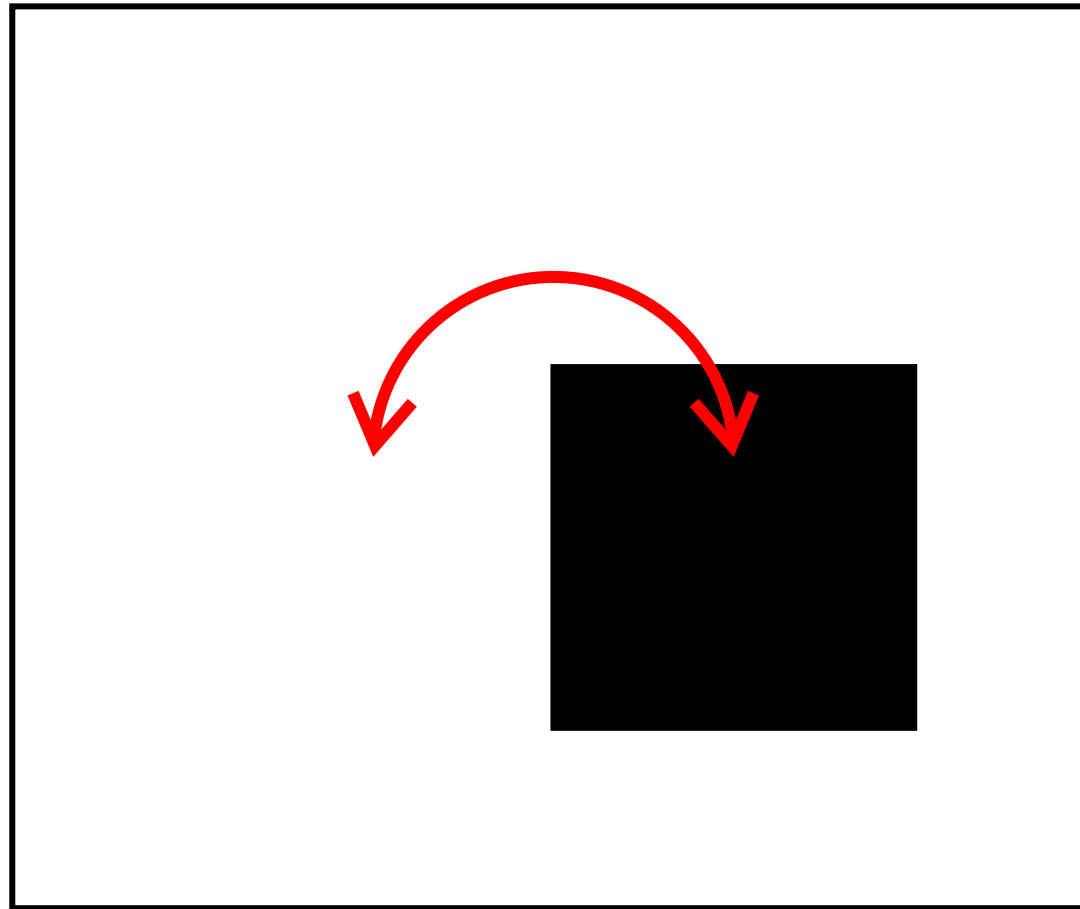


Advanced Molecular Dynamics

Ensembles

May 11, 2021

Sub system



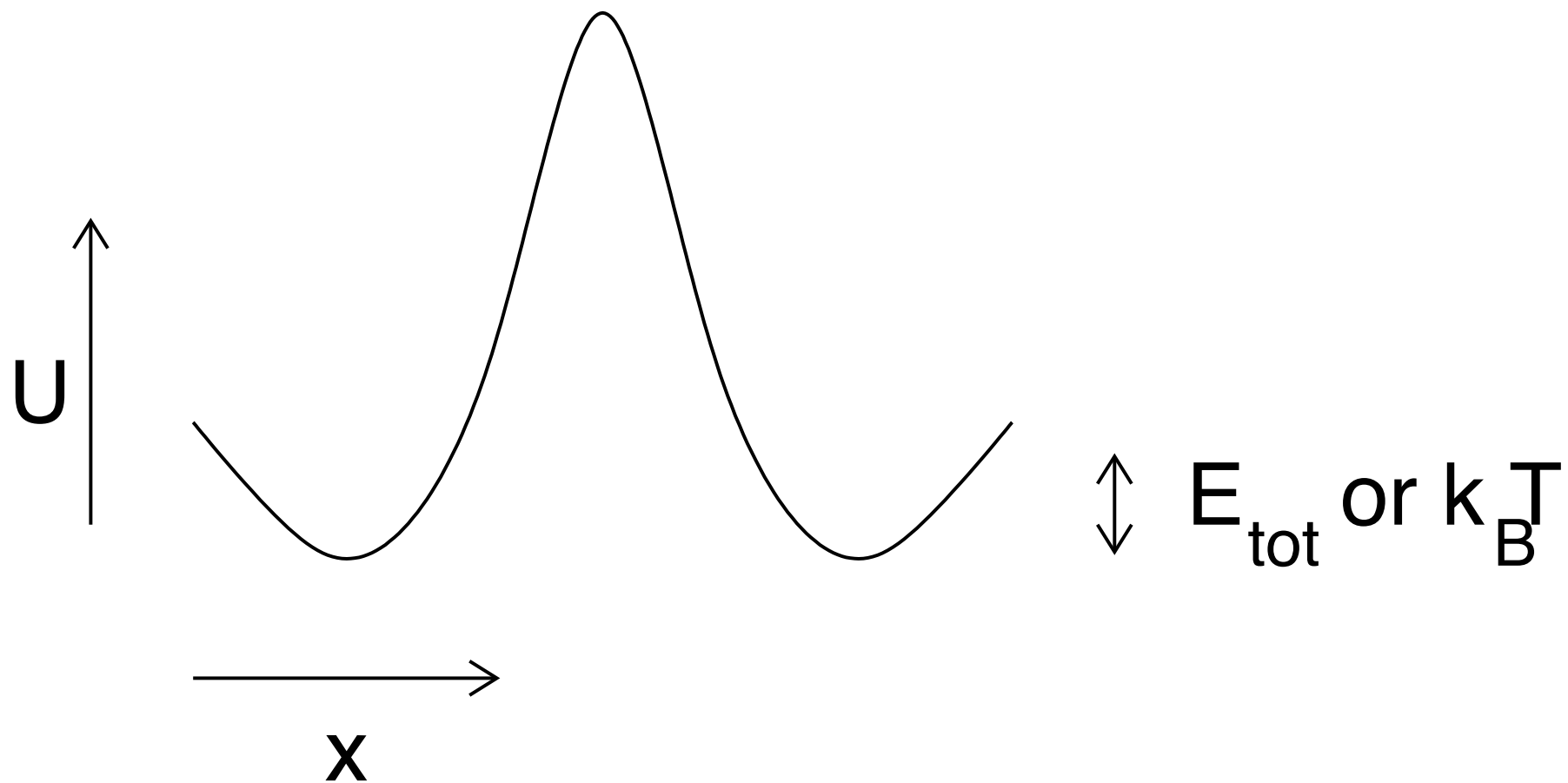
Exchange of “things”

“Pure” Molecular Dynamics

$$m_i \frac{d^2 \mathbf{x}_i}{dt^2} = -\nabla_i V(\mathbf{x}) \quad , \quad i = 1, \dots, N$$

- Plain MD conserves $E_{\text{tot}} = E_{\text{pot}} + E_{\text{kin}} = U + K$
- Plain MD generates a constant NVE, or microcanonical ensemble
- This results in reliable dynamics

Crossing a barrier?



Thermal equilibrium

- In practice systems are in thermal equilibrium with the environment
- Simplest constant-T ensemble:
 - constant NVT or canonical ensemble

$$\rho(\mathbf{x}, \mathbf{v}) = \frac{1}{Z} \exp \left[-\frac{U(\mathbf{x}) + K(\mathbf{v})}{k_B T} \right]$$

partition function:
$$Z = \int \exp \left[-\frac{U(\mathbf{x}) + K(\mathbf{v})}{k_B T} \right] d\mathbf{x} d\mathbf{v}$$

$$\rho(\mathbf{x}) = \frac{1}{Z} \exp \left[-\frac{U(\mathbf{x})}{k_B T} \right]$$

Ensemble averages

What you measure in experiment are ensemble averages

$$\langle g(\mathbf{x}) \rangle = \int g(\mathbf{x}) \rho(\mathbf{x}) d\mathbf{x}$$

For the canonical ensemble:

$$\langle g(\mathbf{x}) \rangle = \int g(\mathbf{x}) \frac{1}{Z} \exp \left[-\frac{U(\mathbf{x})}{k_B T} \right] d\mathbf{x}$$

Different ensembles

- In the limit of large systems all ensembles (or ensemble averages) are identical
 - But how large is large?
 - MD systems are often “small”
 - so you need to think about which ensemble to use

Ergodicity

time average = average over many instances

How to generate a canonical ensemble?

- Add a thermostat
 - for instance a Nose-Hoover thermostat:

$$\frac{d^2 \mathbf{r}_i}{dt^2} = \frac{\mathbf{F}_i}{m_i} - \frac{p_\xi}{Q} \frac{d\mathbf{r}_i}{dt}$$
$$\frac{dp_\xi}{dt} = (T - T_0)$$

Q: mass parameter,
determines coupling
strength (time)

Conserved quantity:

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) + \frac{p_\xi^2}{2Q} + N_f kT\xi$$

Simple velocity scaling

- Nose-Hoover is correct, but second order coupling, this can cause oscillations
- Simple first order velocity scaling (Berendsen thermostat):

$$\frac{dT}{dt} = \frac{T_0 - T}{\tau}$$

velocity scaling factor:

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left\{ \frac{T_0}{T(t - \frac{1}{2}\Delta t)} - 1 \right\} \right]^{1/2}$$

issue: no proper ensemble

Corrected velocity scaling

- Add a stochastic term: Bussi thermostat
(JCP 126:014101,2007)

$$dK = (K_0 - K) \frac{dt}{\tau_T} + 2 \sqrt{\frac{K K_0}{N_f}} \frac{dW}{\sqrt{\tau_T}}$$

W is a Wiener process:
a random process with
expectation zero, which can be
constructed from a random walk

degrees of
freedom

Advantage: nice first order decay of deviations

Stochastic dynamics

- Another option: add friction and noise to every degree of freedom:

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -m_i \overset{\substack{\text{friction coefficient} \\ \swarrow}}{\xi_i} \frac{d\mathbf{r}_i}{dt} + \mathbf{F}_i(\mathbf{r}) + \mathbf{w}_i \quad \nwarrow \text{Wiener process}$$

$$\langle \mathbf{w}_i(t) \mathbf{w}_j(t+s) \rangle = 2m_i \xi_i k_B T \delta(s) \delta_{ij}$$

- Advantage: good ergodicity/equilibration
- Disadvantage: loss of dynamics/inertia

Dissipative particle dynamics

- Stochastic dynamics on velocity differences between particle pairs
 - advantage: preserves hydrodynamics
 - adds some friction (viscosity)
 - you can solve Navier-Stokes equations using particles
 - but pair interactions are more complex and expensive to calculate

Constant pressure

- Constant NPT ensemble
 - one of the most popular ensembles
 - Use a barostat
 - for instance Parrinello-Rahman:

$$\frac{d\mathbf{b}^2}{dt^2} = V\mathbf{W}^{-1}\mathbf{b}'^{-1}(\mathbf{P} - \mathbf{P}_{ref})$$

b: box vectors
W: mass parameter

- disadvantage second order coupling:
volume oscillations

Berendsen pressure coupling

- For equilibration you can use first order Berendsen pressure coupling:

- scale box elements with:

$$\mu_{ij} = \delta_{ij} - \frac{\Delta t}{3 \tau_p} \beta_{ij} \{P_{0ij} - P_{ij}(t)\}$$

compressibility

coupling time

- disadvantage: no proper ensemble and fluctuations
- Conclusion: use Berendsen for equilibration and Parrinello-Rahman for productions

Stochastic cell rescaling

- To get the correct ensemble, again add fluctuations to Berendsen coupling:

Use the strain: $\epsilon = \log(V/V_0)$

$$d\epsilon = -\frac{\beta}{\tau_p}(P_0 - P)dt + \sqrt{\frac{2k_B T \beta}{V \tau_p}} dW$$

- Velocities are scaled reciprocal to the coordinates
- First order coupling and the correct ensemble
- Bernetti, M. and Bussi, G., “Pressure control using stochastic cell rescaling”, J. Chem. Phys., 153, 114107 (2020)

Constant chemical potential

- Constant μ -PT ensemble
 - you can use test particle insertion or particle deletion to determine chemical potential and remove/add particles
 - but this disrupts dynamics
 - and can be complex to implement and use

Reading

- Read Frenkel&Smit 11.6