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# Solvation force in two-dimensional Ising strips

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Finite-size contributions to the free energy of a fluid confined between two parallel walls, separated by a distance $L$, give rise to an excess pressure which is termed the solvation force $f_{\rm solv}(L)$. Using exact transfer-matrix methods we calculate the analog of $f_{\rm solv}$ for a two-dimensional Ising strip of infinite length and finite width $L \equiv na$, where $n$ is the number of layers and $a$ is the lattice spacing, for bulk field $h=0$ and fixed $(+/+)$ and $(+/-)$ boundary conditions on the spins in the surface layers. $+$ and $-$ refer to up and down spins, respectively. $f_{\rm solv}^{(++)}$ is negative (attractive force) for all temperatures $T$ and for a given $L$ has its minimum above the critical temperature $T_c$. The amplitude of the force at the minimum is about 6.6 times the value at $T_c$, the "Casimir" amplitude. In the $(+/-)$ strip a $+-$ interface develops at all subcritical temperatures and entropic repulsion gives rise to a positive $f_{\rm solv}^{(+-)}$ which has its maximum slightly below $T_c$. Universal scaling forms are derived for both cases and accurate approximations, valid for low, near critical, and high temperatures, are obtained. In the scaling limit, $L \to \infty, t[\equiv (T-T_c)/T_c] \to 0$, the minimum of $f_{\rm solv}^{(++)}$ is given by $nt_{\min}=1.2642$ and the maximum of $f_{\rm solv}^{(+-)}$ by $nt_{\max}=-0.2735$. We compare and contrast our results with earlier predictions based on mean-field analyses and scaling arguments.

## I. INTRODUCTION

When a simple fluid, or an Ising magnet, is confined between two parallel plates, or walls, of infinite area which exert local surface fields $h_1$ and $h_n$ the properties of the fluid or magnet depend upon the distance $L$ between the plates and on the nature of the surface fields. A model of this type is standard in fundamental studies of finite-size effects in statistical physics.[1,2] It also serves as an idealized representation of a fluid in a slitlike pore; the local surface fields then model the substrate-fluid interactions which give rise to adsorption phenomena. The phase behavior of fluids confined between identical parallel plates ($h_1=h_n$) has been the subject of several detailed investigations.[3–5] More recently, the case of opposing surface fields ($h_1h_n<0$) has attracted attention because of predictions of phase behavior, very different from that associated with identical walls[6,7] and (for dimension $d<3$) of long-ranged density (magnetization) profiles associated with interfacial fluctuations.[8] One important quantity which arises naturally in the thermodynamics of confined fluids is the solvation force, sometimes called the disjoining pressure, defined by[9]

$$f_{\rm solv} = -(\partial \omega^{\rm ex}/\partial L)_{\mu,T,A}\ , \tag{1.1}$$

where $\omega^{\rm ex}$ is the excess grand potential per unit area and the derivative is performed at constant chemical potential $\mu$, temperature $T$, and surface area $A$. $f_{\rm solv}$ is a generalized force conjugate to the distance $L$ between the plates. For a fluid it is the excess pressure (over the bulk value, fixed by the reservoir) arising from confinement and has the property $f_{\rm solv}(L) \to 0$ in the limit $L \to \infty$. The sign of the solvation force is of particular interest. It is generally the case that for simple fluids confined between identical walls $f_{\rm solv}(L)<0$ for large $L$, i.e., the net force between the plates is attractive for large separations. [This result emerges directly from mean-field (Landau or density functional) analyses.[10,11]] At small plate separations, when excluded volume (packing) effects dominate, $f_{\rm solv}(L)$ exhibits oscillations[9] and such behavior has been observed in force-apparatus measurements.[5,9] Although $f_{\rm solv}(L)>0$, at large $L$, is not observed for simple fluids between identical walls, a repulsive solvation force has been calculated in mean-field treatments of a fluid subject to opposing surface fields.[6,7] When the temperature and surface fields are such that one wall is wet by liquid $(+)$ and the other by gas $(-)$ (for $L=\infty$ at bulk coexistence) a soft-mode or interfacial phase develops at large $L$. This phase exhibits a $+-$ interface near the center of the slit and $f_{\rm solv}(L)>0$ for temperatures above the wetting transition temperature $T_w$.[7] A positive solvation force would appear to be a characteristic of a special type of confined phase; namely one that is dominated by interfacial fluctuations. Alternatively, one might consider $f_{\rm solv}(L)>0$ as simply a manifestation of finite-size effects on the interfacial tension of the $+-$ interface.

In this paper, we explore these ideas further and calculate the "magnetic" solvation force, using exact transfer-matrix methods, for a two-dimensional Ising strip subject to two choices of surface fields: (i) symmetric $(+/+)$ with $h_1=h_n$ and (ii) antisymmetric $(+/-)$ with $h_1=-h_n$. $h_1$ is chosen sufficiently large that a single "wall" ($L=\infty$) would be wet for all sub-critical temperatures, i.e., $0<T<T_c$. Case (i) clearly corresponds to that of identical walls so we expect to find a negative solvation force, whereas the boundary conditions in case (ii) are chosen to ensure that, for bulk field $h=0$ and large $L$, a nearly free $+-$ interface can develop in the strip and mean-field theory then predicts that the solvation force should be positive for all temperatures. Mean-field and scaling arguments also make specific predictions for the temperature variation of the solvation force at fixed (large) $L$.[7] We inquire whether these predictions remain

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valid in the $d=2$ Ising model where fluctuation effects are especially pronounced.

For an Ising system the analog of the solvation force is

$$f_{\mathrm{solv}}(L)=-(\partial f^{\mathrm{ex}}/\partial L)_{h,T} ,$$

where $f^{\mathrm{ex}}(L)\equiv F-Lf_b$ is the excess free energy per unit area, and $f_b$ is the bulk free-energy density. The quantity $f^{\mathrm{ex}}$ contains $L$ independent surface contributions in addition to the finite-size contribution $\delta f^{\mathrm{ex}}(L)$. It is well known that the latter exhibits certain universal or near-universal features when the confined system is at the bulk critical temperature $T=T_c$ and $h=0$. Fisher and de Gennes[12] predicted

$$\frac{\delta f^{\mathrm{ex}}(L)}{k_B T_c}=A_{1n}L^{-(d-1)} , \quad L\to\infty , \tag{1.2}$$

where the amplitude $A_{1n}$ depends on the relative signs of the surface fields $h_1$ and $h_n$, but not on their magnitudes.[13] The slow algebraic decay predicted by (1.2) is associated with *bulk* critical fluctuations, i.e., a divergent bulk correlation length $\xi_b(T)\sim|T-T_c|^{-\nu}$. For the $d=2$ Ising strip the amplitudes have been calculated exactly so that the leading-order decay of the solvation force is known exactly. When the surface fields are identical,[14]

$$\frac{f_{\mathrm{solv}}}{k_B T_c}=-\frac{\pi}{48}L^{-2} , \quad h_1 h_n\geq 0 , \quad T=T_c . \tag{1.3a}$$

When they are of opposite sign,[15]

$$\frac{f_{\mathrm{solv}}}{k_B T_c}=\frac{23\pi}{48}L^{-2} , \quad h_1 h_n<0 , \quad T=T_c \tag{1.3b}$$

for $L\to\infty$.

These confirm that, for $T=T_c$, $f_{\mathrm{solv}}$ is attractive for identical surface fields, for example $(+/+)$, but is repulsive for opposing fields, for example $(+/-)$. Here we are concerned with the form of the solvation force over the whole temperature range, not just at $T_c$. At low temperatures, $T\ll T_c$, interfacial fluctuations (capillary-wavelike) should dominate the large $L$ behavior of $f_{\mathrm{solv}}$ in the $(+/-)$ strip so there are interesting cross-over effects. Some of these have been described in earlier work on the magnetization profile[16] and on the density-density correlation function[17] in the $(+/-)$ strip. We make use of the techniques developed there to analyze the solvation force.

Figure 1 shows an example of our results for $f_{\mathrm{solv}}$. These are calculated for fixed $n=59$ layers, i.e., a strip of width $L\equiv na$, where $a$ is the lattice constant. The temperature dependence shown here is typical. In the $(+/+)$ strip the solvation force is negative for all $T$ and has a minimum above $T_c$, while in the $(+/-)$ strip it is positive and has its maximum slightly below $T_c$. The magnitude of the solvation force is much larger for the $(+/-)$ case and it decays much more slowly with decreasing $T$ below $T_c$.

Our paper is arranged as follows. In Sec. II we describe the theory, which is based on exact results by Au-Yang and Fisher,[18] and details of calculations for the $(+/+)$ strip. Results are presented in both unscaled and scaled forms. A single scaling function accounts accurately for the $T$ and $L$ dependence of $f_{\mathrm{solv}}$ in the neighborhood of $T_c$. For temperatures sufficiently far below $T_c$, $f_{\mathrm{solv}}$ decays as $\exp(-L/\xi_b)$, in agreement with mean-field predictions. The determination of the solvation force in the $(+/-)$ strip is described in Sec. III. Since the results of Ref. 18 do not apply with this boundary condition we calculate the difference between the solvation force in the $(+/-)$ and $(+/+)$ strips directly, using the techniques of Ref. 16 and 17, and combine the result with that for $f_{\mathrm{solv}}$ in the $(+/+)$ strip. An explicit scaling form is deduced which describes accurately the

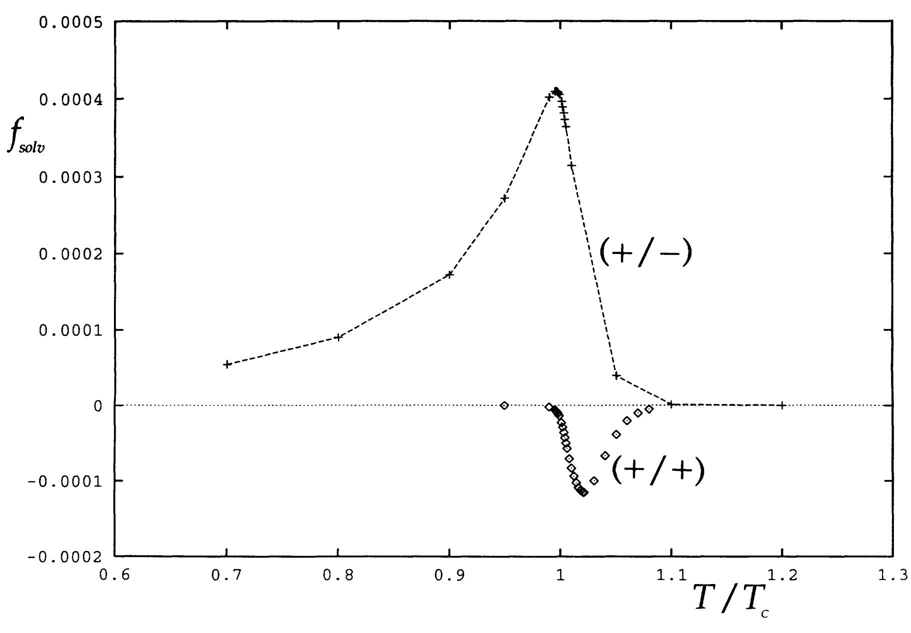


FIG. 1. The solvation force (in units of $kT$) as a function of temperature in the semi-infinite Ising strip with $(+/+)$ and $(+/-)$ boundary conditions. The points for $(+/+)$ were obtained from the finite difference (2.4b) by subtracting data for $n=59$ and $n=60$. [The dashed line for $(+/-)$ is merely a guide to the eye.] At $T=T_c$ the solvation forces take their "Casimir" values (1.3).

position and shape of the maximum of $f_{\text{solv}}$. A discussion of our results is given in Sec. IV.

## II. SOLVATION FORCE IN THE (+/+) STRIP

Following McCoy and Wu[19], Au-Yang and Fisher[18] have given exact formulas for the free energy of a semi-infinite Ising strip with two surface fields $h_1, h_n$ ($h_1 h_n > 0$). The Hamiltonian $H$ of the (isotropic) Ising model is

$$-\beta H = K \sum_{\langle ij \rangle} \sigma_i \sigma_j + h_1 \sum_x \sigma(x,1) + h_n \sum_x \sigma(x,n) , \tag{2.1}$$

where $\beta = 1/kT$, and $K = J/kT$ is the coupling constant. The sum runs over nearest neighbors $\langle ij \rangle$ and the surface fields act only on the spins in row 1 and in row $n$. The fixed (+/+) boundary condition

$$\sigma(x,0) = \sigma(x,n+1) = +1 \; ; \quad \text{all } x \tag{2.2}$$

translates into $h_1 = h_n = K$. Substitution into Eqs. (A7)–(A17) of the Appendix of Ref. 18 gives the free energy per site, in units of $kT$, as

$$f(n,K) = f_b + 2f_w/n + f^*(n)/n , \tag{2.3}$$

where $f_b$ is the bulk free energy, $f_w$ is the ($n$-independent) surface contribution of each wall, and is $f^*$ the finite-size interference term. The latter vanishes for $n \to \infty$. The solvation force introduced in Sec. I is then for our system

$$f_{\text{solv}} = -(\partial f^* / \partial n)_T \tag{2.4a}$$

or, as a finite difference,

$$f_{\text{solv}} = -[f^*(n+1) - f^*(n)] . \tag{2.4b}$$

Here

$$f^* = -(1/\pi) \int_0^{\pi/2} d\varphi \ln[1 + R^{-n} P] , \tag{2.5}$$

where the factor $P$ can be written as

$$P = (p_+/p_-)^2 = \psi^2 (V_p/V_M)$$

with

$$\omega \equiv \sin(\varphi) ,$$

$$\psi \equiv (q_0 q_1 - p_0 p_1 - c + 1 - \omega^2)/(q_0 q_1 + p_0 p_1 + c - 1 + \omega^2) ,$$

$$V_p \equiv q_0 q_1 + p_0 p_1 + c\omega^2 , \quad V_M \equiv q_0 q_1 - p_0 p_1 - c\omega^2 ,$$

$$R \equiv (q_0 + q_1)^4 ,$$

and

$$S \equiv \sinh(2K) , \quad c \equiv \cosh(2K) ,$$

$$p_0 \equiv (1 - S)/(2S)^{1/2} ,$$

$$p_1 \equiv (1 + p_0^2)^{1/2} , \quad q_0 \equiv (p_0^2 + \omega^2)^{1/2} ,$$

$$q_1 \equiv (1 + p_0^2 + \omega^2)^{1/2} .$$

For the discrete version (2.4b) we evaluated the integral

$$f_{\text{solv}} = (1/\pi) \int_0^{\pi/2} d\varphi \ln[(1 + Y/R)/(1 + Y)] , \tag{2.6}$$

with $Y \equiv R^{-n} P$, numerically. Gaussian integration with interval subdivision produced very accurate and stable results. One such curve for $n = 59$ is shown in Fig. 1 and results for several values of $n$ are shown in Fig. 2. $f_{\text{solv}}$ is negative for all temperatures $T$ and shows a minimum *above* the critical temperature $T_c$. For large $n$ we used the differential version (2.4a) which gives

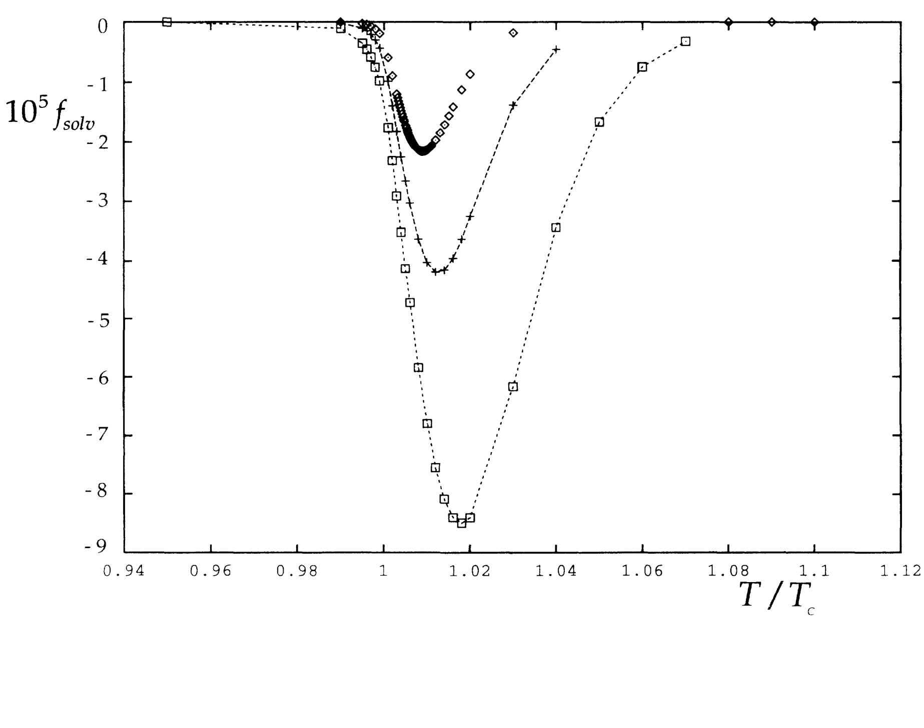


FIG. 2. The solvation force in the (+/+) strip for $n = 69$ (□), $n = 99$ (+), and $n = 139$ (◇). (The dashed lines are guides to the eye.)

$$f_{\mathrm{solv}}=-(4/\pi)\int_0^{\pi/2}d\varphi[Y/(1+Y)]\ln(q_0+q_1) \tag{2.7}$$

again with the abbreviation

$$Y\equiv PR^{-n}=P\exp[-4n\ln(q_0+q_1)] .$$

At sufficiently large $n$ excellent scaling plots were obtained using the scaling variables $n^2f_{\mathrm{solv}}$ and $nt$. Here $t\equiv(T-T_c)/T_c$ and the choice of scaling variables is dictated by the standard finite-size ansatz for the free energy at bulk field $h=0$,[3] i.e., $f=|t|^{2-\alpha}W(nt^{\nu})$ or, equivalently, $f=n^{-d}\tilde{W}(nt^{\nu})$. For the $d=2$ Ising model the critical exponents are $\alpha=0$ and $\nu=1$. The scaling limit corresponds to $n\to\infty$ and $t\to 0$ at constant $\tilde{X}\equiv nt$.

In order to derive the scaling function for the solvation force we introduce the variable $X\equiv p_0 n$, write $d\varphi=dw(1-w^2)^{-1/2}$, and set $ndw=d\xi$, introducing the new integration variable $\xi=nw$. In the scaling limit

$$1-w^2=1-(\xi/n)^2\to 1 , \quad \psi\to 1 , \quad nV_p\to Q_0+X ,$$

$$nV_M\to Q_0-X ,$$

where $Q_0=(\xi^2+X^2)^{1/2}$. Writing

$$R^{-n}=\exp[-4n\ln(q_0+q_1)]$$

and expanding

$$4n\ln[(1+Q_0^2/n^2)^{1/2}+Q_0/n]=4Q_0+\cdots ,$$

we find

$$\tilde{f}_{\mathrm{solv}}=\lim(n^2f_{\mathrm{solv}}) , \tag{2.8}$$

where

$$\tilde{f}_{\mathrm{solv}}=-\frac{4}{\pi}\int_0^{\infty}d\xi\frac{Q_0\exp(-4Q_0)(Q_0+X)}{Q_0-X+\exp(-4Q_0)(Q_0+X)} , \tag{2.9}$$

with $X=2K_c\tilde{X}$. Note that in the limit $t\to 0$, $p_0\approx 2K_ct$ since $\sinh(2K_c)=1$. This scaling function was evaluated by numerical integration. Figure 3 shows $\tilde{f}_{\mathrm{solv}}$ plotted vs $\tilde{X}$ and compared with exact data from (2.4) for $n\in[60,200]$. The agreement is excellent and the corrections to scaling are small on the scale of the graph. The corrections appear to be largest near the minimum of $\tilde{f}_{\mathrm{solv}}$. The scaling curve goes through the known point at $T_c$. Then $X=0$ and (2.9) reduces to

$$\tilde{f}_{\mathrm{solv}}(X=0)=-\frac{1}{4\pi}\int_0^{\infty}dy\,y\frac{1}{e^y+1}=-\frac{1}{48}\pi \tag{2.10}$$

and we recover (1.3a).

Below $T_c$ a semilogarithmic plot reveals the exponential behavior of the solvation force, i.e., $\tilde{f}_{\mathrm{solv}}\sim\exp(-L/\xi_b)$. The decay length is precisely $\xi_b$, the true bulk correlation length of the Ising model. Exponential decay, with decay length $\xi_b$, is obtained from mean-field treatments[10,20,21] of fluids confined between identical walls. The same decay also follows from an exact treatment of the one-dimensional Ising strip subject to two identical surface fields.

This result leads to a very good approximation, valid for negative $\tilde{X}$ and $|\tilde{X}|$ not too large,

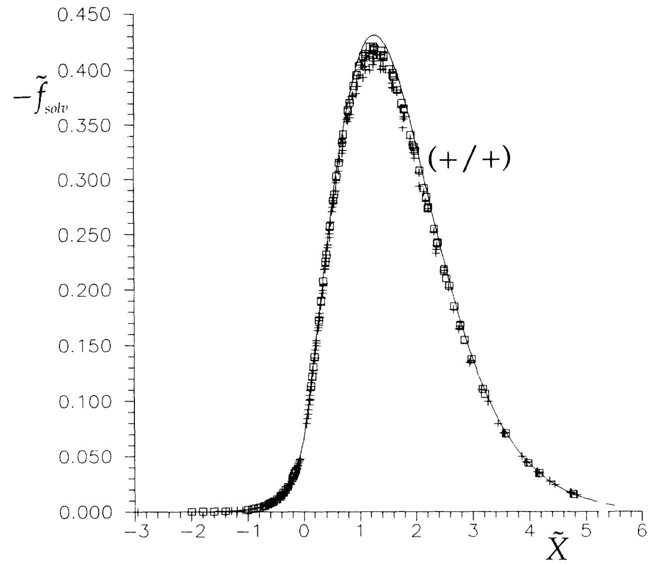


FIG. 3. The modulus of the scaled solvation force $\tilde{f}_{\mathrm{solv}}=n^2f_{\mathrm{solv}}$ vs $\tilde{X}\equiv nt$ for $(+/+)$ strips. The sets of points are obtained from (2.4) and correspond to widths $n\in[60,200]$, while the solid curve is the scaling limit (2.9). Note that the maximum (the minimum of $\tilde{f}_{\mathrm{solv}}$) occurs at $nt_{\mathrm{min}}=1.264\,24$.

$$\tilde{f}_{\mathrm{solv}}\cong-\frac{\pi}{48}\exp[+8K_c\tilde{X}] . \tag{2.11}$$

The universal position of the minimum *above* $T_c$ is given by

$$nt_{\mathrm{min}}=1.264\,24 ,$$

with value $\tilde{f}_{\mathrm{solv}}=-0.430\,516\,312\,656$. Recalling the definition of $t$ it follows

$$T_{\mathrm{min}}/T_c=1+C/n , \tag{2.12}$$

where the value of the constant $C$ is fixed by scaling: $nt_{\mathrm{min}}=C$.

There will be corrections to scaling and these are revealed in semilogarithmic plots of $\tilde{f}_{\mathrm{solv}}$ computed for the same $\tilde{X}=nt$ but for different $n$ and $t$. These corrections are of order $1/n$ in $\tilde{f}_{\mathrm{solv}}$ and will yield nonuniversal corrections to (2.12).

There are three further remarks. First, instead of taking surface fields $h_1=h_n=K$ we can make a system larger by 2 rows, with $n\to n+2$, and put $h_1=h_{n+2}=\infty$ so that $\tanh h_1=\tanh h_{n+2}=1$. The numerical results agree with those obtained using (2.5), as they must on physical grounds.[18]

The second remark concerns free boundary conditions. Putting $h_1=h_n=0$ we obtain, after performing the limiting procedure leading to the scaling form for $\tilde{f}_{\mathrm{solv}}$, an integral identical to (2.9) but with $-X$ substituted for $X$. Thus, in the scaling limit

$$\tilde{f}_{\mathrm{solv}}^{(++)}(X)=\tilde{f}_{\mathrm{solv}}^{(00)}(-X) . \tag{2.13}$$

It follows that at $T=T_c$ the solvation force for free boundaries is the same as for $(+/+)$, see (1.3a). However, the minimum of $\tilde{f}_{\mathrm{solv}}^{(00)}$ occurs below $T_c$ and the position is given by (2.12) with $C$ replaced by $-C$. Although we are not aware of any published derivation of the striking result (2.13) it is likely that this follows as a consequence of duality.

Finally, for the Ising model, where the critical exponent $\alpha=0$, we expect logarithmic terms of the form $X^2\ln X$ to be present in the scaling function. Although corrections to scaling manifest themselves quite visibly in numerical results, the logarithmic term is not visible directly. Note, however, in the integral defining $\tilde{f}_{\rm solv}$ in our $(+/+)$ strip, (2.9), the cases $X>0$ and $X<0$ can be distinguished because the integrand behaves differently. For example for positive $X$, $Q_0-X$ vanishes at $\xi=0^+$, whereas for negative $X$, $Q_0+X$ vanishes at $\xi=0^+$ and $Q_0-X$ does not. This is discussed further in the Appendix, where we extract the $X^2\ln X$ term in $\tilde{f}_{\rm solv}$.

## III. SOLVATION FORCE IN THE $(+/-)$ STRIP

In the semi-infinite Ising strip with a $(+/-)$ fixed boundary condition an interface develops between a latent $(+)$ phase and a latent $(-)$ phase for $T<T_c$. In order to investigate the solvation force in this case we cannot use the exact expressions given in Ref. [18]. These do not apply to this case. However, we can bypass this difficulty by making use of the transfer matrix in the $x$ direction along the strip. This transfer matrix has been formulated and diagonalized for fixed boundary conditions by Abraham and Martin-Löf.[22] Stecki, Maciolek, and Olaussen[16] have applied a projection in order to extract the $(+/-)$ case out of the general solution of Ref. 22, which treats all four possible cases on equal footing. Here we require only the eigenvalues. Now we take $h_1=K$ and $h_n=-K$ in (2.1), corresponding to $\sigma(x,0)=+1$ and $\sigma(x,n+1)=-1$ (in each column) and we introduce the notation $M\equiv n+1$. The highest eigenvalue needed for determining the free energy of a semi-infinite strip is (a) the quantity $\Lambda_0$, as defined in Ref. 22, for the $(+/+)$ strip and (b) $\Lambda_0 e^{-\gamma_1}$ for the $(+/-)$ strip. The free energy *difference* is then given by $\gamma_1(>0)$, i.e., the free energies per site in units of $kT$ are related by

$$f^{(+-)}=f^{(++)}+(1/n)\gamma_1 . \tag{3.1}$$

The solvation force is

$$f^{(+-)}_{\rm solv}=-(\partial/\partial n)(nf^{(+-)})=f^{(++)}_{\rm solv}-(\partial/\partial n)\gamma_1(K,n) . \tag{3.2}$$

For small values of $n$ we can again take the finite difference instead of the derivative. Since $f^{(++)}_{\rm solv}$ is given conveniently by (2.4) and (2.5), we have reduced the problem to calculating the quantity $\gamma_1$. All eigenvalues for the transfer matrix are known in terms of the quantities $\gamma_1,\gamma_2,\ldots$, which are to be calculated from

$$\cosh\gamma_k=\cosh(v_2-v_1)+(1-\cos\omega_k) , \tag{3.3}$$

where $v_2=2K$, $v_1=2K^*$, and the relation $\sinh 2K^*\sinh 2K=1$ defines $K^*(K)$. The angles $\omega_k$ and, in particular $\omega_1$, are obtained from a transcendental equation discussed in detail in Ref. 16 and the allowed interval for $\omega_1$ is $[0,\pi/M]$. In the notation of Ref. 16 this equation is $\delta'(\omega_1)=M\omega_1$. The program for the computation of $\gamma_1(K,n)$ is, therefore, straightforward: for a given temperature $T/T_c$ and a given strip width $M$ solve first the transcendental equation for $\omega_1$ and then invert (3.3) with $k=1$. Before we present the results for the solvation force several remarks are in order. The quantity $\gamma_1$, being the difference of the free energies of a strip with an interface and a strip without, has the obvious interpretation of a surface tension. On the other hand, Onsager[23] showed the surface tension $\sigma_0$ is given by $\sigma_0/kT=v_2-v_1$. It can be seen from (3.3) that the Onsager value is recovered in the limit $\omega_1=0$, i.e., as $M\to\infty$. Moreover, $\gamma_1$ is positive and, from (3.3), $\gamma_1>\sigma_0/kT$. At the critical temperature $T=T_c$ we obtain[17] from the exact equations the following expansion:

$$\gamma_1=\frac{\pi}{2}M^{-1}-\pi\sqrt{2}M^{-2}+\frac{\pi}{4}\left[1-\frac{1}{96}\pi^2\right]M^{-3}+\cdots . \tag{3.4}$$

The first term makes a positive contribution $(\pi/2)M^{-2}$ to $f^{(+-)}_{\rm solv}$. When the negative contribution $-(\pi/48)M^{-2}$ from $f^{(++)}_{\rm solv}$ is added [see (3.2) and (2.10)] we find

$$f^{(+-)}_{\rm solv}=\frac{23\pi}{48}M^{-2}+O(M^{-3})$$

at $T=T_c$, i.e., we recover the known result (1.3b). The other terms in (3.4) represent corrections to scaling. The low-temperature finite-size behavior of $\gamma_1$ is known[24,17]

$$\gamma_1^{\rm FS}=(1/2\beta\Gamma)\pi^2M^{-2}+O(M^{-3}) , \tag{3.5}$$

where the stiffness of the interface $\Gamma/kT=\sinh(\sigma_0/kT)$. Thus, the low-temperature (capillary-wave) contribution of the interface to $f^{(+-)}_{\rm solv}$ is also repulsive

$$-(\partial/\partial M)\gamma_1=(1/\beta\Gamma)\pi^2M^{-3}+O(M^{-4}) . \tag{3.6}$$

Indeed, the repulsive contribution from $\gamma_1$ dominates $f^{(+-)}_{\rm solv}$ for all temperatures. This can be seen in Fig. 1. There is always a maximum of the $-(\partial\gamma_1/\partial M)$ contribution at or slightly below $T_c$ and in the scaling limit the maximum is at $T_c$ exactly. Above $T_c$ the minimum arising from the $(+/+)$ contribution is overwhelmed by the repulsive contribution, which is invariably much larger in magnitude. The origin and location of the maximum of $f^{(+-)}_{\rm solv}$ can also be understood from scaling.

Scaling of $\gamma_1$ has been discussed by several authors.[2,24,17] One of us has recently derived expansions of the scaling functions for $\omega_k$ and $\gamma_k$ for $k=1,2$.[17] The derivation of the scaling limit $M\to\infty$ and $t\to 0$ is straightforward. As $M\to\infty$, $\omega_1\to 0$ and the transcendental equation for $\omega_1$ takes the form

$$\tan(M\omega_1)=\frac{\omega_1}{-v_0+\cdots} , \tag{3.7}$$

where $v_0=v_2-v_1=\beta\sigma_0$. As $t\to 0$, $v_0\cong -4K_c t$. Writing $y=M\omega_1$ we obtain the equation for $y$ in the form $\tan y=y/(-Mv_0)$ or

$$Mt=(4K_c)^{-1}y\coty \ . \tag{3.8}$$

Now for small $\gamma_1$, $\omega_1$, and $v_0$, Eq. (3.3) for $\gamma_1$ can be approximated by $\gamma_1^2=v_1^2+\omega_1^2$, so for the scaled quantity $Z\equiv M\gamma_1$ a parametric representation is

$$Z=\frac{y}{\sin y} \tag{3.9a}$$

and

$$(4K_c)^{-1}y\coty=\tilde{X} \ , \tag{3.9b}$$

where $y\in[0,\pi]$. This defines the scaling function $Z(\tilde{X})$, with $\tilde{X}\equiv Mt$. At $t=0$, $y=\pi/2$ so that $Z(0)=\pi/2$ and $Z'(0)=-4K_c(2/\pi)$. The low-temperature limit, $\tilde{X}\to-\infty$, of the scaling function $Z$ can also be derived,[17] thereby recovering (3.5).

Defining the scaled solvation force in the $(+/-)$ strip by analogy with (2.8) it follows from (3.2) that

$$\tilde{f}^{(+-)}_{\text{solv}}=\tilde{f}^{(++)}_{\text{solv}}+\Delta\tilde{f}_{\text{solv}} \tag{3.10}$$

with

$$\Delta\tilde{f}_{\text{solv}}\equiv-M^2(\partial\gamma_1/\partial M) \tag{3.11}$$

or in terms of the scaling function $Z\equiv M\gamma_1$,

$$\Delta\tilde{f}_{\text{solv}}=Z-\tilde{X}(dZ/d\tilde{X}) \ . \tag{3.12}$$

Figure 4 shows the comparison of results obtained numerically from (3.11), as described earlier, for values of $M\in[60,200]$ with those calculated from (3.12) using the scaling function $Z(\tilde{X})$ given by (3.9). The maximum of the right-hand side of (3.12) occurs precisely at $\tilde{X}=0$, the critical temperature.

In order to analyze these results further it is convenient to introduce, in addition to $\tilde{X}\equiv Mt$, a new variable $\hat{x}\equiv-Mv_0\cong4K_c\tilde{X}$. This quantity appears naturally and is useful because $v_0$ is inversely proportional to the bulk correlation length, i.e., $Mv_0=-Ma/\xi_b$ above $T_c$ and $Mv_0=Ma/2\xi_b$ below $T_c$. [In Sec. II we used the variable $X=\hat{x}/2$, which appeared in the integrand of (2.9).]

As $y\to0^+$, $y\coty\to1$ and $\tilde{X}\to(4K_c)^{-1}$. This point sets the upper limit of the range of the scaling function $Z(\tilde{X})$, which is defined for $-\infty<\tilde{X}<(4K_c)^{-1}$. At higher temperatures we find an exponential decay of $Z$. As is known,[22,16] $\omega_1$ is then purely imaginary, $\cosh\gamma_1$ is given by another equation that replaces (3.3) and we obtain in the scaling limit[25]

$$Z\cong2(\hat{x})^2\exp[-\hat{x}]$$

or

$$M\gamma_1\cong2(Ma/\xi_b)^2\exp[-Ma/\xi_b] \tag{3.13}$$

as the high-temperature behavior. Note that scaling of $\gamma_1$ is free of any singularity associated with the fact that $\alpha=0$ for the Ising model.

Near the maximum of $Z$ we expand the parametric representation (3.9) about $y=\pi/2$ and invert the series for $y\coty$ to obtain an expansion in $\hat{x}$

$$\Delta\tilde{f}_{\text{solv}}=c_0+c_2\hat{x}^2+c_3\hat{x}^3+\cdots \tag{3.14}$$

with the coefficients $c_0=\pi/2$, $c_2=-(-8+\pi^2)/\pi^3$, and $c_3=-8(-48+5\pi^2)/(3\pi^5),\ldots$. At $\tilde{X}=\hat{x}=0$ this function is a maximum and takes the appropriate value $\pi/2$. It approximates $\Delta\tilde{f}_{\text{solv}}$ accurately for small $|\tilde{X}|$.

The genesis of the solvation force in the $(+/-)$ strip is now clear. On adding the positive contribution $\Delta\tilde{f}_{\text{solv}}$ to the negative term $\tilde{f}^{(++)}_{\text{solv}}$ the resultant is positive, with its maximum shifted to negative $\tilde{X}$, i.e., below $T_c$. Figure 5 shows the result of this addition; the upper curve refers

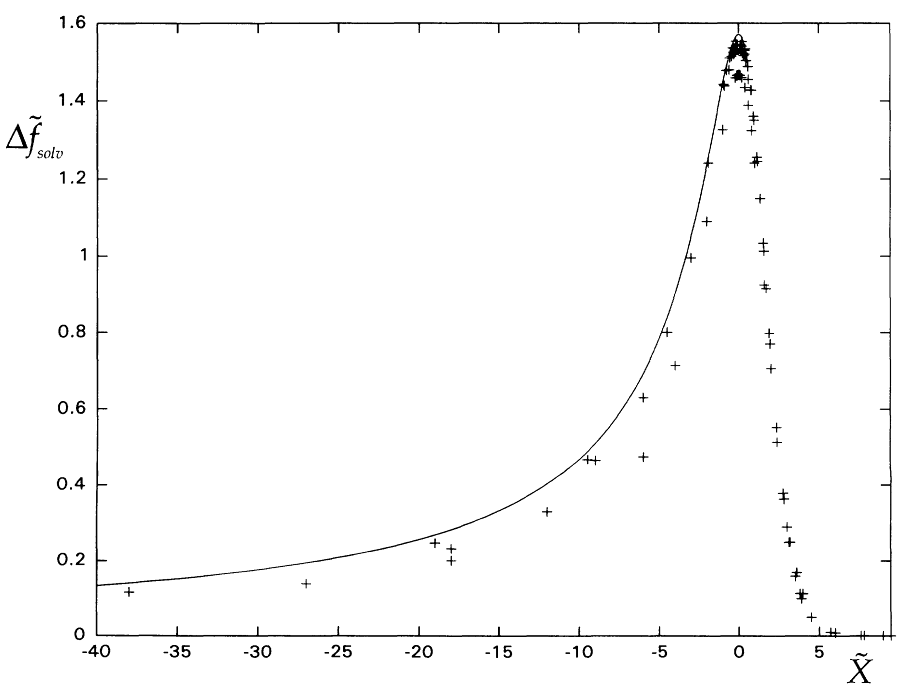


FIG. 4. $\Delta\tilde{f}_{\text{solv}}$, the difference between the scaled solvation forces in the $(+/-)$ and $(+/+)$ strips, vs $\tilde{X}\equiv nt$. The sets of points are obtained from finite differences and correspond to widths $n\in[59,199]$ while the solid line is obtained from the explicit scaling function (3.9) defined for $\tilde{X}<(4K_c)^{-1}$ $(=0.5673)$, see text. Note that the maximum is at $\tilde{X}=0$, the critical temperature.

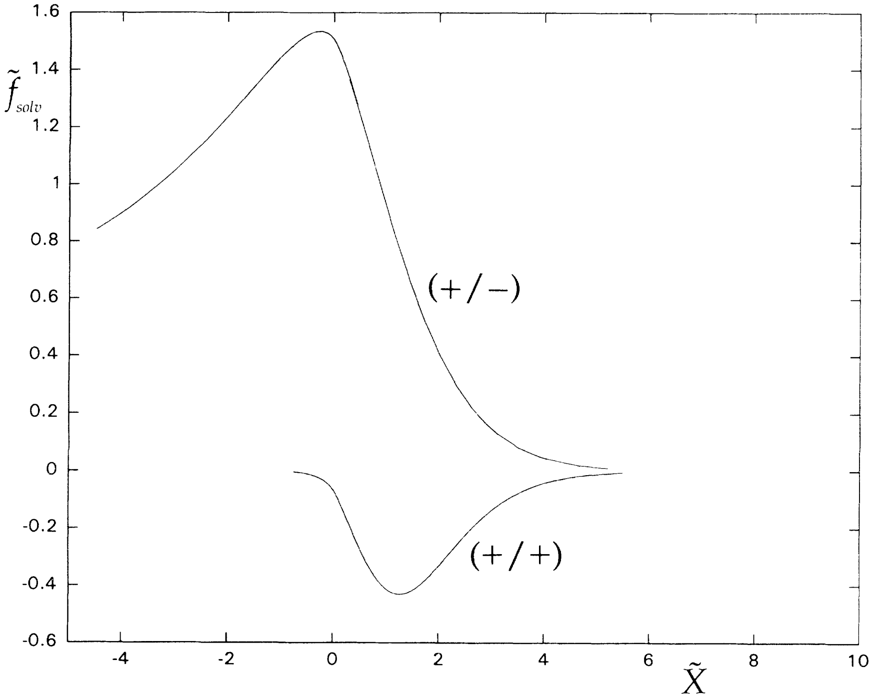


FIG. 5. The scaled solvation force in the $(+/+)$ and $(+/-)$ strips vs $\tilde{X} \equiv nt$. Note that the maximum of $\tilde{f}_{\text{solv}}^{(+/-)}$ occurs at $nt_{\max} = -0.2735$. Two separate portions, valid for low and high temperatures, are used to construct the scaling function for the $(+/-)$ strip, see text.

to $\tilde{f}_{\text{solv}}^{(+-)}(\tilde{X})$ and the lower to $\tilde{f}_{\text{solv}}^{(++)}(\tilde{X})$. The minimum in the latter was located earlier (see Sec. II), while the maximum in the former can be determined by approximating $\tilde{f}_{\text{solv}}^{(++)}$, at negative $\tilde{X}$, by means of (2.11) and $\Delta\tilde{f}_{\text{solv}}$ by (3.14). That is, for $-0.4 < \tilde{X} < 0$, the approximation

$$\tilde{f}_{\text{solv}}^{(+-)} \approx c_0 + c_2\hat{x}^2 + c_3\hat{x}^3 - \frac{\pi}{48}\exp(2\hat{x}) \tag{3.15}$$

is rather accurate and we can locate the maximum at $\tilde{X} \cong -0.2735$ or $\hat{x} \cong -0.482\,111$ with value $\tilde{f}_{\text{solv}}^{(+-)} \cong 1.533\,151\,03$. This result agrees precisely with direct numerical estimate. Thus, for an individual strip of width $M \equiv n+1$, we have, in the scaling limit,

$$T_{\max}/T_c = 1 - \tilde{C}/n \ , \tag{3.16}$$

where the constant $\tilde{C} = 0.2735$ is fixed by scaling. Since there are corrections to scaling, which are again of order $1/n$ in $\tilde{f}_{\text{solv}}$, we can expect nonuniversal corrections to this formula.

The high-temperature portion of $\tilde{f}_{\text{solv}}^{(+-)}$, also shown in Fig. 5, was obtained using (3.13) in (3.12) for $\Delta\tilde{f}_{\text{solv}}$ and the scaling form for $\tilde{f}_{\text{solv}}^{(++)}$. This portion overlaps with the low-temperature portion, given by (3.15), in the region $\tilde{X} \sim 0.5$, where $\tilde{f}_{\text{solv}}^{(+-)} \sim 1.3$.

We should emphasize that our procedure for calculating $f_{\text{solv}}^{(+-)}$, which adds the contribution from $\gamma_1$ to $f_{\text{solv}}^{(++)}$, is physically well motivated and is not just a technical artifact. The free-energy difference between the $(+/-)$ and $(+/+)$ strips must be dominated by the inferface contribution but this contribution is simply $\gamma_1$, the interfacial tension in the finite-size strip. Were we to employ the transfer matrix of Ref. 22 throughout, we would find that the free energy of the $(+/+)$ strip requires *all* quantities $\gamma_k, k = 1, 2, \ldots, n+1$ not just $\gamma_1$. The $\gamma_k$ sum to $2\ln\Lambda_0$ but this quantity is obtained much more easily from the Au-Yang and Fisher[18] approach.

## IV. DISCUSSION

In this paper we have undertaken an investigation of the solvation force in two-dimensional Ising strips subject to two particular $[(+/+)$ and $(+/-)]$ boundary conditions. Our results are restricted to bulk field $h=0$ as the transfer-matrix techniques we have employed are not easily extended to $h \neq 0$. Although we do not have a complete picture of the dependence of $f_{\text{solv}}$ on the thermodynamic fields $L$, $T$, $h$, $h_1$, and $h_n$, our study has revealed several significant features and when combined with the results of mean-field theories,[7,11,27] provides some insight into the global behavior of $f_{\text{solv}}$.

The striking feature of the result for the $(+/+)$ case is that the minimum of $f_{\text{solv}}$ is located at $T > T_c$. The same feature is observed in lattice mean-field calculations,[27] where it is also found that $t_{\min} \equiv (T_{\min} - T_c)/T_c \propto L^{-2}$, consistent with standard finite-size scaling arguments; recall that $\upsilon = 1/2$ in mean field. Such a minimum above $T_c$ is also observed in continuum density-functional results, based on a nonclassical Fisk-Widom-type free energy.[28] It is not immediately obvious why the minimum, at $h=0$, should lie above the bulk critical temperature $T_c$. Recall that for surface fields $h_1 = h_n > 0$ and bulk dimension $d \geq 3$, two phase coexistence occurs in the confined system, with finite (large) $L$, along a line in the $(h,T)$ plane which ends in a (capillary) critical point $(h_{\text{CL}}, T_{\text{CL}})$ that depends on $h_1$. $T_{\text{CL}}$ lies below $T_c$ and $h_{\text{CL}} < 0$.[3–5] The coexistence line has a positive slope and is located at $h < 0$, for example Fig. 12(c) of Ref. 7. $f_{\text{solv}}^{(++)}$ exhibits singular behavior at $(h_{\rm CL}, T_{\rm CL})$.[9] As the structure of $f_{\rm solv}^{(++)}$ for $T > T_{\rm CL}$ and $h < 0$ has not been investigated in any detail we are not able to link the minimum at $T_{\min}$ and $h = 0$ to the singular behavior at $T_{\rm CL}$. Note that the line $h = 0$ corresponds to a single phase region for all temperatures.[29] The situation is similar in $d = 2$. Although there can be no true phase transition for finite $L$ there is still a line of sharp (very weakly rounded) transitions in the Ising strip ending in a pseudocritical point.[30]

Equation (2.12) can be reexpressed as $L/\xi_b^{>}(t_{\min}) = 2.228$, since $\xi_b^{>} \approx a(4K_c t)^{-1}$ for $t > 0$. That is, the minimum of $f_{\rm solv}^{(++)}$ occurs when the strip width $\approx 2.23$ times the bulk correlation length. [Incidentally, this ratio is somewhat smaller than the estimates of Nakanishi and Fisher[4] for the same ratio of length scales at the shifted critical temperature $(h_{\rm CL}, T_{\rm CL})$. For example, for $h_1 = \infty$, they estimate a ratio of 4.61 for the simple cubic Ising model.]

The magnitude of $f_{\rm solv}$ is also important. Since the value of the scaled quantity $\tilde{f}_{\rm solv}^{(++)}(\tilde{X})$ at its minimum (see Figs. 3 and 5) is very different from that at $\tilde{X} = 0$, (the ratio of these quantities is about 6.6) knowing only the value at $T_c$, (1.3a), is not sufficient to estimate the overall strength of the solvation force. We should emphasize that the scaling function $\tilde{f}_{\rm solv}^{(++)}$ is universal, in the sense that it should describe the critical point scaling of $f_{\rm solv}$ for all $h_1 = h_n > 0$. The low temperature behavior will depend on the value of $h_1$. In particular, if $h_1$ is such that a wetting transition occurs, for $L = \infty$ and $h = 0$, at $T_w > 0$ (Ref. 31) then we expect to find specific features in $f_{\rm solv}^{(++)}$ in the neighborhood of $T_w$. These are not present in the scaling function. For free boundaries, $h_1 = h_n = 0$, Ising symmetry requires two-phase coexistence to be at $h = 0$ and it is known that for $d \geq 3$ and large but finite $L$, a line of coexistence extends to the critical temperature $T_{\rm CL} < T_c$ (Refs. 3 and 4), see also Fig. 12(a) of Ref. 7. Thus, we might expect the minimum of $f_{\rm solv}^{(00)}$ to be located at $h = 0$ and $T = T_{\rm CL}$. In the $d = 2$ strip there is no true coexistence or criticality but we would expect the minimum to lie near the pseudocritical point which is below $T_c$. Such an observation is consistent with our result (2.13).

Turning now to the $(+/-)$ strip it is instructive to compare the present results with the predictions of Parry and Evans.[7] The Landau-theory results for the case $h_n = -h_1$, $h = 0$ show $f_{\rm solv}^{(+-)} > 0$ for $T \geq T_w$ with the maximum slightly below $T_c$, see Fig. 10 of Ref. 7. That is, the temperature dependence of $f_{\rm solv}^{(+-)}$ at fixed $L$ is similar to that which we calculate for the $d = 2$ strip. Lattice mean-field calculations indicate that the temperature of the maximum $|t_{\max}| \equiv (T_c - T_{\max})/T_c \propto L^{-2}$, again consistent with standard finite-size scaling.[27] For temperatures in the range $T_w < T \ll T_c$ entropic repulsion, arising from confinement of the $(+-)$ interface, produces a positive solvation force and a scaling ansatz for the free energy predicts $f_{\rm solv}^{(+-)} \sim L^{-1/\beta_s^{\rm co}}$ for large $L$ and $h = 0$.[7] Here $\beta_s^{\rm co}$ is the critical exponent which describes the divergence of the thickness $\ell$ of the wetting film in the approach to complete wetting from off bulk coexistence: $\ell \sim |h|^{-\beta_s^{\rm co}}$. For systems with short-ranged force $\beta_s^{\rm co} = O(\ln)$ for $d \geq 3$. The explicit mean-field result is $f_{\rm solv}^{(+-)} \sim \exp(-L/2\xi_b), L \to \infty$.[7] In $d = 2$, $\beta_s^{\rm co} = 1/3$ and the scaling ansatz predicts $f_{\rm solv}^{(+-)} \sim L^{-3}$. The same result follows from heuristic arguments for the form of the singular contribution to the excess free energy arising from interfacial wandering: $f^{\rm ex} \sim L^{-\tau}$ where $\tau = 2(d-1)/(3-d)$; (with $d < 3$), is the interaction exponent for thermal wandering.[7,8] Our present analysis confirms this prediction for an Ising system since, for $T \ll T_c$, $f_{\rm solv}^{(+-)}$ is dominated by the contribution $-(\partial\gamma_1/\partial M)$ given by (3.6). Note that our result for the amplitude of the leading order term, $\pi^2/\beta\Gamma$, should be valid for all choices of $h_1$, $h_n$ which give rise to complete wetting of wall 1 by $(+)$ phase and wall $n$ by $(-)$ phase. Capillary-wavelike fluctuations of the interface give rise to the slow $L^{-3}$ decay of $f_{\rm solv}^{(+-)}$ in this temperature range. By contrast, in the $(++)$ strip there is no interface, $f_{\rm solv}^{(++)}$ is attractive and decays much faster, as $\exp(-L/\xi_b)$, in this range.

In the neighborhood of $T_c$ cross-over behavior occurs and $f_{\rm solv}^{(+-)}$ decays as $L^{-2}$, characteristic of bulk critical fluctuations. The location of the maximum is determined by (3.16), which can be reexpressed as $L/\xi_b^{>}(|t_{\max}|) = 0.4821$, where we have chosen to measure the reduced temperature in terms of the correlation length for $t > 0$. At first sight one might have expected the maximum of $f_{\rm solv}^{(+-)}$ to be located at $t = 0$ $(T = T_c)$. Were $-(\partial\gamma_1/\partial M)$ the only contribution to the solvation force, this would be the case. It is the presence of the additional term $f_{\rm solv}^{(++)}$ in (3.2) which is responsible for the shift of the maximum to $T < T_c$. Given that the maximum of $f_{\rm solv}^{(+-)}$ also occurs below $T_c$ in mean-field calculations it is natural to propose the following scenario.

Define $\sigma_{(+-)}(L)$ for *arbitrary d*, via

$$f_{(+-)}^{\rm ex}(L) \equiv f_{(++)}^{\rm ex}(L) + \sigma_{+-}(L) , \tag{4.1}$$

where $f^{\rm ex}(L)$ is, as before, the excess free energy per unit area and we are considering the two systems at the same temperature and bulk field $h = 0$.[32] Considerations of magnetization profiles show that, for $T_w < T < T_c$, $f_{(+-)}^{\rm ex}(L) \to 2\sigma_{1+} + \sigma_0$ as $L \to \infty$, whereas $f_{(++)}^{\rm ex}(L) \to 2\sigma_{1+}$ in the same limit.[7] Here $\sigma_{1+}$ $(= \sigma_{n-})$ is the excess free energy of the wall $(h_1)$-up spin interface and $\sigma_0$ is the surface tension of the (free) $+-$ interface. Equation (4.1) then implies $\sigma_{+-}(L) \to \sigma_0$. In the scaling limit, $L \to \infty$, $t \to 0$, each term in (4.1) must have the same scaling form; only the scaling functions are different. The interfacial term $\sigma_{+-}(L)$ is, of course, merely the generalization of $\gamma_1(M)$ introduced in Sec. III so it is tempting to suppose that for $d > 2$ its scaling function also has its maximum precisely at $T = T_c$. Finite-size effects on the interfacial tension of the $+-$ interface should be maximized when $\xi_b = \infty$. Thus, provided $f_{\rm solv}^{(++)}$ always has its minimum above $T_c$, as we have argued above, $f_{\rm solv}^{(+-)}$ should always have its maximum below $T_c$.

We should also remark that Parry and Evans[7] made specific predictions for the behavior of $f_{\rm solv}^{(+-)}$ in the neighborhood of the wetting transition temperature $T_w$; namely that the solvation force, at large $L$ and $h=0$, should, decrease with decreasing $T$, vanish at some $T^* < T_w$ and then take on negative values, with a minimum below $T_w$. Explicit results for the restricted solid-on-solid model confirmed the existence of such a minimum.[7] However, it would be valuable to examine both the solvation force and the magnetization profile in an antisymmetric Ising strip, with $h_1$ ($=-h_n$) chosen so that $T_w > 0$, in order to test the detailed predictions (based on a scaling ansatz for critical wetting) for the behavior of these quantities near $T_w$.[7,8] Our present work is restricted to $T_w=0$ but our methods can be extended to weaker $h_1$ and we shall report results in a future publication.

Finally we note that Krech and Dietrich[33] have recently determined the scaling functions for the finite-size contribution $\delta f^{\mathrm{ex}}(L)$ to the excess free energy using field-theoretical renormalization-group theory. Although a direct comparison of their results with the present is not feasible since these authors do not consider surface fields, it is significant that the scaling functions are positive (repulsive force) for antiperiodic and Dirichlet-Neumann boundary conditions but are negative (attractive) for other choices. Moreover, they find that the scaling functions do not, in general, have their extrema at $T=T_c$.

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## APPENDIX

Denote the scaling function defined by (2.9), as $I$. Assume first $X>0$ and write

$$I=I_1+I_2$$

with

$$I_1 \equiv \int_0^X d\xi \cdots \quad \text{and } I_2 \equiv \int_X^\infty d\xi \cdots \ . \tag{A1}$$

In the first integral $\xi < X$ always so $Q_0 = X[1+(\xi/X)^2]^{1/2}$ can be expanded and the integrand is well behaved everywhere for $\xi \in [0,X]$; no negative powers of $\xi$ appear.

In the second integral $(X/\xi)<1$ so $Q_0$ can be expanded if it is written as $Q_0=\xi[1+(X/\xi)^2]^{1/2}$. Expanding the integrand in powers of $(X/\xi)$ and collecting powers of $X$ we obtain the integrand in the form

$$\sum_{n=0} f_n(\xi)\xi^{-n}X^n \ .$$

Powers $X^0$ and $X^1$ contribute to the nonsingular part. For $n=2$,

$$f_2(\xi)=(1/4)\xi-(8/3)\xi^4+\cdots \tag{A2}$$

and the first term yields

$$(4/\pi)\int_X^{\cdots} d\xi (X/\xi)^2 \tfrac{1}{4}\xi \to -\frac{1}{\pi}X^2\ln|X| \ .$$

The remainder of $f_2(\xi)$, as well as all the other $f_n$, $n=3,\ldots,$ yield terms nonsingular in the limit $X\to 0$. For $X<0$ one obtains similar results with the same coefficient, $-(1/\pi)$, of the singular term. Hence the scaling function $\tilde{f}_{\mathrm{solv}}$ has the form

$$\tilde{f}_{\mathrm{solv}}(X)=Y(X)-(1/\pi)X^2\ln|X| \tag{A3}$$

with $X=2K_c nt$ and $Y(X)$ smooth across $X=0$.

It is not easy to detect this contribution numerically, i.e., in data computed directly from (2.9) and it is even more difficult in data for finite $L\equiv na$, since these contain corrections to scaling of the order of $L^{-1}$ in $\tilde{f}_{\mathrm{solv}}$ or $L^{-3}$ in $f_{\mathrm{solv}}$. Nevertheless, according to (A3), the second derivative obtained from (2.9) must be of the form $Y''-(1/\pi)(2\ln X+3)$ and when this is computed it shows the expected logarithmic divergence as $X\to 0$ with the correct coefficient $2/\pi$. After subtracting the logarithmic term, we find $Y''(X)$ is smooth across $X=0$. Indeed the $d=2$ Ising model has no discontinuous $t^2$ contributions.[2,26]

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