CORRECTIONS TO THE KELVIN EQUATION FOR LONG-RANGE WALL-PARTICLE POTENTIALS

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Abstract. The properties of a simple fluid, or Ising magnet, confined in an $L\times\infty$ geometry, are studied by means of numerical density-matrix renormalization-group techniques. Whereas the particle-particle potential is short ranged, the wall-particle potential is long ranged decaying as h_1/l^p for various values of p-integer, where $l = 1,2,\ldots,L$ labels the columns across the strip and h_1 is the reduced amplitude of the boundary field. For the short-range wall-particle potential, according to the Kelvin equation, the bulk coexistence field scales as $1/L$ for large L; thermodynamics and scaling arguments predict higher-order corrections of the $1/L^2$ and $1/L^{5/3}$ types at partial and complete wetting, respectively. However, at complete wetting for a large range of surface fields and temperatures a correction to scaling of type $1/L^{4/3}$ has been found recently. We discuss the influence of long-range wall-fluid potentials on the scaling. Results are obtained for several values of h_1 for strips of widths up to $L = 690$.

1. Introduction

Wetting phenomena are very common in nature [1]; the most familiar situation is a liquid-vapour system in contact with a solid wall. Usually one considers a semi-infinite geometry with a solid planar wall that preferentially adsorbs one of the phases of a system in thermodynamic equilibrium. Below the bulk critical temperature T_c, the adsorbed phase forms either isolated droplets or a thick macroscopic layer. The first case, known as partial wetting, occurs for temperatures below the wetting temperature T_w, while the second case occurs for $T_w \le T < T_c$ and it is referred to as complete wetting. Here, as a model system the Ising model is considered and both phases, the liquid one and the other the vapour one, correspond to two phases with opposite magnetization. The fact that a wall can favour one of phases, in Ising language, corresponds to introducing surface magnetic field h_1. The bulk magnetic field h refers to the chemical potential of the liquid-vapour system. In the two-dimensional ($d = 2$) Ising model the wetting temperature is known exactly [2] and decreases monotonically with the surface field h_1 (see Fig. 1b).

For finite systems a partial wetting is restricted to temperatures below, so called, the interface delocalisation temperature $T_d(L)$ as shown in Figure 1a. When L grows to infinity $T_d(L)$ scales to the wetting temperature T_w as

$T_d(L) - T_w \approx L^{-1/\beta_s}$, where β_s is the exponent describing the divergence of the thickness of the wetting layer for a semi-infinite system.

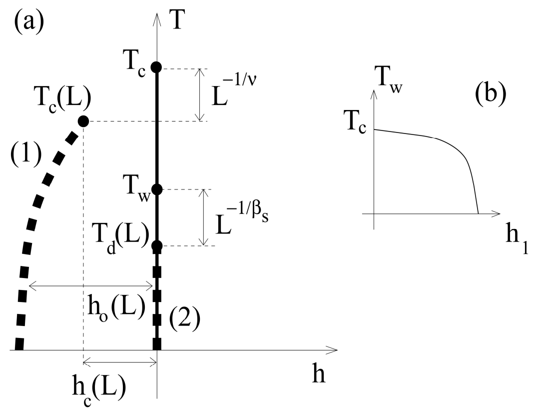

Fig. 1. (a) Phase diagram of the Ising model for a bulk system in the (h,T) plane (solid line). The dashed lines are the phase diagrams of confined systems with identical (1) and opposing (2) boundary fields. (b) Dependence of the wetting temperature on the field h_1 for the short-range wall-particle potential

In this paper we analyse the effect of wetting on the thermodynamics of the Ising model confined in an $L\times\infty$ geometry with identical boundaries. For the short-range wall-particle potential, if $L\to\infty$, i.e. in the bulk, phase coexistence occurs for temperatures $T < T_c$ and for vanishing bulk magnetic field $h = 0$. It is well known that the combined effect of surface fields and confinement shifts phase coexistence to a finite value of the bulk magnetic field $h = h_0(L) \neq 0$, which for large L scales, according the Kelvin equation [3], as

$$h_0(L) = \frac{\sigma_0 \cos\theta}{m_b} \frac{1}{L} \tag{1}$$

where: σ_0, m_b and θ are the surface tension, the bulk spontaneous magnetization and the contact angle, respectively. In other words, to have equilibrium between two phases, or phase coexistence, one needs a bulk field of the order of $1/L$ that compensates the effect of the surface fields. This phenomenon is analogous to the capillary condensation for a fluid confined between parallel surfaces, where the gas-liquid transition occurs at a lower pressure than in the bulk.

To complete the picture it is worth adding that the finite size scaling predicts that the capillary critical point $[hc(L), Tc(L)]$ (see Fig. 1a) scales as

$$T_c(L) - T_c \approx L^{-1/\nu} \quad \text{and} \quad h_c(L) \approx L^{-(d-\beta/\nu)} \tag{2}$$

where d is the dimensionality, ν and β are the correlation length and magnetization exponents [4].

Albano *et al.* [5] and Parry and Evans [6] analysed the next order correction term to the Kelvin equation. Both studies, using scaling and thermodynamics arguments, concluded that at partial wetting, the leading correction to scaling term is of type $1/L^2$. In the case of complete wetting the correction is expected to be non-analytic due to a singularity of the surface free energy. For the $d = 2$ Ising model [5, 6] the predicted correction term is proportional to $1/L^{5/3}$. Monte Carlo simulations on $M\times L$ lattices with $M >> L$ were also performed [5]; the dominant $1/L$ scaling of the Kelvin equation was well verified, but the data were not accurate enough to convincingly test the type of corrections to scaling.

Next, using density-matrix renormalization-group (DMRG) techniques, it was found [7] that for a large range of surface fields and temperature higher order corrections are of type $1/L^{4/3}$. This apparent disagreement is due to the fact that even for the large sizes considered ($L \sim 150$) the wetting layer has a limited thickness, so that the singular part of the surface free energy which determines the correction to scaling behaviour is dominated by the contacts with the walls. In this cases a simple random walk argument indeed predicts a correction-to-scaling term of the type $1/L^{4/3}$ for a thin wetting layer [7].

However, it is known [8] that long-range forces modify the wetting behaviour significantly. Therefore, in the present paper, we study an Ising model with a long-range wall-particle potential. It is reasonable to expect that for such a potential the wet layer should be thicker with respect to the short ranged wall-particle interactions, which is likely to shrink the region with anomalous corrections to the Kelvin equation.

2. Model

In spite of the name, the DMRG has only some analogies with the traditional renormalization group being essentially the numerical, iterative basis, truncation method. It was proposed by White in 1992 as a new tool for the diagonalization of quantum chain spin Hamiltonians [9]. Later, it was adopted by Nishino for $d = 2$ classical systems at non-zero temperatures [10]. The DMRG method allows to study much larger systems than it is possible with standard exact diagonalization method (up to $L = 20 \div 30$ for Ising strips) and provides data with remarkable accuracy. While applying the DMRG method for classical $d = 2$ spin systems, symmetric transfer matrices are considered. Comparisons with exact results for the case of vanishing bulk magnetic field and boundary fields acting only on spins in the surface layers show that this technique gives very accurate results in a wide range of temperatures [11]. Recently the method has been also applied to an Ising film subject to long ranged boundary fields to study the solvation force behaviour [12].
The Ising model has played a central role in the theory of critical phenomena. It can model many interesting physical situations and it is simple enough to be studied in great detail. Moreover in $d = 2$ this model is amenable to the systematic

investigations for arbitrary boundary and bulk fields by means of the DMRG method.

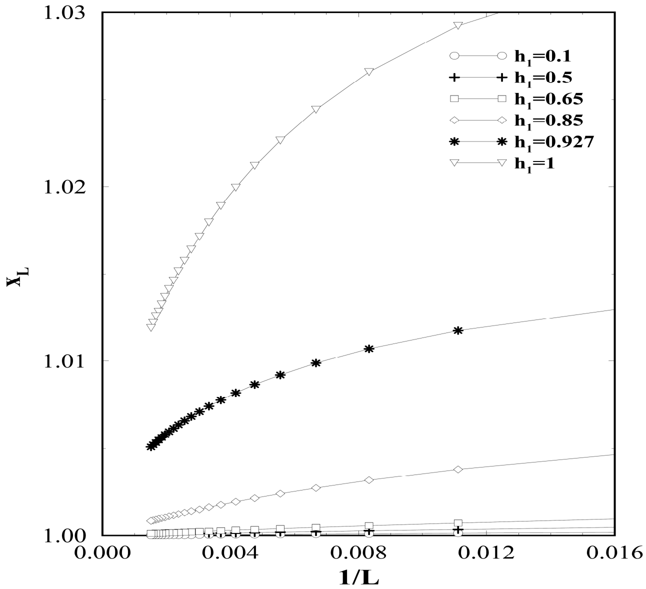

Fig. 2. The plots of x_L versus $1/L$ for the short-range wall-particle potential ($p = 9$)

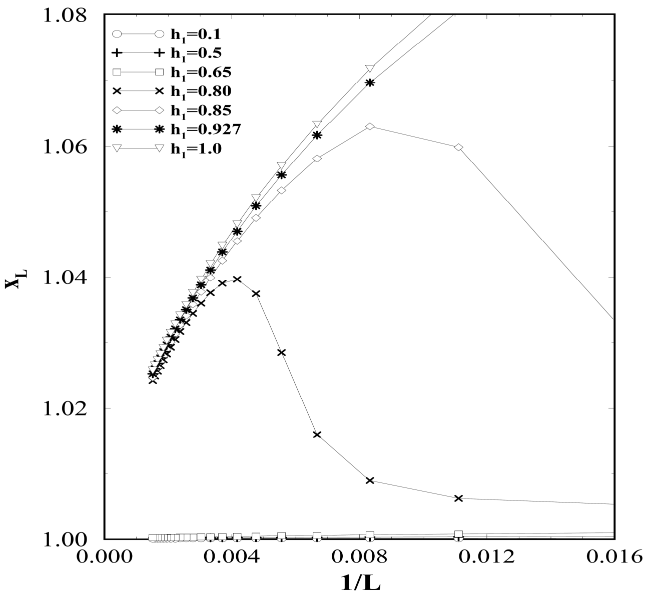

Fig. 3. The plots of x_L versus $1/L$ for the long-range wall-particle potential ($p = 3$)

We consider an Ising model in a slit geometry subject to identical boundary fields. Our results refer to the $d = 2$ strip defined on the square lattice of the size

$M \times L$, $M \to \infty$. The lattice consists of L parallel columns at spacing $a = 1$, so that the width of the strip is $La = L$. We label successive columns by the index l. At each site, labeled (k,l), there is an Ising spin variable taking the value $\sigma_{kl} = \pm 1$. We assume nearest-neighbour interactions of strength J and Hamiltonian of the form

$$H = -J\left\{ \sum_{\langle kl,k'l' \rangle} \sigma_{kl}\sigma_{k'l'} + h\sum_{kl}\sigma_{kl} + \sum_{l=1}^{L} H_l \sum_{k}\sigma_{kl} \right\} \tag{3}$$

where h and H_l are in units of the coupling constant J. The first term in (3) is a sum over all nearest-neighbour pairs of sites, while in the second term h is the bulk magnetic field. The value $H_l = H_l^s + H_{L+1-l}^s$ is the total boundary magnetic field experienced by a spin in column l. The single-boundary field H_l^s is assumed to have a form $H_l^s = h_1 / l^p$ with $p > 0$, and the reduced amplitude of the boundary field $h_1 \geq 0$.

3. Results

In order to find the corrections to the Kelvin equation it is preferable to consider only temperatures not too close to T_c, where DMRG iterations converge very quickly. Moreover, when one is far below $T = T_c$, one avoids the effect of crossover from an initial scaling (for small L) of the type (2) towards the final scaling (for enough large L) according to the Kelvin equation. In the present study we have calculated a series of values of $h_0(L)$ up to $L = 690$ with different values of boundary fields at $T = 1$.

We assume the following expansion for the bulk magnetic field h_0, which restores the phase coexistence:

$$h_0(L) = \frac{A}{L^\alpha} + \frac{B}{L^\gamma} + \ldots \tag{4}$$

where we expect $\alpha = 1$ and A given by the Kelvin equation (1). In order to calculate the exponents α and γ we define the logarithmic derivatives

$$x_L \equiv -\frac{\ln[h_0(L)] - \ln[h_0(L+30)]}{\ln L - \ln(L+30)} \tag{5}$$

for $L = 30, 60, \ldots, 690$ (in steps of $L = 30$). Then introducing the expansion (4) into the definition (5) one has to the lowest orders in $1/L$

$$x_L = \alpha\left(1 - \frac{B}{A}\frac{1}{L^{\gamma-\alpha}} + \ldots\right) \tag{6}$$

Figures 2 and 3 show plots of x_L versus $1/L$ for different values of surface fields at $p = 9$ and 3, respectively. For the first case the wall-particle potential decays so fast that there we expect the short ranged boundaries behaviour. From the exact solution by Abraham one knows that for the wetting temperature $T_w = 1$ the corresponding value of the surface field equals to $h_1 \approx 0.927$. Therefore it is clear that the plots in Figure 2 for $h_1 < 0.927$ correspond to the case of partial wetting, where the scaling behaviour of x_L should be linear in $1/L$ since one expects $\gamma = 2$ and $\alpha = 1$ in Eq. (6). The fact that the data follow straight lines confirms the behaviour predicted by the theory for the short-range case ($p = 9$). It is worth noticing that at $h_1 = 0.85$, the data follows a straight line only for large L. Therefore, we can conclude that the closer h_1 is to the coexistence line value (at $h \approx 0.927$ here), the larger L is necessary to reach an asymptotic regime.

A clearly different behaviour is observed for the long-range wall-particle potential in Figure 3 (at $p = 3$), where the linear dependence occurs only below $h_1 = 0.80$. Therefore, it seems that here the phase coexistence appears for a lower value of restricted boundary field h_1. In details the influence of the long ranged boundary potential on the coexistence line $T_w(h_1)$ will be presented elsewhere.

As one can see in Figures 2 and 3 the values of the scaling exponent α obtained from the DMRG converge very well to the expected value 1 (the detailed extrapolation will be presented elsewhere). Thus, the Kelvin equation dependence is of fairly general character and it does not depend on the range of the wall-particle potential, which is in agreement with the Monte Carlo results [5]. To consider higher-order corrections (setting $\alpha = 1$) one obtains from the equation (6)

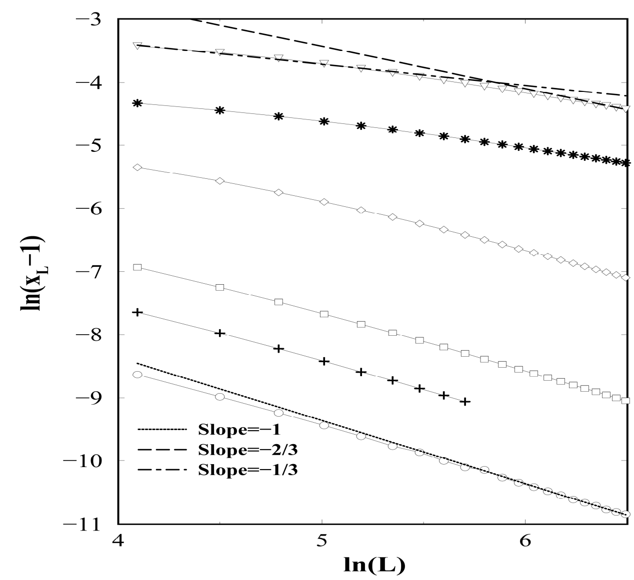

Fig. 4. The plots of $\ln(x_L-1)$ versus $\ln L$ for the short-range wall-particle potential ($p = 9$). The meaning of the symbols is the same as in Figure 2

$$\ln(x_L - 1) = \ln\left|\frac{B}{A}\right| - (\gamma - 1)\ln L + \dots \qquad (7)$$

Figures 4 and 5 show plots of $\ln(x_L-1)$ versus $\ln L$ for different values of surface fields at p = 9 and 3, respectively. In both cases the behaviour at partial and complete wetting can be clearly distinguished.

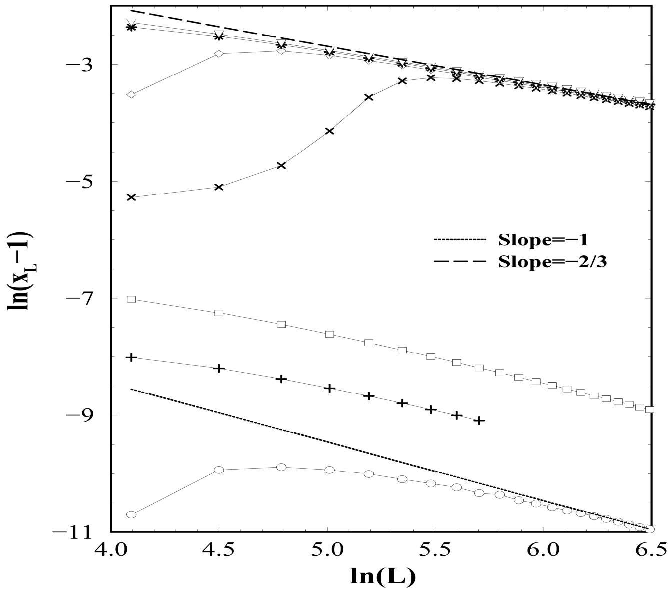

Fig. 5. The plots of $\ln(x_L-1)$ versus $\ln L$ for the long-range wall-particle potential (p = 3). The meaning of the symbols is the same as in Figure 3

At partial wetting the straight dotted lines with slope –1 fit very well the asymptotic behaviour, so $\gamma = 2$ here. At complete wetting for large L the plots are well fitted with dashed lines with slope –2/3 ($\gamma = 5/3$) in agreement with the current theory. However, one can notice that the smaller the range of the boundary potential is, the larger L is necessary to reach the asymptotic regime. Therefore, in agreement with the previous results [7], in Figure 4 (a short-range wall-particle case for p = 9) the data for a large range of L (more or less up to L = 250) are well fitted by straight lines with slope –1/3 ($\gamma = 4/3$). It is in consistence with the previous explanation that even for large system sizes, like L = 100÷200, the wetting layer has a limited thickness, so the singular part of the surface free energy that determines the corrections-to-scaling behaviour is dominated by the contacts with the walls. In this case a simple random walk argument predicts a correction of the type $\gamma = 4/3$ for a thin wetting layer [7]. When the range of the wall-particle potential grows, then a wetting layer is getting thicker and for smaller L the asymptotic limit ($\gamma = 5/3$) is reached.

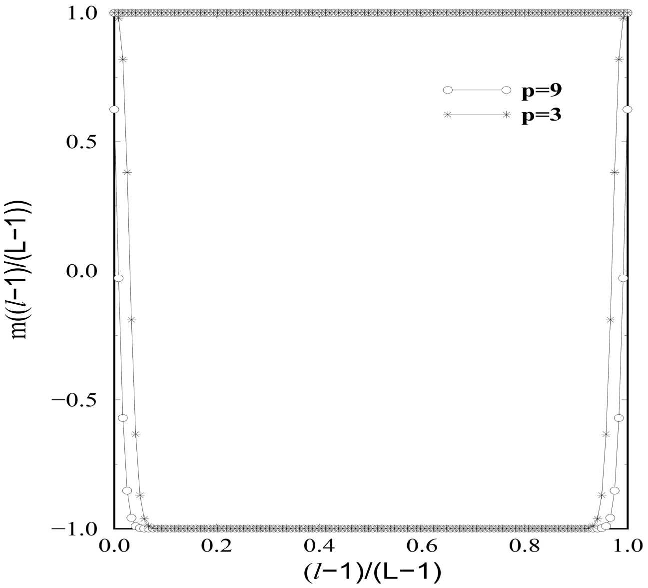

Fig. 6. The magnetization profiles of the two coexisting phases at $T = 1$ and $h_1 = 1$ (for $L = 120$), approaching complete wetting, for different ranges of the wall-particle potential

The above arguments are illustrated in Figure 6, where the magnetization profiles for two coexisting phases are presented. The magnetizations are plotted as a function of the scaled variable $(l–1)/(L–1)$ at $T = 1$ and $h_1 = 1$; this corresponds to a regime of complete wetting $[T_w(h_1 = 1) = 0]$. We should also stress that the profiles refer to bulk fields slightly lower and higher than the coexistence field $h_0(L)$. For bulk field exactly equal to $h_0(L)$ the magnetizations of the two coexisting phases are averaged and it is not possible to distinguish between them. The negative bulk field favours a bulk phase with negative magnetization (vapour) but the positive boundary fields favour the adsorption of positive spins (liquid) at the boundaries. Since $T \geq T_w$ the positive spins form a layer that wets the walls. Obviously for a long-range wall-particle potential ($p = 3$) the wetting layer is thicker than for the short-range case ($p = 9$).

4. Conclusions

In this paper we have analysed the influence of a long-range wall-particle potential on the thermodynamics of an Ising model in a strip geometry. We confirmed that the bulk coexistence field scales according to the Kelvin equation and we verified the previous results for leading correction terms at partial and complete wetting. The comparison of results for different ranges of a wall-particle potential confirms the previously proposed scenario to explain the origin of the anomalous corrections to the Kelvin equation at complete wetting.

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