CE 530 Molecular Simulation

Lecture 13
Molecular Dynamics in Other Ensembles

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Review

- Molecular dynamics is a numerical integration of the classical equations of motion
- Total energy is strictly conserved, so MD samples the NVE ensemble
- Dynamical behaviors can be measured by taking appropriate time averages over the simulation
  - Spontaneous fluctuations provide non-equilibrium condition for measurement of transport in equilibrium MD
  - Non-equilibrium MD can be used to get less noisy results, but requires mechanism to remove energy via heat transfer
- Two equivalent formalisms for EMD measurements
  - Einstein equation
  - Green-Kubo relation
time correlation functions
Molecular Dynamics in Other Ensembles

- Standard MD samples the NVE ensemble
- There is need enable MD to operate at constant T and/or P
  - with standard MD it is very hard to set initial positions and velocities to give a desired T or P with any accuracy
  - NPT MD permits control over state conditions of most interest
    - NEMD and other advanced methods require temperature control
- Two general approaches
  - stochastic coupling to a reservoir
  - feedback control
- Good methods ensure proper sampling of the appropriate ensemble
What is Temperature?

- **Thermodynamic definition**
  \[
  \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N}
  \]
  - temperature describes how much more **disordered** a system becomes when a given amount of energy is added to it
    - high temperature: adding energy opens up **few** additional microstates
    - low temperature: adding energy opens up **many** additional microstates
  \[
  \frac{1}{kT} = \frac{\partial}{\partial E} \ln \Omega(E,V,N)
  \]

- **Thermal equilibrium**
  - entropy is maximized for an isolated system at equilibrium
  - total entropy of two subsystems is sum of entropy of each: \( S_{tot} = S_1 + S_2 \)
  - consider transfer of energy from one subsystem to another
    - if entropy of one system goes up more than entropy of other system goes down, total entropy increases with energy transfer
    - equilibrium established when both rates of change are equal \( T_1 = T_2 \)
      - (temperature is guaranteed to increase as energy is added)
Momentum and Configurational Equilibrium

- Momentum and configuration coordinates are in thermal equilibrium
  - $E(r^N, p^N) = K(p^N) + U(r^N)$
  - momentum and configuration coordinates must be “at same temperature” or there will be net energy flux from one to other

- An arbitrary initial condition $(p^N, r^N)$ is unlikely to have equal momentum and configurational temperatures
  - and once equilibrium is established, energy will fluctuate back and forth between two forms
  - ...so temperatures will fluctuate too

- Either momentum or configurational coordinates (or both) may be thermostatted to fix temperature of both
  - assuming they are coupled
An Expression for the Temperature 1.

- Consider a space of two variables
  - *schematic representation of phase space*
- Contours show lines of constant $E$
  - *standard MD simulation moves along corresponding $3N$ dimensional hypersurface*
- Length of contour $E$ relates to $\Omega(E)$
- While moving along the $E_A$ contour, we’d like to see how much longer the $E_B$ contour is
- Analysis yields

$$\frac{1}{kT} = \frac{\nabla_x^2 E}{|\nabla_x E|^2}$$

*Relates to gradient and rate of change of gradient*
Momentum Temperature

- **Kinetic energy**
  \[
  K(p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m}
  \]

- **Gradient**
  \[
  \nabla_p K = \sum_{i=1}^{N} \left( \frac{p_{ix}}{m} \hat{e}_{ix} + \frac{p_{iy}}{m} \hat{e}_{iy} \right) \quad d = 2
  \]

- **Laplacian**
  \[
  \nabla_p \cdot \nabla_p K = \sum_{i=1}^{N} \left( \frac{1}{m} + \frac{1}{m} \right) = \frac{Nd}{m}
  \]

- **Temperature**
  \[
  kT = \frac{\left| \nabla_p K \right|^2}{\nabla_p^2 K}
  \]
  \[
  = \frac{1}{Nd / m} \sum_{i=1}^{N} \left( \frac{p_{ix}^2}{m^2} + \frac{p_{iy}^2}{m^2} \right)
  \]
  \[
  kT = \frac{1}{Nd} \sum_{i=1}^{N} \frac{p_i^2}{m}
  \]

**The standard canonical-ensemble “equipartition” result**
Configurational Temperature

- **Potential energy** \( U(r^N) \)

- **Gradient** \( \nabla_r U = \sum_{i=1}^{N} \left( \frac{\partial U}{\partial r_{ix}} \hat{e}_{ix} + \frac{\partial U}{\partial r_{iy}} \hat{e}_{iy} \right) = -\sum_{i=1}^{N} \left( F_{ix} \hat{e}_{ix} + F_{iy} \hat{e}_{iy} \right) \)

- **Laplacian** \( \nabla_r \cdot \nabla_r U = -\sum_{i=1}^{N} \left( \frac{\partial F_{ix}}{\partial r_{ix}} + \frac{\partial F_{iy}}{\partial r_{iy}} \right) \)

- **Temperature** \( kT = \frac{|\nabla_r U|^2}{\nabla_r^2 U} \)

\[
= \sum_{i=1}^{N} \frac{F_i^2}{-\sum_{i=1}^{N} \left( \frac{\partial F_{ix}}{\partial r_{ix}} + \frac{\partial F_{iy}}{\partial r_{iy}} \right)}
\]

Lennard-Jones Configurational Temperature

- Spherically-symmetric, pairwise additive model

\[ U(r^N) = \sum_{i=1}^{N} \sum_{j<i} u_{ij}(r_{ij}) \]

\[ u_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

- Force

\[ F_i = -\sum_{j \neq i} \frac{\mathbf{r}_{ij}}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \]

\[ \frac{r}{r} \frac{du_{LJ}}{dr} = \frac{48\varepsilon}{\sigma^2} \left[ \left( \frac{\sigma}{r} \right)^{14} - \frac{1}{2} \left( \frac{\sigma}{r} \right)^{8} \right] \]

- Laplacian

\[ \frac{\partial F_{i\alpha}}{\partial r_{i\alpha}} = -\sum_{j \neq i} \left[ \frac{r_{ij}^2}{r_{ij}} \frac{\partial}{\partial r_{ij}} \left( \frac{1}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \right) - \frac{1}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \right] \]

\[ \frac{1}{r} \frac{d}{dr} \left( \frac{1}{r} \frac{du_{LJ}}{dr} \right) = \frac{672\varepsilon}{\sigma^4} \left[ \left( \frac{\sigma}{r} \right)^{16} - \frac{2}{7} \left( \frac{\sigma}{r} \right)^{10} \right] \]

N.B. Formulas not verified
Thermostats

- All NPT MD methods thermostat the momentum temperature
- Proper sampling of the canonical ensemble requires that the momentum temperature fluctuates
  - *momentum temperature is proportional to total kinetic energy*
  - *energy should fluctuate between K and U*
  - *variance of momentum-temperature fluctuation can be derived from Maxwell-Boltzmann*
    - fluctuations vanish at large N
    - rigidly fixing K affects fluctuation quantities, but may not matter much to other averages

- All thermostats introduce unphysical features to the dynamics
  - *EMD transport measurements best done with no thermostat*
    - use thermostat equilibrate \( r \) and \( p \) temperatures to desired value, then remove
Isokinetic Thermostatting 1.

- Force momentum temperature to remain constant
- One (bad) approach
  - at each time step scale momenta to force $K$ to desired value
    - advance positions and momenta
    - apply $p_{\text{new}} = \lambda p$ with $\lambda$ chosen to satisfy $\sum \frac{(\lambda p_i)^2}{m} = NdkT$
    - repeat
  - “equations of motion” are irreversible
    - “transition probabilities” cannot satisfy detailed balance
  - does not sample any well-defined ensemble
Isokinetic Thermostating 2.

○ One (good) approach
  
  • *modify equations of motion to satisfy constraint*
    \[ \dot{r}_i = \frac{\mathbf{p}_i}{m} \]
    \[ \dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda \mathbf{p} \]
  
  • *λ is a friction term selected to force constant momentum-temperature*
    \[ K = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} \]
    \[ \frac{dK}{dt} = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot \dot{\mathbf{p}}_i}{m} \]
    \[ = \sum_{i=1}^{N} \frac{\mathbf{p}_i \cdot (\mathbf{F}_i - \lambda \mathbf{p}_i)}{m} \equiv 0 \quad \rightarrow \quad \lambda \equiv \frac{\sum_{i=1}^{N} \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{F}_i}{\sum_{i=1}^{N} \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{p}_i} \]

○ Time-reversible equations of motion
  
  • *no momentum-temperature fluctuations*
  
  • *configurations properly sample NVT ensemble (with fluctuations)*
  
  • *temperature is not specified in equations of motion!*
Thermostatting via Wall Collisions

- Wall collision imparts random velocity to molecule
  - *selection consistent with (canonical-ensemble) Maxwell-Boltzmann distribution at desired temperature*

  \[
  \pi(p) = \frac{1}{(2\pi mkT)^{d/2}} \exp\left(-\frac{p^2}{2mkT}\right)
  \]

- Advantages
  - *realistic model of actual process of heat transfer*
  - *correctly samples canonical ensemble*

- Disadvantages
  - *can’t use periodic boundaries*
  - *wall may give rise to unacceptable finite-size effects*
    - not a problem if desiring to simulate a system in confined space
  - *not well suited for soft potentials*
Andersen Thermostat

- Wall thermostat without the wall
- Each molecule undergoes impulsive “collisions” with a heat bath at random intervals
- Collision frequency $\nu$ describes strength of coupling
  - Probability of collision over time $dt$ is $\nu dt$
  - Poisson process governs collisions $P(t;\nu) = \nu e^{-\nu t}$
- Simulation becomes a Markov process
  - $\Pi = (\nu \Delta t) \Pi_{NVT} + (1 - \nu \Delta t) \Pi_{NVE}$
  - $\Pi_{NVE}$ is a “deterministic” TPM
    - It is not ergodic for NVT, but $\Pi$ is
- Click here to see the Andersen thermostat in action
Nosé Thermostat 1.

- **Modification of equations of motion**
  - *like isokinetic algorithm (differential feedback control)*
  - *but permits fluctuations in the momentum temperature*  
  - *integral feedback control*

- **Extended Lagrangian equations of motion**
  - *introduce a new degree of freedom, \( s \), representing reservoir*
  - *associate kinetic and potential energy with \( s \)*

\[
L_{\text{Nosé}} = \sum_{i=1}^{N} \frac{m_i (s \dot{r}_i)^2}{2} - U(r^N) + \frac{Q}{2} s^2 - gkT \ln s
\]

- *momenta* \( \mathbf{p}_i = \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i \)

\[
p_s = \frac{\partial L}{\partial s} = Q \dot{s}
\]

\[
U_s = -gkT \ln s \quad K_s = \frac{1}{2} Qs^2
\]

*effective mass*
Nosé Thermostat 2.

- Extended-system Hamiltonian is conserved
  \[ H_{\text{Nose}} = \sum_{i=1}^{N} \frac{p_i^2}{2m_i s^2} + U(r^N) + \frac{p_s^2}{2Q} + gkT \ln s \]

- Thus the probability distribution can be written
  \[ \pi(r^N, p^N, s, p_s) = \delta(H_{\text{Nose}} - E) \]

- What does this mean for the sampling of coordinates and momenta? How does this ensure a canonical distribution?
Nosé Thermostat 3.

\[ Q_{\text{Nosé}} = \frac{1}{N!} \int dp_s ds dp^N dr^N \delta(H_{\text{Nosé}} - E) \]

\[ = \frac{1}{N!} \int dp_s ds dp'N dr^N s^3 \delta \left[ \sum \frac{p_i'^2}{2m_i} + U(r^N) + \frac{p_s^2}{2Q} + gkT \ln s - E \right] \]

- Get canonical ensemble for \( s, p' \) if \( g = 3(N+1) \)
- \( s \) can be interpreted as a time-scaling factor
  - \( \Delta t_{\text{true}} = \Delta t_{\text{sim}} / s \)
  - \( s \) varies during simulation, so “true” time step is of varying length
Nosé Thermostat 3.

\[
Q_{\text{Nosé}} = \frac{1}{N!} \int dp_s ds dp^N d\mathbf{r}^N \delta(H_{\text{Nosé}} - E)
\]

\[
= \frac{1}{N!} \int dp_s ds dp^N d\mathbf{r}^N s^{3N} \delta \left[ \sum \frac{p_i^2}{2m_i} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s - E \right]
\]

\[
= \frac{1}{N!} \int dp_s ds dp^N d\mathbf{r}^N s^{3N+1} \frac{1}{gkT} \delta \left[ s - \exp \left( -\frac{1}{gkT} \left( H(\mathbf{p}^N, \mathbf{r}^N) + \frac{p_s^2}{2Q} - E \right) \right) \right]
\]

\[
= \frac{1}{N!} \frac{1}{gkT} e^{\frac{E(3N+1)}{gkT}} \int dp_s e^{\frac{(3N+1)p_s^2}{gkT}} 2^Q d\mathbf{p}^N d\mathbf{r}^N \exp \left( -\frac{3(N+1)}{gkT} H(\mathbf{p}^N, \mathbf{r}^N) \right)
\]

\[
= C \frac{1}{N!} \int d\mathbf{p}^N d\mathbf{r}^N \exp \left( -\frac{3(N+1)}{gkT} H(\mathbf{p}^N, \mathbf{r}^N) \right)
\]

- Get canonical ensemble for \( s \), \( p' \) if \( g = 3(N+1) \)
- \( s \) can be interpreted as a time-scaling factor
  - \( \Delta t_{\text{true}} = \Delta t_{\text{sim}} / s \)
  - \( s \) varies during simulation, so “true” time step is of varying length

\[
p' = \frac{p}{s}
\]

\[
\delta[h(s)] = \frac{\delta(s-s_0)}{h'(s_0)}
\]
Nosé-Hoover Thermostat 1.

- Advantageous to work with non-fluctuating time step

- Scaled-variables equations of motion
  - constant simulation $\Delta t$
  - fluctuating real $\Delta t$

\[
\begin{align*}
\dot{r}_i &= \frac{\partial H}{\partial p_i} = \frac{p_i}{m_i s^2} \\
\dot{p}_i &= -\frac{\partial H}{\partial r_i} = F_i \\
\dot{s} &= \frac{\partial H}{\partial p_s} = \frac{p_s}{Q} \\
\dot{p}_s &= -\frac{\partial H}{\partial s} = \frac{1}{s} \left( \sum_{i=1}^{N} \frac{p_i}{m_i s^2} - gkT \right)
\end{align*}
\]

- Real-variables (′ removed) equation of motion

\[
\begin{align*}
\dot{r}' &= r' \\
p' &= \frac{p}{s} \\
s' &= s \\
\Delta t' &= \Delta t / s
\end{align*}
\]

\[
\begin{align*}
\dot{r}_i &= \frac{p_i}{m_i} \\
\dot{p}_i &= F_i - \frac{sp_s}{Q} p_i \\
\dot{s} &= \frac{sp_s}{Q} \\
\dot{p}_s &= \frac{1}{Q} \left( \sum_{i=1}^{N} \frac{p_i}{m_i} - gkT \right)
\end{align*}
\]
Nosé-Hoover Thermostat 2.

- Real-variable equations are of the form
  \[ \dot{r}_i = \frac{p_i}{m_i} \]
  \[ \dot{p}_i = F_i - \xi p_i \]
  \[ \dot{s} = \frac{s}{s} = \xi \] (redundant; \( s \) is not present in other equations)
  \[ \dot{\xi} = \frac{1}{Q} \left( \sum_{i=1}^{N} \frac{p_i}{m_i} - gkT \right) \]

- Compare to isokinetic equations
  \[ \dot{r}_i = \frac{p_i}{m} \]
  \[ \dot{p}_i = F_i - \lambda p \]
  \[ \lambda = \frac{\sum m_i p_i \cdot F_i}{\sum m_i p_i \cdot p_i} \]

- Difference is in the treatment of the friction coefficient
  - Nosé-Hoover correctly samples NVT ensemble for both momentum and configurations; isokinetic does NVT properly only for configurations
Nosé-Hoover Thermostat 3.

- **Equations of motion**
  \[
  \begin{align*}
  \dot{r}_i &= \frac{p_i}{m_i} \\
  \dot{p}_i &= F_i - \xi p_i \\
  \dot{s} &= \xi \\
  \xi &= \frac{1}{Q} \left( \sum_{i=1}^{N} p_i - gkT \right)
  \end{align*}
  \]

- **Integration schemes**
  - *predictor-corrector algorithm is straightforward*
  - *Verlet algorithm is feasible, but tricky to implement*

At this step, update of $\xi$ depends on $p$; update of $p$ depends on $\xi$.
Barostats

- Approaches similar to that seen in thermostats
  - *constraint methods*
  - *stochastic coupling to a pressure bath*
  - *extended Lagrangian equations of motion*

- Instantaneous virial takes the role of the momentum temperature

\[
P(r^N, p^N) = \frac{NkT_p(p^N)}{V} + \frac{1}{3V} \left\langle \sum_{\text{pairs } i,j} \vec{r}_{ij} \cdot \vec{f}_{ij} \right\rangle
\]

- Scaling of the system volume is performed to control pressure

- Example: Equations of motion for constraint method

\[
\begin{align*}
\dot{r}_i &= p_i / m + \chi(r^N, p^N)r \\
\dot{p}_i &= F_i - \chi(r^N, p^N)p \\
\dot{V} &= 3V \chi(r^N, p^N)
\end{align*}
\]

\(\chi(t)\) is set to ensure \(\frac{dP}{dt} = 0\)
Summary

- Standard MD simulations are performed in the NVE ensemble
  - initial momenta can be set to desired temperature, but very hard to set configuration to have same temperature
  - momentum and configuration coordinates go into thermal equilibrium at temperature that is hard to predict

- Need ability to thermostat MD simulations
  - aid initialization
  - required to do NEMD simulations

- Desirable to have thermostat generate canonical ensemble

- Several approaches are possible
  - stochastic coupling with temperature bath
  - constraint methods
  - more rigorous extended Lagrangian techniques

- Barostats and other constraints can be imposed in similar ways