Wetting Transitions: Nonlocality and the Missing Lengthscale

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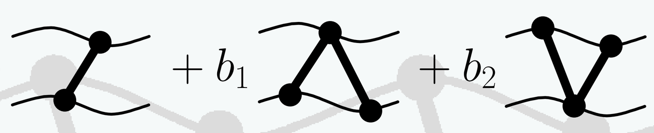
1. What's Wrong With Wetting Theory?

- The theory of short-range wetting in $3D$ has been in *disagreement with simulations* for 20 years [1]!
- The *Nonlocal Model* [2] seems to solve the issue. Why?
- Analysis of a microscopic Landau-Ginzburg-Wilson model reveals a *new lengthscale* ξ_{NL} [3].
- The new lengthscale ξ_{NL} is implicit in the structure of the Nonlocal Model.
- ξ_{NL} allows the Nonlocal Model to *satisfy an exact sum-rule*, unlike previous models [3].
- Fluctuations with wavelength smaller than ξ_{NL} are suppressed, inducing an effective wetting parameter and *restoring agreement with simulations* [3].

3. The Nonlocal Model Works!

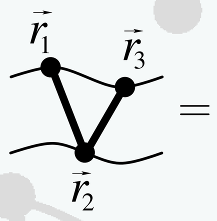
- The derivation of the Interfacial Model from a microscopic model [2] reveals a *nonlocal interaction functional* [2]:

$$W[l] = -a(T_{\mathrm{W}} - T)\ [\text{diagram}] + b_1\ [\text{diagram}] + b_2\ [\text{diagram}] + \cdots \quad (4)$$



with a, b_1 and b_2 constants.

- The diagrams represent integrations over the surfaces (black dots) with the kernel given by the Green's function of the Helmholtz equation ($K(\vec{r}_1, \vec{r}_2)$):



$$[\text{diagram}] = \int \mathrm{d}\vec{S}_{\vec{r}_3} \int \mathrm{d}\vec{S}_{\vec{r}_2} K(\vec{r}_2, \vec{r}_3) \int \mathrm{d}\vec{S}_{\vec{r}_1} K(\vec{r}_1, \vec{r}_2) \quad (5)$$

- This diagram has an *implicit two-body interaction* with range $\xi_{\mathrm{NL}} = \sqrt{l/\kappa}$.
- Monte Carlo simulations of the Nonlocal Model show that full nonuniversal behavior can only be observed for very large systems: the Ising model simulations probed a *pre-asymptotic regime*.

5. Consequences of the Extra Lengthscale.

- *Sum-Rule*: The second moment of the correlation function is changed. It crucially now includes an extra term, in keeping with an exact sum-rule: the Nonlocal Model is thermodynamically consistent.
- *Damping of fluctuations*: Capillary-wave fluctuations with wave-number $q > 1/\xi_{\mathrm{NL}}$ are damped, inducing an effective wetting parameter (Λ is the large wave-number cut-off):

$$\omega_{\mathrm{eff}} \approx \omega \frac{\ln(1 + (\kappa/l\Lambda^2)\mathrm{e}^{\kappa l/\sqrt{2\omega}})}{\ln(1 + \mathrm{e}^{\kappa l/\sqrt{2\omega}})} \quad (7)$$

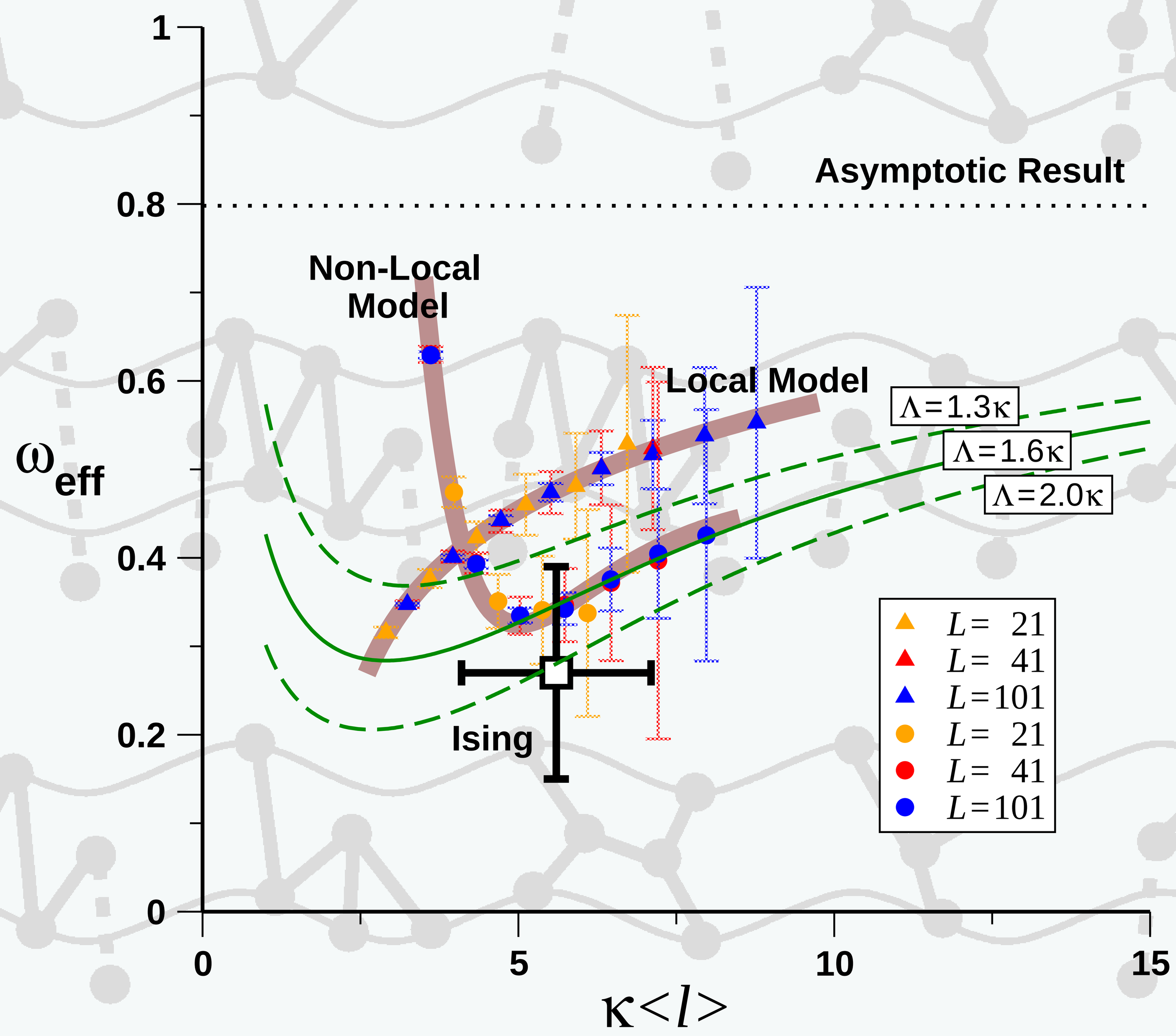


Fig. 2. Effective value of the wetting parameter as a function of the film thickness. Simulations on a $L \times L$ grid of the local (triangles) and Nonlocal Model (circles). The square is the Ising model result. The green lines are the theoretical description (eq. 7 in this box) with different values of Λ. The thick lines are guides to the eye.

2. Wetting Transitions in a Nutshell.

- A *wetting transition* [1] happens when the thickness l of an adsorbed liquid film becomes *infinite* (macroscopic). See Fig. 1.

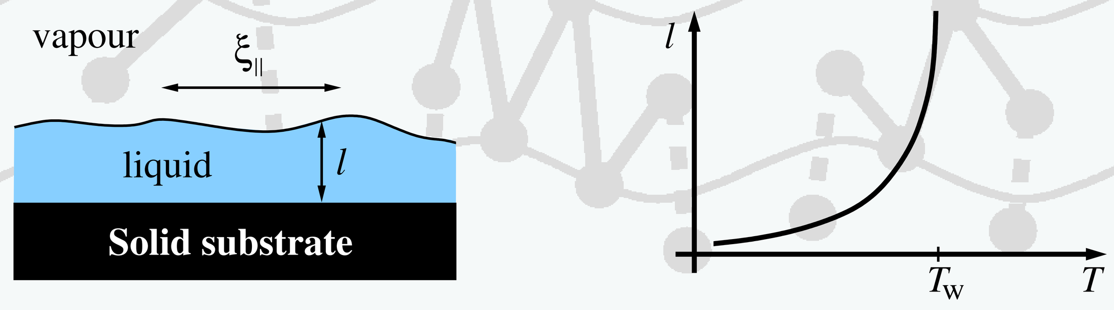


Fig. 1. The thickness of a liquid film l diverges to infinity at the wetting temperature T_{w}.

- If the transition is continuous (*critical wetting*) the divergence is characterized by *critical exponents* describing the asymptotic behavior of the thickness l, and the parallel correlation length $\xi_\parallel$ close to T_{w}:

$$l \sim (T_{\mathrm{w}} - T)^{-\beta} \quad (1)$$
$$\xi_\parallel \sim (T_{\mathrm{w}} - T)^{-\nu_\parallel} \quad (2)$$

- In $3D$, the upper critical dimension, the standard theory predicts *nonuniversal critical exponents*, dependent on a wetting parameter

$$\omega = \frac{k_{\mathrm{B}} T \kappa^2}{4\pi\Sigma} \quad (3)$$

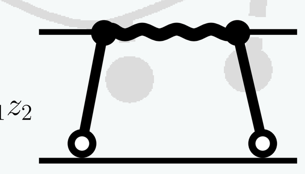
where Σ is the surface tension and κ is the inverse bulk correlation length.

- Ising model ($\omega \approx 0.8$, $\nu_\parallel \approx 3.7$) Monte Carlo simulations could not observe the predicted non-universality. The results are *consistent with a smaller wetting parameter* $\omega = 0.27 \pm 0.12$.
- The standard interfacial model fails to satisfy an exact sum-rule for the second moment of the correlation function, thus being *thermodynamically inconsistent*.

4. Why Does the Nonlocal Model Work!?

- Analysis of the correlations of the Landau-Ginzburg-Wilson model of wetting with Ornstein-Zernike theory reveals the presence of *two* (not one, as previously thought) diverging parallel lengthscales [3].
- The extra lengthscale is the *same* as present in the Nonlocal Model: ξ_{NL}!
- The structure of the correlation function has a *natural interpretation*, and diagrammatic representation, within the Nonlocal Model:

$$G^{\mathrm{sing}}(\vec{r}_1, \vec{r}_2) \propto \partial^2_{z_1 z_2}\ [\text{diagram}] \quad (6)$$



- This diagram is read as follows: the fluctuations at a point (open circles) are correlated to the fluctuations of the interface (thin upper line) by bulk-like fluctuations (thick lines). In turn two points at the interface are correlated by capillary-wave fluctuations (wiggly lines).

6. Take Home Message

- The standard model of wetting predicts strong non-universality with $\omega = 0.8$.
- Ising Model simulations consistent with $\omega = 0.27 \pm 0.12$.
- Nonlocal Model simulations agree better with Ising results. Why?
- Analysis of the correlation function reveals an extra lengthscale, ξ_{NL}.
- ξ_{NL} is the signature of nonlocal effects.
- ξ_{NL} makes the model consistent with exact sum-rules.
- ξ_{NL} cuts-off the fluctuations, restoring agreement with Monte Carlo simulations.

7. References & Acknowledgments

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