Wetting versus layering near the roughening transition in the three-dimensional Ising model

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Ising models with free surfaces where a surface field H_1 competes with the bulk field H exhibit wetting phenomena at temperatures T above the roughening transition temperature T_R, while for $T<T_R$ layering transitions occur. In our previous Monte Carlo study of this model [Phys. Rev. B **37**, 1745 (1988)] we posed the problem of how these two very different surface phase-transition phenomena can be integrated into a common phase diagram. Here we present new Monte Carlo results obtained on very large lattices, using an $L\times L\times D$ thin-film geometry with L up to 512 and D up to 80, where the exchange J_s in the two free $L\times L$ surfaces is allowed to differ from the exchange J in the bulk. For $J_s/J=0.5$ we find that if H_1 is varied for $H=0$ and $T\lesssim T_R$ the layering sequence starts with a transition in the third layer, the first two layers behaving smoothly with H_1. However, for $J_s/J=1$ the layering sequence starts with the second layer and only the first layer behaves smoothly. On the other hand, for J_s slightly exceeding J we find that the layering transitions of the first three layers coincide, and this transition develops into the first-order wetting transition for $T\lesssim T_R$. This latter behavior was not predicted by the previous phenomenological treatment. However, a complete clarification of the surface phase diagram of the Ising model would require extreme effort and cannot yet be provided by present simulation techniques.

I. INTRODUCTION

Wetting and layering transitions can be interpreted in terms of singularities of the surface excess free energy of bulk systems in contact with a wall.[1-5] These phenomena occur for various physical systems (adsorption of gases on walls, surface enrichment in mixtures, surface-induced ordering or disordering at various first-order phase transitions in the bulk, surface melting, etc.) and thus have found much recent interest. A wetting transition can be viewed as an unbinding transition of an interface from the wall, implying that an unbound interface (i.e., far away from the wall deep in the bulk) is rough, i.e., not localized at particular (lattice) planes. In contrast, layering transitions imply well-localized sharp interfaces, which we call nonrough. Since the interface between coexisting bulk phases may undergo a roughening transition upon variation of the temperature,[6] both wetting and layering phenomena may occur in the same physical system (the former above and the latter below the roughening transition temperature T_R). This situation in fact occurs in the nearest-neighbor Ising model, as discussed in our previous work[7] (which hereafter will be referred to as I); the roughening transition has been estimated to occur at[8-12] $J/k_BT_R\approx 0.409\pm 0.004$.

Depending on the ratio between the exchange constant J_s in the free surface plane of the Ising model and the exchange J in the bulk and upon the temperature, one may observe either first- or second-order wetting transitions at $T>T_R$. As in I and in Ref. 11, we restrict attention here to the case where the symmetry-breaking field $H_1<0$ caused by the surface is strictly short in range; it acts in the free surface plane only. The surface excess magnetization m_s increases smoothly as the bulk field H is decreased and ultimately diverges as $H\to 0^+$ (complete wetting[1-5]) if the wetting transition is of second order. In the case of first-order wetting, m_s exhibits a discontinuity when at some critical field $H_c(T)$ one crosses the prewetting line (at this transition the wetting film thickness jumps from a small value to a somewhat larger but still finite value) before the film thickness (defined by $|m_s|/m_b$ where m_b is the bulk magnetization) diverges as $H\to 0^+$.

For $T<T_R$, however, the gradual increase of $|m_s|\to\infty$ as $H\to 0^+$ is replaced by an infinite sequence of first-order layering transitions, which end in layering critical points $T_c(n)$, n being the index of the layer (where $n=1$ is the free surface). It is known[12] that $\lim_{n\to\infty}T_c(n)=T_R$; however, much less is known about the layering transitions for small n near T_R. In particular, one may ask how the prewetting transition emerges from the layering transitions. Neither is the structure of the phase diagram at $H=0$ well understood (see I). Since it was found in I that layering transitions could also be observed at $H=0$ varying H_1, at least for the first few layers $n=1,2,\ldots$, the problem of understanding the phase diagram topology was raised. Figure 1 shows some of the proposed scenarios for the surface phase diagram at phase coexistence ($H=0$) in the Ising model. In the previous Monte Carlo work described in I, it was simply impossible to take data with meaningful accuracy for temperatures close to T_R, because of the dramatic slowing down of interfacial fluctuations; thus, no statement

could be made as to which (if any) of the phase diagrams sketched in Fig. 1 is qualitatively correct.

This limitation has now been overcome and in the present paper we present Monte Carlo data on wetting and layering in the Ising model at temperatures near T_R. As in I, we consider systems in a "thin-film" geometry $L \times L \times D$, with two equivalent free $L \times L$ surfaces and periodic boundary conditions in the two directions parallel to these surfaces. Applying a vectorizing multispin-coding algorithm[13] in every two-dimensional $L \times L$ plane parallel to the free surface together with the technique of preferential surface site selection,[7,11,14] the simulation program performs about two order of magnitude faster (on the CDC Cyber 205 at the University of Georgia) than the conventional program used for the earlier study[7] on serial computers. While in I linear dimensions $L \leq 50$, $D \leq 40$ were considered (i.e., system sizes up to 10^5 Ising spins), we now work with L up to $L_{\max} = 512$ and D up to $D_{\max} = 80$. While we find that near T_R a thickness $D = 40$ is no practical limitation, it would be desirable to work with distinctly larger lateral dimensions L, which is not straightforwardly achievable, since our largest system ($L = L_{\max}$, $D = 40$) already contains more than 10^7 Ising spins.

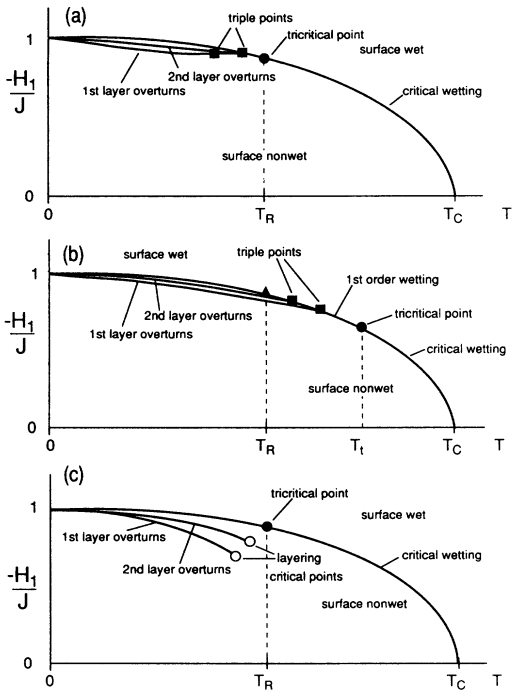

FIG. 1. A series of schematic surface phase diagrams for the nearest-neighbor semi-infinite Ising model exposed to a surface field H_1 opposed to the direction of the spontaneous magnetization. Cases (a) and (c) assume that the wetting transition stays second order for all $T > T_R$, and then the transition at $T = T_R$ has to be a tricritical wetting transition (tricritical points are denoted by full dots in the figure). Case (b) assumes that a tricritical point is already reached for a temperature $T_t > T_R$ (this is the case for $J_s > J$, while for $J_s \leq J$ we have $T_t = T_R$). The line of critical wetting transitions which starts at T_t ends at the bulk critical temperature T_c in all cases. At the point $T = 0$, $H_1/J = -1$ all layering transitions and the wetting transition of the surface merge. The layering transitions of the first, second (and possibly more layers, which are not shown for the sake of clarity) end either in surface triple points [cases (a) and (b)] or in layering critical points $T_c(n)$ [(c), denoted by open circles]. The triple points (denoted by full squares) have to be always at lower temperatures than T_t, which implies they must be at lower temperatures than T_R, if $T_t = T_R$ [case (a)], but they could also be at temperatures $T_R < T_{\text{triple}}(n) < T_t$, if $T_t > T_R$ [case (b)]. If there is an infinite sequence of triple points $T_{\text{triple}}(n)$ where the layering transitions end, we must have $\lim_{n\to\infty} T_{\text{triple}}(n) = T_R$ [this accumulation point of triple points is denoted by a full triangle in (b); in (a) it coincides with T_t]. Similarly, if there were an infinite sequence of layering critical points $T_c(n)$ we must have $\lim_{n\to\infty} T_c(n) = T_R$. Note that this series is by no means meant as an exhaustive classification, but only an illustration of what one possibly can expect. From I, in revised form.

Section II now precisely specifies the model and defines the quantities that are analyzed, and gives some technical details on our data analysis (more of such details can be found in I). Section III presents our results for unchanged surface exchange ($J_s = J$). Section IV describes the results for weakened surface exchange ($J_s = 0.5J$), and Sec. V for enhanced surface exchange. Section VI then contains a discussion of our results and compares them to the speculative phase diagram predictions of Fig. 1.

II. MODEL CALCULATED QUANTITIES AND COMPUTATIONAL TECHNIQUES

The Hamiltonian of our model is

$$H = -J \sum_{\text{bulk}} \sigma_i \sigma_j - J_s \sum_{\text{surfaces}} \sigma_i \sigma_j - H \sum_i \sigma_i - H_1 \sum_{\text{surfaces}} \sigma_1, \quad \sigma_i = \pm 1 . \tag{1}$$

As mentioned above, we study $L \times L \times D$ systems with two free surfaces. While the vectorizing multispin-coding program allows maximum efficiency only for $L = 128$ or larger (integer multiples of 64[13]) D is arbitrary. We typically generated data for $L = 128$ or 256, occasionally also for $L = 64$ or 512.

For most runs 4000 MCS (Monte Carlo steps per site) were first discarded and 12 500 MCS were retained for averages, with spins at the surface sampled ten times as often as those in the bulk. Some much larger runs were made (up to ten times as long) in the vicinity of second-order or "almost" second-order transitions.

Among the quantities we record are the profiles of magnetization m_n, energy U_n, layer susceptibility χ_{nn}, and layer specific heat C_n (n is the layer index which runs from 1 to D, where the lattice spacing is equal to unity). Here both χ_{nn} and C_n are obtained from standard fluctuation relations. A further susceptibility measuring the response of the surface layer magnetization to the bulk field is

$$\chi_1 = \left[\frac{\partial m_1}{\partial H}\right]_T = \frac{L^2 D}{k_B T}\left[\left\langle \frac{1}{2L^2}\sum_{\text{surfaces}}\sigma_k \frac{1}{L^2 D}\sum_i \sigma_i \right\rangle - \left\langle \frac{1}{2L^2}\sum_{\text{surfaces}}\sigma_k \right\rangle \left\langle \frac{1}{L^2 D}\sum_i \sigma_i \right\rangle\right] . \quad (2)$$

We also record a bulk magnetization m_b, bulk energy U_b, bulk susceptibility χ_b, and bulk specific heat C_b defined from an average over the ten innermost layers. We have checked that these estimates are not at all affected by the possible existence of interfaces close to the free surfaces. From the layer quantities we can also obtain the surface excess magnetization m_s, surface excess energy U_s, etc., as follows:

$$2m_s = \sum_{n=1}^{D}(m_b - m_n), \quad 2U_s = \sum_{n=1}^{D}(U_b - U_n), \text{ etc.} \quad (3)$$

Note that the factor 2 simply comes from the fact that we have two free surfaces.

In order to locate first-order layering transitions we often encounter huge hysteresis. As an example, Fig. 2 presents our data for the case $J_s/J = 1.02$ and $J/k_B T = 0.44$. In this case a pronounced first-order transition occurs between a state where the surface is "nonwet" (even the layer magnetization m, is still positive) to a state where several layers are overturned. In the example shown in Fig. 2, two or three layers are overturned because we used the states $m_1 = m_2 = m_3 = -1$, $m_4 = \cdots = m_{D-3} = +1$, $m_{D-2} = m_{D-1} = m_D = -1$ or $m_1 = m_2 = -1$, $m_3 = \cdots = m_{D-2} = +1$, $m_{D-1} = m_D = -1$ as initial conditions; however, an initial condition with more overturned layers remains stable, or metastable, over the same range of H_1. In contrast, states with one overturned layer only turned out to be unstable and develop either into the state with all layers up (for $H_1/J > -0.94$) or into the state with two layers down. At such low temperatures as shown in Fig. 2, it may take an unreasonably long time until a metastable state has decayed to the appropriate equilibrium phase, since each wrongly oriented layer can overturn only via nucleation and growth and the thermal fluctuations needed to start this nucleation process are quite rare, the bulk magnetization being very close to saturation ($m_b = 0.988\,04$) at this temperature.

A determination of which surface phase is stable and which is only metastable requires an estimate of the free-energy difference between those phases. For this purpose, we use standard thermodynamic integration methods.[15] The free-energy difference between two states in the same surface phase and at the same temperature T but two different values of the surface field $H_1^{(1)}, H_1^{(2)}$ is simply obtained from the well-known relation[16] for the surface free energy F_s

$$m_1 = -(\delta F_s/\delta H_1)_T \quad (4)$$

and hence

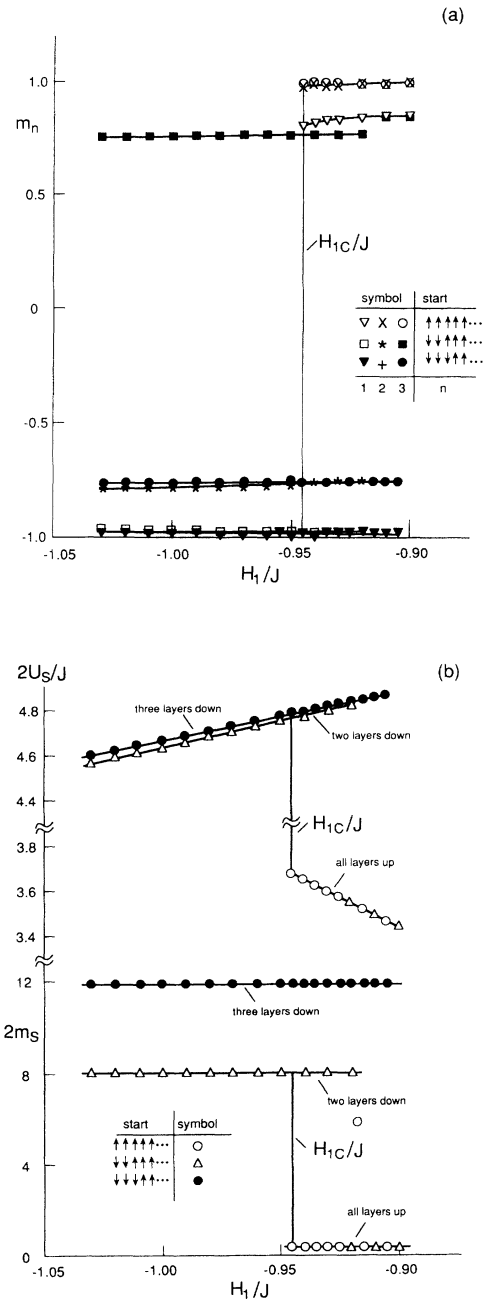

FIG. 2. (a) Layer magnetizations m_n plotted versus surface field H_1/J at $J/k_B T = 0.44$ for $J_s/J = 1.02$, for $n = 1,2,3$. Note that both surfaces are always averaged together (m_n is understood as the average of m_n and m_{D+1-n}), if they are in the same state, in order to improve the statistics. Four initial conditions were used here, either all spins up ($\uparrow\uparrow\uparrow\uparrow\uparrow\cdots$) or one, two, or three layers of down spins at the surfaces and the remaining layers up ($\downarrow\uparrow\uparrow\uparrow\uparrow\cdots$), ($\downarrow\downarrow\uparrow\uparrow\uparrow\cdots$), and ($\downarrow\downarrow\downarrow\uparrow\uparrow\cdots$). Data for ($\downarrow\uparrow\uparrow\uparrow\uparrow\cdots$) are not shown, since this phase turned out to be unstable here. The location of the transition field H_{1c} was found from thermodynamic integration methods, as described in the main text. (b) Surface excess energy $2U_s/J$ (upper part) surface excess magnetization m_s (lower part) plotted vs H_1/J, for the same parameters as shown in case (a). All data are for $L = 128$ and $D = 40$.

$$\Delta F_s = -\int_{H_1^{(1)}}^{H_1^{(2)}} m_1 dH_1 \ . \tag{5}$$

In order to compare the free energy of two different surface phases, we consider two paths varying the temperature from $T=0$ to the desired temperature, keeping the surface field constant at the values $H_1^{(1)}$ in one surface and $H_1^{(2)}$ in the other surface phase. At $T=0$ the free energies are equal to the internal energies, which are trivially known, $F_{s0}^{(1)}=U_{s0}^{(1)}$ and $F_{s0}^{(2)}=U_{s0}^{(2)}$; and at nonzero temperatures we use the integration formula (β=inverse temperature)

$$\beta F_s^{(i)}(\beta)=\beta_0 F_s^{(i)}(\beta_0)+\int_{\beta_0}^{\beta} U_s^{(i)}(\beta')d\beta' \ . \tag{6}$$

Two comments are in order: (i) a reference state $T=0$ for the thermodynamic integration in Eq. (6) would correspond to $\beta_0 \to \infty$ and hence, of course, cannot be used. However, the equality $F_s^{(i)}=U_s^{(i)}$ holds also, as an excellent approximation at very low but finite temperatures, where the layer magnetizations and layer energies differ from their ground-state values only by one part in 10^{-5} or less. Thus, we have found it admissible and practically convenient to use $\beta_0=1.2/J$ as a reference state for the thermodynamic integration where the entropy can still be neglected. (ii) In many cases of interest the surface energies $U_s^{(i)}$ for the various phases $i=1,2,\ldots$ are rather large, while the free-energy differences of interest are much smaller. In the subtraction of two large numbers from each other which were both obtained from Eq. (6) via numerical integration, proliferation of integration errors becomes a problem. However, the simple recipe for this problem is to perform the numerical integration directly on the surface energy difference, $\Delta U_s(\beta')=U_s^{(1)}(\beta')-U_s^{(2)}(\beta')$,

$$\begin{aligned}\beta\Delta F_s(\beta) &\equiv \beta(F_s^{(1)}-F_s^{(2)}) \\ &=\beta_0\Delta F_s(\beta_0)+\int_{\beta_0}^{\beta}\Delta U_s(\beta')d\beta' \ ,\end{aligned} \tag{7}$$

since the free-energy difference $\Delta F_s(\beta)$ is all that is really needed. Figure 3(a) shows that indeed the surface energy differences are much smaller than the surface energies themselves, in particular at low temperatures. From this procedure we obtain free-energy differences ΔF_s between states in different surface phases (different number of overturned layers) and different values $H_s^{(1)}$ and $H_1^{(2)}$, but at the same temperature (including the temperature of interest). These free-energy differences are then combined with Eq. (5) to obtain the free-energy difference between states in different surface phases at the same values of the surface field H_1; see Figs. 3(b) and 3(c). From these figures it is evident that large surface free-energy differences occur between the state with all layers up and the states with two or three layers at the surface being overturned. However, the surface energy and free-energy differences between the state with two and three layers overturned, but otherwise identical conditions, are already very small. We have found that the accuracy of the present investigation is not sufficient to distinguish the free-energy differences between states where three or

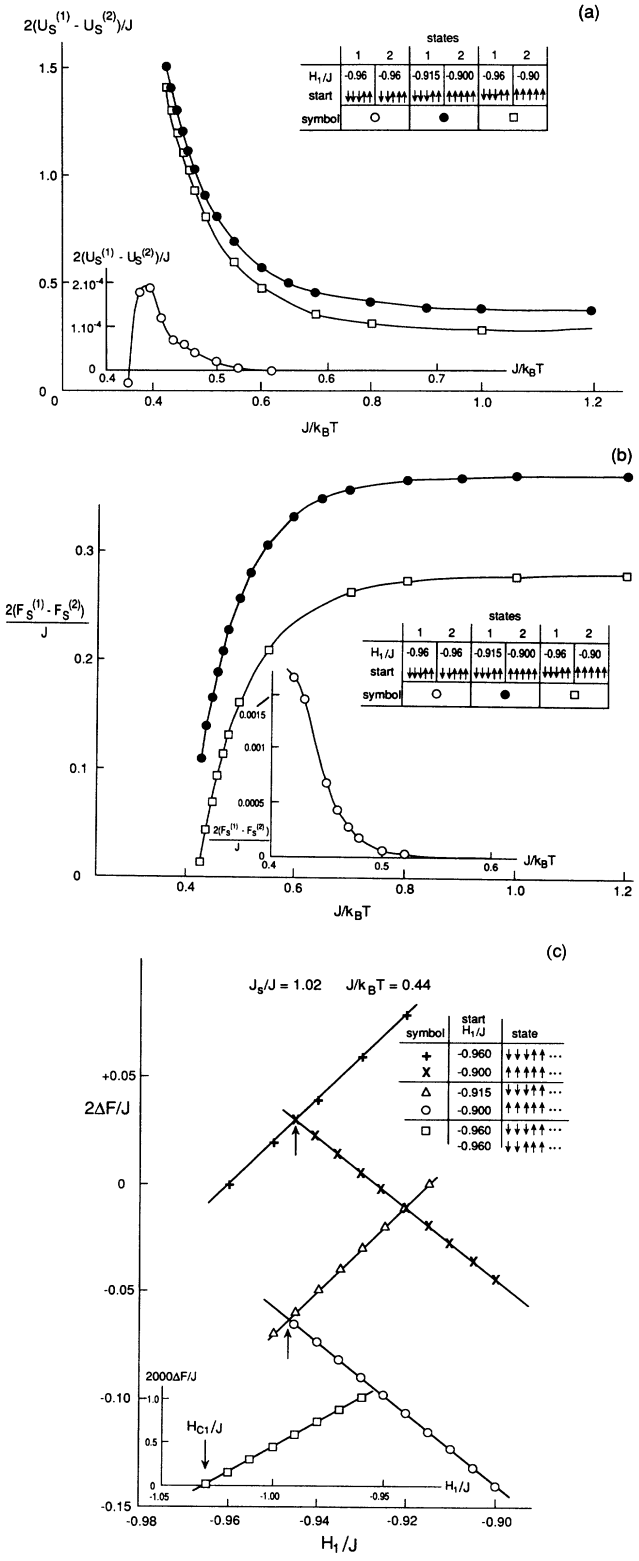

FIG. 3. (a) Surface energy differences $2\Delta U_s/J$ plotted vs inverse temperature, for $J_s/J=1.02$ and several choices of H_1/J and the initial conditions, as indicated in the figure. (b) Surface free-energy differences $2\Delta F_s/J$ resulting from thermodynamic integration of the data shown in (a). (c) Estimation of the critical fields H_{c1}/J and H'_{c1}/J from intersection of free-energy differences between surface states in different phases, as indicated in the figure.

more than three layers are overturned, at all temperatures $T < T_R$.

III. WETTING VERSUS LAYERING IN THE MODEL WITH UNMODIFIED SURFACE EXCHANGE ($J_s = J$)

In I we already tried to study the model defined in Eq. (1) at inverse temperatures $J/k_BT = 0.40$ and $J/k_BT = 0.42$, but the data generated then were so noisy that we could draw no conclusion apart from "the nature of the transitions at $J/k_BT = 0.40$ and $J/k_BT = 0.42$ occurring in our model needs further clarification."

Figure 4 now shows clear evidence that at $J/k_BT = 0.40$, i.e., at a temperature about 2% above the roughening temperatures, we still have a second-order wetting transition, at $H_{1c}/J = -0.94 \pm 0.005$. A non-

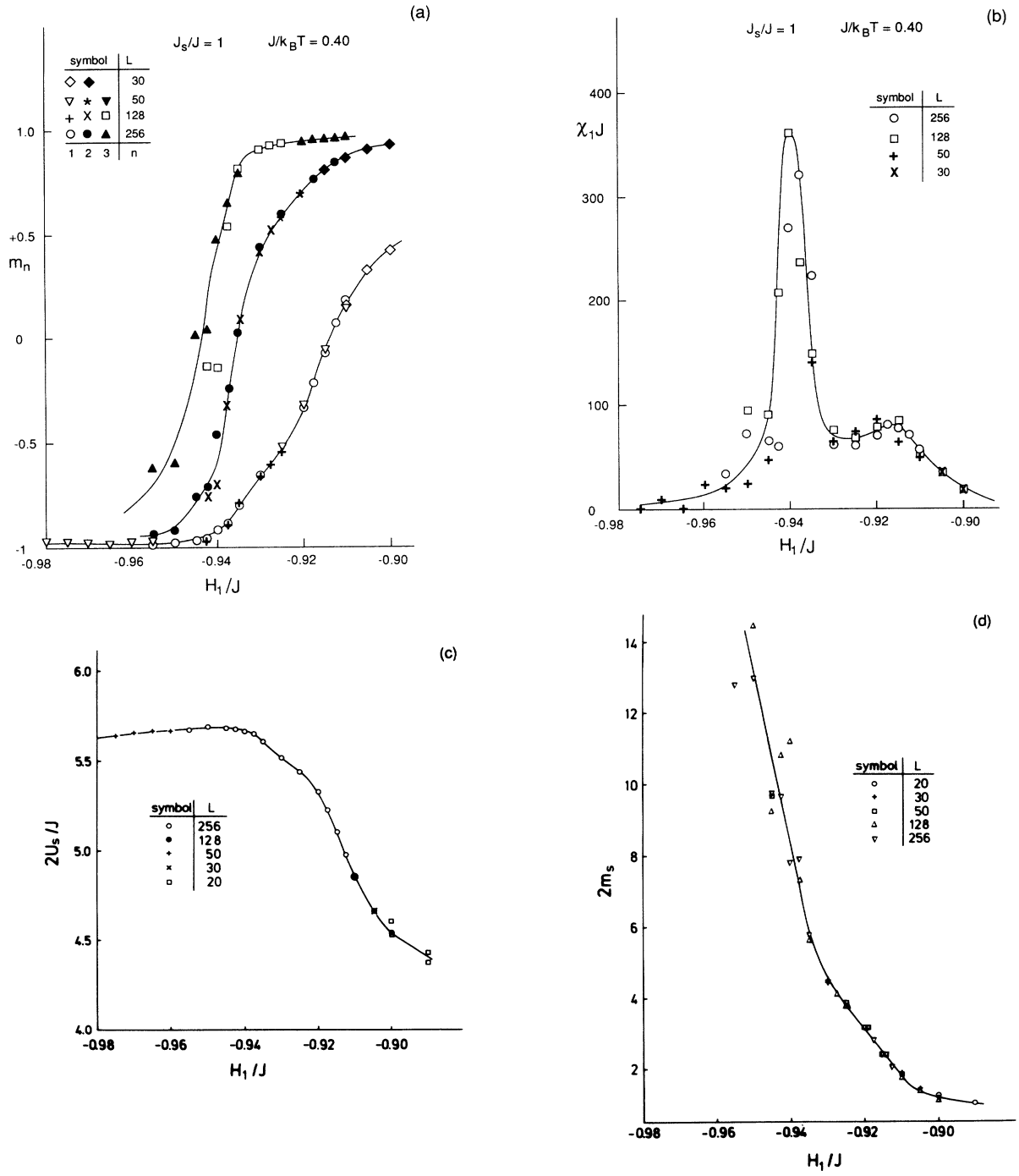

FIG. 4. (a) Layer magnetizations m_1, m_2, and m_3 of the first three layers adjacent to the surface plotted vs surface field H_1 at the inverse temperature $J/k_BT = 0.40$. Different symbols denote the linear dimensions and the layer index, as indicated in the figure. (b) Surface layer susceptibility χ_1 for $J/k_BT = 0.40$ and $J_s/J = 1$ plotted vs H_1/J. (c) Surface excess energy U_s/J plotted vs H_1. (d) Surface excess magnetization plotted vs H_1/J.

singular precursor peak of a layering transition occurs in χ_1 at about $H_{1c}/J \approx -0.92$, Fig. 4(b), and this also shows up in a change of slope in the surface excess energy, Fig. 4(c). The behavior of the layer magnetizations [Fig. 4(a)] and the surface excess magnetization [Fig. 4(d)] are qualitatively the same as presented in previous work[7,11] for higher temperatures. Obviously, except for the region far away from the wetting transition, the data in Fig. 4 are still rather noisy, although most data for small system sizes have been omitted from this plot. Strong finite-size effects and very slow sluggish relaxation of the interface would make it very difficult to study wetting even closer to T_R.

In Figs. 5 and 6 the behavior of U_s and m_s at temperatures slightly below T_R is analyzed. The character of the behavior is now distinctly different: The surface excess magnetization as a function of the surface field now exhibits several steps, which is the signature of layering behavior. But at $J/k_BT=0.42$ and at $J/k_BT=0.43$, the first "step," through which the orientation of the layer $n=1$ is overturned, is perfectly smooth, indicating that these temperatures are above the layering critical temperature $T_c(n=1)$. While at $J/k_BT=0.42$ it is not so clear whether the layering transition of the second layer is also smooth or is weakly of first order, at $J/k_BT=0.43$ the layering transition of the second layer (from the state "one layer down" to the state "two layers down") clearly is of first order. Thus we can conclude that $J/k_BT_c(n=2)\approx 0.42$. At both temperatures, first-order transitions occur from the state with two layers down to

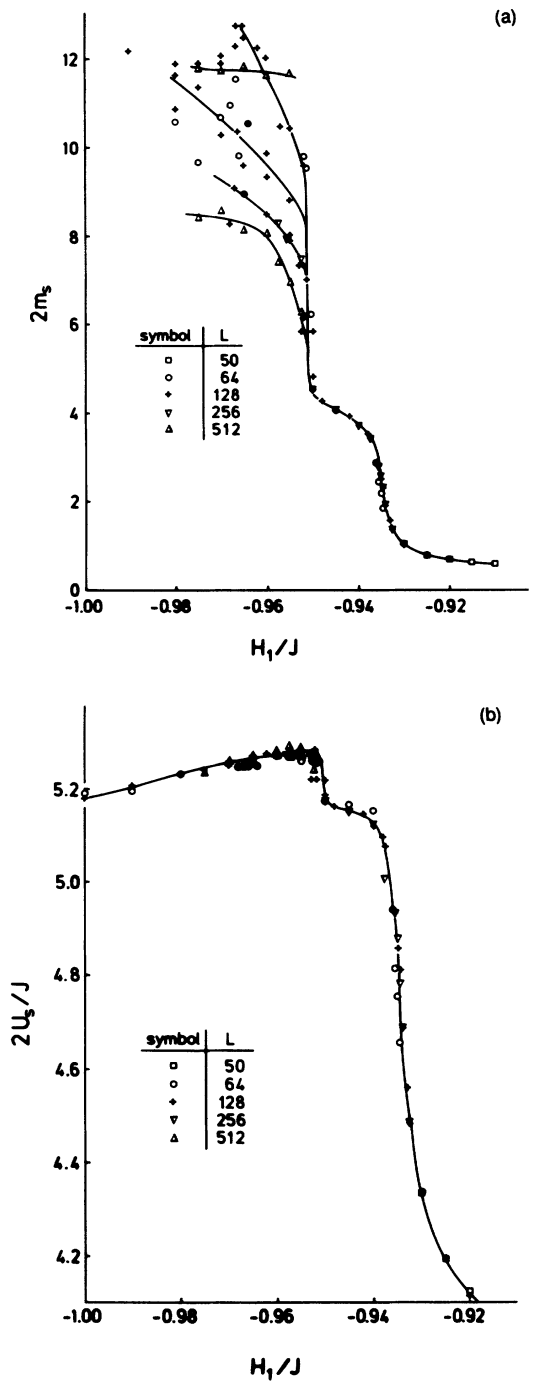

FIG. 5. Surface excess magnetization (a) and surface excess energy (b) plotted vs H_1/J at the inverse temperature $J/k_BT=0.42$ for $J_s/J=1$. Various symbols denote different lattice linear dimensions as shown in the figure. For $L=128$ we used both $D=40$ and $D=80$, while otherwise $D=40$ was used throughout.

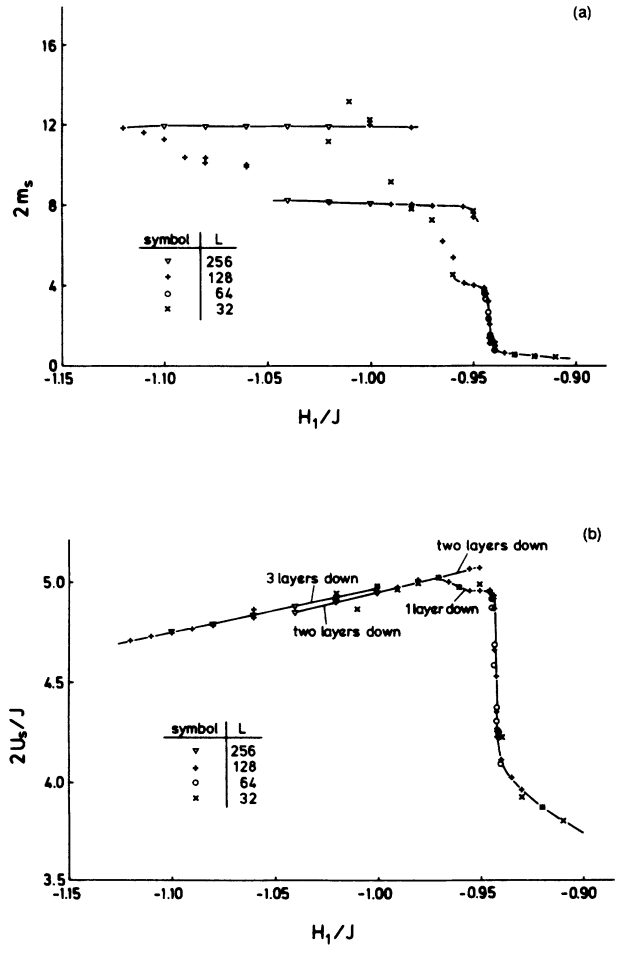

FIG. 6. Same as Fig. 5, but for $J/k_BT=0.43$.

the state with three layers down (note that we cannot really distinguish the latter state from a "wet surface" with many layers adjacent to the surface being overturned, however). Strong hysteresis and sluggish fluctuations prevent more precise statements about the layering transition of the third layer, as is obvious from Fig. 5(a). The proximity of T_R precludes a more definitive study, in spite of our use of systems containing more than 10 million Ising spins.

While the data for $L=32$ shown in Fig. 6(a) are rather scattered, indicating that meaningful information cannot be gathered from such a small system, the data for $L=128$ in the range $-1.09 \leq H_1/J \leq -1.06$ lie systematically in between the branches with two or three overturned layers. Closer inspection of the data reveals that the system has become trapped in a state with unsymmetrical surface conditions, two layers being overturned on the left surface and three layers being overturned at the right. These points in Fig. 6(a) hence may be discarded. Comparing the slope of m_s vs H for the smooth transition of the first layer in Fig. 6(a) to the corresponding part of Fig. 5(a), we see that the curve at $J/k_BT=0.43$ is somewhat steeper than for $J/k_BT=0.42$. Thus one might expect that $J/k_BT=0.43$ is close to the layering critical point of the first layer, and this is in fact borne out by Fig. 7, where data for $J/k_BT=0.44$ are presented. Clear evidence for first-order layering transitions from the state "all layers up" to

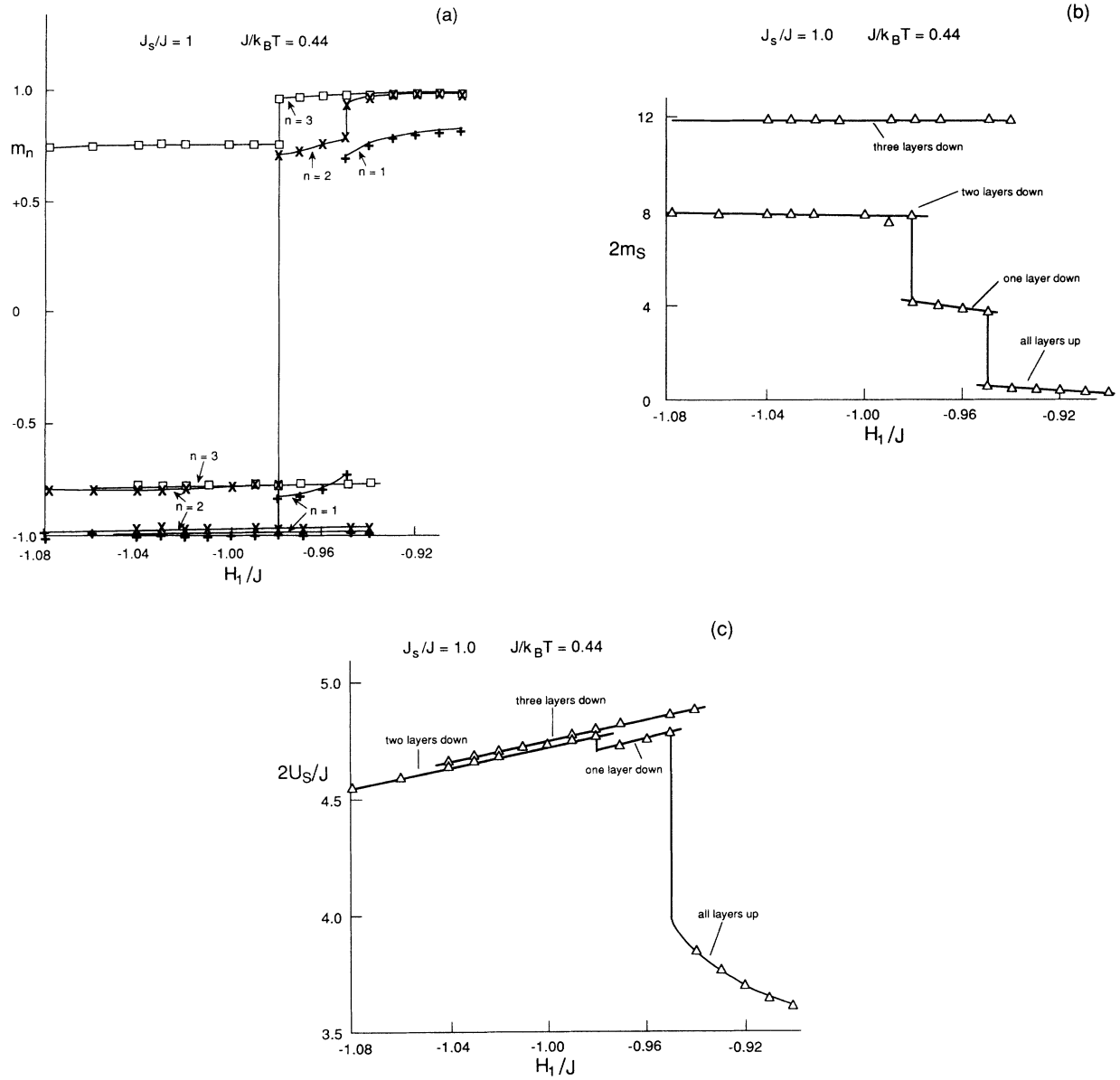

FIG. 7. Layer magnetizations m_n for the first three layers (a), surface excess magnetization (b), and surface excess energy (c) plotted vs surface magnetic field H_1/J at $J/k_BT=0.44$ and $J_s/J=1$. All data refer to the choice $L=128$, $D=40$.

"one layer down" and from there to two layers down and from there to three layers down is visible. The precise location of these layering transitions would require us to obtain the free energy of the various branches, as outlined in Sec. II. This has not been done.

If the temperature is lowered still further, the behavior stays of the same type as seen in Fig. 7. We have taken data for $J/k_BT=0.45$ for much larger systems than in I and confirmed the description which was presented there.

IV. WETTING VERSUS LAYERING IN THE MODEL WITH WEAKENED SURFACE EXCHANGE ($J_s=J/2$)

The weakening of the surface exchange has the effect of basically decoupling the behavior of the first layer from all the following layers. Apart from this phenomenon, the behavior at $J/k_BT=0.40$ is a standard critical wetting behavior (Fig. 8), similar to Fig. 4. As is evident from Fig. 8(b), the overturning of the magnetization m_1 of the first layer is smeared out over a very wide regime of H_1, from $H_1/J\approx 0$ to $H_1/J\approx -2$, and only when the first layer is nearly saturated at the negative value of the spontaneous magnetization do the other layers follow, in much the same way as in the case $J_s=J$. Comparing Figs. 8(a) and 4(a), we see that there is a great similarity between the layers $n=1,2,3$ ($J_s=J$) and $n=2,3,4$ ($J_s=J/2$), apart from the shift in scale for H_1. The behavior of U_s is also of interest: while a smooth round peak occurs at $H_1/J\approx -1.1$, where the magnetization m_1 has just passed zero, the behavior at the wetting transition itself ($H_{1c}/J\approx -2.7\pm 0.1$) is very smooth.

A similar discussion applies to temperatures slightly below the roughening transition, $J/k_BT=0.42$ (Fig. 9):

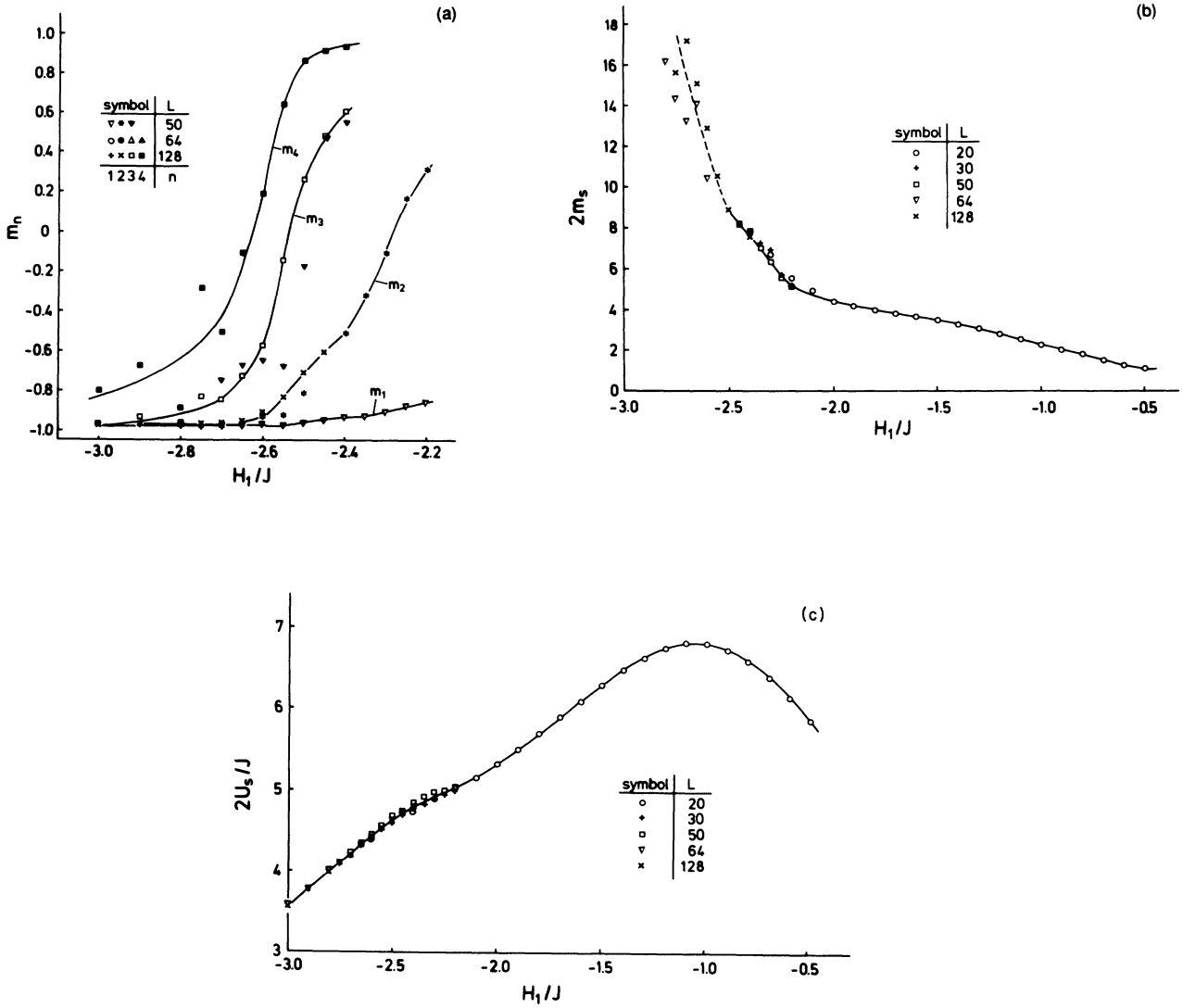

FIG. 8. Layer magnetizations m_n for the first four layers (a), surface excess magnetization (b), and surface excess energy (c) plotted vs surface magnetic field H_1/J at $J/k_BT=0.40$ and $J_s/J=0.5$. Various symbols denote different n [in (a)] and different lattice linear dimensions as indicated in the figure. For $H_1/J<-2.5$ the data are strongly size dependent, and it is not clear if the data for $L=128$ have already converged to the thermodynamic limit. The dashed part of the curve in (b) is thus only a plausible extrapolation.

we now have layering behavior, with a smooth variation m_2 vs H_1 for the second layer, and distinct first-order layering transitions in the third and fourth layer. At lower temperatures, the layering of the second layer also turns into a first-order transition [see Fig. 16(b) of I]. We estimate that $J/k_BT_c(n=2)$ only slightly exceeds 0.42 also in this case, similar to the case $J_s/J=1$. Thus, the reduction of J_s strongly affects the first layer, but has little effect on higher layers apart from the change of scale for H_1.

Note that our characterization of the nature of the various transitions always is based on an examination of all the quantities discussed in Sec. II, such as, e.g., the layering susceptibilities χ_{nn} [Fig. 9(d)]. We emphasize that, for the sake of saving space, only a small fraction of all the data generated is shown here.

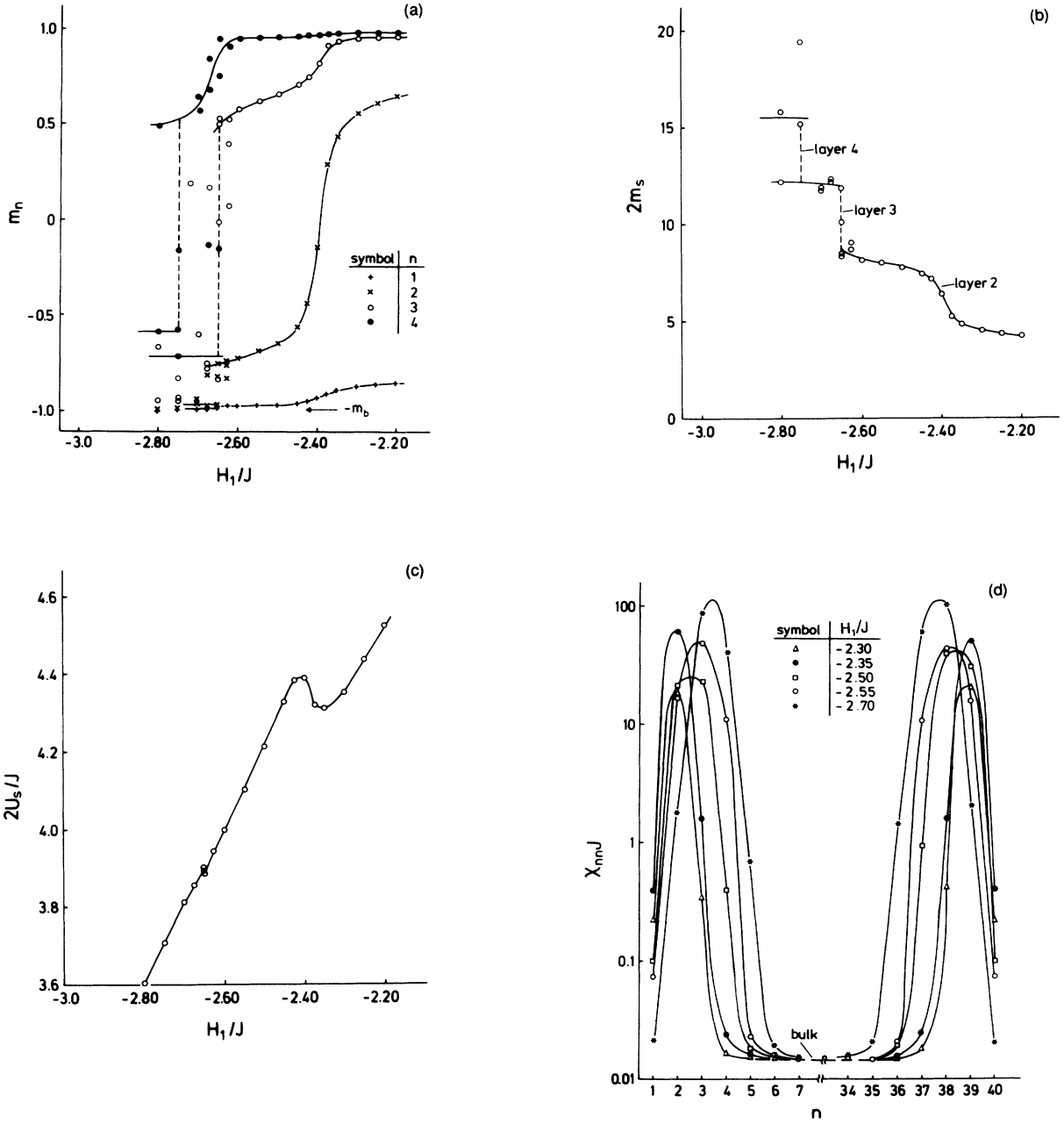

FIG. 9. Layer magnetizations m_n for the first four layers (a), surface excess magnetization (b), and surface excess energy (c) plotted vs surface magnetic field H_1/J at $J/k_BT=0.42$ and $J_s/J=0.5$. All data refer to the choice $L=128$, $D=40$. (d) Profile of the layer susceptibility χ_{nn} at $J/k_BT=0.42$, $J_s/J=0.5$ for $L=128$, $D=40$ and several choices of the surface field. Curves are only guides to the eye. Note the logarithmic ordinate scale. It is clearly seen that the peak of χ_{nn} moves towards inner layers n as H_1 becomes more negative. Due to statistical inaccuracy, there is no complete symmetry between n and $D+1-n$. Very close to the transition fields indicated in (a) and (b) $\chi_{nn}J$ shoots up to the order of nearly 10^4, clearly indicative of first-order layering transitions.

V. WETTING VERSUS LAYERING IN THE MODEL WITH ENHANCED SURFACE EXCHANGE ($J_s > J$)

Extensive calculations have been made for $J_s/J=1.02$, while only preliminary explorations were made for $J_s/J=1.05$ and 1.20. It turns out that a dramatic change of behavior occurs in going from $J_s/J=1$ to $J_s/J=1.02$, while for still larger J_s/J there is no further qualitative change. Thus, only data for $J_s/J=1.02$ will be mentioned here.

In Fig. 10 data are shown for $J/k_BT=0.40$, i.e., a temperature slightly above the roughening transition temperature. One sees evidence for a single phase transition which is strongly of first order. Note that even if one starts the system in a state with three layers down ($\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow$), one quite often [Fig. 10(a)] ends up in a state with (roughly) four layers down (in fact, the values of m_s do not really correspond to integer numbers of layers, and such integers also would not be expected since $T>T_R$). Interestingly, the surface energy in the two "branches" discernible in Fig. 10(a) is indistinguishable, $U_s^{\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow}=U_s^{\downarrow\downarrow\downarrow\downarrow\uparrow}$. Since we know that for $T>T_R$ and interface between bulk coexisting phases would be rough (delocalized) and that such a delocalized interface has more configurational entropy than an interface that is localized close to the wall, we can conclude $F_s^{\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow}=U_s^{\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow}-TS^{\downarrow\downarrow\downarrow\uparrow\uparrow\uparrow} > F_s^{\downarrow\downarrow\downarrow\downarrow\uparrow}=U_s^{\downarrow\downarrow\downarrow\downarrow\uparrow}-TS^{\downarrow\downarrow\downarrow\downarrow\uparrow} > F_s^{\rm wet}$, where $F_s^{\rm wet}$ refers to the free energy of a surface with a large number of overturned layers. As a consequence, Fig. 10 gives compelling evidence for a first-order wetting transition.

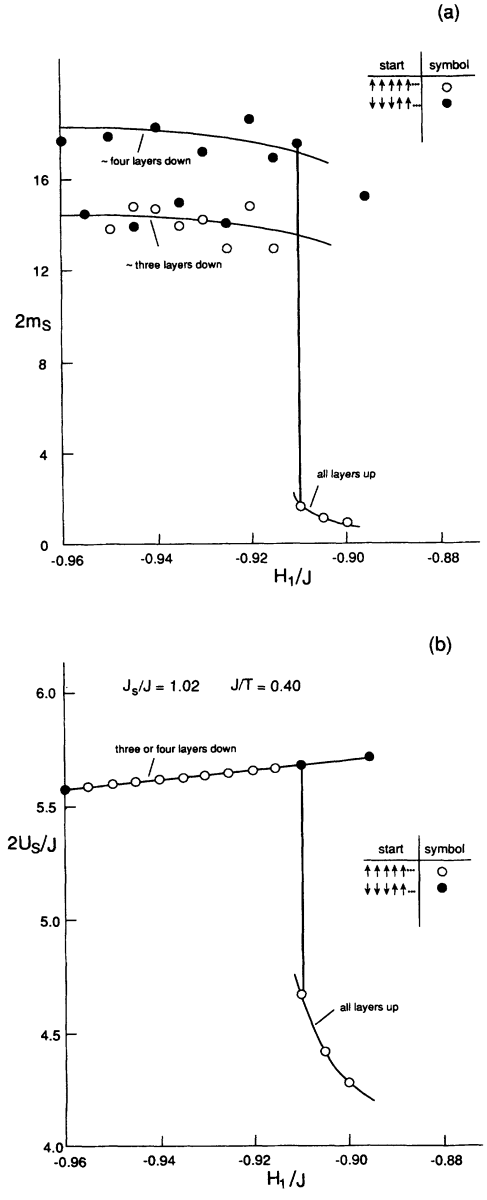

FIG. 10. Surface excess magnetization (a) and surface excess energy (b) plotted vs surface field at $J/k_BT=0.40$, $J_s/J=1.02$. All data refer to choice $L=128$, $D=40$.

Data for $J/k_BT=0.42$ (not shown) are qualitatively similar to those of Fig. 10; even stronger fluctuations are seen in the vicinity of the roughening transition. Thus we suggest that a first-order transition also occurs from a state where the surface is nonwet (even m_1 being still positive) to a state where it is wet. Of course, if we would approach the wet surface by varying the bulk field H and letting $H\to 0$, we would observe a sequence of layering transitions here since $T<T_R$.

At still lower temperatures such as $J/k_BT=0.44$ (Fig. 2) the first-order wetting behavior as a function of H_1 is replaced by layering transitions. The analysis presented in Sec. II shows that one first goes from a nonwet state of the surface (all $m_n>0$) to a state with the topmost two layers overturned, at $H_{1c}/J=-0.945\pm0.003$, while the second transition (to three or more overturned layers) occurs at $H'_{1c}/J=-1.030\pm0.003$. At this point, we emphasize that the distinction in this layering behavior between $J_s/J>1$ and $J_s/J<1$ is not straightforwardly interpretable in terms of ground-state properties of the model: as discussed in I, the state $T=0$, $H_{1c}/J=1$ is a degenerate transition point from which all layering transition lines $H_{1c}(T)/J$ have to start, irrespective of J_s/J (see Fig. 1).[17]

VI. DISCUSSION

In this work, the surface phase behavior of the Ising model exposed to a surface field oppositely oriented to the magnetization in the bulk was studied near the roughening temperature, performing large-scale Monte Carlo simulations using a very fast vectorizing multispin coding algorithm. Particular attention was paid to the influence of varying the ratio between surface coupling J_s and bulk coupling J. Our results can be summarized as follows.

(i) We verify the expectation that wetting transitions occur in the Ising model at all temperatures above T_R, even very close to T_R, irrespective of the value of J_s/J. If $J_s/J\le 1$, critical wetting is observed, while for $J_s/J>1$ the wetting transition is first order. The layering behavior which takes over for $T<T_R$ already shows up in certain precursor effects at $T>T_R$; e.g., the suscepti-

bility χ_1 develops a rounded maximum of finite height at a field H_1 close to the critical field where for $T < T_R$ the layering transition of the first layer appears. We find that the value of J_s/J (for $J_s/J \leq 1$) mainly affects the behavior of the first layer. The lower J_s/J is, the more $k_B T_c(n=1)/J$ is suppressed to lower temperatures, and the more negative H_1 must become in order to induce a wetting transition; but when H_1 is sufficiently negative to bring m_1 close to the value of $-m_n$ for $n \geq 2$, the behavior is always qualitatively the same.

(ii) At temperatures slightly below T_R, the layering "transitions" of the first and second layer are still smooth (i.e., nonsingular), which already rules out the scenario of Fig. 1(a) and rather favors the scenario of Fig. 1(c). Unfortunately, the accuracy of the present study is not sufficient to distinguish the layering of the third (and subsequent) layers from the first-order transition to the wet state of the surface.

(iii) If $J_s/J > 1$, we find that the first-order wetting transition which then occurs for $T > T_R$ is replaced by a sequence of transitions for $T < T_R$ where the first two layers jump together from positive magnetization (nonwet state of the surface) to negative magnetization, while at a surface field H_1 still more negative the transition of the third (and possibly additional layers) occurs. This possibility, that layering of the first layer is suppressed in favor of a transition where at once a layer of two lattice planes thickness forms, was not foreseen in the phase diagram scenarios proposed in I. The same feature that several layers may experience a common transition has also been seen in recent work on layering in the presence of long-range surface forces.[18]

In conclusion, some—but by no means all—questions left open in I have now been resolved. This problem is very difficult, even if a large amount of CPU effort is invested, for several reasons: near the roughening transition there are dramatic finite-size effects, due to an exponential increase of the correlation length, and there is very pronounced slowing down. While the latter problem could be better handled by a recently developed cluster algorithm,[19] it remains to be shown that this algorithm is also useful for free surfaces exposed to a surface field H_1 and having a modified surface exchange. Another problem is the small free-energy difference ΔF_s between phases having n layers of overturned spins and $n+1$ layers of overturned spins near the surface at low temperatures, in particular for $n \geq 3$. The smallness of these free-energy differences results from the exact degeneracy of all these layering states at $T=0$, $H_1 = H_{1c} = J$. While for $n=2$ it was shown that thermodynamic integration methods can still be successfully used, if one uses suitable surface energy differences ΔU_s [Eq. (7)] or surface layer magnetization differences Δm_1 to avoid estimation of small ΔF_s from subtracting large numbers; for larger n the basic differences $\Delta U_s, \Delta m_1$ become too small to be estimated reliably with the present statistical effort. Thus, a substantial extension of the present study will need significantly faster computers and/or more efficient algorithms.

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[17] In I in the presentation of possible schematic phase diagrams it was erroneously stated that $H_{1c}(T=0)/J=2$ and thus the ordinate scales in the schematic figure, Fig. 20, of I are in error by a factor of 2.

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