

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

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N}$$

Number of microstates having given E

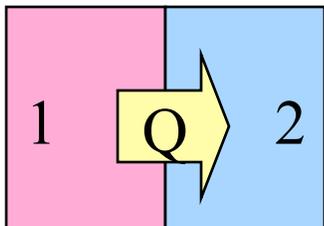
$$\frac{1}{kT} = \frac{\partial}{\partial E} \ln \Omega(E, V, N)$$

Disordered: more ways to arrange system and have it look the same

- *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

○ 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*



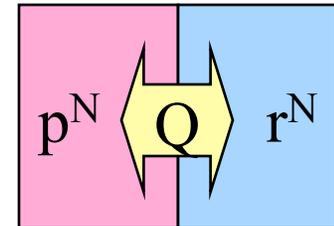
if entropy of one system goes up more than entropy of other system goes down, total entropy increases with energy transfer

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

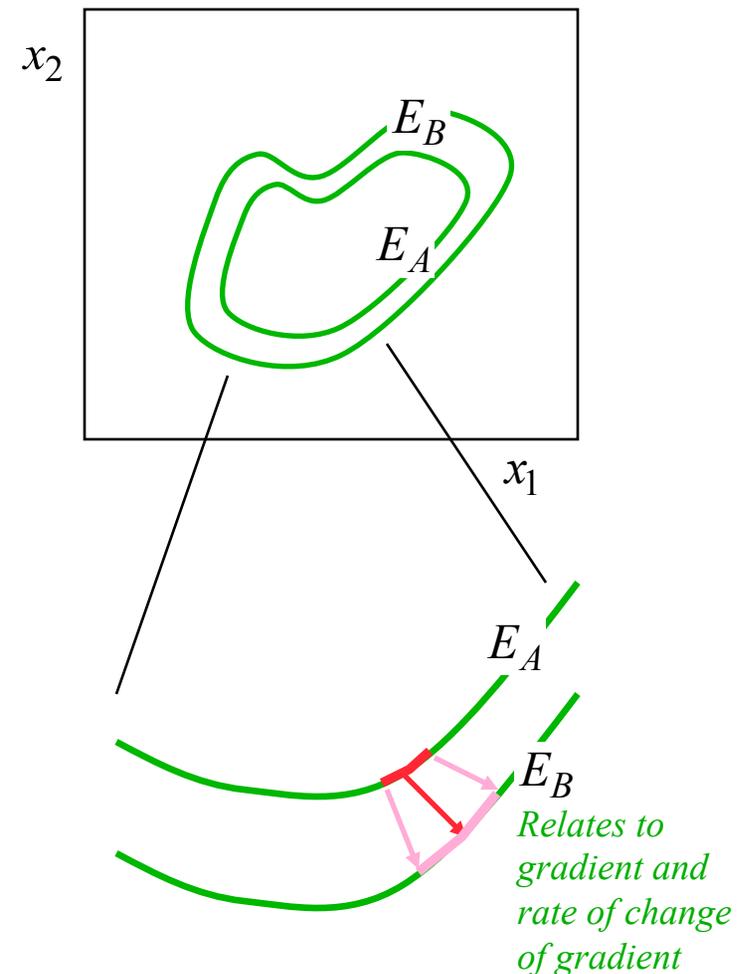


- $E(r^N, p^N) = K(p^N) + U(r^N)$
 - *momentum and configuration coordinates must be “at same temperature” or there will be net energy flux from one to other*
- An arbitrary initial condition (p^N, r^N) is unlikely to have equal momentum and configurational temperatures
 - *and once equilibrium is established, 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

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



Momentum Temperature

○ Kinetic energy $K(\mathbf{p}^N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}$

○ Gradient $\nabla_{\mathbf{p}} K = \sum_{i=1}^N \left(\frac{p_{ix}}{m} \hat{\mathbf{e}}_{ix} + \frac{p_{iy}}{m} \hat{\mathbf{e}}_{iy} \right) \quad d = 2$

○ Laplacian $\nabla_{\mathbf{p}} \cdot \nabla_{\mathbf{p}} K = \sum_{i=1}^N \left(\frac{1}{m} + \frac{1}{m} \right) = \frac{Nd}{m}$

○ Temperature $kT = \frac{|\nabla_{\mathbf{p}} K|^2}{\nabla_{\mathbf{p}}^2 K}$

$$= \frac{1}{Nd/m} \sum_{i=1}^N \left(\frac{p_{ix}^2}{m^2} + \frac{p_{iy}^2}{m^2} \right)$$

$$kT = \frac{1}{Nd} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m}$$

*The standard canonical-ensemble
“equipartition” result*

Configurational Temperature

○ Potential energy $U(\mathbf{r}^N)$

○ Gradient $\nabla_{\mathbf{r}}U = \sum_{i=1}^N \left(\frac{\partial U}{\partial r_{ix}} \hat{\mathbf{e}}_{ix} + \frac{\partial U}{\partial r_{iy}} \hat{\mathbf{e}}_{iy} \right) = - \sum_{i=1}^N (F_{ix} \hat{\mathbf{e}}_{ix} + F_{iy} \hat{\mathbf{e}}_{iy})$

○ Laplacian $\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{r}}U = - \sum_{i=1}^N \left(\frac{\partial F_{ix}}{\partial r_{ix}} + \frac{\partial F_{iy}}{\partial r_{iy}} \right)$

○ Temperature $kT = \frac{|\nabla_{\mathbf{r}}U|^2}{\nabla_{\mathbf{r}}^2U}$

$$= \frac{\sum_{i=1}^N \mathbf{F}_i^2}{-\sum_{i=1}^N \left(\frac{\partial F_{ix}}{\partial r_{ix}} + \frac{\partial F_{iy}}{\partial r_{iy}} \right)}$$

Butler, B. D., G. Ayton, O. G. Jepps, and D. J. Evans. 1998. Configurational temperature: verification of Monte Carlo simulations. *J. Chem. Phys.* **109**, 6519.

Lennard-Jones Configurational Temperature

- Spherically-symmetric, pairwise additive model

$$U(\mathbf{r}^N) = \sum_{i=1}^N \sum_{j<i} u_{ij}(r_{ij}) \quad u_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

- Force

$$\mathbf{F}_i = - \sum_{j \neq i} \frac{\mathbf{r}_{ij}}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \quad \frac{\mathbf{r}}{r} \frac{du_{LJ}}{dr} = \mathbf{r} \frac{48\epsilon}{\sigma^2} \left[\left(\frac{\sigma}{r} \right)^{14} - \frac{1}{2} \left(\frac{\sigma}{r} \right)^8 \right]$$

- Laplacian

$$\frac{\partial F_{i\alpha}}{\partial r_{i\alpha}} = - \sum_{j \neq i} \left[\frac{r_{ij}^2}{r_{ij}} \frac{\partial}{\partial r_{ij}} \left(\frac{1}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \right) - \frac{1}{r_{ij}} \frac{du_{ij}}{dr_{ij}} \right] \quad \frac{1}{r} \frac{d}{dr} \left(\frac{1}{r} \frac{du_{LJ}}{dr} \right) = \frac{672\epsilon}{\sigma^4} \left[\left(\frac{\sigma}{r} \right)^{16} - \frac{2}{7} \left(\frac{\sigma}{r} \right)^{10} \right]$$

N.B. Formulas not verified

Thermostats

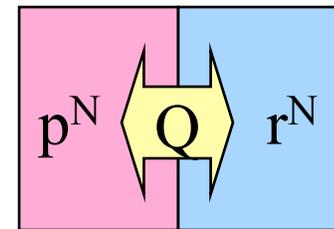
- All NPT MD methods thermostat the momentum temperature
- Proper sampling of the canonical ensemble requires that the momentum temperature fluctuates

- *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

$$kT = \frac{1}{Nd} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m} = \frac{2}{Nd} K$$



$$\frac{\sigma_{T_p}^2}{\langle T_p \rangle^2} = \frac{2}{3N}$$

- All thermostats introduce unphysical features to the dynamics
 - *EMD transport measurements best done with no thermostat*
 - *use thermostat equilibrate \mathbf{r} and \mathbf{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 $\mathbf{p}^{\text{new}} = \lambda \mathbf{p}$ with λ chosen to satisfy $\sum \frac{(\lambda \mathbf{p}_i)^2}{m} = NdkT$
 repeat
 - “*equations of motion*” are irreversible
 “transition probabilities” cannot satisfy detailed balance
 - *does not sample any well-defined ensemble*

Isokinetic Thermostatting 2.

○ One (good) approach

- *modify equations of motion to satisfy constraint*

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \lambda \mathbf{p}_i$$

- *λ is a friction term selected to force constant momentum-temperature*

$$K = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m}$$

$$\frac{dK}{dt} = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \dot{\mathbf{p}}_i}{m}$$

$$= \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \cdot (\mathbf{F}_i - \lambda \mathbf{p}_i) \equiv 0 \quad \Longrightarrow \quad \lambda = \frac{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{F}_i}{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{p}_i}$$

○ 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

Gaussian

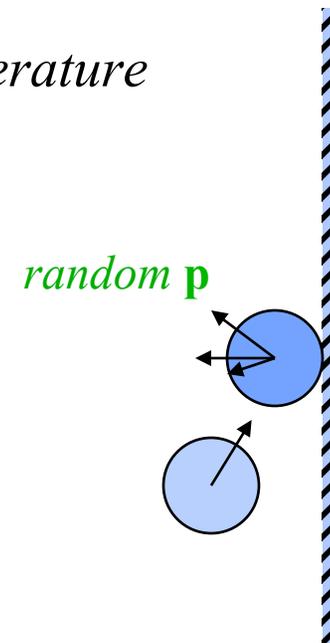
$$\pi(\mathbf{p}) = \frac{1}{(2\pi mkT)^{d/2}} \exp\left(-\frac{\mathbf{p}^2}{2mkT}\right)$$

○ 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*

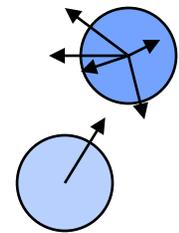


Wall can be made as realistic as desired

Andersen Thermostat

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

random \mathbf{p}



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*

$$L_{Nose} = \sum_{i=1}^N \frac{m_i (s \dot{\mathbf{r}}_i)^2}{2} - U(\mathbf{r}^N) + \frac{Q}{2} \dot{s}^2 - gkT \ln s$$

$$U_s = -gkT \ln s$$

$$K_s = \frac{1}{2} Q \dot{s}^2$$

*effective
mass*

- *momenta*

$$\mathbf{p}_i \equiv \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$$

$$p_s \equiv \frac{\partial L}{\partial \dot{s}} = Q \dot{s}$$

Nosé Thermostat 2.

- Extended-system Hamiltonian is conserved

$$H_{Nose} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s$$

- Thus the probability distribution can be written

$$\pi(\mathbf{r}^N, \mathbf{p}^N, s, p_s) = \delta(H_{Nose} - E)$$

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

Nosé Thermostat 3.

$$\mathbf{p}' = \frac{\mathbf{p}}{s}$$

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

$$\delta[h(s)] = \frac{\delta(s - s_0)}{h'(s_0)}$$

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

○ 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

$$\mathbf{p}' = \frac{\mathbf{p}}{s}$$

Nosé Thermostat 3.

$$\begin{aligned}
 Q_{\text{Nosé}} &= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^N d\mathbf{r}^N \delta(H_{\text{Nosé}} - E) & \delta[h(s)] &= \frac{\delta(s-s_0)}{h'(s_0)} \\
 &= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^N d\mathbf{r}^N s^{3N} \delta \left[\sum \frac{\mathbf{p}'_i{}^2}{2m_i} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s - E \right] \\
 &= \frac{1}{N!} \int dp_s ds d\mathbf{p}'^N d\mathbf{r}^N \frac{s^{3N+1}}{gkT} \delta \left[s - \exp \left(-\frac{1}{gkT} \left(H(\mathbf{p}'^N, \mathbf{r}^N) + \frac{p_s^2}{2Q} - E \right) \right) \right] \\
 &= \frac{1}{N!} \frac{1}{gkT} e^{\frac{E(3N+1)}{gkT}} \int dp_s e^{-\frac{(3N+1)p_s^2}{gkT 2Q}} d\mathbf{p}'^N d\mathbf{r}^N \exp \left(-\frac{3(N+1)}{gkT} H(\mathbf{p}'^N, \mathbf{r}^N) \right) \\
 &= C \frac{1}{N!} \int d\mathbf{p}'^N d\mathbf{r}^N \exp \left(-\frac{3(N+1)}{gkT} H(\mathbf{p}'^N, \mathbf{r}^N) \right)
 \end{aligned}$$

○ 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

$$H_{Nose} = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}^N) + \frac{p_s^2}{2Q} + gkT \ln s$$

Nosé-Hoover Thermostat 1.

$$\mathbf{r}' = \mathbf{r}$$

$$\mathbf{p}' = \mathbf{p} / s$$

$$s' = s$$

$$\Delta t' = \Delta t / s$$

○ Advantageous to work with non-fluctuating time step

○ Scaled-variables equations of motion

- constant simulation Δt
- fluctuating real Δt

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i} = \frac{\mathbf{p}_i}{m_i s^2}$$

$$\dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = \mathbf{F}_i$$

$$\dot{s} = \frac{\partial H}{\partial p_s} = \frac{p_s}{Q}$$

$$\dot{p}_s = -\frac{\partial H}{\partial s} = \frac{1}{s} \left(\sum_{i=1}^N \frac{p_i^2}{m_i s^2} - gkT \right)$$

○ Real-variables (' removed) equation of motion

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \frac{sp_s}{Q} \mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \frac{sp_s}{Q}$$

$$\frac{\partial(sp_s / Q)}{\partial t} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - gkT \right)$$

$$\begin{aligned} \frac{d\mathbf{r}'}{dt'} &= s \frac{d\mathbf{r}}{dt} \\ &= s \frac{\mathbf{p}}{ms^2} \\ &= \frac{\mathbf{p}}{ms} \\ &= \frac{\mathbf{p}'}{m} \end{aligned}$$

Nosé-Hoover Thermostat 2.

- Real-variable equations are of the form

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \xi \quad (\text{redundant; } s \text{ is not present in other equations})$$

$$\dot{\xi} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - gkT \right)$$

- Compare to isokinetic equations

$$\begin{aligned} \dot{\mathbf{r}}_i &= \mathbf{p}_i / m & \lambda &= \frac{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{F}_i}{\sum \frac{1}{m_i} \mathbf{p}_i \cdot \mathbf{p}_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i - \lambda \mathbf{p} \end{aligned}$$

- 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

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

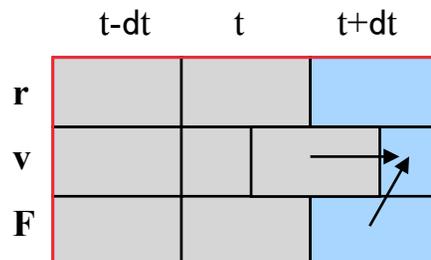
$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\frac{\dot{s}}{s} = \xi$$

$$\dot{\xi} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - gkT \right)$$

○ Integration schemes

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



At this step, update of ξ depends on p ; update of p depends on ξ

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \xi \mathbf{p}_i$$

$$\dot{\xi} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{p_i^2}{m_i} - gkT \right)$$

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

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

- Scaling of the system volume is performed to control pressure
- Example: Equations of motion for constraint method

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m + \chi(\mathbf{r}^N, \mathbf{p}^N) \mathbf{r}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \chi(\mathbf{r}^N, \mathbf{p}^N) \mathbf{p}$$

$$\dot{V} = 3V \chi(\mathbf{r}^N, \mathbf{p}^N)$$

$\chi(t)$ is set to ensure $dP/dt = 0$

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