Some Representative Issues in Multiscale Modeling

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Supported by DOE, ONR and NSF.
Plan

- General remarks
- Issues in coupled atomistic-continuum methods (boundary conditions, consistency, stability)
- Electronic structure analysis

Focus on multiscale, *multi-physics* modeling.
Traditional vs. multiscale approaches to modeling

Challenges

Electronic structure analysis

Linear and sublinear scaling algorithms
Example: Modeling of incompressible fluids

Conservation of mass:
\[ \nabla \cdot \mathbf{u} = 0 \]

Conservation of momentum:
\[ \rho \left( \frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla) \mathbf{u} \right) = \nabla \cdot \mathbf{\tau} \]

\[ \mathbf{\tau} = 3 \times 3 \text{ stress tensor which represents forces acting on surfaces due to molecular interaction.} \]

To close the system, need to express \(\mathbf{\tau}\) in terms of \(\mathbf{u}\).

Example: \(\mathbf{\tau} = -p \mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)\)

- Works well for simple fluids.
Complex fluids

Nightmare for complex fluids (e.g. polymer fluids).

- Too complicated.
- Too many parameters.
- No information about the conformation of the polymers.
Another class of examples: Local singularities

Example: The contact line problem

\[ \gamma_1 \quad \theta_s \quad \gamma_2 \]

Solid

Fluid 1 \quad \text{Fluid 2}

The static case: Young’s relation (partial wetting)

\[ \gamma \cos \theta_s = \gamma_1 - \gamma_2 \]
Difficulty for the moving contact line (MCL) problem: The Huh-Scriven singularity

Hydrodynamic equation (steady Stokes)

\[
\begin{cases}
-\eta_i \Delta u + \nabla p = f \quad \text{in } V_i \\
\nabla \cdot u = 0
\end{cases}
\]

No-slip boundary condition

interface condition

\[
\psi = r ((C \phi + D) \cos \phi + (E \phi + F) \sin \phi)
\]

\[
\nabla u \sim \frac{1}{r}, \quad \int |\nabla u|^2 dV = +\infty
\]

“corner singularity”

Infinite energy dissipation rate – certainly non-physical
The guessing game: ad hoc models

1. Navier boundary condition: \( \beta u_s = -\eta \partial_z u \)
2. zero tangential stress
3. \( u_s = \) prescribed profile, e.g. \( u_s = u_0 e^{-\frac{|x|}{s}} \)
4. diffusive interface model (phase-field)

Fluid 1
\[ u=0 \]
\[ u_z=0 \]
Fluid 2
\[ u=0 \]

Question: What is REALLY going on near CL?
These issues occur almost everywhere

- equation of state in gas dynamics
- collision cross-section in kinetic theory
- turbulence models
- stress-strain relation for solids
- plasticity models
- cohesive zone models for cracks
- empirical potentials in molecular dynamics
- crack dynamics
- triple junctions
- ......
Simple models may or may not work:

- Either: strike of a genius.
- Or: sweeping things under the rug.

Usually:

- works well for simple systems;
- becomes nightmare for complex systems.
Multi-physics philosophy

Develop a hierarchy of consistent models that can be used either

▸ individually, or

▸ simultaneously (coupled formulation).

Multi-physics hierarchy

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This philosophy is not new:

Classical examples:

- Quantum mechanics-Molecular mechanics methods (1975, Warshel and Levitt)
- Car-Parrinello molecular dynamics (1985, avoid empirical potentials, compute force fields directly from electronic structure information)
- Kinetic schemes (algorithms for gas dynamics based on kinetic theory).

What is new is the realization that multiscale, multi-physics modeling is a general concept. It is relevant to all areas of science, engineering and even technology.

Good for math: Specific applications and general principles.
Do not expect quick results

*Major difficulty*: Microscopic models, such as molecular dynamics and electronic structure models, are very poorly understood.
Traditional vs. multiscale approaches to modeling

Challenges

Electronic structure analysis

Linear and sublinear scaling algorithms
Molecular dynamics

\[ m_j \frac{d^2 x_j}{dt^2} = F_j = -\frac{\partial V}{\partial x_j} \]
Boundary conditions: Phonon reflection from MD simulation of solids

Dirichlet type of boundary condition is used.

Boundary conditions for MD and QM models

Super-cell: making things periodic.

Effect of boundary condition more pronounced due to the fact that we can only simulate rather small systems.

Imagine what would it be like if we only knew how to deal with periodic boundary conditions for PDEs.
Boundary condition for MD simulation of solids

Main objective: Use a small system to mimic the behavior of much larger system.

Obvious analogy with ABC (absorbing boundary condition for wave equation)

Key differences:

- Small $k$ expansion not enough, phonons exist for all $k$.
- Finite temperature: Also need to take phonons from the environment.
Problem formulation

Eliminate heat bath variables
The right perspective: Mori-Zwanzig formalism

A simple linear example

\[
\frac{dp}{dt} = A_{11}p + A_{12}q,
\]
\[
\frac{dq}{dt} = A_{21}p + A_{22}q.
\]

Objective: Obtain a closed model for \( p \).

\[
q(t) = e^{A_{22}t} q(0) + \int_0^t e^{A_{22}(t-\tau)} A_{21} p(\tau) \, d\tau.
\]

\[
\frac{dp}{dt} = A_{11}p + A_{12} \int_0^t e^{A_{22}(t-\tau)} A_{21} p(\tau) \, d\tau + A_{12} e^{A_{22}t} q(0)
\]
\[
= A_{11}p + \int_0^t K(t - \tau) p(\tau) \, d\tau + f(t),
\]

- \( K(t) = A_{12} e^{A_{22}t} A_{21} \) is the memory kernel
- \( f(t) = A_{12} e^{A_{22}t} q(0) \) is the noise term, if we think of \( q(0) \) as a random variable.
General Mori-Zwanzig formalism

1. Projection operator (conditional expectation),

\[ \mathcal{P} g = E(g|\text{retained variables}), \quad Q = I - \mathcal{P}. \]

2. For any function of the retained variables: \( \varphi \),

\[ \frac{d}{dt} \varphi(t) = e^{tL} L \varphi(0) = e^{tL} \mathcal{P} L \varphi(0) + e^{tL} Q L \varphi(0), \]

3. Dyson’s formula,

\[ e^{tL} = e^{tQL} + \int_0^t e^{(t-s)L} \mathcal{P} L e^{sQL} ds. \]

4. Generalized Langevin equation:

\[ \frac{d}{dt} \varphi(t) = e^{tL} \mathcal{P} L \varphi(0) + \int_0^t e^{(t-s)L} K(s) ds + R(t). \]

\[ R(t) = e^{tQL} Q L \varphi(0), \quad K(t) = \mathcal{P} L R(t). \]

Recent literature: Chorin et al. on “Optimal prediction”.
- Universal strategy for eliminating degrees of freedom.
- By itself, it is almost useless. The key is to make approximations.
Mori-Zwanzig formalism for MD (Xiantao Li and E)

Partition of the system: \( \mathbf{u} = (\mathbf{u}_I, \mathbf{u}_J), \quad \mathbf{v} = (\mathbf{v}_I, \mathbf{v}_J) \)

The thermodynamic force: \( e^{t \mathcal{L}} \mathcal{P} \mathcal{L} \mathbf{v}_I(0) = -\frac{\partial W}{\partial \mathbf{u}_I} \).

The effective free energy:

\[
W(\mathbf{u}_I, T) = -k_B T \ln Z, \quad Z = \int e^{-\frac{V(\mathbf{u}_I, \mathbf{u}_J)}{k_B T}} d\mathbf{u}_J,
\]

The memory term: \(- \int_0^t \Theta(\tau) \mathbf{u}_I(t - \tau) d\tau.\)

The generalized Langevin equation:

\[
m \ddot{\mathbf{u}}_I = -\nabla_{\mathbf{u}_I} W - \int_0^t \Theta(\tau) \mathbf{u}_I(t - \tau) d\tau + R(t) + f^{\text{ex}}(t).
\]
Example:

\[
\begin{align*}
\ddot{u}_j &= \phi'(u_{j+1} - u_j) - \phi'(u_j - u_{j-1}) \\
\dot{u}_j &= u_{j+1} - 2u_j + u_{j-1}, \quad j \leq 0.
\end{align*}
\]
Example:

\[ \ddot{u}_0 = \phi'(u_1 - u_0) - \int_0^t \theta(\tau) \dot{u}_0(t-\tau) \, d\tau + R. \]

\[ \theta(t) = \frac{J_2(2t)}{t}. \]
Local memory kernels

(E and Huang, 2001; Li and E, 2006–2007)

- the memory kernel is independent of the temperature
- at zero temperature, similar to absorbing BC for wave equations

Basic principles:

1. Efficiency: local kernels
2. Stability: positive-definite kernels
3. Consistency: fluctuation-dissipation theorem
Variational approach at $T = 0$

*Given the stencil (cost), find the best approximate kernels.*
Note the lack of a small parameter.

1. Express $\Theta(t)$ in the form of,

$$\Theta(t) = \int_{-\infty}^{+\infty} \Gamma(s) \Gamma(t + s)^T ds.$$ 

$\Gamma(t)$ is local:

$$\Gamma_{ij}(t) = 0, \text{ if } |\mathbf{r}_i - \mathbf{r}_j| > r_c, \text{ or } |t| > t_c.$$ 

2. Objective functions

$$\min_{\Gamma(t)} \int e(\omega; \Gamma) W(\omega) d\omega.$$ 

3. Choose the functional: e.g. Total energy of reflected phonons.
Sample the random noise

The random noise \( R(t) \) is a stationary Gaussian process. The fluctuation-dissipation theorem is satisfied:

\[
\langle R(t)R(0)^T \rangle = k_B T \Theta(t).
\]

Let \( W(t) \) be white noise with variance \( k_B T \), then,

\[
R(t) = \sum_k \int \Gamma(s)W(t - s)ds.
\]
Case studied 1: fracture simulation

Fixed boundary condition.  
Variational boundary condition.
Case studied 2: finite temperature in 3D BCC Iron

System temperature.

Velocity autocorrelation.
Case studied 3: finite temperature crack simulation

At zero temperature
Case studied 3: finite temperature crack simulation

At finite temperature 500K
Comparison with the idea of using border region.
Consistency between the MD and the continuum model

Outside region (eliminated region) is not just a heat bath, but a piece of material modeled by continuum equations (with a temperature field).

Will look at a special case:
Quasicontinuum method (Tadmor et al. 1996)

- Temperature = 0
- No dynamics
Quasicontinuum method

- An adaptive mesh and model refinement procedure
- Based on linear finite elements
- Representative atoms define the triangulation
- Near defects, the mesh becomes fully atomistic
- Local (continuum) and nonlocal (atomistic) regions
Consistency

- Consistency in the bulk: For simple systems, the two models should produce consistent results.
- Consistency at the local-nonlocal interface.
Consistency between atomistic and continuum models

Nonlinear elasticity theory:

\[ E(u) = \int_{\Omega} W(\nabla u) \, dx \]

\( W(\cdot) = \) stored energy density.

In linear elasticity, \( W = \) a quadratic function of \( \nabla u \).

\[ E(\{y_1, \cdots, y_N\}) = \sum_{i,j} V_2(y_i, y_j) + \sum_{i,j,k} V_3(y_i, y_j, y_k) + \cdots \]

Question: Can we relate \( W \) to the atomistic model?
The Cauchy-Born rule

Given $A$, a $3 \times 3$ matrix, $W(A) =$?

Deform the crystal uniformly: $\mathbf{y}_j = \mathbf{x}_j + A\mathbf{x}_j = (I + A)\mathbf{x}_j$

$W(A) =$ energy density of deformed unit cell, computed according to the given atomistic or electronic structure model.
Application: The local Cauchy-Born rule

- Left: Compression of Carbon nano-tube computed using the atomistic model (Tersoff potential).
- Right: Same problem computed using a continuum nonlinear elasticity model derived using the local Cauchy-Born rule (Jerry Yang and W. E).
Validity of Cauchy-Born rule: Consistency

One dimension model: $x_k = k\epsilon$.
Assume: $y_k = x_k + u(x_k)$ and $u$ is a smooth function.

$$V = \frac{1}{2} \sum_{i \neq k} V_0(y_i - y_k)$$

$$\approx \frac{1}{2} \sum_i \left( \sum_{k \neq i} V_0(1 + \frac{du}{dx}(x_i)) k\epsilon \right)$$

$$= \sum_i W \left( \frac{du}{dx}(x_i) \right) \epsilon \approx \int W \left( \frac{du}{dx}(x) \right) dx,$$

where

$$W(A) = \frac{1}{2\epsilon} \sum_k V_0((1 + A)k\epsilon)$$

Validity of Cauchy-Born rule: Counterexample

Example: Lennard-Jones potential, next nearest neighbor interaction

- Triangular lattice, Cauchy-Born rule is valid
- Square lattice, Cauchy-Born gives negative shear modulus (unstable), can’t speak of elasticity theory.
Validity of Cauchy-Born rule: Stability

- **Continuum** level (Born criteria) – *Elastic stiffness tensor* is positive definite

- **Atomic** level (Lindemann criteria) – *Phonon spectra* (dispersion relation for the lattice waves) remain “positive definite”

- **Electronic** level – Dispersion relation for the *charge-density waves* and *spin waves*
Phonons: Dispersion relation of lattice waves

Linearization at the undeformed or uniformly deformed states

\[ m \frac{d^2 y_j}{dt^2} = -\frac{\partial V}{\partial y_j} = V'(y_{j+1} - y_j) - V'(y_j - y_{j-1}), \]

Let \( y_j = j \varepsilon + \tilde{y}_j \), linearizing the above equation, we get

\[ m \frac{d^2 \tilde{y}_j}{dt^2} = V''(\varepsilon)(\tilde{y}_{j+1} - 2\tilde{y}_j + \tilde{y}_{j-1}). \]

Let \( \tilde{y}_j(k) = e^{i(k x_j - \omega t)} \), we obtain

\[ \omega^2(k) = \frac{4}{m} V''(\varepsilon) \sin^2 \frac{k \varepsilon}{2}, \]

where \( k = \frac{2\pi \ell}{M \varepsilon} \) with \( \ell = -\lfloor M/2 \rfloor, \ldots, \lfloor M/2 \rfloor \).
Phonon spectra

Acoustic branch: dynamics of the Bravais lattice

Optical branch: relative motion of the internal degrees of freedom

1st Brillouin zone: Voronoi cell of the origin of the dual lattice
Under these conditions, the Cauchy-Born continuum model and the atomistic model are consistent.

- E and Ming (2007), molecular mechanics models.
- E and Lu (2008), several classes of quantum mechanics models.

These conditions are sharp!!
Violation of the stability conditions signals onset of plastic deformation or structural (or electronic) phase transformation.

Similar conditions given by Ju Li, Sidney Yip
Ryan Elliott
Consistency at the loca-nonlocal interface

The issue of “ghost force” (e.g. in quasicontinuum methods)

- **Left side:** using continuum model based on the Cauchy-Born rule (effectively a nearest neighbor model).
- **Right side:** Using full atomistic model, next nearest neighbor interaction.
1. The deformation gradient has $\mathcal{O}(1)$ error at the interface.
2. The influence of the ghost force decays exponential fast away from the interface.
3. Away from an interfacial region of width $\mathcal{O}(\varepsilon |\log(\varepsilon)|)$, the error in the deformation gradient is of $\mathcal{O}(\varepsilon)$ (see also recent work of Dobson and Luskin).
\[ \hat{y}_\varepsilon \equiv y_{qc} - x. \]

\[ f(z) = 14 + 5z, \quad g(z) = 11 + 4z, \quad \gamma = g(\omega_1) + \beta g(\omega_2) \]

\[ \omega_1 = (3 + \sqrt{5})/2, \quad \omega_2 = -(3 + \sqrt{5})/2 \]

\[ \hat{y}_i^\varepsilon = \begin{cases} 
(i + N)\gamma + \alpha f(\omega_1) + \beta f(\omega_2) + \alpha \omega_1^{i+N} + \beta \omega_2^{i+N}, & \text{if } i = -N, \ldots \\
(i - N - 1)\gamma & \text{if } i = 1, \ldots, N 
\end{cases} \]

Define: \[ D^+ y_i = (y_{i+1} - y_i)/\varepsilon, \]

\[ D^+ \hat{y}_i^\varepsilon = \begin{cases} 
\frac{\gamma}{\varepsilon} + \frac{\alpha}{\varepsilon} \omega_1^{i+N} (\omega_1 - 1) + \frac{\beta}{\varepsilon} \omega_2^{i+N} (\omega_2 - 1), & \text{if } i = -N, \ldots \\
- \frac{2\gamma}{N} - \frac{\alpha f(\omega_1) + \beta f(\omega_2)}{\varepsilon} - \frac{\alpha \omega_1^N + \beta \omega_2^N}{\varepsilon}, & \text{if } i = 0, \\
\gamma/\varepsilon, & \text{if } i = 1, \ldots, N 
\end{cases} \]
Removing the ghost force

Ghost force may induce numerical artifacts (e.g. plastic deformation) at the interface.

- Force-based approach (Tadmor et al.)
- Quasi-nonlocal atoms (Jacobson et al.)
- Geometrically consistent scheme (E, Lu and Yang)

Classical numerical analysis viewpoint:
- Truncation error $= O(\varepsilon)$ in a weak sense
- Stability conditions (similar to the ones discussed above)
Uniform $O(\varepsilon)$ accuracy for smooth solutions.
Ghost force for the coupled OF-DFT/EAM method
(Choly, Lu, E, Kaxiras)
Loss of fluctuations

Example: Coupled KMC-continuum models of epitaxial crystal growth (Schulze, Smereka and E):

- Around the step-edges, use KMC, since fluctuations are important
- On the terraces, use continuum (e.g. diffusion) models
Mean position and variance of step edge

Figure 6: The time and space averaged surface adatom density for the KMC simulations (diamonds) and the hybrid scheme (crosses) using cell-widths \( M = \{20, 25, 40\} \).

Figure 7: The standard deviation (in time) of the surface averaged adatom density as a function of the ratio \( D/F \). The solid curve (diamonds) are from the KMC simulations and the remaining curves are for the hybrid scheme with cell-widths \( M = \{20, 25, 40\} \) sites per cell.

Other examples: See work of Garcia, Bell and Doney, et al.
Stability of coupled continuum/MD methods

Work of Weiqing Ren (NYU)

- Example of fluids
- General strategy: Domain decomposition (with overlap)
- Coupling:
In continuum region (I, III): \( \rho u_t - \mu u_{zz} = 0 \)

In particle region (II): \( m \frac{d^2x_j}{dt^2} = f_j \)

Four coupling schemes:
1. velocity(MD)-velocity(C),
2. velocity(MD)-flux(C),
3. flux(MD)-velocity(C),
4. flux(MD)-flux(C)
Particular features as a domain decomposition method

- The MD (molecular dynamics) domain is very small.
- Statistical error cannot be avoided
Numerical solutions for equilibrium states

Upper panel: velocity-velocity
Lower panel: flux-velocity

Upper panel: velocity-flux
Lower panel: flux-flux
Steady-state calculation: $T_c = \infty$

Amplification factors $k$ for the four schemes:

- velocity-velocity, flux-velocity

$$u_n(z) = \sum_{i=1}^{n} k^{n-i} \xi_i \frac{1-z}{1-a}, \quad \langle \| u_n \|_2 \rangle \leq \left( \frac{1}{3(1-k^2)} \right)^{1/2} \sigma_v$$

$\xi_i$: Statistical errors in velocity BC; $\sigma_v = \langle \xi_i^2 \rangle$

$k = \frac{a(1-b)}{b(1-a)}$ for velocity-velocity; $k = \frac{a}{a-1}$ for flux-velocity

- velocity-flux, flux-flux

$$u_n(z) = \sum_{i=1}^{n} k^{n-i} \xi(z-1)$$

$k = \frac{b-1}{b}$ for velocity-flux; ($k > 1 \rightarrow$ Diverge)

$k = 1$ for flux-flux $\rightarrow \langle \| u_n \|_2 \rangle \leq 3^{-1/2}(1 - a)n^{1/2}\sigma_T$
Stability: Finite $T_c$

**Figure:** The amplification factor $k$ versus $T_c/\Delta t$ for the four schemes: VV (squares), FV (diamonds), VF (triangles) and FF (circles).
Summary:

- There are many different variants of atomistic/continuum coupling schemes.
- Errors and artifacts difficult to understand.
- What I have described are examples of efforts to try to put things on a solid foundation.

Other related work: Gunzburger et al., Lehoucq et al., W. K. Liu et al., W. Cai et al.
Traditional vs. multiscale approaches to modeling

Challenges

Electronic structure analysis

Linear and sublinear scaling algorithms
Density functional theory (Kohn and Sham, 1965)

\[ \{ \psi_k = \psi_k(\mathbf{y}), k = 1, \cdots, N \} = \text{A set of } N \text{ orthonormal orbitals:} \]

\[ l_\varepsilon(\{\psi_k\}) = \varepsilon^2 \sum_{k=1}^{N} \int_{\mathbb{R}^3} |\nabla \psi_k(\mathbf{y})|^2 \, d\mathbf{y} + \int_{\mathbb{R}^3} \epsilon_{xc}(\rho)\rho(\mathbf{y}) \, d\mathbf{y} \]

\[ + \frac{\varepsilon}{2} \int \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{(\rho - m)(\mathbf{y})(\rho - m)(\mathbf{y}')}{|\mathbf{y} - \mathbf{y}'|} \, d\mathbf{y} \, d\mathbf{y}'. \]

\[ \varepsilon = \text{atomic length scale, e.g. the lattice constant.} \]

\[ \rho(\mathbf{y}) = \sum_k |\psi_k|^2(\mathbf{y}) \text{ is the electron density.} \]

Input to the model: The atoms. \( m(\mathbf{y}) = \sum_{\mathbf{y}_i \in \mathcal{E} \cap \Omega} m^a_i(\mathbf{y} - \mathbf{y}_i) = \) (pseudo)-ionic potential (describing the atoms in the system).

- \( \{ \mathbf{y}_j \} = \text{positions of the nuclei (ions).} \)
- \( \{ m^a_j \} = \text{describe the types of atoms} \)
Illustration: Al in the presence of vacancy

C. Garcia, J. Lu and W. E
Some basic issues

- What is the right formulation?
- Metals vs. insulators?
- Asymptotics?
- Behavior of solutions?
- Stability issues?
- Relations between different models?
- Better functionals?
Algorithmic issues

- Linear scaling algorithms?
- Accuracy?
- Using asymptotics to develop algorithms?
- Convergence of nonlinear iterations?
Relevance

- Energy issues (e.g. band-gap of materials)
- Materials (peculiarity at the nano-scale, chemistry-motivated materials, molecular electronics)
Ansatz (first variable is Eulerian, second is Lagrangian):

\[
\psi_\alpha(y, \frac{x}{\varepsilon}) = \frac{1}{\varepsilon^{3/2}} \psi_{\alpha,0}(y, \frac{x}{\varepsilon}) + \frac{1}{\varepsilon^{1/2}} \psi_{\alpha,1}(y, \frac{x}{\varepsilon}) + \varepsilon^{1/2} \psi_{\alpha,2}(y, \frac{x}{\varepsilon}) + \cdots
\]

\[
\rho(y, \frac{x}{\varepsilon}) = \frac{1}{\varepsilon^3} \rho_0(y, \frac{x}{\varepsilon}) + \frac{1}{\varepsilon^2} \rho_1(y, \frac{x}{\varepsilon}) + \frac{1}{\varepsilon} \rho_2(y, \frac{x}{\varepsilon}) + \cdots
\]

\[
\phi(y, \frac{x}{\varepsilon}) = \phi_0(y, \frac{x}{\varepsilon}) + \varepsilon \phi_1(y, \frac{x}{\varepsilon}) + \varepsilon^2 \phi_2(y, \frac{x}{\varepsilon}) + \cdots
\]

\(\psi_\alpha(y, z)\) decays for large \(z\)

\(\rho(y, z)\) and \(\phi(y, z)\) are periodic in \(z\).

Electron density distribution of Al
Leading order: Electronic structure of a uniformly deformed infinite lattice

\[ \{ \psi_\alpha \}, \text{ where } \alpha \text{ numbers the valence electrons in a unit cell.} \]

\[ \nabla_1 = \nabla_y, \nabla_2 = \nabla_z. \]

\[ - \Delta_2^x \psi_{\alpha,0}(y, z) + V_{xc,0}(\rho_0) \psi_{\alpha,0}(y, z) - \phi_0(y, z) \psi_{\alpha,0}(y, z) \]

\[ + \sum_{\alpha', z_j \in L} \lambda_{\alpha\alpha', 0}(y) \psi_{\alpha',0}(y, z - z_j) = 0; \]

\[ - \Delta_2^x \phi_0(y, z) = 4\pi (m_0 - \rho_0)(y, z); \]

\[ \int_{\mathbb{R}^3} \psi_{\alpha,0}(y, z) \psi_{\alpha',0}(y, z - z_j) \, dz = \delta_{\alpha\alpha'} \delta_{0j} / \det(I + \nabla u(x)). \]

\[ \Delta_2^x = ((I + \nabla u(x))^{-1}) \nabla_2)^2, \text{ the coefficients come from the coordinate change, } y = x + u(x). \]

- This is a system of equations in \( z \) – the fast variables. \( y \) enters only as parameters.

- It is a periodic system, but the equation is formulated over the whole space.
The continuum limit and the Cauchy-Born rule

\[ E(u) = \int_{\Omega} W_{\text{CB}}(\nabla u(x)) \, dx \]

Variational formulation

\[ W_{\text{CB}}(A) = \inf_{\{\psi\}} W(A, \{\psi_\alpha(\cdot; A)\}) = \inf_{\{\psi\}} \frac{\det(I + A)}{|\Gamma|} I_A(\{\psi\}) \]

\[ I_A = \sum_\alpha \int_{\mathbb{R}^3} |(I + A)^{-T} \nabla \psi_\alpha(z; A)|^2 \, dz + \int_{\Gamma} \varepsilon_{xc,0}(\rho(z; A))\rho(z; A) \, dz \]

\[ + \frac{1}{2} \int \int_{\Gamma \times \Gamma} (\rho - m_{\text{CB}})(z; A) G(z - z'; A)(\rho - m_{\text{CB}})(z'; A) \, dz \, dz'. \]

\[ \Gamma = \text{unit cell}, \ G \text{ is the periodic Green's function.} \]
Next order equations:

\[- \Delta_2^x \psi_{\alpha,1}(y, z) + V_{xc,0}(\rho_0) \psi_{\alpha,1}(y, z)\]
\[+ V_{xc,1}(\rho_0, \rho_1) \psi_{\alpha,0}(y, z) - \phi_0 \psi_{\alpha,1}(y, z) - \phi_1 \psi_{\alpha,0}(y, z)\]
\[+ \sum_{\alpha', z_j \in L} \left( \lambda_{\alpha \alpha' j, 0} \nabla_1 \psi_{\alpha', 0}(y, z - z_j)(I + \nabla u) \cdot z_j \right) \]
\[+ \lambda_{\alpha \alpha' j, 0} \psi_{\alpha', 1}(y, z - z_j) + \lambda_{\alpha \alpha' j, 1} \psi_{\alpha', 0}(y, z - z_j) \right) = 0;\]
\[- \Delta_2^x \phi_1(y, z) = 4\pi(m_1(y, z) - \rho_1(y, z));\]
\[\int_{R^3} \psi_{\alpha,0}(y, z) \psi_{\alpha', 1}(y, z - z_j) \]
\[+ \psi_{\alpha,0}(y, z) \nabla_1 \psi_{\alpha', 0}(y, z - z_j)(I + \nabla u) \cdot z_j \, dz = 0.\]

Again, this is a set of equations in the fast variable. Differentiation in $y$ only enters through the forcing term in the constraint equation.
Traditional vs. multiscale approaches to modeling

Challenges

Electronic structure analysis

Linear and sublinear scaling algorithms
Linear scaling algorithms

Cost $\sim$ number of degrees of freedom

Examples:
- Multi-grid method
- Fast multipole method
- Linear scaling algorithms in electronic structure analysis
- ......
Sublinear scaling algorithms

Cost $\ll$ number of degrees of freedom (in the microscopic) model

- Quasicontinuum method
- AtC methods

Most multiscale methods are sublinear scaling algorithms.
Sub-linear scaling algorithm for electronic structure analysis

García-Cervera, Lu and E (2007)

Electron density distribution of Al in the presence of vacancies

A slice of the electron density (modulated problem).
An analogy: Wave propagation and geometric optics

\[ \partial_t^2 u = C(x)^2 \Delta u; \]

\[ u(x, 0) = A_0(x)e^{i\frac{\phi_0(x)}{\epsilon}}. \]

Solving the wave equation directly: \( O(\epsilon^{-1}) \) operations (linear scaling algorithm).
Geometric optics approximation:

Ansatz: \( u(x, t) = A(x, t) \exp \left( i \frac{\varphi(x, t)}{\epsilon} \right) + \cdots \)

\[
\partial_t \varphi + C(x) |\nabla \varphi| = 0;
\]

\[
\partial_t A + C(x) \frac{\nabla \varphi \cdot \nabla A}{|\nabla \varphi|} + \frac{C(x)^2 \Delta \varphi - \partial^2_t \varphi}{2C(x)|\nabla \varphi|} A = 0.
\]

Solving these equation require \( O(1) \) (independent of \( \epsilon \)) operations.

In the general case, solve these limit equations away from caustics, and solve the original problem near caustics. This requires \( o(\epsilon^{-1}) \) operations, hence sub-linear scaling algorithm.

Combine asymptotic analysis and numerical methods
Some open questions

- Consistency in the presence of fluctuations
- Accuracy of QM-MM methods (even at $T=0$)
- Accuracy analysis for linear scaling methods for DFT
Concluding remarks

- Multiscale modeling is a way of introducing RIGOR into the modeling process.
- Some of the fundamental challenges are mathematical in nature.
- More efforts needed to better understand microscopic models, such as electronic structure models, molecular dynamics and Monte Carlo methods.

1. Introduction
2. Analytical methods
3. Multiscale representation
4. Classical multiscale algorithms
5. The hierarchy of physics models
6. Examples of multi-physics models
7. Capturing the macroscale behavior
8. Resolving local events and singularities
9. Elliptic equations with multiscale coefficients
10. Rare events