CE 530 Molecular Simulation

Lecture 24

Non-Equilibrium Molecular Dynamics

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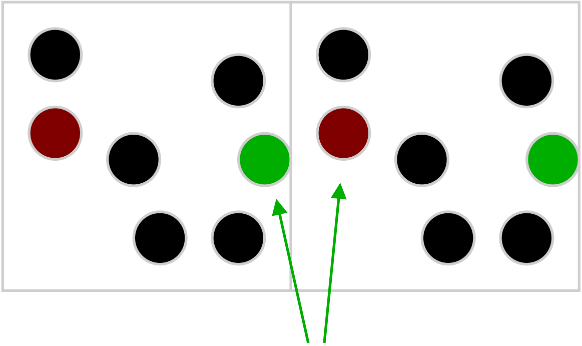
Summary
from Lecture 12

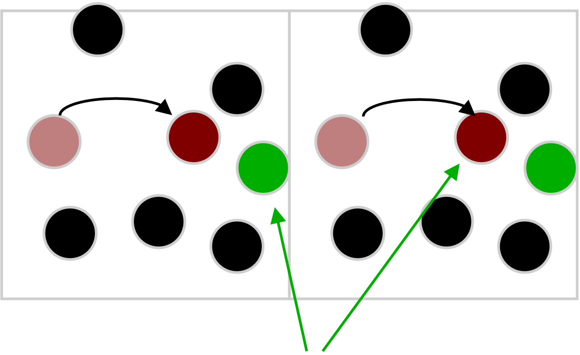
- Dynamical properties describe the way collective behaviors cause macroscopic observables to redistribute or decay
- Evaluation of transport coefficients requires non-equilibrium condition
  - *NEMD imposes macroscopic non-equilibrium steady state*
  - *EMD approach uses natural fluctuations from equilibrium*
- Two formulations to connect macroscopic to microscopic
  - *Einstein relation describes long-time asymptotic behavior*
  - *Green-Kubo relation connects to time correlation function*
- Several approaches to evaluation of correlation functions
  - *direct: simple but inefficient*
  - *Fourier transform: less simple, more efficient*
  - *coarse graining: least simple, most efficient, approximate*

Limitations of Equilibrium Methods

- Response to naturally occurring (small) fluctuations
- Signal-to-noise particularly bad at long times
  - *but may have significant contributions to transport coefficient here*
- Finite system size limits time that correlations can be calculated reliably



correlations between these two…



…lose meaning once they've traveled the length of the system

Non-Equilibrium Molecular Dynamics

- Introduce much larger fluctuation artificially
  - *dramatically improve signal-to-noise of response*
- Measure steady-state response
- Corresponds more closely to experimental procedure
  - *create flow of momentum, energy, mass, etc. to measure…*
  - *…shear viscosity, thermal conductivity, diffusivity, etc.*
- Advantages
  - *better quality of measurement*
  - *can also examine nonlinear response*
- Disadvantages
  - *limited to one transport process at a time*
  - *may need to extrapolate to linear response*

One (Disfavored) Approach

- Introduce boundaries in which molecules interact with inhomogeneous momentum/mass/energy reservoirs
- Disadvantages
  - *incompatible with PBC*
  - *introduces surface effects*
  - *inhomogeneous*
  - *difficult to analyze to obtain transport coefficients correctly*
- Have a look with a thermal conductivity applet
- Better methods rely on linear response theory

Linear Response Theory: Static

- Linear Response Theory forms the theoretical basis for evaluation of transport properties by molecular simulation
- Consider first a static linear response
- Examine how average of a mechanical property A changes in the presence of an external perturbation f
  - *Unperturbed value* $\langle A \rangle_0$
  - *Apply perturbation to Hamiltonian* $H = H_0 - \lambda B(p^N, q^N)$
  - *New value of A*

$$\langle A \rangle_0 + \langle \Delta A \rangle = \frac{\int d\Gamma A e^{-\beta(H_0 - \lambda B)}}{\int d\Gamma e^{-\beta(H_0 - \lambda B)}}$$

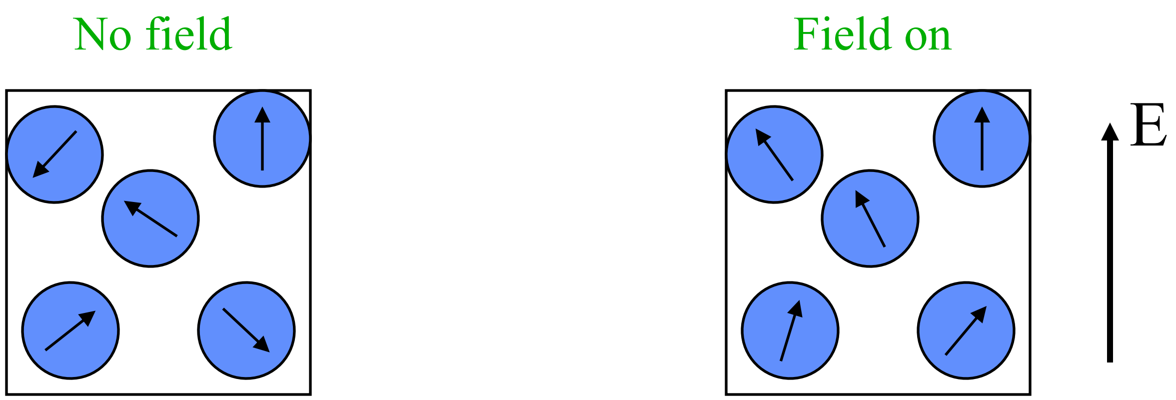
  - *Linearize*

$$\left(\frac{\partial(\Delta A)}{\partial \lambda} \right)_{\lambda=0} = \beta\left[\langle AB \rangle_0 - \langle A \rangle_0 \langle B \rangle_0 \right]$$

Susceptibility describes first-order static response to perturbation

Example of Static Linear Response

- Dielectric response to an external electric field
  - *coupling to dipole moment of system, M_y* $\Delta H = -E_y M_y(\mathbf{q}^N)$
  - *interest in net polarization induced by field* $\langle M_y \rangle$
  - *thus $A = B = M_y$*



$\langle M_y \rangle = 0$ $\langle M_y \rangle \neq 0$

- *susceptibility* $\beta\left[\langle M_y^2 \rangle_0 - \langle M_y \rangle_0^2\right]$

Linear Response Theory: Dynamic 1.

- Time-dependent perturbation $F_e(t)$
- Consider situation in which F_e is non-zero for $t < 0$, then is switched off at $t = 0$
- Response ΔA decays to zero

$$\langle \Delta A(t) \rangle = \frac{\int d\Gamma A(t) e^{-\beta(H_0 - \lambda B)}}{\int d\Gamma e^{-\beta(H_0 - \lambda B)}}$$

$$= \beta\lambda \langle B(0) A(t) \rangle$$

Ensemble average over (perturbation-weighted) initial conditions

Linear Response Theory: Dynamic 2.

- Now consider a more general time-dependent perturbation $F_e(t)$
- Simplest general form of linear response

$$\langle \Delta A(t) \rangle = \int_{-\infty}^{t} dt' \chi_{AB}(t-t') F_e(t')$$

Value at time t is a sum of the responses to the perturbation over the entire history of the system

- For the protocol previously discussed (shut off field at t = 0)

$$\langle \Delta A(t) \rangle = \lambda \int_{-\infty}^{0} dt' \chi_{AB}(t-t')$$

$$= \lambda \int_{t}^{\infty} d\tau \chi_{AB}(\tau)$$

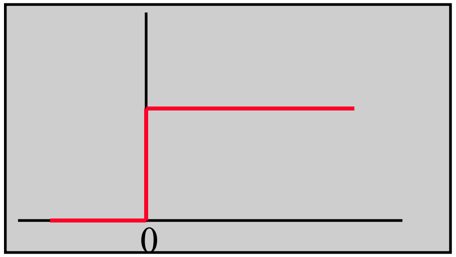
- *thus*

$$\int_{t}^{\infty} d\tau \chi_{AB}(\tau) = \beta \langle B(0) A(t) \rangle \Rightarrow \boxed{\chi_{AB}(t) = -\beta \langle B(0) \dot{A}(t) \rangle}$$

Perturbation-Response Protocols

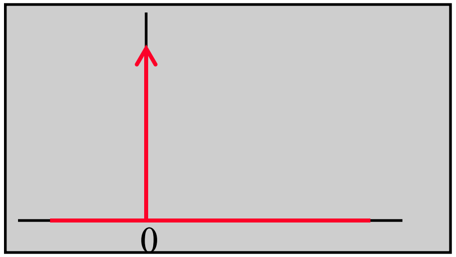
$$\boxed{\left\langle \Delta A(t) \right\rangle = \int_{-\infty}^{t} dt' \left\langle B(0)\dot{A}(t') \right\rangle F_e(t')}$$

- Turn on perturbation at t = 0, and keep constant thereafter
  - *measured response is proportional to integral of time-integrated correlation function*



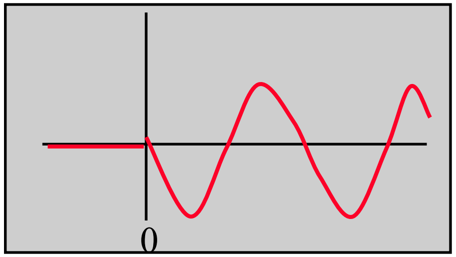
$$\left\langle \Delta A(t) \right\rangle = -\beta \int_{0}^{t\to\infty} dt' \left\langle B(0)\dot{A}(t') \right\rangle$$

- Apply as δ-function pulse at t = 0, subsequent evolution proceeding normally
  - *measured response proportional to time correlation function itself*



$$\left\langle \Delta A(t) \right\rangle = -\beta \left\langle B(0)\dot{A}(t) \right\rangle$$

- Use a sinusoidally oscillating perturbation
  - *measured response proportional to Fourier-Laplace transformed correlation functions at the applied frequency*
  - *extrapolate results from several frequencies to zero-frequency limit*



$$\left\langle \Delta A(t) \right\rangle = -\beta \int_{0}^{t\to\infty} dt' e^{i\omega t} \left\langle B(0)\dot{A}(t') \right\rangle$$

Synthetic NEMD

- Perturb usual equations of motion in some way
  - *Artificial "synthetic" perturbation need not exist in nature*
- For transport coefficient of interest L_{ij}, $J_i = L_{ij}X_j$
  - *Identify the Green-Kubo relation for the transport coefficient*

$$L_{ij} = \int_0^\infty \langle J_i(\tau) J_j(0) \rangle d\tau$$

e.g., $D = \int_0^\infty \langle v_x(\tau) \cdot v_x(0) \rangle d\tau$

  - *Invent a fictitious field F_e, and its coupling to the system such that the dissipative flux is J_j* $\dot{H}_0^{ad} = -J_j F_e$
  - *ensure that*

    equations of motion correspond to an incompressible phase space

    equations of motion are consistent with periodic boundaries

    equations of motion do not introduce inhomogeneities
  - *apply a thermostat*
  - *couple F_e to the system and compute the steady-state average* $\langle J_i(t) \rangle$
  - *then*

$$\boxed{L_{ij} = \lim_{F_e \to 0} \lim_{t \to \infty} \frac{\langle J_i(t) \rangle}{F_e}}$$

Phase Space

- Underlying development assumes that equations of motion correspond to an incompressible phase space

$$\nabla \cdot \dot{\Gamma} = \nabla_{\mathbf{q}} \cdot \dot{\mathbf{q}} + \nabla_{\mathbf{p}} \cdot \dot{\mathbf{p}} = 0$$

- This can be ensured by having the perturbation derivable from a Hamiltonian

$$H^{ne} = H + \mathbf{A}(\mathbf{p},\mathbf{q}) \cdot \mathbf{f}(t)$$

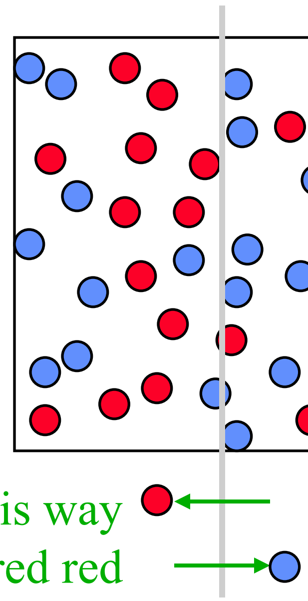
$$\dot{\mathbf{q}} = \frac{\partial H^{ne}}{\partial \mathbf{p}} = \mathbf{p}/m + \mathbf{A}_{\mathbf{p}} \cdot \mathbf{f}(t)$$

$$\dot{\mathbf{p}} = -\frac{\partial H^{ne}}{\partial \mathbf{q}} = \mathbf{F}(\mathbf{q}) - \mathbf{A}_{\mathbf{q}} \cdot \mathbf{f}(t)$$

- Most often the equations of motion are not derivable from a Hamiltonian
  - *but are still formulated to be compatible with an incompressible phase space*

Diffusion: An Inhomogeneous Approach

- Artificially distinguish particles by "color"
- Introduce a species-changing plane



Molecules moving this way across wall get colored red

Those crossing this way get blue

Diffusion: An Inhomogeneous Approach

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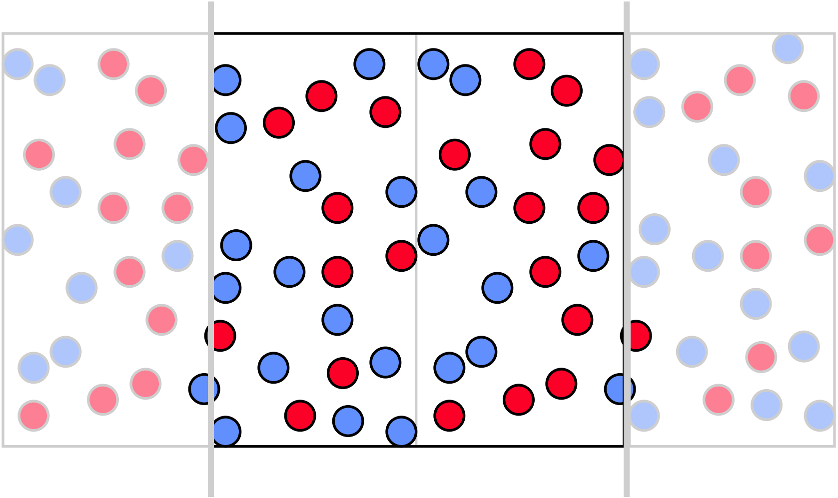


Considering periodic boundaries,
this creates a color gradient

- Problems
  - *Difficult to know form of inhomogeneity in color profile*
  - *Cannot be extended to multicomponent diffusion*

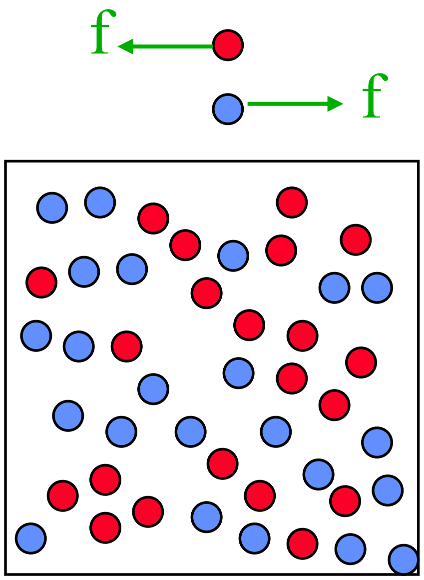
Self-Diffusion: Perturbation

- Green-Kubo relation

$$D = \int_0^\infty \langle v_x(\tau)\cdot v_x(0)\rangle d\tau = \int_0^\infty \langle \dot{r}_x(\tau)\cdot v_x(0)\rangle d\tau$$

- Label each molecule with one of two "colors"
  - *each color given to half the molecules*
- Apply Hamiltonian perturbation

$$H = H_0 - \sum_{i=1}^{N} c_i r_{ix} f(t)$$



- New equations of motion

$$\dot{\mathbf{q}} = \mathbf{p}/m$$

$$\dot{\mathbf{p}} = \mathbf{F}(\mathbf{q}) - \mathbf{A}_{\mathbf{q}}\cdot\mathbf{f}(t) \begin{cases} \dot{p}_{ix} = F_{ix} + c_i f(t) \\ \dot{p}_{i(y,z)} = F_{i(y,z)} \end{cases}$$

- System remains homogeneous

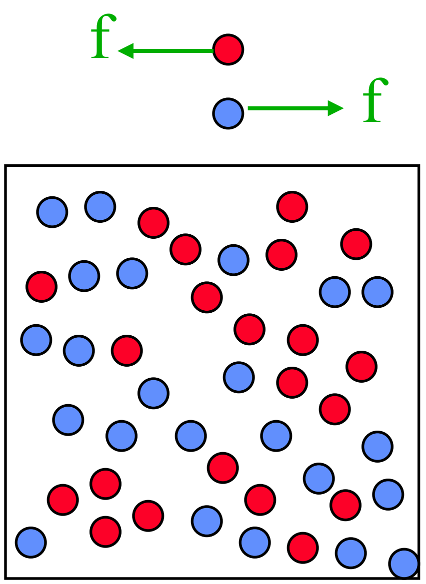
Self-Diffusion: Response

- Appropriate response variable is the "color current"

$$J_x(t) = \frac{1}{V}\sum_{i=1}^{N} c_i v_{ix}(t)$$

- According to linear response theory

$$\langle J_x(t)\rangle = \beta V \int_0^t ds \langle J_x(t-s) J_x(0)\rangle_0 f(s)$$



- In the canonical ensemble

$$\begin{aligned}\langle J_x(t) J_x(0)\rangle &= \frac{1}{V^2}\sum_{i,j} c_i c_j \langle v_{xi}(t) v_{xj}(0)\rangle \\ &= \frac{1}{V^2}\sum_{i} c_i^2 \langle v_{xi}(t) v_{xi}(0)\rangle \\ &= \frac{N}{V^2}\langle v_x(t) v_x(0)\rangle\end{aligned}$$

- Back to Green-Kubo relation

$$\boxed{D = \frac{1}{\beta\rho}\lim_{t\to\infty}\lim_{f\to 0}\frac{\langle J_x(t)\rangle}{F}}$$

Thermostatting

- External field does work on the system
  - *this must be dissipated to reach steady state*
- Thermostat based on velocity relative to total current density
  - *"peculiar velocity"*

$$\hat{p}_{ix} = p_{ix} - c_i \tfrac{1}{Nm} \sum c_j p_{jx}$$
$$= p_{ix} - c_i J_x / m\rho$$

  - *constrain kinetic energy*

$$\sum \hat{\mathbf{p}}^2 / m = 3NkT$$

  - *modified equations of motion*

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{e}_x c_i f - \alpha \hat{\mathbf{p}}_i$$

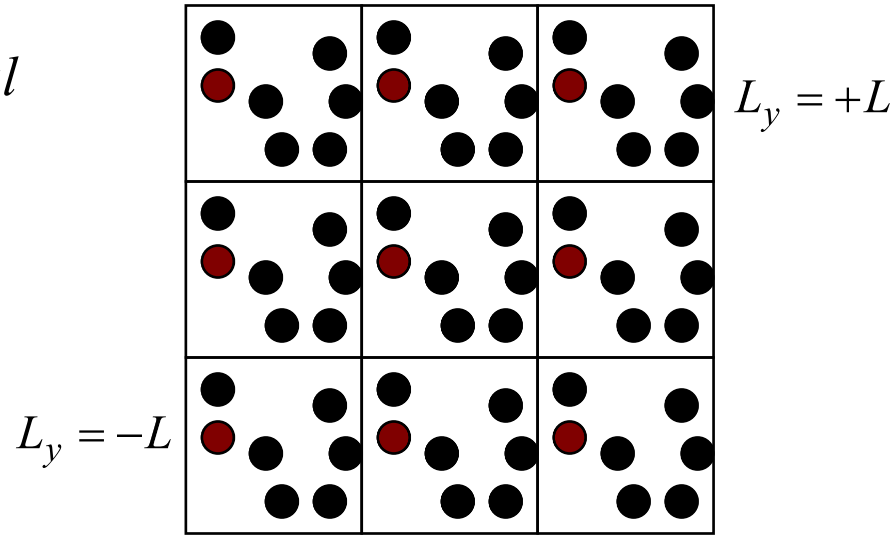
  - *thermostatting multiplier*

$$\alpha = \frac{\sum m\mathbf{F}_i \cdot \hat{\mathbf{p}}_i}{\sum \mathbf{p}_i \cdot \hat{\mathbf{p}}_i}$$

Shear Viscosity: Boundary-Driven Algorithm

- Homogeneous algorithm for boundary-driven shear is possible
  - *unique to shear viscosity*
- Lees-Edwards shearing periodic boundaries (sliding brick)
  - *Image cells in plane above and below central cell move*
  - *Image velocity given by shear rate* $\gamma = \dfrac{dv_x}{dy}$
  - *Peculiar velocity of all images equal*

$$\hat{p}_{ix} = p_{ix} - \gamma L_y$$



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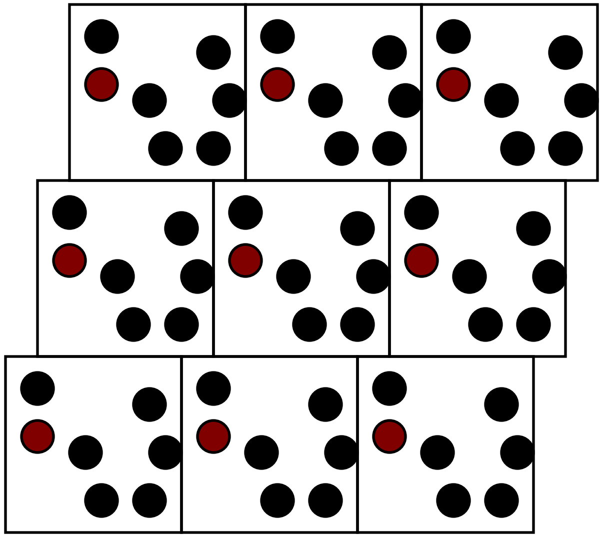

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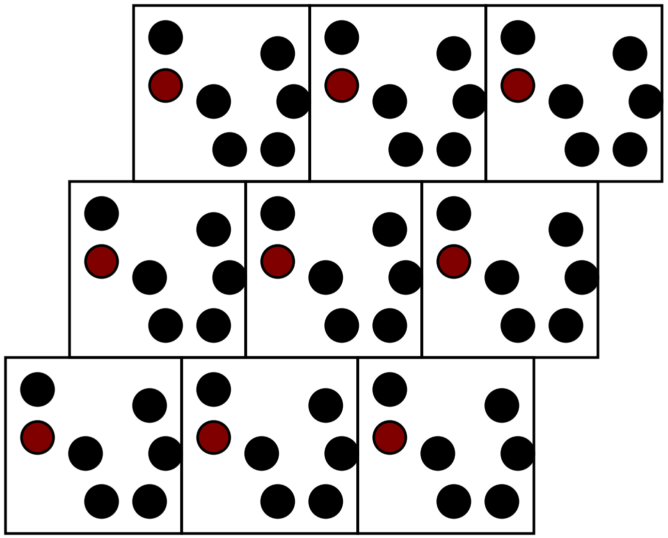

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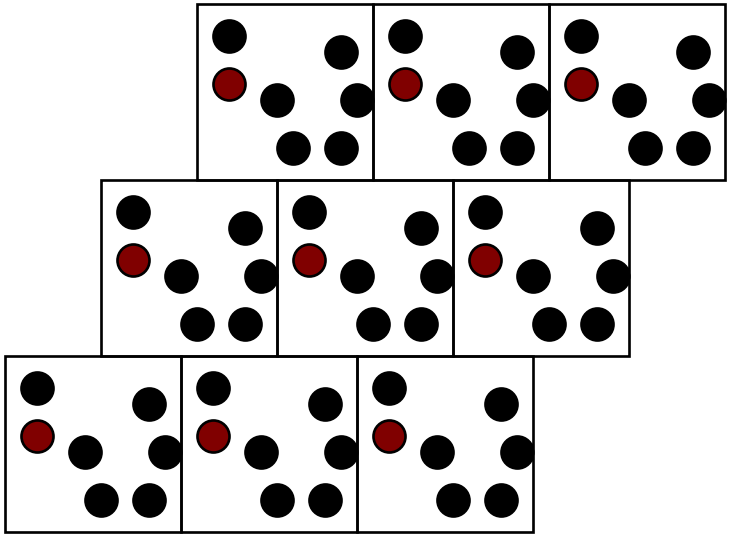
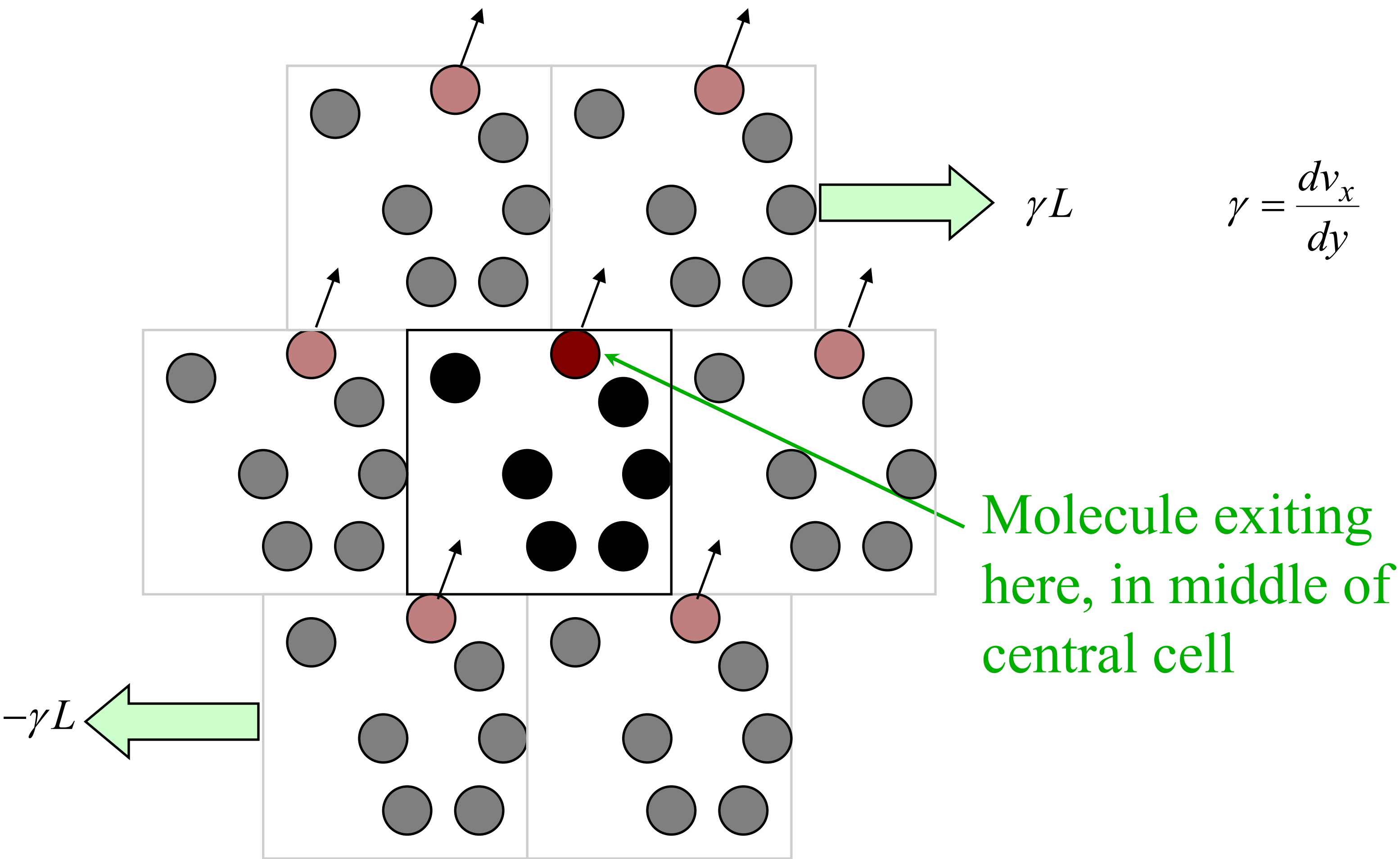
$$\hat{p}_{ix} = p_{ix} - \gamma L_y$$

- Try the applet



Lees-Edwards Boundary Conditions



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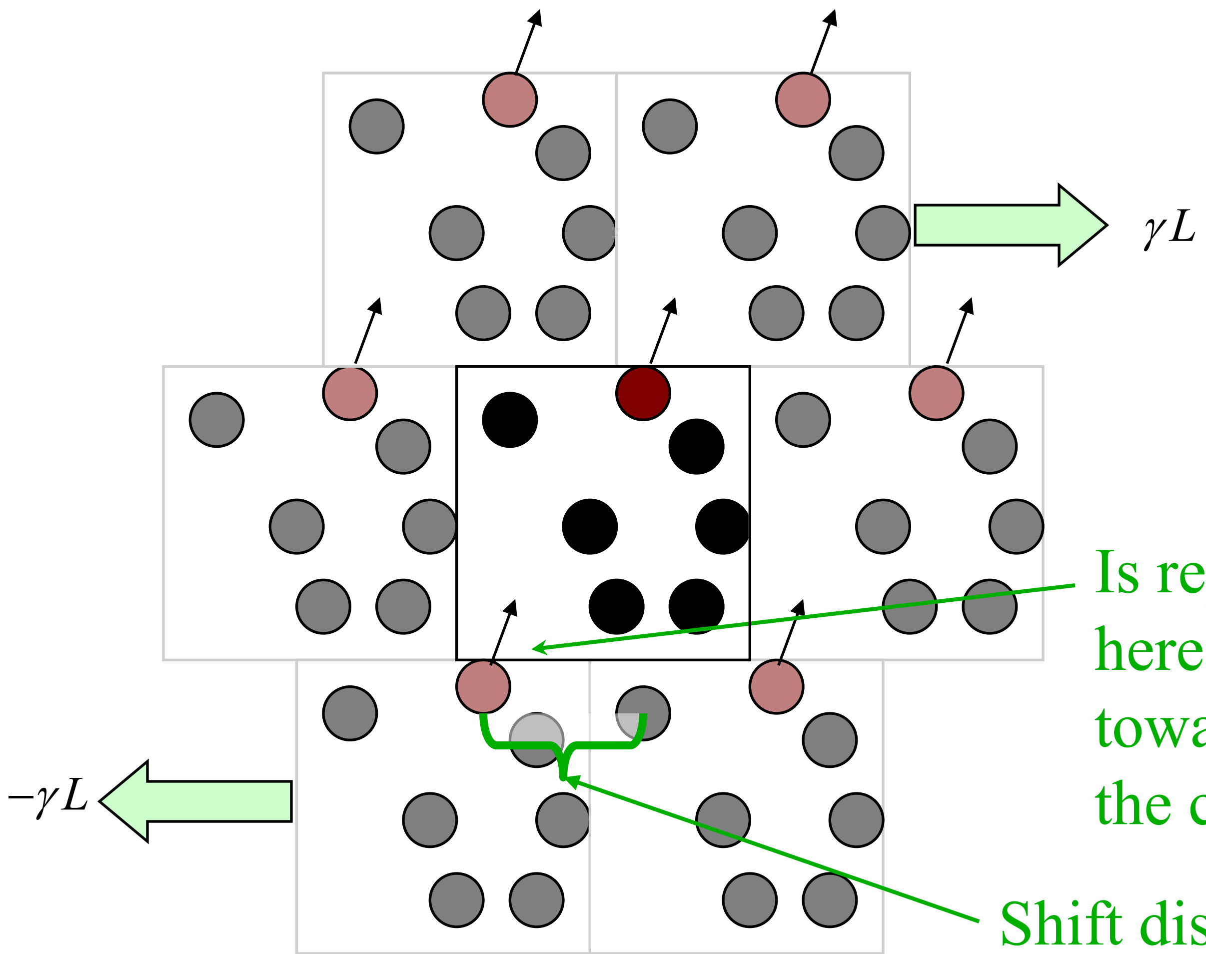
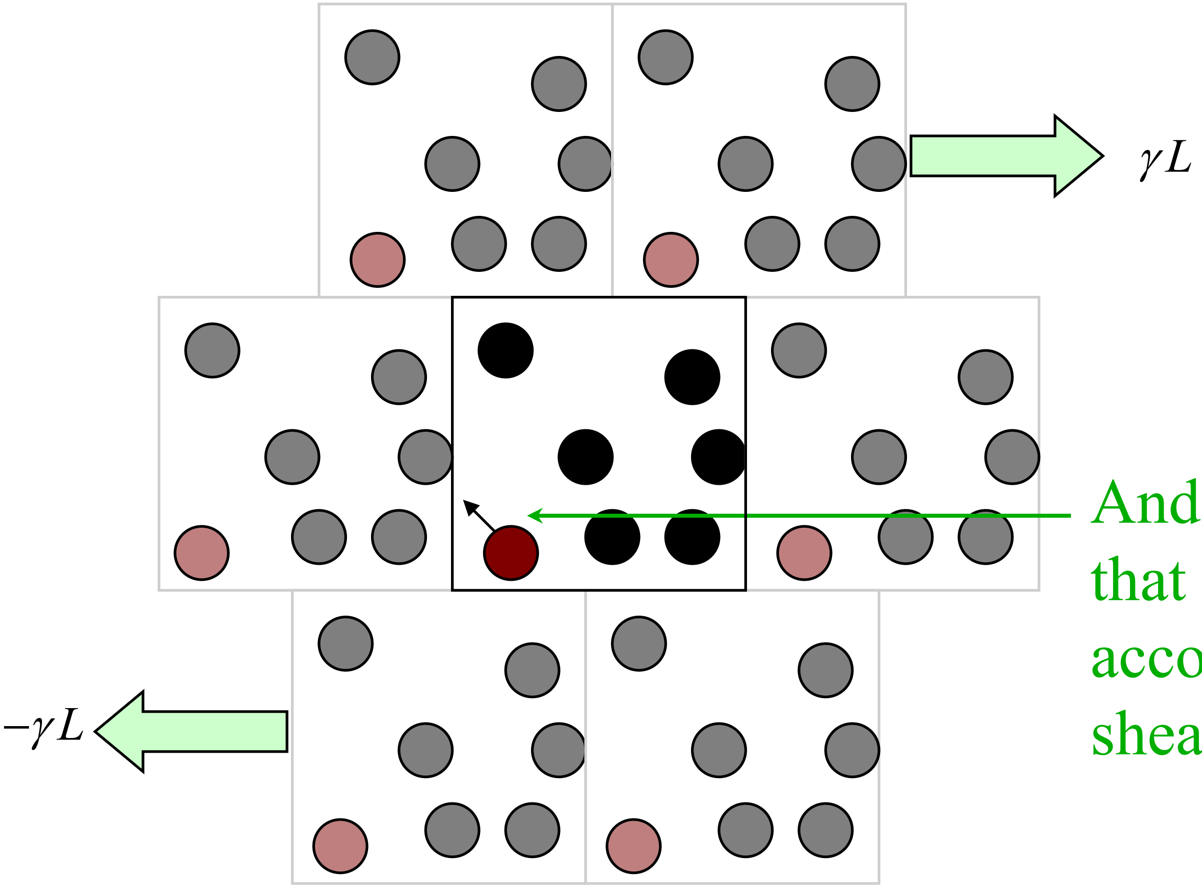


$$\gamma = \frac{dv_x}{dy}$$

Is replaced by one here, shifted over toward the edge of the cell

Shift distance = γLt

Lees-Edwards Boundary Conditions

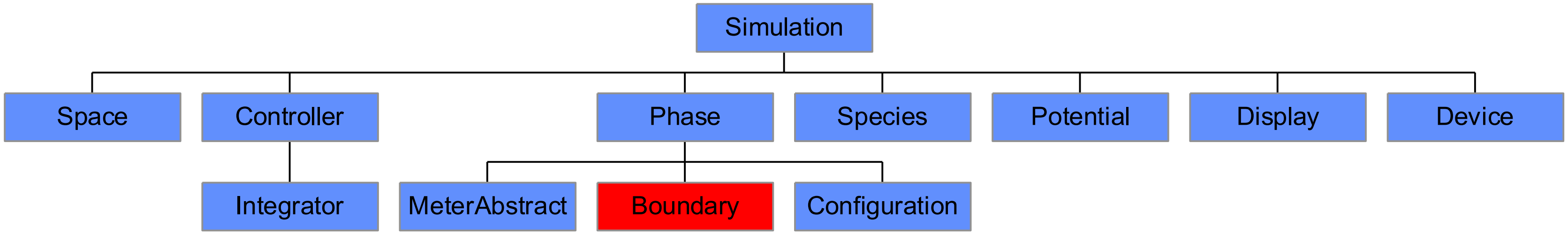


$$\gamma = \frac{dv_x}{dy}$$

And with a velocity that is modified according to the shear rate

Lees-Edwards Boundary: API

User's Perspective on the Molecular Simulation API



Lees-Edwards Boundary: Java Code

```
public class Space2D.BoundarySlidingBrick extends
        Space2D.BoundaryPeriodicSquare
```

```
public void nearestImage(Vector dr) {
  double delrx = delvx*timer.currentValue();
  double cory;
  cory = (dr.y > 0.0) ? Math.floor(dr.y/dimensions.y+0.5):Math.ceil(dr.y/dimensions.y-0.5);
  dr.x -= cory*delrx;
  dr.x -= dimensions.x * ((dr.x > 0.0) ? Math.floor(dr.x/dimensions.x+0.5) :
                          Math.ceil(dr.x/dimensions.x-0.5));
  dr.y -= dimensions.y * cory;
}


public void centralImage(Coordinate c) {
  Vector r = c.r;
  double cory = (r.y > 0.0) ? Math.floor(r.y/dimensions.y) : Math.ceil(r.y/dimensions.y-1.0);
  double corx = (r.x > 0.0) ? Math.floor(r.x/dimensions.x) : Math.ceil(r.x/dimensions.x-1.0);
  if(corx==0.0 && cory==0.0) return;
  double delrx = delvx*timer.currentValue();
  Vector p = c.p;
  r.x -= cory*delrx;
  r.x -= dimensions.x * corx;
  r.y -= dimensions.y * cory;
  p.x -= cory*delvx;
}
```

Limitations of Boundary-Driven Shear

- No external field in equations of motion
  - *cannot employ response theory to link to viscosity*
- Lag time in response of system to initiation of shear
  - *cannot be used to examine time-dependent flows*
- A fictitious-force method is preferable

DOLLS-Tensor Hamiltonian: Perturbation

- An arbitrary fictitious shear field can be imposed via the DOLLS-tensor Hamiltonian

$$H = H_0 + \sum_{i=1}^{N} \mathbf{q}_i \mathbf{p}_i : \left(\nabla \mathbf{u}(t)\right)^T$$

- Equations of motion

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{q}_i \cdot \nabla \mathbf{u}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \nabla \mathbf{u} \cdot \mathbf{p}_i$$

  - *must be implemented with compatible PBC*

- Example: Simple Couette shear

$$\nabla \mathbf{u} = \begin{pmatrix} 0 & 0 & 0 \\ \gamma & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \gamma q_{iy} \mathbf{e}_x$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \gamma p_{ix} \mathbf{e}_y$$

DOLLS-Tensor Hamiltonian: Response

- Appropriate response variable is the pressure tensor

$$\mathbf{P}(t) = \frac{1}{V}\sum_{i=1}^{N}\tfrac{1}{m}\mathbf{p}_i\mathbf{p}_i - \tfrac{1}{2}\sum_{i,j}^{N}\mathbf{r}_{ij}\mathbf{F}_{ij}$$

- According to linear response theory

$$\langle \mathbf{P}(t)\rangle = -\beta V\int_0^t ds \langle \mathbf{P}(t-s)\mathbf{P}(0)\rangle_0 : \nabla\mathbf{u}(s)$$

- Shear viscosity, via Green-Kubo

$$\boxed{\eta = \lim_{t\to\infty}\lim_{\gamma\to 0}\frac{\langle -P_{xy}(t)\rangle}{\gamma}}$$

SLLOD Formulation

- DOLLS-tensor formulation fails in more complex situations
  - *non-linear regime*
  - *evaluation of normal-stress differences*
  - *a simple change fixes things up*
- SLLOD Equations of motion

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{q}_i \cdot \nabla \mathbf{u}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u}$$

Only change

DOLLS

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m + \mathbf{q}_i \cdot \nabla \mathbf{u}$$
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \nabla \mathbf{u} \cdot \mathbf{p}_i$$

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$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \gamma p_{ix} \mathbf{e}_y$$

- Methods equivalent for irrotational flows $\nabla \mathbf{u} = (\nabla \mathbf{u})^T$

Application

- NEMD usually introduces exceptionally large strain rates
  - *10^8 sec^{-1} or greater*
  - *dimensionless strain rate* $\gamma^* = \gamma\left(\frac{m\sigma^2}{\varepsilon}\right)^{1/2}$
  - *thus, e.g.,*

    m = 30g/mol; σ = 3A; ε/k = 100K; γ* = 1.0 → $\gamma = 5 \times 10^{11}$ sec^{-1}
- Shear-thinning observed even in simple fluids at these rates
- Very important to extrapolate to zero shear