

Phase field modelling of interfaces from first principles

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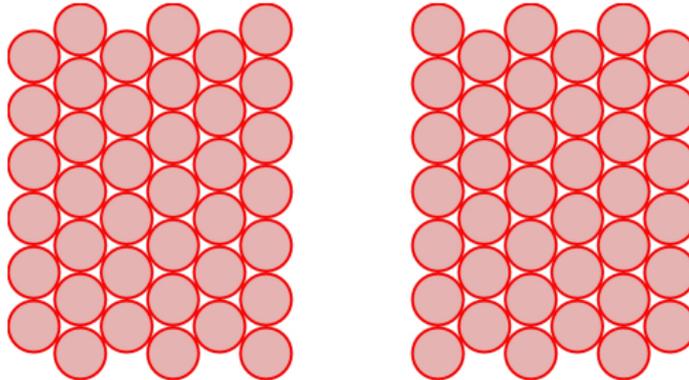
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EMRS Spring Meeting, Strasbourg, May 2007

Outline

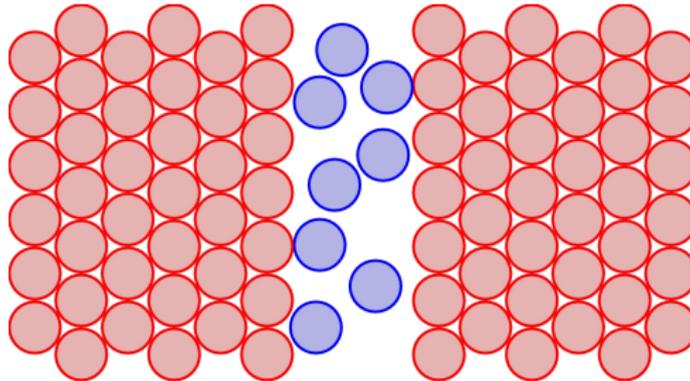
- 1 Introduction
- 2 classical DFT in general
- 3 From DFT to Phase Field Modelling
- 4 Summary

Model



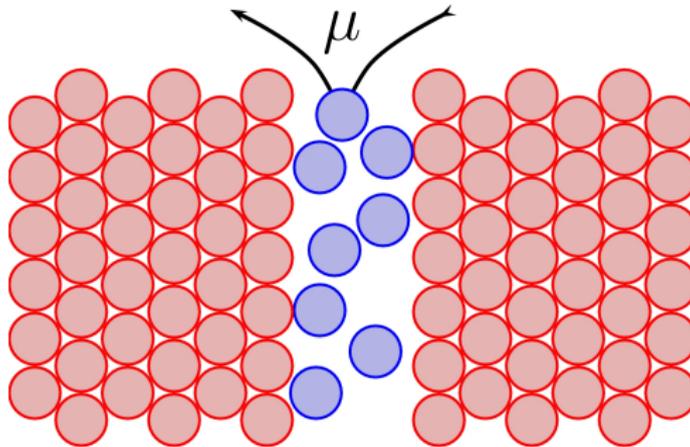
- Two **confining** lattices (3D)
- Interface: **liquid layer** in between
- Reservoir: **chemical potential** μ

Model



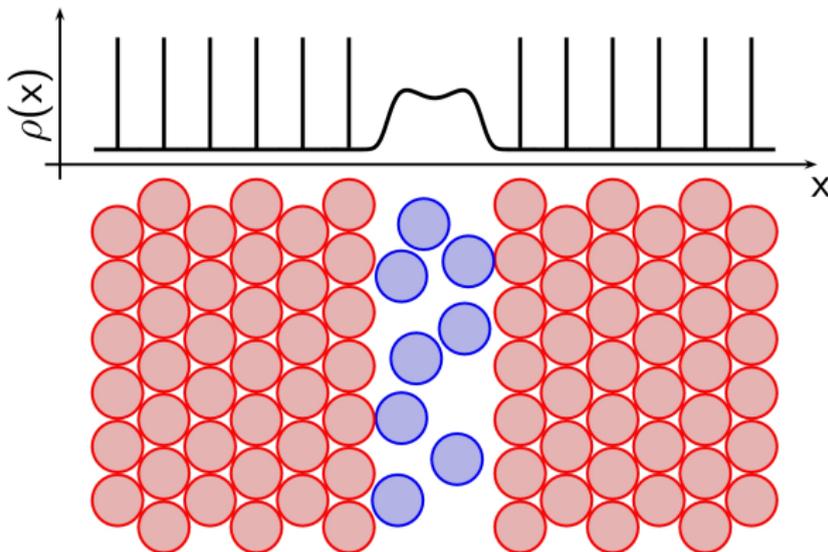
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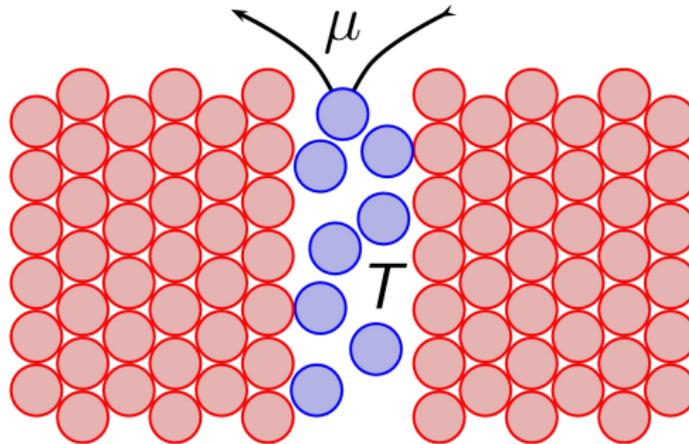
Observables and Parameters



- Key observables

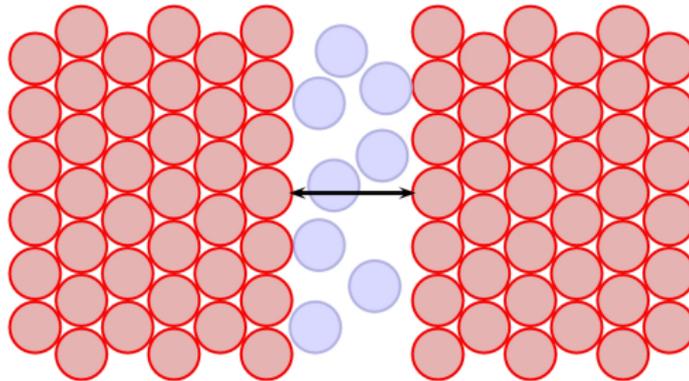
- Density profile $\rho(\vec{x})$
- Thermodynamic properties (grand potential, steric forces, pressure...)

Observables and Parameters



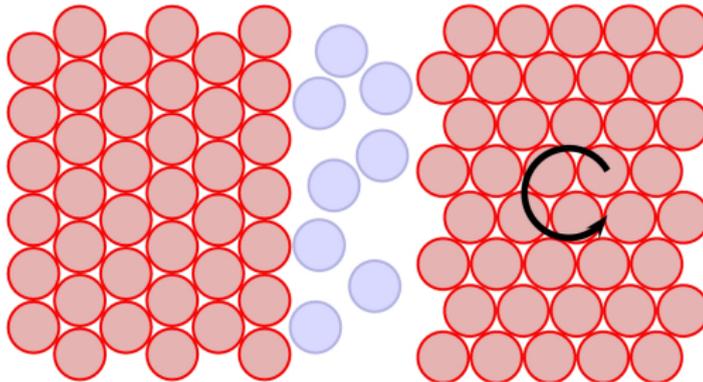
- Key observables: Density profile, potentials, pressure ...
- Parameters
 - temperature, chemical potential, ...
 - relative lattice orientation: gap, tilt, twist

Observables and Parameters



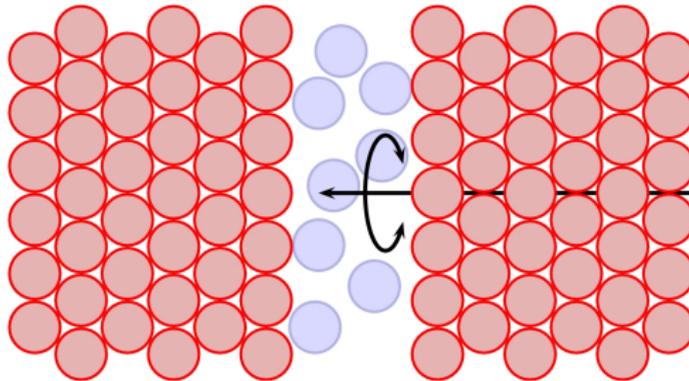
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Introduction

Key ideas of classical DFT

Classical Density Functional Theory

- Given a stable (metastable?) thermodynamic system ...
- ... write down a (mock-) free energy (grand potential)
- External potential is a **unique** functional of the density profile
- Solve self-consistency equation (i.e. find root, minimise potential)
- Microscopic theory, (can be) very hard to solve (numerics)

Introduction

Key ideas of Phase Field Modelling

Phase Field Modelling of grain boundaries

- Identify relevant interactions reproducing observations
- Identify symmetries and write down (mock-) free energy
 - ... in terms of an order parameter: the crystallinity ϕ
 - **Derive dynamics minimising free energy**
- Integrate “equation of motion”
- **Not** a microscopic theory
well established techniques

Idea: Provide solid thermodynamic foundation of phase field modelling through DFT

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The key equation of DFT

DFT

Free energy functional $F[\rho]$ of the system given.

Solution for

$u(\mathbf{r})$ (one-body local potential) at given density profile $\rho(\mathbf{r})$

$\rho(\mathbf{r})$ at given $\tilde{u}(\mathbf{r})$

is found by minimising the “non-equilibrium grand potential”

$$\tilde{W}[\rho, \tilde{u}] = F[\rho] - \int d^d r \tilde{u}(\mathbf{r}) \rho(\mathbf{r})$$

with respect to ρ . Solve $u(\mathbf{r})[\rho] = \tilde{u}(\mathbf{r})$ plus technicalities.

Different flavours of DFT have **different** methods of constructing **grand potential** \tilde{W} .

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

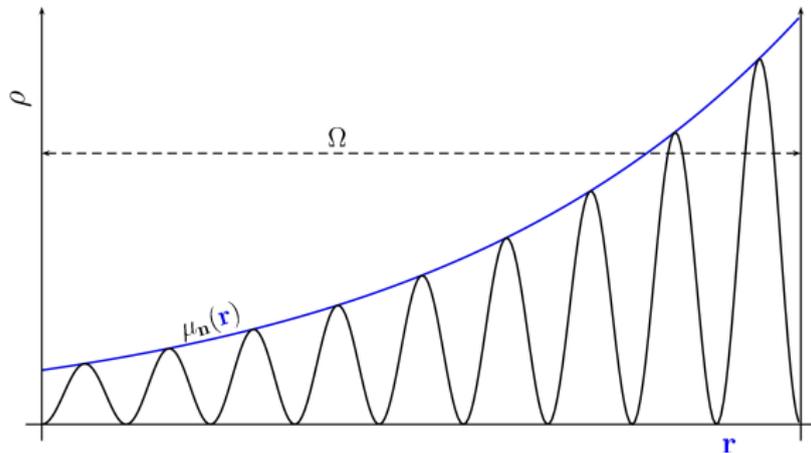
$$\ln\left(\frac{\rho(\mathbf{r})}{\rho_0}\right) = \int d^d r' C^{(2)}(\mathbf{r}' - \mathbf{r})(\rho(\mathbf{r}') - \rho_0)$$

using **direct correlation function** $C^{(2)}(\mathbf{r})$, *i.e.* **structure factor**

- To be solved with certain boundary conditions.
- Re-parametrise $\rho(\mathbf{r})$:

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

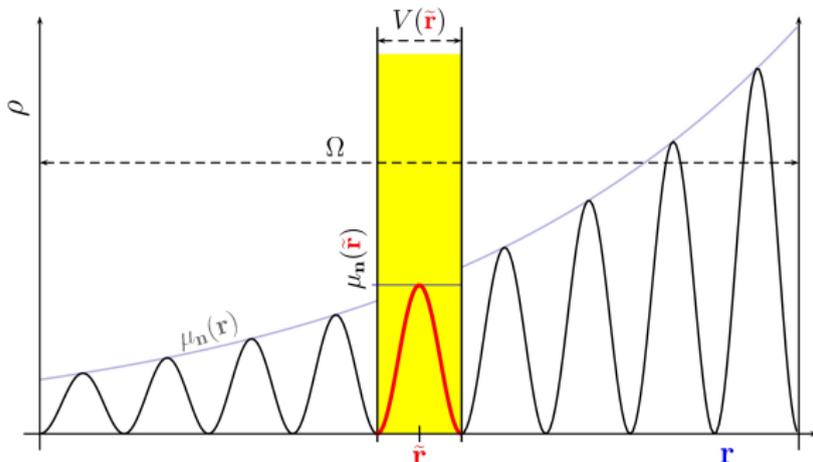
Separation of length scales



Full density profile:

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

Separation of length scales

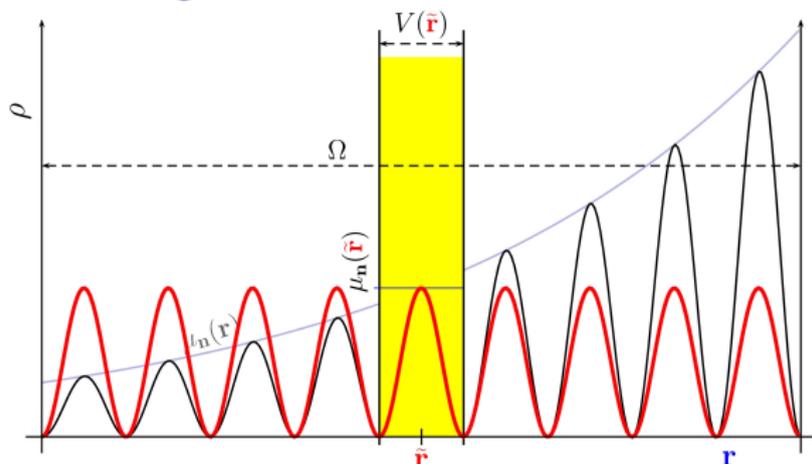


Separation of length scale:

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

Haymet and Oxtoby: Separation of length scales works for physical reasons

Separation of length scales

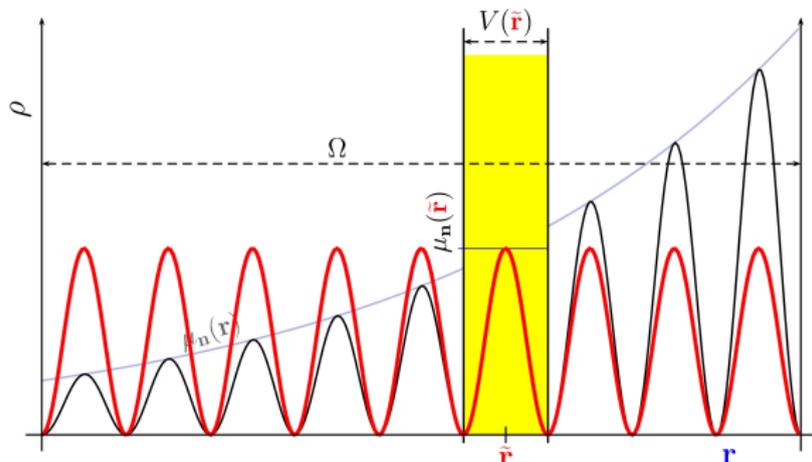


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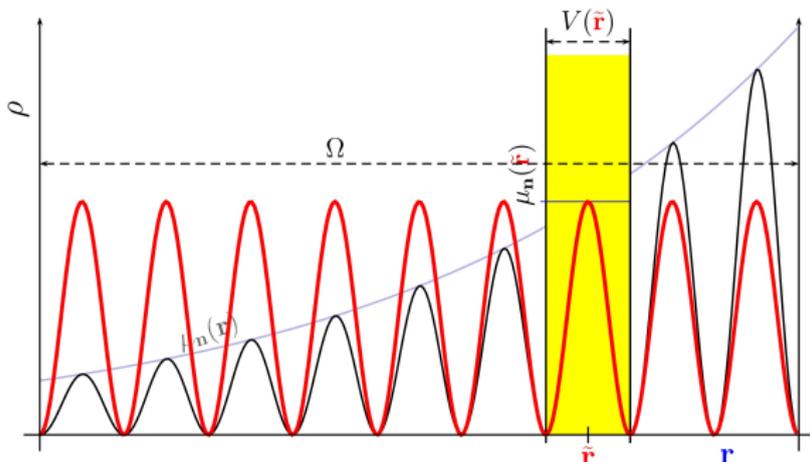


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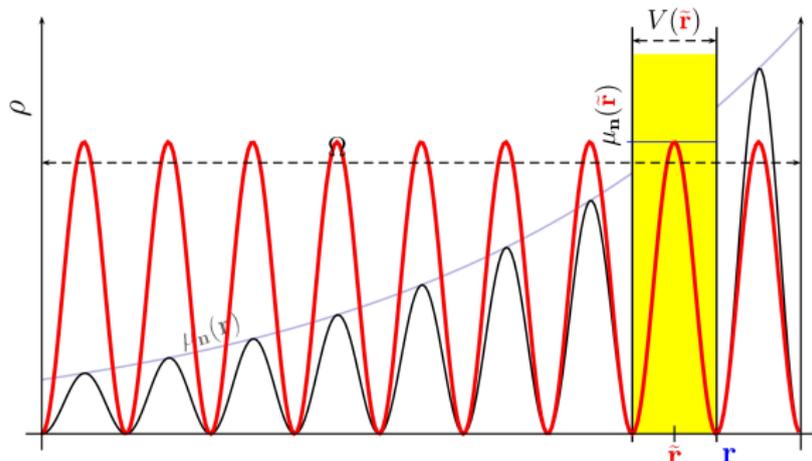


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The principles of Classical Density Functional Theory

Haymet and Oxtoby, 1981 and 1982

Classical Density Functional Theory

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

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

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

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

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Classical Density Functional Theory

- Now Fourier transform

$$V^{-1} \int d^d r e^{-i\mathbf{k}_m \cdot \mathbf{r}} \ln \left(1 + \sum_n \mu_n(\tilde{\mathbf{r}}) e^{i\mathbf{k}_n \cdot \mathbf{r}} \right) = \\ V'' \rho_0 (c_m \mu_m(\tilde{\mathbf{r}}) - i \nabla c_m \nabla \mu_m(\tilde{\mathbf{r}}) - \dots)$$

Approximations and assumptions so far

- **Functional expansion** of the effective one particle potential
Range V'' should be small
- **Taylor expansion** of the Fourier coefficients $\mu_n(\tilde{\mathbf{r}})$
Slow changes of $\mu_n(\tilde{\mathbf{r}})$ only and Fourier domain V small
- **Separation of length scales**
- Crystal structure must be known (**choice of \mathbf{k} -vectors**)
- **Structure** across the system **constrained** by set of \mathbf{k} -vectors

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Constraints by assumed crystalline structure

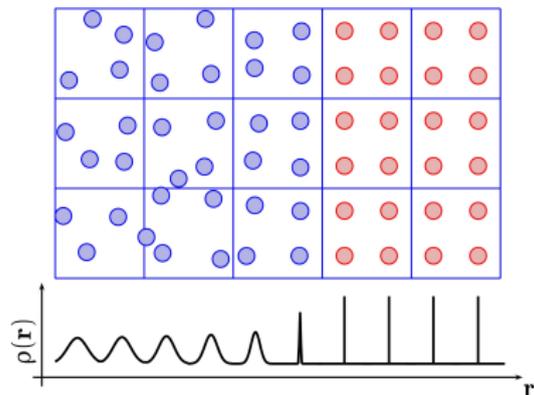
Solid-liquid interface

Density profile:

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

Boundary Condition:

Fix $\mu_n(\mathbf{r})$ on the far right.



Parametrisation of the **right hand boundary condition** does not seriously constrain **liquid**, because

- Density profile is an ensemble *average*
- Set of \mathbf{k} -vectors can be extended (completed)
- Domain can be extended

Constraints by assumed crystalline structure

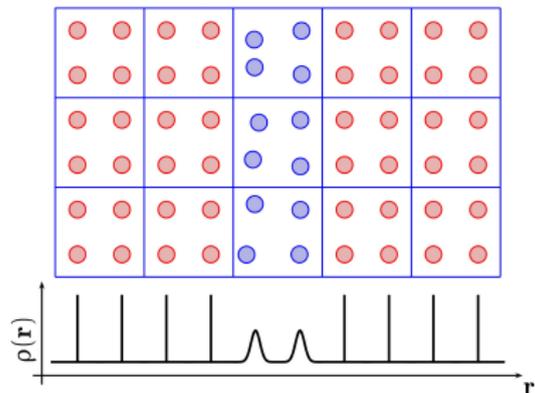
Grain boundary

Density profile:

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Boundary Conditions:

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



Parametrisation must capture both **right hand boundary condition** and **left hand boundary condition**

- Amorphous region easily represented
- “Conflicting” boundary conditions, requiring different sets of **k**-vectors.
- **Σ -boundaries** can be handled naturally, $\tan(\alpha/2) \in \mathbb{Q}$

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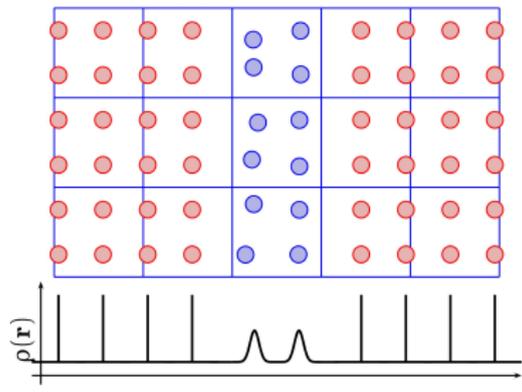
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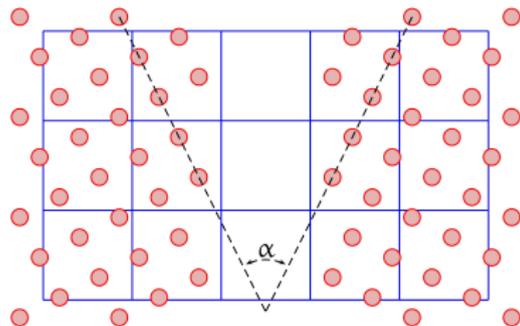
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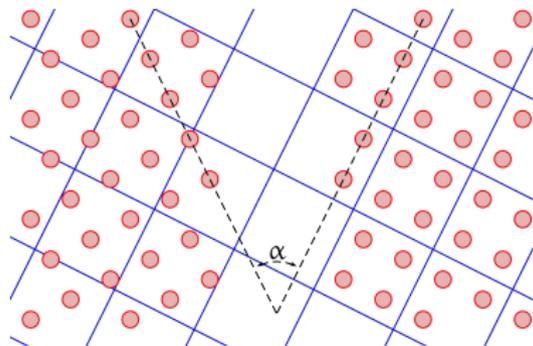
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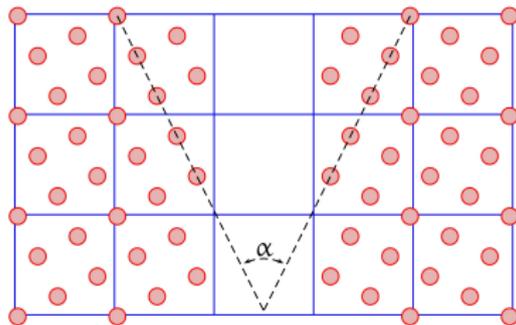
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Intermediate Summary

- DFT by Haymet and Oxtoby can be adapted to grain boundaries
- Systematic approximations
- Set of \mathbf{k} -vectors to be chosen carefully

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The Allen Cahn phase field model

Free energy functional by symmetry and conservation arguments

$$\tilde{W}[\phi] = \int_{\Omega} d^d r w(\phi) + \frac{\epsilon^2}{2} (\nabla\phi)^2$$

Grain boundaries: ϕ is the **crystallinity**

Minimal dynamics:

$$\dot{\phi} = -M_{\phi} \frac{\delta}{\delta\phi} \tilde{W} = -M_{\phi} \left(\frac{\partial w}{\partial \phi} - \epsilon^2 \nabla^2 \phi \right)$$

Can DFT explain the physics of ϕ ?

Can DFT help to determine the coupling ϵ ?

Rewriting Haymet and Oxtoby's DFT

Step 1

Originally: Separation of length scales applied to self-consistency equation

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

Instead: Separation of length scales on the level of the grand potential:

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Instead: Separation of length scales on the level of the grand potential:

$$\begin{aligned} & \tilde{\mathcal{W}}([\rho_i], [u_i \equiv \beta \mu]) \\ = & \int_{\Omega} d^d \tilde{\mathbf{r}} V^{-1} \int_{V(\tilde{\mathbf{r}})} d^d r' \left(\ln\left(1 + \sum_n \mu_n(\tilde{\mathbf{r}}) e^{i\mathbf{k}_n r'}\right) - 1 \right) \rho_0 \left(1 + \sum_n \mu_n(\tilde{\mathbf{r}}) e^{i\mathbf{k}_n r'}\right) \\ & - \Phi_0 + \int_{\Omega} d^d r' C_0 \rho_0 \\ & - \frac{1}{2} \rho_0^2 V'' \int_{\Omega} d^d \tilde{\mathbf{r}} \sum_n \mu_{-\mathbf{n}}(\tilde{\mathbf{r}}) \left[\mu_{\mathbf{n}}(\tilde{\mathbf{r}}) c(\mathbf{k}_{\mathbf{n}}) - \nu (\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}}) \mu_{\mathbf{n}}(\tilde{\mathbf{r}}) c(\mathbf{k}_{\mathbf{n}}) - \frac{1}{2} (\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{k}})^2 \mu_{\mathbf{n}}(\tilde{\mathbf{r}}) c(\mathbf{k}_{\mathbf{n}}) + \dots \right] \end{aligned}$$

Rewriting Haymet and Oxtoby's DFT

Step 2

Re-parametrisation: $\phi(\tilde{\mathbf{r}})$ is the **amplitude** of a set of $\mu_{\mathbf{n}}$ associated with the **\mathbf{k} -vectors** of the solid phases:

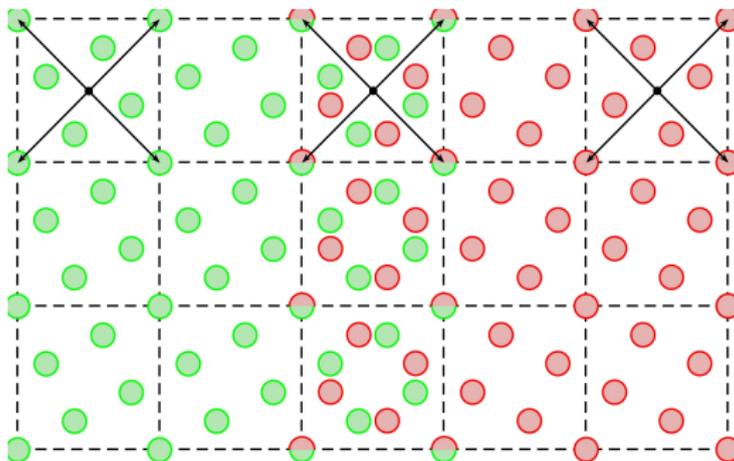
$$\mu_{\mathbf{n}}(\tilde{\mathbf{r}}) = \phi(\tilde{\mathbf{r}})\mu_{\mathbf{n}}^0$$

Use in non-equilibrium grand potential $\tilde{\mathcal{W}}$:

$$\begin{aligned}\tilde{\mathcal{W}}_{\text{AC}}([\phi]) &= \int_{\Omega} d^d r \left(w(\phi(\mathbf{r})) \right. \\ &\quad \left. + \frac{1}{4} \rho_0^2 V'' \left(\epsilon_l \mu_0^l{}^2 + \epsilon_r \mu_0^r{}^2 - 2\epsilon_{\text{I}} \mu_0^l \mu_0^r \right) \phi \nabla^2 \phi \right)\end{aligned}$$

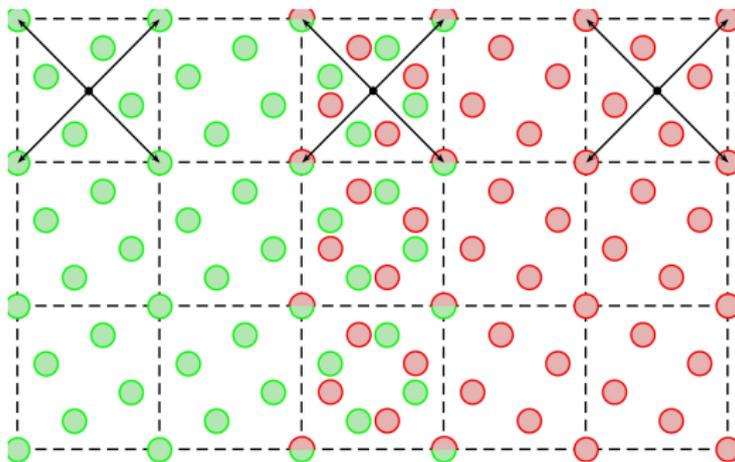
All physics in couplings ϵ_l , ϵ_r and ϵ_{I} to be calculated for closed set of **\mathbf{k} -vectors**.

Couplings



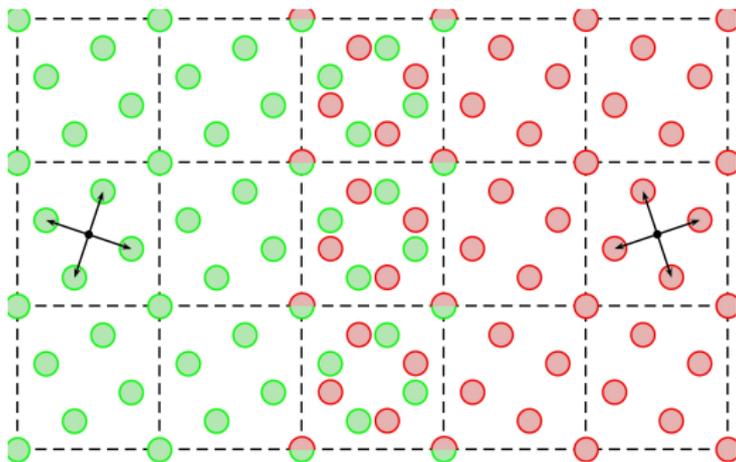
- ϵ_l and ϵ_r is **proportional to the order of the symmetry group** of the solid in the boundary condition. Here $\epsilon_l = \epsilon_r \sim 4$
- ϵ_{\parallel} is proportional to the **number of \mathbf{k} -vectors common to both lattices**. Here $\epsilon_{\parallel} \sim 4$
- Another set of \mathbf{k} -vectors, $\epsilon_{\parallel} \sim 0$

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Finally: Use “non-equilibrium grand potential”

$$\begin{aligned} \tilde{W}_{AC}([\Phi]) = \int_{\Omega} d^d r \left(w(\phi(\mathbf{r})) \right. \\ \left. + \frac{1}{4} \rho_0^2 V'' \left(\epsilon_l \mu_0^l{}^2 + \epsilon_r \mu_0^r{}^2 - 2\epsilon_{\text{I}} \mu_0^l \mu_0^r \right) \phi \nabla^2 \phi \right) \end{aligned}$$

for minimal dynamics

$$\begin{aligned} \dot{\phi} &= -M_{\phi} \frac{\delta}{\delta \phi} \tilde{W} \\ &= -M_{\phi} \left(\frac{\partial}{\partial \phi} w(\phi) - \frac{1}{2} \rho_0^2 V'' \left(\epsilon_l \mu_0^l{}^2 + \epsilon_r \mu_0^r{}^2 - 2\epsilon_{\text{I}} \mu_0^l \mu_0^r \right) \nabla^2 \phi \right) \end{aligned}$$

Couplings depend on order of underlying symmetry

Summary

- Density Functional Theory by Haymet and Oxtoby **extended to grain boundaries**
- Key ingredient: **Direct correlation function** (+ thermodynamics)
- Key step: **Separation of length scales**
- Instead of self-consistency, **grand potential** can be derived using the same approximations
- Introduction of **phase field variable ϕ as common amplitude**
- Couplings proportional to **order of underlying point symmetry group**
- Amounts to **first microscopic derivation** of phase field model for grain boundaries

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