Classical Density Functional Theory for Intergranular Films

Gunnar Pruessner   Adrian Sutton

Department of Physics
Imperial College London

INCEMS Meeting, Stuttgart, March 2006

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Outline

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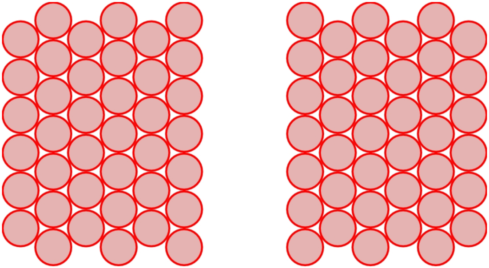
Model



- Two confining lattices (3D)
- Interface: liquid layer in between
- Reservoir: chemical potential μ

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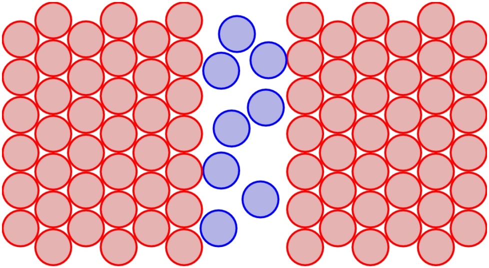

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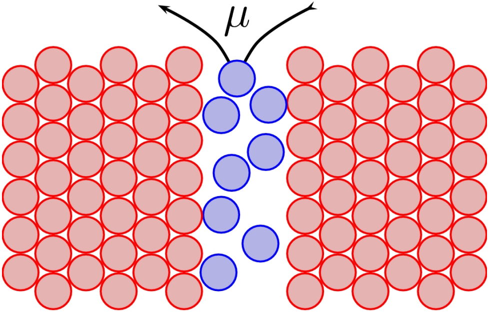

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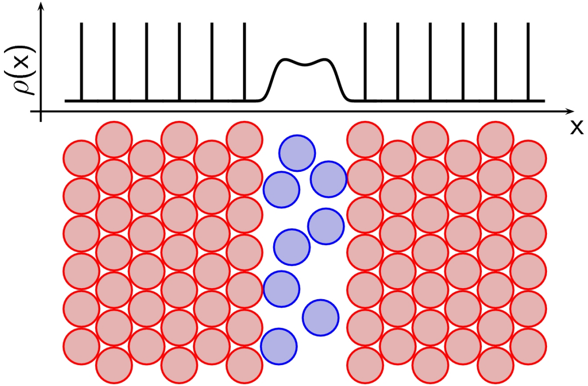
Observables and Parameters



- Key observables
  - Density profile $\rho(\vec{x})$
  - Thermodynamic properties (grand potential, steric forces, pressure. . .)

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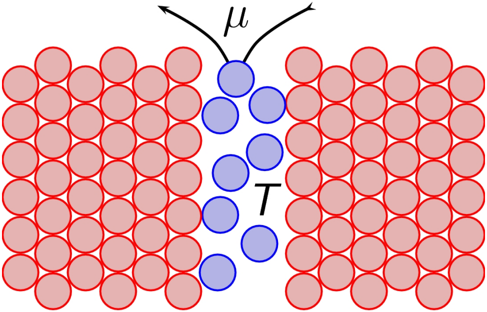
Observables and Parameters



- Key observables: Density profile, potentials, pressure ...
- Parameters
  - temperature, chemical potential, ...
  - relative lattice orientation: gap, tilt, twist

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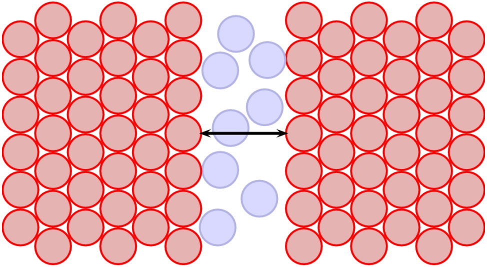

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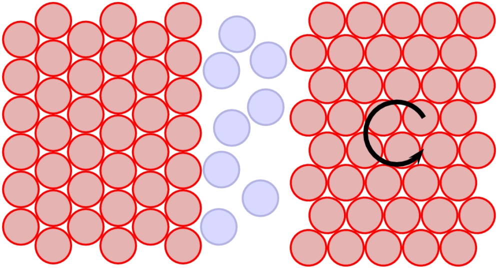

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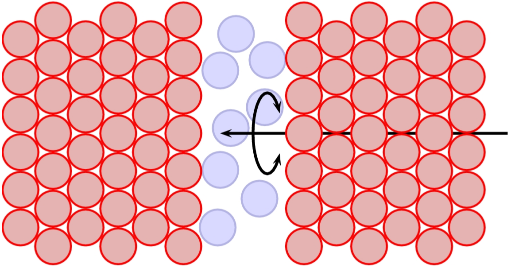

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The principles of Classical Density Functional Theory

Classical Density Functional Theory

- The **dimensionless, local potential** $u(\vec{x}) = \beta(\mu - U(\vec{x}))$ is a **unique functional** of the density $\rho(\vec{x})$.
- **Minimise the functional**

$$\widetilde{W}([u],[\widetilde{\rho}]) = F([\widetilde{\rho}]) - \int d^d x\, u(\vec{x})\widetilde{\rho}(\vec{x})$$

- Find $\widetilde{\rho}_0$ that satisfies

$$\left.\frac{\delta}{\delta\widetilde{\rho}}\right|_{\widetilde{\rho}\equiv\widetilde{\rho}_0} \widetilde{W}([u],[\widetilde{\rho}]) \equiv 0$$

- At minimum: $\widetilde{W}\left([u],[\widetilde{\rho}=\widetilde{\rho}_0]\right) = W([u])$, the **grand potential**

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The rôle of the effective potential

Rôle of the effective potential $C(\vec{x})$

- **Effective potential** $C(\vec{x})$: Difference between ideal potential $\ln(\Lambda\rho(\vec{x}))$ and local potential $u(\vec{x})$
- **Standard approximation**:
  Expand $C(\vec{x})$ in functional Taylor series
- **Perturbation theory** about the infinite, uniform liquid
- All interaction within the liquid enters solely through $C(\vec{x})$
  $\rightarrow$**Direct correlation function**
- Test beds of increasing complexity:
  Hard rods, hard spheres, Silicon

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1. Motivation – Model, Observables, Parameters
   - Model
   - Observables and Parameters

2. Classical Density Functional Theory
   - Principles
   - An Example
   - From DFT to Phase Field Models

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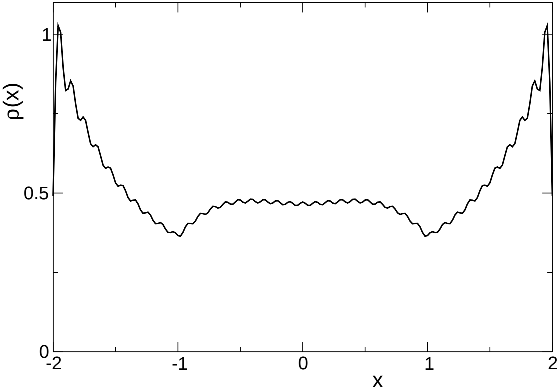
DFT calculation for a confined 1D liquid

with S. Dungey and N. Gnanathas



Density profile for $L = 4$, $\rho_0 = 0.46$

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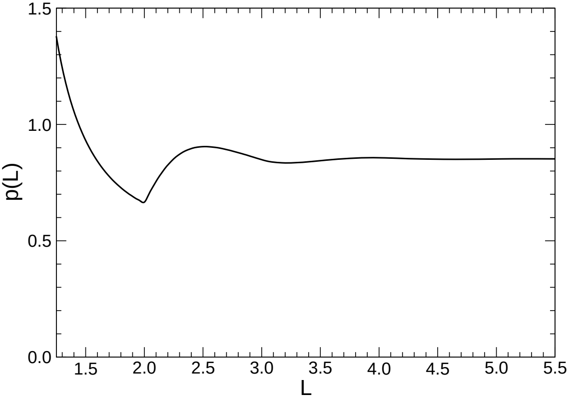

Pressure as a function of wall separation

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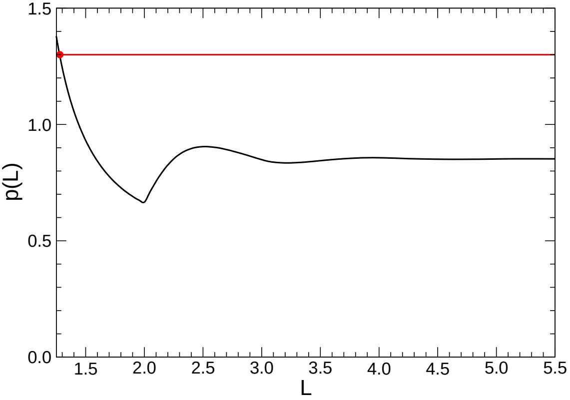

Equilibrium width due to external walls

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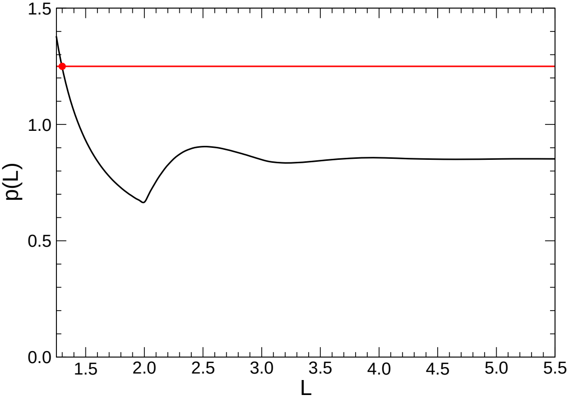

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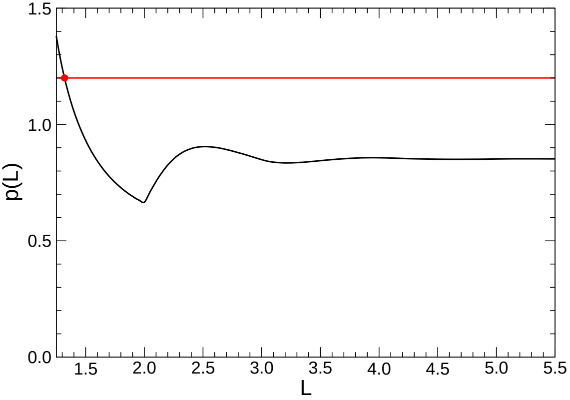

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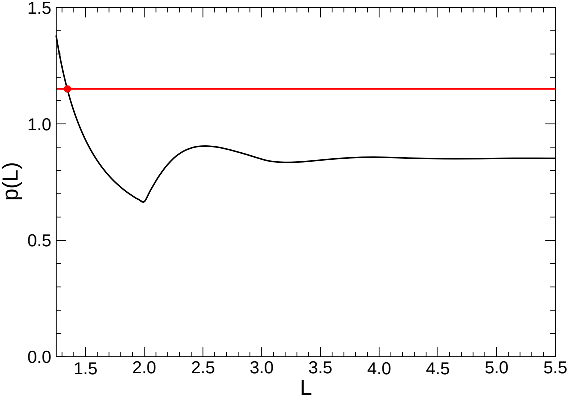

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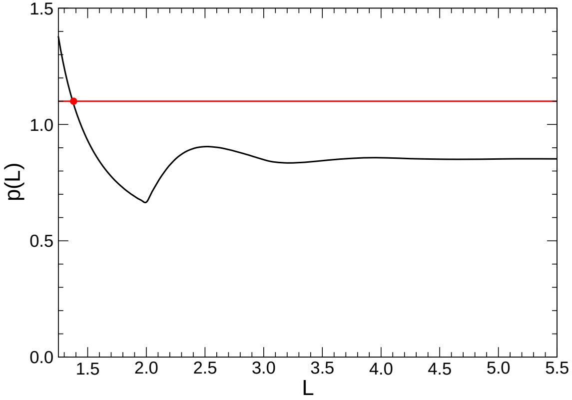

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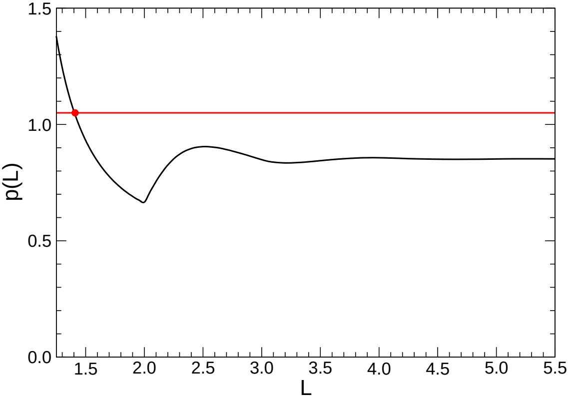

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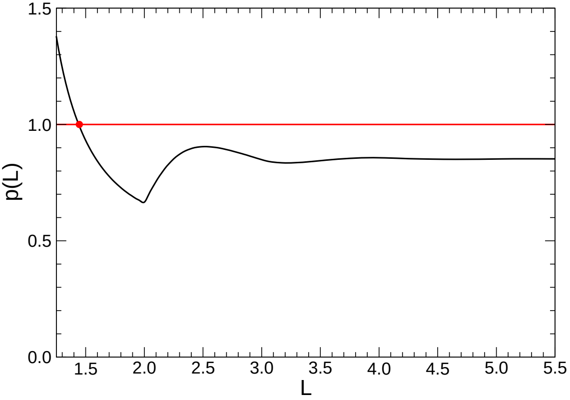

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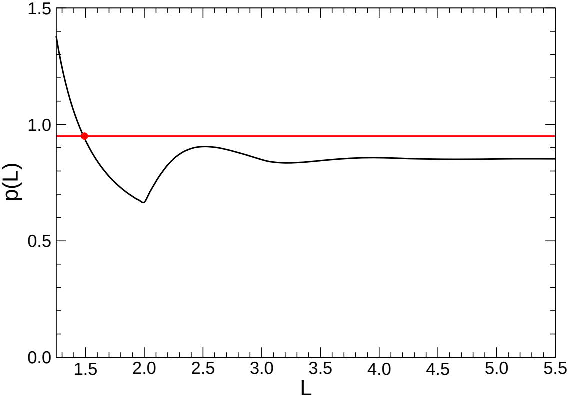

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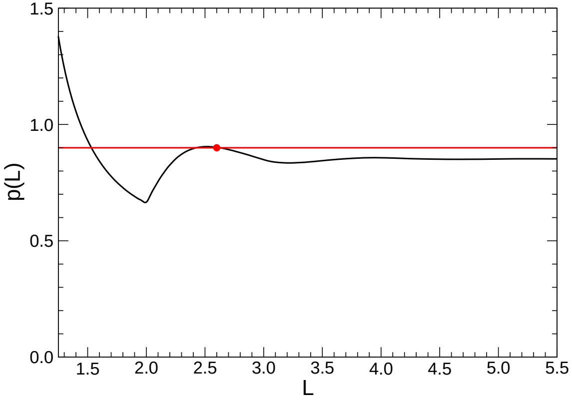

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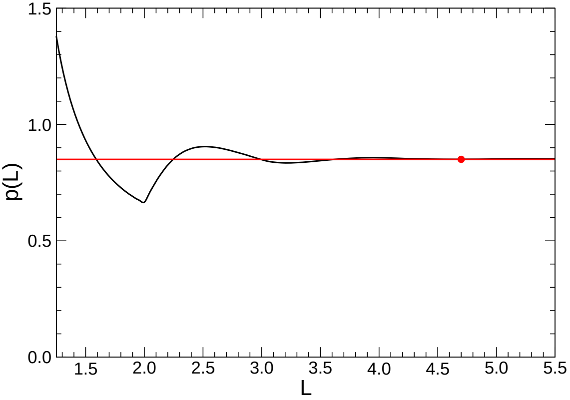

Equilibrium width due to external walls

Outline

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Phase Field Models

Features of Phase Field Models

- Study dynamical and equilibrium properties of phase boundaries
- Avoid boundary problems and no-overhang approximation
- Phase field $\phi(\vec{x})$ describes “degree of liquid-ness”
- Provides equation of motion for phase changes and their interfaces
- Problem: Functional *ad hoc*, physical meaning of ϕ unclear

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Phase Field Model from DFT

Based on (Haymet and Oxtoby 1981, Oxtoby and Haymet 1982)

- **Standard method**: Write density ρ as a Fourier sum,

$$\rho(\vec{x}) = \rho_0 \left(1 + \eta + \sum_{\{\vec{k}\}} \mu_k e^{i\vec{k}\vec{x}}\right)$$

- Characterise liquid/solid by **spatially varying coefficients** $\mu_{\vec{k}}(\vec{x})$
- Oxtoby and Haymet:
  Find solution of **integro-differential equation**
- Alternatively, **minimise** with respect to $\widetilde{\eta}$ and $\widetilde{\mu}_k$

$$\widetilde{W} = \int d^d x\, f(\widetilde{\eta}, \widetilde{\mu}_n) + \frac{1}{4} c_0'' \left(\vec{\nabla}\widetilde{\eta}\right)^2 + \frac{1}{4} \sum_{\{\vec{k}\}} c_k'' \left(\hat{\vec{k}}\vec{\nabla}\widetilde{\mu}_k\right)^2 - u\widetilde{\rho}$$

- $\widetilde{\mu}_k(\vec{x})$ **is a phase field!** — Resulting **equation of motion**

$$\dot{\widetilde{\mu}}_k = -\frac{\delta}{\delta \widetilde{\mu}_k} \widetilde{W}$$

is a **phase field model** . . . animation

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