# Simulation Evidence for Nonlocal Interface Models: Two Correlation Lengths Describe Complete Wetting

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# Simulation evidence for non-local interface models: Two correlation lengths describe complete wetting

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Monte Carlo simulations of (fluctuating) interfaces in Ising models confined between competing walls at temperatures above the wetting transition are presented and various correlation functions probing the interfacial fluctuation are computed. Evidence for the non-local interface Hamiltonian approach of A. O. Parry et al. [Phys. Rev. Lett. **93** (2004) 086104] is given. In particular, we show that two correlation lengths exist with different dependence on the distance $D$ between the walls.

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Interfaces between coexisting fluid phases interacting with solid walls occur in many different contexts: wetting phenomena [1–4], heterogeneous nucleation [5–7], nanofluidic devices [8], capillary imbibition [9], use of mesoporous materials for separation [10], capillary condensation [11–13] and related phenomena where liquid bridges [10, 13–15] matter for nanoconfinement, etc. Due to the inhomogeneous character of the fluid in such circumstances, a precise theoretical understanding of all these phenomena is difficult to achieve. Certain problems (e.g. "critical wetting" [16–25]) have been heavily debated for a long time. An atomistic, detailed description (based on Hamiltonians via density functional theory [26]) involves mean-field-type approximations that often are inadequate in view of the reduced dimensionality of these problems. Thus, coarse-grained models of the interfaces are required in order to allow a description of interfacial fluctuations. The "standard model" of interfaces has been the (local) interface Hamiltonian describing the interaction between a (fluctuating) interface at position $z = \ell(x, y)$ above a planar wall at cartesian coordinate $z = 0$ in terms of a local potential $V(\ell(x, y))$ [1–4, 27]. This theoretical approach yielded predictions for critical wetting that were contradicted by the results of both simulation and experiment. However, Parry et al. [22–24, 28] pointed out various intrinsic inconsistencies of this description and suggested use of a non-local functional $W\{\ell(x, y)\}$. This implies that the interface at the point $z = \ell(x, y)$ does not just "feel" a potential from the wall at the point $\vec{r} = (x, y, z = 0)$ underneath, but every point at the interface $z = \ell(x, y)$ interacts with every point $\vec{r}'$ of the wall. Note that this description naturally generalizes to the interaction of interfaces with non-planar walls as well [23, 28].

Despite the possible wide-reaching consequences of this suggestion for the description of interfacial phenomena, the evidence in favor of this new theory so far is scarce. Basically, the slow crossover from mean-field to non-classical critical behavior seen in Monte Carlo studies of critical wetting [19] is all the (indirect) evidence that exists (this slow crossover is compatible with the non-local theory [23–25]). However, more direct evidence so far has been lacking.

Indeed, while critical wetting (for systems with short range surface forces) is a somewhat special problem and is difficult to realize in nature [29], a much more common situation is complete wetting [1–4] (Fig. 1): at temperatures where the liquid (at liquid-vapor equilibrium) is above its wetting transition temperature, the interface is (for conditions where the vapor is slightly off vapor-liquid coexistence) at a finite distance $\bar{\ell}$ from the wall. Now, the theory of Parry et al. [25] also predicts important consequences of non-locality for this case. We first define the site-site correlation function $C(z_1, z_2, r)$ as the correlation between sites at height $z_1$ and $z_2$ and separated by a lateral distance $r$. Consider the fourier transformed correlation function $G(z_1, z_2, q) \equiv \int dr_x \int dr_y \exp(iq_x r_x + q_y r_y) C(z_1, z_2, r)$ where $(r_x, r_y)$ are $x$ and $y$ coordinates of the distance $\vec{r}$ in Fig. 1)}. Parry et al. [25] predict that only the correlation function $G(\bar{\ell}, \bar{\ell}, q)$ which has small q behavior

$$G(\bar{\ell}, \bar{\ell}, q) \propto (1 + q^2 \xi_{\|}^2)^{-1}, \tag{1}$$

is the same as for the local theory. In Eq. (1) $\xi_{\|}$ is the correlation length of interfacial fluctuation in $x, y$ directions. However, **two** other correlation functions $C(0, \bar{\ell}, r)$ and $C(0, 0, r)$, or their Fourier transforms $G(0, \bar{\ell}, q)$ and $G(0, 0, q)$, acquire a more complicated, non-trivial structure [25],

$$G(0, \bar{\ell}, q) \propto \exp(-q^2 \xi_{NL}^2/2)/(1 + q^2 \xi_{\|}^2) \quad , \tag{2}$$

$$G(0, 0, q) \propto \exp(-q^2 \xi_{NL}^2)/(1 + q^2 \xi_{\|}^2) \quad , \tag{3}$$

where a second correlation length $\xi_{NL}$ appears. This new correlation length, $\xi_{NL}$, is **completely absent**, in the

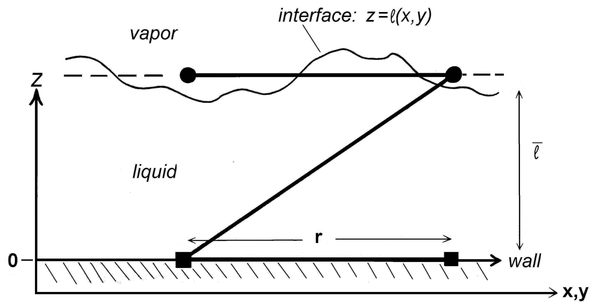

FIG. 1: Coarse-grained picture of an interface at height $z = \ell(x, y)$ above a planar wall at $z = 0$. For a situation close to complete wetting, the average height $\bar{\ell}$ is much larger than all molecular dimensions, and hence the interface is simply described by the single-valued function $\ell(x, y)$ separating liquid from vapor, disregarding the "intrinsic" structure of the interface. The thick lines indicate three correlation functions $C(z_1, z_2, r)$, $r$ being the lateral distance: $C(\bar{\ell}, \bar{\ell}, d)$ [line connecting two dots]; $C(0, 0, r)$ [line connecting two squares]; and $C(0, \bar{\ell}, r)$ [line connecting square and dot, respectively). (Note: $\vec{r} = (r_x, r_y)$ is a vector having $x$ and $y$ components.)

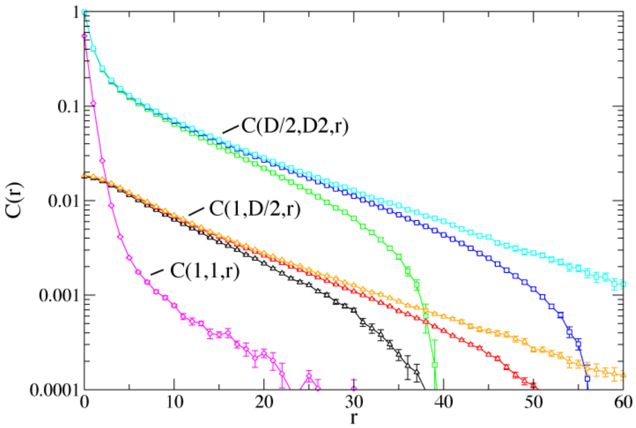

FIG. 2: Correlation functions $C(D/2, D/2, r)$ {open squares}. $C(1, D/2, r)$ {triangles} and $C(1, 1, r)$ {diamonds} plotted vs. distance $r$, for a system with $D = 12$,and $L = 128, 256$, and 512. (Data for $L = 128$ curve downwards at large $r$, but for $L = 512$ pure exponential behavior is seen for large $r$. Surface fields $H_1/J = -H_D/J = 0.55$ and $J/k_BT = 0.244$. Note that due to the discreteness of the lattice the surface fields act on layers $n = 1$ and $n = D$, respectively, and the interface plane occurs in between $n = D/2$ and $n = D/2 - 1$ (for even $D$). Where not shown, error bars are smaller than the symbols.

framework of the theory based on the standard interface Hamiltonian. We note, however, that on a qualitative level Eqs. (1)-(3) also have been derived from the standard mean-field square gradient theory using the double-parabola approximation[25]. This length $\xi_{NL}$, can be written as $\xi_{NL} = (\bar{\ell}/\kappa)^{1/2}$, where $\kappa^{-1}$ describes the (exponential) decay of the (short range) wall potential $V(\ell)$, $V(\ell) \propto \exp(-\kappa\ell)$, in the "standard model" of the wall-interface interaction [25]. In the present Letter we, hence, wish to fill this gap, providing evidence for the non-local theory of Parry et al. [23–25, 28] by testing the predictions given in Eqs. 2, 3 and obtaining $\xi_{NL}$. However, for a computer simulation a slight modification of the setup sketched in Fig. 1 is more convenient: rather than confining the interface at a finite distance $\bar{\ell}$ from a wall by working slightly off coexistence in a semi-infinite geometry, we consider a thin film of thickness $D$ confined by strictly antisymmetric walls and exactly at coexistence [30, 31]. Then, $\bar{\ell} = D/2$ and $\xi_{\|} \propto \exp(\kappa D/4)$ [32] while then $\xi_{NL} = (D/2\kappa)^{1/2}$. Varying $D$ we then obtain very direct evidence for both lengths $\xi_{\|}$, $\xi_{NL}$ and their very different dependence on film thickness.

Following previous studies of thin Ising films with competing walls [31], we simulate $L \times L \times D$ simple cubic Ising lattices, choosing surface fields $H_1/J = -H_D/J = -0.55$ and an inverse temperature $J/k_BT = 0.244$; since it is known that for this choice of surface fields critical wetting [19] occurs at $J/k_BT_w = 0.250$ ($\pm 0.001$), this choice corresponds to complete wetting, and $\kappa^{-1}$ is still small ($\kappa^{-1} \approx 2$ [32], measuring all lengths in units of the lattice spacing). We choose systems with $D = 6, 8, 10, 12$ and 14 layers, and the lateral linear dimension $L = 256$ (choosing periodic boundary conditions throughout). Multiple runs are made with different starting configurations and different random number seeds to determine statistical errors and to detect any systematic errors. Typically, a toatal of around $10^8$ MCS/site were kept for computing averages of the correlation functions. To check for finite size effects, for $D = 12$ the choices $L = 128$ and 512 were also considered.

Fig. 2 shows typical data for the correlation functions $C(D/2, D/2, r)$, $C(1, D/2, r)$ and $C(1, 1, r)$ at an inverse temperature of $J/k_BT = 0.244$. Since the two surfaces are equivalent, the squares are obtained as averages $[C(D/2, D/2, r)+C(D/2+1, D/2+1, r)]/2$, the diamonds are averages $[C(1, 1, r) + C(D, D, r)]/2$, and the triangles averages $[C(1, D/2, r)+C(D, D/2+1, r)]/2$. As expected, the correlations of spins within the interface are largest, but the asymptotic decay of all three correlations is governed by the exponential decay $\exp(-r/\xi_{\|})$. However, since the initial decay clearly is non-exponential, and the behavior for large $r$ is affected both by finite size effects and statistical errors, a quantitative analysis of these correlations in real space is difficult.

Fortunately, the behavior of the Fourier transforms $G(D/2, D/2, q)$ and $G(1, D/2, q)$ yields a clearer picture (Fig. 3). Finite size effects are still seen for $q \leq 0.05$, but they are negligible for larger $q$. When we examine the ratio $G(1, D/2, q)/G(D/2, D/2, q)$, we no longer find any systematic differences due to the finite size of $L$. Eqs. 1 and 2 imply that this ratio should simply be proportional to $\exp(-q^2\xi_{NL}^2/2)$. Our results are compatible with this prediction (Fig. 3b), and the fact that finite size effects are no longer present supports the plausible conclusion that only the very large correlation length $\xi_{\|}(D)$ is affected by finite size but not the much smaller length $\xi_{NL}(D)$. Fig. 4 shows that ,$\xi_{NL}(D)$ indeed increases with $D$ according to a power law, although the theoretical exponent ($\xi_{NL}^2 \propto D$) is not verified. Note, however, that the asymptotic region $\kappa D \gg 1$ unfortunately has not yet been reached. Nevertheless, we consider Fig. 3 and Fig.4 as offering fairly strong evidence in favor of the non-local theory of Parry et al. [23–25]. Recall that according to Parry et al. [24, 25, 28] $\xi_{NL}$ directly controls the range of the effective repulsion generated by the nonlocal interaction between the surface and the interface: this range diverges when $\bar{\ell}$ in Fig.1, or D in our geometry, tends to infinity, while the range $1/\kappa$ of the local interaction stays finite. The presence of this nonlocal repulsive interaction cuts off long range interfacial fluctuations, and thus affects the observability of non-universal critical wetting with short range forces. In addition, the presence of this length strongly alters the description of interactions between two curved interfaces, and hence should lead to interesting (but as yet, to our knowledge, unexplored) consequences for interface unbinding from rough surfaces: we speculate that roughness will be averaged out if the scale of corrugation is smaller than $\xi_{NL}$ but needs to be accounted for explicitly otherwise.

In conclusion, using large scale Monte Carlo simulations of the Ising model in a thin film geometry with competing surface fields, we have been able to measure several correlation functions describing interfacial fluctuations with sufficient accuracy to put the nonlocal interface Hamiltonian description of Parry et al. [23–25, 28] to a test. We have obtained evidence that two correlation lengths, $\xi_{\|}(D)$ and $\xi_{NL}(D)$, do indeed control the behavior of the correlation function. While $\xi_{\|}(D) \propto \exp(\kappa D/4)$ is predicted already by the naive interface Hamiltonian description [30, 32], and this result has also been verified by earlier simulations [34], the present work yields the first evidence for the role of the second correlation length, $\xi_{NL}(D)$. However, taking into account that $\kappa/2 \approx 0.25$ [32] the actual values observed for $\xi_{NL}(D)$ {Fig. 4} differ from the theoretical prediction, $\xi_{NL}^2(D) = D/2\kappa = D$. More work will be needed to clarify this remaining problem, and to extend our study to other systems and related problems. Indeed, experimental evidence for a length $\xi_\perp$ proportional to $\sqrt{\bar{\ell}}$ or $\sqrt{D}$ has been seen both in thin films of polymer blends [35] and in wetting layers of phase separated colloid-polymer mixtures [36]: this length $\xi_\perp$ is a measure of transverse interfacial fluctuations, however, and $\xi_\perp \propto \sqrt{\bar{\ell}} \propto \sqrt{D}$ already is derived from the standard interface Hamiltonian model, for short range wall forces. Thus these systems would also be well suited to test Eqs. 2 and 3 experimentally. We hope that our study will encourage such work.

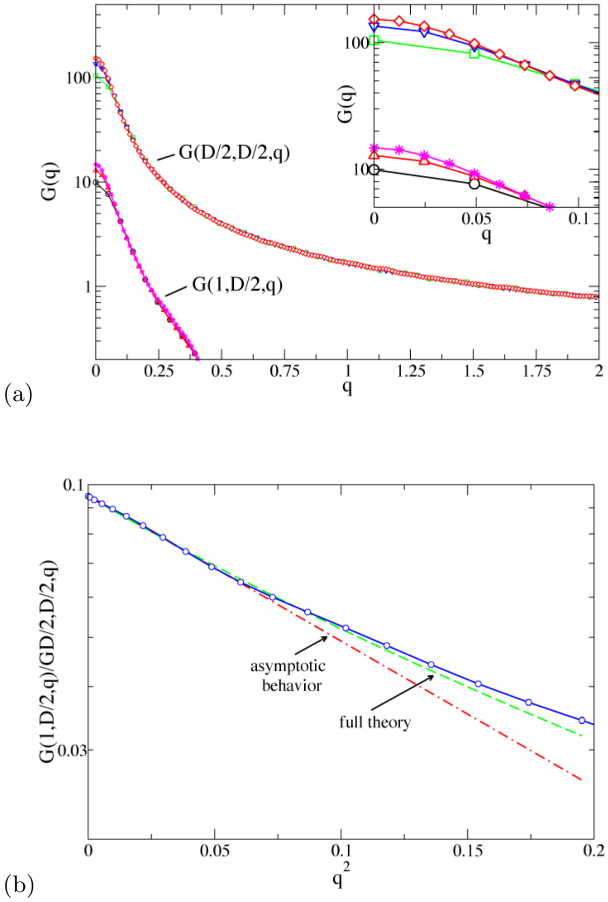

FIG. 3: (a) Correlation functions $G(D/2, D/2, q)$ [upper set of curves] and $G(1, D/2, q)$ [lower set of curves] plotted vs. $q$, for D = 12, $H_1/J = -H_D/J = -0.55$, $J/k_BT = 0.244$ and three choices of $L$, as indicated. The inset shows an amplification of the region for small values of $q$. The circles and squares represent results of $L = 128$, the triangles (both up and down) represent $L = 256$, while the stars and diamonds represent $L = 512$. (b) Ratio $G(1, D/2, q)/G(D/2, D/2, q)$ plotted vs. $q^2$, using the data of Fig. 3(a). Where not shown, error bars are smaller than the symbols. Broken curve in part (b) shows the full theory[33], namely the function $\exp\{\xi_{NL}^2\kappa[\kappa - \sqrt{q^2+\kappa^2}]\}$ which reduces to the asymptotic behavior $\exp(-q^2\xi_{NL}^2/2)$ for small q, also shown as dash-dotted curve.

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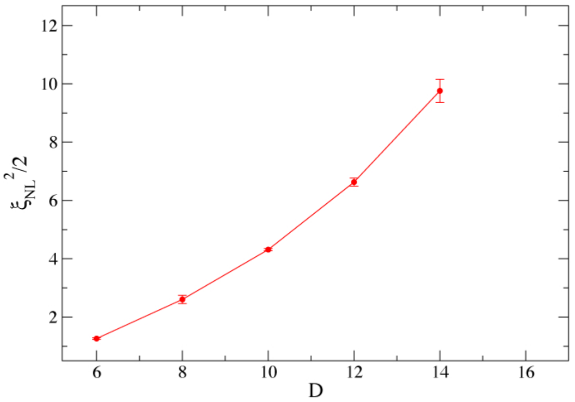

FIG. 4: Plot of $\xi^2_{NL}/2$ versus $D$, using data such as shown in Fig. 3b, for $D = 6, 8, 10, 12$ and 14. The data can be fitted to $\xi_{NL} \propto D^x$ with $x$ close to unity, but for the small values of D accessible here this exponent $x$ clearly is an effective exponent.

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