12th US National Congress on Computational Mechanics, Raleigh, NC

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Atomistic-to-Continuum Modeling of the Electric Double Layer

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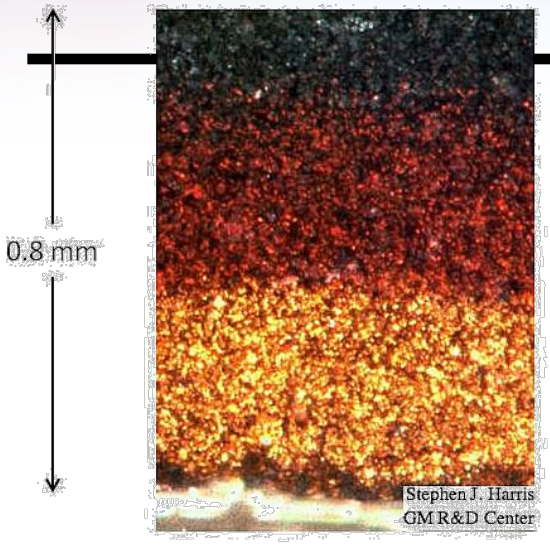
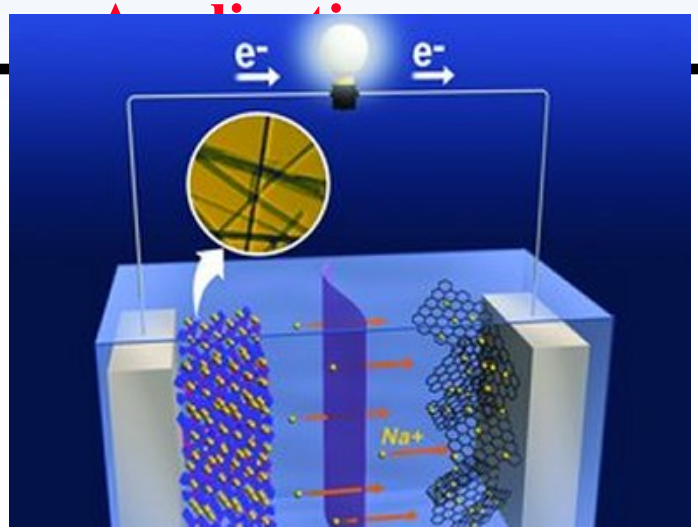
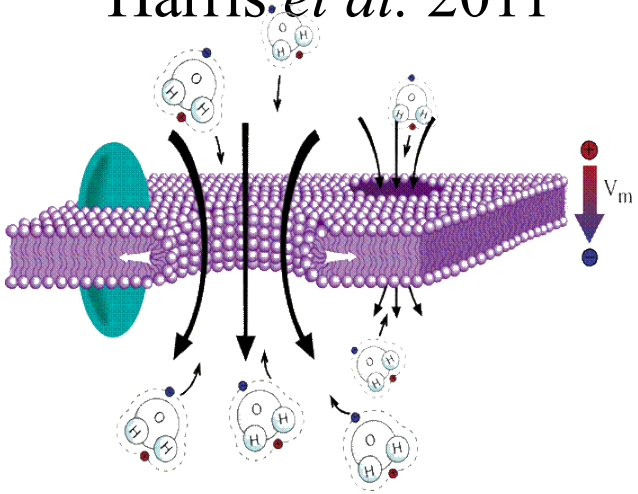




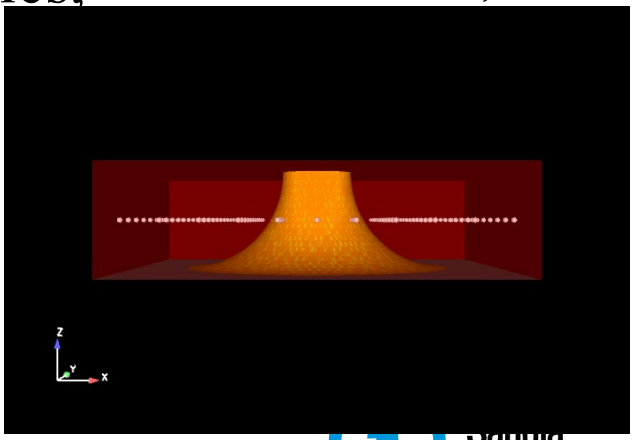
Lithiation of Graphite, Harris *et al.* 2011

Rechargeable Sodium Ion Batteries, Cao *et al.* 2011

Induced-Charge Electro-Osmosis,

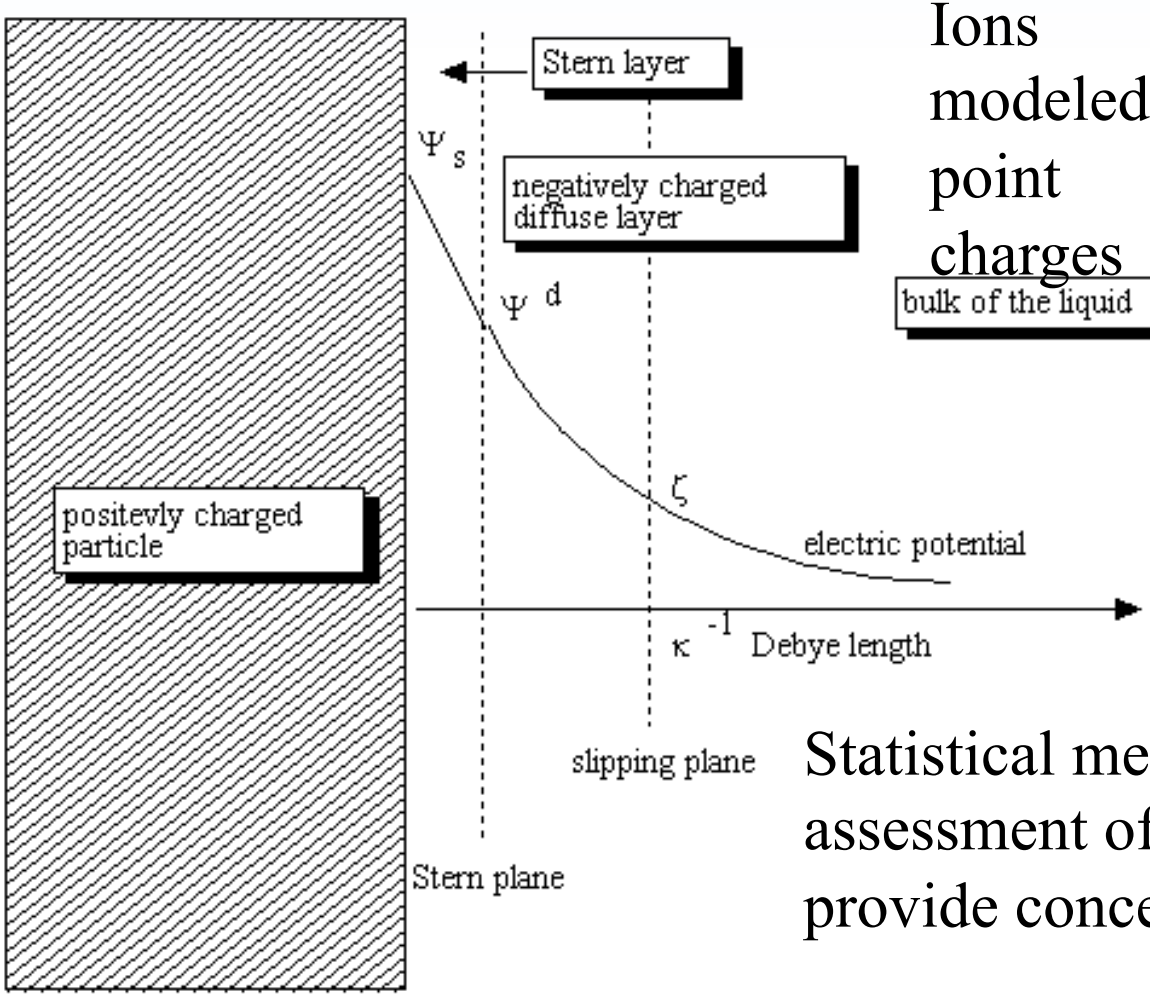


Ion Transport through cell walls, Pilskin *et al.*



Poisson-Boltzmann Theory

Electric potential coupled to ion distributions and surface charge



Ions modeled as point charges

Statistical mechanics assessment of energies to provide concentrations

A. Dukhin

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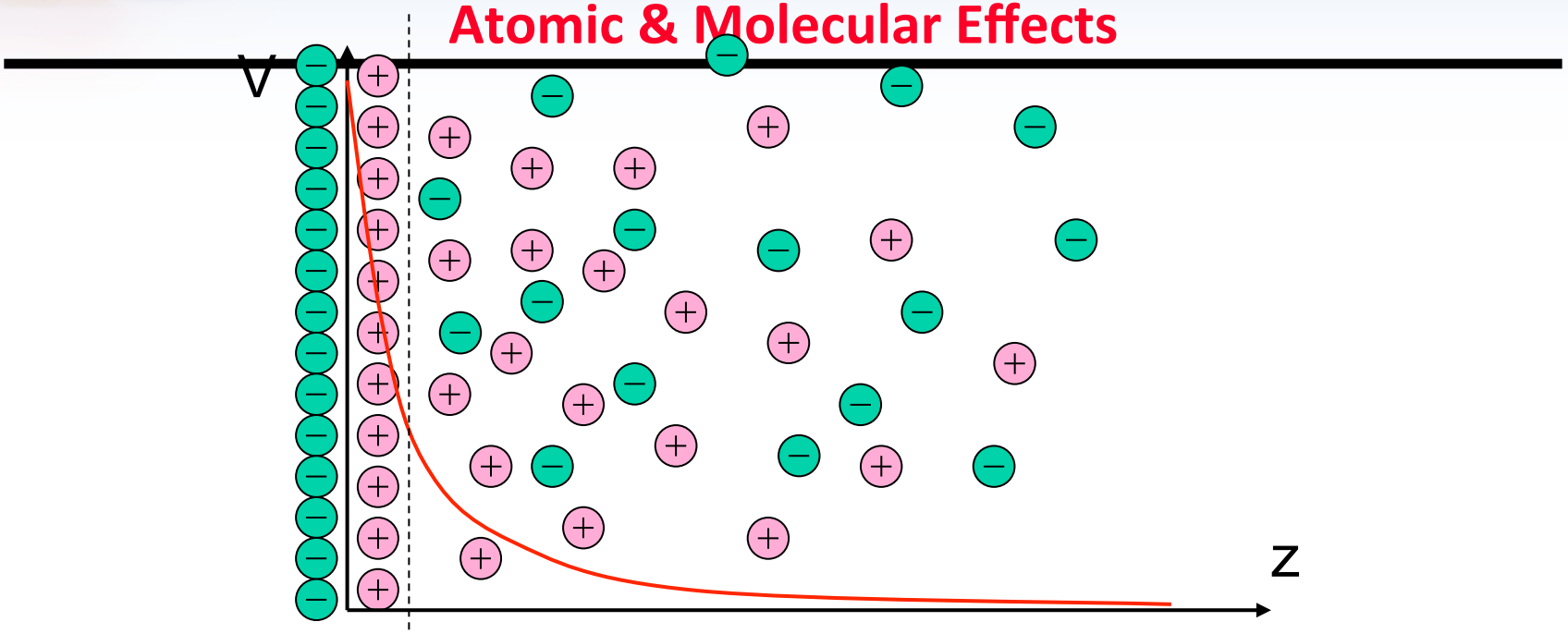
Atomic & Molecular Effects



Poisson Boltzmann (PB) does not include

- Atomic size
- Solvent & molecular effects
- Changes in mechanical and electrical properties
- Electro-chemistry

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Ingredients List

1) Mass Transport – solvent and solute particles

2) Momentum Transport – electrokinetics

3) Thermal Transport – define equilibrium and bulk

4) Electric Potential – spans all scales

More on EDL physics in

- **Mandadapu *et al.*,** *Polarization as a field variable from molecular dynamics simulations.* **Session 8.2, 7/24 @ 5:50**
- **Lee *et al.*,** *Atomistic effects in electric double layers at high voltages.* **Session 4.2, 7/23 @ 3:00**

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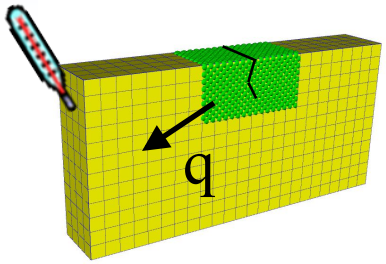
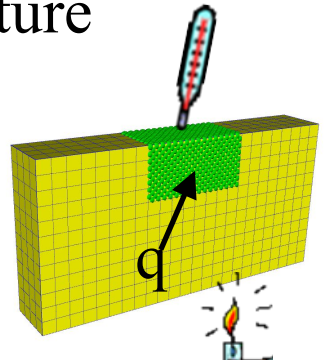
Two-Way Coupling for Heat Transfer



Fine-to-coarse: Fine scale vibrational energy from the MD region should f low into the surrounding FE region and be accounted for as temperature



Coarse-to-fine: Temperature of the FE model (θ) should have an effect on the MD region, through e.g. thermal excitation of atoms

Two interdependent parts of coupling strategy:

1. Modification of finite element equation to incorporate effects of atoms on θ
2. Thermostat to transfer information from the temperature field θ to atoms

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Continuum Heat Equation

Heat equation with Fourier heat conduction arising from Boltzmann Transport equation for energy conservation:

$$\frac{\partial}{\partial t}\left(\rho c_v \theta\left(\mathbf{x},t\right)\right) = \nabla\cdot\left(\kappa\nabla\theta\left(\mathbf{x},t\right)\right)$$

Finite element discretization leads to a set of ODE's for the nodal temperatures

$$\theta^h\left(\mathbf{x},t\right) = \sum_I N_I\left(\mathbf{x}\right)\theta_I\left(t\right) \implies \frac{\partial}{\partial t}\left(\mathbf{M}\theta\right) = \mathbf{K}\theta$$

$$M_{IJ} = \int_\Omega \rho c_v N_I N_J \, dV$$

$$K_{IJ} = \int_\Omega \kappa \nabla N_I \cdot \nabla N_J \, dV$$

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MD Temperature Definition

We have to relate the dynamics of atoms to the nodal temperature field

$$E^{MD} = \sum_{\alpha} \frac{1}{2} m_\alpha \left|\mathbf{v}_\alpha\right|^2 + \Phi \implies \begin{aligned} e^k_\alpha &\approx m_\alpha \left|\mathbf{v}'_\alpha\right|^2 / \Delta V_\alpha \\ e^t_\alpha &\approx \left(m_\alpha \left|\mathbf{v}'_\alpha\right|^2 / 2 + \phi'_\alpha \right) / \Delta V_\alpha \end{aligned}$$

Define restriction operation: MD particles → Nodal field

E.g. projection, averaging, shape functions…

One way: minimize difference between MD and continuum energies

$$\min_{\theta_I} \sum_{\alpha \in \text{atoms}} \left(e_\alpha \Delta V_\alpha - \sum_{I \in \text{nodes}} \rho c_v N_{I\alpha} \theta_I \Delta V_\alpha \right)^2 \Longrightarrow \boxed{\theta_I = \sum_\alpha \hat{N}_{I\alpha} T_\alpha}$$

$$\rho \equiv \frac{m_\alpha}{\Delta V_\alpha}, \quad c_v \equiv \frac{3k_B}{m_\alpha}$$

Dulong-Petit expression for heat capacity of a mono-atomic solid or dense fluid above the Debye temperature

Using row-sum lumping (localization) and atomic quadrature for mass matrix in MD region (thermodynamic consistency)

$$\hat{N}_{I\alpha} = \frac{N_{I\alpha}}{\sum_\beta N_{I\beta}}$$

$$T_\alpha = \frac{1}{3k_B} e_\alpha \Delta V_\alpha$$

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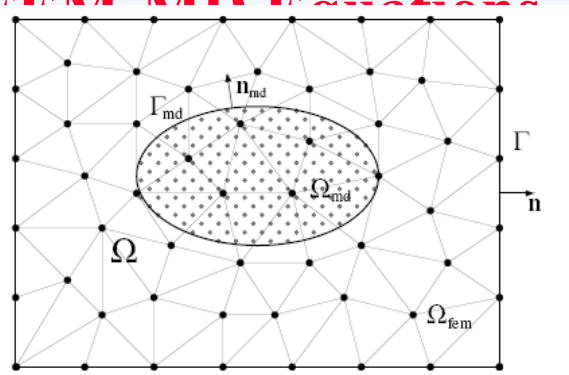
Derivation of Coupled FEM-MD Equations



Apply Galerkin method to entire domain:

Decompose domain:

$$\int_{\Omega} N_I(\mathbf{x}) \frac{\partial}{\partial t}\left(\rho c_v \theta^h(\mathbf{x})\right) dV = \int_{\Omega_{\text{fem}}} N_I(\mathbf{x}) \frac{\partial}{\partial t}\left(\rho c_v \theta^h(\mathbf{x})\right) dV + \sum_{\alpha} \frac{\partial}{\partial t}\left(N_{I\alpha} \rho c_v \theta^h_\alpha \Delta V_\alpha\right)$$

Use atomic energy density:

$$\int_{\Omega_{\text{fem}}} N_I(\mathbf{x}) \frac{\partial}{\partial t}\left(\rho c_v \theta^h(\mathbf{x})\right) dV + \sum_{\alpha} \frac{\partial}{\partial t}\left(N_{I\alpha} \rho c_v \theta^h_\alpha \Delta V_\alpha\right) = \int_{\Omega_{\text{fem}}} N_I(\mathbf{x}) \frac{\partial}{\partial t}\left(\rho c_v \theta^h(\mathbf{x})\right) dV + \sum_{\alpha} \frac{\partial}{\partial t}\left(N_{I\alpha} e_\alpha \Delta V_\alpha\right)$$

Apply physics:

$$\int_{\Omega_{\text{fem}}} N_I(\mathbf{x}) \frac{\partial}{\partial t}\left(\rho c_v \theta^h(\mathbf{x})\right) dV + \sum_{\alpha} \frac{\partial}{\partial t}\left(N_{I\alpha} \rho c_v \theta^h_\alpha \Delta V_\alpha\right) =$$

$$\int_{\Omega_{\text{fem}}} N_I \nabla \cdot \kappa \nabla \theta^h \, dV + \sum_{\alpha} N_{I\alpha}\left(\mathbf{v}_\alpha \cdot \mathbf{f}_\alpha + \dot{\phi}'_\alpha\right) + \sum_{\alpha} \left(\nabla N_{I\alpha} \cdot \mathbf{v}_\alpha\right) e_\alpha \Delta V_\alpha$$

Discretize:

$$\sum_J \frac{\partial}{\partial t}\left(M_{IJ}\theta_J\right) = \sum_J K_{IJ}\theta_J + \sum_{\alpha} N_{I\alpha}\left(\mathbf{v}_\alpha \cdot \mathbf{f}_\alpha + \dot{\phi}'_\alpha\right) + \sum_{\alpha} \left(\nabla N_{I\alpha} \cdot \mathbf{v}_\alpha\right) e_\alpha \Delta V_\alpha$$

Coupling MD Thermostat

Effects of FEM on MD can be included by prescribing constraints relating the FE and MD dynamics:

Temperature constraint

$$\sum_{\alpha} N_{I\alpha}\mathbf{v}_{\alpha}\cdot\mathbf{f}_{\alpha}+\sum_{\alpha} N_{I\alpha}\phi'_{\alpha}+\sum_{\alpha}\left(\nabla N_{I\alpha}\cdot\mathbf{v}_{\alpha}\right)e_{\alpha}\Delta V_{\alpha}-\sum_{J}\frac{\partial}{\partial t}\left(M^{MD}_{IJ}\theta_{J}\right)=0$$

Heat flux constraint

$$\sum_{\alpha} N_{I\alpha}\left(\frac{\partial\Phi}{\partial\mathbf{x}_{\alpha}}\cdot\mathbf{v}_{\alpha}+\mathbf{v}_{\alpha}\cdot\mathbf{f}_{\alpha}\right)+\int_{\Gamma_{MD}} N_{I\alpha}\mathbf{n}_{md}\cdot q^{h}\,dA=0$$

Thermostat force exactly cancels the FE boundary flux for the total temperature definition, otherwise there is a partial residual

Governing Equation for the Lagrange Multiplier

Application of Gauss' principle of least constraint to atomic forces yields an elliptic-like equation for the Lagrange Multiplier:

$$\sum_{\alpha} N_{I\alpha} K_{\alpha} \sum_{J} N_{J\alpha} \lambda_J = R_I^c$$

Variable λ is a continuum field defined on the nodes:

$$\lambda\left(\mathbf{x}_{\alpha}\right) = \sum_{I} N_{I\alpha} \lambda_I$$

Implies a modification to the MD force

$$\mathbf{f}_{\alpha} = \mathbf{f}_{\alpha}^{MD} - \frac{m_{\alpha}}{2} \lambda\left(\mathbf{x}_{\alpha}\right) \mathbf{v}_{\alpha}$$

So atomic degrees of freedom are governed by

$$m_{\alpha} \dot{\mathbf{v}}_{\alpha} = \mathbf{f}_{\alpha}^{MD} - \frac{m_{\alpha}}{2} \sum_{I} N_{I\alpha} \lambda_I \mathbf{v}_{\alpha}$$

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Combined System

Result is set of coupled FEM/MD equations

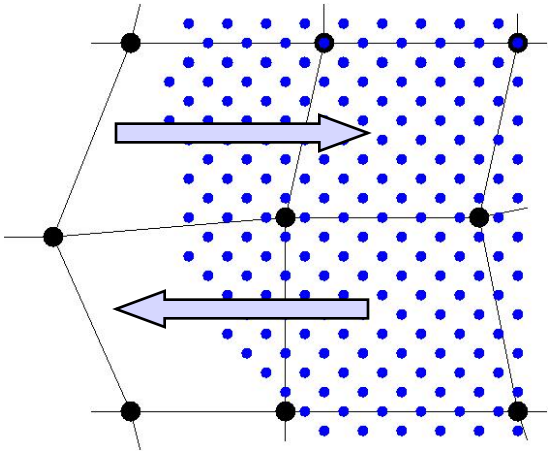
$$\sum_J \frac{\partial}{\partial t}\left(M_{IJ}\theta_J\right) = \sum_J K_{IJ}\theta_J + 2\sum_\alpha N_{I\alpha}\mathbf{v}_\alpha \cdot \left(\mathbf{f}_\alpha^{MD} + \frac{1}{2}\mathbf{f}_\alpha^{\lambda}\right)$$

$$m_\alpha \dot{\mathbf{v}}_\alpha = \mathbf{f}_\alpha^{MD} - \frac{m_\alpha}{2}\sum_I N_{I\alpha}\lambda_I \mathbf{v}_\alpha$$

Coupling parameter (temperature/flux constraint)

Combined MD/FEM system has two-way coupling:

Atoms contribute to nodal heat equation



Heat at nodes affects MD energy through thermostat

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Motivation for the Fractional Step Method

Fractional step originally developed by A. Chorin (1968) to exactly satisfy elliptic constraints on a hyperbolic problem, including different integration methods for different terms

In this case there are several complicating factors

Discrepancy in evolution of kinetic energy in atomic system

$$\Delta K_\alpha = \Delta t \mathbf{v}_\alpha \cdot \mathbf{f}_\alpha + \frac{\Delta t^2}{2} \mathbf{f}_\alpha \cdot \mathbf{f}_\alpha$$

No direct evaluation of the time derivative of the potential

$$\frac{\partial \phi_\alpha}{\partial t} = ?$$

Drift between change in shape functions and convection

$$\nabla N_{I\alpha} \cdot \mathbf{v}_\alpha \neq \Delta N_{I\alpha}$$

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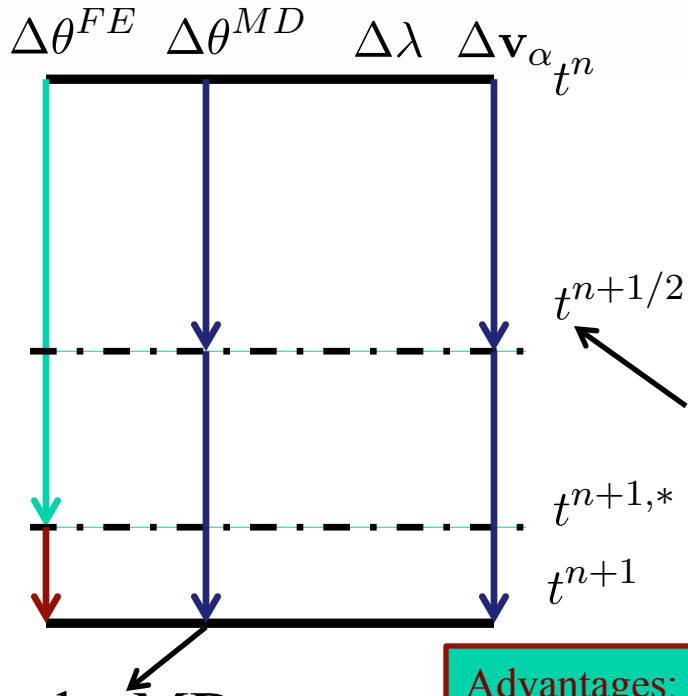
Fractional Step Method for Time Integration



Gear update for FE dynamics, predictor/corrector requires:

$$\dot{\theta}^{FE} = M_{IJ}^{-1} K_{IK} \theta_K$$

at time $t^{n+1,*}$

Velocity-Verlet update for MD, two-step update requires:

$$\dot{\mathbf{v}}_\alpha = m_\alpha^{-1} \mathbf{f}_\alpha^{MD}$$

at time $t^{n+1/2}$

Use a consistent update for the MD contribution to the FE temperature, two-step update based on incremental

$$\Delta\theta_I = M_{IJ}^{-1} \sum_\alpha N_{I\alpha} e_\alpha \Delta V_\alpha \big|_{t^{n+1}} - M_{IJ}^{-1} \sum_\alpha N_{I\alpha} e_\alpha \Delta V_\alpha \big|_{t^n}$$

$$\Delta E_I = \sum_\alpha N_{I\alpha} \left(\Delta t \mathbf{v}_\alpha \cdot \mathbf{f}_\alpha + \frac{\Delta t^2}{2} m_\alpha^{-1} \mathbf{f}_\alpha \cdot \mathbf{f}_\alpha + \phi'_\alpha \big|_{t^{n+1}} - \phi'_\alpha \big|_{t^n} \right)$$

Advantages:

- Enables general temperature definitions to be used
- Eliminates temperature drift between FE and MD systems

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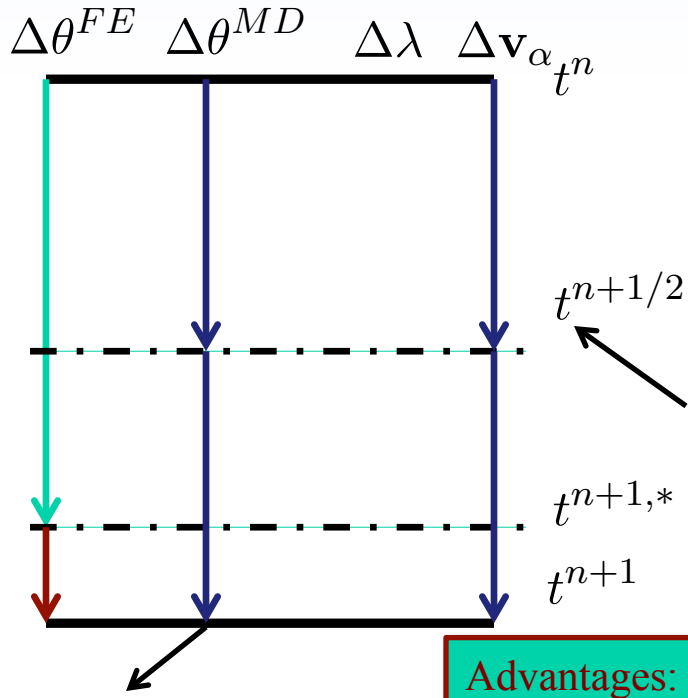
Fractional Step Method for Time Integration



Gear update for FE dynamics, predictor/corrector requires:

$$\dot{\theta}^{FE} = M_{IJ}^{-1} K_{IK} \theta_K$$

at time $t^{n+1,*}$

Velocity-Verlet update for MD, two-step update requires:

$$\dot{\mathbf{v}}_\alpha = m_\alpha^{-1} \mathbf{f}_\alpha^{MD}$$

at time $t^{n+1/2}$

Update Lagrange multipliers after the prediction phase by solving the non-

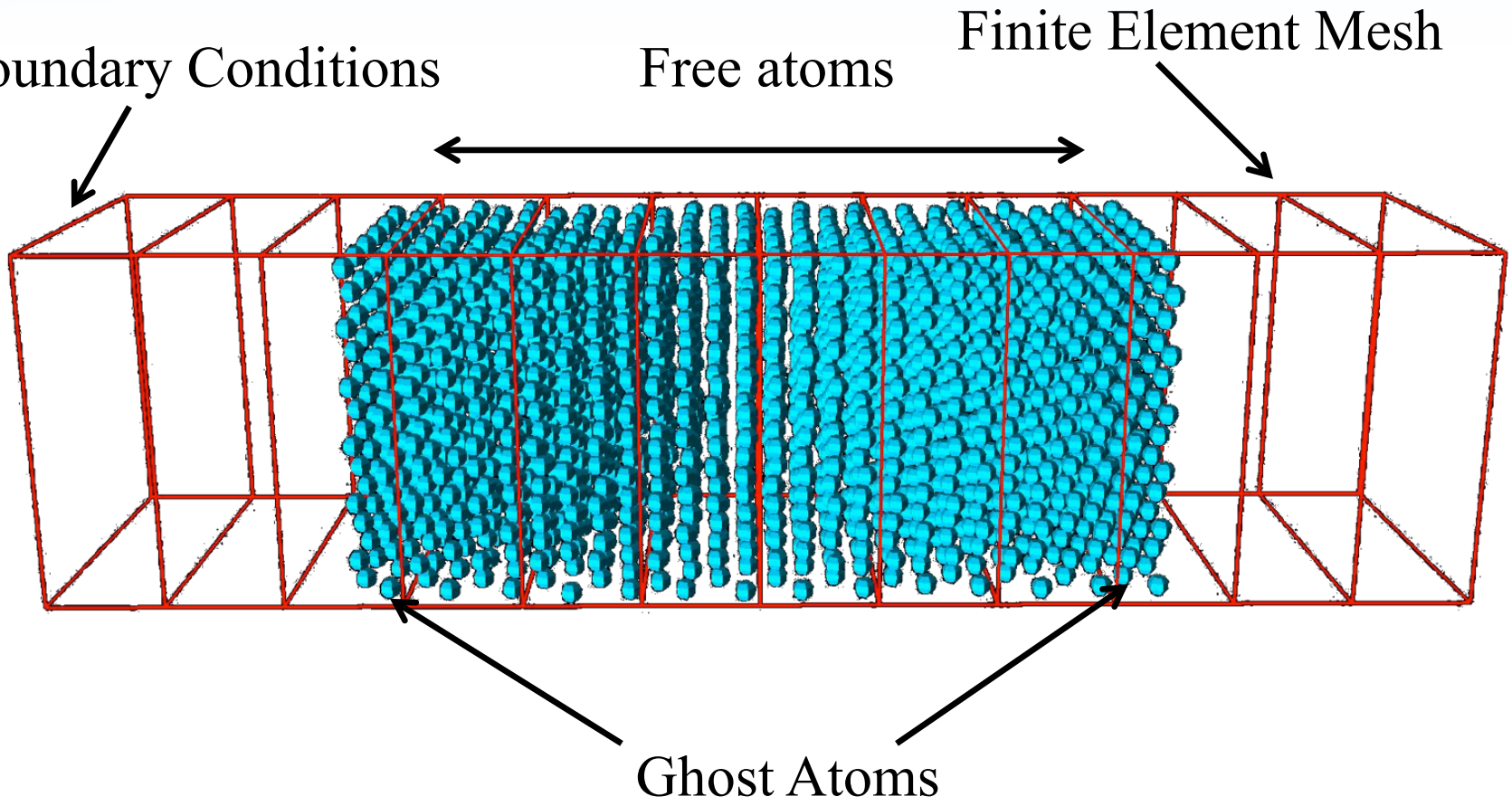
$$\Delta t \sum_\alpha N_I^\alpha K_\alpha \sum_J N_J^\alpha \lambda_J - \frac{\Delta t^2}{4} \sum_\alpha N_I^\alpha K_\alpha \left(\sum_J N_J^\alpha \lambda_J \right) \left(\sum_K N_K^\alpha \lambda_K \right) = R_I^c$$

Apply resulting force at three time increments: t^n, $t^{n+1/2}$, and $t^{n+1,*}$

Advantages:

- Solvability criteria for timestep: $\Delta t \lambda < 1$
- Efficient solution by iterative methods
- Eliminates drift between MD and FE temperatures
- Enables exact energy conservation

Demonstration Problem



2016 Lennard-Jones argon atoms with equilibrium FCC spacing of ~5 Ang at 20 K

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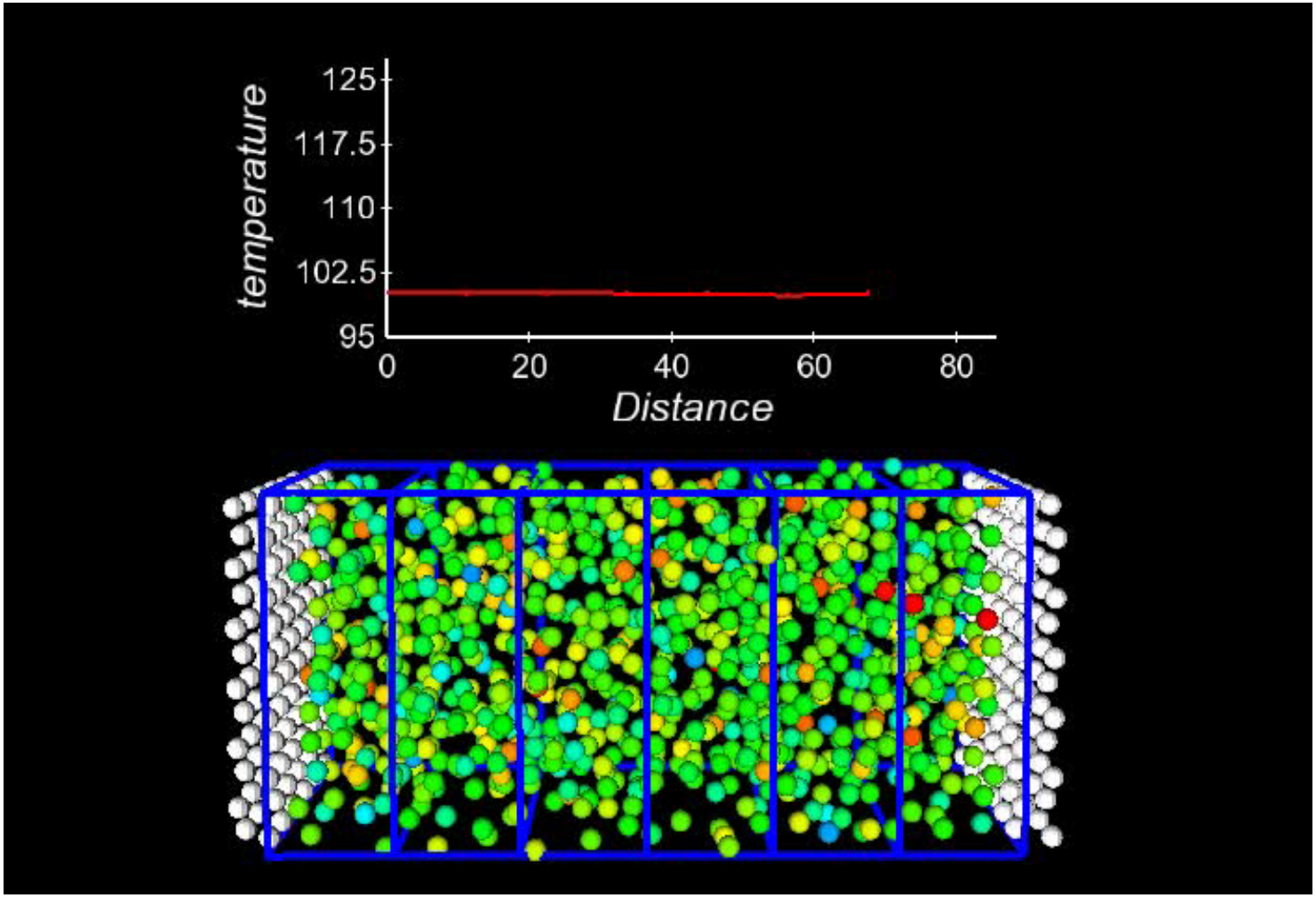
Liquid Argon Temperature BCs



$$\kappa = 1.54 \times 10^{-9} \text{ AMU/fs}^3 \text{ K}$$

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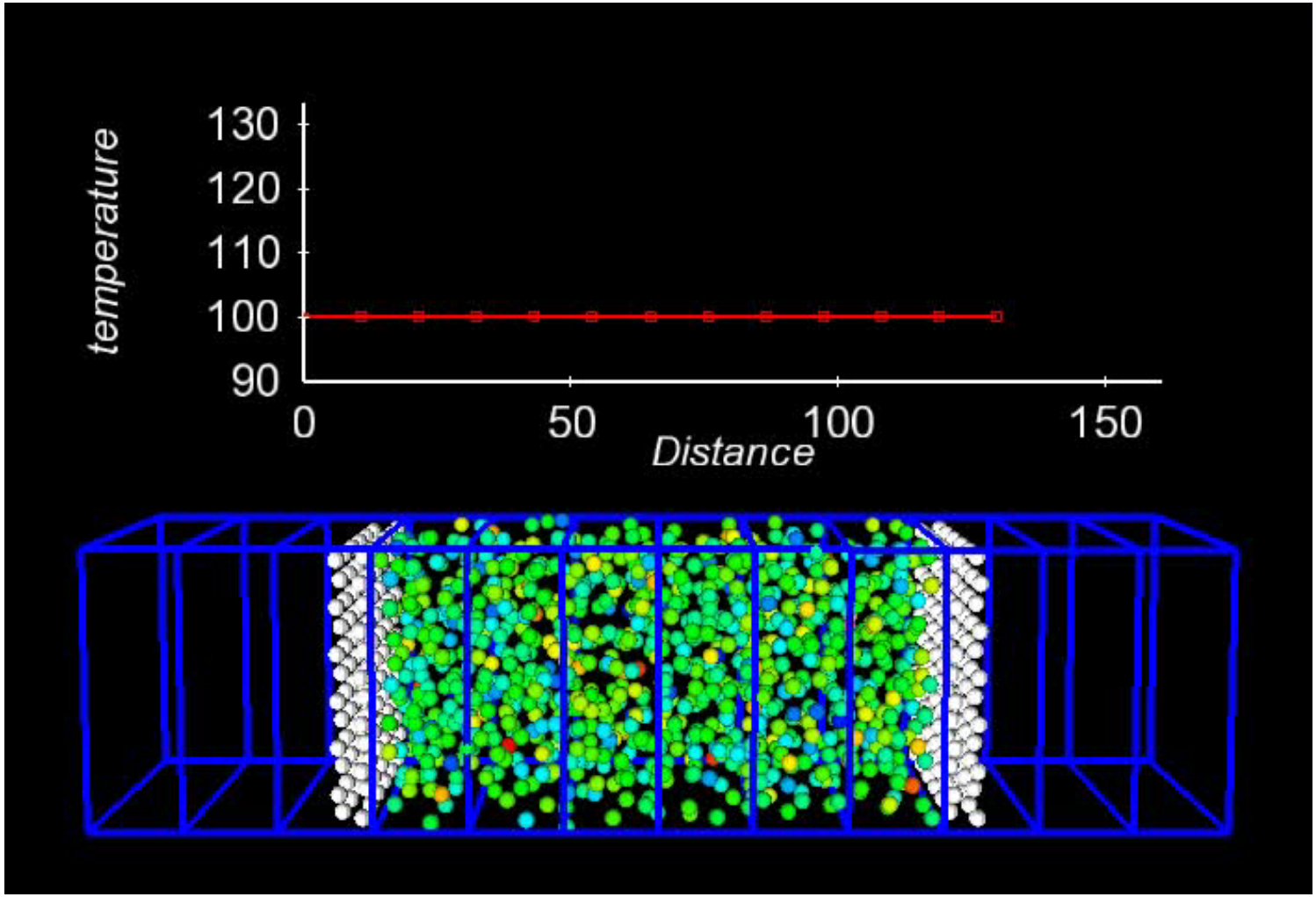
Liquid Argon Flux Coupling



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Coupled Momentum & Temperature Equations

- Continuum equations of motion,

$$\frac{D}{Dt}\left(\rho \mathbf{V}(\mathbf{x},t)\right) = -\nabla P + \nabla \cdot \mu \nabla \mathbf{V}(\mathbf{x},t)$$

$$\frac{D}{Dt}\left(\rho c_p T\left(\mathbf{x},t\right)\right) = \nabla \cdot \left(\kappa \nabla T\left(\mathbf{x},t\right)\right)$$

- Discretized using the finite element method,

$$\mathbf{V}^h\left(\mathbf{x},t\right) = \sum_I N_I\left(\mathbf{x}\right)\mathbf{V}_I\left(t\right) \implies \frac{D}{Dt}\left(M\dot{\mathbf{V}}\right) = \int_\Omega P_I \nabla N_I \, dV - K\mathbf{V}$$

$$M_{IJ} = \int_\Omega \rho N_I N_J \, dV \qquad K_{IJ} = \int_\Omega \mu \nabla N_I \cdot \nabla N_J \, dV$$

- Corresponding atomic quantities

$$\mathbf{p}_\alpha \Delta V_\alpha = m_\alpha \mathbf{v}_\alpha \qquad T_\alpha \Delta V_\alpha = \frac{1}{3k_B} m_\alpha \left|\mathbf{v}'_\alpha\right|^2$$

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Coarse-Graining of Atomic Quantities

- Minimize least-squares error between MD & FE:

$$\min_{\mathbf{v}_I} \frac{1}{2} \int_\Omega \left(\mathbf{p} - \sum_{I \in \text{nodes}} \rho N_I \mathbf{v}_I \right)^2 dV \approx \min_{\mathbf{v}_I} \frac{1}{2} \sum_{\alpha \in \text{atoms}} \left(\mathbf{p}_\alpha - \sum_{I \in \text{nodes}} \rho N_{I\alpha} \mathbf{v}_I \right)^2 \Delta V_\alpha$$

- Results in mapping between atomic and nodal variables:

$$\mathbf{v}_I = \sum_\alpha \hat{N}_{I\alpha} m_\alpha \mathbf{v}_\alpha \qquad \hat{N}_{I\alpha} = \frac{N_{I\alpha}}{\sum_\beta N_{I\beta} m_\beta}$$

- As well as dynamics driven by atomistic quantities

$$\sum_J \frac{D}{Dt} \left(M_{IJ} \mathbf{v}_J \right) = \sum_\alpha N_{I\alpha} \mathbf{f}_\alpha + \sum_\alpha \left(\nabla N_{I\alpha} \cdot \mathbf{v}_\alpha \right) m_\alpha \mathbf{v}_\alpha$$

$$\sum_J \frac{D}{Dt} \left(M_{IJ} T_J \right) = 2 \sum_\alpha N_{I\alpha} \mathbf{v}'_\alpha \cdot \mathbf{f}'_\alpha + 2 \sum_\alpha \left(\nabla N_{I\alpha} \cdot \mathbf{v}_\alpha \right) m_\alpha \mathbf{v}' \cdot \mathbf{v}'$$

- BCs and sources specify the left-hand side

Gaussian Least Constraints for Combined Momentum/Temperature Coupling

- Create an augmented cost function using Lagrange multipliers

$$J = \sum_{\alpha} \left| \mathbf{f}_{\alpha}^{MD} - \mathbf{f}_{\alpha} \right|^2 - \sum_{I} \lambda_I^{\mathbf{V}} \cdot \left(\mathbf{V}_I^{RHS} - \mathbf{V}_I^{LHS} \right) - \sum_{I} \lambda_I^{T} \left(T_I^{RHS} - T_I^{LHS} \right)$$

- Which implies an augmented force:

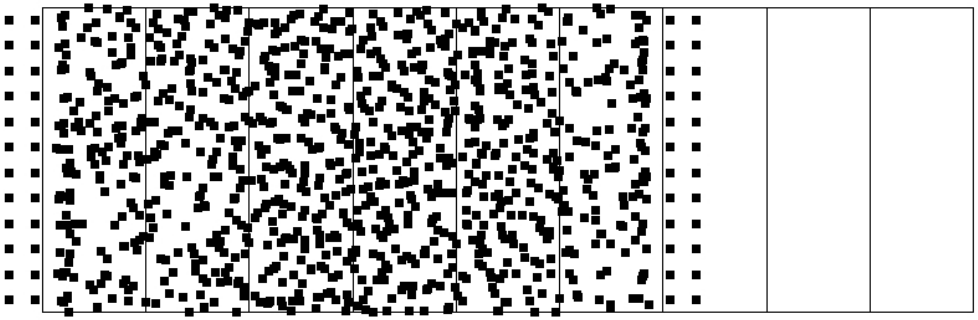
$$m_\alpha \dot{\mathbf{v}}_\alpha = \mathbf{f}_\alpha^{MD} - m_\alpha \sum_I N_{I\alpha} \lambda_I^{\mathbf{V}} - \frac{m_\alpha}{2} \sum_I N_{I\alpha} \lambda_I^T \mathbf{v}'_\alpha$$

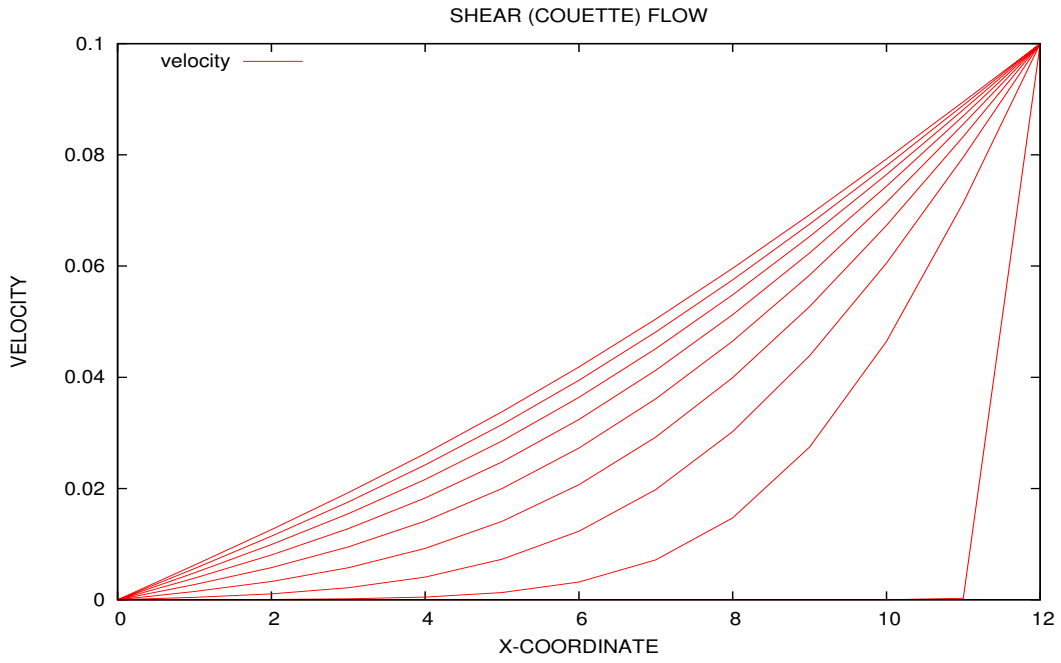
- Where λ satisfies the following matrix equation

$$\sum_\alpha N_{I\alpha} M_\alpha \sum_J N_{J\alpha} \lambda_J^{\mathbf{V}} + \frac{1}{2} \sum_\alpha N_{I\alpha} \mathbf{P}'_\alpha \sum_J N_{J\alpha} \lambda_J^T = R_I^{\mathbf{V}}$$

$$\sum_\alpha N_{I\alpha} K'_\alpha \sum_J N_{J\alpha} \lambda_J^T + \frac{1}{2} \sum_\alpha N_{I\alpha} \mathbf{P}'_\alpha \sum_J N_{J\alpha} \lambda_J^{\mathbf{V}} = R_I^T$$

Shear Flow





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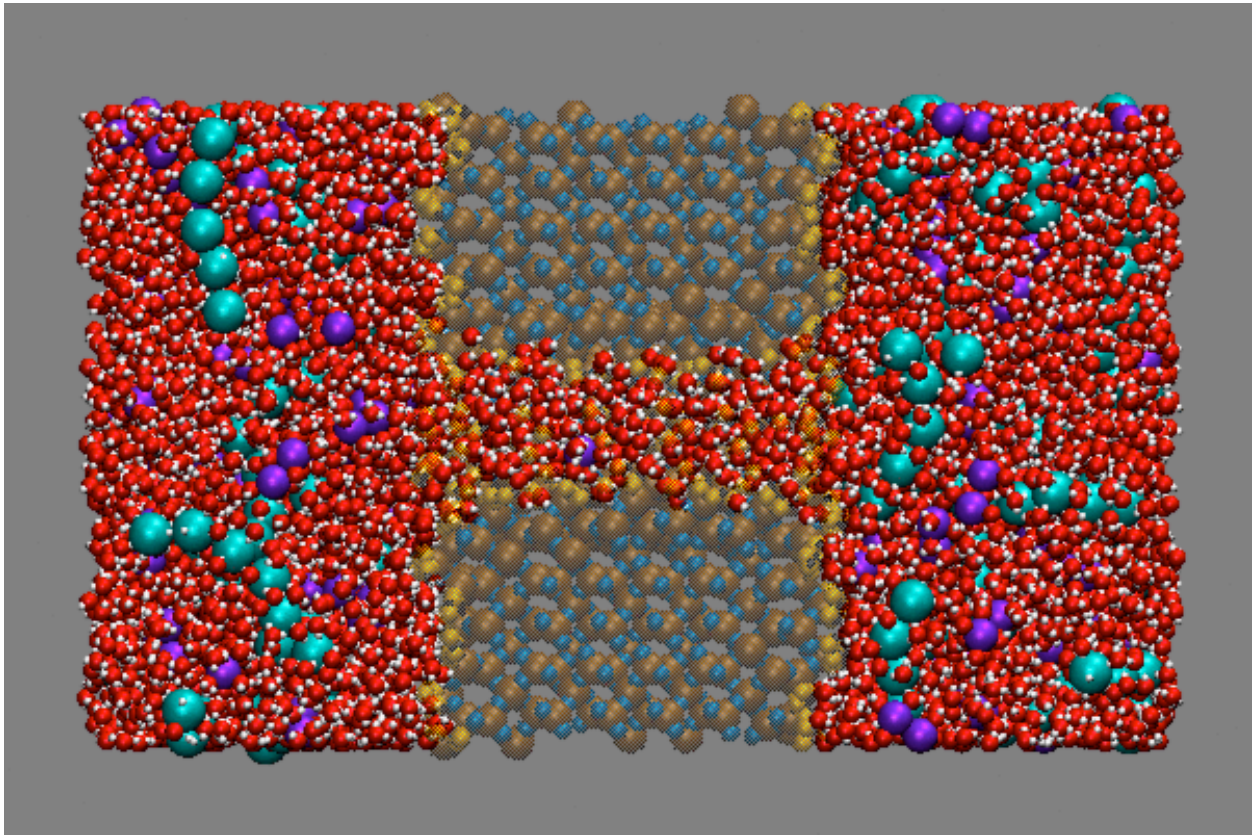
Concentration Control

+V

-V



Particle insertions/ deletions based on minimal energy locations

In collaboration with F. Rizzi (Johns-Hopkins)

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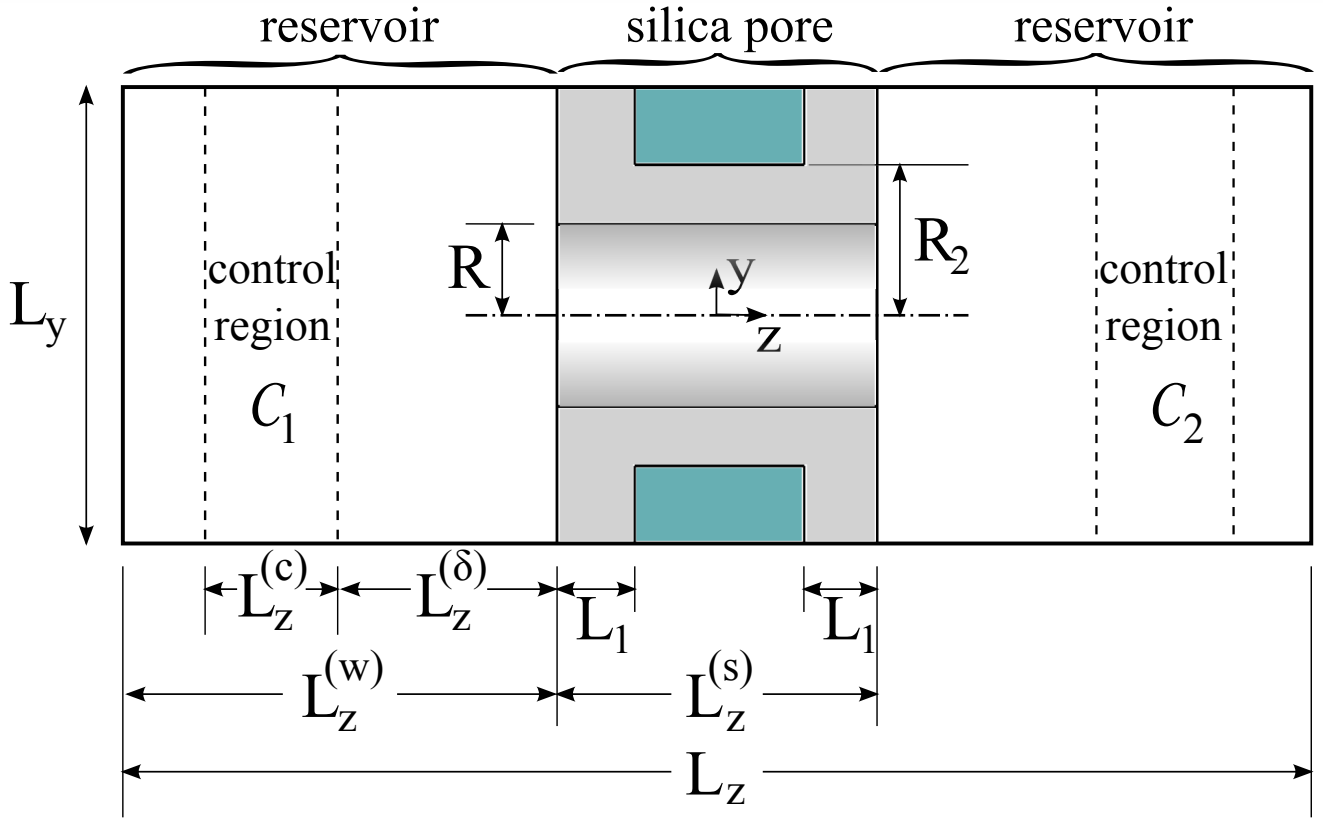
Example: Flow in a Nanopore



Control regions maintain temperature and concentration while preserving momentum

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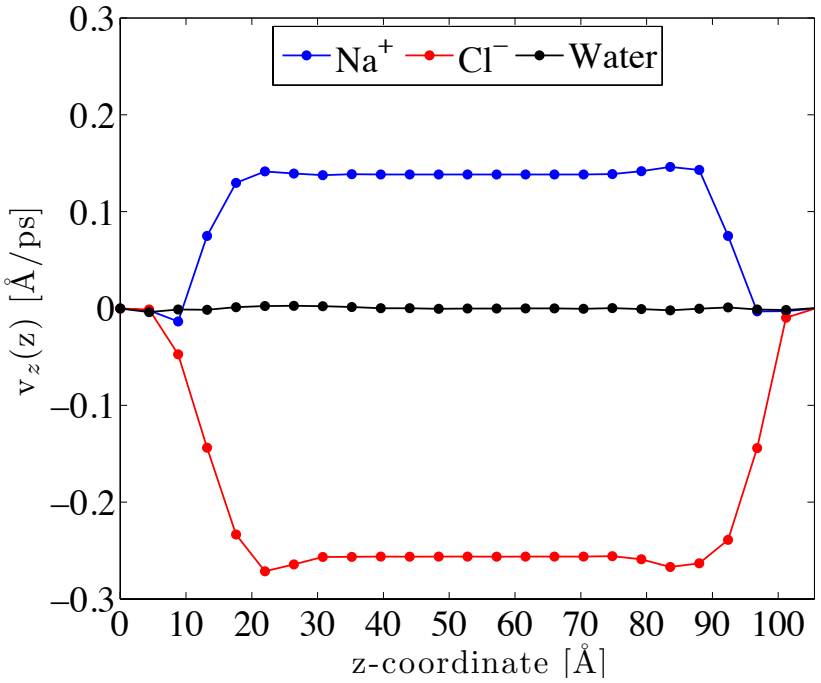
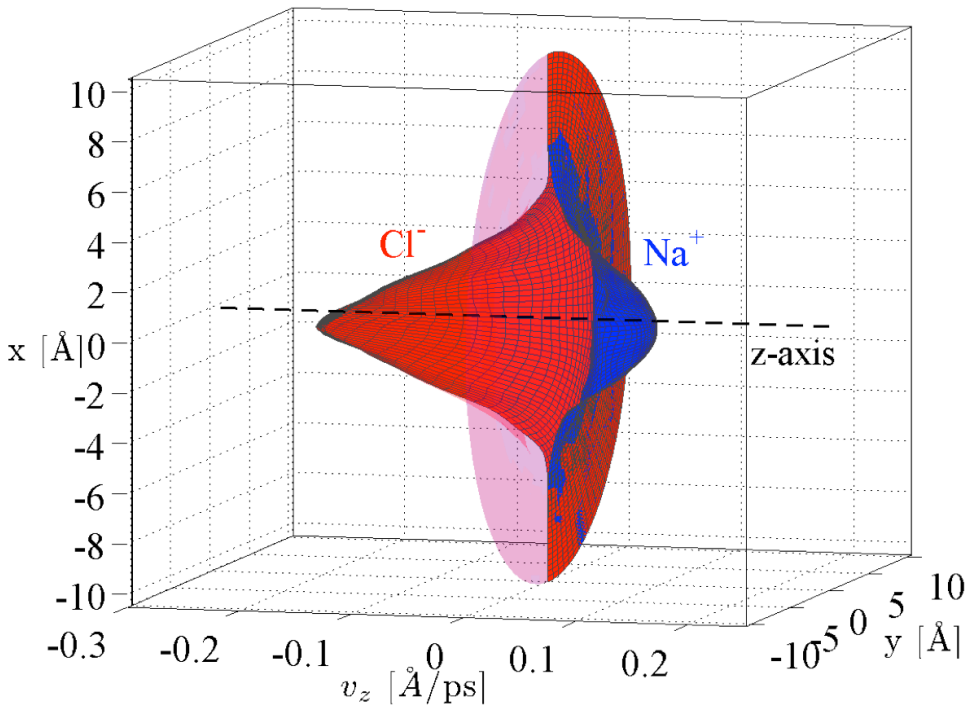
Example: Flow in a Nanopore

Mean Velocities



Velocity Distributions



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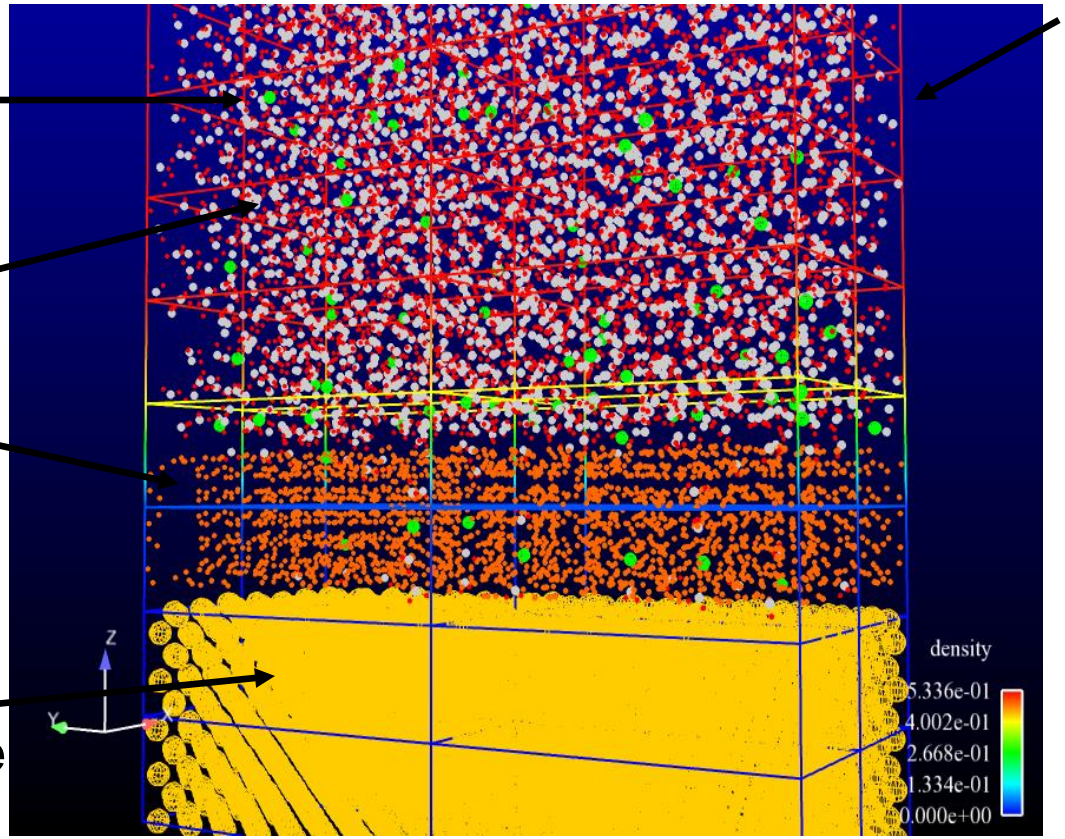
AtC Model for Long-range Electrostatics



FE Mesh Enables

1. Coarse-scaling MD for increased physical understanding
2. Solves for electric field with
   a) Upscale FE source terms
   b) Downscale MD electric forces

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Finite Element Electric Potential

FE equation for nodal electric potential:

$$\sum_{J\in\mathcal{F}} \int_{\Omega} \nabla N_I \cdot \nabla N_J \phi_J \, dV = \frac{1}{\varepsilon_0} \int_{\Omega} N_I \rho \, dV - \int_{\Gamma} N_I \mathbf{E} \cdot \mathbf{n} \, dS$$

Includes source from continuous charge density and natural boundary conditions associated with the electric field.

Define nodal charge density through row-sum lumped projection:

$$\int_{\Omega} N_I \rho \, dV \approx \sum_{\alpha} N_I^{\alpha} q^{\alpha}$$

Arrive at a FE potential equation with multiscale source:

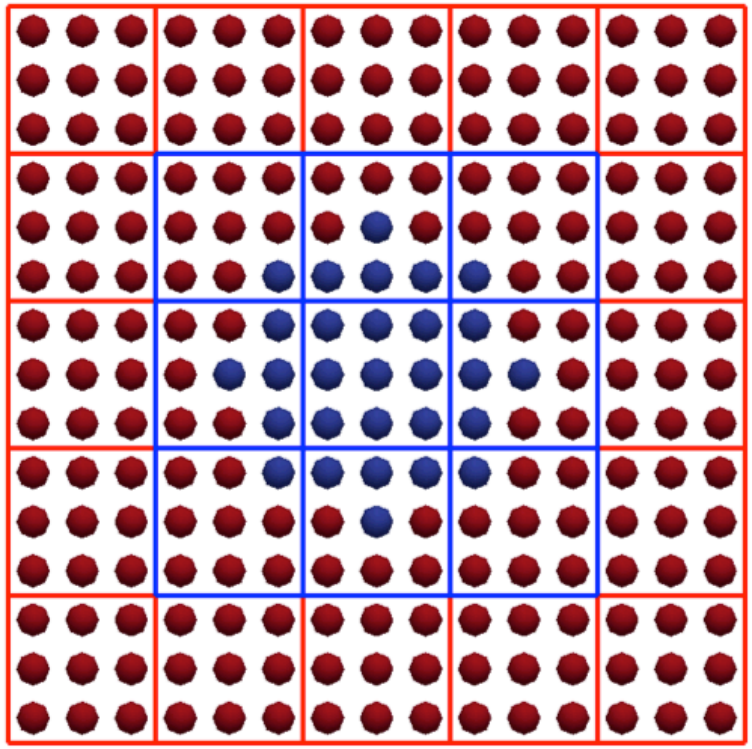
$$\sum_{J\in\mathcal{F}} \int_{\Omega} \nabla N_I \cdot \nabla N_J \phi_J \, dV = \frac{1}{\varepsilon_0} \sum_{\alpha} N_I^{\alpha} q^{\alpha} - \int_{\Gamma} N_I \mathbf{E} \cdot \mathbf{n} \, dS$$

subject to appropriate boundary conditions.

Short-Range/Long-Range Decomposition

$$\mathbf{f}^{\alpha} = \underbrace{\sum_{\beta \in \mathcal{N}_{\alpha}} \frac{k q^{\alpha} q^{\beta}}{r_{\alpha\beta}^{2}} \mathbf{r}'_{\alpha\beta}}_{\text{short range Coulombic}} - \underbrace{q^{\alpha} \nabla \phi\left(\mathbf{x}^{\alpha}\right)}_{\text{long range electrostatic}} + \underbrace{q^{\alpha} \sum_{\beta \in \mathcal{N}_{\alpha}} \nabla \phi^{\beta}\left(\mathbf{x}^{\alpha}\right)}_{\text{correction to long range forces}}$$

Atoms outside neighbor list contribute only through long range FE potential solved on the entire mesh.



Atoms in neighbor list have interactions corrected with short range FE potential computed on local nodes using Green's functions.

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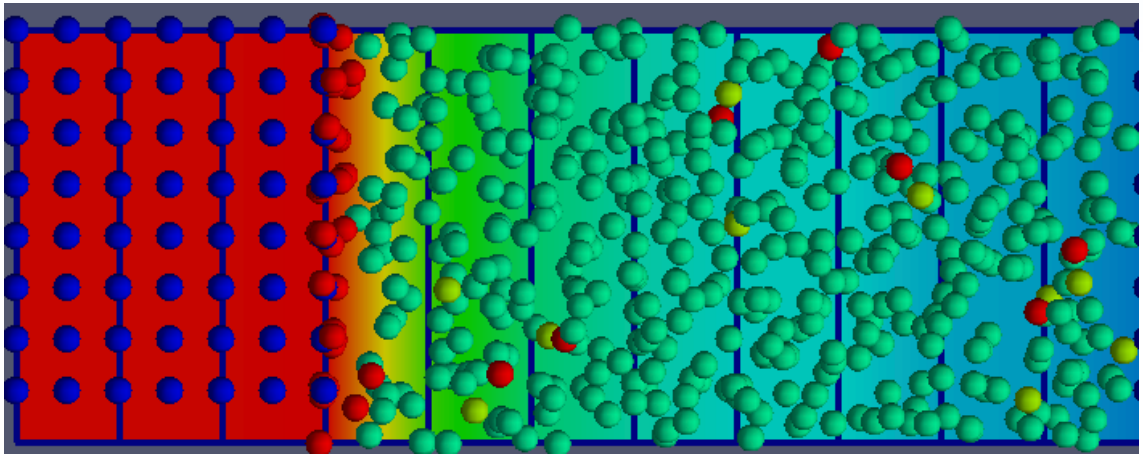
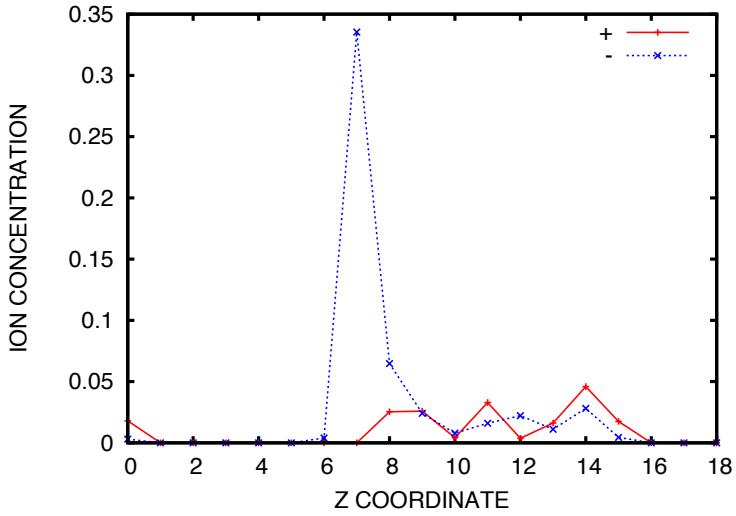
Boundary Conditions



Far-field electric potential boundary conditions

Ghost charges mimic conducting surface



Concentration controlled to prescribed values

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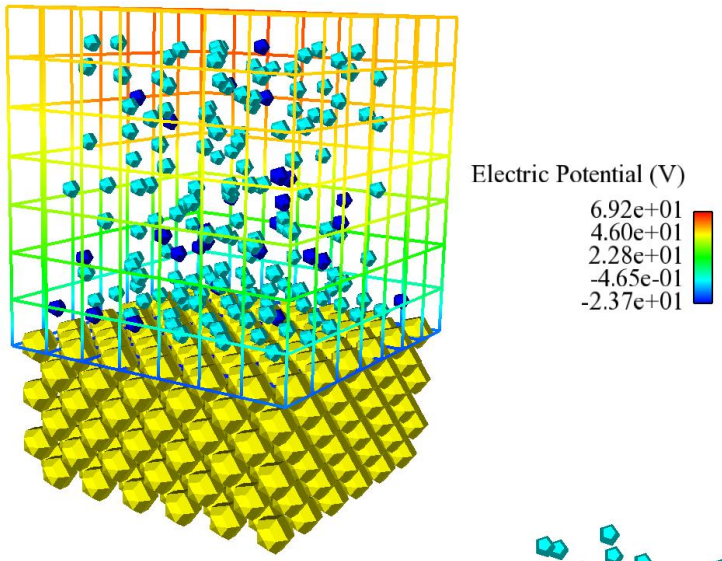
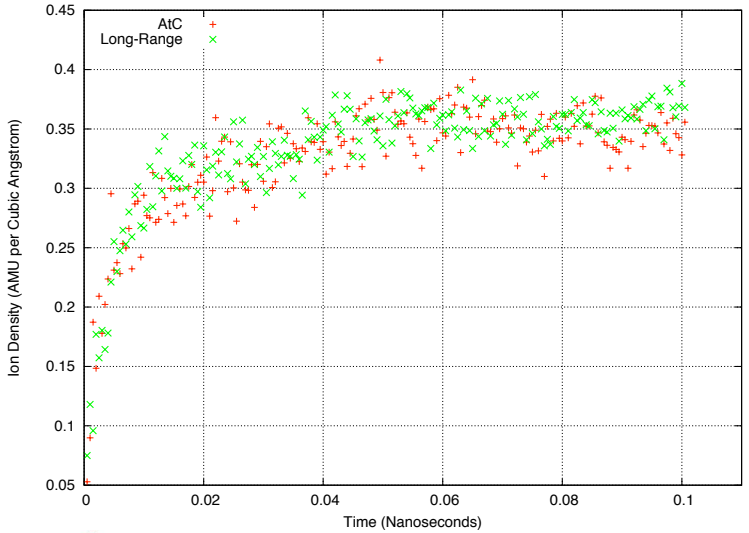
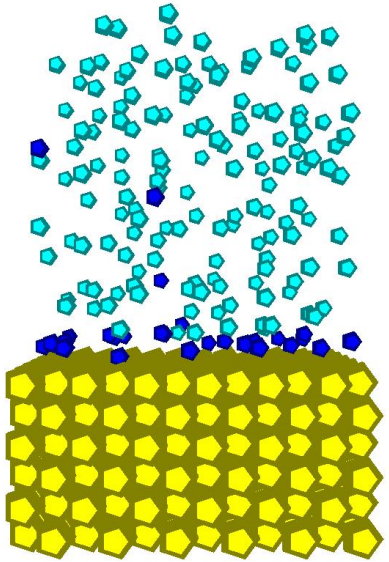
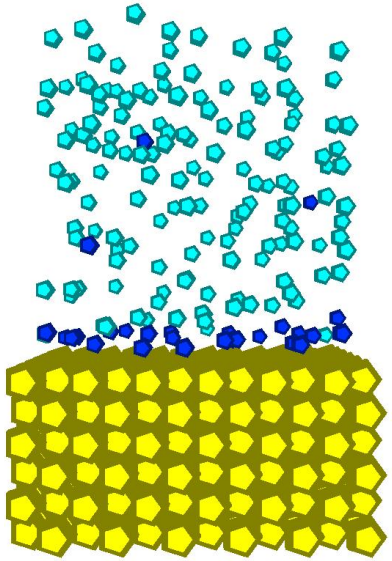
Boundary Condition Assessment





AtC Final State





Long Range Final State

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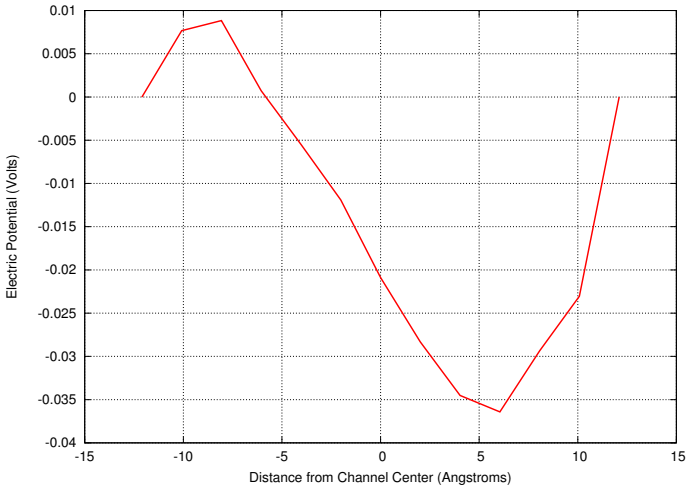
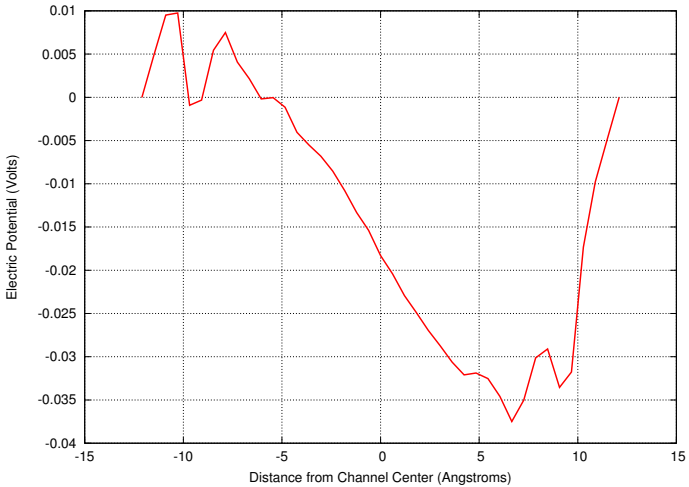
Silicon Nanochannel Simulation

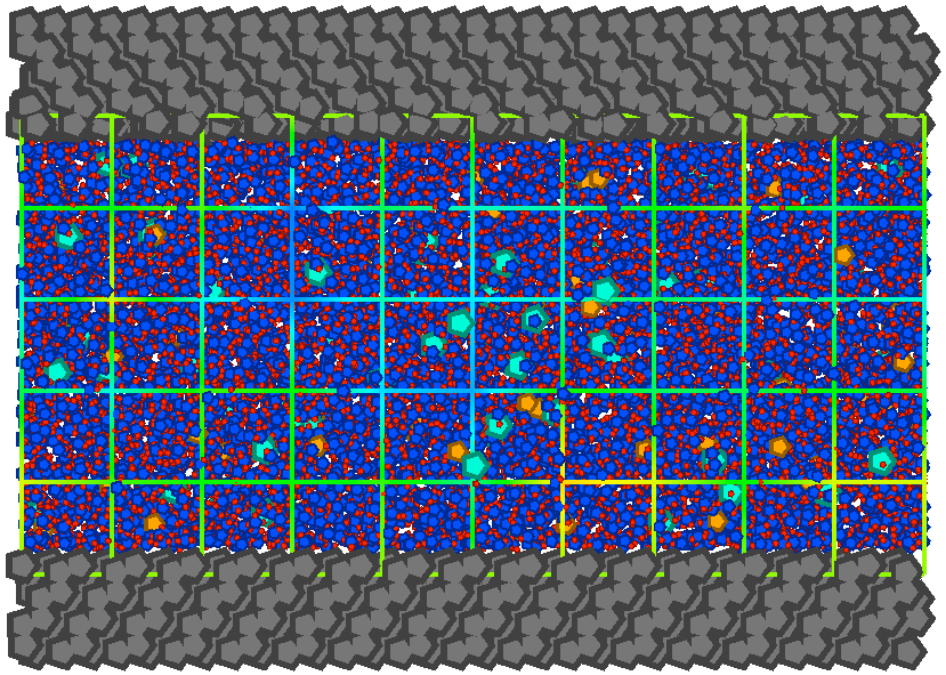
12 wall-normal elements



40wall-normal elements



Geometry and potentials based on Qiao & Uluru, *J. Chem. Phys.* (2003)



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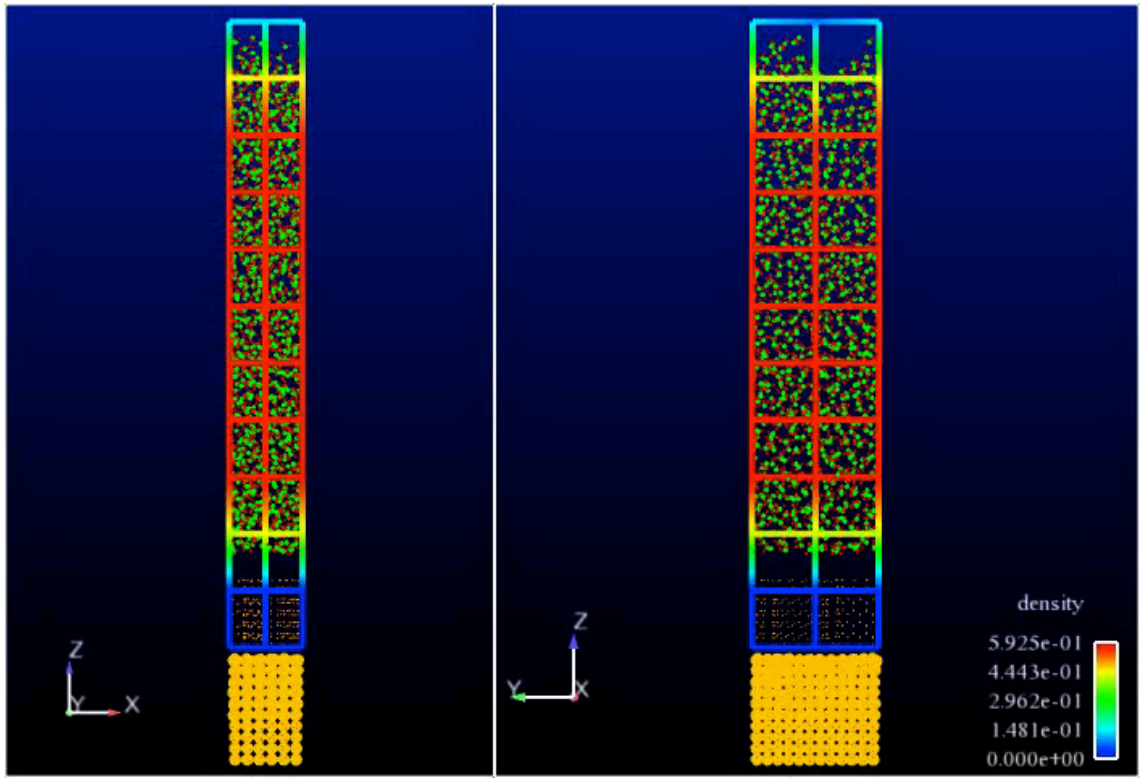
Other Physical Models: Fluidic Species Transport

- Define coupling in Eulerian frame rather than Lagrangian
- Track individual species to understand particle agglomeration and diffusion
- Example problem: transport of saltwater into nanotubes



- Future work: energy storage devices

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Selected AtC References

Thermal coupling

- Wagner *et al.*, *Comp. Meth. Appl. Mech. Eng.* (2008)
- Templeton, Jones, & Wagner, *Model. Simul. Mater. Sci. Eng* (2010)

Hardy post-processing

- Zimmerman, Jones, & Templeton, *J. Comp. Phys.* (2010)
- Jones & Zimmerman, *J. Mech. Phys. Solids* (2010)
- Jones *et al.*, *Phys. Condens. Matter* (2010)

Two-temperature modeling

- Jones *et al.*, *Int'l J. Numer. Meth. Eng.* (2010)

Long-range electrostatics

- Templeton *et al.*, *J. Comput. Theor. Chem.* (2011)

Simulations performed with LAMMPS MD code:

http://lammps.sandia.gov

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