Mathematics of Multiscale Materials
Research Proposal

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13th February 2012

Outline

- Background
  - Statistical Mechanics
  - Coarse-Graining
  - Cauchy–Born rule
- Finite Temperature Cauchy–Born
- Comparison of Methods
- Analysis
- Different Boundary Conditions
- Closing Remarks

Background: Statistical Mechanics

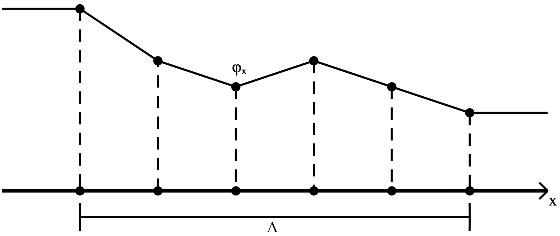
Statistical Mechanics: The Interface Model

Fix a (finite) reference lattice

$$\Lambda \subset \mathbb{Z}^d$$

Configuration

$$\varphi \colon \Lambda \to \mathbb{R}^m$$



Statistical Mechanics: The Gibbs Distribution

Hamiltonian

$$H_\Lambda^\Psi = \sum_{\substack{x,y\in\Lambda \\ |x-y|=1}} W(\varphi_x - \varphi_y)$$

Gibbs Distribution

$$\gamma_\Lambda^\Psi(\mathrm{d}\varphi) = \frac{1}{Z_\Lambda^\Psi} e^{-\beta H_\Lambda^\Psi} \prod_{x\in\Lambda} \mathrm{d}\varphi_x \prod_{z\in\Lambda^c} \delta\Psi_z(\mathrm{d}\varphi_z)$$

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Statistical Mechanics: The Free Energy

Free Energy

$$F_\Lambda(\Psi) = -\frac{1}{\beta|\Lambda|} \log Z_\Lambda^\Psi$$

Thermodynamic Limit

$$\Lambda \to \mathbb{Z}^d$$

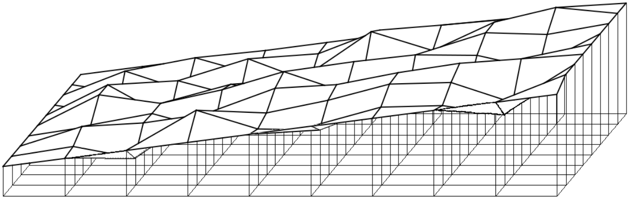
Gibbs Measure

$$\mu(\cdot|\Lambda^c)(\Psi) = \gamma_\Lambda^\Psi(\cdot)$$

Statistical Mechanics: Tilt

Tilt Condition

$$\mathbb{E}_{\mu}\left[\varphi_x - \varphi_y\right] = \langle u, x - y \rangle. \quad u \in \mathbb{R}^d$$



Statistical Mechanics: Tilted Partition Function

Tilted Partition Function

$$Z_\Lambda(u) = \int \exp\left[-\beta \sum_{x\in\Lambda} \sum_{i=1}^{d} W\left(\nabla_i \varphi(x) - u_i\right)\right]$$

Background: Coarse-Graining

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Coarse-Graining: Canonical Average

Ergodic property

$$\mathbb{E}[A] = \lim_{T\to\infty} \int_0^T A(X_t)\,\mathrm{d}t = \int_{\Omega^N} A(x)\,\mathrm{d}\mu(x),$$

hence we can write

$$\mathbb{E}[A] = \frac{\int_{\Omega^N} A(u)\exp(-\beta H(u))\,\mathrm{d}u}{\int_{\Omega^N} \exp(-\beta H(u))\,\mathrm{d}u}.$$

Coarse-Graining: Canonical Average

Let $u = (u_r, u_c)$, where u_r are the repatoms and u_c are the coarse-grained atoms then we can rewrite the expectation as

$$\mathbb{E}[A] = \frac{\int_{\Omega^{N_r}} A(u_r) \exp(-\beta H_{CG}(u_r)) \,\mathrm{d}u_r}{\int_{\Omega^{N_r}} \exp(-\beta H_{CG}(u_r)) \,\mathrm{d}u_r}.$$

where

$$H_{CG}(u_r) = -\frac{1}{\beta} \log \int_{\mathbb{R}^{3N_c}} \exp(-\beta H(u_r, u_c)) \,\mathrm{d}u_c$$

is the coarse grained free energy.

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Coarse-Graining: Canonical Average

We fix N_r the number of repatoms and we let the number of coarse-grained atoms go to infinity. Under modest conditions on the interaction potential W we have the following result for F_N the free energy per particle

$$F_N(x) + \frac{1}{\beta} \log \frac{z}{N} \to F_\infty(x) \text{ in } L^p_{\text{loc}} \ \forall p \in [1, \infty),$$

with

$$F_\infty(x) = \frac{1}{\beta} \sup_{\xi \in \mathbb{R}} \left(\xi x - \log \left(z^{-1} \int_{\mathbb{R}} \exp(\xi y - \beta W(y)) \, \mathrm{d}y \right) \right) \text{ and}$$

$$z = \int_{\mathbb{R}} \exp(-\beta W(y)) \, \mathrm{d}y.$$

Coarse-Graining: For Observables

We also have the result when A is an observable:

$$\mathbb{E}[A] = A(y^*) + \frac{\sigma^2}{2N} A''(y^*) + o\left(\frac{1}{N}\right),$$

where

$$y^* = \frac{\int_{\mathbb{R}} y \exp(-\beta W(y))\,\mathrm{d}y}{\int_{\mathbb{R}} \exp(-\beta W(y))\,\mathrm{d}y},$$

and

$$\sigma^2 = \frac{\int_{\mathbb{R}} (y - y^*)^2 \exp(-\beta W(y))\,\mathrm{d}y}{\int_{\mathbb{R}} \exp(-\beta W(y))\,\mathrm{d}y}.$$

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Background: The Cauchy–Born Rule

Cauchy–Born

Physically at low temperatures atoms in solids form a crystal.

Bravais Lattice

$$L(\{e_i\}, o) = \left\{ x : x = o + \sum_{i=1}^{d} \alpha_i e_i, \alpha_i \in \mathbb{Z} \right\},$$

Consider $\mathcal{L} = \Lambda \cap \Omega_R$.

Cauchy–Born: The Minimisation Problem

Consider the elastic energy of the deformed lattice

$$H[\{y(x)\}_{x\in\mathcal{L}}] = \sum_{i,j} W_1\left(\frac{y_i}{h}, \frac{y_j}{h}\right) + \sum_{i,j,k} W_2\left(\frac{y_i}{h}, \frac{y_j}{h}, \frac{y_k}{h}\right) + \dots,$$

Our problem is to find:

$$\min_y H[\{y(x)\}_{x\in\mathcal{L}}],$$

subject to

$$y(x) = \mathbf{F}x \text{ on } \partial\mathcal{L},$$

where

$$\partial\mathcal{L} = \{x \in \mathcal{L} : \exists\, i \in \{1, \dots, d\} \text{ s.t } x + e_i \notin \mathcal{L}\},$$

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Cauchy–Born: The Cauchy–Born Rule

One can compute the elastic energy per unit volume

$$E(\mathbf{F}) := \lim_{R\to\infty} \min_{\substack{y \\ y(x)=\mathbf{F}x \text{ on } \partial\mathcal{L}}} \frac{H[\{y(x)\}_{x\in\mathcal{L}}]}{\mathrm{vol}(\Omega_R)},$$

using the simpler formula

$$E_{CB}(\mathbf{F}) := \lim_{R\to\infty} \frac{H[\{\mathbf{F}x\}_{x\in\mathcal{L}}]}{\mathrm{vol}(\Omega_R)}.$$

Finite Temperature Cauchy–Born Rule

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There is currently no widely accepted Cauchy–Born rule for systems in finite temperature.

Suggested Rule

$$F_H^T(\mathbf{F}) = \int_\Omega w_C(\mathbf{F})\,\mathrm{d}\Omega + C_0^T \times \log\left(C_1^T\,\bar{D}(\mathbf{F}(X)))^{\frac{1}{2n}}\right).$$

Finite Temperature Cauchy–Born Rule

Questions

(T1) Justify the assumptions; are they physically relevant or pertinent to real systems?

(T2) Is it feasible to change this model to be more realistic without excessive complications?

1D Rod Cauchy–Born at Finite Temperature: Diagram

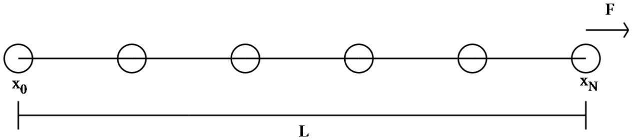


Figure: Applying a deformation **F** to a rod

Finite Temperature Cauchy-Born Rule

(T3) For the 1D rod, simplify the free energy formula given above for nearest neighbour and next nearest neighbour interactions. Derive an explicit formula.

1D Rod Cauchy–Born Simulations at Finite Temperatures

Questions

(FT1) Calculate the free energy for the nearest neighbour interaction model with the temperature Cauchy–Born rule and compare with molecular dynamics simulations for a range of deformations $\mathbf{F}$.

(FT2) Repeat (FT1) with next-nearest neighbour interactions.

(FT3) Derive an approximation for the order of the error between the molecular dynamics energy and the energy calculated using the temperature Cauchy–Born rule.

Comparison of Methods

Comparison of Methods on a Regular 2D Triangular Lattice

We wish to compare different techniques of calculating the free energy for a range of deformations.

Molecular Dynamics

A computational technique using the laws of classical physics. This method is computationally expensive.

Statistical Mechanics

We need to consider an infinite lattice. With an appropriate choice of interaction potential, the free energy can be calculated explicitly.

Comparison of Methods on a Regular 2D Triangular Lattice

Coarse-Graining

We use coarse-grained techniques to calculate the gradient of free energy and use thermodynamic integration to obtain the free energy.

Temperature Cauchy–Born

Use answer to Question (T2).

Comparison of Methods on a Regular 2D Triangular Lattice

Question

(C1) Initially, consider the model where the potentials are zero on the boundary. We also choose a potential which is quadratic and use a gradient model. Under these assumptions it should be possible to calculate estimates for the free energy from each of these methods. Taking molecular dynamics as the standard, compare the error of the other three methods for a range of deformations.

Analysis

Calculating the Partition Function for a More General Potential

Question

(A1) Consider the potential W and investigate whether weakening some of the conditions on it still give rise to the existence of Z and F.

Analytical Bounds on the Error: Zero Temperature

Zero Temperature

(A2) Is it possible to analytically derive a bound for the error between the Cauchy–Born approximation and the exact solution (assuming it exists)?

Analytical Bounds on the Error: Finite Temperature

Finite Temperature

(A3) In the setting described in questions (FT1) – (FT3) is it possible to derive analytic bounds on the error between the temperature Cauchy–Born approximation and the true value for free energy in terms of the magnitude of the deformation?

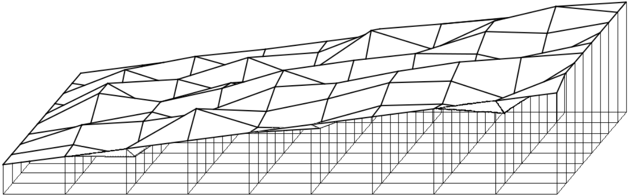
(A4) Make precise qualifications on how the distance between the deformation and the $SO(2)$ group affects the validity of the Cauchy–Born rule.

Different Boundary Conditions

Different Boundary Conditions

Dirichlet Boundary Condition

For non-zero boundary conditions, in statistical mechanics, we apply a tilt u to the boundary such that the lattice deforms to a plane.



Different Boundary Conditions

Frozen Lattice

Particles inside the box still interact with particles outside the box but we do not consider the exterior particles in our calculations.

Different Boundary Conditions

Question

(BC1) Calculate the free energy using the temperature Cauchy–Born rule, statistical mechanics, and coarse graining for

- Dirichlet boundary conditions, and
- Frozen lattice boundary conditions

and compare the differences.

Closing Remarks

Closing Remarks

Further work

- Fix **F** and increase system size,
- Periodic boundary condition,
- Extend analysis of Cauchy–Born error (zero and finite temperature) to 2D.

Acknowledgements

We are grateful to Stefan Adams and Christoph Ortner for their guidance, ideas, and support throughout the course of this project.

Any Questions?