Coarse Graining of Electric Field Interactions with Materials

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*Figure: http://www.themolecularuniverse.com/mile/mile1.htm
Overview of the talk

Goal and introduction

Continuum limit calculations

Multiscale formulation

Results

Discussions

Future work
Goal

1. Electrostatics in nanostructures

2. Electrostatics in random media

3. Multiscale method for ionic solids at finite temperature
Motivation

- Electrostatics interaction
  - Storage devices
  - Ferroelectric RAM
  - Piezoelectric sensors

- Finite temperature
  - Thermal fluctuations of atoms
  - Coupling of deformation, electric field with temperature

(a) Hard drive
(b) Ferroelectric RAM
(c) Piezoelectric sensor
Long range interactions

Energy density at $X = \int_{Y} G(X, Y) f(Y) dY$

Field at $X$ due to charge/dipole at $Y$  
Charge/dipole at $Y$

Charge distribution  
Quadrupole distribution  
Dipole distribution

$W \approx \sum_{r=1}^{\infty} \frac{1}{r} \times r^2 = \sum_{r=1}^{\infty} r$

$W \approx \sum_{r=1}^{\infty} \frac{1}{r^5} \times r^2 = \sum_{r=1}^{\infty} \frac{1}{r^3}$

$W \approx \sum_{r=1}^{\infty} \frac{1}{r^3} \times r^2 = \sum_{r=1}^{\infty} \frac{1}{r}$

Figure: Jason Marshall and Kaushik Dayal
Long range interactions...

Linear Elasticity
\[ W(\mathbf{x}) = \frac{1}{2} \varepsilon(\mathbf{x}) \cdot \mathbb{C} \varepsilon(\mathbf{x}) \]

Electrostatics
\[ W(\mathbf{x}) = \nabla \phi(\mathbf{x}) \cdot \nabla \phi(\mathbf{x}) \]
\[ \nabla \cdot \nabla \phi = \nabla \cdot \rho \]

Energy density depends on polarization field over whole material domain
Long range interactions...

\[ E = V(q) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{n} \frac{Q_i Q_j}{|q_i - q_j|} \]

Continuum limit of electrostatic energy

\[ E = V(q) + \frac{1}{2} \int_{\mathbb{R}^3} |\nabla \phi|^2 \]

\[ \nabla^2 \phi = \nabla \cdot \mathbf{p} \quad \in \mathbb{R}^3, \mathbf{p} = 0 \quad \in \mathbb{R}^3 - \Omega \]

\( \mathbf{p} \): polarization field in a material
Multiscale in a material

(a) macroscale

(b) atomic scale

Piezoelectric material

- Deformation is slowly varying field
- Displacement of charges cause change in electric field
- Change in electric field causes deformation of material
- Except near loading, variation of deformation field is at higher scale than the scale at which atoms displace
Multiscale method

Atomistic region

Coarse mesh as we move away from defect
We use interpolation for atoms within element
Finite temperature

➢ Observation of property at time scale >> time scale at which system change state

➢ Phase average → need probability distribution function $p$

➢ for each state → $p$ is the probability of system being at that state

$$f_{\text{observed}} := \int_{\Gamma} f(\mathbf{q}, \mathbf{p}) p(\mathbf{q}, \mathbf{p}) d\mathbf{q} d\mathbf{p} \quad p(\mathbf{q}, \mathbf{p}) = \exp\left[-\frac{H(\mathbf{q}, \mathbf{p})}{\beta T}\right]$$

Position of all atoms 
Momenta of all atoms
Length scales

- Continuum Length scale: $L$
- Size of material point: $\epsilon$
- Atomic spacing: $l$

Macroscopic field vary at the scale $\frac{\epsilon}{L}$

Interested in limit

- $\epsilon \ll L$ Fields vary at fine scale compared to size of material
- $l \ll \epsilon$ Atomic spacing is fine compared to scale at which fields vary
Continuum limit

\[ E_{\text{limit}} = \lim_{r \to \infty} \left\{ \frac{1}{\text{vol}(B_r(0))} \sum_{i,j} \Phi(x_i - x_j) \right\} \rightarrow \text{Average energy of atoms in Sphere } B_r(0) \]

Two equivalent approach

(a.) \( r \to \infty \) keeping \( l = 1 \) fixed
(b.) \( l \to 0 \) keeping \( r = 2 \) fixed

Scaled potential

\[ \Phi_l(\mathbf{x}) = \Phi \left( \frac{\mathbf{x}}{l} \right) \]
Continuum limit...

Energy of domain

\[ E(\Omega) \approx \text{vol}(\Omega) \times E_{\text{limit}} \]

Accuracy increases as \( \frac{\text{diam}(\Omega)}{l} \) increases
Electrostatics energy

\[ \rho : \Omega \times \mathbb{R}^3 \to \mathbb{R} \text{ charge density field} \]

Small scale dependence: \[ \rho_l(x, y) = \rho(x, y/l) \]

Electrostatics energy

\[ E = \sum_a E(a) \]

\[ E(a) = \left[ \text{energy due to interactions of charges within material point } a \right] \]
\[ + \left[ \text{energy due to interactions of charges outside material point } a \right] \]
Random media: Charge density field

- $\rho : \Omega \times \mathbb{R}^3 \times D \rightarrow \mathbb{R}$ random field
- Stationary: $\bar{\rho} : \Omega \times D \rightarrow \mathbb{R}$ such that $\rho(x, y, \omega) = \bar{\rho}(x, Ty\omega)$
- $\rho$ is ergodic
- Scaled charge density field:
  $$\rho_l(x, y, \omega) = \rho(x, y/l, \omega) = \bar{\rho}(x, Ty/l\omega)$$

We find later: Scaling is not correct

$$\text{need } \rho_l(x, y, \omega) = \frac{\rho(x, y/l, \omega)}{l}$$
Random media: Local energy

\[
E_{local} = \frac{4\pi}{3} \sum_{x \in \Omega_c} \epsilon^3 l^2 \left( \frac{1}{|B_{e/l}(x)|} \int_{z \in B_{e/l}(x)} \rho(x, z, \omega) h(x, z, \omega) dV_z \right)
\]

Ergodic theorem

We don't want energy to go to zero or infinity trivially

**Correct scaling**: \( \rho_l(x, y, \omega) = \frac{\rho(x, y/l, \omega)}{l} \)

*we had assumed earlier \( \rho_l(x, y, \omega) = \rho(x, y/l, \omega) \)
Random media: Non-local energy

After change of variable and dividing and multiplying \(vol(B_{\varepsilon/l}(x))vol(B_{\varepsilon/l}(x'))\)

\[
E_{\text{nonlocal}} = \left(\frac{4\pi}{3}\right)^2 \sum_{\substack{x, x' \in \Omega, \\ x \neq x'}} \varepsilon^6 \left(\frac{1}{l^2} \frac{1}{|B_{\varepsilon/l}(x)|} \frac{1}{|B_{\varepsilon/l}(x')|} \int_{\substack{z \in B_{\varepsilon/l}(x), \\ z' \in B_{\varepsilon/l}(x')}} \frac{\rho(x, z, \omega) \rho(x', z', \omega)}{|x +lz - x' -lz'|} dV_z dV_{z'}\right)
\]

Taylor's series expansion

\[
\frac{1}{|x +lz - x' -lz'|} = \frac{1}{|x - x'|} + \left[ \frac{\partial}{\partial y} \frac{1}{|y|}\right]_{y = x - x'} l \cdot (z - z') + \left[ \frac{\partial^2}{\partial y^2} \frac{1}{|y|}\right]_{y = x - x'} l^2 : (z - z') \otimes (z - z') + O(l^3)
\]

Zeroth order term

\[
\frac{1}{l^2} \left\{ \frac{1}{|B_{\varepsilon/l}(x)|} \int_{B_{\varepsilon/l}(x)} \rho(x, z, \omega) dV_z \right\} \times \left\{ \frac{1}{|B_{\varepsilon/l}(x')|} \int_{B_{\varepsilon/l}(x')} \rho(x', z', \omega) dV_{z'} \right\}
\]

Second order term

Goes to infinity, unless the term in bracket is zero

Charge neutrality condition

\[
\lim_{\varepsilon/l \to \infty} \frac{1}{|B_{\varepsilon/l}(x)|} \int_{B_{\varepsilon/l}(x)} \rho(x, z, \omega) dV_z = 0 \quad \forall x \in \Omega
\]

By Ergodic theorem

\[
E[\rho(x, y, \cdot)] = 0 \quad \forall x \in \Omega, y \in \mathbb{R}^3
\]
Random media: Result

Assume that $\rho$ is ergodic and stationary, and also satisfies charge neutrality condition. Let $\rho_l$ be scaled field. Then, electrostatics energy, in the limit is given by

$$
E = E_{local} + E_{nonlocal}
$$

$$
E_{local} = \mathbb{E} \left[ \int_{x \in \Omega} \left( \int_{\mathbb{R}^3} \frac{\rho(x, 0, \cdot) \rho(x, z', \cdot)}{|0 - z'|} dV_{z'} \right) dV_x \right]
$$

$$
E_{nonlocal} = \int_{x, x' \in \Omega, \frac{x}{x'} \neq x'} \mathbb{K}(x - x') : \hat{p}(x) \otimes \hat{p}(x') dV_x dV_{x'}
$$

where $\hat{p}(x)$ is dipole moment at $x$ and is independent of $\omega$.

$$
\hat{p}(x) = p(x, w) = \lim_{r \to \infty} \frac{1}{|B_r(x)|} \int_{z \in B_r(x)} \rho(x, z, \omega) z dV_z
$$
Nanostructures

- Cross-section is of few atomic thickness
- Long in axial direction
- Translational, and/or rotational symmetry

Nanostructure and macroscopically thick structures in a continuum limit

Nanotube Image: http://nano-bio.ehu.es/areas/nanostructures-and-nanotubes
**Nanostructures: Geometry**

- cross-section is \([0, l]^2\)
- Let \(Q\) be rotation and \(e_1\) be unit translation
- for periodic nanorod: \(Q = I\)

**Symmetry**
\[
\rho(x, Q^k y + k e_1) = \rho(x, y)
\]

**Scaling**
\[
\rho_l(x, y) = \rho(x, y/l)
\]

Correct scaling will be determined by condition that local energy is finite in the limit
Nanostructures: Result

\[ E = \int_{x \in \Omega} E_{\text{local}}(x) \, dx + \int_{x, x' \in \Omega, x \neq x'} E_{\text{nonlocal}}(x, x') \, dx \, dx' \]

\[ E_{\text{nonlocal}}(x, x') = \frac{q(x)q(x')}{|xe_1 - x'e_1|} = 0 \]

If net charge in unit cell is zero

Net charge \( q(x) := \int_{u \in xe_1 + [0,1]^3} \tilde{\rho}(x,u) \, dV_u = 0 \)

We assume there exist \( \tilde{\rho} \) such that

\[ \rho_l(x,y) = \frac{\tilde{\rho}(x,y/l)}{l^2} \]

No long-range interaction
Nanostructures/thin films behave differently

Field at $x$ due to dipole $d$ at origin is $K(x)d$\quad $K(x) = -\frac{1}{4\pi|\mathbf{x}|^3}\left\{I - 3\frac{\mathbf{x}}{|\mathbf{x}|}\otimes\frac{\mathbf{x}}{|\mathbf{x}|}\right\}$

Estimate of dipole energy for 1-D, 2-D and 3-D materials

\begin{align*}
W &= \sum_{r=1}^{\infty} \frac{1}{r^3} \times 1 = \sum_{r=1}^{\infty} \frac{1}{r^3} \\
W &= \sum_{r=1}^{\infty} \frac{1}{r^3} \times r = \sum_{r=1}^{\infty} \frac{1}{r^2} \\
W &= \sum_{r=1}^{\infty} \frac{1}{r^3} \times r^2 = \sum_{r=1}^{\infty} \frac{1}{r}
\end{align*}

At distance $r$ net dipole is 1

Along the circumference of circle of $r$, net dipole is $2\pi r$

At the surface of sphere of radius $r$, net dipole is $4\pi r^2$

Dipole field kernel decays fast for 1-D and 2-D materials
Phase average of a function

- $H(q, p)$: Hamiltonian of system
- $q$: position vector of all atoms
- $p$: momenta vector of all atoms
- $p_{exact}(q, p)$: exact probability density function
- $F_{exact}$: exact free energy
- $f(q, p)$: phase function

Canonical ensemble

- $\langle f \rangle = \frac{1}{N!h^{3N}} \int_T f(q, p)p_{exact}(q, p)dqd\mathbf{p}$
- $p_{exact}(q, p) = \frac{1}{Z_{exact}} \exp[-\frac{H(q, p)}{k_BT}]$
- $F_{exact} = -k_BT \log[Z_{exact}]$
Monte Carlo approximation

\( (q^0, p^0) \): initial state of system

For \((n + 1)^{st}\) step

Let \( (q, p) \) be randomly choosen state and \( x \) random number in \([0, 1]\)

\[
(q^{n+1}, p^{n+1}) = \begin{cases} 
(q, p) & \text{if } H(q, p) - H(q^n, p^n) \leq 0, \\
(q, p) & \text{if } H(q, p) - H(q^n, p^n) > 0 \\
(q^n, p^n) & \text{and } \exp\left[-\frac{H(q, p) - H(q^n, p^n)}{k_B T}\right] \geq x, \\
(q^n, p^n) & \text{if } H(q, p) - H(q^n, p^n) > 0 \\
(q^n, p^n) & \text{and } \exp\left[-\frac{H(q, p) - H(q^n, p^n)}{k_B T}\right] < x
\end{cases}
\]

\[
\langle f \rangle_{\text{Monte-Carlo}} = \frac{1}{N} \sum_{i=1}^{N} f(q^i, p^i) N p(q^i, p^i)
\]

**max-ent approach**

We use *max-ent* method developed by Kulkarni, Knapp and Ortiz*

1. **Mean position and mean momenta**
   \[
   \langle q_i \rangle = \bar{q}_i \\
   \langle |q_i - \bar{q}_i|^2 \rangle = 3\tau_i^2
   \]

2. **Maximum entropy principle \(\rightarrow\) Probability density function**
   \[
   S[p] = -\frac{k_B}{N!h^{3N}} \int_{\Gamma} p \log pd\Gamma
   \]

3. **Variational mean field theory \(\rightarrow\) minimization problem**
   \[
   F_p := \langle H(q, p) \rangle_p - TS[p] \geq F_{exact}
   \]

---

Minimization problem

Free energy

\[ F_p := F_p(\bar{q}, \omega, T) = \langle H \rangle_p - TS[p] = \sum_i \frac{3}{2} k_B T + \sum_i < V_i >_p + \sum_{i \neq j} \frac{1}{2} < \frac{Q_i Q_j}{|q_i - q_j|} >_p - \sum_i TS_i \]

Determine the mean state

\[
\min_{q,\omega} F_p(q, \omega; T) + F_{ext}(q, \omega; T)
\]

\[ \omega_i := \frac{\sigma_i}{\tau_i} \quad \text{mean frequency of atom } i \]

Assumption: quasi-static problem

\[ \bar{P}_i = 0 \]
Quasi-harmonic approximation

\[ V(\{q_i\}) = V(\{\bar{q}_i\}) + \sum \frac{\partial V(\{q_i\})}{\partial q_i} \bigg|_{q_i=\bar{q}_i} (q_i - \bar{q}_i) 
+ \frac{1}{2} \sum \frac{\partial^2 V(q)}{\partial q_i^2} \bigg|_{q_i=\bar{q}_i} (q_i - \bar{q}_i) \otimes (q_i - \bar{q}_i) \]

Phase average

\[ < V > = V(\{\bar{q}_i\}) + \frac{1}{2} \sum \frac{\sigma_i^2}{\omega_i^2} I : H_{ii} \]

For Coulombic interaction \( I : H_{ii} = 0 \)

\[ \min_{\omega} F_p(q, \omega, T) \Rightarrow \omega_i^2 = \frac{1}{3} I : H_{ii} \]

QC code

- Extended Jason Marshall’s code to finite temperature
- Object oriented
- New more efficient algorithm to compute phase average of EAM like potential

### Quasi-harmonic approximation: QC code

**Ar Lennard Jonnes**

<table>
<thead>
<tr>
<th>Size</th>
<th>Type</th>
<th>Constant a</th>
<th>Potential</th>
<th>Temperature</th>
<th>Initial freq.</th>
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<td>LJ 3.4</td>
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DB: node_quasi_1_load_number_00000.ptf.gz

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## Results

**Quasi-harmonic approximation: QC code**

**Ar Lennard Jonnes**

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<tr>
<th>Size</th>
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<td>100K</td>
<td>288.2</td>
</tr>
</tbody>
</table>

QC Code minimization

Analytical frequency
Frequency minimization

Frequency which minimizes free energy should be independent of initial value.

**Mesh:** 24x24x12 – 6x6x6

Initial frequency
1. 288.2
2. 230.5
3. 192.1
4. 164.7

**Mesh:** 8x8x8

Initial frequency
1. 576.3
2. 230.5
3. 192.1
4. 144.1
5. 115.1
6. 96.05
Frequency minimization

Mean frequency should increase with the temperature

Mesh: 8x8x8
Frequency minimization

Mean frequency should increase with the temperature

Mesh: 8x8x8

Mesh: 24x24x24-6x6x6

Temperature: \{10K, 20K, \ldots, 150K\}
Frequency minimization

Mean frequency should increase with the temperature

Mesh: 64x64x32-6x6x6
Temperature
{10K, 30K, 50K, 70K, 90K, 100K, 120K, 150K}

Mesh: 256x256x128-10x10x10
Temperature
{50K, 80K, 90K, 100K}
Frequency minimization: Discussion

\[ \omega = \frac{\sigma}{\tau}, \quad \sigma = \sqrt{2k_B T} \]

if \( \tau \) is very small

\( f_\omega \) due to entropy dominates and it is uniform

if \( \tau \) is very large

\( f_\omega \) due to interatomic potentials dominates and it is very large

we find that when initial frequency is such that \( f_\omega \) due to interatomic potential and entropy is of the same order the code converges.
Electrostatics implementation

For small $\tau$, phase average of energy would be very close to the energy at mean configuration!

Gallium nitride 6-lattice core-shell model

<table>
<thead>
<tr>
<th>Size</th>
<th>Type</th>
<th>Potential</th>
<th>Temperature</th>
<th>Initial freq.</th>
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<td>Constant a</td>
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<td>Wurtzite</td>
<td>Core-shell 6 lattice model*</td>
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<tr>
<td>2x2x2</td>
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## Electrostatics implementation

**NiAl: Artificial charge +1 at Ni and -1 at Al**

<table>
<thead>
<tr>
<th>Size (Atomistic)</th>
<th>Type</th>
<th>Constant Potential</th>
<th>Temperature</th>
<th>Initial freq.</th>
</tr>
</thead>
<tbody>
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<td>SC</td>
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<tr>
<td>2x2x2</td>
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</tbody>
</table>

Zero temp QC (Old Code)  
Finite temp QC (New code), $\tau = 0.001$

Discussion

No long range interactions in nanostructures and thin films
Agrees with Gioia and James calculation for thin film

In case of random media, we find that nonlocal energy, does not depend on fluctuations.

- Fluctuations are happening at the scale of $l$
- Whereas nonlocal energy is due to the interaction between material points which are $\epsilon$ apart.
- Coulombic interaction is linear.

Our QC calculation show that initial frequency should be in range such that frequency force from different interactions is of the same order

We also show that minimizing frequency is independent of initial frequency.

Point defects play an important role in semiconductor devices. We would like to model the single charge point defect in a large crystal and see how it interacts with surrounding.

The multi-scale formulation is for finite constant temperature problems. Doing non-equilibrium in a multiscale framework is still a challenge.

Groups like Tadmor group and Knapp group are working on this challenge.

For non-equilibrium temperature problem, we may have to revisit the ergodic and Stationary assumption on charge density field.

- If charge density field is not ergodic then computation of dipole moment \( p(x) \) is not clear.
- If there is a gradient of temperature, the charge density field may not be stationary, as stationarity requires that statistical properties, e.g. mean, should be independent of spatial location.
Future works...

Experiments can be carried out to find the critical ratio of length of nanotube to the size in cross-section, such that above the critical ratio, nanotube does not show long-range electrical interactions. This will be useful if the goal is to develop multiscale models for nanostructures.

We can also estimate the rate at which difference between actual electrostatics energy, and continuum limit of electrostatics energy, goes to zero with respect to ratio macroscopic length and atomic spacing.
Thank you!