

Classical Density Functional Theory

Towards interfaces in crystalline materials

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Outline

- 1 Introduction
 - Aims
 - Roots
- 2 cDFT in general
 - General considerations
 - Ideal System
 - Perturbation Theory
- 3 Application to interfaces
 - cDFT for interfaces: Haymet and Oxtoby
 - Application to IGFs

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Introduction

cDFT: What for?

Aims of classical density functional theory

- Determine thermodynamic properties: (surface) free energy, density profiles, phases, potentials, etc. without simulation or experiments
- Determine (few) relevant degrees of freedom
- Minimal input (here: direct n -point correlation function)
- Controlled approximation scheme (perturbation theory...)
- Here: Given two crystalline orientations at $x = \pm\infty$, what is the density profile in between? (notice: *structured walls!*)

Introduction

cDFT: Based on what?

Theoretical basis of 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, i.e. minimise mock potential)
- Relation to electronic DFT: Ground state wave-function is a unique functional of density profile

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The key equation of DFT

DFT

Given the full free energy functional $F[\rho]$ of the system, the unique potential $u(\vec{r})$ (intrinsic chemical potential) at given density profile $\rho(\vec{r})$, or one possible solution $\rho(\vec{r})$ at given $\tilde{u}(\vec{r})$ is found by minimising

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

with respect to ρ (i.e. $\frac{\delta}{\delta \rho} \tilde{W} \equiv 0$) which is equivalent to solving

$$u(\vec{r})[\rho] = \tilde{u}(\vec{r})$$

plus technicalities (LHS: equilibrium potential, RHS: imposed potential). If ρ is the equilibrium profile for \tilde{u} then $\tilde{W}[\rho, \tilde{u}]$ is the grand potential.

Flavours of DFT

- Impose that the free energy has square gradient form
- Density expansion (expansion about bulk; HNC [here] and PY closure)
- LDA: $F = \int d^d r f(\rho)$
- Expansion about bulk; van der Waals
- WDA: $F = \dots + \int d^d r \rho(\vec{r}) f(\vec{r})[\rho]$ (Tarazona Mark I, Mark II, Curtin-Ashcroft, ...)
- Rosenfeld's fundamental-measure theory
- ...

General considerations I

- Hamiltonian of an N -particle system:

$$H_N = V_N(\vec{r}_1, \dots, \vec{r}_N) + \sum_i^N \left(\frac{p_i^2}{2m} + U(r_i) \right)$$

- Grand canonical partition sum:

$$\begin{aligned} \mathcal{Z} &= \sum_N \frac{1}{N!} e^{\beta \mu N} \tilde{\Lambda}^{-Nd} \int d^d p_1 d^d x_1 \dots \int d^d p_N d^d x_N e^{-\beta H_N} \\ &= \text{Tr} \frac{1}{N!} e^{\beta \mu N} \tilde{\Lambda}^{-Nd} e^{-\beta H_N} \end{aligned}$$

where $\tilde{\Lambda}$ is the phase space volume element. Integrate out (Gaussian) p_i 's ($\dots \sqrt{2m\pi/\beta}$) and absorb into $\tilde{\Lambda}^d \rightarrow \Lambda$.

General considerations II

- Introduce density operator:

$$\hat{\rho}_N(\vec{r}; \vec{r}_1, \dots, \vec{r}_N) = \sum_i^N \delta(\vec{r} - \vec{r}_i)$$

and write $\sum_i U(r_i) - \mu N = \int d^d r \hat{\rho}_N(U(\vec{r}) - \mu)$.

- Dimensionless (intrinsic chemical) potential $u(\vec{r}) = \beta\mu - \beta U(\vec{r})$ so that

$$e^{\beta\mu N} e^{-\beta \sum_i U(\vec{r}_i)} = e^{\int d^d r \hat{\rho}_N(\vec{r}; \dots) u(\vec{r})}$$

- Grand canonical partition sum now

$$\mathcal{Z} = \text{Tr} \frac{1}{N!} \Lambda^{-N} e^{-\beta V_N(\dots)} e^{\int d^d r \hat{\rho}_N u}$$

General considerations III

- Grand potential $W = -\ln \mathcal{Z}$
- so that

$$\rho(\vec{r}) = \langle \hat{\rho}(\vec{r}; \dots) \rangle = -\frac{\delta}{\delta u(\vec{r})} W$$

and $\langle N \rangle = -\beta^{-1} \frac{d}{d\mu} W$

- Grand potential is a functional of the external potential, $W = W(\beta, [u(\vec{r})])$. Its Legendre transform

$$F = F(\beta, [\rho(\vec{r})]) = W + \int d^d r u(\vec{r}) \rho(\vec{r})$$

is the free energy.

- Straight forward to show that

$$\frac{\delta}{\delta \rho(\vec{r})} F = u(\vec{r})$$

Ideal System I

- Ideal system: $V_N \equiv 0$, so partition sum becomes

$$\mathcal{Z}_{\text{id}} = \text{Tr} \frac{1}{N!} \Lambda^{-N} \exp \left(\int d^d r \hat{\rho}_N(\vec{r}; \dots) u(\vec{r}) \right)$$

Because of the missing interaction, the integral factorises and becomes just

$$\left(\int d^d r e^{u(\vec{r})} \right)^N$$

so that

$$\mathcal{Z}_{\text{id}} = \sum_N \frac{1}{N!} \Lambda^{-N} \left(\int d^d r e^{u(\vec{r})} \right)^N = \exp \left(\Lambda^{-1} \int d^d r e^{u(\vec{r})} \right)$$

Ideal System II

- From $\mathcal{Z} = \exp(\Lambda^{-1} \int d^d r \exp(u))$ we have the grand potential:

$$W_{\text{id}}[u(\vec{r})] = -\Lambda^{-1} \int d^d r \exp(u(\vec{r}))$$

and from $\rho = -\frac{\delta}{\delta u} W$ we have the barometric formula:

$$\rho(\vec{r}) = \Lambda^{-1} \exp(u(\vec{r}))$$

- Using this relation between ρ and u one can perform the Legendre transform ($F = W + \int dr \rho u$) to find

$$F_{\text{id}}[\rho(\vec{r})] = \int d^d r (\ln(\rho\Lambda) - 1) \rho$$

Ideal System III

- Now define the excess free energy Φ for an interacting system as

$$\Phi[\rho(\vec{r})] = F_{\text{id}}[\rho(\vec{r})] - F[\rho(\vec{r})]$$

where $F_{\text{id}}[\rho(\vec{r})]$ is the free energy for a given density profile, assuming that the system is ideal.

- Use $\frac{\delta}{\delta\rho} F_{\text{id}} = \ln(\rho\Lambda)$ and $\frac{\delta}{\delta\rho} F = u$ to show that

$$C(\vec{r}) \equiv \frac{\delta}{\delta\rho(\vec{r})} \Phi = \ln(\rho(\vec{r})\Lambda) - u(\vec{r})$$

which is the **effective one particle potential**: It is the additional external potential needed in an ideal system, for it to “mimic” a particular density profile ρ found in an interacting system

$$\rho(\vec{r}) = \Lambda^{-1} e^{u(\vec{r})+C(\vec{r})}$$

Perturbation Theory: cDFT

Standard technique in cDFT: Write down a perturbative expansion of the effective one particle potential about some reference system:

$$C(\vec{r}) = C_0^{(1)}(\vec{r}) + \int d^d r_1 C_0^{(2)}(\vec{r}, \vec{r}_1) (\rho(\vec{r}_1) - \rho_0(\vec{r}_1)) + \dots$$

which, together with

$$C(\vec{r}) = \ln(\rho(\vec{r})\Lambda) - u(\vec{r})$$

immediately gives rise to a self-consistency equation.

Connection to the real world via the n -point direct correlation functions $C_0^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$ of the reference system.

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cDFT for interfaces

Haymet and Oxtoby I — The uniform system

- Consider a continuous family (index \vec{s}) of uniform (uniform Fourier coefficient, i.e. periodic) systems

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

- Every member has its own external potential

$$U(\vec{r}; \vec{s}) = \sum_n U_n(\vec{s}) e^{i\vec{k}_n \vec{r}}$$

- Expand uniform systems about the bulk liquid with bulk density ρ_0 one particle potential C_l and chemical potential μ , so

$$C_u(\vec{r}; \vec{s}) = C_l + \int d^d r' C^{(2)}(\vec{r} - \vec{r}') (\rho(\vec{r}'; \vec{s}) - \rho_0)$$

with $u(\vec{r}; \vec{s}) = \ln(\rho(\vec{r}; \vec{s}) \Lambda) - C_u(\vec{r}; \vec{s})$.

cDFT for interfaces

Haymet and Oxtoby I — Potential

Now use the infinite bulk liquid

$$\beta\mu = \ln(\rho_0\Lambda) - C_l$$

to derive

The potential

$$-\beta U(\vec{r}; \vec{s}) = \ln(\rho(\vec{r}; \vec{s})/\rho_0) - \int d^d r' C^{(2)}(\vec{r} - \vec{r}') (\rho(\vec{r}'; \vec{s}) - \rho_0)$$

cDFT for interfaces

Haymet and Oxtoby II — The interface

- Impose that the family collectively represents a system with varying density profile – the interface:

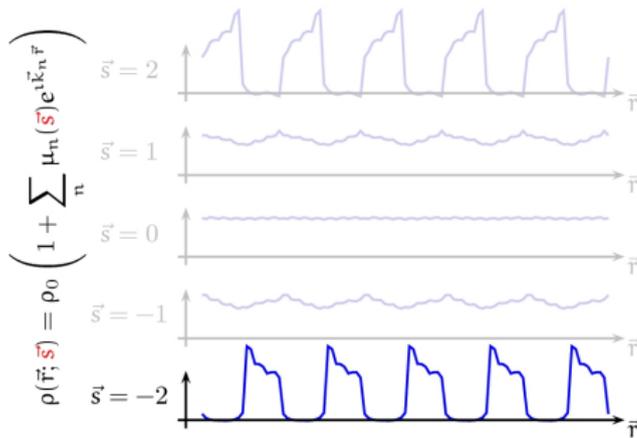
$$\rho_i(\vec{r}) = \rho(\vec{r}; \vec{r}) = \rho_0 \left(1 + \sum_n \mu_n(\vec{r}) e^{i\vec{k}_n \vec{r}} \right)$$

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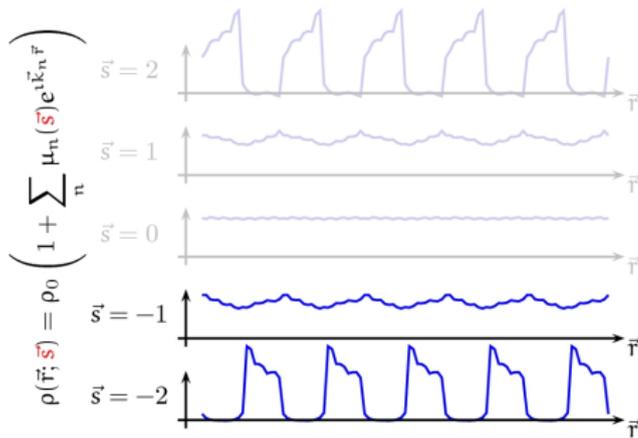


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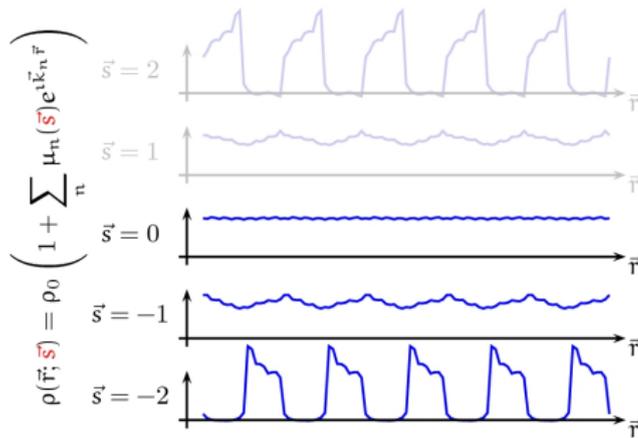


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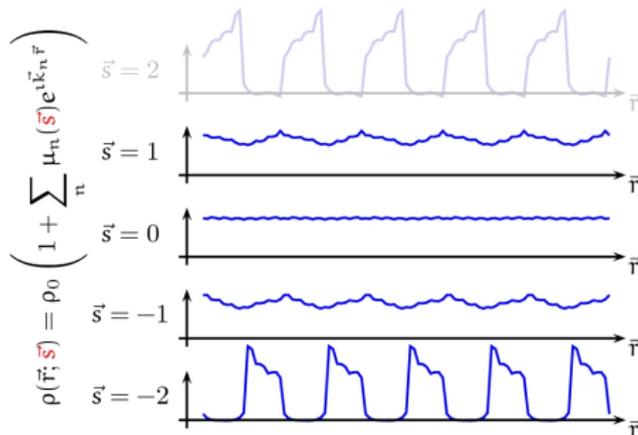


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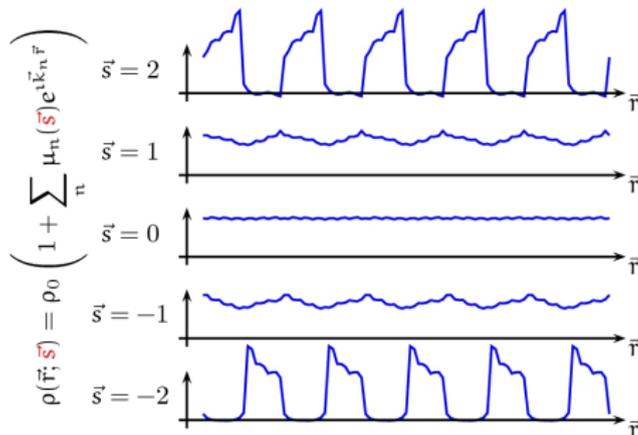


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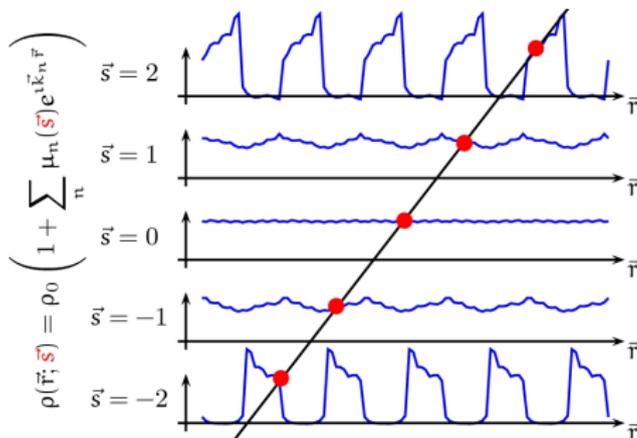


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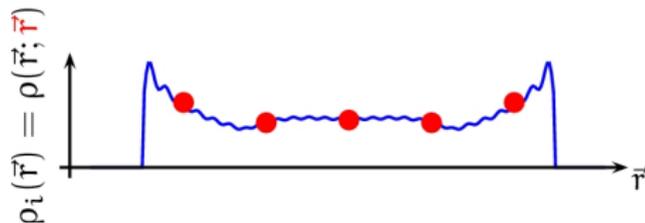


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- What is actually imposed? No potential for interface:

$$\beta\mu = \ln(\rho_i(\vec{r})\Lambda) - C_i(\vec{r})$$

with the effective one particle potential to be expanded about the infinite liquid: $C_i(\vec{r}) = C_l + \int d^d r' C^{(2)}(\vec{r} - \vec{r}')(\rho_i(\vec{r}') - \rho_0)$

- Resulting relation between C_i and C_u :

$$C_i(\vec{r}) - C_u(\vec{r}; \vec{s}) = \int d^d r' C^{(2)}(\vec{r} - \vec{r}')(\rho(\vec{r}'; \vec{r}') - \rho(\vec{r}'; \vec{s}))$$

cDFT for interfaces

Haymet and Oxtoby III — Equation of motion

- Relation between C_i and C_u must be consistent with

$$\beta\mu = \ln(\rho(\vec{r}; \vec{r})\Lambda) - C_i(\vec{r}) \quad (1)$$

$$\beta\mu - \beta U(\vec{r}; \vec{s}) = \ln(\rho(\vec{r}; \vec{s})\Lambda) - C_u(\vec{r}) \quad (2)$$

- Evaluate at $\vec{s} = \vec{r}$

$$-\beta U(\vec{r}; \vec{r}) = \int d^d r' C^{(2)}(\vec{r} - \vec{r}') (\rho(\vec{r}'; \vec{r}') - \rho(\vec{r}'; \vec{r}))$$

This is the external potential to be applied in the uniform system, so that the resulting family of density profiles gives rise to an interface profile with vanishing potential.

- Note: if $\rho(\vec{r}; \vec{s}) \equiv \rho^*(\vec{r})$ independent of \vec{s} , then all uniform systems are the same, no potential, identical to the interface.

cDFT for interfaces

Haymet and Oxtoby III — Equation of motion

Self-consistency above fixes U only at $\vec{s} = \vec{r}$.

Make a convenient choice:

The equation of motion

$$-\beta U(\vec{r}; \vec{s}) = \int d^d r' C^{(2)}(\vec{r} - \vec{r}') (\rho(\vec{r}'; \vec{r}' + \vec{s} - \vec{r}) - \rho(\vec{r}'; \vec{s}))$$

Advantage: Taylor-expand bracket and plug in Fourier-sum for $\rho(\vec{r}; \vec{s}) \dots$

cDFT for interfaces

Haymet and Oxtoby IV — The central result

Equation of motion for an interface across z :

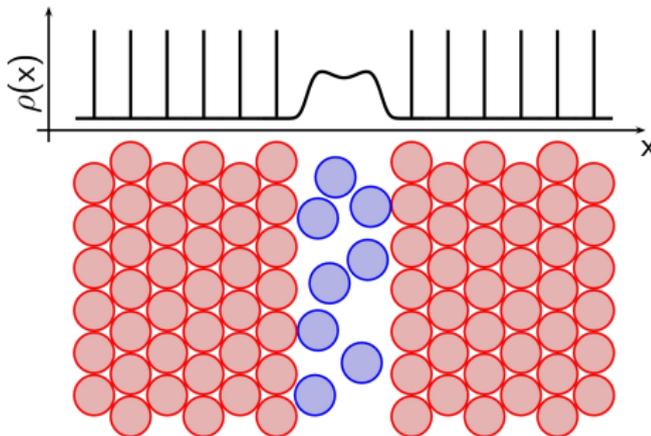
$$-\beta U_n(z) = -\rho_0 V \left\{ \mu_n'(z) \nu C^{(2)'}(\vec{k}_n) + \frac{1}{2} \mu_n''(z) C^{(2)''}(\vec{k}_n) + \dots \right\}$$

Potential:

$$\begin{aligned} -\beta U_n(z) = & V^{-1} \int_V d^d r e^{-i\vec{k}_n \vec{r}} \ln \left(1 + \sum_n \mu_n(z) e^{i\vec{k}_n \vec{r}} \right) \\ & -\rho_0 V C^{(2)}(\vec{k}_n) \mu_n(z) \end{aligned}$$

Application to IGFs

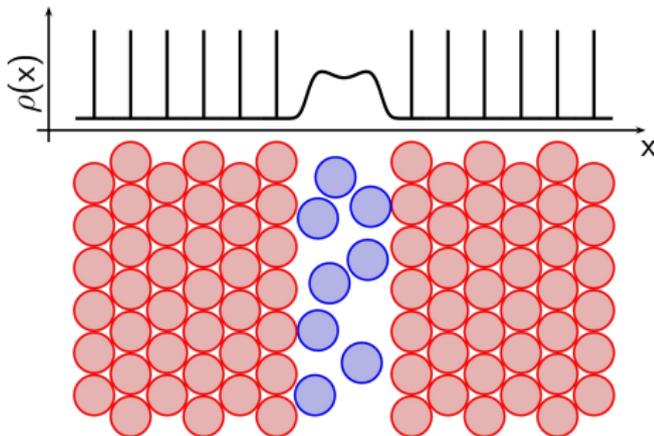
- Apply appropriate boundary conditions for $\mu_n(z \rightarrow \pm\infty)$



- Find appropriate parametrisation capable of capturing both sides of the interface
- Find direct correlation function for bulk-liquid phase
- Solve self-consistency (i.e. integrate equation of motion) ... Done!

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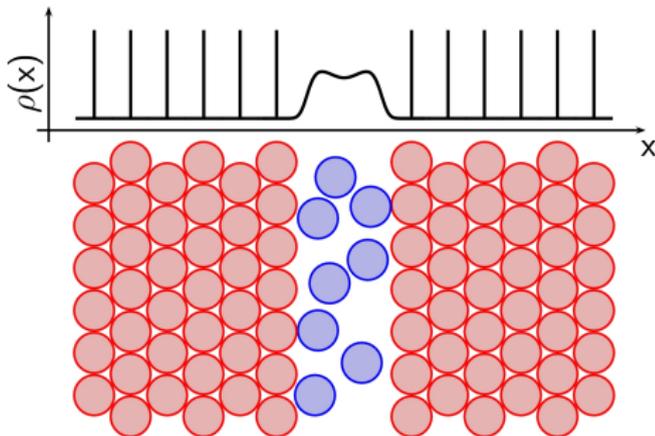
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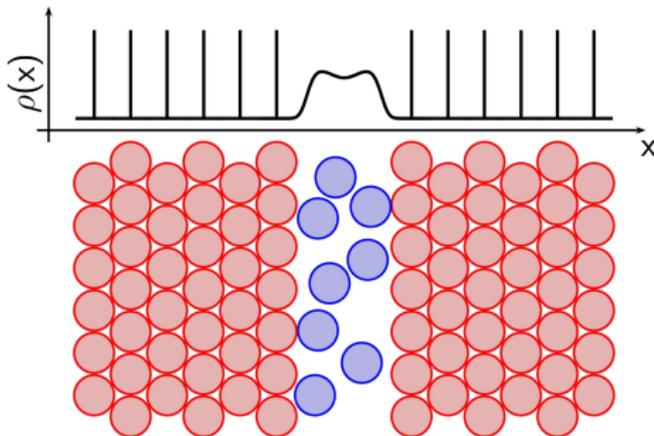
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Problems with O&H's original approach

Parametrisation

- **Fourier sum makes physical sense and makes the convolution factorise**
- Parametrisation must be capable to capture different translations and orientations on both sides (Fourier transform breaks symmetry)
- Parametrisation must make sure that a stable, uniform configuration is equally stable in any orientation and translation
- All possible degrees of freedom should (but cannot) be accessible – even those that break symmetry (numerical inaccuracies help)
- Solid phase not necessarily stable (reference system: liquid)

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What to do next?

- Find a parametrisation that keeps the solid stable in any translation and orientation
- Expand about a (stable) solid, i.e. take the direct correlation function from the stable solid
- $C^{(2)'}$ and $C^{(2)''}$ à la Debye Waller
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