Critical wetting transitions: A scientific soap opera?

Nelson R. Bernardino

Max-Planck-Institut für Metallforschung
Stuttgart, Germany

Düsseldorf, 10-07-2008

Motivation

- Why replace this:

$$W(\ell) = a\,\mathrm{e}^{-\kappa\ell} + b\,\mathrm{e}^{-2\kappa\ell}$$

- with this:

$$W[\ell,\psi] = a \iint d\vec{s}_\psi d\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} + b \int d\vec{s}_\psi \left[\int d\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} \right]^2$$

- or this

$W[\ell,\psi] = a$ $+\, b$

Motivation

- Why replace this:

$$W(\ell) = a\,\mathrm{e}^{-\kappa\ell} + b\,\mathrm{e}^{-2\kappa\ell}$$

- with this:

$$W[\ell,\psi] = a \iint \mathrm{d}\vec{s}_\psi \mathrm{d}\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} + b \int \mathrm{d}\vec{s}_\psi \left[\int \mathrm{d}\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} \right]^2$$

- or this

$W[\ell,\psi] = a$ $+\, b$

Motivation

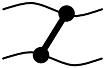
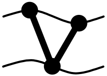
- Why replace this:

$$W(\ell) = a\,\mathrm{e}^{-\kappa\ell} + b\,\mathrm{e}^{-2\kappa\ell}$$

- with this:

$$W[\ell,\psi] = a \iint \mathrm{d}\vec{s}_\psi \mathrm{d}\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} + b \int \mathrm{d}\vec{s}_\psi \left[\int \mathrm{d}\vec{s}_\ell \frac{\kappa \mathrm{e}^{-\kappa|\vec{r}_\psi - \vec{r}_\ell|}}{2\pi|\vec{r}_\psi - \vec{r}_\ell|} \right]^2$$

- or this

$W[\ell,\psi] = a$  $+\, b$ 

Outline

1 Historical Background
- Phenomenology of Wetting
- 3D Wetting Transitions
- The Nonlocal Model

2 A Closer Look at the Nonlocal Model
- A New Lengthscale
- Derivation of the Nonlocal Model

Outline

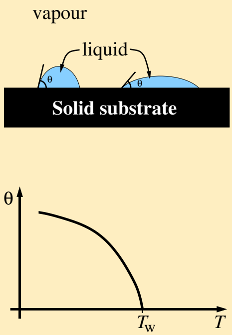
1. Historical Background
   - Phenomenology of Wetting
   - 3D Wetting Transitions
   - The Nonlocal Model
2. A Closer Look at the Nonlocal Model
   - A New Lengthscale
   - Derivation of the Nonlocal Model

Next...

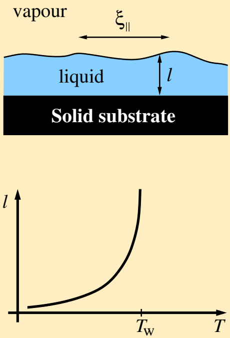
1. Historical Background
   - Phenomenology of Wetting
   - 3D Wetting Transitions
   - The Nonlocal Model
2. A Closer Look at the Nonlocal Model
   - A New Lengthscale
   - Derivation of the Nonlocal Model

The Wetting Transition (Cahn; Ebner & Saam 1977)

Contact angle goes to zero



Film thickness goes to infinity



Show Movie

Critical Exponents

Diverging lengthscales at critical wetting

- $\ell \sim (T - T_w)^{-\beta}$
- $\xi_{\parallel} \sim (T - T_w)^{-\nu_{\parallel}}$

Mean-field results (for short-range forces)

- $\beta = 0$ (log divergence)
- $\nu_{\parallel} = 1$
- Upper critical dimension = 3

Critical Exponents

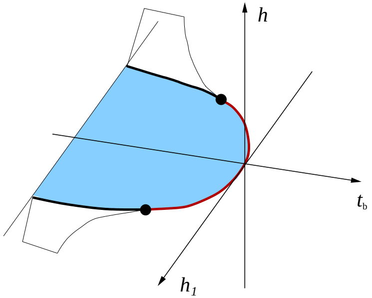
Diverging lengthscales at critical wetting

- $\ell \sim (T - T_w)^{-\beta}$
- $\xi_{\parallel} \sim (T - T_w)^{-\nu_{\parallel}}$

Mean-field results (for short-range forces)

- $\beta = 0$ (log divergence)
- $\nu_{\parallel} = 1$
- Upper critical dimension = 3

Global Phase Diagram of Nakanishi and Fisher (1982)



- Thick red lines = critical wetting transitions.
- Thick black lines = first order wetting transitions.
- Thick points = tricritical wetting transitions.

Next...

1. Historical Background
   - Phenomenology of Wetting
   - 3D Wetting Transitions
   - The Nonlocal Model
2. A Closer Look at the Nonlocal Model
   - A New Lengthscale
   - Derivation of the Nonlocal Model

The Interfacial Model

Interfacial Hamiltonian:

$$H_I = \int \mathrm{d}\vec{x} \left[\frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell) \right]$$

with the binding potential

$$W(\ell) = a\,\mathrm{e}^{-\kappa\ell} + b\,\mathrm{e}^{-2\kappa\ell}$$

The form of $W(\ell)$ is reasonable but not rigorously derived from a more microscopic model!

The Interfacial Model

Interfacial Hamiltonian:

$$H_I = \int \mathrm{d}\vec{x} \left[\frac{\Sigma}{2} (\nabla \ell)^2 + W(\ell) \right]$$

with the binding potential

$$W(\ell) = a\,\mathrm{e}^{-\kappa\ell} + b\,\mathrm{e}^{-2\kappa\ell}$$

The form of $W(\ell)$ is reasonable but not rigorously derived from a more microscopic model!

Renormalization Group Results (Brezin, Halperin & Leibler 1983)

- RG results depend on wetting parameter $\omega = \frac{k_B T \kappa^2}{4\pi\Sigma}$.
- $\nu_\parallel = (1-\omega)^{-1}$ if $0 \leq \omega < 1/2$.
- $\nu_\parallel = (\sqrt{2} - \sqrt{\omega})^{-2}$ if $1/2 < \omega < 2$.
- For the Ising model $\omega \approx 0.8$.
- For the Ising model we expect to see $\nu_\parallel \approx 4$ ($\nu_\parallel^{\mathrm{MF}} = 1$).

Monte Carlo Ising Model Results (Binder & Landau 1986-89)

- Extensive Monte Carlo simulations of the Ising Model:
  - observe the wetting transition.
  - confirm the global wetting phase diagram of Nakanishi and Fisher.
  - measure only very mild deviations from Mean-Field, consistent with $\omega \approx 0.3$!
- Simulations of the Interfacial Model (Gomper & Kroll, 1988) observe full non-universal results, consistent with RG.

A Refined Hamiltonian (Fisher & Jin, 1991-93)

- Careful derivation of interfacial Hamiltonian from a Landau-Ginzburg-Wilson Hamiltonian.
- Use perturbative method, expanding on the small-gradient of the interface.
- Hamiltonian with position-dependent stiffness:

$$H_{\mathrm{FJ}} = \int \mathrm{d}\vec{x} \left[\frac{\Sigma(\ell)}{2} (\nabla \ell)^2 + W(\ell) \right]$$

with

$$\Sigma(\ell) = \Sigma + a\mathrm{e}^{-\kappa\ell} - 2b\kappa\ell\mathrm{e}^{-2\kappa\ell}$$

and $W(\ell)$ as before.

Results of Fisher & Jin: Successes and Problems

Successes

- Systematization and rigorous derivation of interfacial model.
- "Critical wetting is a first-order transition!"

Problems

- No signature of a first-order phase transition in simulations.
- Same reasoning implies first-order wetting becomes critical wetting ⇒ inversion of the Nakanishi-Fisher global phase diagram (confirmed by simulations).

Paradox

Why does a better, more rigorous model gives contradictory results?

Results of Fisher & Jin: Successes and Problems

Successes

- Systematization and rigorous derivation of interfacial model.
- “Critical wetting is a first-order transition!”

Problems

- No signature of a first-order phase transition in simulations.
- Same reasoning implies first-order wetting becomes critical wetting ⇒ inversion of the Nakanishi-Fisher global phase diagram (confirmed by simulations).

Paradox

Why does a better, more rigorous model gives contradictory results?

Results of Fisher & Jin: Successes and Problems

Successes

- Systematization and rigorous derivation of interfacial model.
- “Critical wetting is a first-order transition!”

Problems

- No signature of a first-order phase transition in simulations.
- Same reasoning implies first-order wetting becomes critical wetting $\Rightarrow$ inversion of the Nakanishi-Fisher global phase diagram (confirmed by simulations).

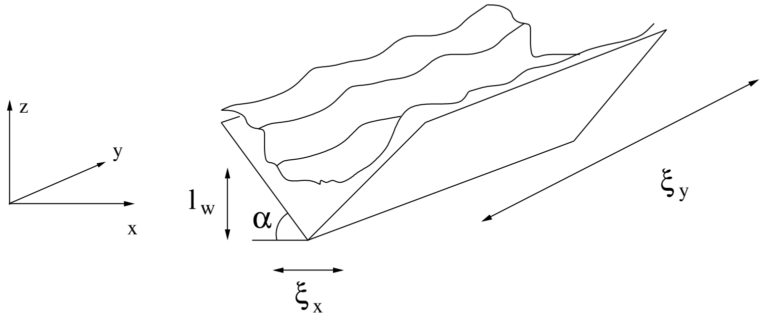
Paradox

Why does a better, more rigorous model gives contradictory results?

Next...

1. Historical Background
   - Phenomenology of Wetting
   - 3D Wetting Transitions
   - The Nonlocal Model
2. A Closer Look at the Nonlocal Model
   - A New Lengthscale
   - Derivation of the Nonlocal Model

Wedge Filling



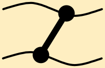
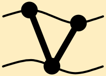
- Standard interfacial model gives wrong results for acute wedges.
- Need to develop interfacial Hamiltonian for nonplanar surfaces.

Definition of the Nonlocal Model

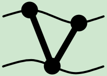
The Nonlocal Model

$$H_{\mathrm{NL}} = \Sigma A + W[\ell, \psi]$$

with

$W[\ell, \psi] = a$  $+\, b$ 

Diagrammatic representation

 $\equiv \int \mathrm{d}\vec{s}_\psi \left[\int \mathrm{d}\vec{s}_\ell \; K(|\vec{r}_\psi - \vec{r}_\ell|) \right]^2$

Implications of the Nonlocal Model

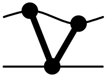
- Recovers Fisher-Jin model for planar wall and small-gradient limit.
- Better agreement with Ising Model simulations (why?).
- Consistent results for wedge filling.
- General framework for wetting on nonplanar substrates.
- Agrees with exact results for wetting on spheres and cylinders.
- Satisfies exact sum-rule at complete wetting.

Next...

1 Historical Background
- Phenomenology of Wetting
- 3D Wetting Transitions
- The Nonlocal Model

2 A Closer Look at the Nonlocal Model
- A New Lengthscale
- Derivation of the Nonlocal Model

A New Lengthscale


$$\approx \iint \mathrm{d}\vec{s}_1 \, \mathrm{d}\vec{s}_2 \, \mathrm{e}^{-2\kappa\bar{\ell}} S(x_{12};\bar{\ell})$$

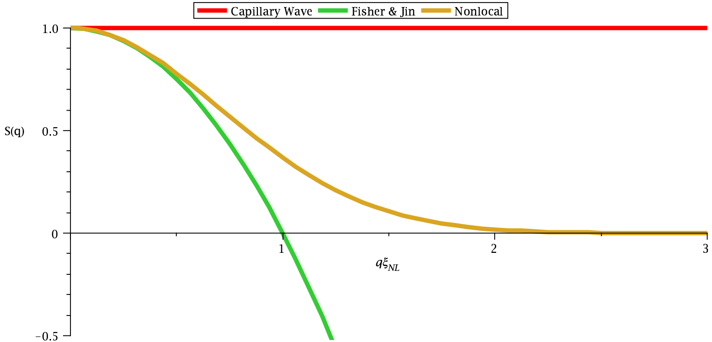
with

$$S(x_{12};\bar{\ell}) = \frac{\mathrm{e}^{-x_{12}^2/4\xi_{\mathrm{NL}}^2}}{4\pi\xi_{\mathrm{NL}}^2} \; ; \quad \bar{\ell} = \frac{\ell_1 + \ell_2}{2}$$

New Lengthscale

$$\xi_{\mathrm{NL}} = \sqrt{\frac{\bar{\ell}}{\kappa}}$$

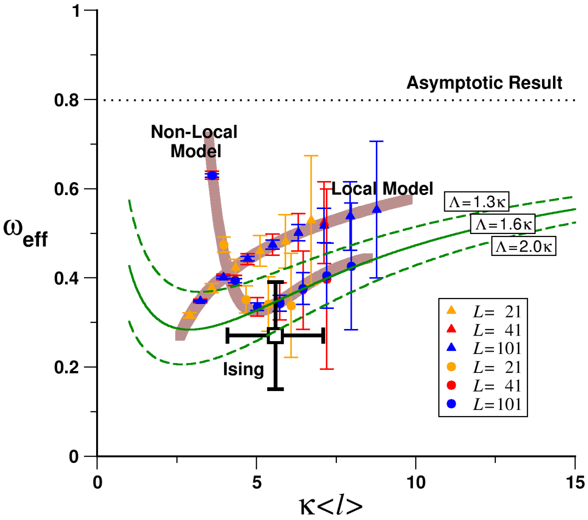
Influence of the New Lengthscale



Importance of the New Lengthscale

- ξ_{NL} acts as an effective short-wavelength cutoff.
- Repulsion weaker than original model.
- Less fluctuations, smaller critical regime.
- ξ_{NL} also present in the Landau-Ginzburg-Wilson model.
- ξ_{NL} essential for consistency with exact sum rule.
- Effects interpreted as effective ω.

Comparison With Simulations



Next...

1. Historical Background
   - Phenomenology of Wetting
   - 3D Wetting Transitions
   - The Nonlocal Model
2. A Closer Look at the Nonlocal Model
   - A New Lengthscale
   - Derivation of the Nonlocal Model

Derivation of the Nonlocal Model

Recipe of Fisher & Jin

1. Choose interfacial configuration.
2. Calculate mean-field density profile (non-perturbatively for Nonlocal Model).
3. Insert density profile in LGW model.
4. Result is the Interfacial Model.

Summary

- Short-range wetting transitions are difficult because we are at the upper critical dimension.
- A proper derivation of the interfacial Hamiltonian reveals a nonlocal interaction.
- There is a new lengthscale in the Nonlocal Model that explains the results of the simulations.
- The new lengthscale is essential for the thermodynamic consistency of the model.

Thanks to

Work done with

- Andy Parry (PhD Supervisor),
  Imperial College London, UK.
- Carlos Rascón,
  Universidad Carlos III, Madrid, Spain.
- José Manuel Romero-Enrique,
  Universidad de Sevilla, Sevilla, Spain.

Movie provided by

- Oleg Vasilyev,
  MPI Stuttgart, Germany

Is the Nonlocal Model the last episode
or
is a new twist just around the corner?

Don't miss the next episode of:
"The Wetting Soap Opera"

Thank you.

Is the Nonlocal Model the last episode
or
is a new twist just around the corner?

Don't miss the next episode of:
"The Wetting Soap Opera"

Thank you.

To Know More

A. O. Parry, C. Rascón, N. R. Bernardino and J. M. Romero-Enrique,
Derivation of a non-local interfacial Hamiltonian for short-ranged wetting I: Double-Parabola approximation,
Journal of Physics: Condensed Matter, **18**, 6433 (2006).

A. O. Parry, C. Rascón, N. R. Bernardino and J. M. Romero-Enrique,
3D short-ranged wetting and nonlocality,
Physical Review Letters, **100**, 136105 (2008).