Wetting in a Nutshell

Interfacial Phase Transitions in Planar and Non-Planar Geometries

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A O Parry, C Rascon, N R Bernardino, J M Romero-Enrique,
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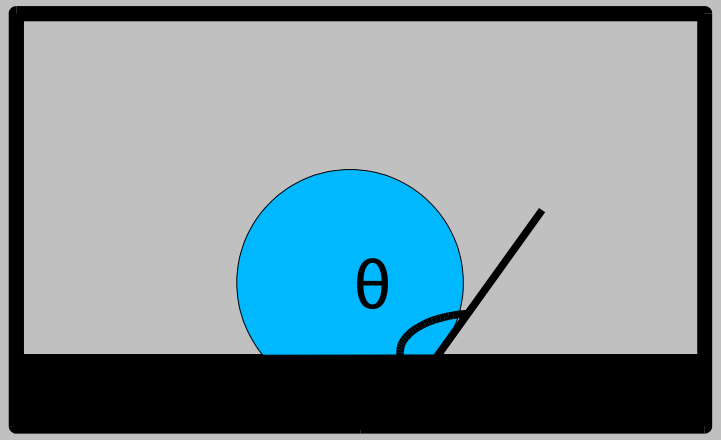
Outlook

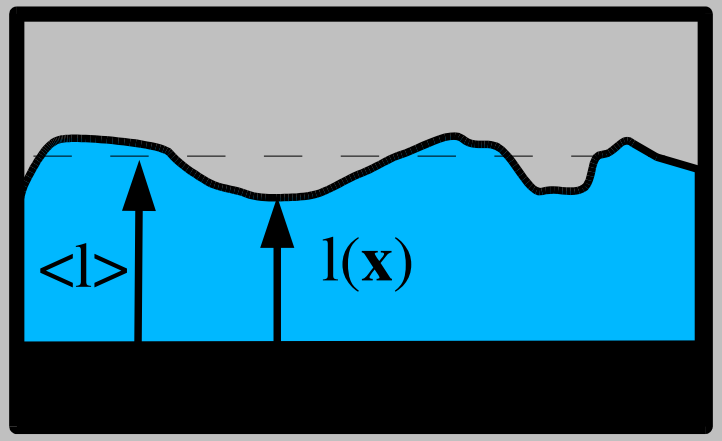
- Basic Concepts of Wetting
- Review of Critical Phenomena
- Interfacial Model (Ad Hoc Version)
- Interfacial Model Revisited (Systematic)
- Interfacial Model Revisited (Again!!!)
- New Results and Their Meaning

Wetting

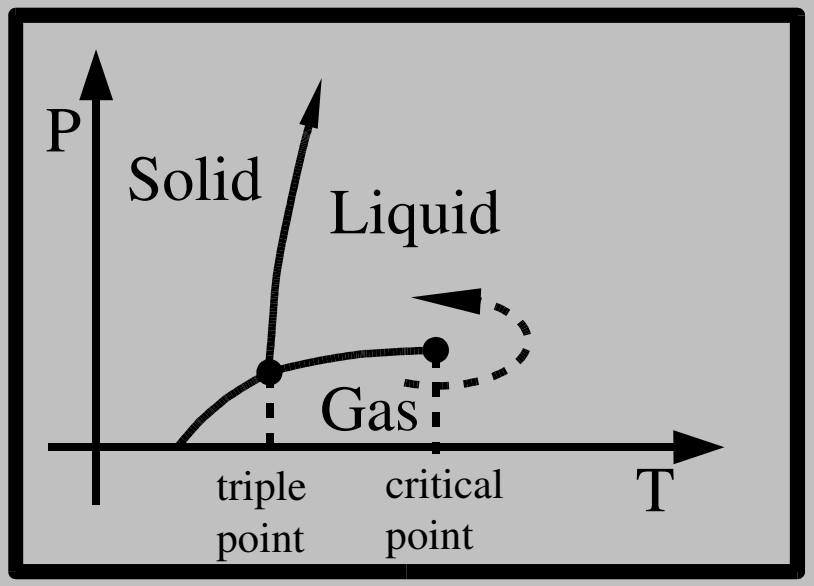
- Interfacial phase transition
- Contact angle goes to zero
- Mean interfacial height goes to infinity

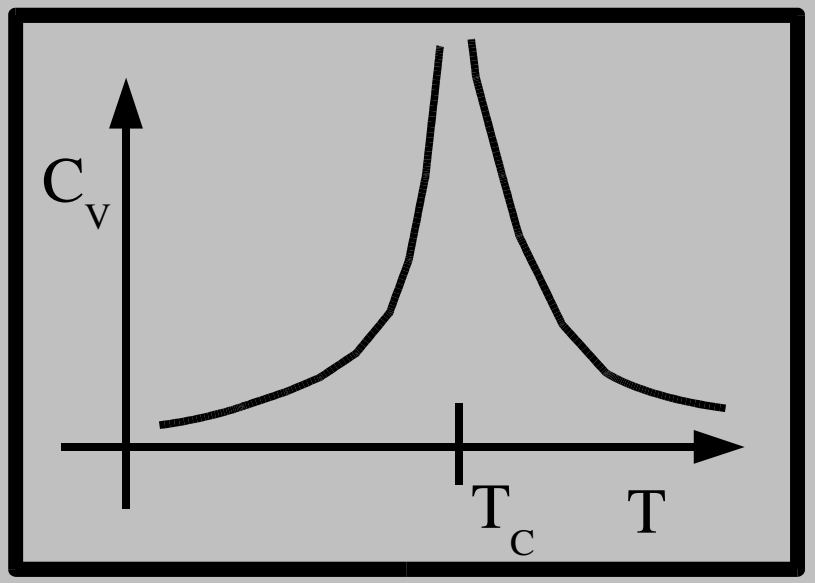


In the grand-canonical ensemble:



Critical Phenomena





- Free-energy is non-analytic
- Fluctuations are HUGE!!!
- Power-law singularities described by a set of critical exponents, e.g. $C_V \sim |T - T_C|^{-\alpha}$

Landau-Ginzburg-Wilson Theory I

- Model:

$$H_{LGW} = \int d\boldsymbol{r} \left[\frac{(\nabla m(\boldsymbol{r}))^2}{2} + \Phi(m(\boldsymbol{r})) \right]$$

$$\Phi(m) = -t\frac{m^2}{2} + u\frac{m^4}{4} \quad \text{or} \quad \Phi^{DP}(m) = \frac{k^2}{2}(|m| - m_0)^2$$

- Statistical Physics:

$$Z = \int D_m e^{-\beta H}$$

- Thermodynamics:

$$F = -k_B T \ln Z$$

Landau-Ginzburg-Wilson Theory II

- Mean-Field Theory (MF) = Minimize H_{LGW}
  - Wrong critical exponents
  - Underestimates fluctuations
  - OK (usually) far from critical point

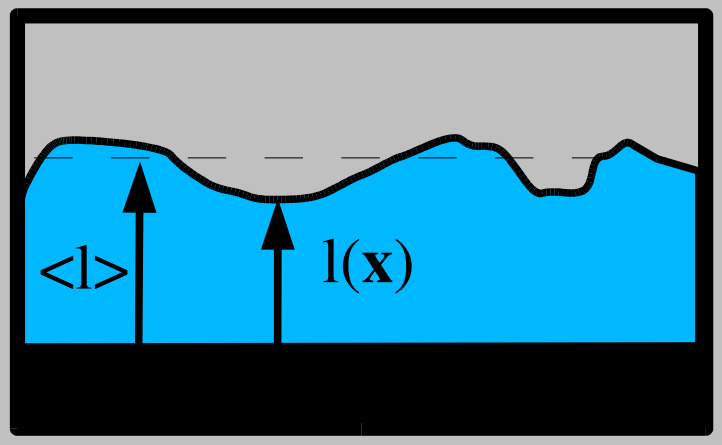
- Renormalization Group Theory (RG)
  - Accounts correctly for fluctuations
  - **Universality**!!!
  - Predicts MF is correct for $d>d_c$ (**upper critical dimension**)

Interfacial Model

- LGW model is too difficult - translational invariance broken.

- Phenomenological theory: focus on interface, described as stretched membrane.

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



$$W(l) = -a e^{-kl} + b e^{-2kl}$$

Interfacial Model II

- Upper Critical Dimension = 3
- RG predicts non-universal (detail dependent) results in *3D* (Brezin *et al*, 1983)

Simulations of Interfacial model agree with RG (Gompper & Kroll, 1988)

Simulations of LGW model agree with MF (Binder *et al*, 1986)

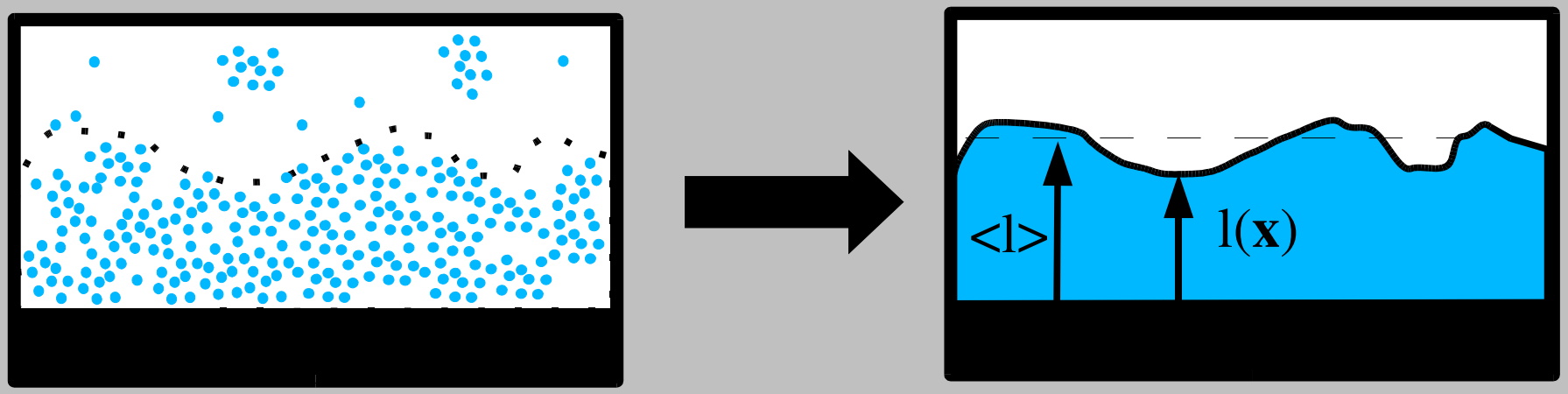
Something is **wrong** with the **details** of the interfacial model!!!

Interfacial Model III

- Exact statistical mechanics results (Sum Rules) are not satisfied by the interfacial model.
- Sum Rules imply a position dependent stiffness, $\sum(l)$.
- The expression for the potential, $W(l)$ is pretty much an educated guess.
- Non-physical results for non-planar substrates (e.g. parabola or wedge)

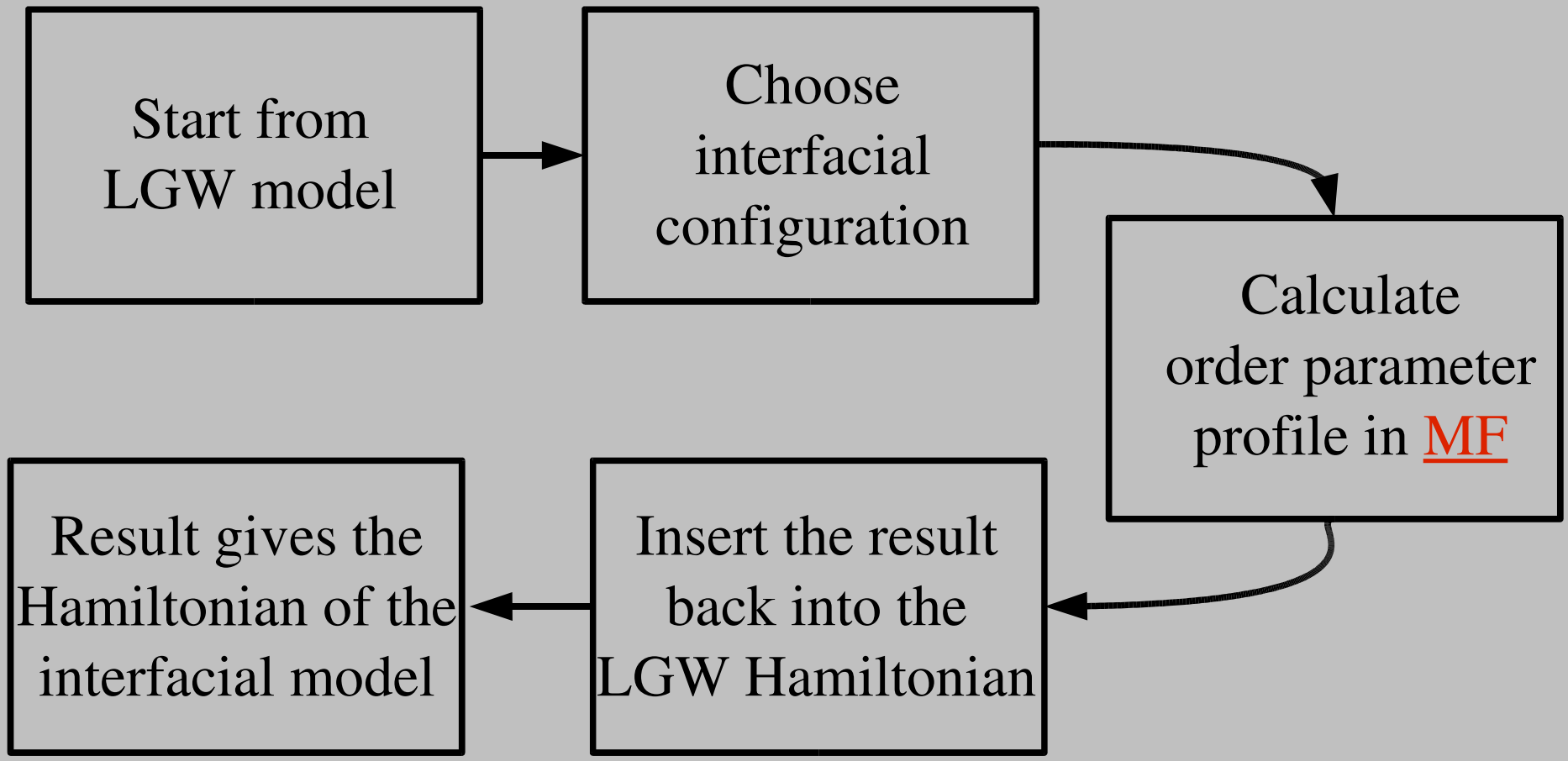
Interfacial Model Revisited (a la Fisher and Jin)

- How to derive the interfacial model from the LGW model?



"Integrate out" irrelevant details.
(Fisher & Jin, 1992)

Systematic Definition of the Interfacial Model I



Systematic Definition of the Interfacial Model II

- Functional minimization of H_{LGW} (with specified interface) leads to:

$$\nabla^2 m_\Xi = k^2 (m_\Xi \pm m_0)$$

with boundary conditions:

$$m_\Xi(\infty) = -m_0 \qquad m_\Xi(l) = 0 \qquad m_\Xi(\Psi) = m_1$$

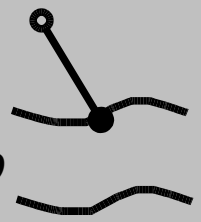
Results of Fisher and Jin

- F J get perturbative solution for small fluctuations around the planar interface.
- Position dependent stiffness, $\Sigma(l)$.

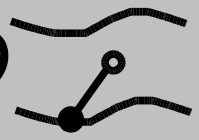
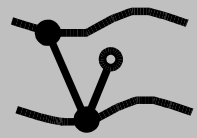
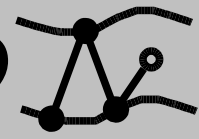
But...

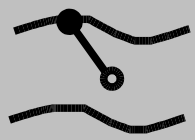
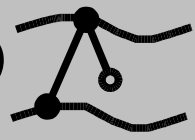
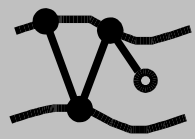
- RG results show that fluctuations change the order of the transition (no sign of this in the simulations).
- No physical explanation for the l dependence of $\Sigma(l)$ or $W(l)$.
- Again, non-physical results for wedge.

Solving the Helmholtz Equation

$m_{\Xi} = -m_0 + m_0$  ; above the interface

$m_{\Xi} = m_0$

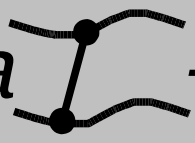
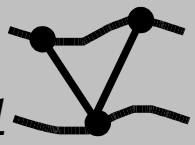
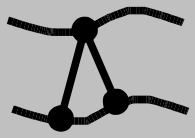
$+ (m_1 - m_0)$  $+ m_0$  $+ (m_1 - m_0)$  $+ \cdots$

$- m_0$  $- (m_1 - m_0)$  $- m_0$  $- \cdots$

; below the interface

The Result and its Meaning

- Replacing back in the LGW Hamiltonian:

$$W[l,\Psi] = a$$  $$+ b_1$$  $$+ b_2$$  $$+ \cdots$$

- **Nonlocal** (Important Physics)
- Obeys exact statistical mechanical results (sum rules)
- Can be interpreted as interactions due to tube-like fluctuations (Kadanoff-Wu anomaly of 2D Ising model).

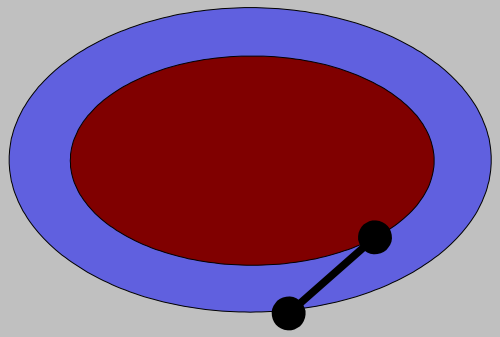
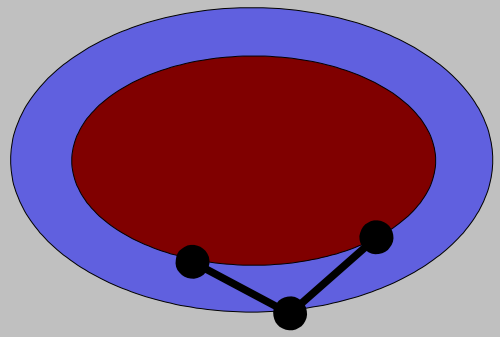
Brave New World!!!

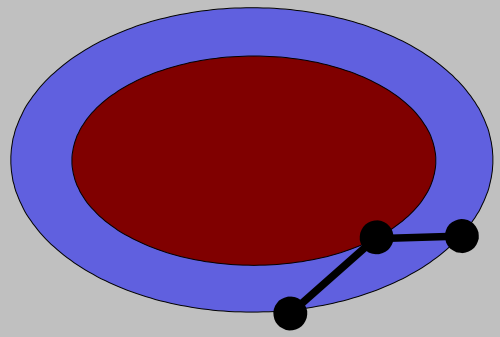
- Renormalization results are same as standard model but critical region is too small – only MF will be observed.
- Non-ambiguous framework to study wetting in non-planar substrates.
- Easy to generalize the formalism:
  - Perturbation theory
  - Surface field
  - Tricritical wetting
  - Arbitrary bulk field

Take Home Message

- At the upper critical dimension proceed with caution.
- The standard interfacial model is too simplistic and an intermediate level of description is needed.
- Careful derivation of the interfacial model uncovers important physical effects: **nonlocal** model.
- The nonlocal model allows us to do **wetting in curved substrates**, among other things...

How to do Wetting in a Nutshell?

$W = a_1$  $+ b_1$ 

$+ b_2$  $+ \cdots$

Done With

- Andy Parry (Imperial)
- Laura Morgan (Imperial)
- Carlos Rascon (Madrid)
- Jose Manuel Romero-Enrique (Sevilla)

"Problems worthy of attack prove their worth by fighting back."

Piet Hein (1905–1996)

Thank you for listening