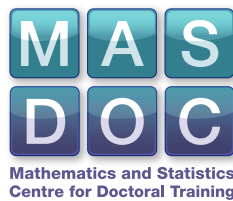


Mathematics of Multiscale Materials
Research Proposal

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Figure 1: From left to right: Stefan Adams and Christoph Ortner

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1 Introduction

The equilibria states of a thermodynamic system minimise the free energy, which is a measure of how much useful work can be extracted from the system. Since we are considering the structure of materials, we are interested in their equilibrium properties, so free energy is an important quantity to calculate. The aim of this proposal is to extend results of free energy error estimates from zero temperature systems to finite temperature systems. Whilst some results have been established numerically [7], we wish to place these results on a firmer analytical basis.

We focus on techniques to obtain error estimates of free energy for finite temperature systems using three different methods: statistical mechanics, a variant of the Cauchy–Born rule and coarse-graining. To begin with, the zero temperature case in the one-dimensional setting with nearest neighbour and next-nearest neighbour interactions is considered in Section 3. We propose to calculate the free energy using the Cauchy–Born rule and then to compare the results to molecular statics. We also propose extending this to the finite temperature case.

We will introduce a Cauchy–Born rule for finite temperatures in Section 3.2. Then in Section 3.3, we look at comparing different methods of calculating the free energy for finite temperature regimes in 1D. Specifically, one end of a chain of atoms is fixed and a deformation is applied to the other end. We would like to analyse the difference in free energy as given by statistical mechanics, coarse-graining and a temperature-related Cauchy–Born rule. This is expanded in Section 4.2 to analytically derive an estimate of the order of the error of the temperature-related Cauchy–Born rule in terms of the size of the deformation.

In Section 4.3, we also intend to compare free energy in finite temperature systems in 2D as given by the temperature-related Cauchy–Born rule, statistical mechanics and coarse-graining techniques with molecular dynamics for varying boundary conditions.

A background of the Cauchy–Born rule, statistical mechanics and coarse-graining is given in Section 2. Throughout this proposal, we assume some knowledge of molecular dynamics. A small introduction to this area is given in Appendix A.

Throughout this proposal, we sometimes refer to a lattice at finite temperature. By this we mean that the atoms’ equilibrium positions are on a lattice.

A recommended plan of action to tackle our proposal is given in Appendix B.

2 Background

2.1 The Cauchy–Born Rule

The Cauchy–Born rule or the Cauchy–Born hypothesis is an assumption which links the deformation of a continuum object to the corresponding atomistic model.

From here on we assume that the temperature of the solid is zero. Physically, as the temperature tends to zero, solids form a crystalline structure in which the atoms form a lattice. There are two types of lattices: a simple or Bravais lattice takes the form

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

where e_i are basis vectors, o is a particular lattice point, and d is the dimension. The other type are complex lattices which are a union of simple lattices:

$$L(\{e_i\}, o) \cup L(\{e_i\}, o + p_1) \cup \dots \cup L(\{e_i\}, o + p_k),$$

where p_1, \dots, p_k are *shift vectors*, each of which translates one simple lattice to another.

Let the undeformed configuration be given by $\mathcal{L} = \Lambda \cap \Omega_R$ where Λ is a lattice and $\Omega_R = \{Rx : x \in \Omega, R \in \mathbb{R}^+\}$ with Ω being an open domain in \mathbb{R}^d . Let x be the position of an atom in the undeformed lattice. A *deformation* of the lattice is described by a vector field $y : \mathcal{L} \rightarrow \mathbb{R}^d$, so $y(x)$ is the position of the atom after deformation. The atoms in the lattice interact via some potential, which differs according to the kind of material one is trying to model. Associated with a deformation is the elastic energy of the deformed lattice

$$H[\{y(x)\}_{x \in \mathcal{L}}] = \sum_{i,j} W_1\left(\frac{y_i}{h}, \frac{y_j}{h}\right) + \sum_{i,j,k} W_2\left(\frac{y_i}{h}, \frac{y_j}{h}, \frac{y_k}{h}\right) + \dots, \quad (1)$$

where $W_i, i = 1, 2, \dots$ are the interaction potentials, h is the equilibrium length, and $\{y_i\} \subset \mathcal{L}$. For examples of potentials, see [12]. Suppose we apply a deformation $y(x) = \mathbf{F}x$ to the boundary of \mathcal{L} where \mathbf{F} is a $n \times n$ matrix. We are interested in how all the atoms deform. Systems tend to stay in the state with the lowest energy, therefore the problem of finding the deformed configuration is a minimisation problem:

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

subject to

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

where

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

is the boundary of \mathcal{L} . Under this setting the Cauchy–Born rule can be stated as in [3] [5]:

Cauchy–Born Rule The minimiser to (1) is given by $y(x) = \mathbf{F}x$ for all $x \in \mathcal{L}$; that is, when a crystal is subjected to a deformation prescribed at the boundary then all atoms will follow this deformation.

One can then compute the elastic energy per unit volume

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

using the simpler formula

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

The validity of the Cauchy–Born rule is an important issue as it provides a simple way to calculate E which can be used to derive other quantities such as stress [7]. Friesecke and Theil [3] have studied the problem in the special case of a 2D square lattice interacting via harmonic potentials between nearest and next-nearest neighbours. They have shown that the Cauchy–Born rule is valid for certain parameters of spring constants and equilibrium lengths for \mathbf{F} in an open neighbourhood of $SO(2)$. They have also identified for certain sets of parameters the Cauchy–Born rule fails to give the minimiser. Conti et al. [5] generalised this to a d -dimensional cubic lattice under certain assumptions on H_{cell} (the energy required to deform a unit cell in the lattice). However, they have not provided any negative results. They have also remarked that proving the result for a general Bravais lattice is similar.

The work of the two above are concerned with global minimisers of the elastic energy. E and Ming [12] on the other hand, observed that fractured states can have lower energy than the Cauchy–Born state and hence considered local minimisers of the energy and proved that the Cauchy–Born rule is always valid for elastically deformed crystals which are only local minimisers of the energy in general. More precisely, they proved that under certain assumptions on the lattice and deformation, the minimiser (1) of the atomistic model is closely approximated by the minimiser of the energy in the Cauchy–Born model.

It is interesting to note that all of these results are in the setting of zero temperature and that the extension to non-zero temperature is an open problem.

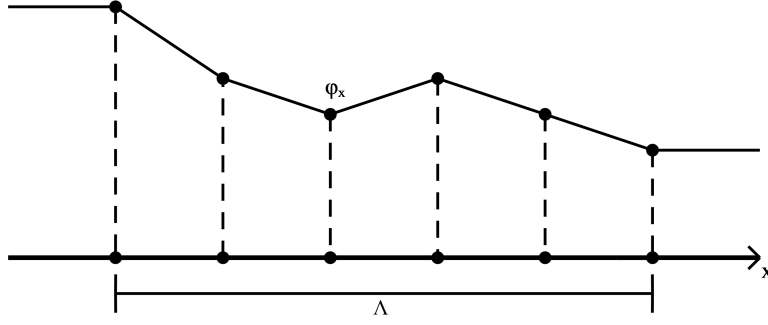


Figure 2: An interface in \mathbb{Z}

2.2 Statistical Mechanics

In this section, we concentrate on statistical mechanical models that describe the interface between co-existing phases (for example, water and ice at 0°C). In contrast to the previous section statistical mechanics is a probabilistic technique used for finite temperature systems.

Fix a (finite) reference lattice $\Lambda \subset \mathbb{Z}^d$ and a *configuration* $\varphi: \Lambda \rightarrow \mathbb{R}^m$ defined on the lattice. If $m = 1$, one can think of φ as specifying the position of the interface: for each site $x \in \Lambda$, we call $\varphi(x) =: \varphi_x \in \mathbb{R}$ the *height* of the interface at x . See Figure 2 for a visualisation. For $m = d$, we have an equivalent notion of viewing φ as defining a deformation of the reference lattice.

The *Hamiltonian*

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

represents the energy in the system, where $W: \mathbb{R}^d \rightarrow \mathbb{R}$ is the *interaction potential*, which we assume to be bounded from below and strictly convex. Here, Ψ denotes the boundary conditions of the lattice. That is, $\Psi = \varphi$ on the boundary $\partial\Lambda$. When one chooses an H that depends on differences in the heights of adjacent sites then the model is said to be *gradient-based*. The significance of such models shall be made clear below after we introduce further concepts.

The Hamiltonian is used to define the *Gibbs distribution*:

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

where Z_Λ^Ψ is the normalisation constant (called the *partition function*) that makes γ_Λ^Ψ a probability distribution, β is the inverse temperature and $\Lambda^c = \mathbb{Z}^d \setminus \Lambda$.

The quantity of interest for us in such systems is the *free energy*

$$F_\Lambda(\Psi) = -\frac{1}{\beta|\Lambda|} \log Z_\Lambda^\Psi. \quad (2)$$

The above equations pertain to finite lattices. We are interested in the thermodynamic limit; that is, we wish to take $\Lambda \rightarrow \mathbb{Z}^d$ and find expressions analogous to Gibbs distributions and free energy. These corresponding expressions are *Gibbs measures* and *specific free energy* respectively. We say that μ is a Gibbs measure at inverse temperature β if its conditional probability satisfies

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

for every finite $\Lambda \subset \mathbb{Z}^d$. This means that the Gibbs measure given the boundary conditions Ψ coincides with the Gibbs distribution γ . The specific free energy is given by taking the limit of the free energy (2) as $\Lambda \rightarrow \mathbb{Z}^d$.

We specified that the energy should depend only on gradients. This is because such models are invariant in the sense that if the interface is shifted up or down by a constant amount ($\varphi_x \rightarrow \varphi_x + c$, $c \in \mathbb{R}$, for all x), the energy does not change. This is a property exhibited by physical systems. Further to this constraint we also force W to be strictly convex with $0 < c_- \leq W''(x) < c_+ < \infty$ and $c_-, c_+ \in \mathbb{R}$. This is to ensure the existence of gradient Gibbs measures for all dimensions $d \geq 1$ [8], a fact which does not hold for general potentials.

For a detailed introduction to gradient Gibbs measure (with slightly different notation) see Chapter 1 in [6].

We now discuss the idea of *tilt* (called *slope* in [6]). This is a way of introducing certain types of boundary conditions. The lattice Λ has an associated average height $\mathbb{E}_\mu[\varphi_x] = h$. We can enforce a tilt $u \in \mathbb{R}^d$ by specifying the boundary condition $\varphi(x) = \Psi_u(x) = \langle u, x \rangle$ for all $x \in \partial\Lambda$.

In 2D, this corresponds to literally tilting the lattice so that it resembles a plane (see Figure 4). For example, it could be the case that all points at one edge are at their original position whilst points on the opposite edge have been shifted upwards by a constant factor. This tilting means that the average height will be increased by an amount depending on the projection of the tilted lattice onto the original lattice, so that the average difference in heights between adjacent sites is

$$\mathbb{E}_\mu[\varphi_x - \varphi_y] = \langle u, x - y \rangle.$$

The effect of the tilt is equivalent to modifying all of the heights φ_x , so we need to alter the untilted Hamiltonian to reflect this change. Sticking with gradient models, if W is the potential with no tilt then the potential with tilt u , W_u , is given by

$$W_{u_i}(\nabla\varphi) = W(\nabla_i\varphi - u_i).$$

Thus the partition function becomes

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

2.3 Coarse-Graining

To calculate expressions like the free energy (2), we need to evaluate an integral that may be difficult to compute because of large dimensions. To overcome this problem, we can use a technique called coarse-graining. Coarse-graining is used to find the average of an observable¹ A as given by (3). The free energy is not an observable, but its derivative is, so coarse-graining can still be used.

The coarse-graining approach aims to make $\mathbb{E}[A]$ easier to compute:

$$\mathbb{E}[A] = \frac{\int_{\Omega^N} A(u) \exp(-\beta H(u)) du}{\int_{\Omega^N} \exp(-\beta H(u)) du}. \quad (3)$$

In the case where A depends only on a subset of the N atoms we divide the set of atoms into the *repatoms* u_r (the atoms upon which A depends) and the *coarse-grained atoms* u_c . So we let $u = (u_r, u_c)$. We can now rewrite $\mathbb{E}[A]$ as

$$\mathbb{E}[A] = \frac{\int_{\Omega^{N_r}} A(u_r) \exp(-\beta H_{CG}(u_r)) du_r}{\int_{\Omega^{N_r}} \exp(-\beta H_{CG}(u_r)) du_r} \quad (4)$$

where

$$H_{CG}(u_r) = -\frac{1}{\beta} \log \int_{\mathbb{R}^{3N_c}} \exp(-\beta H(u_r, u_c)) du_c \quad (5)$$

¹An observable is a property of the system that can be determined experimentally.

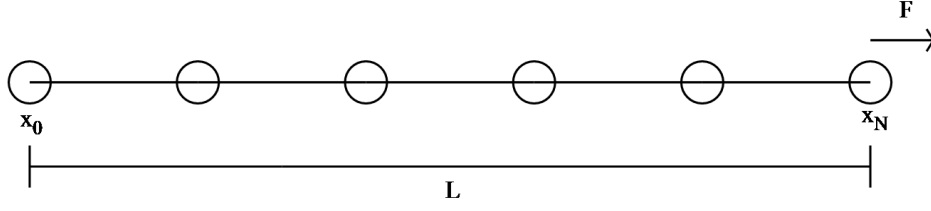


Figure 3: Applying a deformation \mathbf{F} to a rod

Provided we know H_{CG} then $\mathbb{E}[A]$ is cheap to calculate. The difficulty then arises in trying to calculate H_{CG} . Let $F_N(x) = \frac{1}{N}H_{CG}(x)$ be the free energy per particle. In the 1D case with nearest neighbour interactions under modest conditions on the potential W we have

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

with

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

and

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

See [14] for more details on the 1D case and [13] for details on the 2D case. It is also possible to calculate the canonical average. In the 1D setting, by using a change of variables and a central limit theorem we obtain

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

where

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

and

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

In the next-nearest neighbour case and the 2D setting it is still possible to find a x^* and y^* such that $\mathbb{E}[A] \approx A(x^* + y^*)$. Even though x^* and y^* are now more complicated they still only involve 1D integrals. In these cases a Markov chain approach is used and the theory for the 2D case is largely based on the fact that it holds in 1D. Consult [13] and [14] for more details.

3 Cauchy-Born Simulations

This section is not meant to be too demanding but is intended to be an introduction to methodology that is useful later. It should also give results that can be compared with bounds that are analytically established in further sections.

3.1 Zero Temperature Interactions

At zero temperature, there is no thermal contribution so the free energy is equivalent to the interaction energy. Suppose we have a rod of length L consisting of atoms u_0, \dots, u_N at positions x_0, \dots, x_N (see Figure 3). We fix one end of the rod and apply a deformation \mathbf{F} to the other end. Let the resulting deformed atoms be in positions y_0, \dots, y_N .

Nearest neighbour We start by simulating results for energy of one-dimensional systems with nearest neighbour interactions at zero-temperature. The energy of the deformed system is given by

$$H = \sum_{i=1}^N W\left(\frac{y_i - y_{i-1}}{h}\right), \quad (6)$$

where, for example, as in [14], we can choose $W(x) = \frac{1}{2}(x-1)^4 + \frac{1}{2}x^2$, which is convex and converges to infinity and $x \rightarrow \infty$, and h is the average spacing between two adjacent atoms in the original reference lattice.

Assuming that the deformation satisfies the assumptions of Cauchy–Born, we calculate the Cauchy–Born energy as (6) with $y_i - y_{i-1} = \frac{L\mathbf{F}}{N}$.

Question

- (ZT1) Calculate the free energy for the nearest neighbour interaction model with the Cauchy–Born rule and compare with molecular statics simulations for a range of deformations \mathbf{F} . *We expect a very small error between the Cauchy–Born energy calculations and the results from the molecular statics simulations.*

Next-nearest neighbour Let us now look for a comparison of the error between the molecular statics simulation and the energy given by the Cauchy–Born rule when we have next-nearest neighbour interactions, i.e., when the energy is of the form

$$H = \sum_{i=1}^N W_1\left(\frac{y_i - y_{i-1}}{h}\right) + \sum_{i=1}^{N-1} W_2\left(\frac{y_{i+1} - y_{i-1}}{h}\right),$$

where for example, as in [14], the potentials could be chosen to be $W_1(x) = \frac{1}{2}(x-1)^4 + \frac{1}{2}x^2$ and $W_2 = \frac{1}{4}(x-2.1)^4$. The authors chose W_2 of this form because it has a different equilibrium distance to W_1 , so there is some competition between the potentials. Similarly, W_2 converges to infinity as $x \rightarrow \infty$.

Questions

- (ZT2) Calculate the free energy for the next-nearest neighbour interaction model with the Cauchy–Born rule and compare with molecular statics simulations for a range of deformations \mathbf{F} . *The difference between the molecular statics approach and the energy calculated assuming the Cauchy–Born rule should increase as \mathbf{F} increases.*
- (ZT3) By making estimates on the error from the molecular statics approach derive an approximation for the order of the error between the molecular statics energy and the energy calculated using the Cauchy–Born rule.

3.2 Finite Temperature Cauchy–Born

We previously discussed the zero temperature Cauchy–Born rule. Now let us turn our attention to the finite temperature case. At non-zero temperature, we can no longer assume that lattice points are fixed due to thermal oscillations. We therefore need a method of incorporating the vibrational energy of lattice points into our model. In [7], the authors extended the original Cauchy–Born rule to finite temperatures under the further assumption that all atoms can be modelled as harmonic oscillators with frequencies independent of each other. The proposed extension states:

Finite temperature Cauchy–Born rule At a given temperature, when a deformation \mathbf{F} is applied to a solid, the lattice deforms homogeneously and each of the atoms has the same local vibration mode. The formula for free energy as given in [7] is

$$F_H(\mathbf{F}, T) = \int_{\Omega} E(\mathbf{F}) \, d\Omega + nk_B T \sum_{i=1}^{N_q} n_i^q \times \log \left(\frac{\hbar(\bar{D}(\mathbf{F}(X_i^q)))^{\frac{1}{2n}}}{2\pi k_B T} \right),$$

where n is the number of degrees of freedom of each atom, N_q is the number of quadrature points in the continuum model in which one quadrature point X_i^q represents n_i^q atoms, and \bar{D} is the determinant of the matrix that has its eigenvalues equal to the frequencies of the atoms.

In the case for fixed temperature and just one repatom X , this free energy formula simplifies to

$$F_H^T(\mathbf{F}) = \int_{\Omega} E(\mathbf{F}) \, d\Omega + C_0^T \times \log \left(C_1^T \bar{D}(\mathbf{F}(X))^{\frac{1}{2n}} \right), \quad (7)$$

where C_0^T and C_1^T are temperature dependent constants. The paper presents strong numerical evidence by way of comparisons to molecular dynamics simulations to validate this finite-temperature rule.

Questions

- (T1) Justify the assumptions the paper makes; are they physically relevant or pertinent to real systems?
- (T2) Based on your answer to (T1), is it feasible to change this model to be more realistic without excessive complications?
- (T3) For the 1D rod, simplify the free energy formula (7) for nearest neighbour and next-nearest neighbour interactions. Derive an explicit formula.

3.3 Finite Temperature Interactions

As with Section 3.1, we want to generalise our 1D rod to finite temperatures in nearest neighbour and next-nearest neighbour regimes. Using the background given in Section 2.2, we propose comparisons to be done of the temperature Cauchy–Born free energy with molecular dynamics simulations.

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} . *We expect a very small error between the temperature Cauchy–Born energy calculations and the results from the molecular dynamics simulations.*

- (FT2) Calculate the free energy for the next-nearest neighbour interaction model with the temperature Cauchy–Born rule and with molecular dynamics simulations for a range of deformations \mathbf{F} . *The difference between the molecular dynamics approach and the energy calculated assuming the temperature Cauchy–Born rule should increase as \mathbf{F} increases.*
- (FT3) By making estimates on the error from the molecular dynamics approach derive an approximation for the order of the error between the molecular dynamics energy and the energy calculated using the temperature Cauchy–Born rule.

4 Projects

4.1 Comparisons of Methods

For one of our main proposals, consider a regular 2D triangular lattice. We choose a triangular lattice because only nearest neighbour interactions need to be taken into account. We would like to compare free energy estimates as given by different methods. Specifically, compute the free energy using molecular dynamics, statistical mechanics, coarse-graining and the temperature Cauchy–Born rule. To do this, deform the lattice by stretching it in one coordinate direction and make the assumption that the Cauchy–Born rule holds, i.e., assume that the lattice deforms uniformly. For molecular dynamics, Cauchy–Born, and coarse-graining, we use a finite lattice, and for statistical mechanics, we use an infinite lattice. The interaction potential between atoms is nearest neighbour and quadratic. Notice that once we have the deformed lattice, we no longer require the original lattice for these calculations except for the statistical mechanics case.

Molecular dynamics Molecular dynamics is a computational technique where atoms in the lattice are simulated using the laws of classical physics. One can simulate the phase space trajectories, calculate the gradient of free energy and from this calculate the free energy using thermodynamic integration. This method is computationally expensive and simulating a large number of atoms is of excessive cost.

Statistical mechanics To calculate free energy in statistical mechanics, we use the formulae given above in Section 2.2. Unlike the other cases, as we are taking the thermodynamic limit we need to consider an infinite lattice. With an appropriate choice of interaction potential, the free energy can be calculated explicitly.

Coarse-graining As briefly discussed in Section 2.3, coarse-graining is an indirect way of calculating free energy. We cannot take free energy as our observable, however we can use the gradient of free energy. The canonical ensemble average for the gradient can be calculated using the results given in Section 2.3. The free energy is obtained by thermodynamic integration and averaging over non-repatom.

Temperature Cauchy–Born As mentioned above, at non-zero temperature atoms are no longer at a fixed position on the lattice due to thermal oscillations. A variant of the Cauchy–Born rule was introduced which can be used to model thermal effects. Given a certain temperature and a deformation of the lattice the temperature related Cauchy–Born rule assumes that the lattice deforms homogeneously, as in the zero temperature case, plus a further assumption that each of the atoms have the same vibration mode. The free energy is then given by (7).

Question

- (C1) Initially, consider the model where the potentials are zero on the boundary. We choose a potential which is quadratic and use a gradient model for ease of calculations and to guarantee the existence

of the partition function (and therefore the free energy). 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.

4.2 Analysis

4.2.1 Statistical Mechanics

In Section 2.2 we constrained the potential W to be strictly convex so that the partition function and the free energy exist. This is a sufficient condition to guarantee existence of gradient Gibbs measures, but it may not be necessary. On the other hand, for the free energy (2) to exist, clearly the Hamiltonian H needs to tend to infinity as $|x|$ tends to infinity, but whether this is sufficient is another question.

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 . For example, does the second derivative of W need to be bounded above? Are there other constraints it needs to satisfy? Is there a more general class of functions than those that are strictly convex?

4.2.2 Cauchy–Born

In questions (ZT1) – (ZT3) we discussed the error in the Cauchy–Born approximation for the 1D rod in the zero temperature case with nearest neighbour and next-nearest neighbour interactions. In the next-nearest neighbour case the Cauchy–Born hypothesis should hold on the interior of the rod but not near the boundary. So any error in assuming the Cauchy–Born rule will be in the boundary. This could be verified by running simulations with a larger number of atoms.

Question

- (A2) Is it possible to analytically derive a bound for the error between the Cauchy–Born approximation and the exact solution (assuming it exists)? Compare this bound to the simulations done in (ZT2) and the order of the error made in question (ZT3).

A more challenging problem is to consider the finite temperature case. Friesecke and Theil [3] showed the validity of the Cauchy–Born rule at zero temperature for a certain model in 2D when the deformation is close to $SO(2)$; we would like to investigate more closely the relationship of the distance to the SO group on the rule. You will probably have to make further assumptions when calculating the “true” value on the oscillations of the atoms (for example, assume that they are oscillating homogeneously).

Questions

- (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 to the $SO(2)$ group affects the validity of the Cauchy–Born rule.

4.3 Boundary Conditions

We want to compare free energy estimates in a 2D square lattice calculated by three different methods for the two cases of different boundary conditions described below.

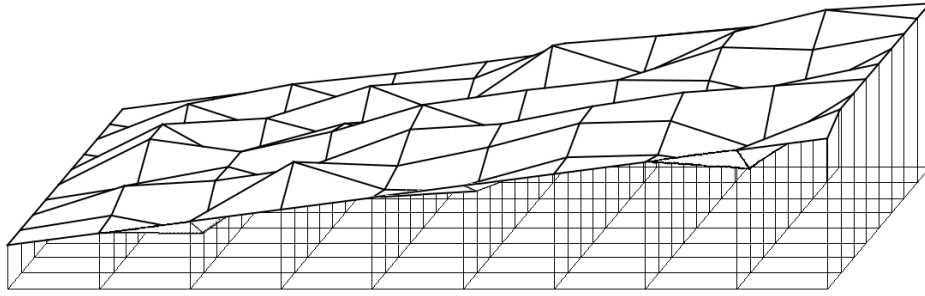


Figure 4: An interface in 2D showing tilt

Dirichlet boundary conditions We recommend starting with zero boundary conditions — this is easy to implement so we do not discuss it. For non-zero boundary conditions, in statistical mechanics, we apply a tilt u to the boundary such that the lattice deforms to a plane (i.e., fix one side to have zero boundary conditions and its opposite side to be non-zero on the boundary, and the other two boundaries connect linearly; see Figure 4). As with zero boundary conditions, coarse-graining and Cauchy–Born are easy to implement here.

Frozen lattice boundary conditions Here, the lattice is extended to infinity but such that the domain is restricted to a finite box, i.e., the outside of the box is “frozen”. Particles inside the box still interact with particles outside the box but we do not consider the exterior particles in our calculations. For coarse-graining, the integral remains the same but there is an extra term in the energy coming from the interactions of particles outside the box. We conjecture that the Cauchy–Born rule remains unchanged. In statistical mechanics, we have to include terms from interactions with particles outside the domain.

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.

5 Closing Remarks

In Section 3, we proposed changing the deformation \mathbf{F} whilst keeping the system size fixed. In further work, one could instead keep \mathbf{F} fixed whilst varying the system size and analyse the error bounds.

In Section 4.2, where we considered the temperature Cauchy–Born rule analytically, we suggested bounding the error in a system that can hopefully be explicitly solved. Depending on the difficulty of this, it might be feasible to extend the analysis from 1D to 2D lattices. If an analytic error bound is not derivable, molecular dynamics could be used to provide an estimate for the true value.

We neglected periodic boundary conditions in our comparisons, which could provide an extra source of problems.

Appendices

A Molecular Dynamics

Molecular dynamics is a widely used computational method for sampling the phase space trajectories and calculating the ensemble average of a thermodynamic quantity of interest over the simulated trajectories.

Consider a molecular system of N particles with positions given by $(x_1, \dots, x_N) = x \in \mathbb{R}^{3N}$ with pair potential interactions $W(x_i, x_j), i \neq j$ (for example the Lennard-Jones potential). To calculate thermodynamic quantities such as the free energy in the canonical ensemble setting, we want to sample from the Gibbs probability measure

$$d\mu(x) = Z^{-1} \exp(-\beta W(x)) dx.$$

To sample from μ we can use many techniques. In the main text of the proposal and the references the technique used for comparison is overdamped Langevin dynamics. To sample particle trajectories we use solutions of the following stochastic differential equation

$$dX_t = -\nabla W(X_t)dt + \sqrt{2\beta^{-1}} dB_t,$$

where B_t is $3N$ -dimensional Brownian motion. The basic idea is that if one allows the system to evolve in time indefinitely, that system will eventually pass through all possible states. If this is the case, experimentally relevant information concerning structural, dynamic and thermodynamic properties may then be calculated using a reasonable amount of computer resources. Because the simulations are of fixed duration, one must be certain to sample a sufficient range of phase space. Under suitable assumptions, we have the ergodic property

$$\lim_{T \rightarrow \infty} \int_0^T \phi(X_t) dt = \int \phi(x) d\mu(x)$$

for almost all initial conditions X_0 . One goal, therefore, of a molecular dynamics simulation is to generate enough representative states such that this equation is satisfied.

B Schedule

Tasks	Skills	Aim	Time	Useful sources
(ZT1) – (ZT3)	MS, CB, NN and NNN models, approximate bounds on error between MS and CB	Introduction to CB	1-2 days	[3], [12]
(T1) – (T3)	Derivation and discussion of finite temperature CB	Stating concisely finite temperature CB	1-2 days	[7]
(FT1) – (FT3)	Finite temperature CB, MD, approximate error bounds between MD and TCB	Repeat of (ZT1) – (ZT3) but in finite temperature setting. Uses results from (T1) – (T3)	1-2 days	Appendix A, [7]
(C1)	2D triangular lattice, TCB, coarse-graining, statistical mechanics and MD, comparison of errors	To compare different methods for calculating free energy on a 2D triangular lattice.	2 weeks	Appendix A, [13], [7], [2]
(A1)	Statistical mechanics, analysis	Investigating conditions on the potential to guarantee existence of the partition function and free energy.	2 weeks	[2] [8], [4]
(A2)	CB	In a system where an exact solution exists, compare the error between the CB approximation at zero temperature analytically. Comparison with (ZT2) – (ZT3)	2 weeks.	[5], [3]
(A3) – (A4)	Finite temperature CB, analytic error bounds	Try to determine an analytical bound on the error of the TCB approximation in terms of the distance to the $SO(n)$ group	3 weeks	[3], [7]
(BC1)	CB, statistical mechanics, coarse-graining	Comparing free energy for a variety of techniques for Dirichlet and frozen lattice boundary conditions	3 weeks	Appendix A [6]

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