Universal phase boundary shifts for corner wetting and filling

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The phase boundaries for corner wetting (filling) in square and diagonal lattice Ising models are exactly determined and show a universal shift relative to wetting near the bulk criticality. More generally, scaling theory predicts that the filling phase boundary shift for wedges and cones is determined by a universal scaling function \( R_d(\psi) \) depending only on the opening angle \( 2\psi \). \( R_d(\psi) \) is determined exactly in \( d = 2 \) and approximately in higher dimensions using non-classical local functional and mean-field theory. Detailed numerical transfer matrix studies of the the magnetisation profile in finite-size Ising squares support the conjectured connection between filling and the strong-fluctuation regime of wetting.

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The wetting of structured and chemically heterogeneous substrates has recently drawn a great deal of interest. This is motivated not only by the possible relevance to emerging technologies such as micro-fluidics\textsuperscript{[1]} but also from a more fundamental statistical physics perspective since surface structure may induce new types of interfacial phase transition. Examples of these are morphological phenomena on heterogeneous substrates\textsuperscript{[2,3]} and filling transitions for fluids adsorbed near corners, wedges and cones\textsuperscript{[4–10]}. Recent continuum effective interfacial Hamiltonian studies indicate that the conditions for observing continuous wedge and cone filling are much more relaxed than for continuous (critical) wetting. These studies also indicate that fluctuation effects at filling are characterised by a high degree of universality which persists even in the presence of long-ranged forces. For example, the filling of a three dimensional wedge is characterised by a universal roughness exponent\textsuperscript{[11]} while for two dimensional corners (in both ordered and disordered systems\textsuperscript{[11,12]}) and three dimensional cones\textsuperscript{[11]} fluctuation effects mimic, quite precisely, behaviour predicted to occur for the strong-fluctuation (SFL) regime of critical wetting\textsuperscript{[12]}.

Here we go beyond the effective Hamiltonian approach and investigate surface phase diagrams and fluctuation effects at filling using microscopic theory. We present exact results\textsuperscript{[13]} for two dimensional \((d = 2)\) Ising models which improve upon previous low temperature, solid-on-solid (SOS) studies\textsuperscript{[14,15]} and show that, near the bulk critical point, the shift of the phase boundary (relative to wetting) is universal, determined only by the corner opening angle. The results of detailed numerical transfer matrix studies, which test the proposed connection between two dimensional filling and the SFL, are discussed at length and predictions for phase boundary shifts for wedges and cones in \( d = 3 \) are made.

Consider a two dimensional corner with opening angle \( 2\psi \) (with \( \psi \in (0, \pi/2) \)) in contact with a bulk phase \( A \) which is at two-phase bulk \( AB \) coexistence. Thus \( \psi = \pi/4 \) is a right angle corner whilst \( \psi = \pi/2 \) is a flat, semi-infinite interface. Thermodynamic arguments\textsuperscript{[14]} indicate that the corner is completely filled by phase \( B \) when the contact angle \( \theta \) satisfies

\[
\theta(T) = \frac{\pi}{2} - \psi
\]

implying that filling precedes wetting. The same condition applies for the filling of three-dimensional wedges and cones and is confirmed by effective Hamiltonian studies\textsuperscript{[1,2]}.

\[
\theta(T) = \frac{\pi}{2} - \psi
\]

Note that \( T(T) \) can be identified as a universal scaling function provided we allow for a non-universal metric factor \( \delta \). It follows that near the bulk critical point the filling phase boundary satisfies

\[
ah_1^f(T) = W^{-1}(\frac{\pi}{2} - \psi)\text{ generalising the well known result for the wetting phase boundary (denoted } h_1^w(T) \text{) corresponding to } \psi = \pi/2 \text{.}
\]

Consequently the phase boundary shift defined as

\[
\lim_{T \to T_c} h_1^w(T) = R_d(\psi)
\]

should be universal depending only on the opening angle and dimensionality. Implicit in this definition is the assumption that both the wetting and filling transitions are continuous. This requirement is not restrictive in the two dimensional systems, which are the main concern of this paper, since both the filling and wetting transitions are continuous at all temperatures. In three dimensions we emphasise that both wedge and cone filling may be continuous even if the wetting transition is first-order. To continue, it follows that for fixed, small values of the surface field

\[
\frac{T_c - T_w}{T_c - T_f} = R_d(\psi)^{1/\Delta_1}
\]

which provides a useful means of estimating \( T_f \) provided \( T_w \) is known. Moreover, whilst the character of the filling...
transitions for the $d = 3$ wedge and cone are different, the location of the phase boundary obeys the same thermodynamic condition $f(\psi) = 0$ and the shift function $R_3(\psi)$ is unique.

To test the scaling theory we consider square and diagonal lattice right-angle Ising corners which are natural extensions of Abraham’s semi-infinite model [18,19] (see Fig.1). We assume isotropic interactions in order to preserve reflection symmetry about the apex diagonal so that both boundaries behave as identical walls. The reduced interaction strength between nearest neighbour spins is $K = 1/L$, except they are modified to $K = h_1/T$ in the bottom row and far left column. The boundary spins are fixed to $+1$ whilst the bulk magnetisation (infinitely far from the boundaries) is supposed negative.

\[ f^S(T) = \tau^S_p - \tau^D_p/2 \] and \[ f^D(T) = \tau^D_p - \tau^S_p. \] At filling \[ f(T_f) = 0, \] leading to the exact conditions

\[ \cosh 2\tilde{K} = \cosh 2K - e^{-2K} \sinh^2 2K \] \[ \sinh^2 2\tilde{K} = \frac{\sinh(2K - 1)(1 - e^{-2K})}{2} \]

for the square and diagonal lattices respectively (see Fig. 2). Both types of corner show the same universal phase boundary shift with

\[ R_2(\pi/4) = \frac{1}{\sqrt{2 + \sqrt{2}}} \]

in agreement with scaling theory. The low temperature behaviour is also revealing. For the square lattice there

\[ h^w(T) \sim 1 - \frac{T}{2} \ln 2 \]

is a strong entropic effect arising from the energetic degeneracy of domain configurations and away from the bulk critical regime we find

\[ h^f(T) \sim 1 - \frac{T}{2} \ln 2 \]

which is precisely the SOS result obtained earlier by Duxbury and Orrick [14] and Lipowski [15]. For the diagonal lattice on the other hand such entropic effects influence the wetting but not filling phase boundary. The SOS limit for this lattice has not been considered before but is very easily constructed. Assuming the interface sticks to the walls (as shown) outside of the filled region the probability distribution for diagonal interfacial height follows as

- \[ P^D(T) = \frac{(e^K (\cosh 2K - \cosh 2\tilde{K}) - e^{-K} \sinh 2K)^2}{(\cosh 2K - \cosh 2\tilde{K}) \sinh 2K} \]

\[ F^S(T) = \frac{\sinh^2 2K - 1 - 2 \sinh^2 2\tilde{K}}{\sinh^2 2K} \]

which vanish at wetting. Next note that for large $L$ the excess free-energy of the corner must contain a term $f(T)L$ arising from surface tension contributions with

\[ \cosh \tau_p = \cosh \tau - \frac{1}{2} f(T) \]

where $\tau^S = 2K + \ln \tanh K$ and $\tau^D = 2 \ln(\sinh 2K)$ denote the free interfacial tensions. The singular contributions to the free energy are

\[ F^D(T) = \frac{(e^K (\cosh 2K - \cosh 2\tilde{K}) - e^{-K} \sinh 2K)^2}{(\cosh 2K - \cosh 2\tilde{K}) \sinh 2K} \]

\[ F^S(T) = \frac{\sinh^2 2K - 1 - 2 \sinh^2 2\tilde{K}}{\sinh^2 2K} \]

\[ \tau_p = \tau - \frac{1}{2} f(T) \]
\[ P(z) = \frac{e^{-z/(\langle z \rangle)}}{\langle z \rangle} \tag{10} \]

where \( \langle z \rangle \sim (h_1 - h_1^*)^{-1} \) and \( \lim_{T \to 0} h_1^* = 1/2 \) true to the exact Ising result. Notice that the scaling of \( P(z) \) is precisely the same as that predicted for the SFL regime of critical wetting in agreement with continuum effective Hamiltonian studies of filling in open wedges [16].

Returning to the Ising phase boundary, we note that the above results allow us to determine the exact \( R_2(\psi) \) even though it is not always possible to (easily) construct Ising lattices with arbitrary opening angle. Near the bulk critical temperature the Ising model recovers fluid isotropy and the incremental free-energy \( \tau_p \) may be identified with \( \tau \cos \theta \). Using the thermodynamic condition for filling [16] we obtain, after a little manipulation, the elegant expression

\[ R_2(\psi) = \sqrt{2} \sin \frac{\psi}{2} \tag{11} \]

which recovers the result for the right-angle corner quoted above as a special case. Note that for a corner with 120° opening angle we predict \( R_2(\pi/3) = 1/\sqrt{2} \), which may be tested using the triangular lattice Ising model which naturally forms corners of this type. Also [11] is consistent with the general requirement for the open wedge (\( \psi \to \pi/2 \)) limit \( 1 - R_2(\psi) \sim (\pi/2 - \psi)^{2\alpha_s} \) which follows from [16]. Here \( \alpha_s \) denotes the critical wetting specific heat exponent which is zero for the planar Ising model [18].

![FIG. 3. Numerical transfer matrix results for the magnetisation profile in the finite-size Ising square for \( N = 24 \), \( T = 1.6 \) and different surface fields above, below and (nearly) at the filling phase boundary.](image)

To test the connection between filling and the SFL regime for the full Ising model we consider a finite-size square lattice Ising square of side length \( N \) with weakened bonds around the perimeter. The boundary spins are fixed to +1 (-1) along the bottom (top) rows and left (right) columns respectively so that the domain wall runs from the upper left to lower right corner (see inset Fig.3).

In the limit of \( N \) tending to infinity the system decouples into two separate corner lattices, each of which exhibit a filling transition by the opposite bulk phase at the same temperature, \( T_f \). For finite \( N \) this anti-symmetric choice of boundary conditions frustrates the interface analogous to behaviour in infinite Ising strips with opposing surface fields [21,22]. Far above the filling transition the interface stretches from the top left to bottom right corners across the middle of the square and has an r.m.s width of order \( \sqrt{N} \). In contrast, far below the transition temperature we anticipate pseudo phase coexistence, since the interface may be bound to either the top-right or the lower-left corner. The cross-over between these different types of interfacial behaviour occurs when \( T_f - T \sim N^{-1/\beta_o} \) reflecting the influence of length-scales associated with the filling transition.

The conjectured connection between filling and SFL-wetting suggests that at \( T = T_f \) the magnetisation profile along the diagonal \( m(z) \) is universal and characterised by the same scaling function describing the profile for an infinite Ising strips with opposing surfaces fields at \( T = T_w \). Thus exactly at \( T = T_f \) and for asymptotically large \( z, N \) with arbitrary \( z/N \in (0, 1) \), we expect the SFL-like scaling behaviour [22,23]

\[ m(z) = m_0 \left( 1 - \frac{2z}{N} \right) \tag{12} \]

where \( m_0 \) is the bulk spontaneous magnetisation. Notice that at the filling temperature the r.m.s. width of the interface now scales with \( N \) compared to \( \sqrt{N} \) for \( T \geq T_f \) which reflects the additional excitations present near filling [16]. Using numerical transfer matrix techniques [13] we have calculated the exact magnetisation profile in the Ising square for systems up to \( N = 24 \). The results verify the qualitative character of the interface delocalisation discussed above and are in excellent quantitative agreement with the scaling of the profile at \( T_f \). Indeed, testing for the most linear profile turns out to be a highly efficient numerical method of determining the phase boundary up to \( T = 1.6 \) (see Fig.2) beyond which the influence of the bulk critical point becomes apparent and larger systems sizes are required to see the scaling of \( m(z) \). At low temperatures the exact Ising results are very well described by the SOS approximation and for this model we have numerically computed \( m(z) \) for systems up to \( N = 180 \). Again there is excellent agreement with the scaling prediction (11) for the profile at \( T = T_f \) and the SOS phase boundary \( h_1^*(T) \) is recovered to four significant figures.

It is straightforward to derive an expression for \( R_d \) using mean-field (MF) theory. This serves not only as point of comparison with the exact Ising result but also
indicates the $d$ dependence. We omit the details and only quote the final result (which is independent of $d$) obtained using Landau theory:

$$\sin \psi = \frac{3}{2} R(1 - \frac{R^2}{3})$$

which we anticipate to be correct for $d > 4$. This is a remarkably good approximation to the exact $d = 2$ result (yielding $R(\pi/4) = 0.518$ and $R(\pi/3) = 0.684$) and strongly suggests that the dimension dependence of $R_d(\psi)$ is rather weak. Unfortunately no $\epsilon$ expansion results for the pertinent surface tensions are available to systematically estimate $R_d$ in lower dimensions; though progress can be made using approximate non-classical local-functional theory which is usually a reliable treatment of bulk and surface criticality. Strictly speaking the theory fails for $d \leq 3$ when $\psi$ is very close to $\pi/2$ since it does not account for capillary-wave like fluctuations which alter the Landau MF value of $\alpha_\perp$ (equal to zero). However, the asymptotic critical regime for wetting in three dimensions, where such effects are important, is extremely small and the value of $R_d(\psi)$ will be uninfluenced by capillary-waves for all but the shallowest of wedges. The local functional theory we use is a simple extension and application of the Fisk-Widom theory.

Again we omit the details of the calculation and only quote the result for three dimensions which is conveniently written as the expansion

$$\sin \psi \approx \frac{7}{2\sqrt{6}} R_3^2 \left(1 - \frac{R_3^2}{4} - \frac{9R_3^4}{160} + \ldots\right)$$

valid provided $R_3$ is not extremely close to unity. For the right-angle wedge the local theory predicts $R_d(\pi/4) \approx 0.53$ which lies close to and between the $d = 2$ and $d = 4$ (MF) results and is presumably reliable to within a few per cent. This may be used to estimate the location of the filling phase boundary for Ising model right angle wedges with weak surface fields which are natural generalisations of models used to study wetting. Again, as in $d = 2$, there are two ways of constructing this wedge with a simple cubic lattice with cross sections the same as shown in Fig.1 (and translational invariance in the other spatial direction). Away from the critical region we anticipate that, for the analogue of the (S) lattice, entropic effects are important and the phase boundary is determined by a linear law similar to $\psi = \psi_d$. This prior knowledge of the phase boundary may be useful when studying the large scale fluctuation effects predicted for wedge filling characterised by the universal critical exponent $\beta_0 = 1/4$.

In summary we have presented exact results for corner wetting in $d = 2$ and approximate results in higher dimensions, highlighting the universal shift of the phase boundary relative to wetting in the bulk critical region. In $d = 2$ numerical transfer matrix studies of the finite-size scaling of the magnetisation profile in Ising squares strongly support the conjectured relation between filling and the SFL regime.