

# Short Course on Molecular Dynamics Simulation

## Lecture 10: Non Equilibrium MD

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# High Level Course Outline

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1. MD Basics
2. Potential Energy Functions
3. Integration Algorithms
4. Temperature Control
5. Boundary Conditions
6. Neighbor Lists
7. Initialization and Equilibrium
8. Extracting Static Properties
9. Extracting Dynamic Properties
10. Non-Equilibrium MD

# Non Equilibrium MD

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- Why use NEMD?
  - Improve efficiency of transport coefficient calculations
    - Time correlation functions in equilibrium MD are subject to significant statistical error because they represent the average response to naturally occurring fluctuations which are relatively small
    - With NEMD, we artificially impose a much larger fluctuation and measure the response
  - Examine the system response to a large perturbation

# Non Equilibrium MD

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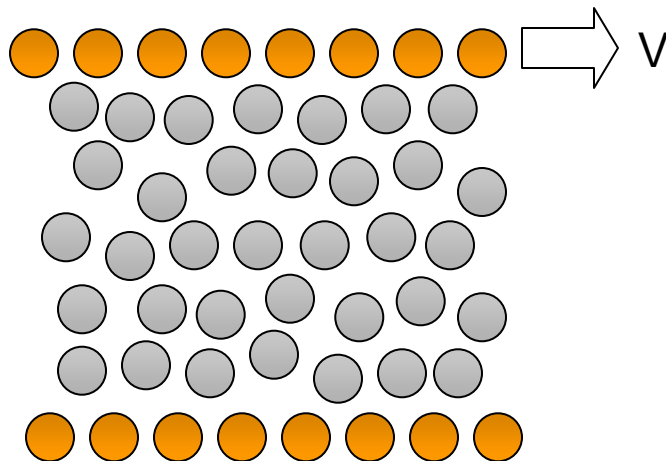
- General NEMD types
  - Direct measurement - Introduce boundaries where particles interact with external momentum
    - Introduce surface/boundary effects
  - Modified dynamics - Perturb the equations of motion
    - Constant perturbation
    - Pulse perturbation
    - Sinusoidal oscillating perturbation

# NEMD

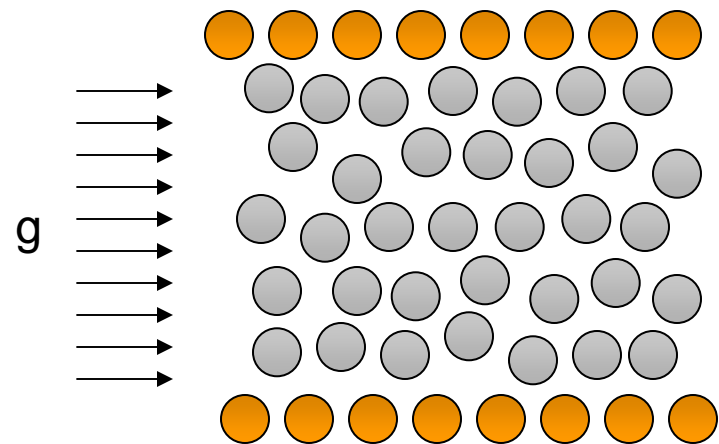
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- Classic systems with boundaries

- Couette flow



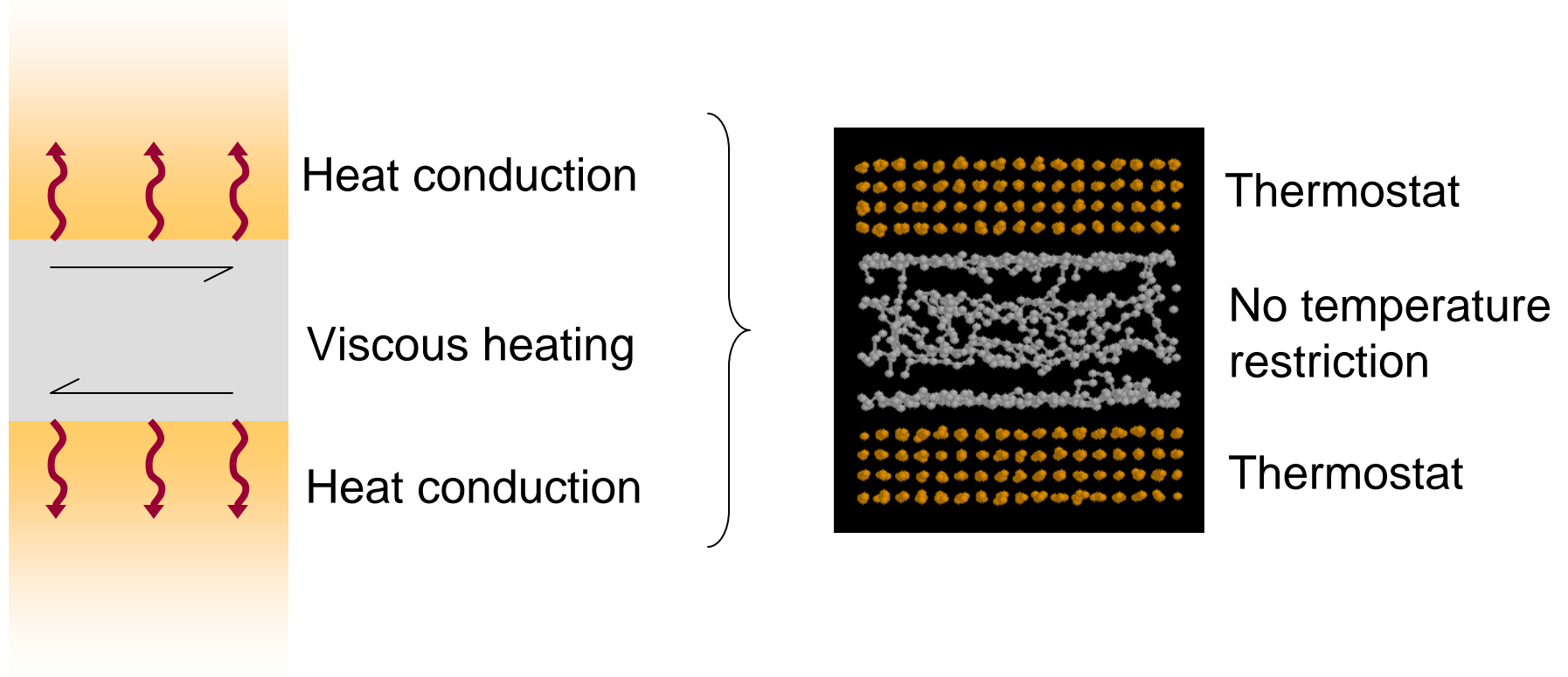
- Poiseuille flow



# NEMD

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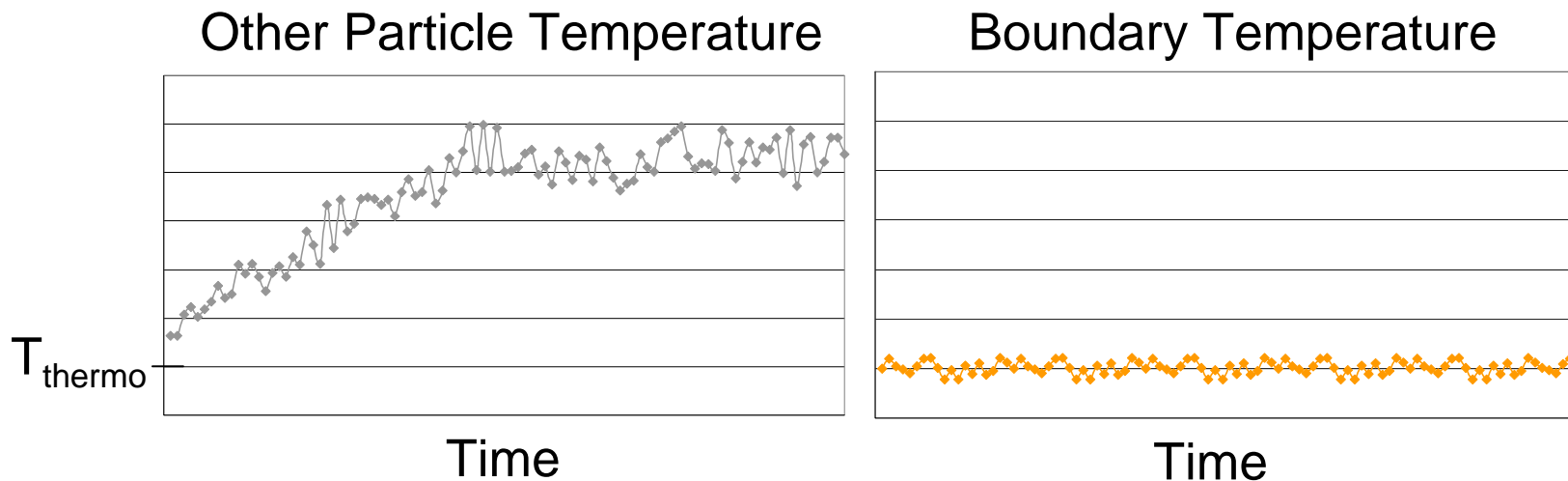
- Thermostat wall atoms only
  - Temperature is controlled
  - Motion of the particles of interest is not modified



# NEMD

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- Boundary will oscillate about the reservoir temperature
- Temperature of the other particles will increase and then stabilize

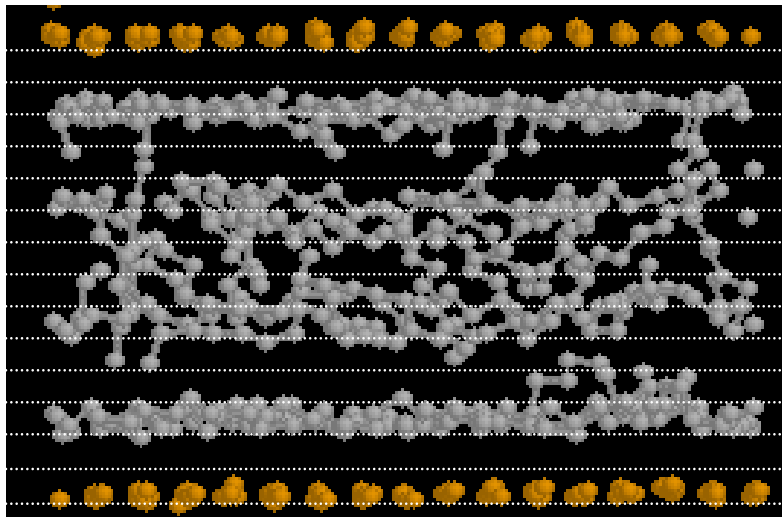


# NEMD

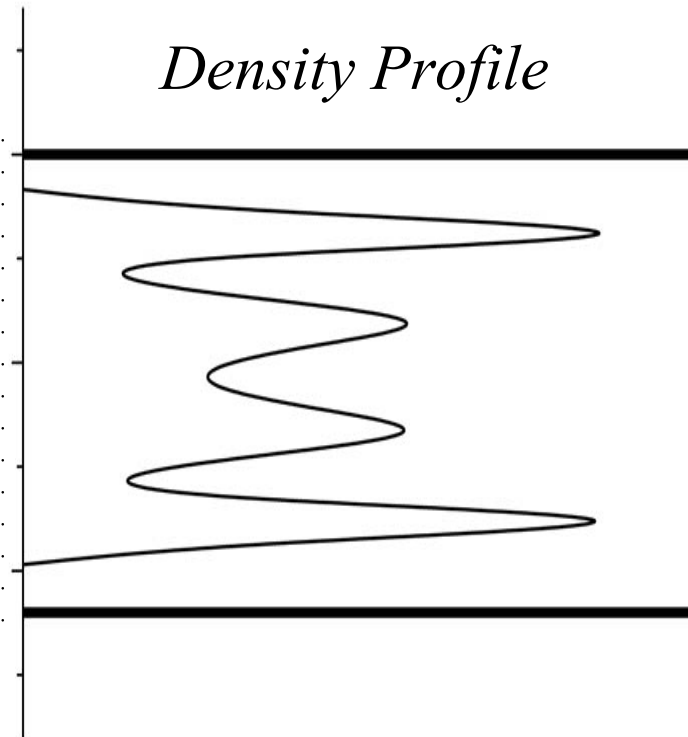
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- Profiles are calculated by dividing the volume into “bins” and averaging the properties of the atoms in each bin over time

*Snapshot Cross-section*

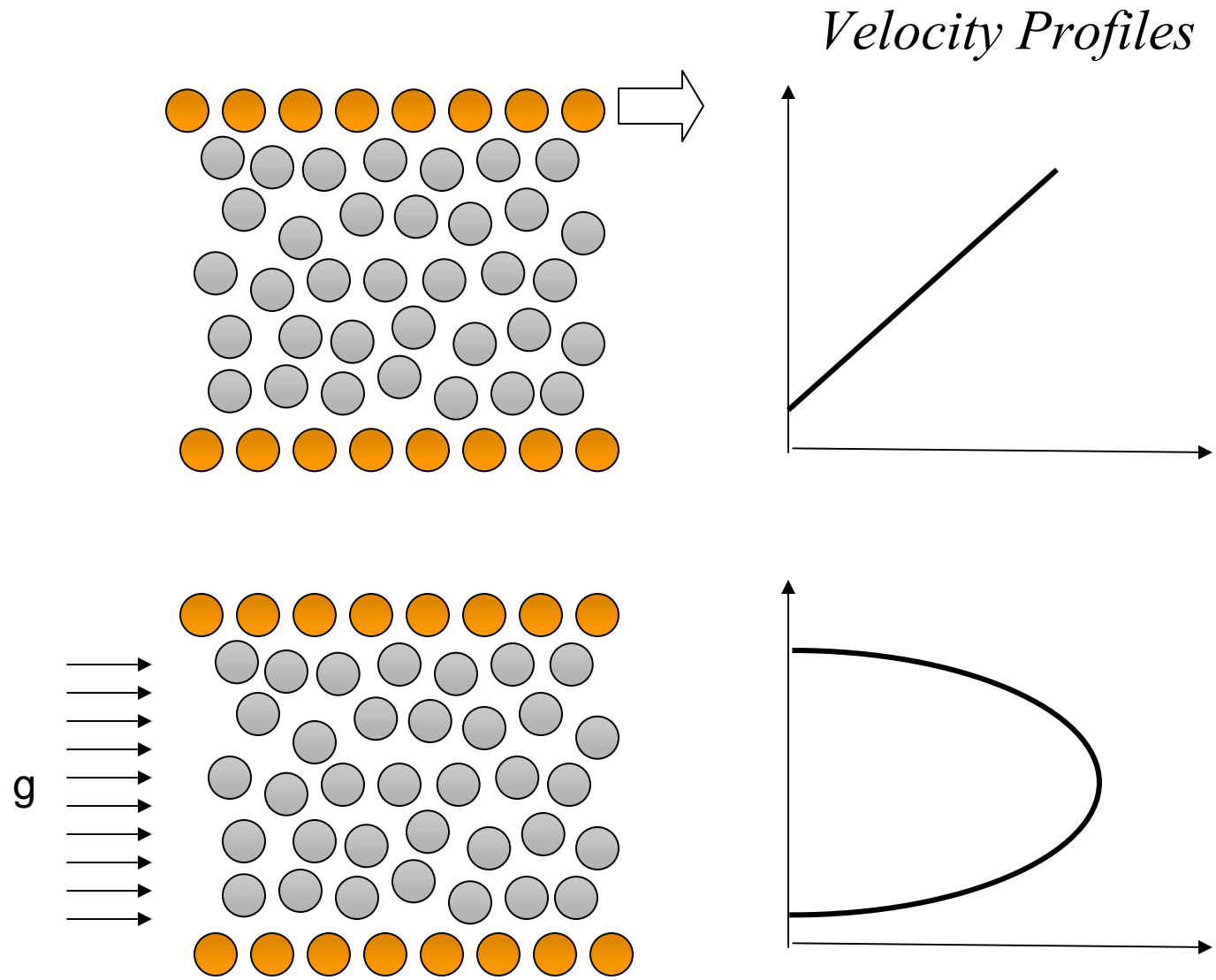


*Density Profile*



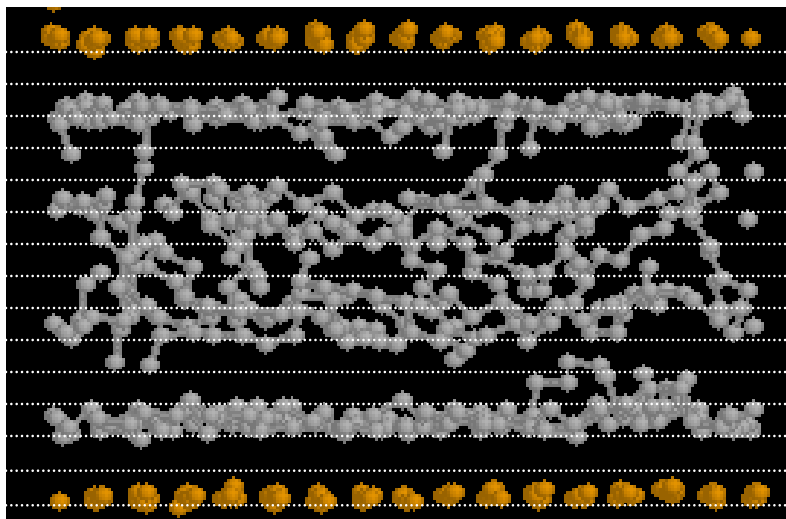


# NEMD

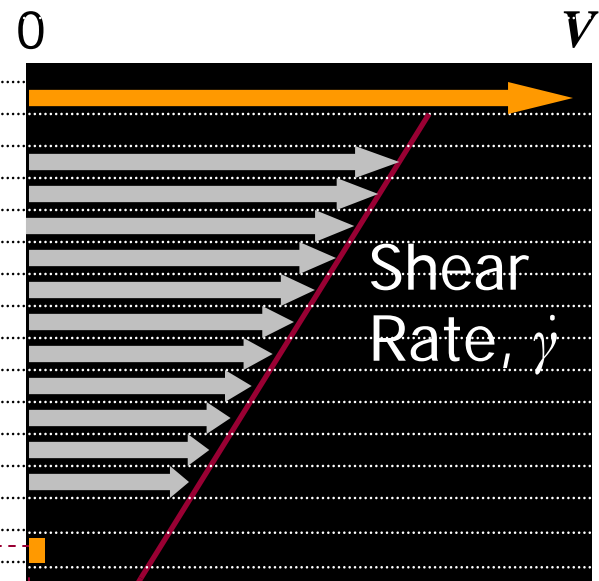


# Couette Flow

*Snapshot Cross-section*



*Velocity Profile*



Slip Length

$L_s$

Slip Magnitude:

$$v_s = L_s \dot{\gamma}$$

or

$$L_s = v_s / \dot{\gamma}$$

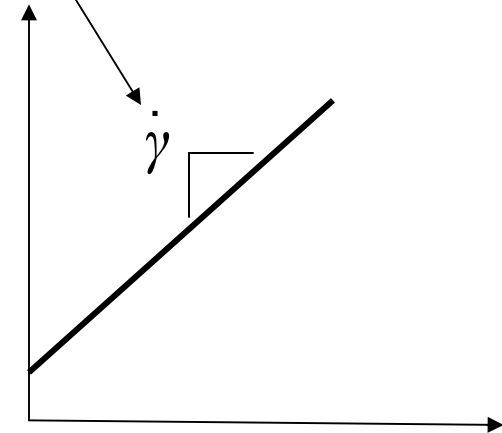
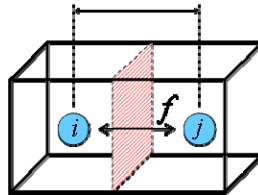
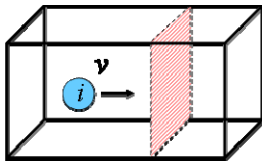
Slip Velocity,  $v_s$

# Couette Flow

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- Viscosity = Stress / Strain Rate

$$\sigma_{\alpha\beta} = m \sum_i^N v_{i\alpha} v_{i\beta} + \frac{1}{2} \sum_{i \neq j}^N r_{ij\beta} F_{ij\alpha}$$

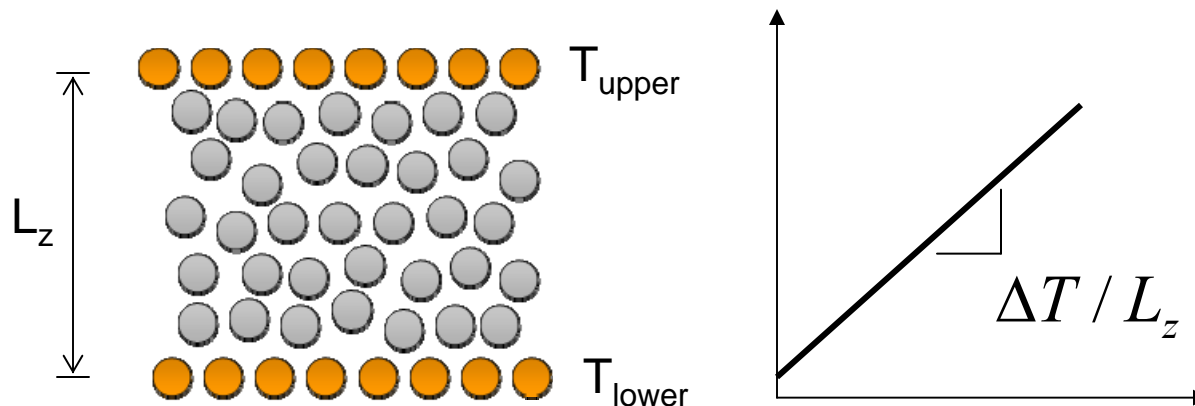


# Couette Flow

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- Thermal Conductivity = Rate of heat (KE) transfer / temperature gradient

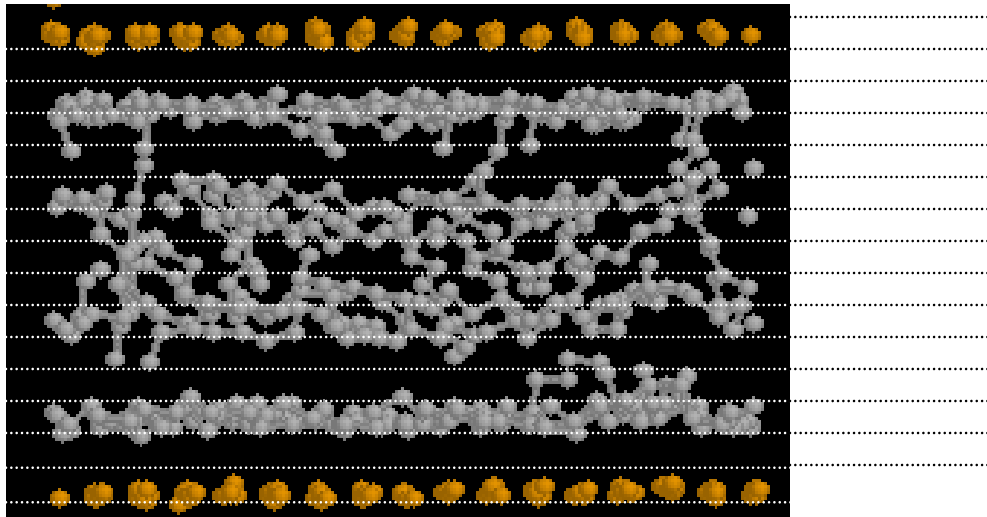
$$\lambda = \frac{\Delta KE}{2tA\Delta T / L_z}$$



# Poiseuille Flow

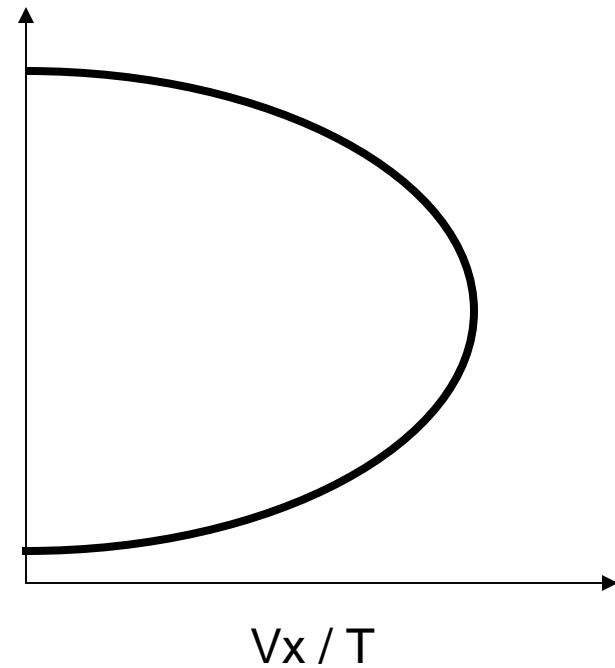
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*Snapshot Cross-section*



→ X

*Velocity/Temperature Profile*



# Poiseuille Flow

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- Navier Stokes and Heat Conduction
  - Viscosity from second-degree polynomial fit
  - Thermal conductivity from fourth-degree polynomial fit

$$v_x(z) = \frac{\rho g L_z^2}{2\eta} \left[ \frac{1}{4} - \left( z - \frac{1}{2} \right)^2 \right]$$

Shear Viscosity

Channel width

$$T(z) = T_w + \frac{\rho^2 g^2 L_z^4}{2\lambda\eta} \left[ \frac{1}{16} - \left( z - \frac{1}{2} \right)^4 \right]$$

Wall temperature

Thermal Conductivity

# Perturbation Methods

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- General types

- Constant perturbation; system response proportional to time-integrated correlation functions
- Pulse perturbation; system response proportional to the correlations functions themselves
- Sinusoidal oscillating perturbation; system response proportional to real and imaginary parts of the Fourier-Laplace transformed correlation functions

- Basic concept

- Additional term in the Hamiltonian

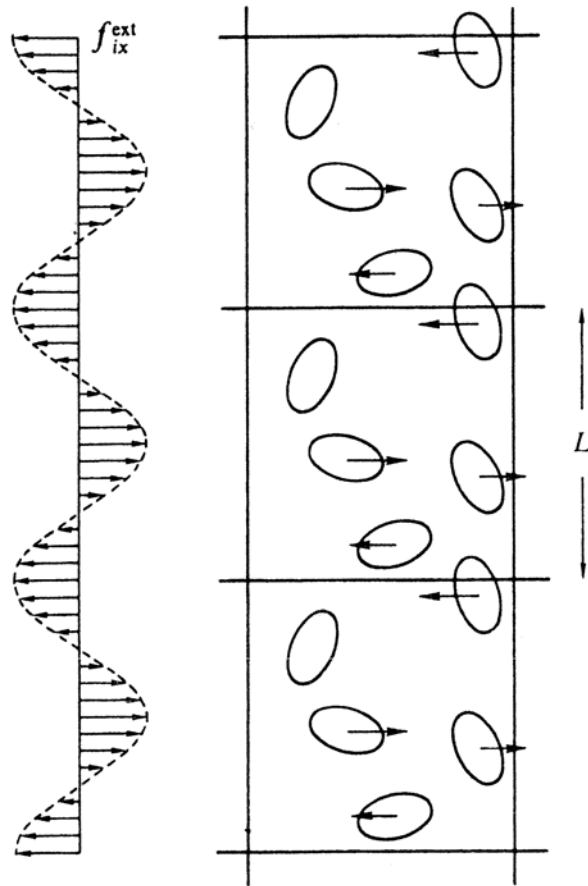
$$H_{NEMD} = H + A(r, p) \cdot F(t)$$

3N-vector is the time-dependent applied field

3Nx3N matrix coupling the field to the molecules

# Perturbation Methods

- Shear flow; e.g. oscillatory velocity profile



$$f_{ix}^{ext} = F \cos(2\pi n r_{iy} / L)$$

Constant

- Fit average MD results to calculate viscosity

$$\langle v_x(r_y) \rangle \approx (\rho / k^2 \eta) F \cos(k r_y)$$

$$\vec{k} = (0, 2\pi n / L, 0)$$



# Perturbation Methods

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## □ Others

- Diagonal components of the stress tensor
  - Expansion/contraction
- Thermal conductivity
  - Induce an energy flux
- Diffusion coefficient
  - Advisable for multi-component systems
  - Apply a “charge” to the atoms ( $z_i = -1, +1$ )
  - Diffusion related to correlation with the current charge

$$p_{ix} = f_{ix} + z_i F(t)$$

$$D = \frac{k_B T}{\rho F} \langle j_x^z(t \rightarrow \infty) \rangle \quad j_x^z(t) = \frac{1}{V} \sum_i z_i v_{ix}(t)$$

# NEMD

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## □ Comments

- NEMD is much more efficient for calculating individual transport coefficients
- In general, large perturbations (much larger than in an experiment) are needed to obtain reasonable signal-to-noise ratio
- May not be able to extrapolate to zero or low perturbation characteristics
  - Typical NEMD for viscosity calculation is limited to meters-per-second imposed velocities