Non-locality and short-range wetting phenomena

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We propose a non-local interfacial model for 3D short-range wetting at planar and non-planar walls. The model is characterized by a binding potential functional depending only on the bulk Ornstein-Zernike correlation function, which arises from different classes of tube-like fluctuations that connect the interface and the substrate. The theory provides a physical explanation for the origin of the effective position-dependent stiffness and binding potential in approximate local theories, and also obeys the necessary classical wedge covariance relationship between wetting and wedge filling. Renormalization group and computer simulation studies reveal the strong non-perturbative influence of non-locality at critical wetting, throwing light on long-standing theoretical problems regarding the order of the phase transition.

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Density functional [1] and interfacial Hamiltonian models [2] are complementary approaches to the theory of confined fluids. Mean-field, non-local density functionals give an accurate description of structural properties but are unable to account correctly for long-wavelength interfacial fluctuations. To understand these it is usually necessary to employ mesoscopic interfacial Hamiltonians based on a collective coordinate l(x), measuring the local interfacial thickness. These models are essentially local in character containing a surface energy term proportional to the stiffness Σ of the unbinding interface and a binding potential function W(l). In more refined theories the stiffness also contains a position dependent term Σ, which, it is has been argued, may drive the wetting transition first-order [4]. Despite progress over the last few years there are a number of outstanding problems particularly for wetting with short-ranged forces. In addition, recent studies of fluids in wedge-like geometries have uncovered hidden connections or wedge covariance relations between observables at planar wetting and wedge filling transitions [5], which have yet to understood at a deeper level. In this paper we argue that analogous to filling transitions [5], which, it is has been argued, may drive the wetting transition first-order [4]. Despite progress over the last few years there are a number of outstanding problems particularly for wetting with short-ranged forces. In addition, recent studies of fluids in wedge-like geometries have uncovered hidden connections or wedge covariance relations between observables at planar wetting and wedge filling transitions [5], which have yet to understood at a deeper level. In this paper we argue that analogous to filling transitions [5], which, it is has been argued, may drive the wetting transition first-order [4]. 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where \( h \) is proportional to the bulk field. There is no explicit position dependent tension but rather a binding potential functional with three leading contributions

\[
W[l, \psi] = -a\Omega^1_w[l, \psi] + b_1\Omega^2_w[l, \psi] + b_2\Omega^2_\Omega[l, \psi]
\]

where \( a, b_1 \) and \( b_2 \) are best regarded as phenomenological parameters to be identified later. Each \( \Omega^\mu \) represents integrated two-point interactions between \( \mu \) and \( \nu \) points on the wall and interface mediated by the (rescaled) bulk OZ correlation function \( K(r) = \kappa e^{-\kappa r}/2\pi r \). These can be viewed as contributions to the free-energy of a constrained thin-film arising from tube-like fluctuations of the bulk phase which tunnel from the interface to the wall. The first term involves only one tube

\[
\Omega^1_w[l, \psi] = \int ds_1^w \int ds_2^w K(r_{12})
\]

where \( ds_\mu = \sqrt{1 + (\nabla l(x_\mu))^2} dx_\mu \) etc and \( r_{12} = \sqrt{l(x_1)^2 + (\psi(x_1) - l(x_2))^2} \) is the distance between two points on the interface and wall. The last two terms

\[
\Omega^2_w[l, \psi] = \int ds_1^w \left\{ \int ds_2^w K(r_{12}) \right\}^2
\]

\[
\Omega^2_\Omega[l, \psi] = \int ds_1^\Omega \left\{ \int ds_2^\Omega K(r_{12}) \right\}^2
\]

involve two tubes and may be viewed as a self-interaction between points on the same interface or wall induced by the presence of a second surface. Each contribution can be represented diagrammatically as shown in Fig. 1. The upper and lower lines represent typical non-planar configurations of the interface and wall. The undulated line joining them represents the interaction function \( K(r_{12}) \) whilst the solid dots imply integration over the area of each surface. For general wall and interfacial configurations all contributions to \( W[l, \psi] \) are NL. Simplifications arise when one or both are planar. If both the wall and interface are flat, \( \psi(x) = 0 \), \( l(x) = l \) the Hamiltonian per unit area \( W(l) = W[l, 0]/A \) reduces to

\[
W(l) = -ae^{-\kappa l} + (b_1 + 2b_2)e^{-2\kappa l}
\]

which recovers the standard form of the binding potential appearing in local models. For the more general case of a non-planar interface near a planar wall, two contributions to the binding potential functional are local since

\[
\Omega^1_\mu[l, 0] = \int ds_1^\mu e^{-\mu l(x_1)}, \quad \mu = 1, 2
\]

However \( \Omega^2_\Omega \) remains NL and can be rewritten as a two-body repulsive interaction

\[
\Omega^2_\Omega[l, 0] = \int \int ds_1^\Omega ds_2^\Omega S((l(x_1); t) \Omega^2_\Omega[l, 0] = \int \int ds_1^\Omega ds_2^\Omega S((l(x_1); t)
\]

where \( t = |l(x_1) + l(x_2)|/2 \) and \( S(x; t) \) is:

\[
S(x; t) = \frac{\kappa^2}{2\pi} \int_{2\pi} dt e^{-\sqrt{t^2 + \kappa^2 x^2}} \approx \frac{\kappa}{4\pi t} e^{\frac{\kappa}{2} - 2\kappa x^2 + \kappa^2 x^2 / 4}
\]

valid for \( \kappa t \gg 1 \). In the small gradient limit, \( |\nabla| \ll 1 \), the NL term can be expanded and the model reduces to

\[
H[l, 0] = \int dx \left\{ \frac{\Sigma(l)}{2} (\nabla l)^2 + W(l) \right\}
\]

with stiffness coefficient

\[
\Sigma(l) = -ae^{-\kappa l} - 2b_1\kappa e^{-2\kappa l} + ...
\]

precisely recovering the FJ model and uniquely identifying \( a, b_1 \) and \( b_2 \). In particular \( a \) measures the deviation from the MF critical wetting temperature, \( b_2 \propto a^2 \) and the sign of \( b_1 \) determines the order of the MF transition. Thus the origin of the \( \kappa e^{-2\kappa l} \) contribution, crucial in the FJ analysis, can be traced directly to a perturbative treatment of the NL contribution \( \Omega^2_\Omega \).

Now consider fluid adsorption in a wedge geometry (\( \psi = \tan \sigma(x) \)). The NL model satisfies the necessary requirement of classical wedge covariance known from numerical studies of the microscopic model. Classical wedge covariance refers to the relationship between observables at MF critical wetting and MF wedge filling transitions. Let \( l_w(\theta) \) denote the MF thickness of the critical wetting layer written as a function of the contact angle. Let \( l_w(\theta, \alpha) \) denote the thickness of the filling layer above the wedge mid-point. Numerical minimization of the LGW Hamiltonian shows that \( l_w(\theta, \alpha) = l_w(\theta - \alpha) \) as \( \theta \to \alpha \), for both shallow and acute wedges. This relation cannot be explained using an approximate local Hamiltonian in which the interface interacts with the (closest) wall via a binding potential dependent on the normal distance. Such models predict the incorrect behavior \( l_w(\theta, \alpha) = \sec \alpha l_w(\theta - \alpha) \). In contrast the NL model obeys the correct wedge covariance relation. The reason for this can be traced to the structure of the NL binding potential. Since filling precedes wetting (\( \alpha \neq 0 \)), the dominant term is \( \Omega^1_\mu \). Now for a flat interfacial configuration \( l(x) = l_0 \) near a non-planar wall both \( \Omega^1_\mu \) and

FIG. 1: Schematic illustration of the diagrams which represent the leading order contributions to \( W[l, \psi] \).
\[ \Omega[l, \psi]|_{l=0} = \int dx \sqrt{1 + (\nabla \psi)^2} e^{-\kappa (l_0 - \psi(x))} \] (13)

showing that the effective local interaction occurs via the vertical distance to the surface. Near the filling phase boundary the interface is essentially flat in the filled section of the wedge and the \( \Omega_1^0 \) contribution must be of the above form. This is sufficient to ensure covariance. We also remark that for wetting at more general non-planar walls the NL model reproduces the precise form of the stiffness matrix appearing in approximate two-field models [11] valid for \(|\nabla l| \ll 1\) and \(|\nabla \psi| \ll 1\). This means that in application to complete wetting the NL theory satisfies exact sum rules [12].

Finally we turn to the controversy surrounding fluctuation effects at planar critical wetting. The standard capillary wave (CW) model, obtained by setting \( \Sigma(l) = \Sigma \) in Eq. (11), famously predicts non-universal criticality dependent on the wetting parameter \( \omega = k_B T c^2 / 4\pi \Sigma \) [13]. However, this strongly disagrees with Ising model simulation studies [14] which show only minor deviations from MF-like critical wetting behavior (for the experiments, see Ref. [13]). The more refined FJ model provides a possible explanation of this discrepancy since the \( \Sigma(l) \) term drives the transition first order for physical values of \( \omega \).

Here we show that the stiffness instability is not a robust mechanism since the wetting transition change due to the NL model remains continuous. A linear RG theory can be constructed provided we first expand \( 1 + (\nabla l)^2 \) to square gradient order. The local terms \( \Omega_{\mu}^0 \) generate effective binding potential and position-dependent stiffness contributions which renormalize as in Refs. [11,13]. We focus on the renormalization of the NL potential \( S(x;l) \) which controls the order of the phase transition since it is responsible for the \(-l e^{-2\kappa l} \) term in the perturbative \(|\nabla l| \ll 1\) limit. After renormalizing up to a scale \( b = e^t \) the NL term \( \Omega_1^0 \) retains its two-body form but with a modified potential \( S_t(x;l) \) satisfying the flow equation:

\[ \frac{\partial S_t}{\partial t} = 4S_t + x \frac{\partial S_t}{\partial x} + \omega e^{-2} \left( \frac{1 + J_0(\Lambda x)}{2} \right) \frac{\partial^2 S_t}{\partial l^2} \] (14)

where \( J_0(x) \) is a Bessel function of first kind and \( \Lambda \) is the momentum cutoff. This equation has the formal solution:

\[ S_t(x;l) = e^{4t} \int_{-\infty}^{\infty} \frac{k S_0(x e^t, l)}{\sqrt{4\pi k \Phi(\Lambda x, \Lambda x)}} \exp \left( \frac{-k (\kappa - k)^2}{\Phi(\Lambda x, \Lambda x)} \right) \] (15)

where \( \Phi(a, b) = \int_0^\infty dt [1 + J_0(t)]/2t \). We choose \( S_0(x, l) = \Theta(l) S(x, l) \), with \( \Theta(l) \) the Heaviside step function and \( S(x, l) \) given by Eq. (10). As \( t \to \infty \), \( S_t(x;l) \) becomes increasingly localized around \( x \). Using a matching technique we renormalize to a scale \( e^{-\gamma t} \) at which the curvature of the effective binding potential \( W_t(l) \) at its global minimum is of order \( \Sigma \kappa^2 \). Our \( W_t(l) \) has a local contribution due to the \( \Omega_1^0 \) and \( \Omega_2^0 \) processes, and a NL contribution which is obtained from the expansion of \( \Omega_1^0 \) in powers of \( \nabla l \):

\[ W_t^{NL}(l) = 2\pi \int_0^\infty dx x S_t(x;l) \] (16)

Numerical integration of the RG flow equation show that the wetting transition is always second order, and quantitatively similar to the non-universality exhibited by the CW model. This fact can be rationalized by noting that \( \Phi(\Delta x, \Delta x) \sim t \) as \( t \to \infty \) and \( \kappa x \lesssim e^{-t} \), which is the range where \( S_0(\Delta x, \Delta x) \) is non-negligible. Consequently, in our NL model there is no stiffness instability. The difference with the RG predictions of the FJ model arises specifically from non-locality. Mathematically the FJ flow equations can be recovered from Eq. (15) if we approximate the Bessel function term by its quadratic expansion in \( x \). However this is not valid at large distances and invalidates the stiffness instability.

In order to check the RG predictions, we have performed Monte Carlo simulations of the CW, FJ and NL
Hamiltonians (with the approximation $\sqrt{1+(\nabla l)^2} \approx 1 + (\nabla l)^2/2$). Following Ref. [10] we discretize by introducing a $L \times L$ lattice of spacing $\sigma$ with periodic boundary conditions in the directions parallel to the surface, but treating the interfacial position height as continuous variables. We chose $\sigma = 3.1023 \kappa^{-1}$ so that $\Lambda \kappa^{-1} \sim \pi/\kappa \sigma \lesssim 1$, and also set $\omega = 0.8$ and $b_1 = 2.5 \kappa^2 k_B T$ which are reasonable Ising-like parameters. We anticipate the critical wetting phase boundary remains MF ($a = 0$) for the CW and NL theories [13], whilst the FJ exhibits a first-order transition at higher temperatures [4]. Fig. 2 describes the behavior of the mean wetting layer thickness $\langle l \rangle$ and the surface magnetization-like operator $\Delta m_1 = \langle e^{-\kappa \ell} \rangle$ along the MF critical wetting isotherm $a = 0$, $h \to 0$. The FJ model clearly describes wetting in this limit consistent with a fluctuation-induced first-order transition. On the other hand the CW and NL models are qualitatively similar, showing continuous wetting. The divergence of the film thickness is well described by the RG result $\kappa \langle l \rangle \sim -\sqrt{\ln h}$ even for moderately thick wetting layers. However the surface magnetization shows a much larger preasymptotic critical regime. The asymptotic non-universal behavior $\Delta m_1 \sim h^{1-1/2\nu||}$, with $\nu|| = (\sqrt{2} - \sqrt{\omega})^{-2}$ is not observed until the wetting layer $\kappa \langle l \rangle \sim 10$ for very large lattice sizes $\kappa L \sim 300$. This is strongly suggesting that current Ising model simulations will not be able to observe significant deviation from MF behavior provided they focus on surface quantities.

We conclude by mentioning extensions and limitations of our theory. It is straightforward to generalize the model to describe wetting at heterogeneous substrates with, for example, hydrophilic and hydrophobic domains [17]. For such geometries all the contributions to $W[l, \psi]$ will be NL and may influence mesoscopic wetting behavior. The same is true for other types of homogeneous sculpted substrates as, for example, wedges of parabolic cross section [18]. However, even for the simple case of wetting at homogeneous planar walls, systematic improvements of the theory can be envisaged. The binding potential functional $\mathcal{K}$ is only valid for wetting layers many times larger than $\kappa^{-1}$. If the wetting layer is only a few bulk correlation lengths thick, the interaction function $K(r)$ should be replaced by the correlation function defined within the constrained profile. This would modify the form of the binding potential functional at short distances and may influence how the asymptotic critical regime is approached.

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