Multiscale Modeling

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Outline

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Introduction

- Physical systems can be modeled at different levels of detail:
  - Continuum mechanics, e.g., Navier-Stokes equations, Continuum Elasticity.
  - Kinetic Theory, e.g., Boltzmann equation.
  - Molecular Dynamics.
  - Quantum Mechanics, e.g. Schrödinger equation, DFT, GW, etc.
- Full solution impractical/undesirable.
- Objectives of Multiscale Modeling:
  - Analytical connection between different levels.
  - Systematic coarse-graining: Error control.
  - Development of efficient numerical methodologies.

Types of Multiscale Problems

A. Macroscopic description fails in a localized region.
   - Defects in crystals.
   - Contact line dynamics.

B. Macroscopic model is not fully known.
   - Flow in a porous medium.
   - Complex fluids.
   - Composite materials.

Multiscale approaches and algorithms

- Classical multiscale algorithms:
  - Multigrid method[1].
  - Multiresolution analysis and wavelets[2]
  - Domain Decomposition: Quasicontinuum method[3].
- General frameworks make use of scale separation:
  - Homogenization and multiple-scale asymptotics.
  - Equation-free approaches[4].
  - Heterogeneous Multiscale Method[5].

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[1] A. Brandt, *Math. Comp.*, 31 (1977); W. Hackbusch, *Computing*, 20 (1978)

[2] A. Harten, *J. Appl. Numer. Math.*, 12 (1993); I. Daubechies, *Ten Lectures on Wavelets*

[3] Tadmor, Ortiz, Phillips, *Philosophical Magazine A*, 73 (1996)

[4] I.G. Kevrekidis, C.W. Gear, J.M. Hyman, P.G. Kevrekidis, O. Runborg. C. Theodoropoulos, *Comm. Math. Sci.*, 1 (2003)

[5] W. E, B. Engquist, *Comm. Math. Sci.*, 1 (2003); W. E, B. Engquist, X. Li, W. Ren, E. Vanden-Eijnden, *Commun. Comp. Phys.*, 2 (2007); A. Abdulle, W. E, B. Engquist, E. Vanden-Eijnden, *Acta Numerica*, 21 (2012)

Multiscale/Multiphysics Phenomena

- Complex Fluids, e.g., Polymers.

$$\begin{aligned} \frac{\partial U}{\partial t} + (U \cdot \nabla) U &= \text{div } \sigma + \nabla P, \\ \text{div } U &= 0. \end{aligned}$$

  - U is the velocity.
  - P is the pressure.
  - σ is the stress tensor $\longleftrightarrow$ Interparticle interactions.
  - Constitutive relation: $\sigma = \sigma(\nabla U)$.
  - What is the microscopic foundation of the constitutive relation?.

Multiscale/Multiphysics Phenomena (cont.)

- Elasticity.

$$\min \int_{\Omega} \left(W(u) - f \cdot u \right) \, dx.$$

  - u represents the displacement.
  - f is the external force.
  - Constitutive relation, e.g., Hooke's law: $W(u) = \frac{1}{2} \epsilon^T \cdot C \cdot \epsilon$, where
    - $\epsilon = \frac{1}{2} \left(\nabla u^T + \nabla u \right)$ is the strain.
    - C is a tensor consisting of elastic constants.
  - Can $W(u)$ be derived from microscopic interactions? From quantum mechanics?.

Homogenization: Multiple-scale asymptotics approach

Consider $0 < m \leq a(x,y) \leq M$ periodic in y with period p, and

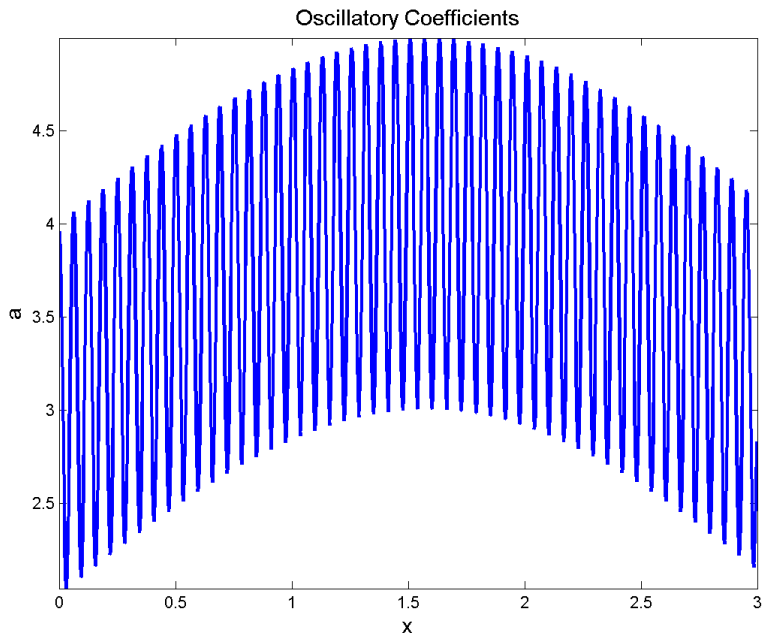
$$\begin{aligned} \frac{d}{dx}\left(a\left(x,\frac{x}{\epsilon}\right)\frac{du^\epsilon}{dx}\right) &= f(x), \quad x \in [0,1] \\ u(0) &= 0; \quad u(1) = 0. \end{aligned}$$

What does the solution look like when $\epsilon \to 0$?

- Notice that $a\left(x,\frac{x}{\epsilon}\right) \rightharpoonup < a > (x) = \frac{1}{p}\int_0^p a(x,y)\,dy$.
- Does u^ϵ converge to the solution of $\frac{d}{dx}\left(< a > (x)\frac{du}{dx}\right) = f$?

Multiple-scale asymptotics (cont.)

Does u^ϵ converge to the solution of $\frac{d}{dx}\left(< a > (x)\frac{du}{dx}\right) = f$? No!



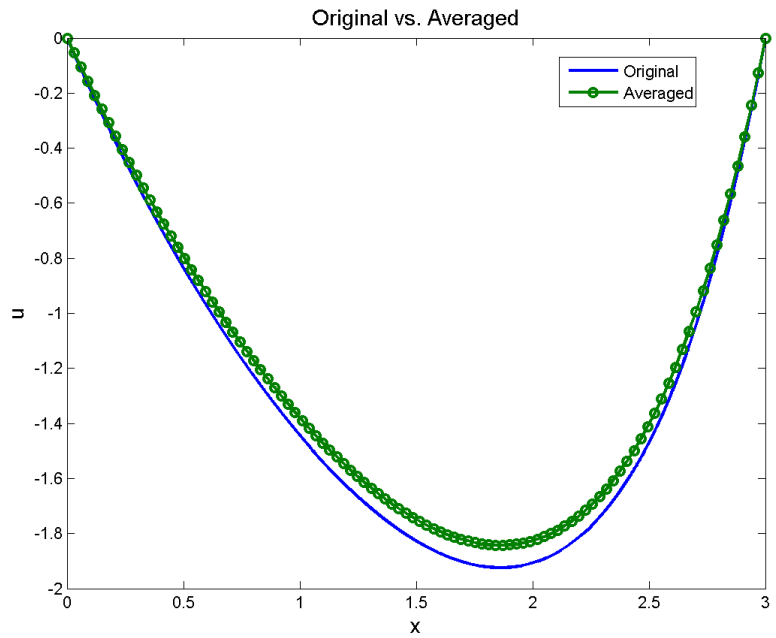


Figure: Left: $a = 3 + \sin(x) + \cos(x/\epsilon)$; Right: Solution of Averaged Equation.

Multiple-scale asymptotics (cont.)

- Introduce two (independent) scales: $z = x$, $y = x/\epsilon$.
- $\frac{d}{dx} \Rightarrow \frac{\partial}{\partial z} + \frac{1}{\epsilon}\frac{\partial}{\partial y}$.
- Assume $u = u_0(x,y) + \epsilon u_1(x,y) + \epsilon^2 u_2(x,y) + O(\epsilon^3)$, periodic in y.

$$f = \left(\partial_x + \frac{1}{\epsilon}\partial_y\right)\left(a(x,y)\left(\partial_x u_0 + \epsilon\partial_x u_1 + \frac{1}{\epsilon}\partial_y u_0 + \partial_y u_1 + \epsilon\partial_y u_2\right)\right)$$

- Collect terms:

$$O\left(\epsilon^{-2}\right): \quad \partial_y\left(a(x,y)\partial_y u_0\right) = 0 \Rightarrow \boxed{u_0 = u_0(x)}$$

$$O\left(\epsilon^{-1}\right): \quad \partial_x\left(a(x,y)\partial_y u_0\right) + \partial_y\left(a(x,y)(\partial_x u_0 + \partial_y u_1)\right) = 0$$

$$\Rightarrow u_1(x,y) = u_1(x,0) - \partial_x u_0 y + g(x)\int_0^y \frac{dz}{a(x,z)}$$

$$\overset{\text{Periodicity}}{\Rightarrow} \boxed{u_0'(x) = g(x)\frac{1}{p}\int_0^p \frac{dz}{a(x,z)}}$$

Multiple-scale asymptotics (cont.)

$$O\left(\epsilon^{-1}\right): \quad \boxed{u_0'(x) = g(x)\frac{1}{p}\int_0^p \frac{dz}{a(x,z)} = g(x) < a^{-1} >}$$

$$O\left(1\right): \quad \partial_x\left(a(x,y)\left(\partial_x u_0 + \partial_y u_1\right)\right) + \partial_y\left(a(x,y)(\partial_x u_1 + \partial_y u_2)\right) = f$$

$$\Rightarrow g'(x) + \partial_y\left(a(x,y)(\partial_x u_1 + \partial_y u_2)\right) = f$$

$$\overset{Compatibility}{\Rightarrow} g'(x) = f(x)$$

$$\Rightarrow \boxed{\frac{d}{dx}\left(< a^{-1} >^{-1} \frac{du_0}{dx}\right) = f}$$

Notice that in general,

$$< a^{-1} >^{-1} \neq < a >!$$

Multiple-scale asymptotics (cont.)

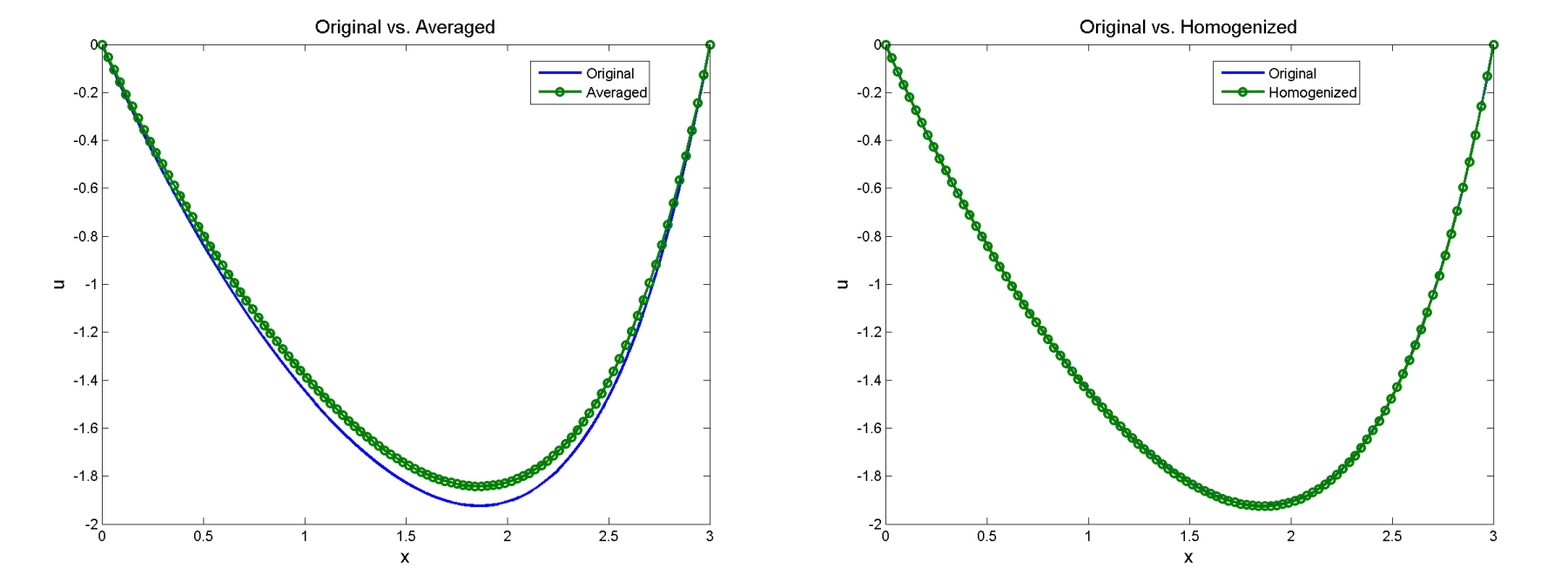


Figure: Left: Averaged equation; Right: Homogenized Equation.

Multiple-scale asymptotics (cont.)

- In higher dimensions: Homogenized coefficients obtained by solving a cell problem (more on this later).
- Intuitive; Leads to effective macroscopic equations and provides *systematic* improvement.
- In some cases it can be formalized[1].
- Widely used in the study of composite materials, photonics, etc....

[1] Asymptotic Analysis for Periodic Structures, A. Bensoussan, J.-L. Lions, G. Papanicolaou

Heterogeneous Multiscale Method (HMM)[1]

- Systematic procedure for multiscale modeling.
- Main ingredients:
  - Macroscopic Model: $U_t = F(U, D)$, D is unknown.
  - A way to estimate D from microscopic data.
    - Microscopic Model: $u_t = f(u)$.
    - Reconstruction Operator: $u = R(U)$.
    - Compression Operator: $U = Q(u)$.

[1] E, Engquist, Comm. Math. Sci. 1(1), 2003

Example: Complex Fluids[1]

- Macroscopic model: Navier-Stokes equations.

$$\begin{aligned} \partial_t U + (U \cdot \nabla) U - \nabla P &= \text{div } \sigma, \\ \text{div } U &= 0, \end{aligned}$$

  where U is the velocity, P is the pressure, and σ is the viscous stress.

- Constitutive relation:

$$\sigma = \mu \left(\nabla U + (\nabla U)^T \right).$$

  - Very successful for Newtonian fluids.
  - Inaccurate for complex fluids, e.g. polymers.

[1] Weiqing Ren, National University of Singapore

Example: Complex fluids (cont.)

- At the microscale, the system can be modeled by molecular dynamics:

$$m_i \ddot{x}_i = F_i = -\nabla_{x_i} V(x_1, x_2, \ldots, x_N), \ i = 1, 2, \ldots, N$$

- Large number of degrees of freedom: $N = O(10^{23})$.
- Small time step required, $\delta t = O(10^{-15})$.

Macro solver: Projection Method[1]

Denote the velocity field at time t^n by U^n, then U^{n+1} is computed following the two-step procedure:

- Compute intermediate value U^*:

$$\frac{U^* - U^n}{\Delta t} + \nabla \cdot (U^n \otimes U^n) = \nabla \cdot \sigma.$$

- Project U^* onto the divergence-free space:

$$\frac{U^{n+1} - U^*}{\Delta t} + \nabla P^{n+1} = 0,$$

where P^{n+1} solves

$$\Delta P^{n+1} = \frac{1}{\Delta t} \nabla \cdot U^*$$

with Neumann boundary conditions.

[1] A.J. Chorin, *Math. Comp.*, 22 (1968); ....

Spatial discretization: Staggered grid

Spatial derivatives are discretized using finite difference on staggered grid:

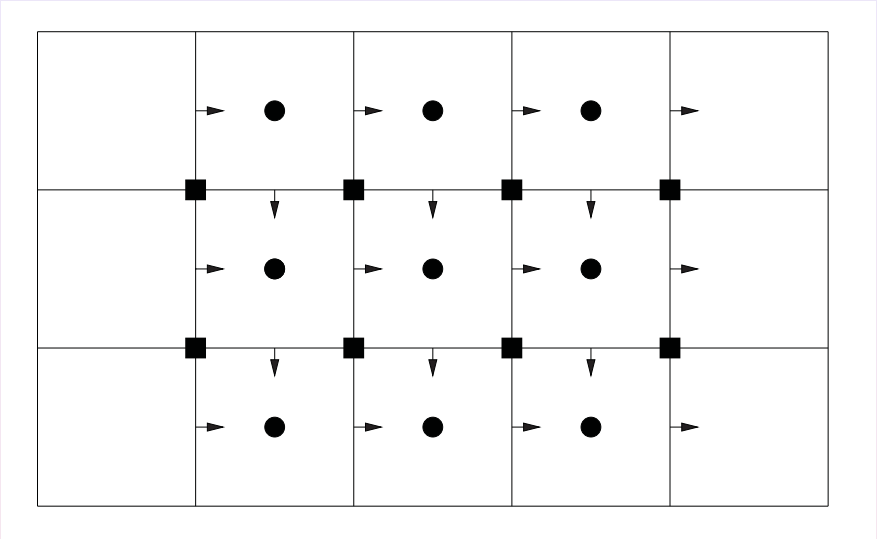


Figure: Staggered grid (courtesy of W. Ren)

Denote the two components of U by (u, v).

- u defined at $(x_i, y_{j+1/2})$, v at $(x_i, y_{j+1/2})$; normal stress at $(x_{i+1/2}, y_{j+1/2})$, and shear stress at (x_i, y_j).

Computing stress from MD

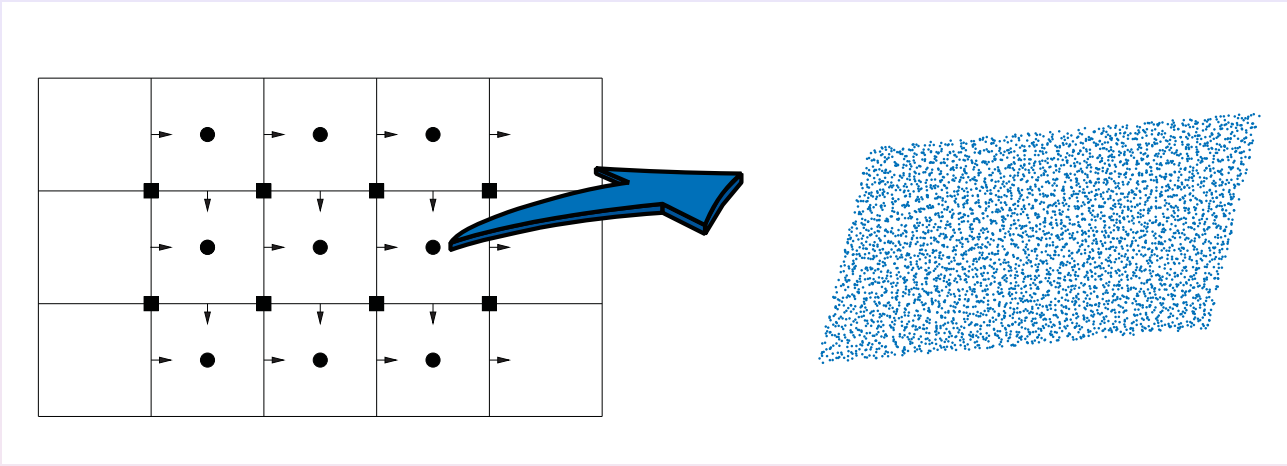


Figure: Local computation (courtesy of W. Ren)

- Each point where stress is needed is associated with an MD system.
- Assume stress depends only on local velocity gradient ∇U. Then the MDs are constrained by ∇U.

The HMM algorithm for fluids

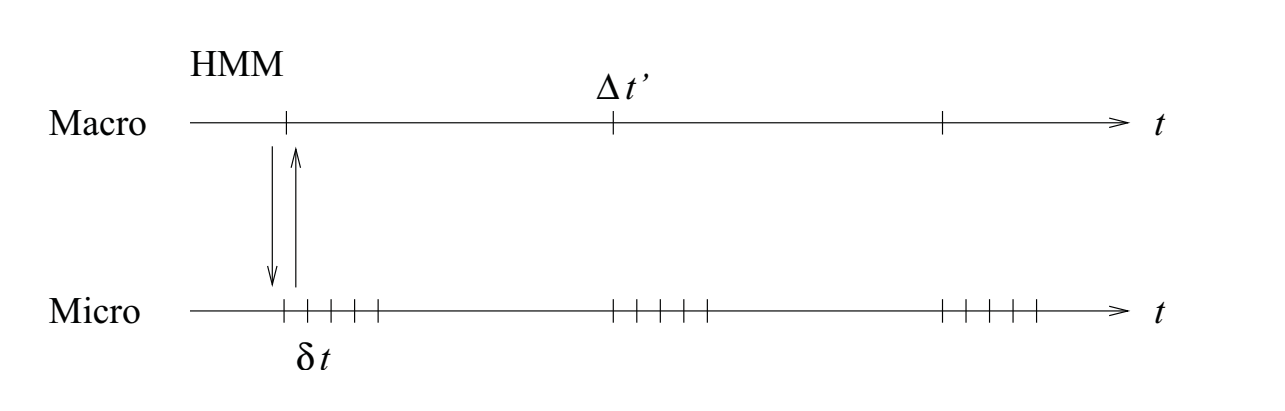


Figure: The HMM schematically (courtesy of W. Ren)

- Compute the velocity gradient $A^n = \nabla U^n$ at each point where the stress is needed.
- Initialize an MD at each point where stress is needed.
- Evolve each MD constrained by A^n for M steps with a micro time step $\delta\tau$.
- Compute the stress from the MD results.
- Evolve the macro model using the estimated stress for one macro time step Δt, to obtain U^{n+1}.

Constrained molecular dynamics

- Set up MD whose averaged velocity coincides with local macroscale velocity field.
- The MD box deforms according to the given velocity gradient:

$$\dot{X} = AX, \quad A = \nabla U.$$

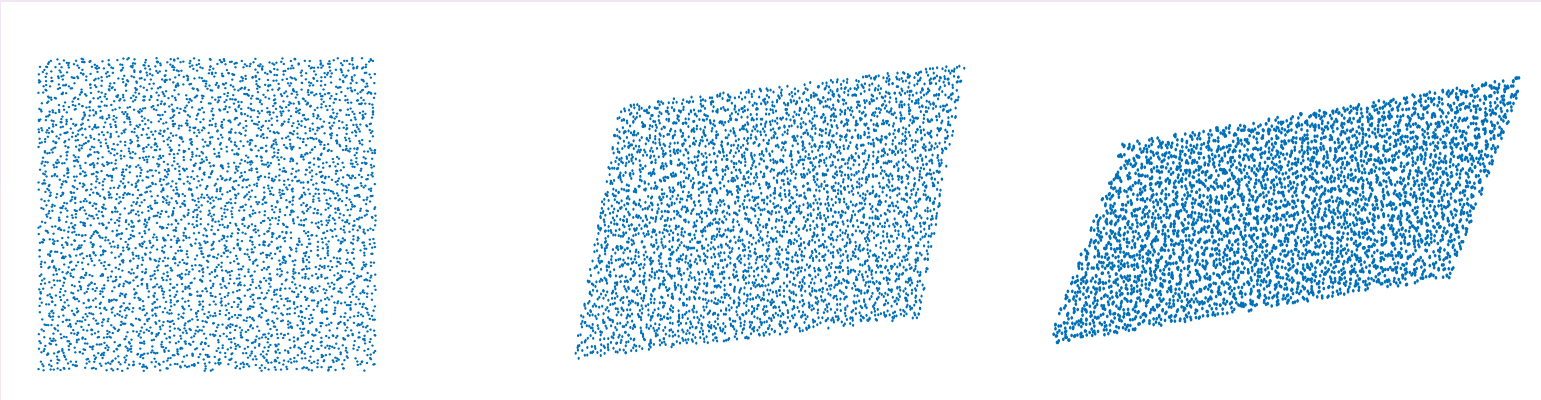


Figure: Constrained MD (courtesy of W. Ren)

- Periodic boundary conditions on the deforming box.
- Temperature controlled using Langevin thermostat.

Stress estimation

- Compute stress using the Irving-Kirkwood formula:

$$\widetilde{\sigma}(x, n\delta\tau) = -\sum_i m v_i(\tau) \otimes v_i(\tau)\delta(x - q_i * \tau))$$
$$-\frac{1}{2}\sum_{j\neq i}(q_j(\tau)-q_i(\tau))\otimes f_{ij}(\tau)\int_0^1 \delta(x-(1-\lambda)q_j(\tau)-\lambda q_i(\tau))\, d\lambda, \tag{1}$$

  where $\{v_i\}$ are the thermal velocity of the particles.

- The stress is obtained by averaging $\widetilde{\sigma}$ over the MD box:

$$\sigma(n\Delta' t) = \frac{1}{|\omega|}\int_\omega \widetilde{\sigma}(x, n\delta\tau)\, dx,$$

  where ω is the MD simulation box.

Driven-cavity flow[1]

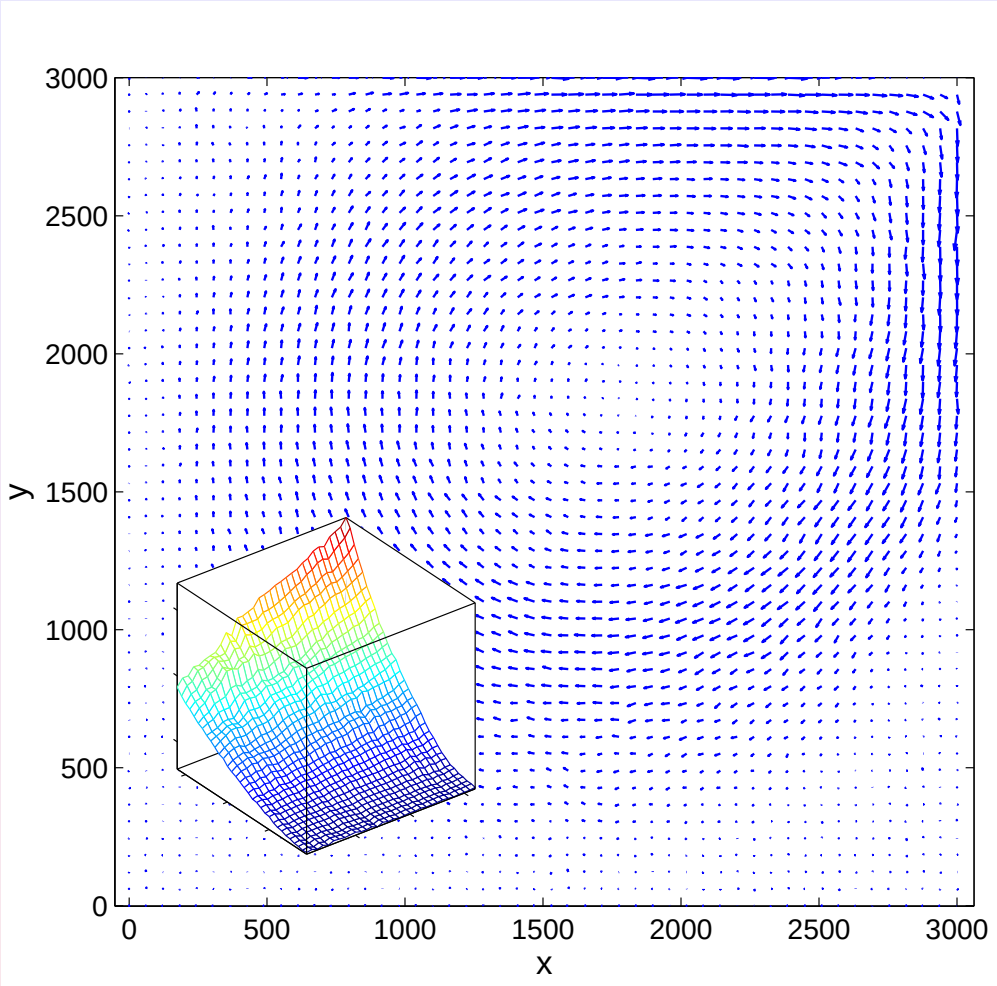
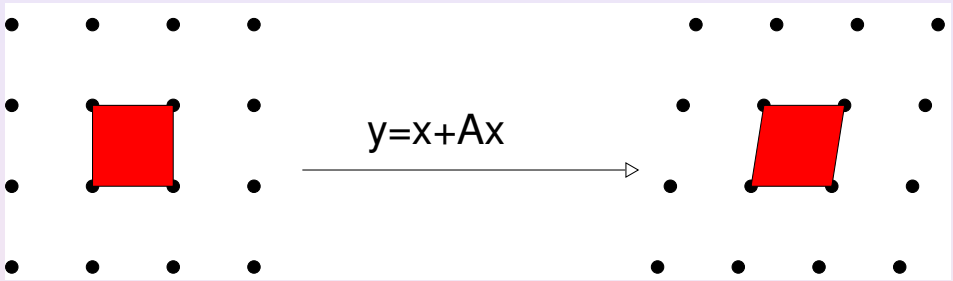


Figure: Velocity field at steady state in the driven cavity flow. Inset in the figure is one of the normal stress as a function of 2d velocity gradient.

[1] W. Ren, W. E, *J. Comp. Phys.*, **204** (2005); CJGC, W. Ren, J. Lu, W. E, *Commun. Comput. Phys.*, **4** (2008); W. E, W. Ren, E. Vanden-Eijnden, *J. Comput. Phys.* (2009)

Cauchy-Born rule for a simple lattice[1]

$\mathbf{A} \in \mathbb{R}^{3\times 3}$ $\qquad$ $W(\mathbf{A}) = ?$



- The microscopic state is determined by the macroscopic deformation.
- $W_{\mathrm{CB}}(\mathbf{A})$ is computed by first deforming an infinite crystal uniformly with displacement gradient $\mathbf{A}$, and then setting $W_{\mathrm{CB}}(\mathbf{A})$ to be the energy of the deformed unit cell:

[1] M. Born and K. Huang, Oxford University Press, Oxford, 1954

Cauchy-Born rule for a simple lattice (cont.)

- Example: 1d simple lattice with Lennard-Jones potential

$$W_{\mathrm{CB}}(A) = \frac{\zeta^2(6)}{\zeta(12)}\left(|1+A|^{-12} - 2|1+A|^{-6}\right)$$

  $\zeta =$ Riemann-zeta function

- Validity of Cauchy-Born: Under certain lattice stability conditions[1]

$$\|u_{\mathrm{CB}} - \mathbf{y}\| \leq C\epsilon^2,$$

  where $\epsilon =$ lattice constant/diam(Ω).

[1] Theil and Friesecke, *J. Nonl. Sci*, 12, (2002); E, Ming, *Arch. Rat. Mech. Anal.*, 183 (2006); Van Koten and Ortner (2012)

Thermodynamic limit

- More generally: How does one define the energy of a crystal? Thermodynamic limit[1].
- Quantum mechanical description:
  - Does there exist a limit for the energy per unit volume $\frac{1}{N}E_N$ as $N \to \infty$?
  - Does the minimizing electronic density ρ_N approach a limit ρ_∞ in some sense?
  - Does the limit density ρ_∞ have the same periodicity as the assumed periodicity of the nuclei?
- Proved in the context of Thomas-Fermi[2], Thomas-Fermi-von Weiszacker and Hartree-Fock[3].

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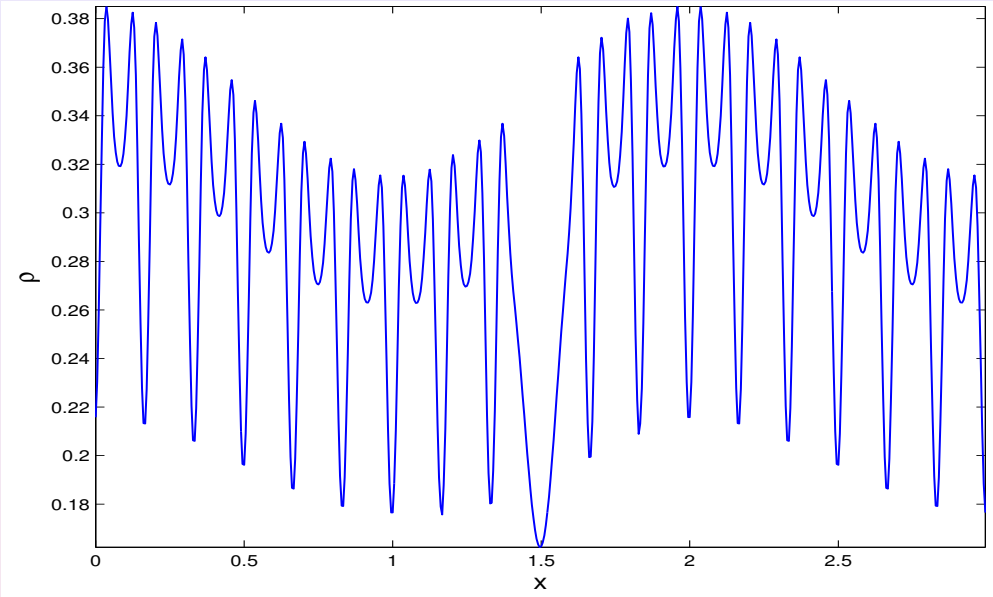
[1] Blanc, Le Bris, Lions, *Arch. Rat. Mech. Anal.*, 164 (2002)

[2] Lieb, Simon, *Adv. Math.*, 23 (1977)

[3] Catto, Le Bris, Lions (2001), Cancès, Lahbabi, Lewin (2012)

Cauchy-Born in Quantum Mechanics[1]

Consider the electronic density around a vacancy in an Aluminium crystal:



- The effect of the vacancy is very localized (more on this later).
- Two scales:
  - Fast scale: Interatomic distance (lattice constant).
  - Slow scale: Elastic deformation
- Multiple-scale behavior motivates the use of asymptotic analysis: homogenization.

[1] Lu, E, *Comm. Math. Sci.*, 5 (2007); García-Cervera, Lu, E, *Comm. Math. Sci.*, 5 (2007); Lu, E, *Memoirs AMS*, (2012)

Cauchy-Born: Orbital-Free DFT case

We choose units so that the diameter of the domain is $O(1)$, and introduce $\varepsilon = \text{Lattice constant}/diam(\Omega)$. The energy becomes:

$$E[u] = \frac{\varepsilon^2}{2}\int_\Omega |\nabla u|^2 + \varepsilon^2 C_{TF}\int_\Omega u^{10/3} + F_{XC}[\varepsilon^3 u^2] + \frac{\varepsilon}{2}\int_\Omega\int_\Omega \frac{(u^2-m)\cdot(u^2-m)}{|x-y|}.$$

Euler-Lagrange equations:

$$\begin{aligned} -\varepsilon^2\Delta u + \frac{5}{3}\varepsilon^2 u^{7/3} - \phi u + \varepsilon^2 V_{XC}[\varepsilon^3 u] + \lambda u &= 0, \\ -\Delta\phi &= 4\pi\varepsilon(m-u^2), \end{aligned}$$

- λ is a Lagrange multiplier for the normalization constraint.
- ϕ is the Coulomb potential generated by the electrons and the ions.
- Equation set in $\varphi(\Omega)$, with $\varphi : \Omega \to \mathbb{R}^3$ elastic deformation.

Cauchy-Born (cont.)

For smooth elastic deformations:

$$
\begin{aligned}
u &= u(y, \frac{x}{\varepsilon}) = \frac{1}{\varepsilon^{3/2}} u_0\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^{1/2}} u_1\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^{1/2} u_2\left(y, \frac{x}{\varepsilon}\right) + \cdots, \\
\phi &= \phi\left(y, \frac{x}{\varepsilon}\right) = \phi_0\left(y, \frac{x}{\varepsilon}\right) + \varepsilon\phi_1\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^2\phi_2\left(y, \frac{x}{\varepsilon}\right) + \cdots, \\
\lambda &= \lambda_0 + \varepsilon\lambda_1 + \varepsilon^2\lambda_2 + \cdots
\end{aligned}
$$

- $x = x(y) = \varphi^{-1}(y)$ is the Euler-Lagrange map: It gives the Lagrangian coordinate corresponding to y.
- $u(y, z)$ and $\phi(y, z)$ are functions defined on $\mathbb{R}^3 \times \Gamma$ and are periodic in the second variable on Γ (unit cell).

Leading order equations:

$$
\begin{aligned}
-\Delta_2^x u_0 + \frac{5}{3} u_0^{7/3} - \phi_0 u_0 + \lambda_0 u_0 &= 0, \\
-\Delta_2^x \phi_0 &= 4\pi(m_0 - u_0^2).
\end{aligned}
$$

These are the Euler-Lagrange equations for the *periodic* problem, on the deformed cell $\mathbf{A}\Gamma$, with $\mathbf{A} = \nabla\varphi(x)$: Cauchy-Born rule.

Kohn-Sham Density Functional Theory

$$E_{KS}[\{\psi_j\}] = 2\sum_{j=1}^{N}(-\frac{1}{2})\int \psi_j\,(\Delta\psi_j)\;dx + \frac{1}{2}\int\int \frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy$$
$$+ \int V_{ext}(x)\rho(x)\,dx + \int \rho\varepsilon(\rho) + \frac{1}{2}\sum_{i\neq j}\frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|},$$

where

$$\rho(x) = 2\sum_{j=1}^{N}|\psi_j(x)|^2$$

Kohn-Sham DFT:

$$\min_{(\psi_i,\psi_j)=\delta_{ij}} E_{KS}[\{\psi_j\}]$$

Asymptotics in the Kohn-Sham framework

Euler-Lagrange equations:

$\varepsilon =$ Lattice Constant/Diameter of the domain.

$$\begin{aligned} -\frac{\varepsilon^2}{2}\Delta\psi_k + V_{XC}(\varepsilon^3\rho)\psi_k - \phi\psi_k &= \lambda_k\psi_k; \\ -\Delta\phi &= 4\pi\varepsilon(m-\rho), \end{aligned}$$

$$\rho(\times) = 2\sum_{j=1}^{N} |\psi_j(\times)|^2. \tag{2}$$

Asymptotic expansion for $\varepsilon \ll 1$:

$$\begin{aligned} \psi_\alpha\left(y, \frac{x}{\varepsilon}\right) &= \frac{1}{\varepsilon^{3/2}}\psi_{\alpha,0}\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^{1/2}}\psi_{\alpha,1}\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^{1/2}\psi_{\alpha,2}\left(y, \frac{x}{\varepsilon}\right) + \\ \rho\left(y, \frac{x}{\varepsilon}\right) &= \frac{1}{\varepsilon^3}\rho_0\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^2}\rho_1\left(y, \frac{x}{\varepsilon}\right) + \frac{1}{\varepsilon^1}\rho_2\left(y, \frac{x}{\varepsilon}\right) + \cdots \\ \phi\left(y, \frac{x}{\varepsilon}\right) &= \phi_0\left(y, \frac{x}{\varepsilon}\right) + \varepsilon\phi_1\left(y, \frac{x}{\varepsilon}\right) + \varepsilon^2\phi_2\left(y, \frac{x}{\varepsilon}\right) + \cdots . \end{aligned}$$

Asymptotics in the Kohn-Sham framework (cont.)

Leading order:

$$\rho_0(y,z) = 2\sum_{\alpha}\sum_{z_j\in L}|\psi_{\alpha,0}(y,z-z_j)|^2.$$

$$\int_{\mathbb{R}^3}\psi^*_{\alpha,0}(y,z-z_i)\psi_{\alpha',0}(y,z-z_j)\,dz = \delta_{\alpha\alpha'}\delta_{ij}/\det(\nabla\varphi(x)).$$

$$-\frac{1}{2}\Delta_2^x\psi_{\alpha,0}(y,z) + V_{XC}(\rho_0)\psi_{\alpha,0}(y,z) - \phi_0(y,z)\psi_{\alpha,0}(y,z) + \sum_{\alpha',z_j\in L}\lambda_{\alpha\alpha',z_j0}\psi_{\alpha',0}(y,z-z_j) = 0;$$

$$-\Delta_2^x\phi_0(y,z) = 4\pi(m_0-\rho_0)(y,z).$$

These are the Euler-Lagrange equations for the *periodic* problem, on the deformed cell: Cauchy-Born rule.

Precomputing W_{CB}[3]

- Concurrent computation of the electronic density is impractical.
- Stress is a function of the strain: This is a function of six variables.
- This can be precomputed and stored in a table from where we can interpolate, in the context of the Heterogeneous Multiscale Method (HMM)[1].
- An effective way of doing this is using a **sparse representation**.
- Can be used to assess accuracy of empirical potentials[2].

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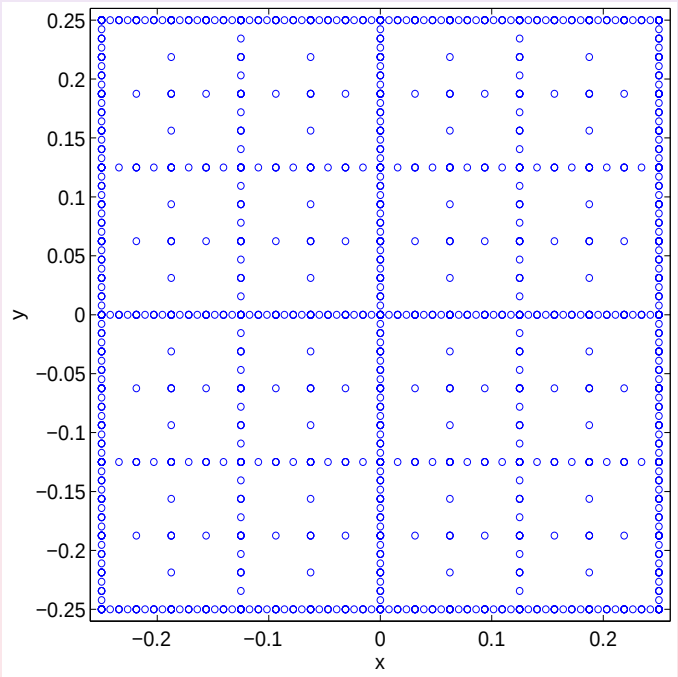
[1] W. E, B. Engquist, *Comm. Math. Sci.*, 1 (2003)

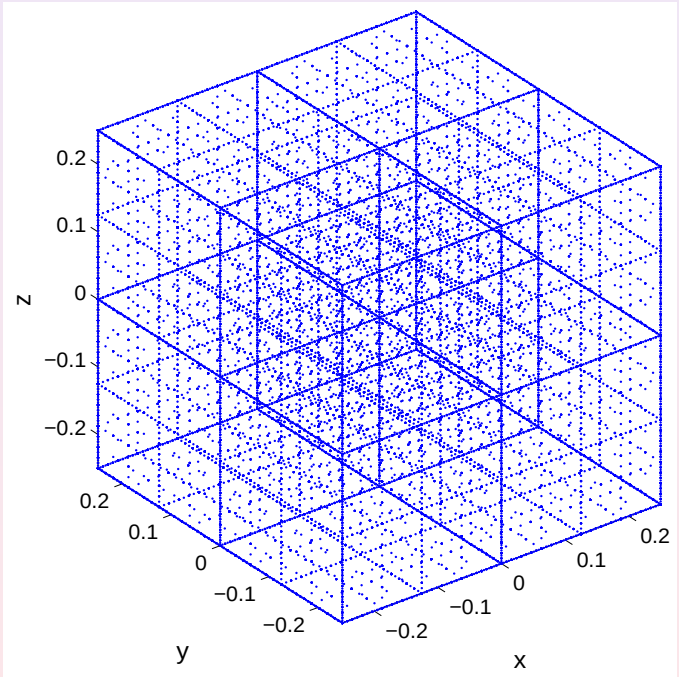
[2] G. Wu, G. Lu, CJGC, and W. E, *Phys. Rev. B*, 79 (2009)

[3] CJGC, Ren, Lu, and E, *Comm. Comp. Phys.*, 4 (2008)

Sparse representation

- If we attempt to represent a function of d variables using a uniform grid, we would need $O(2^{nd})$ grid points.
- Using sparse grids, we need only $O(n^{d-1}2^n)$ points[1].





[1] Bungartz and Griebel, *Acta Numerica (2004)*

Elastic deformation of a solid

Given a deformation $u : \Omega \to \mathbb{R}^3$, we denote by $F = \nabla u$ the deformation tensor, and define the elastic energy density as

$$\omega[F] = \frac{1}{|V_0|} W_{\mathrm{CB}}[F], \tag{3}$$

where the Cauchy-Born energy, $W_{\mathrm{CB}}[F]$, is the energy of the deformed unit cell, obtained by transforming the basis vectors as $b_i = Fa_i$, $i = 1, 2, 3$. Due to frame indifference, the elastic energy depends only on the right Cauchy-Green strain tensor (RCGST), $C = F^T F$.

Computational Cost

- $2,572,288$ grid points were used, which provided up to four digits of accuracy.
- To achieve the same accuracy with a regular grid, $128^6 \geq 4 \times 10^{12}$ grid points would be required.

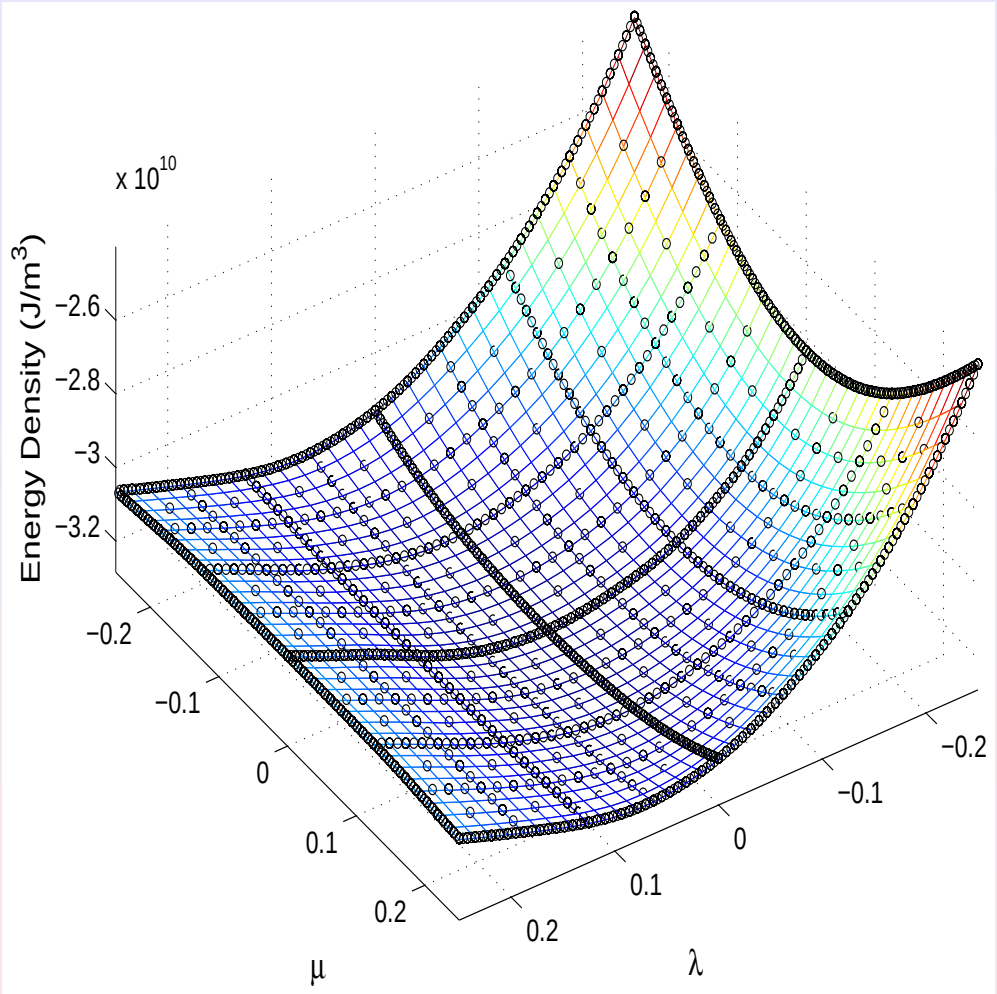


Figure: Elastic energy for the shear and expansion deformation. We plot the energy interpolated to a uniform grid. The sparse grid nodes are superimposed.

Domain Decomposition: Quasicontinuum

- Domain decomposition: Quasicontinuum[1]
  - Domain decomposed into a local and nonlocal region.
  - Local region: Cauchy-Born elasticity.
  - Nonlocal region: Fully atomistic.
  - Interface matching: Can produce *ghost forces*[2].
  - Extended to Quantum-Mechanical models[3].

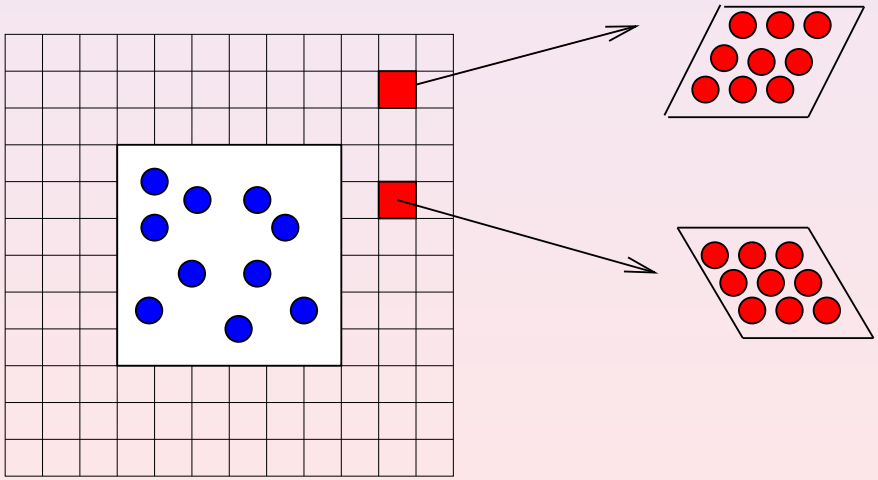
[1] Tadmor, Ortiz, Phillips, *Philosophical Magazine A*, **73** (1996)

[2] Tadmor, Phillips, Ortiz ('96), E, Ming ('05), E, Lu, Yang ('06), Dobson and Luskin ('07)

[3] E, Lu, Kaxiras ('06), Hayes, Ho, Ortiz, and Carter ('06), G-C, Lu, E ('07), Gavini, Bhattacharya and Ortiz ('07), Peng, Zhang, Hung, Carter, Lu ('08)

The Quasicontinuum Method[1]

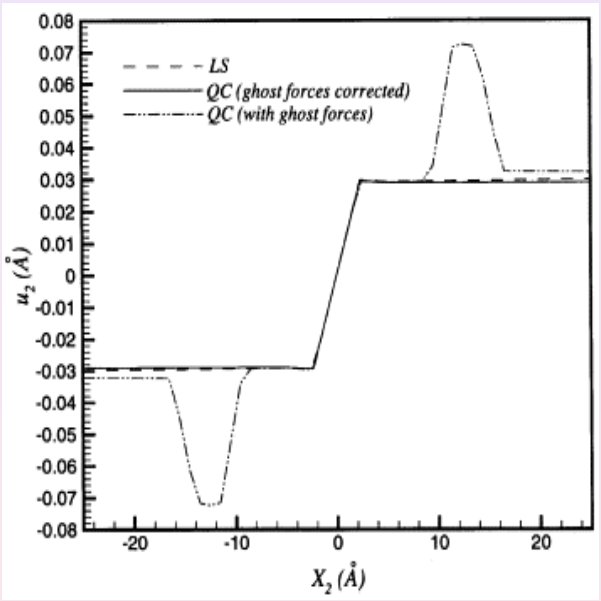
- Consider a material sample with a defect, e.g., a crack, vacancy, dislocation, etc.
- Decompose the domain into a **nonlocal** region containing the defect, and a **local** region, containing the rest.
- In the nonlocal region, atoms are treated directly.
- In the local region, representative atoms (rep-atoms) and Cauchy-Born elasticity is used.



[1] Tadmor, Ortiz, Phillips, *Philosophical Magazine A*, **73** (1996)

The Quasicontinuum Method (cont.)

- Overcomes some limitations of Cauchy-Born.
- Matching at the atomistic/continuum interface is difficult: Ghost forces[1] (Nonzero force for equilibrium configuration).



- Energy-based correction[2], Force-based correction [3].
- No general method to remove ghost forces is available to date.

[1] Shenoy, Miller, Tadmor, Rodney, Phillips, Ortiz, *J. Mech. Phys. Solids*, 47 (1999)

[2] E, Lu, Yang *Phys. Rev. B* 74 (2006).

[3] Luskin, Dobson, *Math. Modelling Num. Anal.* 42 (2008).

The Mori-Zwanzig Formalism[1]

- General strategy to eliminate degrees of freedom.
- Produces an exact reduced model.

[1] Mori, Prog. Theor. Phys. 33(3) 1965; Zwanzig, J. Stat. Phys. 9(3) 1973

Example: Collision of a gas atom with a surface[1]

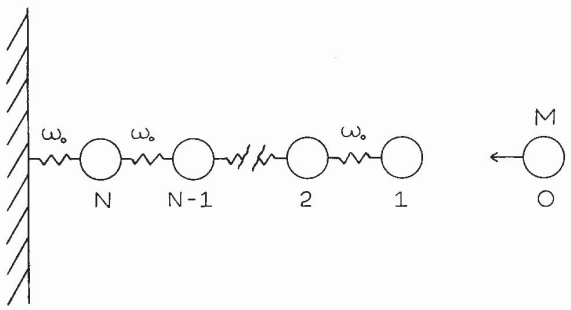


FIG. 1. Schematic representation of a gas atom (particle O) collidin with a one-dimensional harmonic chain. The mass of the incident particle is M and that of the chain atoms is unity. The chain's harmonic interaction is of frequency ω_0. The number of atoms in the chain, N, is generally assumed to tend to infinity.

$$H(P,Q,p,q) = \frac{P^2}{2} + U(Q) + \sum_j \frac{1}{2}p_j^2 + \sum_j \frac{1}{2}\omega_j^2(q_j - \frac{\gamma_j}{\omega_j^2}Q)^2$$

The Hamilton equations are

$$\frac{dQ}{dt} = P; \quad \frac{dP}{dt} = -U'(Q) + \sum_j \gamma_j^2(q_j - \frac{\gamma_j}{\omega_j^2}Q),$$

$$\frac{dq_j}{dt} = p_j; \quad \frac{dp_j}{dt} = -\omega_j^2 q_j + \gamma_j Q.$$

[1] S.A. Adelman, J.D. Doll, J. Chem. Phys., 61(10) 1974

Example: Collision of a gas atom with a surface (cont.)

- Integrating the equations for q_j and p_j,

$$q_j(t) = q_j(0)\cos(w_j t) + \frac{p_j(0)}{\omega_j}\sin(\omega_j t) - \frac{\gamma_j^2}{\omega_j}\int_0^t \sin(\omega_j(t-s))Q(s)\,ds.$$

- We can therefore eliminate q_j:

$$\begin{aligned}\frac{dQ}{dt} &= P,\\ \frac{dP}{dt} &= -U'(Q) + \int_0^t \xi(t-s)P(s)\,ds + F(t),\end{aligned}$$

where

$$\begin{aligned}\xi(t) &= -\sum_j \frac{\gamma_j^2}{\omega_j^2}\cos(\omega_j(t)),\\ F(t) &= \sum_j \left(\gamma_j\left(q_j(0) - \frac{\gamma_j}{\omega_j^2}Q(0)\right)\cos(\omega_j t) + \frac{\gamma_j}{\omega_j}p_j(0)\sin(\omega_j t)\right)\end{aligned}$$

Example: Collision of a gas atom with a surface (cont.)

- The procedure is exact.
- $\xi(t)$ is a memory kernel:
  - Describes dissipation in the system.
  - Dynamics are not Markovian.
- $\{q_j(0)\}$, $\{p_j(0)\}$ appear only in $F(t)$.
- Assume system is initially in equilibrium, with initial positions and momenta sampled from a Gibbs distribution

$$G(P, Q, \{q_j\}, \{p_j\}) \sim exp\{-H(P, Q, \{q_j\}, \{p_j\})/k_B T\}.$$

  then $F(t)$ is a random term.
- Fluctuation-dissipation theorem:

$$\begin{aligned} < F(t) > &= 0, \\ < F(t)F(s) > &= k_B T \xi(t-s). \end{aligned}$$

- Generalized Langevin equation.

Mori-Zwanzig Formalism: Applications

- In general, the random noise and memory terms are extremely complicated.
- Approximations are needed to simplify the model
- Can be used to find effective boundary conditions for MD simulations[1]
  - Atomistic/Continuum coupling.
  - Avoid phonon reflection.
  - Atoms removed should act as a thermal bath.

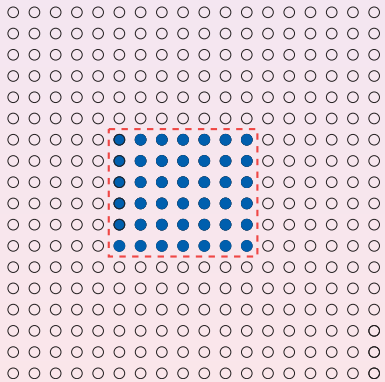


Figure: MD Setup for Mori-Zwanzig approach (courtesy of X. Li)

[1] X. Li, W. E, *Phys. Rev. B* **76**, 104107 (2007)

Mori-Zwanzig Formalism: Applications (cont.)

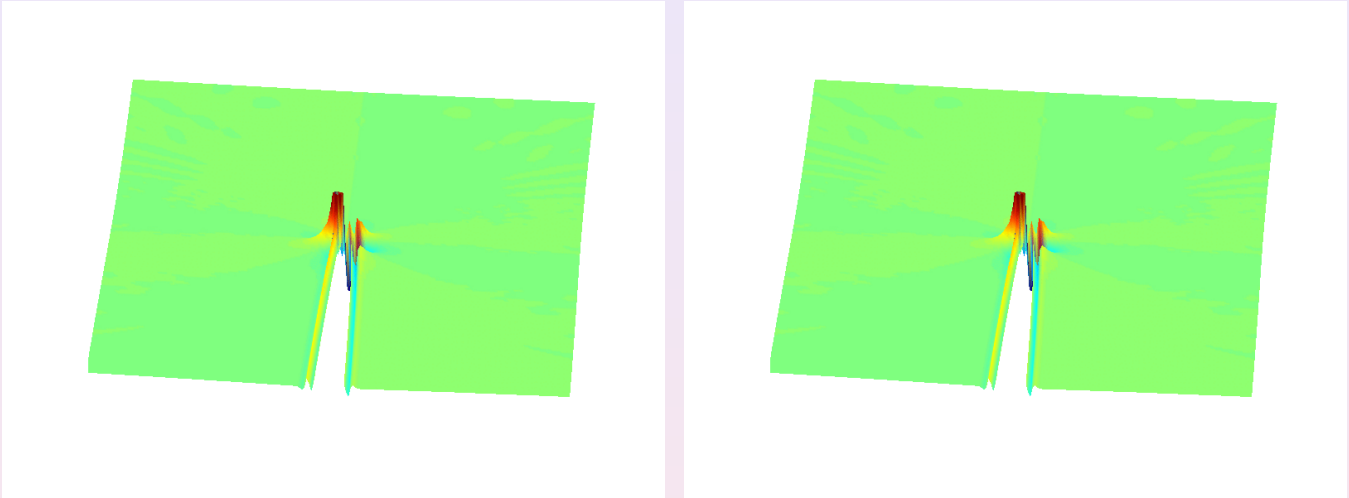


Figure: Phonons generated from a crack (courtesy of X. Li)

Mori-Zwanzig Formalism: Applications (cont.)

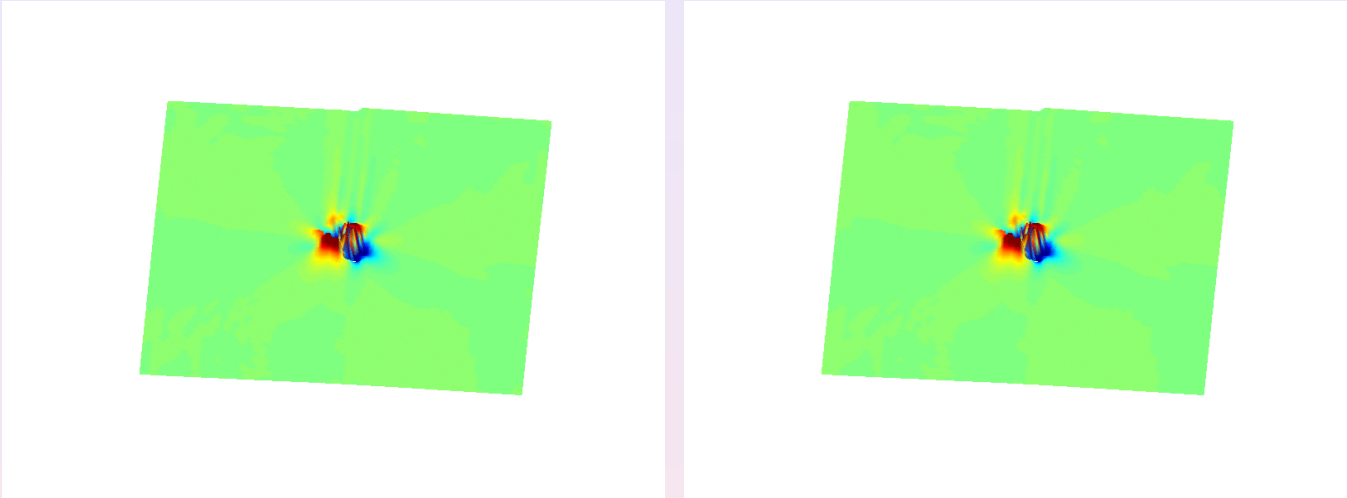


Figure: Phonons generated from a crack (courtesy of X. Li)

Additional Literature on Mori-Zwanzig

- A.J. Chorin, O.H, Hald, R. Kupferman, *PNAS*, **97** (2000).
- X. Li, *J. Comp. Phys.*, **227** (2008).
- C. Hijón, P. Español, E. Vanden-Eijnden, R. Delgado-Buscalioni, *Faraday Discussions*, **144** (2010).
- M. Chen, X. Li, C. Liu, *arXiv:1403.6543* (2014).

Thank you!