H)$ as a function of the field H at $T = T_c$ is *weaker* than the extremum of the function $f_{solv}(T)$ at $H = 0$. The location of the minimum of the solvation force seems to be gov-

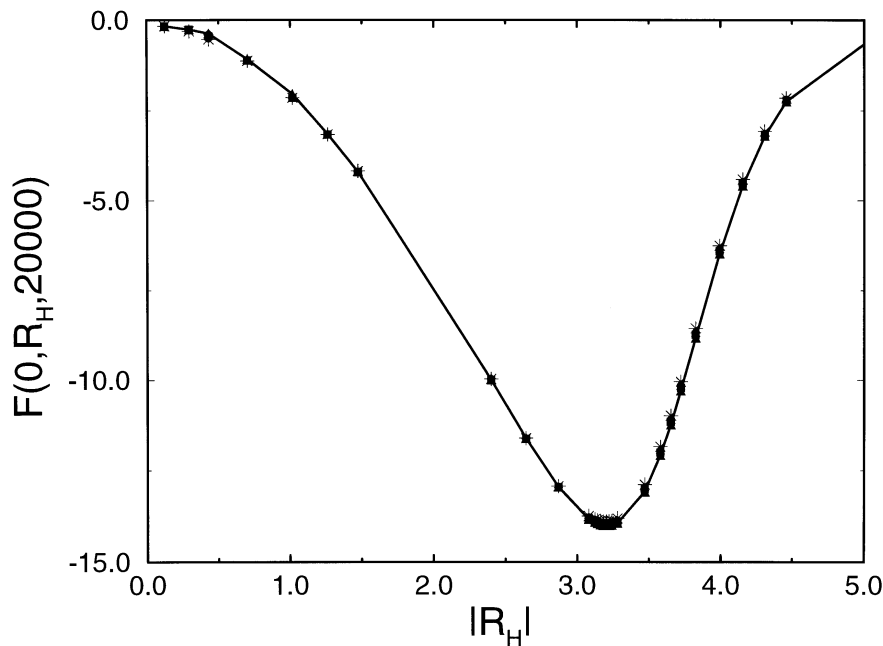


Figure 5. Scaling function of the solvation force $F(0, R_H, 20000)$ calculated for 2D Ising films at $T = T_c$ of widths $L = 100$ (stars), 124 (circles), 150 (squares), 174 (diamonds) and 200 (triangles). Calculations for each L were performed at the suitable value of surface fields $H_1 = H_L$ to meet the condition $R_{H_1} = L |H_1|^{v/\Delta_1} = 20000$ (normal transition).

erned not by the bulk correlation length but rather by the longitudinal spin-spin correlation length ξ_{\parallel} , since at the minimum $L \approx 2.7 \times \xi_{\parallel}$. ξ_{\parallel} is defined from two largest eigenvalues of the transfer matrix Λ_0 and Λ_1 . $\xi_{\parallel}^{-1}(\tau, H; L, H_1) = -\ln [\Lambda_1/\Lambda_0]$ and describes the spin-spin correlation in a finite system in a direction parallel to the walls. For H around the minimum of the solvation force, ξ_{\parallel} is much bigger than ξ_b , due to the presence of broad interfaces between thin layers of a liquid-like phase near walls and a gas-like phase in the middle of the film in a crossover regime. Another interesting feature is that for weak H the solvation force is a linear function of the bulk field. The finite size scaling implies that in this “linear regime” f_{solv} very weakly depends on the width of the film L , *i.e.*, $f_{solv} \sim L^{-d+\Delta/\nu}$ with the exponent equal to -0.125 in $d=2$. Similarly to the case of free boundary conditions, the minimum of the solvation force is associated with highly inhomogeneous profile (see Fig. 6).

Several features of the solvation force for adsorbing walls are not obvious. For example, why the minimum of the solvation force should lie *above* the bulk critical temperature T_c or why the solvation force is much stronger for states, which lie slightly *off bulk coexistence*, with $H < 0$ or why for weak H $f_{solv}(T = T_c)$ is a linear function of H . Recall that systems with surface fields $H_1 = H_L > 0$ are thermodynamically very different from the systems with $H_1 = H_L = 0$, due to the phenomenon of capillary condensation that takes place for $H_{co}(T) < 0$. The f_{solv} exhibits a discontinuous

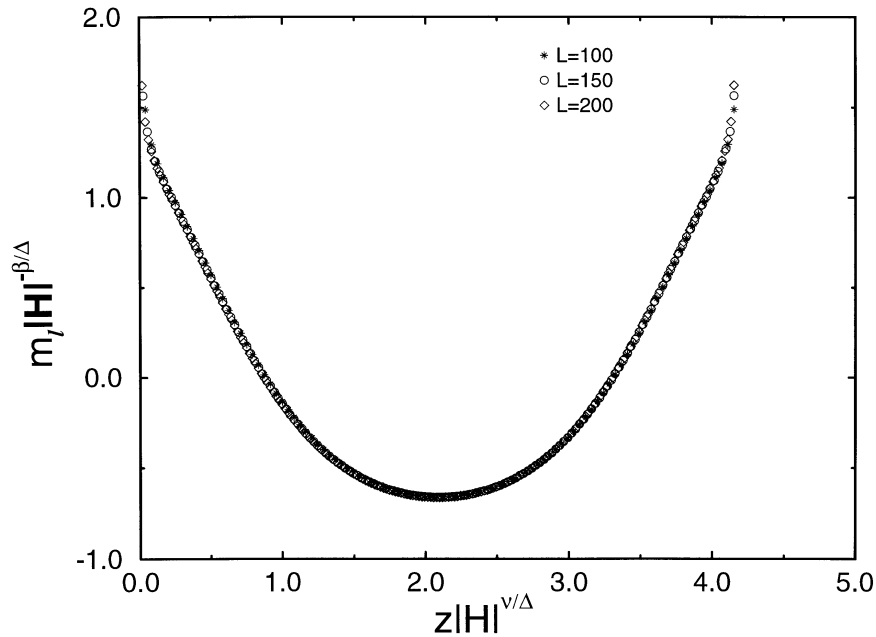


Figure 6. Scaling functions of typical magnetization profile for 2D Ising films at $T = T_c$ in the crossover regime for the scaling variable $\text{sgn}(H)R_H = \text{sgn}(H)L|H|^{v/\Delta} = -3.2$, *i.e.* at the minimum of the solvation force. Calculations for each L were performed at the suitable value of surface fields $H_1 = H_L$ to meet the condition $R_{H_1} = L|H_1|^{v/\Delta} = 20000$.

jump on crossing the coexistence (capillary condensation) line and singular behaviour at the capillary critical point (H_{cL}, T_{cL}) . In order to link the minimum of the solvation force as a function of T at T_{min} and $H = 0$ to the singular behavior at H_{cL} and to clarify the surprising behavior of the solvation force, a detailed investigation of f_{solv} as a function of H for different temperatures above and below T_c was performed using the DMRG method [16].

For low temperatures (in a regime of capillary condensation) the solvation force exhibits a very weakly rounded jump from zero to some negative value (see Fig. 7). As mentioned earlier, a discontinuous jump is characteristic of the solvation force at a first-order capillary condensation phase transition. The calculated gradients of f_{solv} at the three lowest temperatures in Fig. 7 agree with the approximation for the jump of the solvation force ((8), with $\rho_l - \rho_g$ replaced by $2m^*(T)$). Also, the prediction of the decrease of the magnitude of the jump in the same fashion as the interfacial tension, as T increases at fixed L (9) is confirmed. For higher temperatures a change in the behaviour of f_{solv} is observed. As the temperature increases, the jump of f_{solv} gradually transforms into a minimum, whose depth decreases and moves monotonically towards $H = 0$. Even above T_c at the temperature at which f_{solv} exhibits a minimum as a function of τ for $H = 0$, the minimum of f_{solv} as a function of H is still present and its depth is about 4.8 times bigger than $|f_{solv}(H = 0)|$. For temperatures up to the critical temperature, the magnetization profiles for small $|H|$ are similar to that of a “con-

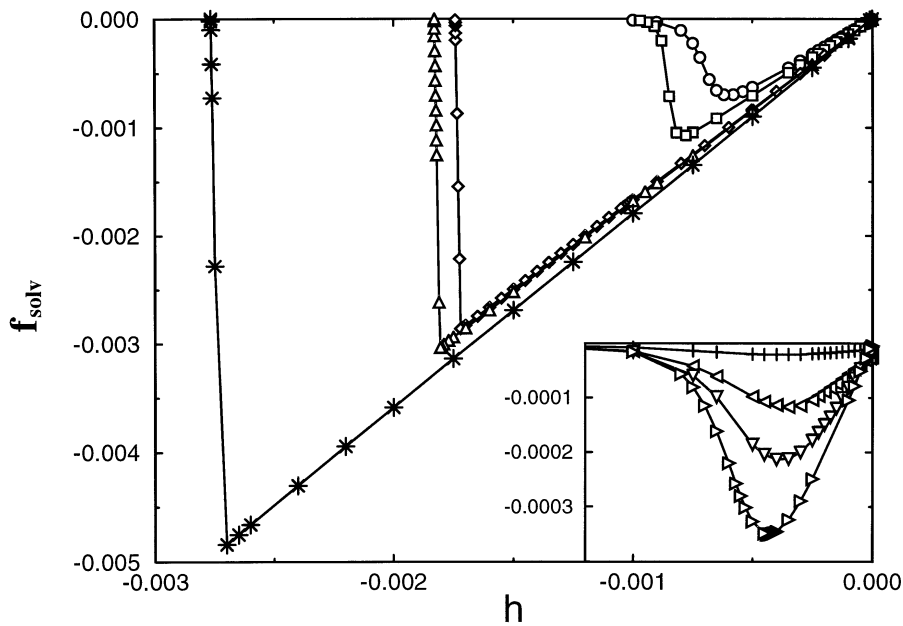


Figure 7. Solvation force as a function of the bulk magnetic field H (both quantities in units of J) for an Ising strip of width $L = 200$, surface fields $H_1 = H_2 = 10$ and several reduced temperatures $\tau \equiv (T - T_c)/T_c \approx$: (+) 0.0135, (\triangleleft) 0.0063, (∇) 0.0031, (\triangleright) 0.0, (o) -0.0063, (T) -0.0126, (\diamond) -0.0505, (Δ) -0.0546, (*) -0.1011.

densed" (+) (liquid) phase. Moreover, f_{solv} still varies linearly with H , as is implied by the approximate treatment above, although the linear region does shrink as $\tau \rightarrow 0^-$. Thus, the behavior of the solvation (Casimir) force in the neighbourhood of the critical point is strongly influenced by capillary condensation, which occurs below the bulk critical temperature T_c . At T slightly below and slightly above T_c , a small bulk field $H < 0$, which favours gas, or (-) phase, leads to residual condensation and a solvation force, which is much more attractive (at the same large wall separation) than that found exactly at the critical point. Again the strongest variation of the solvation force is associated with profiles, which are highly nonuniform across the whole film.

VI. CONCLUDING REMARKS

As emphasized in the introduction, this article has concentrated on the near-critical properties of $d = 2$ Ising films. Exact solutions and the approximate DMRG method have made a striking input into fundamental understanding of the near-critical behavior of the solvation force in two dimensions. Do the results obtained in $d = 2$ have any relevance for $d = 3$? The general features of f_{solv} for identical walls as a function of the temperature at $H = 0$ seem to be the same in $d = 3$, for both, ordinary and normal transitions. The field theoretical renormalization group calculations to first order in ϵ for the free energy of a system with ordinary-ordinary boundary condition [32] give the scaling function qualitatively very similar to the corresponding scaling function for an Ising strip in $d = 2$. The same similarity was found in the case of the normal transition. For the (+/+) boundary condition, the scaling function at $H = 0$ was determined in the mean-field theory. In the mean-field, the minimum of the scaling function $F_{++}(R_\tau)$ occurs for $L \sim 3.7\xi$ and the amplitude is about 1.4 times $F_{++}(0)$ [33,37]. Borjan and Upton [34] have calculated $F_{++}(R_\tau)$ in $d = 3$, using local functional methods and they find the minimum at $L \sim 3.1\xi$, and the amplitude at the extremum is about 2.1 times $F_{++}(0)$. For $d = 3$ there are no published results for the behavior of the near-critical solvation force in the case of a nonvanishing bulk magnetic field. We expect that in $d = 3$, where there is a true coexistence for $T < T_{cL}$, f_{solv} should behave in a similar fashion to what is observed in $d = 2$, but now the jumps of f_{solv} will be discontinuous. Explicit mean-field results for a Landau (square-gradient) theory support our expectations for $T < T_{cL}$ and for $T > T_{cL}$, where $f_{solv} \approx 2Hm^*(T)$ for $H \rightarrow 0^-$ [35].

We have stressed the connections between the extrema of the solvation force near the bulk critical point and the high nonuniformity of the magnetization profiles for values of T and H in the neighbourhood of these extrema. Recall that below the capillary critical point (H_{cL}, T_{cL}), there is a connection between $f_{solv}(L)$ and the adsorption $\Gamma(\mu)$, *i.e.*, the excess magnetization; first-order phase transitions are signalled by discontinuous jumps in these functions and criticality by divergence in their first and second derivatives [11].

Results in $d = 2$ imply that the solvation force in a real confined fluid at temperatures near T_c and at reservoir densities slightly below the critical value (or compositions slightly away from the critical composition in a binary mixture) should be much more attractive than the Casimir value for the same L , although the effect may be less pronounced than in $d = 3$. Thus, experiments which aim to measure the Casimir force and future theoretical work should focus on the τ and H dependence of f_{solv} , *i.e.*, the scaling function, not just the Casimir amplitude.

Solvation forces, induced by the confined fluid, are not restricted to the planar geometry of the confining walls. The fluid confined between two colloidal particles should also lead to a solvation force between the confining surfaces, which in this case correspond to the spherical surfaces of the colloids. For large radii R of the colloid particles, $R/\sigma \rightarrow \infty$, where σ is the molecular diameter of the solvent particles, the curvature of the surfaces is not of primary importance. The qualitative properties of the solvation force should be similar as in the case of the planar geometry. Hence, effective attraction between the colloidal particles should be induced by the fluid confined between them. This attraction should be long-ranged when the solvent is near its critical point, and the magnitude of this force should be particularly large when the solvent is slightly off the criticality. Effective attraction between the colloidal particles should affect the equation of state of the colloidal suspension. Measurements of the second virial coefficient for the suspension, when the solvent is near criticality, should allow for estimation of the effective force between the colloids [36]. In this way one could confirm experimentally the theoretical predictions reviewed above.

Finally we note that the existence of a long-ranged, strongly attractive solvation force between two large colloidal particles immersed in a near-critical fluid can have ramifications for aggregation or flocculation of the particles [37]. Studies summarized above should indicate where aggregation is potentially the strongest.

Acknowledgments

The paper is dedicated to Professor Jan Stecki, our teacher, on the occasion of his 70th birthday. We are grateful to R. Evans and A. Drzewiński for the fruitful collaboration. This work was partially funded by the Polish State Committee for Scientific Research (grants No. 2P03B10616 and No. 3T09A07316).

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