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The critical wetting saga: how to draw the correct conclusion

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Abstract

A long-standing problem in condensed matter physics concerns the nature of the critical wetting phase transition in the Ising model or, more generally, in 3D systems with short-ranged forces. This is of fundamental interest because 3D corresponds to the upper critical dimension of the transition and it is not clear *a priori* whether the behaviour of the system will be mean-field-like or fluctuation-dominated. Renormalization group studies of the standard coarse-grained effective interfacial Hamiltonian model famously predict strong non-universal critical exponents which depend on the value of the so-called wetting parameter ω. However, these predictions are at odds with extensive Monte Carlo simulations of wetting in the Ising model, due to Binder, Landau and coworkers, which appear to be more mean-field-like. Further amendments to the interfacial Hamiltonian, which included the presence of a position-dependent stiffness, worsened the problem by paradoxically predicting fluctuation-induced first-order wetting behaviour.

Here we show from re-analysis of a microscopic Landau–Ginzburg–Wilson model of 3D short-ranged wetting that correlation functions are characterized by two diverging parallel length scales, not one, as previously thought. This has a simple diagrammatic explanation using a non-local interfacial Hamiltonian and yields a thermodynamically consistent theory of wetting in keeping with exact sum rules. The non-local model crucially contains long-ranged two-body interfacial interactions, characterized by the new length scale, which were missing in earlier treatments. For critical wetting the second length cuts off the spectrum of interfacial fluctuations determining the repulsion from the wall. We show how this corrects previous renormalization group predictions for fluctuation effects, based on local interfacial Hamiltonians. In particular, lowering the cut-off leads to a substantial reduction in the effective value of the wetting parameter controlling the non-universality and also prevents the transition being driven first-order. Quantitative comparison with the Ising model simulation studies is also made.

(Some figures in this article are in colour only in the electronic version)

New phase behaviour emerges when a system (fluid, magnet, superconductor, etc) is geometrically confined. Perhaps the most important example is the wetting transition, which occurs when one of two coexisting phases α and β (think up-spin/down-spin or liquid/vapour) is energetically preferred by the confining walls of the system [1]. Far from being a technical detail, the wetting transition has deep implications since it is intrinsically linked to the vanishing of the contact angle formed by a drop of one of the phases, and plays a crucial role in nanotechnology. From a theoretical perspective, the wetting transition is of fundamental interest since fluctuation effects associated with the thermal excitation of long-wavelength, capillary-wave-like modes of the unbinding interface may have a profound influence on critical singularities.

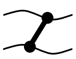
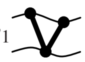
Imagine bringing a planar wall in contact with a bulk phase α. In general, a microscopic layer of the preferred phase β will intrude between the wall and the α phase.

At a wetting transition [2, 3], the thickness of this layer ℓ diverges, i.e. becomes macroscopic. This situation occurs on approaching two-phase coexistence and the wetting temperature T_w, and may be first-order or continuous (critical wetting). Alternatively, the divergence of ℓ on approaching two-phase coexistence for $T > T_w$ is termed complete wetting (see figure 1). As the film thickens, a fluid interface between phases α and β is subject to increasingly large fluctuations characterized by parallel $\xi_\parallel$ and perpendicular $\xi_\perp$ correlation lengths. For critical and complete wetting, these length scales diverge continuously and are described by critical exponents [1]. It turns out that the upper critical dimension for both these transitions is $d = 3$ for systems with short-ranged forces, i.e. for $d > 3$, the critical exponents take their classical values, as determined by mean-field (MF) theory, while for $d < 3$ they are fluctuation-dominated. Predicting what will happen exactly at the upper critical dimension is a stringent test for theory and it is here that the interest and ensuing controversy concerning critical wetting begins [4]. Renormalization group (RG) studies of critical wetting based on the standard, coarse-grained, interfacial Hamiltonian predict strong non-universality in which critical exponents depend on the wetting parameter

$$\omega = k_B T / 4\pi \Sigma \xi^2 \qquad (1)$$

where Σ is the interfacial stiffness and ξ is the correlation length of the bulk β phase [5]. For example, the divergence of the parallel correlation length along path (C) is given by $\xi_\parallel \sim (T_w - T)^{-\nu_\parallel}$, where $\nu_\parallel(\omega) = (1-\omega)^{-1}$ for $\omega < 1/2$ and $\nu_\parallel(\omega) = (\sqrt{2} - \sqrt{\omega})^{-2}$ for $1/2 < \omega < 2$. The ideal testing ground for these predictions is the Ising model for which independent studies have accurately estimated $\omega \approx 0.8$ close to T_c [6], suggesting $\nu_\parallel \approx 3.7$, much larger than the MF value $\nu_\parallel = 1$. In sharp contrast to this, extensive simulation studies by Binder *et al* [7] found only minor deviations from MF theory, attributable to a much smaller effective value $\omega_{\rm eff} \approx 0.27 \pm 0.12$, lying somewhere between MF and RG expectations [8]. Unfortunately, early attempts to explain this discrepancy failed and the situation was confounded by a further refinement of the model due to Fisher and Jin [9] who included a position-dependent stiffness in their refinement of the interfacial model and predicted that, paradoxically, fluctuations drive the transition first-order, in disagreement with the qualitative findings of the simulations.

Progress has recently been made towards resolving this problem using a non-local (NL) interfacial Hamiltonian [10–12]. Within this description, the energetic binding between the interface and the wall is represented diagrammatically:

$W = a_1$  $+ b_1$  $+ \cdots \qquad (2)$

and may be visualized arising from tube-like fluctuations that zigzag between the surfaces. Numerical and renormalization group (RG) studies of critical wetting using this NL Hamiltonian [10] are in better agreement with the Ising model simulations [7, 8]. However, the fundamental physical mechanism behind this agreement has remained obscure. Here we show that non-locality explains the existence of a new diverging length scale, previously overlooked in the phenomenology of wetting but which is present in more microscopic theories. This leads to a breakdown of simple scaling and provides a mechanism by which the effective value of ω is reduced.

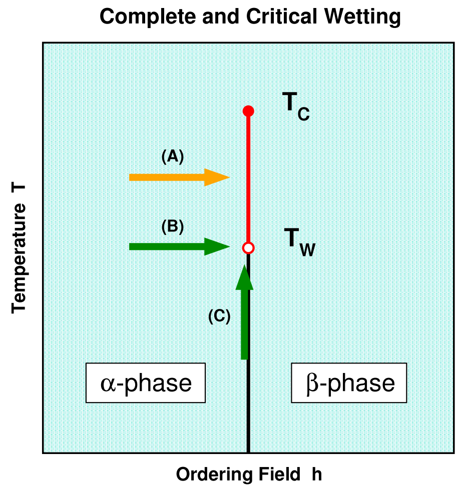


Figure 1. Surface phase diagram with a critical wetting transition at T_w (thermodynamic paths (B) and (C)) and complete wetting (path (A)). The bulk ordering field is denoted h while T_c is the critical temperature.

To begin, we return to the starting point of wetting theory and, using a magnetic notation, consider a microscopic Landau–Ginzburg–Wilson model [2, 3]

$$\mathcal{H}[m] = \int d\mathbf{r}\{\tfrac{1}{2}(\nabla m)^2 + \phi(m)\} \qquad (3)$$

which has a bounding wall in the $z = 0$ plane. A potential $\phi(m)$ describes the coexistence of bulk phases α and β where, in zero field, $m_\beta = -m_\alpha = m_0$. The bulk ordering field $h \leqslant 0$ so the bulk phase is α. Minimization of (3) determines the MF equilibrium profile $\langle m \rangle = m(z)$. With a fixed wall magnetization $m = m_1 > 0$, the model exhibits critical wetting when $m_1 = m_0(T_w)$, leading to the phase diagram figure 1.

Next consider the correlation function $G(\mathbf{r}_1, \mathbf{r}_2) = \langle m(\mathbf{r}_1) m(\mathbf{r}_2)\rangle - \langle m(\mathbf{r}_1)\rangle\langle m(\mathbf{r}_2)\rangle$ and its transverse Fourier transform (FT) $\mathcal{G}$, which, at MF level, satisfies

$$(-\partial_{z_1}^2 + \phi''(m(z_1)) + q^2)\, \mathcal{G}(z_1, z_2; q) = \delta(z_1 - z_2) \qquad (4)$$

where we have set $k_B T = 1$. This can be solved within the double-parabola (DP) approximation $\phi(m) = \kappa^2(|m| - m_0)^2/2 - hm$ which is known to describe the physics of continuous wetting transitions [12]. Here, κ is the inverse bulk correlation length. Within the DP approximation, the MF thickness (defined as $m(\ell) = 0$) is $\kappa\ell \approx \ln(-t/2 + \sqrt{t^2/4 - \tilde{h}})$, where $t \equiv m_1/m_0 - 1$ and $\tilde{h} \equiv h/(m_0\kappa^2)$ are dimensionless scaling fields. This displays the well-known logarithmic divergences of ℓ at critical and complete wetting. The result for $\mathcal{G} = \mathcal{G}_{\rm sing} + \mathcal{G}_{\rm reg}$ separates conveniently into singular and regular parts. The regular part contains no diverging length scales and can be identified as the structure factor of a film of β-like phase with fixed magnetization

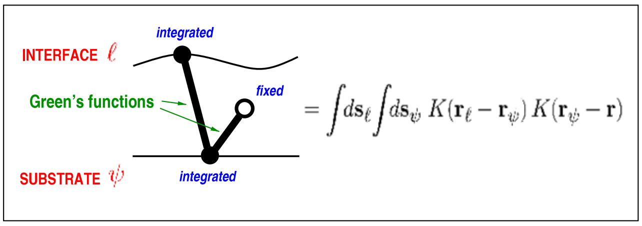


Figure 2. Wetting diagram and its algebraic expression.

boundary conditions $m(0) = m_1$ and $m(\ell) = 0$ at both sides. The singular term is

$$\mathcal{G}_{\text{sing}}(z_1, z_2; q) = \frac{\Psi(z_1; q)\Psi(z_2; q)}{E(\ell; q)} \tag{5}$$

where, in the relevant long-wavelength limit ($q \ll \kappa$), $\Psi(z, q) \approx m_0\kappa \mathrm{e}^{-\kappa_q(\ell - z)}$ and

$$E(\ell; q) \approx 2m_0\kappa|h| + 2m_0^2\kappa^3 \mathrm{e}^{-2\kappa\ell}\mathrm{e}^{-q^2\ell/\kappa} + \sigma_{\alpha\beta}q^2. \tag{6}$$

Here, $\kappa_q = \sqrt{\kappa^2 + q^2}$ and $\sigma_{\alpha\beta} = m_0^2\kappa$ is the DP result for the interfacial tension/stiffness. It is clear from (5) that the correlation function is determined by two diverging transverse length scales; the parallel correlation length $\xi_\parallel = (\sigma_{\alpha\beta}/E(\ell; 0))^{1/2}$ and also a second length $\xi_{\text{NL}} = (\ell/\kappa)^{1/2}$. For example, in the approach to critical wetting at $h = 0^-$ (path (C)) and near the interface:

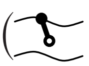
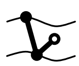
$$\mathcal{G}(\ell, \ell; q) \approx \frac{\mathcal{G}(\ell, \ell; 0)}{\mathrm{e}^{-q^2\xi_{\text{NL}}^2} + q^2\xi_\parallel^2} \tag{7}$$

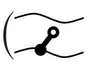
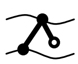
where $\mathcal{G}(\ell, \ell; 0) = \kappa^2 m_0^2 \xi_\parallel^2/\sigma_{\alpha\beta}$, while near the wall

$$\mathcal{G}_{\text{sing}}(0, 0; q) \approx \frac{1}{2\kappa}\frac{\mathrm{e}^{-q^2\xi_{\text{NL}}^2}}{\mathrm{e}^{-q^2\xi_{\text{NL}}^2} + q^2\xi_\parallel^2}. \tag{8}$$

Importantly, the singular contribution to $\mathcal{G}$ near the wall is dampened strongly when $q > \xi_{\text{NL}}^{-1}$. This damping factor also emerges beyond the DP approximation. The existence of two diverging transverse length scales corresponds to a breakdown of simple scaling and sheds new light on two long-standing puzzles for complete and critical wetting.

All the above is captured by the NL model, which describes wetting both for planar and non-planar walls [11]. A collective coordinate $\ell(\mathbf{x})$ denotes the location of a surface of iso-magnetization $m(\mathbf{r}_\ell) = 0$, where $\mathbf{r}_\ell = (\mathbf{x}, \ell)$ is an arbitrary point on the interface. A trace over irrelevant fluctuations identifies $H[\ell] = \mathcal{H}[m_\Xi]$ [9], where $m_\Xi(\mathbf{r})$ is the profile that minimizes (3) subject to the boundary conditions. For the DP potential

$m_\Xi(\mathbf{r}) - m_\beta = -m_\beta$ ( −  + ⋯)

+ $(m_1 - m_\beta)$ ( −  + ⋯) (9)

where the thick straight line denotes the Green's function $K(\mathbf{r}) = \kappa\,\mathrm{e}^{-\kappa r}/2\pi r$ and the wavy lines represent the interfacial configuration (top) and wall (bottom). A black

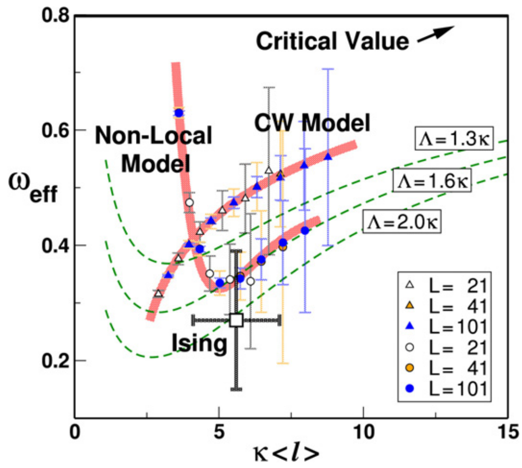
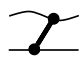


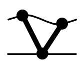
Figure 3. Effective value of the wetting parameter as a function of the wetting thickness. Simulations of the discretized local (triangles) and non-local (circles) interfacial models were performed on an $L \times L$ grid. Here L is measured in units of $3.1623/\kappa$ [10]. The thick lines are guides for the eye. The continuous and dashed lines are predictions of the continuum approximation (17) for different Λ. The value of ω_{eff} obtained from Ising model simulations [8] is also shown (square).

dot on a surface means one must integrate over all points on that surface with the appropriate infinitesimal area element (figure 2). The NL Hamiltonian is

$$H[\ell] = \sigma_{\alpha\beta}A_{\alpha\beta} + 2m_0|h|V_\beta + W_{\text{NL}}[\ell] \tag{10}$$

where $A_{\alpha\beta}$, V_β are the interfacial area and the volume of the β layer, respectively, and $W_{\text{NL}}[\ell]$ is given in (2). The geometry-independent coefficients are $a_1 = 2t\sigma_{\alpha\beta}$, $b_1 = \sigma_{\alpha\beta}$. The structure of W_{NL} is largely unchanged beyond DP and when coupling to a surface field is allowed, although the values of a_1, b_1 are slightly altered [12]. When the interface and wall are planar, $W_{\text{NL}}[\ell] = A_{\alpha\beta}\, W(\ell)$, where $W(\ell) = a_1\mathrm{e}^{-\kappa\ell} + b_1\mathrm{e}^{-2\kappa\ell}$ is the usual binding potential function [4]. For more general interfacial configurations, the diagrams further simplify to

 $= \int d\mathbf{s}\, \mathrm{e}^{-\kappa\ell}$ (11)

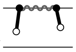
 $= \int\int d\mathbf{s}_1\, d\mathbf{s}_2\, \mathrm{e}^{-2\kappa\bar{\ell}}\, S(x_{12}; \bar{\ell})$ (12)

where $\bar{\ell} \equiv (\ell(\mathbf{x}_1) + \ell(\mathbf{x}_1))/2$ and $d\mathbf{s}$ is the appropriate infinitesimal area element at the interface. Here

$$S(x; \ell) = \frac{1}{4\pi\xi_{\text{NL}}^2}\mathrm{e}^{-x^2/4\xi_{\text{NL}}^2} \tag{13}$$

is an effective two-body interfacial interaction whose range is the new length scale ξ_{NL} discussed earlier. It is natural to interpret $\xi_{\text{NL}} \propto \ell^{1/2}$ as the rms width arising from the thermal wandering of a tube of length ℓ.

The MF expression for G_{sing} can be recovered from the interfacial correlation function $\langle\delta\ell(\mathbf{x}_1)\delta\ell(\mathbf{x}_2)\rangle$, where $\delta\ell \equiv \ell - \langle\ell\rangle$. Using the constrained profile (9) to reconstruct magnetization correlations, we are led to the diagrammatic formula

$$\frac{G_{\rm sing}(\mathbf{r}_1, \mathbf{r}_2)}{m_0^2} = \partial^2_{z_1 z_2}$$  . (14)

Here, the horizontal lines denote the equilibrium MF positions of the interface and wall, while the thick line and open/black dots are as before. The wiggly line represents $\langle \delta\ell(\mathbf{x}_1)\delta\ell(\mathbf{x}_2)\rangle$ and, therefore, shows magnetization correlations arising from the interaction between tubes and capillary waves. The transverse FT of equation (14) leads to the same expression for $G_{\rm sing}$ obtained in the Landau theory, equation (5). This demonstrates its robustness beyond the DP approximation. The standard local interfacial theory is recovered when one approximates $\xi_{\rm NL} \approx 0$.

We are now in a position to re-examine two long-standing problems of wetting theory. For complete wetting (path (A) in figure 1), the correlation function near the wall is

$$\mathcal{G}_{\rm sing}(0, 0; q) \propto \frac{h^2}{2m_0\kappa|h| + \sigma_{\alpha\beta}q^2} {\rm e}^{-q^2\xi_{\rm NL}^2} \qquad (15)$$

which remains valid beyond MF. Expanding in powers of q^2, including the exponential damping term, we identify the second moment $\mathcal{G}_2(0, 0) \propto \sigma_{\alpha\beta} + \sigma_{\rm sing}$ which contains correctly both the $\alpha\beta$ and the singular contributions $\sigma_{\rm sing} \sim h \ln|h|$ to the total surface tension of the wall–α interface. The presence of these two terms is an exact sum-rule requirement [13] which is known to be breached by the standard interfacial model of wetting. Non-locality and the consequent existence of the new length scale $\xi_{\rm NL}$ offer a fully consistent solution to this problem.

Armed with these insights, we now return to the problem of non-universality at critical wetting. The key observation here is that $\xi_{\rm NL}$ serves to cut-off the spectrum of interfacial interactions that control the repulsion from the wall. This is already present in the LGW model results (7) and (8) for the MF correlation function. For instance, near the interface and for wavevectors in the range $1/\xi_{\rm NL} \lesssim q \lesssim \kappa$, we find $\mathcal{G}(\ell, \ell; q) = \kappa^2 m_0^2/\sigma_{\alpha\beta}q^2$ which is the same as for a free $\alpha\beta$ interface, independent of the presence of the wall. Similarly, near the wall, the exponential damping kills the singular contribution for $q \gtrsim 1/\xi_{\rm NL}$. All these effects can be traced to the two-body interaction (13) controlling the repulsion. The FT of the interaction is $\tilde{S}(q) \approx \exp(-q^2\xi_{\rm NL}^2)$, which suppresses strongly the repulsion for wavevectors $q \gtrsim 1/\xi_{\rm NL}$. We are now in a position to critically re-assess previous predictions for fluctuation effects [5, 9]: (A) if we take the ultra-long-wavelength approximation $\tilde{S}(q) \approx 1$, the diagram (12) reduces to the local interaction $\int {\rm d}\mathbf{x}\, {\rm e}^{-2\kappa\ell}$, appearing in the original interfacial theory [5]. However, this approximation is only valid provided we restrict wavevectors to $q < \Lambda_{\rm NL}$, where $\Lambda_{\rm NL} \sim 1/\xi_{\rm NL}$ is an effective momentum cut-off. This contrasts with the original assumption [5] that $q < \Lambda$, where $\Lambda \sim \kappa$ is the high-momentum cut-off (which remains valid for the attractive term (11)). This implies that the renormalized repulsion should be [14, 15]

$$R[{\rm e}^{-2\kappa\ell}] \approx \frac{1}{\sqrt{2\pi}\, w_\perp} \int_0^\infty {\rm d}t\, {\rm e}^{-2\kappa t - (\ell - t)^2/2w_\perp^2} \qquad (16)$$

determined by a reduced width $\kappa^2 w_\perp^2 = \omega \ln(1 + \xi_\parallel^2 \Lambda_{\rm NL}^2)$. Equivalently, the wetting parameter controlling the renormalized repulsion takes a lower effective value

$$\frac{\omega_{\rm eff}}{\omega} \approx \frac{\ln(1 + \xi_\parallel^2 \Lambda_{\rm NL}^2)}{\ln(1 + \xi_\parallel^2 \Lambda^2)}, \qquad (17)$$

which, for thick wetting films, reduces to

$$\omega_{\rm eff} = \omega - \sqrt{2\omega^3} \frac{\ln(\kappa\ell)}{\kappa\ell} + \cdots \qquad (18)$$

where we have assumed that $\omega > 1/2$ as appropriate to the Ising model. (B) The precise same mechanism prevents the possibility of a stiffness instability subsequently predicted for models which allow for a position-dependent stiffness [9]. Indeed, the Fisher–Jin model can be recovered explicitly from the NL theory if we approximate $\tilde{S}(q) \approx 1 - q^2\xi_{\rm NL}^2$ [11]. Again, this is only valid for $q < \Lambda_{\rm NL} \sim 1/\xi_{\rm NL}$ and with this corrected cut-off the flow equations studied in [9] no longer drive the transition first-order. There is no stiffness instability. Thus, the NL theory preserves the Nakanishi–Fisher global phase diagram showing first-order, critical and tri-critical wetting [3]. All these considerations are consistent with the more detailed analysis based on the numerical renormalization of the two-body interaction (13) given in [10, 15].

It is this reduced value $\omega_{\rm eff}$ which determines the singularities of the first-layer magnetization and susceptibility along the critical wetting isotherm, which were studied in simulations of the Ising model [7] and NL Hamiltonian [10]. In figure 3, we plot $\omega_{\rm eff}$ versus the film thickness $\kappa\ell$ as obtained from simulation studies and the above theory. In the simulation studies of the interfacial models, $\omega_{\rm eff}$ has been extracted from the singularity of the surface magnetization $m_1 \sim |h|^{1-1/2\nu_\parallel(\omega_{\rm eff})}$ along the critical wetting isotherm. This is more difficult for the Ising model and we have used the estimate taken from the surface susceptibility critical amplitude [8]. As can be seen, the NL theory is in better agreement with the Ising model simulation result due to the slower crossover. Theoretical predictions for $\omega_{\rm eff}$ are also shown for different values of Λ. This is close to the simulation findings and substantially lower than the asymptotic critical value $\omega = 0.8$. It is interesting to note that, within the NL model, $\omega_{\rm eff}$ has a minimum value of approximately 0.3 when the film thickness is approximately five bulk correlation lengths. For thinner wetting films, the effective value actually increases. Similar qualitative behaviour is found in equation (17). Unfortunately, in the original Ising simulation studies, this regime corresponds to wetting layers of less than one or two lattice spacings for which a continuum description is doubtful. However, this limitation can be overcome in future simulations at temperatures closer to $T_{\rm c}$, where the bulk correlation length is much larger.

In conclusion, we have shown that 3D short-ranged wetting transitions are characterized by two diverging parallel length scales, and not one, as previously thought. The new length scale can be seen explicitly in the analytical expression derived for the mean-field magnetization correlation function within an LGW model. This is not accounted for in the original effective Hamiltonian description of wetting, but appears naturally in the present NL description, where it emerges from a two-body interfacial interaction. The nature of this interaction and the new length ξ_{NL} appears to resolve long-standing puzzles in critical wetting theory. In particular, for critical wetting, it suppresses long-wavelength interfacial modes, implying that critical singularities are necessarily much closer to mean-field predictions in keeping with Ising model simulation results.

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