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9: Common Non-Equilibrium Calculations

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Why Non-Equilibrium MD (NEMD)?

- Classical Molecular Dynamics often used as a thermodynamic equilibrium technique
  - Newton's Equations + pairwise central forces conserve energy
    - At long times (depending on IC's and BC's) → Microcanonical Ensemble
- We are interested in non-equilibrium properties
  - Transport: rheology

$$\boldsymbol{\sigma} = \eta\dot{\boldsymbol{\gamma}}$$

- How to obtain?
  - Near equilibrium or fluctuations about equilibrium
    - Linear response regime
      - Effectively zero rate transport coefficients
      - Need long-time for good statistics
- What about far from equilibrium?
  - High rates, large gradients
  - General time dependent behavior

Non-Equilibrium Ensemble Averages

- Rheological observables – `compute pxy`, `fix ave/spatial`
  - Stress and strain-rate (linear regime)
    - Irving-Kirkwood (1950) *J Chem Phys*, v. 18, p. 817

$$\sigma_{\alpha\beta} = \left\langle \frac{1}{V} \sum_{i=1}^{N} \left[\sum_{j \neq i} \frac{r_{ij}^{\alpha} f_{ij}^{\beta}}{2} + m_i (v_i^{\alpha} - u^{\alpha})(v_j^{\beta} - u^{\beta}) \right]; f^{N}(\mathbf{r}, \mathbf{p}, t) \right\rangle$$

$$\dot{\gamma} = \left[\nabla \left\langle \sum_{i=1}^{N} \mathbf{v}_i \delta(\mathbf{r}_i - \mathbf{r}) \right\rangle \right]_{\alpha\beta} = \left[\nabla \mathbf{u}(r) \right]_{\alpha\beta} \qquad \sigma_{\alpha\beta} \Big/ \dot{\gamma} = \eta$$

    - Again, in practice these become time averages
    - How long is long enough?

Evans and Morris, *Statistical Mechanics of Nonequilibrium Liquids*

Non-Equilibrium Steady States

- What happens when a constant force (through boundary conditions – applied gradient, or external field) is applied to Equilibrium System following Newton's Equations for particle dynamics?
  - E.g., cause particles to flow
    - For pairwise central forces, Newton's Equations conserve energy
    - Constant force gives constant acceleration so kinetic energy (temperature) increases with time
- What to do for constant (steady-sate) temperature?
  - Thermostat (on fluctuations about average) to balance energy input
    - Section 6.16 of How to

$$k_B T = \frac{3(N-1)}{2} \left\langle \sum_i m_i (\mathbf{v}_i(t) - \mathbf{u}(r,t))^2 \right\rangle$$

Typical NEMD Techniques (Rheology)

- Non-Hamiltonian Systems – “perturb” equations of motion
  - SLLOD + Parrinello-Rahman: shear flow
    - `fix nvt/sllod` + `fix deform`
- Boundary Modifications
  - Lees-Edwards
    - Steady Couette Flow
  - Muller-Plathe: shear or heat flow
    - `fix viscosity`
    - `fix thermal/conductivity`
  - Deletion and insertion
    - Mass flow

Perturbations to Equations of Motion

- General Approach

$$\dot{\mathbf{q}} = \mathbf{p}/m + \mathbf{A}_{\mathbf{p}}(\mathbf{q},\mathbf{p}) \cdot \mathcal{F}(t)$$

$$\dot{\mathbf{p}} = \mathbf{F} - \mathbf{A}_{\mathbf{q}}(\mathbf{q},\mathbf{p}) \cdot \mathcal{F}(t)$$

- Shear
- Heat flow

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m_i$$

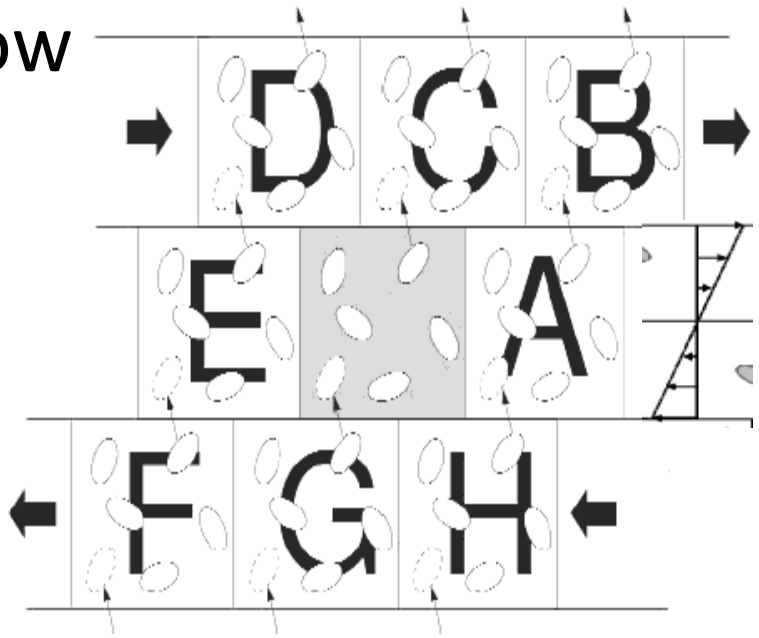
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \delta\varepsilon_i \mathcal{F}(t) + \frac{1}{2}\sum_j \mathbf{F}_{ij}(\mathbf{r}_{ij} \cdot \mathcal{F}(t)) - \frac{1}{2N}\sum_j \sum_k \mathbf{F}_{jk}(\mathbf{r}_{jk} \cdot \mathcal{F}(t))$$

- Diffusion

Allen and Tildesley, *Computer Simulation of Liquids*

Lees-Edwards Boundary Conditions

- Remap positions and velocities of particles crossing PBC
- Steady Shear (Couette) Flow
- Thermostat
  - E.g., Nose-Hoover
- No time dependent flow



Evans and Morris, *Statistical Mechanics of Nonequilibrium Liquids*

SLLOD + Parinello-Rahman

- Apply Shear Perturbation to each particle
  - Deform Box/particle positions

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m_i + \mathbf{q}_i \cdot \nabla \mathbf{u}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u}$$

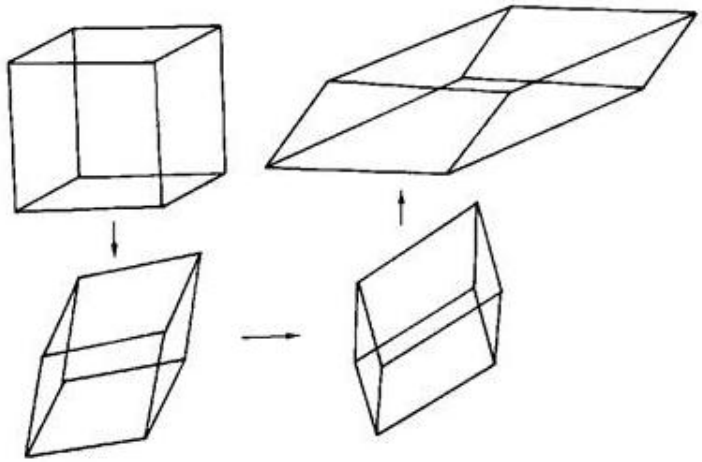
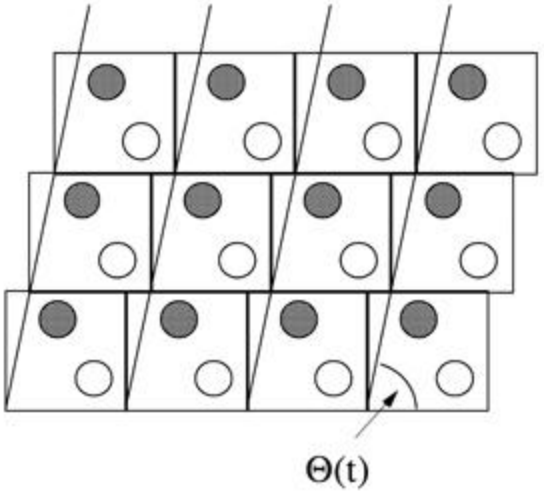
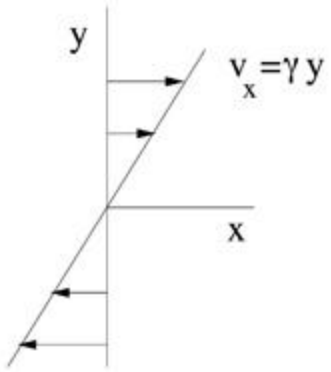


Fig. 7.3 Changing box-shape.

Evans and Morris, *Statistical Mechanics of Nonequilibrium Liquids*

- Remap positions and/ velocities across PBC
- Thermostat!
  - E.g., Nose-Hoover





$$\nabla \mathbf{u}(\mathbf{r},t) = \begin{bmatrix} 0 & 0 \\ \gamma & 0 \end{bmatrix}$$

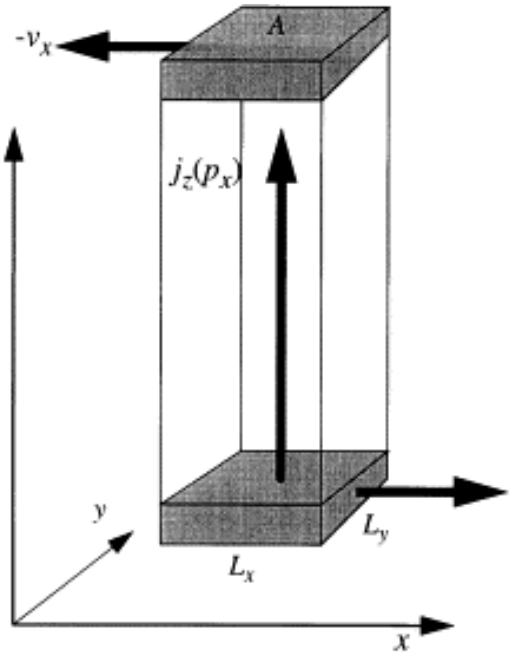
- Profile biased vs. profile unbiased

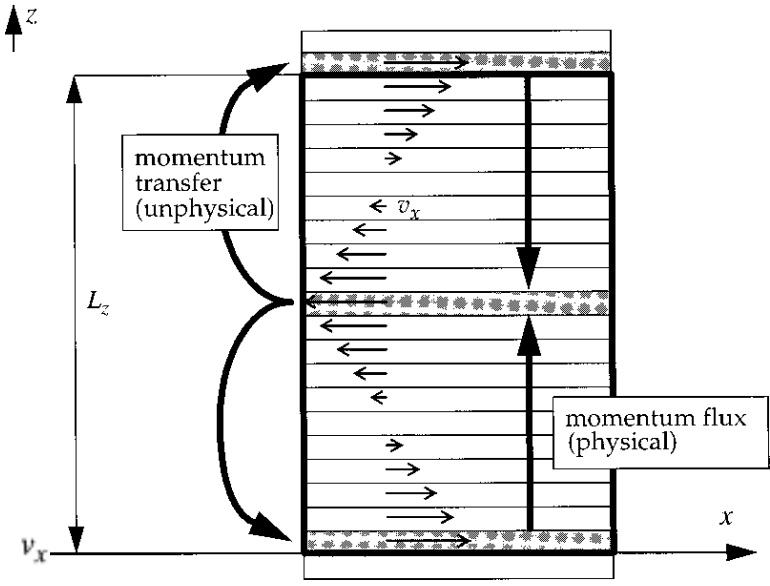
Muller-Plathe Approach

- Bin system in z
- Viscosity: swap opposed velocities in top and middle bins
  - `fix viscosit`
  - `fix ave/spat`

$$j_z(p_x) = -\eta \frac{\partial v_x}{\partial z}$$

$$j_z(p_x) = \frac{P_{tot}}{2tL_xL_y}$$



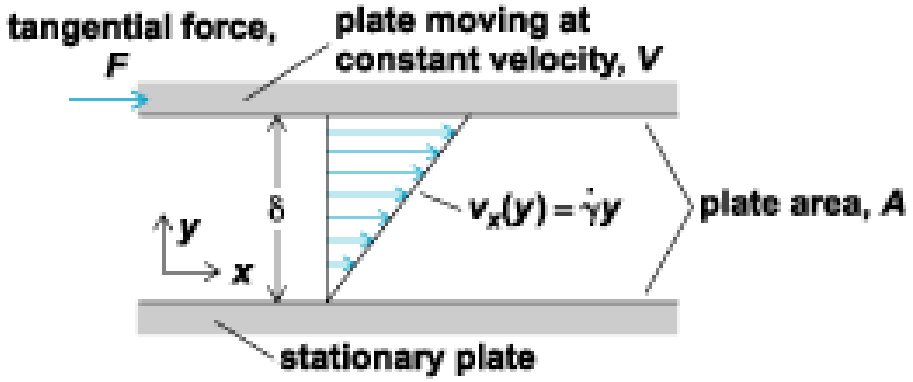


- Can swap "hot" and "cold" (difference in squared velocity magnitude) atoms for thermal conductivities

Muller-Plathe (1999) *Phys Rev E*, v. 59, p. 4894-4898

Additional Rheology Relevant NE Simulations

- Initial and boundary conditions
  - Oscillatory
    - Large amplitude, high frequency
  - Failure, crazing
  - Phase changes
  - Concentration gradients
    - Dispersion stability
  - Evaporation
  - Shock



Rheology Applications

- What's possible?
- Practical issues
  - Long time averages – how long is long enough!
  - statistics