Filling Transition: Exact Results for Ising Corners

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We obtain the exact solution for a two-dimensional rectangular Ising ferromagnet forming a corner with a surface field applied to the spins on edges. We establish the existence of the filling transition and give the condition for the filling temperature. We discuss the basic properties of the transition.

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Adsorption of a fluid on solid substrates equipped with modified geometrical structure has become increasingly important for many modern applications and technologies [1]. For instance, the surface of solid substrates can be channeled and grooved by mechanical and electrochemical means. Moreover, the chemical behavior resulting from noncovalent bonding can be modulated down to the nanoscale using microlithographic technique [2,3]. Recent studies, both experimental and theoretical, have shown that such systems have radically altered wetting characteristics [4], an example of which is the filling of wedges or corners. Phenomenological modeling shows that the *wedge fills with the liquid at a lower temperature than that at which the liquid wets an otherwise identical flat surface.* In fact, one can adjust the opening angle of the wedge to obtain filling at any temperature which solves $\Theta_c(T) = \alpha$, where α is the wedge tilt angle and $\Theta_c(T)$ is the contact angle of a liquid drop on the planar substrate [5–8]; the condition for *planar* wetting is $\Theta_c(T) = 0$. A considerable amount of work has been done recently on fluctuation effects, scaling regimes, and universality classes of filling transitions and how these compare with wetting [9–11]. There are conjectures on the universality of the filling transition and the behavior of the interfacial height probability distribution and other quantities based on heuristic scaling arguments and approximate interfacial models *in the limit of small tilt angle.* However, the evidence for the occurrence of the filling transition in a model system of a fluid at a molecular scale in the wedge geometry is still lacking, not to mention detailed verification of the predictions [12]. Here we propose a two-dimensional lattice gas model of a fluid confined by adsorbing walls forming a corner which can be solved exactly. We demonstrate existence of two different transitions taking place below the wetting temperature T_w of a single wall, one of which can be identified with filling.

Consider a rectangular lattice $N \times M$ with spins $\sigma(x, y) = \pm 1$ located at the sites of the lattice and interacting via coupling $K = \beta J > 0$. We consider two cases. In case (a), a field h is applied *to the spins on all edges*; for case (b), this field is reversed both on the edge $x = 1$ for $y = 1, \ldots, m$ and on $y = 1$, for $x = 1, \ldots, n$. Thus, in case (b) a domain wall, or interface, running from $(n, 1)$ to $(1, m)$ which can be bound to the surface by a suitable choice of h. Alternatively, it can gain entropy by choosing more direct routes. The standard edge wetting problem, having the interface beginning and ending on the edge, but far from the corner, has been solved exactly [13]. We establish an analogous phase transition for the corner case, beginning with the thermodynamics.

The incremental free energy of the domain wall is a canonical partition function ratio for the boundary conditions (a) and (b). We calculate this exactly using the transfer matrix technique. We consider the transfer in the $(1, 0)$ direction and use the spectrum of the transfer matrix with boundary fields h [14]; this has been obtained by the extension of the method of Kaufman [15] which we give in lattice-fermion language. For the symmetrized transfer matrix V', we have

$$V' = \exp\left\{-(1/2)\sum_k \gamma(k)[2X(k)^\dagger X(k) - I]\right\}, \quad (1)$$

where $\gamma(k)$ is Onsager's function given by

$$\cosh\gamma(k) = \cosh 2K \cosh 2K^* - \cos k, \quad (2)$$

with

$$\exp(-2K^*) = \tanh K. \quad (3)$$

The operators $X(k)$ satisfy Fermi anticommutation relation $[X(k_1)^\dagger, X(k_2)]_+ = \delta_{k_1,k_2}$ and $[X(k_1), X(k_2)]_+ = 0$. The $X(k)$ are given by

$$X(k) = N_k \sum_{m=0}^{2M+1} y'_m(k)\Gamma_m, \quad (4)$$

where N_k are normalization factors, with

$$\Gamma_{2m} = -i(f_m^\dagger - f_m), \qquad \Gamma_{2m-1} = f_m^\dagger + f_m. \quad (5)$$

$f_m = \mathcal{P}_{m-1}(\sigma_m^x - i\sigma_m^y)/2$, $\mathcal{P}_0 = 1$, $\mathcal{P}_m = \prod_{j=0}^m(-\sigma_j^z)$ which is the Jordan-Wigner transformation of the spin operators, σ_m^α, $\alpha = x, y, z$, to fermion operators. Here the basis for the transfer matrix representation is given by eigenvectors of σ_j^x. The $y'_m(k)$ are

$$y'_{2m-1}(k) = e^{i\delta(k)}e^{-i(m-1)k} + e^{i\delta'(k)}e^{imk}, \quad (6)$$

$$iy'_{2m}(k) = e^{i\delta(k)}e^{i\delta'(k)}e^{-i(m-1)k} + e^{imk} \quad (7)$$

for $m = 1, \ldots, M$; $y'_0(k)$ and $y'_{2M+1}(k)$ are given later. Thus, there is a phase shift between even and odd lattice points where $\delta'(k)$ is an angle of the Onsager hyperbolic triangle [16]. The boundary bonds are incorporated by combining elements with opposite wave numbers as suggested by the reflection symmetry, with a phase shift of $\exp i\delta(k)$ where

$$e^{i\delta(k)} = e^{i\delta'(k)}(we^{ik} - 1)/(e^{ik} - w). \quad (8)$$

Here w is a usual wetting parameter $w = \exp 2K(\cosh 2K^* - \sinh 2K^* \cosh h)$ [13]. The k values are quantized by $\exp iMk = s \exp i\delta(k)$ with $s = \pm 1$ being determined by the reflection characteristics of the associated $y'(k)$. Finally, the boundary values of the eigenvectors y' are given by

$$y'_0(k) = i\frac{\sinh 2h \cosh K_1^*}{\sinh\gamma(k)}(e^{i\delta(k)} + e^{i\delta'(k)}e^{ik}), \quad (9)$$

with $y'_{2M+1}(k) = isy'_0(k)$. The first deduction, essential for the physics, is that for $w > 1$ there are two asymptotically degenerate imaginary wave numbers $k = iv \pm \mathcal{A}(v)e^{-vM}$, where $e^v = w$ defines v and $\mathcal{A}$ is some M independent real function of v.

The following remarks, which will be crucial in understanding corner filling, refer to the strip geometry. The incremental free energy per unit length associated with a domain wall running from $(1, 1)$ to $(n, 1)$ is, as $M \to \infty$, $n \to \infty$ given by $f^x = \gamma(iv)$ [13]. An analogous calculation for a domain wall crossing the strip with terminations at $(1, 1)$ and (n, M) with n, M proportional and large is

$$F \sim n\gamma(iv) + Mv + O(1). \quad (10)$$

Both of these results are a direct consequence of the existence of imaginary wave number modes.

We anticipate physically that local thermodynamic equilibrium and overall free energy minimization imply that the interface will subtend the contact angle Θ_c with the walls so that (10) could equally well be written up to leading order as

$$F \sim M\csc\Theta_c\tau(\Theta_c) + M(1 - \cot\Theta_c)f^x, \quad (11)$$

where f^x is the interfacial free energy of a portion of the interface pinned to the wall, as shown in the previous paragraph. Using the modified Young's equation $\tau(\Theta)\cos\Theta - \tau'(\Theta)\sin\Theta = f^x$ and the implicit form of the angle-dependent surface tension [17] $\tau(\Theta) = \cos\Theta\gamma(iv_s(\Theta)) + \sin\Theta v_s(\Theta)$ with $\gamma(iv_s(\Theta)) = i\tan\Theta$ shows, with some effort, that (10) and (11) are indeed the same.

The final fact needed to set the stage for our new results is to obtain the probability P_m of a *pinned* interface passing at the distance m from the wall, using the "domain wall state" idea [18] extended to this new geometry. The domain wall state, which localizes the interface up to the scale of the bulk correlation length, can be taken as $|m\rangle = \Gamma_{2m-1}|\Phi\rangle$, from which it follows that

$$P_m = |\langle\Phi|X(c)\Gamma_{2m-1}|\Phi\rangle|^2, \quad (12)$$

with $X(c)$ given by (4) with $k = iv$. This form factor is easily obtained as before giving $P_m \sim \exp(-2mv)$. By appealing to the angle-dependent surface tension and contact angle formulas, were we to calculate P_m by Helmholtz fluctuation theory, our result for P_m is generated by a blob of adsorbed matter of isosceles triangular form with the apex at $(0, m)$ and feet at $(\pm m\cot\Theta_c, 0)$; the incremental free energy $\delta f(m) = -m\cot\Theta_c f^x + m\csc\Theta_c\tau(\Theta_c)$; some analysis shows that $\delta f(m) = 2mv$ as it should be. Moreover, the inverse length scale $2v$ agrees exactly with the film thickness of Ref. [13]. This series of remarks summarizes the wetting transition on an edge using the parallel transfer matrix, rather than the perpendicular one; it also brings in the contact angle Θ_c in a natural way [19].

We return to the boundary conditions for the corner given in the second paragraph of this Letter. Imagine a domain wall starting at $(1, m)$ and ending at $(n, 1)$ with $n \to \infty$ *first.* Clearly, there will be a depinning transition off $(\infty, 1)$ at $w = 1$, or $T = T_w$. What is considerably more surprising is that there is a phase transition in which the *domain wall on* $(1, m)$ *is depinned* as $m \to \infty$ at $T = T_1$ for $T_1 < T_w$ (the inequality is strict); for $T_1 < T < T_w$, the interface forms a wedge at the corner, the base angle of which can be calculated.

Such a problem is readily formulated in transfer matrix language. The incremental free energy is

$$e^{-F} = \lim_{M\to\infty}\frac{\langle\Phi_\infty|\Gamma_{2m}\tilde{V}_1X(c)^\dagger|\Phi\rangle}{\langle\Phi_\infty|\tilde{V}_1|\Phi\rangle}, \quad (13)$$

where $\tilde{V}_1 = \exp i\vartheta\sum_{j=1}^{M}\Gamma_{2j-1}\Gamma_{2j}$, $|\Phi_\infty\rangle$ is a boundary state with all spins parallel in the x direction and $\vartheta = 2h^* - K^*$, where h^* is dual to h. The extra difficulty is determination of the form factors when the in and out states are different; this has already been encountered in the corner problem *with free boundaries* [20], but here it is considerably more complicated, even though the basic technique is, once seen, rather obvious. First, we note that $\tilde{V}_1^{-1}\Gamma_{2m}\tilde{V}_1 = i\Gamma_{2m}\cosh\vartheta + \Gamma_{2m-1}\sinh\vartheta$ and then we develop the right-hand side of (13) in terms of the $X^\dagger(k)$ and $X(k)$. This gives

$$e^{-F} = \lim_{M\to\infty}\sum_{\pi>k>-\pi}N_ke^{imk}(\cosh\vartheta + e^{i\delta'(k)}\sinh\vartheta) \times\frac{\langle\Phi_\infty|\tilde{V}_1X^\dagger(k)X^\dagger(c)|\Phi\rangle}{\langle\Phi_\infty|\tilde{V}_1|\Phi\rangle} - N_ce^{-mv}(\cosh\vartheta - e^{i\delta'(v)}\sinh\vartheta). \quad (14)$$

To evaluate the $\langle\Phi_\infty|\tilde{V}_1X^\dagger(k)X^\dagger(c)|\Phi\rangle$, we consider the equation $\langle\Phi_\infty|(\Gamma_{2j} + i\Gamma_{2j+1}) = 0$ for $j = 1, \ldots, M$; this follows because $|\Phi_\infty\rangle$ has all spins parallel in the x direction. The next step is to evaluate $\tilde{V}_1^{-1}(\Gamma_{2j} + i\Gamma_{2j+1})\tilde{V}_1$ and then to expand the result in the $X^\dagger(k)$ and the $X(k)$. This gives

$$\sum_{0<k<\pi} N_k(e^{-ijk}e^{i\delta'(k)} - e^{ijk})\chi(k) \times \langle\Phi_\infty|\tilde{V}_1 X^\dagger(k)X^\dagger(c)|\Phi\rangle = -N_c(e^{-jv} + se^{-(M-j)})\chi_1(-iv), \tag{15}$$

where $\chi(k) = -\tanh\vartheta(e^{ik} - e^{i\delta'(k)}) + 1 - e^{ik}e^{i\delta'(k)}$ and $\chi_1(k) = -\tanh\vartheta(e^{-ik} + e^{-i\delta'(k)}) + 1 + e^{-ik}e^{-i\delta'(k)}$. Equations (14) and (15) can be simplified further by noting that $X(-k) = \exp -i[k + \delta(k) + \delta'(k)]X(k)$, giving

$$\sum_{-\pi<k<\pi} N_k^2 e^{ijk} K_M(k) = -N_c e^{-jv}\chi_1(-iv), \tag{16}$$

where

$$K_M(k) = \frac{\chi(k)}{N_k}\frac{\langle\Phi_\infty|\tilde{V}_1 X^\dagger(k)X^\dagger(c)|\Phi\rangle}{\langle\Phi_\infty|\tilde{V}_1|\Phi\rangle}. \tag{17}$$

Multiply (16) by z_1^{-j} with $|z_1| > 1$ and sum, getting as $M \to \infty$ with $K(z) = K_\infty(z)$

$$\frac{1}{2\pi i}\oint_{|z|=1}\frac{K(z)dz}{z - z_1} = \frac{2N_c w^{-1}\chi_1(-iv)}{z_1 - w^{-1}}. \tag{18}$$

This equation determines only the part analytic outside the unit circle in a Laurent decomposition of K. This is supplemented by the equation $K(z^{-1}) = -e^{i\delta(k)}K(z)$ which follows from reversing k; the Wiener-Hopf method gives the unique result:

$$K(z) = -\frac{2N_c\chi_1(-iv)(z^2 - 1)}{(z - w^{-1})[(z - A)(z - B)]^{1/2}}, \tag{19}$$

where $A = \exp 2(K + K^*)$ and $B = \exp 2(K - K^*)$. Using the same $k \to -k$ idea, (14) becomes

$$e^{-F} = \frac{1}{4\pi}\int_{-\pi}^{\pi} d\omega e^{im\omega}(\cosh\vartheta + \sinh\vartheta e^{i\delta'(\omega)})\frac{K(e^{i\omega})}{\chi(\omega)} - e^{-mv}(\cosh\vartheta - \sinh\vartheta e^{i\delta'(iv)}). \tag{20}$$

Thus, to obtain $\lim_{m\to\infty} F/m$, we must examine the singularities of the integral in (20). The branch cut at $\omega = i\log B$ generates the bulk phase correlation length. It is always dominated by either the singularity $\omega = iv$ or that generated by zeros of $\chi(\omega)$. A detailed analysis locates them as simple poles at $\omega = i\log\gamma(iv)$. It follows that the incremental free energy per unit length is

$$f = \min(\gamma(iv), v), \tag{21}$$

and that there is a first order phase transition at the locus of points in the (h, K) plane where, below the transition, the free energy behaves as $\gamma(iv)$, indicating that the domain wall is bound to both edges meeting at the corner, whereas above the transition, the free energy behaves as v, indicating a domain wall unbound from the vertical wall crossing the lattice at the contact angle at the horizontal edge. At this transition point, the contact angle is $\pi/4$; this angle decreases on increasing the temperature, vanishing when $v = 0$ (the usual wetting transition). The mathematical mechanism for this first order transition is the crossing of poles on the imaginary ω axis.

The basis for investigating the filling transition is to take a domain wall running from $(n, 1)$ to $(1, m)$ with the wetting condition on each edge, secured by taking $w > 1$ and now to take n, m to infinity together. *Analysis of this requires the full limiting two-point form factor*

$$K(k_1, k_2) = \lim_{M\to\infty}\frac{\chi(k_1)\chi(k_2)\langle\Phi_\infty|\tilde{V}_1 X^\dagger(k)X^\dagger(c)|\Phi\rangle}{N(k_1)N(k_2)\langle\Phi_\infty|\tilde{V}_1|\Phi\rangle}. \tag{22}$$

This has been obtained by a conceptually straightforward generalization of the vacuum condition trick above, the details of which will be given elsewhere. The conclusion is

$$K(k_1, k_2) = \frac{\chi(iv)}{\chi(-iv)}K(e^{ik_1})K(e^{ik_2})[1 - S(e^{ik_1}, e^{ik_2})], \tag{23}$$

where

$$S(z_1, z_2) = \frac{(e^{-\gamma(iv)} - z_2)(e^{-\gamma(iv)}z_2 - 1)}{(e^{-\gamma(iv)} - w)(e^{-\gamma(iv)} - w^{-1})}\frac{(z_1 - w)(z_1 - w^{-1})}{(z_1 - z_2)(z_1 z_2 - 1)}. \tag{24}$$

That this result is, in fact, antisymmetric in k_1 and k_2, as it should be, is a most significant test since the calculation places k_1 and k_2 on an entirely different footing. The singularity structure of (23) is of great relevance. There are simple poles at $k_1 = \pm k_2$ which produce the desired asymptotics, "bulk" branch points and singularities at $k_j = \pm i\gamma(iv)$, $j = 1, 2$. The latter ones arise because $\chi[i\gamma(iv)] = 0$; they give the required $\exp -m\gamma(iv)$ term. A detailed inspection then shows that the free energy is

$$F \sim (m + n)\gamma(iv) + O(1). \tag{25}$$

In addition to these simple pole terms, there is also a saddle point path. On raising the temperature, the pole at $k = i\gamma(iv)$ crosses this path. The integrands in the single integrals resulting from the $k_1 = \pm ik_2$ residues mentioned above contain a factor $\exp[-n\gamma(k) + imk]$; the saddle point mentioned above is located at the solution of $\gamma'(k) = im/n$. To see what relevance this has, the location of the domain wall can be found by using the domain wall states $|m\rangle$ again. The probability of a domain wall passing through (m_1, n_1) is

$$P_{m_1,n_1} = \frac{\langle \Phi_\infty | \tilde{V}_1 \tilde{R_m} (V')^{n_1} | m_1 \rangle \langle m_1 | (V')^{n-n_1} \tilde{R_0} | \Phi \rangle}{\langle \Phi_\infty | \tilde{V}_1 \tilde{R_m} (V')^n \tilde{R_0} | \Phi \rangle}. \quad (26)$$

This is developed by expanding the $|m\rangle$ and $\tilde{R_m} = \tilde{V_1}^{-1}\Gamma_0 \tilde{V}_1$ in terms of the $X^\dagger(k)$ and $X(k)$. The second matrix element in (26) generates the leading term $\sim \exp-[(n-n_1)\gamma(iv) + m_1 v]$. For the first matrix element, some detailed calculation gives the leading behavior $\exp-[m\gamma(iv) - m_1\gamma(iv) + n_1 v]$. Thus, the overall decay is

$$P_{nm} \sim \exp-(n+m)[v - \gamma(iv)]. \quad (27)$$

The factor premultiplying the exponent is independent of m and n; this is because the asymptotic form is generated by poles in the integrand. The result for P_{nm} shows that it is constant on lines normal to (1, 1), and the inverse length scale is $\ell^{-1} = v - \gamma(iv)$, where $\exp v = w$. Thus, from (2), ℓ^{-1} will vanish when $2\cosh v = \cosh 2K \cosh 2K^*$, that is, when $\exp v = \sinh 2K$. Coupling this with $\exp v = w$ gives a transition at $K = K_f$ where

$$\cosh 2h = \cosh 2K_f - e^{-2K_f}\sinh^2 2K_f, \quad (28)$$

confirming a conjecture [11]. Further, as $K \to K_f^+$, $\ell \sim (K - K_f)^{-1}$. There is additional physical meaning: for an otherwise free interface inclined at an angle $\pi/4$, the surface tension satisfies $\tau(\pi/4) = [\gamma(iv_s) + v_s]/\sqrt{2}$ with $\gamma'(iv_s) = i$ as the saddle point condition; this implies that $v_s = \gamma(iv_s)$ and $\exp v_s = \sinh 2K$. Thus, at the point where the length scale ℓ diverges, the binding free energy at the wall and $\tau(\pi/4)$ allow the bound interface to detach on each edge and cross at exactly an angle $\pi/4$, producing interface fluctuations which are much larger in spatial extent than the capillary ones encountered heretofore. Thermodynamically, the transition is of first order, but the corner fills with adsorbate *continuously* as $K \to K_f^+$.

In summary, we have established the existence and basic properties of a corner filling transition in a planar lattice gas model by exact solution of the equilibrium statistical mechanics. The mathematical details, which are extensive and rather technical, will be given elsewhere.

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