Wetting and interfacial adsorption in the Blume-Capel model on the square lattice

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Abstract. We study the Blume-Capel model on the square lattice. To allow for wetting and interfacial adsorption, the spins on opposite boundaries are fixed in two different states, “+1” and “-1”, with reduced couplings at one of the boundaries. Using mainly Monte Carlo techniques, of Metropolis and Wang-Landau type, phase diagrams showing bulk and wetting transitions are determined. The role of the non-boundary state, “0”, adsorbed preferably at the interface between “-1” and “+1” rich regions, is elucidated.

PACS. 75.10.Hk Classical spin models – 05.50+q Lattice theory and statistics (Ising, Potts. etc.) – 05.10.Ln Monte Carlo method, statistical theory

1 Introduction

Critical interfacial phenomena have been studied extensively in the last decades, both experimentally and theoretically \([1234]\). A well-known example is wetting, where the macroscopically thick phase, e.g., the fluid, is formed between the substrate and the other phase, say, the gas. Liquid and gas are separated by the interface. The scenario may be mimicked, in Statistical Physics, in a simple way by the two-state Ising model, with the state “+1” representing, say, the fluid, and “-1” the gas.

An interesting complication arises when one considers the possibility of more than two phases. A third phase may be formed at the interface between the two other phases. An experimental realization is the two-component fluid system in equilibrium with its vapor phase \([2,5]\). The situation may be mimicked in a simplified fashion in three-state models, like Potts \([6]\) or Blume-Capel models \([7]\). The formation of the third phase in such models has been called “interfacial adsorption”.

In the following article, we shall consider wetting in the (3-state) Blume-Capel model, with spin \(S = 1\), on the square lattice, paying special attention to possible interfacial adsorption. The present analysis has been motivated by the closely related recent Monte Carlo (MC) study \([8]\). In that thorough study, wetting had been imposed by symmetric surface fields. Here, spins at opposite boundaries are fixed in two different states, reducing, in addition, the couplings to one of the boundaries. Thence, there will be no ambiguity in the wetting phenomenon occurring only relative to the boundary with reduced couplings. Similar boundary conditions have been used before for describing interfacial phenomena in Ising \([9]\) and Potts \([10]\) models.

The outline of the article is as follows: In the next section the model and the methods, especially, MC simulations of Metropolis and Wang-Landau type, will be introduced, followed by the discussion of our main results in section 3. The summary, section 4, will conclude the article.

2 Model and Methods

The Blume-Capel (BC) model on the square lattice is a classical spin-1 Ising model described by the Hamiltonian \([11,12]\)

\[
H = -J \sum_{(i,j)} S_{i,j} S_{i \pm 1,j \pm 1} + D \sum_{i,j} S_{i,j}^2,
\]

where the spin variable \(S_{i,j}\), at site \((i,j)\), takes on the values -1, 0, or +1, with the sums running over the entire lattice. The exchange interaction between neighboring spins is ferromagnetic \(J > 0\); \(D\) denotes the strength of the single-ion anisotropy term, where \(D \geq 0\).

The bulk phase diagram of the model has been studied extensively and carefully, using approximate, but highly accurate methods \([13,14]\). From these analyzes, the BC model is known to order, at low temperatures, ferromagnetically for \(D < 1\), whereas it becomes of first-order at \(D > 1\). At \(D_t = 1.9655(10)\) and \(k_B T_t / J = 0.610(5)\) \([13]\), a tricritical point occurs.
To study wetting, we shall employ special boundary conditions, modifying, in addition, the exchange interaction at one of the boundaries: As sketched in figure 1, the spins of the lattice with \( L \times M \) sites are fixed on one of the boundaries, say, the left boundary, in state \( S_L = -1 \), while the spins on the opposite boundary are fixed to be \( S_R = 1 \). The two boundaries are separated by \( L \) sites. Top and bottom boundaries are connected by periodic boundary conditions. Obviously, then an interface between regions of predominantly -1 and +1 spins may be formed. To allow for wetting or (de)pinning of the interface, the couplings at one of the boundaries may be modified, for example by introducing, at the left hand side, the surface coupling \( \alpha J \) between the boundary spins and the neighboring bulk spins, with \( 0 \leq \alpha \leq 1 \). Otherwise, the couplings between neighbors are always \( J \) [8]. Wetting may then take place when the “-1” rich region spreads from the left hand side towards the center of the lattice. In the limiting case \( \alpha = 0 \), i.e., assuming free boundary condition at the left boundary, there will be, of course, no wetting. When \( \alpha = 1 \), the interface will be de-pinned at arbitrarily low temperatures. Interfacial adsorption will show up with spins in the state “0” being preferably adsorbed at the interface between “-1” and “+1” rich regions [6][7]. We shall mainly deal with the case \( 0 < \alpha < 1 \), where both wetting and interfacial adsorption may play an interesting role.

To analyze the model, studying both critical bulk and wetting phenomena, we used large-scale MC simulations, augmented by rather straightforward energy considerations for the ground state, \( T = 0 \), and for low temperature excitations.

In particular, to determine accurately the bulk transition temperatures for our special choices of the strength of the single-ion anisotropy, \( D \), we implemented a modified version [17][18][19] of the Wang-Landau (WL) algorithm [20]. The modifications have been proposed to cope with the huge number of energy states for large lattices and to deal with the important aspect of detailed balance. More concretely, a combination of several stages of the WL process has been suggested. In short, we carry out a starting multi-range (multi-R) stage, in a very wide energy space, and up to a certain level of the WL random walk. The WL refinement is \( G(E) \rightarrow fG(E) \), where \( G(E) \) is the density of states (DOS), and we follow the usual modification factor adjustment \( f_{j+1} = \sqrt{f_j} \) and \( f_1 = \epsilon \). This preliminary stage consists of the levels \( j = 1, \ldots, 18 \) and to improve accuracy the process is repeated several times. The process continues in two further stages, using now the high WL iteration levels, where the modification factor is very close to unity and there is not any significant violation of the detailed balance condition. In the first (high-level) stage, we follow again a repeated several times (typically \( \sim 5 - 10 \)) multi-R WL approach, carried out now in a restricted energy subspace obtained form the preliminary stage, following the prescription of references [17][18]. The WL levels may be now chosen as \( j = 18, 19, 20 \) and as an appropriate starting DOS for the corresponding starting level the average DOS of the preliminary stage at the starting level may be used. Finally, the second (high-level) stage is applied in the refinement WL levels \( j = j_1, \ldots, j_1 + 3 \) (typically \( j_1 = 21 \)), where we use an one-range approach, where the adjustment of the WL modification factor follows the rule \( \ln f \sim t^{-1} \), where \( t \) the MC time [21].

On the other hand, to investigate the wetting transition, we applied the simpler standard Metropolis MC algorithm, as had been done before [8]. We still achieved a good accuracy, performing runs of sufficient length, as we checked, for instance, by comparing WL and Metropolis data for the specific heat and magnetic susceptibility.

3 Results

3.1 Phase diagram

The phase diagram of the BC model on the square lattice comprises the bulk phase transition, \( k_B T_c/J \), and, usually at lower temperature, the wetting transition, \( k_B T_w/J \).

Of course, \( T_c \) depends only on the strength of the single-ion anisotropy term, \( D/J \), but not on the reduction factor of the boundary couplings, \( \alpha \). As depicted in figure 2, we studied the cases \( D/J = 1.0, 1.4, 1.7, \) and 1.98, with \( \alpha \) ranging from 0.2 to 0.95, using MC techniques.

For continuous bulk transitions, \( D/J < D_t/J \), the wetting line is found to decrease monotonically with increasing \( \alpha \), where \( T_w(\alpha = 0) = T_c \) and \( T_w(\alpha = 1) = 0 \). Interestingly, for bulk transitions of first-order, \( D/J = 1.98 \), the wetting line \( T_w(\alpha) \) ends, at non-vanishing value of \( \alpha \), in the bulk transition, as has been observed in the two-dimensional BC model for wetting induced by surface fields [5].

In the following, we shall discuss these main findings in detail.

3.2 Bulk transition

The square-lattice BC model, equation (1), at the crystal-field values \( D/J < D_t/J \) undergoes a second-order phase transition between the ferromagnetic and paramagnetic
phases, expected to be in the universality class of the two-dimensional Ising model [14]. This aspect had been verified recently by high-accuracy WL type of simulations for single-ion anisotropy values in the range $D/J = [0 - 1.8]$ [15,16].

Here we study the bulk transition in the second-order regime of the phase diagram for three values of $D/J$, namely $D/J = 1.0, 1.4,$ and $1.7$. Using the above sketched WL MC approach we simulated quadratic systems with periodic boundary conditions and linear sizes $L$ ranging from 20 to 100. Moreover, to increase statistical accuracy, we averaged, for each pair $(L, D/J)$, over at least 50 independent runs.

The case $D/J = 1.0$ has been investigated before [14,16], and so a direct comparison is possible. For the other two cases, we present new estimates for the critical temperatures. As we shall see below, they agree well with the, presumably, best previous estimates for nearby values of the single-ion anisotropy [14].

For each value of $D/J$, we performed a standard finite-size scaling analysis in order to estimate the critical temperature $T_c$. For reasons of brevity, we show here only the typical case of $D/J = 1.4$ in figure 3 below (similar analysis has been performed for the other two cases). In the following we use the abbreviation $K = J/(k_B T)$ for the inverse temperature. $E$ denotes the energy, and $m = \langle |m| \rangle$ is the magnetization, with the number of lattice sites $N = L^2$. In figure 3 we plot the shift-behavior of different “pseudo-critical” temperatures corresponding to the peak positions of four quantities: The specific heat

\[ C = K^2 N^{-1} \left[ \langle E^2 \rangle - \langle E \rangle^2 \right], \]

the magnetic susceptibility

\[ \chi = KN \left[ \langle m^2 \rangle - \langle |m| \rangle \right], \]

and the derivative of the absolute value of the magnetization

\[ \frac{\partial \langle |m| \rangle}{\partial K} = \langle |m| \rangle - \langle |m| \rangle \langle \mathcal{H} \rangle, \]

and the logarithmic derivative of the second moment of the magnetization

\[ \frac{\partial \ln \langle m^2 \rangle}{\partial K} = \frac{\langle m^2 \mathcal{H} \rangle}{\langle m^2 \rangle} - \langle \mathcal{H} \rangle. \]

Fitting simultaneously our data for the larger lattice sizes to the expected asymptotic power-law behavior $T = T_c + b L^{-\nu}$, and taking, by invoking Ising universality, $\nu = 1$, we obtain the following estimates for the critical temperatures $k_B T_c/J = 1.3957(7)$, 1.2098(8), and 1.0033(7) at $D/J = 1.0, 1.4,$ and $1.7$, respectively. The error bars take into account the dependence of the estimates for $T_c$ on the system sizes included in the fits.

We now turn to the case $D/J = 1.98 > D_i/J = 1.9965$, where the bulk transition is of first-order. There, in accordance with the finite-size scaling theory of first-order phase transitions [22,23,24], the MC data for the peak positions may be fitted according to the double Gaussian approximation. We then obtain for the bulk transition temperature $k_B T_c/J = T^* = 0.5533(9)$. This finding is corroborated by an analysis of the distribution function of the energy density, with two distinct peaks of equal height at the transition [25,26].

Our estimates for the bulk transition temperatures are marked by the solid lines in figure 3, where the thickness of the lines is larger than the error bars we stated.

Closing this subsection on the bulk transition of the BC model for the four distinct values of $D/J$, a few comments may be added. Regarding the accuracy of our final estimates: Our estimate for $T_c$ at $D/J = 1.0$ agrees well with the previous estimate, 1.398(2) of [16], and the estimates for $D/J = 1.4$ and 1.7 are fully compatible with the previous estimate, 1.398(2) of [16].
those given in Table I of reference [14] for nearby values of \( D/J \). Also, in the first-order transition regime, the value of the transition temperature for \( D/J = 1.98 \) interpolates reasonably well between the estimates \( T^*(D/J = 1.969) = 0.60 \) and \( T^*(D/J = 1.999) = 0.55 \) of [14] (see also [15]). Regarding the type of phase transitions: As expected, the transitions of second order are observed to be in the universality class of the two-dimensional Ising model, with, e.g., the maximal susceptibility growing with the exponent \( 7/4 \). For the first-order transition, we confirmed the expected finite-size scaling behavior, e.g., of the maximal susceptibility, \( \sim L^2 \), as seen in our WL data for \( D/J = 1.98 \).

### 3.3 Wetting

To study wetting in the BC model, we mainly performed Metropolis MC simulations, augmented by rather straightforward ground-state and low-temperature energy considerations.

At \( T = 0 \), for \( 0 < \alpha < 1 \) either all spins are in the state \( "+1" \) or, if

\[
D/J \geq 2 - \alpha,
\]

there is a single line of spins in the state \( "0" \) next to the left hand boundary, see figure 1. This “pre-wetting” phenomenon had been observed before for \( \alpha = 1 \) [24]. At non-zero temperatures, the pre-wetting may be enhanced, or reduced. Indeed, if \( D/J \geq 2 - (\alpha/2) \), it costs less energy to flip a \( "+" \) spin next to the line of \( "0" \)’s to the state \( "0" \) than to do the reverse flip for a spin in the pre-wetting line. In any event, the possible effect of pre-wetting by \( "0" \)’s on the critical wetting, at \( T_w > 0 \), will be discussed below.

For critical wetting, one expects that the \( "-1" \) spins on the left side boundary of the lattice will impose, at \( T \geq T_w \), a region of macroscopic extent, with, predominantly, \( "-1" \) spins in the left part of the system. The wetting transition should be indicated by anomalies and singularities in various quantities [2].

To identify and analyze the wetting transition, we performed MC simulations for lattices with \( N = L \times M \) sites or spins, see figure 1. Critical properties of the transition are believed to be affected by the two different correlation lengths parallel and perpendicular to the interface between the \( "-1" \) and \( "+1" \) rich regions. The resulting anisotropic scaling is taken into account by simulating lattices with \( M \propto L^2 \) [8], i.e., with a constant generalized aspect ratio \( c = M/L^2 \). The factor of 2 corresponds to the ratio of the critical exponents of the two correlation lengths [8].

Specifically, we studied lattices with \( c = 1 \), with \( L \) ranging from 6 to 30, and \( M \) ranging, accordingly, from 36 to 900. To obtain data of the desired accuracy, runs with \( 10^5 \) to \( 6 \times 10^5 \) MC steps per spin were done. To estimate error bars, averages over runs with different random numbers were taken. In fact, for the data depicted in the figures, error bars turned out to be smaller than the symbol sizes, and are not shown.

The wetting transition is signalled by a variety of physical quantities, as illustrated in figures 4-8. Examples are the specific heat \( C \), equation (2), the susceptibility \( \chi \), equation (5), and the second moment of the magnetization \( \langle m^2 \rangle \). Furthermore, we recorded the fraction of spins in the state \( n, f_n \)

\[
f_n = \frac{1}{LM} \sum_{(i,j)} \delta_S(i,j),n.
\]

Another interesting quantity is the interfacial adsorption, \( W_0 \) [6]. \( W_0 \) measures the surplus of \( "0" \) spins due to the interface between the \( "-1" \) and \( "+1" \) rich regions induced by the fixed boundary conditions:

\[
W_0 = L(f_0 - F_0),
\]

where \( F_0 \) is the fraction of spins in state \( "0" \) when the fixed boundary spins have always the same sign, say, \( "+1" \). The behavior of the above quantities at the wetting transition will be discussed in detail below. In addition, we recorded and monitored several other quantities, as had been done before [8], like magnetization histograms and profiles, as well as the Binder cumulant [25]. Of course, in contrast to wetting induced by symmetric boundary fields [8], the magnetization histograms are no longer symmetric around zero magnetization due to the reduced couplings at one of the boundaries. Finally, typical MC equilibrium configurations are helpful in illustrating wetting.

The fraction of spins in the state \( n = 0, \pm 1, f_n \), shows the wetting transition in the, perhaps, clearest way. As seen from figure 4, \( f_{-1} \) increases quite drastically close to \( T_w \), reflecting the spreading of the \( "-1" \) rich region from the left boundary. This behavior holds at all values of \( D/J \) and \( \alpha \) we studied. \( f_1 \) displays the corresponding inflection point near \( T_w \), now due to the quite drastic decrease in the number of \( "+1" \) spins. Of course, there are finite-size effects in \( f_1 \) and \( f_{-1} \), with more pronounced changes approaching \( T_w \) for larger lattices.
It is worthwhile to take a closer look at \( f_0 \). As seen in figure 4, one obtains \( f_0(T = 0) = 1/L \) in the case of prewetting at the left boundary by a single line of “0” spins, in particular for \( D/J = 1.7 \) and 1.98. There is no prewetting in case of \( D/J = 1.4 \) and \( \alpha = 0.4 \), in accordance with the considerations mentioned above, equation (9). For \( D/J = 1.98 \) and \( \alpha = 0.95 \), \( f_0 \) is seen to grow rather rapidly with increasing temperatures. Inspection of typical MC equilibrium configurations show an initial expansion of the “0” rich region at the left boundary. However, eventually the “0” region will be bordered by “+1” as well as “-1” domains, allowing for a meandering of both interfaces. This “entropic repulsion” of the two interfaces has been discussed before in the framework of critical interfacial adsorption [8].

It is interesting to note that \( f_0 \), like \( f_{-1,1} \), exhibits a, comparably weak, inflection point close to \( T_w \). Again, finite-size effects enhance the anomaly for larger lattices. We shall return to the aspect when discussing \( W_0 \).

It has been suggested that, in simulations, the analysis of \( \langle m^2 \rangle \) may lead to reliable estimates of \( T_w \) in the two-dimensional BC model [8]. Like related quantities, such as other moments of the magnetization and the Binder cumulant, \( \langle m^2 \rangle \) displays for two lattices of different sizes an intersection point, approaching \( T_w \) when enlarging the lattices sizes. The rather small finite size effects and the high statistical accuracy of MC data for \( \langle m^2 \rangle \) have been argued to be in favor of using this quantity to determine \( T_w \). [8] Indeed, we confirmed the suggestion done for wetting imposed by surface fields in our study on wetting induced by fixed boundary spins.

Typical results are shown in figure 5, taking \( D/J = 1.0 \) and \( \alpha = 0.2 \), with \( L \) ranging from 6 to 24 (thence, \( M \) from 36 to 576). There are well-defined intersection points, with only weak finite-size effects. The resulting estimates for \( T_w \) for this and other choices of \( D/J \) and \( \alpha \) are depicted in fig 5.

Our estimates for \( T_w \), as obtained from the various quantities discussed in this section are, indeed, compatible with the findings on the wetting transition temperature based on \( \langle m^2 \rangle \).

As exemplified in figure 6, the specific heat \( C \) in our MC study is found to display a maximum near the wetting transition \( T_w \). However, in contrast to the peak close to the bulk transition, \( T_c \), the height of the peak shrinks for larger lattices. In fact, at \( T_c \) one expects for sufficiently larger systems, a logarithmic divergence of the peak height for continuous transitions in the universality class of the two-dimensional Ising model. At the bulk transition of first-order, the maximal specific heat is expected to diverge even more strongly with a power-law in the number of sites. The lowering of the height of the maximum, when enlarging \( L \), is consistent with the corresponding critical exponent being negative. In fact, one expects a value of \(-2\) [8]. The position of the maximum in \( C \) is shifted towards higher temperatures with increasing \( L \), approaching \( T_w \).

Typical MC data close to \( T_w \) for the susceptibility \( \chi \) are depicted in figure 7, for various values of \( D/J \) and \( \alpha \). Obviously, \( \chi \) exhibits a pronounced maximum of height \( \chi^{(max)} \), there, increasing rapidly with system size, \( L \). From analyzes of \( \chi^{(max)}(L) \propto L^\omega \), we find that \( \omega \) seems to approach 3 for large lattices, in agreement with the previous result [8].

It is worth mentioning, that the maxima in \( C \) and \( \chi \) may be useful to show the ending of the wetting line, \( T_w \), in the bulk transition line, \( T_c \), see figure 2. For instance, at \( D/J = 1.98 \) and \( \alpha \leq 0.6 \), we observe that the specific heat \( C \) displays a unique maximum close to the bulk transition, whose height increases significantly more strongly than logarithmically with \( L \). This behavior indicates the bulk transition of first-order. Likewise, \( \chi \) exhibits a unique maximum, with the size-dependent effective exponent \( \omega \) increasing with \( L \), up to about 2 for the sizes we studied.
Finally, let us discuss the MC findings on the interfacial adsorption $W_0$, equation [5], near the wetting transition. As mentioned above, the fraction of spins in state “0”, $f_0$, displays an inflection point near $T_w$. With the interface between the “-1” and “+1” rich regions moving towards the center of the lattice, the interface may fluctuate or meander more strongly, and the number of “0” spins may grow more rapidly. To disentangle bulk and interface effects on the “0” spins, we consider $W_0$, measuring, roughly, the width of the (fictitious) stripe of “0” spins due to the interface [6].

As depicted in figure 8 for the example $D/J = 1.0$ and $\alpha = 0.8$, the temperature derivative of $W_0$, $dW_0/d(k_BT/J)$, shows, in fact, a clear maximum near $T_w$. For larger $L$, the position of the maximum moves towards $T_w$, with increasing height. The MC data seem to be consistent with a singularity at $T_w$ in the thermodynamic limit. The height of the maximum may diverge, with $L$, either logarithmically or in form of a power law with a small exponent, $\leq 0.2$. We observed similar features for other choices of $D/J$ and $\alpha$ as well. The detailed analysis is desirable, but it would require much more computational efforts. Accordingly, it is beyond the scope of the present study.

4 Summary

We studied the Blume-Capel model on the square lattice, with nearest neighbor exchange interactions, $J$, and the single-ion anisotropy term, $D$. We used, mainly, Monte Carlo simulations, both of Metropolis and Wang-Landau type. For selected cases of $D/J$, we determined accurately the bulk phase transition temperature, $T_c$, by applying a modified Wang-Landau scheme.

Wetting has been induced by appropriate boundary conditions. Spins at two opposite boundaries are fixed in the different states “-1” and “+1”. Moreover, at one of the boundaries, say, the one with “-1” spins, the exchange interaction is reduced by the factor $\alpha$, where $0 < \alpha < 1$.

Wetting lines, $T_w$, have been determined for various values of $D/J$, yielding continuous or bulk transitions of first-order. To estimate $T_w$, the second moment of the magnetization, $\langle m^2 \rangle$ turned out to be a useful quantity, showing only weak finite-size effects. The spreading of the “-1” rich region near $T_w$ may be clearly monitored by the fraction of spins in state “-1”, $f_{-1}$. The “0” spins may lead to pre-wetting next to the “-1” boundary depending on $D/J$ and $\alpha$.

For continuous bulk transition, the wetting line, at fixed $D/J$, $T_w(\alpha)$ is found to decrease monotonically with the reduction factor $\alpha$, where $T_w(0) = T_c$ and $T_w(1) = 0$. In the case of a bulk transition of first-order, we observe that the wetting line ends at the bulk transition line at a non-zero value of $\alpha$. Especially, for $D/J = 1.98$, the merging seems to occur close to $\alpha = 0.6$.

Critical properties at the wetting agree with those obtained recently for wetting imposed by surface fields, including anisotropic scaling and critical exponents of the susceptibility and specific heat.

Last, but not least, we monitored the adsorption of “0” spins at the interface between “-1” and “+1” rich regions. Due to the strong meandering of the interface, the adsorption, $W_0$, grows rapidly near $T_w$, associated, possibly, with a singularity in the temperature derivative of $W_0$.

Our study has been motivated by an inspiring talk of Kurt Binder on wetting. It is a pleasure to thank him for a very useful correspondence on this topic as well. N.G. Fytas is grateful to the Departamento de Física Teórica I, Universidad Complutense de Madrid (Spain), for providing access to computing resources, where part of the current simulations has been performed.
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