# What can and cannot be done with classical DFT at interfaces?

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# Outline


1. Introduction
   - Model
   - Observables and Parameters
   - Classical DFT
   - Relation to phase field modelling
2. Applying DFT to Intergranular Films
   - Parametrisation
   - Technical limitations
   - Summary: Doable and not doable


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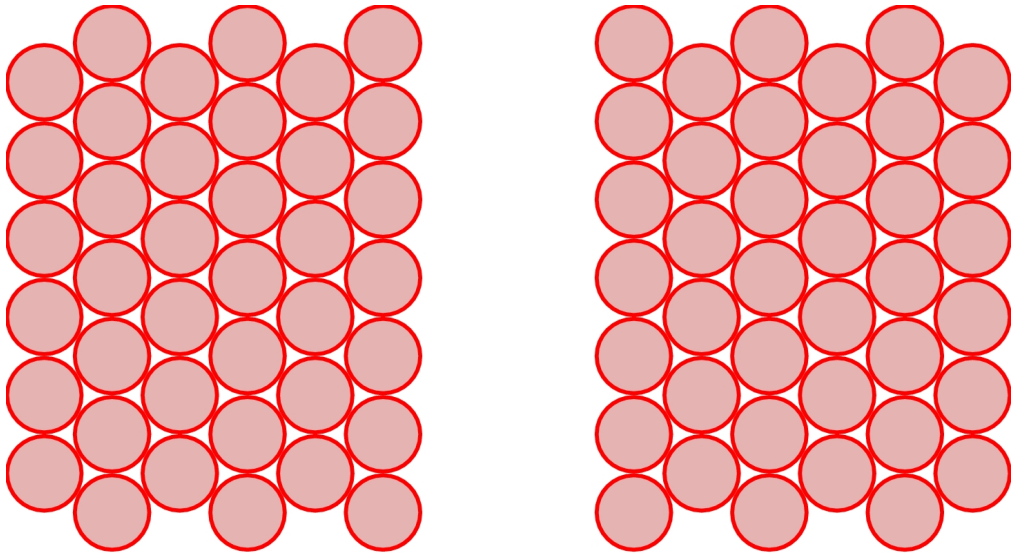
# Model



- Two confining lattices
- Interface: freely rearranging, "liquid" layer in between
- Reservoir: chemical potential $\mu$

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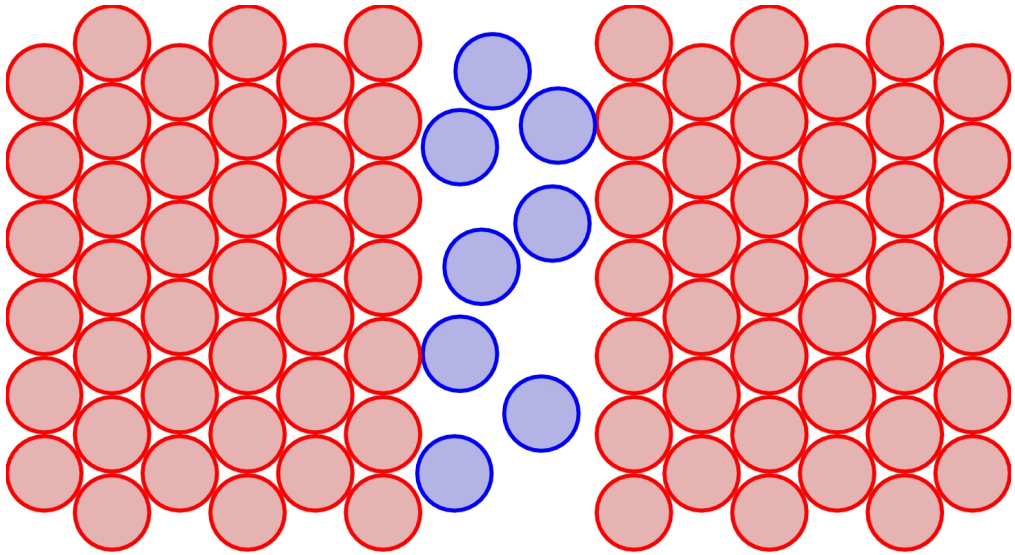

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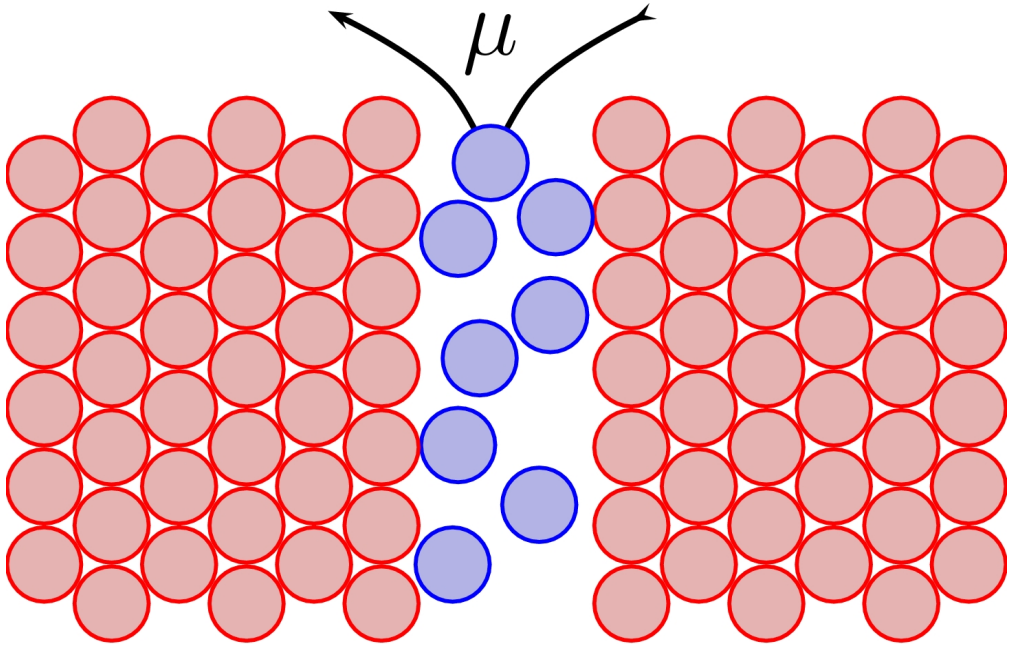


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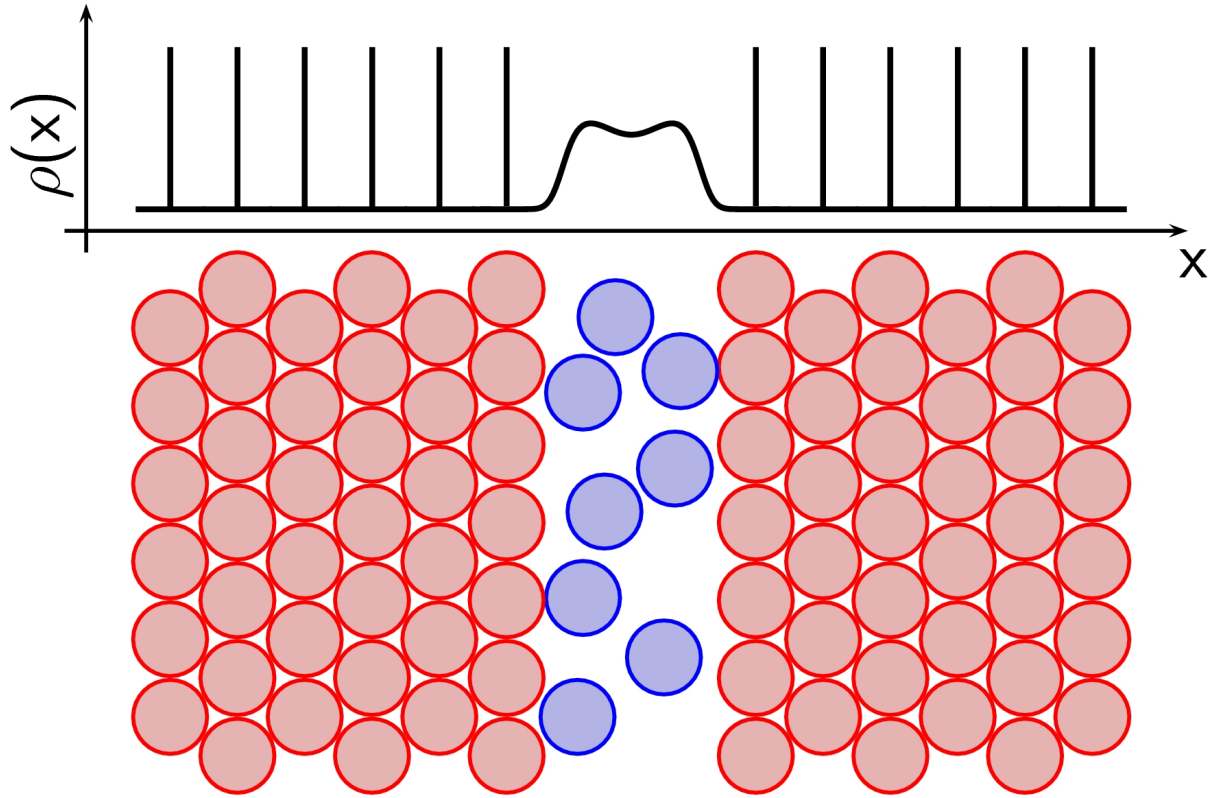


- Key observables
  - Density profile $\rho(\vec{x})$
  - Thermodynamic properties (grand potential, steric forces, pressure...)

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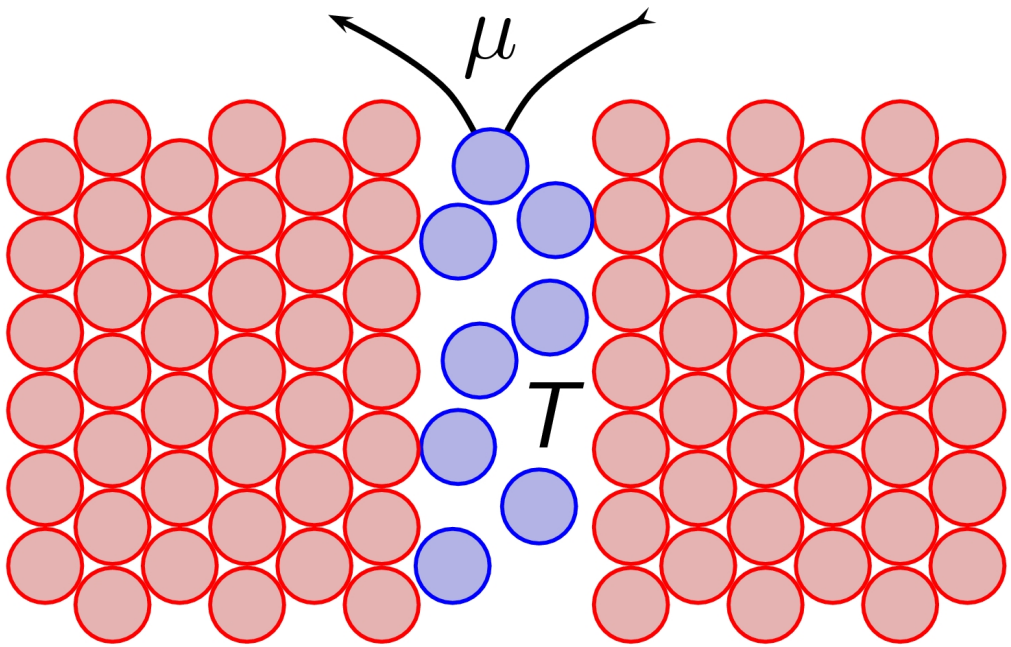


- Key observables: Density profile, potentials, pressure ...
- Parameters
  - temperature, chemical potential, ...
  - relative lattice orientation: gap (phase), tilt, twist

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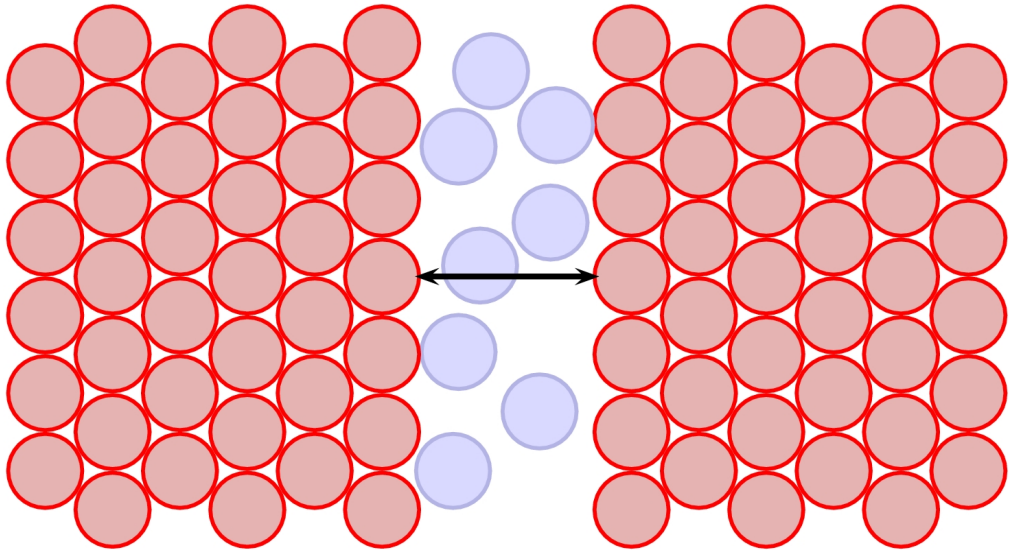

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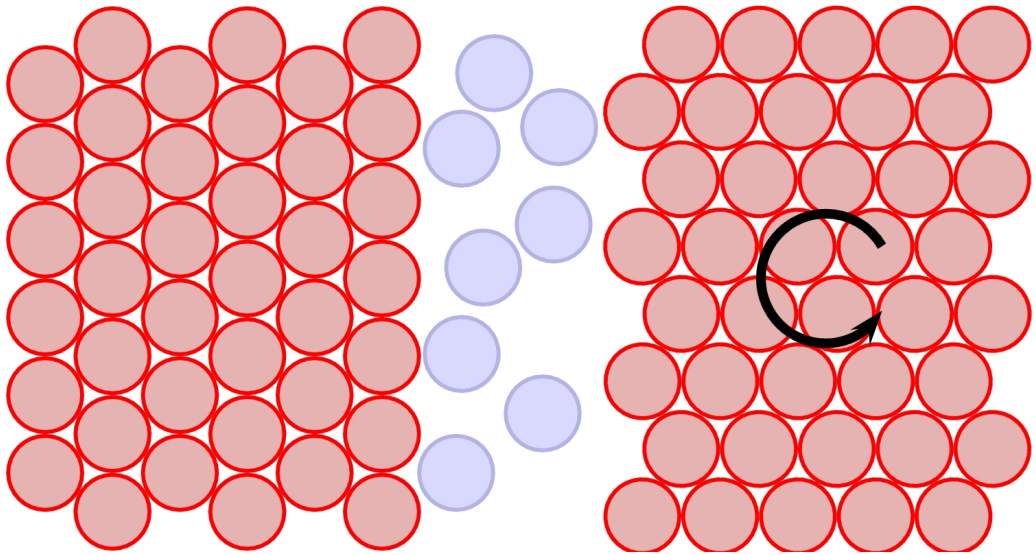

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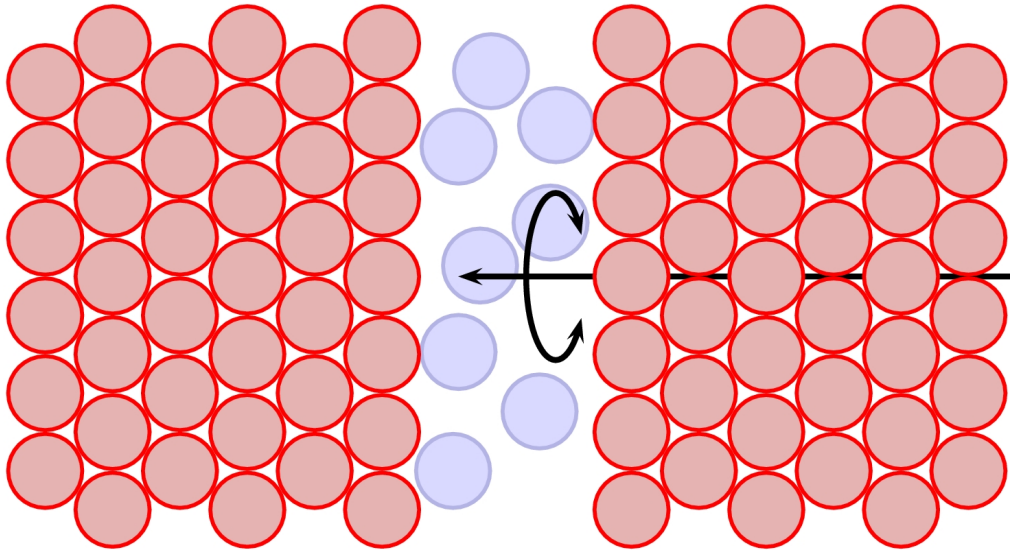

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# The principles of Classical Density Functional Theory

Haymet and Oxtoby, 1981 and 1982

## **Classical** Density Functional Theory

- Functional Taylor series of effective one particle potential of complicated liquid over reference (bulk) system

$$\ln\left(\frac{\rho(\mathbf{r})}{\rho_0}\right) = \int d^d r' \; C^{(2)}(\mathbf{r}' - \mathbf{r})(\rho(\mathbf{r}') - \rho_0)$$

  using direct correlation function $C^{(2)}(\mathbf{r})$
- To be solved with certain boundary conditions.
- Reparametrise $\rho(\mathbf{r})$:

$$\rho(\mathbf{r}) = \rho_0 \left(1 + \sum_n \mu_n(\mathbf{r}) e^{\imath \mathbf{k}_n \mathbf{r}}\right)$$

Separation of length scales.

# The principles of Classical Density Functional Theory

Haymet and Oxtoby, 1981 and 1982

## **Classical** Density Functional Theory

- Expand $\mu_n(\mathbf{r}')$ about $\mathbf{r}' = \mathbf{r}$ and use Fourier coefficients of $C^{(2)}$:

$$\ln\left(1 + \sum_n \mu_n(\mathbf{r}) e^{\imath \mathbf{k}_n \mathbf{r}}\right) = \sum_n e^{\imath \mathbf{k}_n \mathbf{r}} V'' \rho_0 \left(c_n \mu_n(\mathbf{r}) - \imath \nabla c_n \nabla \mu_n(\mathbf{r}) - \ldots\right)$$

- Problem: All $\mu_n$ on both sides, need to decouple
- Idea: Demand for all $\widetilde{\mathbf{r}}$:

$$\ln\left(1 + \sum_n \mu_n(\widetilde{\mathbf{r}}) e^{\imath \mathbf{k}_n \mathbf{r}}\right) = \sum_n e^{\imath \mathbf{k}_n \mathbf{r}} V'' \rho_0 \left(c_n \mu_n(\widetilde{\mathbf{r}}) - \imath \nabla c_n \nabla \mu_n(\widetilde{\mathbf{r}}) - \ldots\right)$$

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# The principles of Classical Density Functional Theory

Haymet and Oxtoby, 1981 and 1982

## **Classical** Density Functional Theory

- Now Fourier transform

$$V^{-1}\int d^d r\; e^{-\imath \mathbf{k}_m \mathbf{r}} \ln\left(1+\sum_n \mu_n(\widetilde{\mathbf{r}})e^{\imath \mathbf{k}_n \mathbf{r}}\right) =$$

$$V''\rho_0\left(c_m\mu_m(\widetilde{\mathbf{r}}) - \imath\nabla c_m \nabla\mu_m(\widetilde{\mathbf{r}}) - \ldots\right)$$

- Surprise: Equivalent to Allen-Cahn phase field model.

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# Phase field modelling derived from DFT

## Recipe

- Start with (and keep it) the full grand potential in terms of $\rho(\mathbf{r})$
- Reparametrise and expand (functionally and in space)
- Simplify: Within a unit cell $\mu_n(\mathbf{r})$ is nearly constant
  Separation of length scales
- Results in Allen-Cahn phase field model:

$$\mathcal{W} = \int_\Omega d^d r \; f(\phi(\mathbf{r})) - \frac{\epsilon^2}{2}\phi(\mathbf{r})\nabla^2\phi(\mathbf{r})$$

non-conserved order parameter
Kobayashi, Warren, Carter (2000) [with orientation field integrated out]

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# What does the parametrisation mean physically?

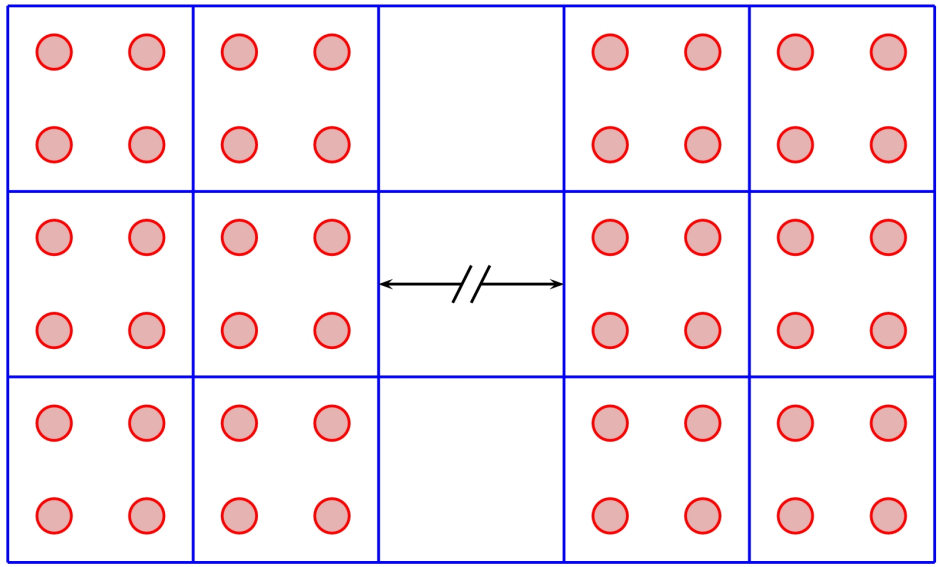
Density profile: $\rho(\mathbf{r}) = \rho_0 \left(1 + \sum_n \mu_n(\mathbf{r}) e^{\imath \mathbf{k}_n \mathbf{r}}\right)$

Boundary Conditions: Fix $\mu_n(\mathbf{r})$ on the far left and the far right.

Shift/Gap: No problem!

What if orientations are different on both sides?

Change Fourier domain!



Possible if $\Sigma$ boundary; Feasible if small enough ($\rightarrow$ number of coefficients).

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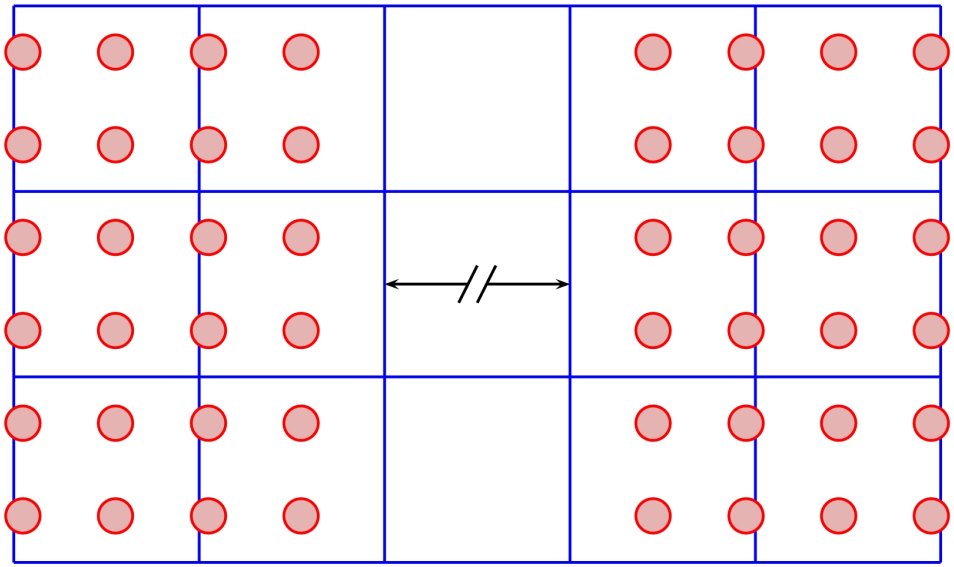

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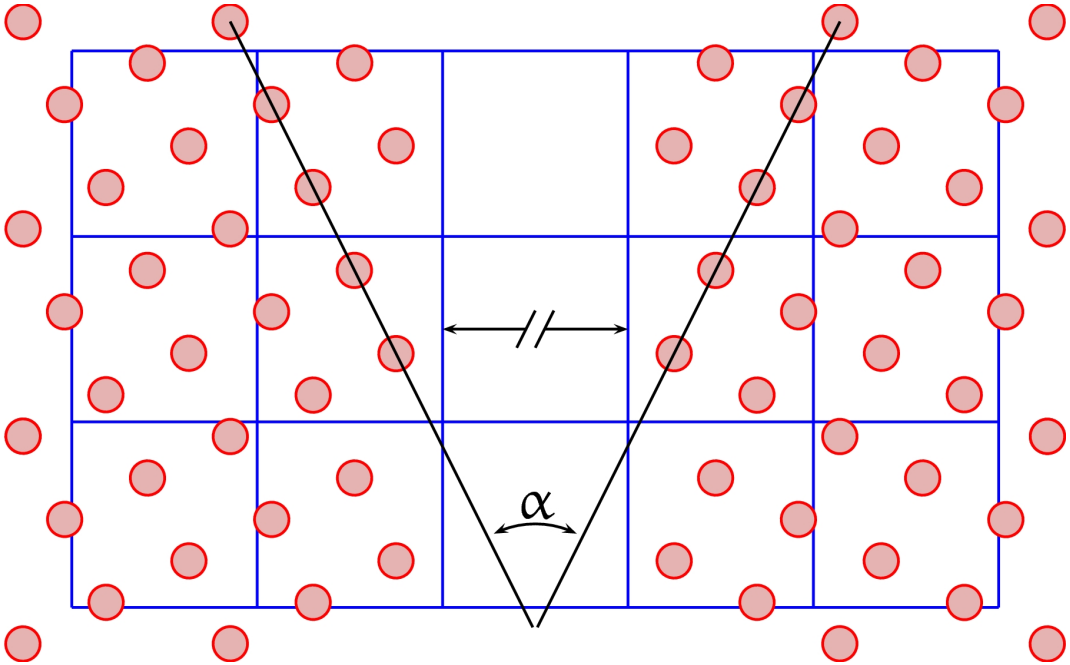


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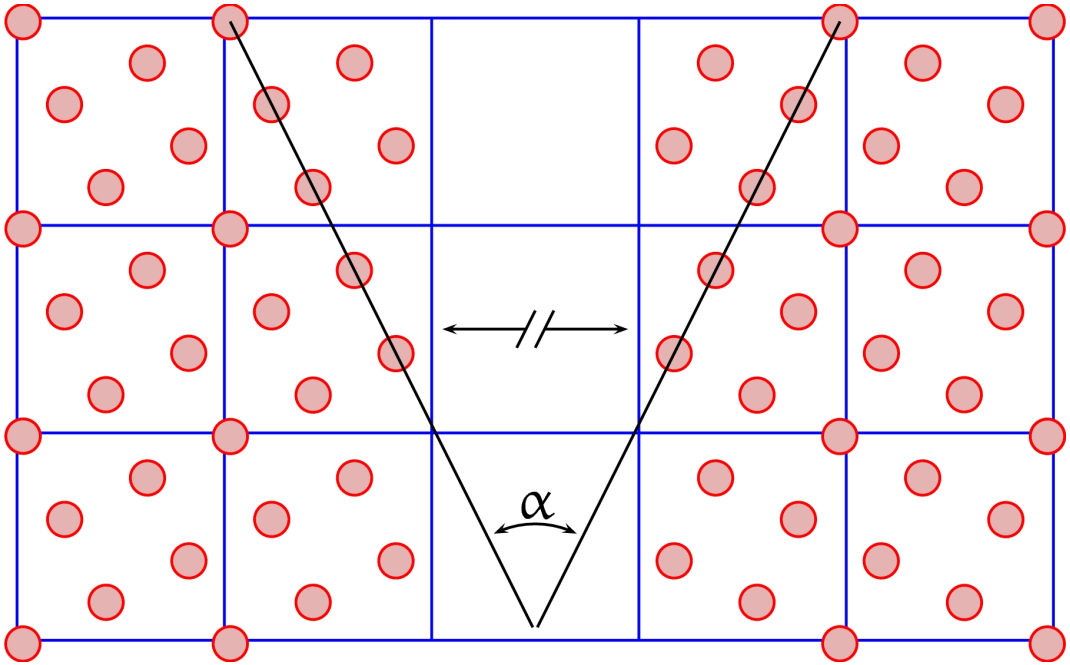


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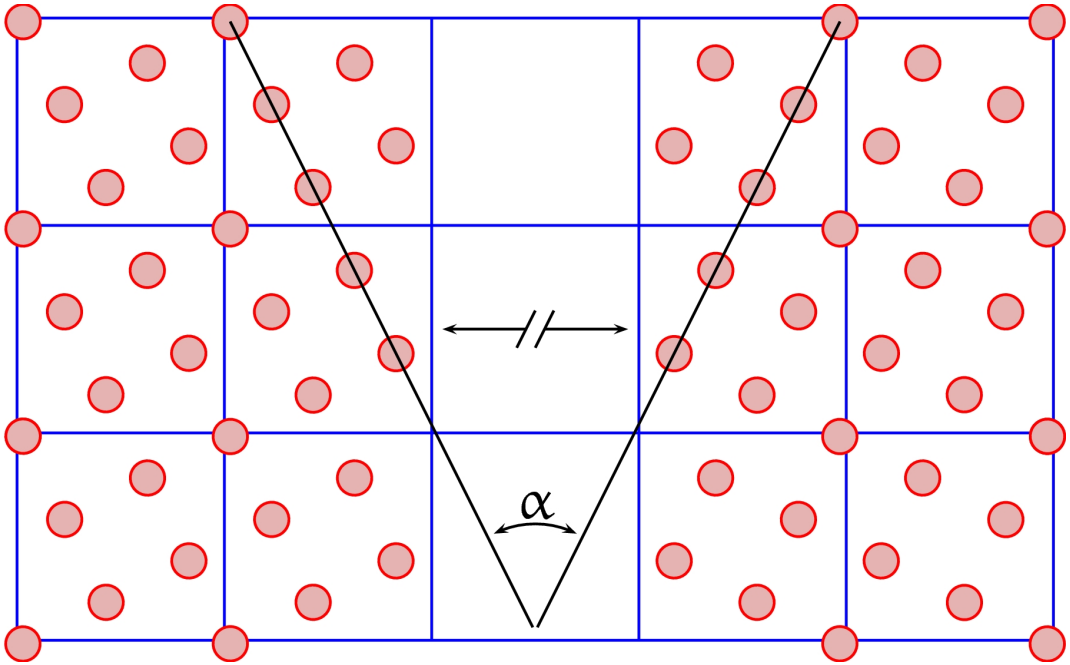


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# What are the technical obstacles?

Key obstacles:

- Can only cope with one Fourier domain (practically excludes different crystal structures).
- Need to have stable solid phases (an issue in itself), *i.e.* $\mu_n$ of the solid phase must be a solution of

$$\int d^d r \; e^{\imath \mathbf{k}_m \mathbf{r}} \ln\left(1 + \sum_n \mu_n e^{\imath \mathbf{k}_n \mathbf{r}}\right) = V'' \rho_0 c_m \mu_m$$

- Numerical convergence during root-finding
- Complicated geometry, *i.e.* setup
- Improving expansion systematically ($C^{(3)}$, $\nabla^3$, higher modes) is possible but might ruin convergence.

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# Results so far

- Clear mathematical foundation of the theory
- Appropriate parametrisation for grain boundaries ($\Sigma$ only, twist and tilt)
- Grand potential functional to be globally minimised (std. minimisation methods)
- Relation to phase field modelling (observables, parameters, limitations; publication in preparation [contribution to D3.2])
- Implementation for gaps (not yet convergent)

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# Doable

- Complete theory for Σ boundaries
  contribution to INCEMS M3.4 (general description) — relevance?
- Probably: Convergence for single species, at least in single mode or common amplitude approximation
- Narrow boundaries using **r**-independent $\mu_n$
- Closed, dense structures. BCC, FCC.

## [Probably] Not doable

- Multiple species (lack of reliable data, non-convergence of numerics, too many parameters)
- Open, network structures (require 3 and higher body interactions)
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