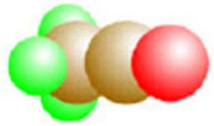
Applied Statistical Mechanics
Lecture Note - 13

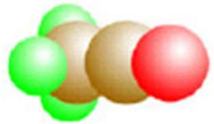


고려대학교

Molecular Dynamics Simulation

고려대학교
화공생명공학과
강정원

Contents



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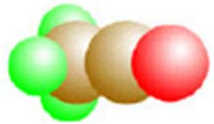
I. Basic MD Simulation - MC vs. MD



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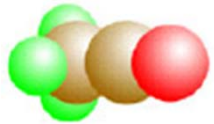
- MC
  - Probabilistic simulation technique
  - Limitations
    - require the knowledge of an equilibrium distribution
    - rigorous sampling of large number of possible phase-space
    - gives only configurational properties (not dynamic properties !)

$$\langle A \rangle = \frac{\int dr^N A(r^N) \exp\{-\beta U(r^N)\}}{\int dr^N \exp\{-\beta U(r^N)\}}$$

- MD
  - Deterministic simulation technique
  - Fully numerical formalism
    - numerical solution of N-body system

I. Basic MD Simulation - The Idea



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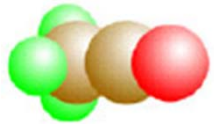
- Follow the exactly same procedure as real experiments
  - Prepare sample
    - prepare N particles
    - solve equation of motions
  - Connect sample to measuring instruments (e.g. thermometer, viscometer,…)
    - after equilibration time, actual measurement begins
  - Measure the property of interest for a certain time interval
    - average properties
- Example : measurement of temperature

$$\left\langle \frac{1}{2} m v_\alpha^2 \right\rangle = \frac{1}{2} k_B T \quad \longrightarrow \quad T(t) = \sum_i \frac{m_i v_i^2(t)}{k_B N_f}$$

I. Basic MD Simulation - Equation of Motion



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- Classical Newton's equation of motion
  - Three formulation
    - Newtonian
    - Lagrangian
    - Hamiltonian
  - Hamiltonian preferred for many-body systems
    - solution of 2N differential equations

$$\frac{\partial \mathbf{r}_i}{\partial t} = \frac{\mathbf{p}_i}{m_i}$$

$$\frac{\partial \mathbf{p}_i}{\partial t} = \mathbf{F}_i$$

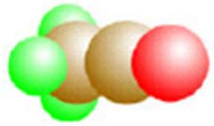
$$\mathbf{r} = \mathbf{r}(r_x, r_y, r_z)$$

$$\mathbf{p} = \mathbf{p}(p_x, p_y, p_z)$$

$$\mathbf{F}_i = \sum_{\substack{j=1 \\ j \neq i}} \mathbf{F}_{ij}$$

→ **Solution methods : Finite Difference Method**

I. Basic MD Simulation - Verlet Algorithm



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- Verlet (1967) : Very simple, efficient and popular algorithm

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \frac{1}{m}\mathbf{p}(t)\delta t + \frac{1}{2m}\mathbf{F}(t)\delta t^2 + \frac{1}{3!}\dddot{\mathbf{r}}(t)\delta t^3 + O(\delta t^4)$$

$$\mathbf{r}(t-\delta t) = \mathbf{r}(t) - \frac{1}{m}\mathbf{p}(t)\delta t + \frac{1}{2m}\mathbf{F}(t)\delta t^2 - \frac{1}{3!}\dddot{\mathbf{r}}(t)\delta t^3 + O(\delta t^4)$$

$$\downarrow$$

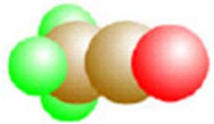
$$\mathbf{r}(t+\delta t) + \mathbf{r}(t-\delta t) = 2\mathbf{r}(t) + \frac{1}{m}\mathbf{F}(t)\delta t^2 + O(\delta t^4)$$

$$\downarrow$$

$$\mathbf{r}(t+\delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\delta t) + \frac{1}{m}\mathbf{F}(t)\delta t^2 + O(\delta t^4)$$

feature : update without calculating momentum (p)

I. Basic MD Simulation - Leapfrog Algorithm



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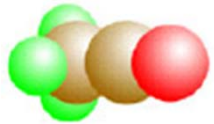
- Hockeny (1970), Potter (1972)
- Half-step leap-frog algorithm
- Mathematically equivalent to Verlet algorithm

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \mathbf{v}(t+\tfrac{1}{2}\delta t)\delta t$$

$$\mathbf{v}(t+\tfrac{1}{2}\delta t) = \mathbf{v}(t-\tfrac{1}{2}\delta t) + \tfrac{1}{m}\mathbf{F}(t)\delta t$$

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \left[\mathbf{v}(t-\tfrac{1}{2}\delta t) + \tfrac{1}{m}\mathbf{F}(t)\delta t\right]\delta t$$

2. Properties Calculation in MD - Energies



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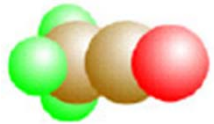
- Potential energy
  - Can be calculated during force calculation
- Kinetic energy

$$K = \sum \frac{1}{2} m v_i^2$$

2. Properties Calculation in MD - Pressures



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- In an MD simulation, calculation of pressure using tensor notation is not the most efficient method.
- For homogeneous systems, there is simple way to calculate pressure (Irving and Kirkwood, 1950)

Kinetic – ideal gas term

Configurational – called "Virial"

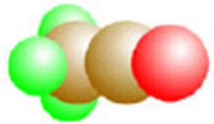
$$P = \frac{1}{V}\left[\sum_i m_i \mathbf{v}_i(t)\mathbf{v}_i(t) + \sum_i \sum_j \mathbf{r}_{ij}(t)\mathbf{F}_{ij}(t)\right]$$

$$= \rho k_B T + \frac{1}{2V}\sum_i \sum_j \mathbf{r}_{ij}(t)\mathbf{F}_{ij}(t)$$

Calculate when force update

Calculate when velocity update

2. Properties Calculation in MD - Transport Properties



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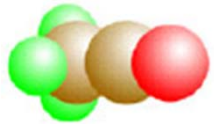
- Approaches for transport properties
  - Method 1 : ***NEMD*** (Non-equilibrium Molecular Dynamics)
    - Continuous addition and removal of conserved quantities
    - Gives high signal-to-noise ratio (good statistics)
  - Method 2 : Equilibrium molecular dynamics
    - Start with anisotropic configuration of mass, momentum and energy
    - Observe natural fluctuations and dissipation of mass, momentum and energy
    - Poor signal-to-noise ration (poor statistics)
    - All transport properties can be measured at once

2. Properties Calculation in MD - Transport Properties



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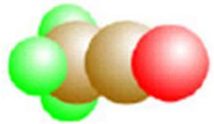
- Differential Balance Equation

Mass	Energy	Momentum
$\frac{\partial c(r,t)}{\partial t} + \nabla \bullet \mathbf{j} = 0$	$c_p \frac{\partial T(r,t)}{\partial t} + \nabla \bullet \mathbf{q} = 0$	$\rho \frac{D\mathbf{v}(r,t)}{Dt} + \nabla \bullet \underline{\underline{\boldsymbol{\tau}}} = 0$

- Constitutive Equations

Fick's Law	Fourier's Law	Newton's Law
$\mathbf{j} = -D\nabla c$	$q = -k\nabla T$	$\tau_{xy} = -v\nabla_y(\rho v_x)$

2. Properties Calculation in MD - Transport Properties



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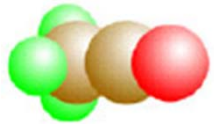
- Purpose : Obtain transport coefficient by molecular simulation
  - Not that the “laws” are only approximation that apply not-too-large gradients
  - In principle transfer coefficients depends on c, T and v

- **Green-Kubo Relation**
  - Relation between transport properties and integral over time-correlation function.

2. Properties Calculation in MD - Transport Properties



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- Consider self-diffusion in a pure substance
- Consider how molecules are dissipated when initial configurations are given as Dirac delta function

- Combine mass balance eqn. With Fick's Law

$$\frac{\partial c(\mathbf{r},t)}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0$$

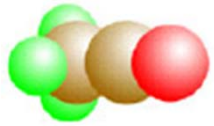
B.C. $\quad c(\mathbf{r},t) = \delta(\mathbf{r})$

Dimensionality of given system

Solution

$$c(\mathbf{r},t) = (2\pi Dt)^{-2/d} \exp(-\frac{r^2}{2Dt})$$

2. Properties Calculation in MD - Transport Properties



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We do not need concentration itself c(r,t) - just diffusion coefficient (D)

$$< r^2(t) >= \int c(\mathbf{r},t) r^2 dr$$

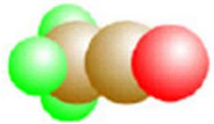
$$\int c(\mathbf{r},t) dr = 1$$

$$\frac{\partial c(\mathbf{r},t)}{\partial t} - D\nabla^2 c(\mathbf{r},t) = 0$$

$$\frac{\partial < r^2(t) >}{\partial t} = 2dD$$

$$< r^2(t) >= \frac{1}{N}\sum (r_i(t))^2 = 2dDt$$

2. Properties Calculation in MD - Transport Properties



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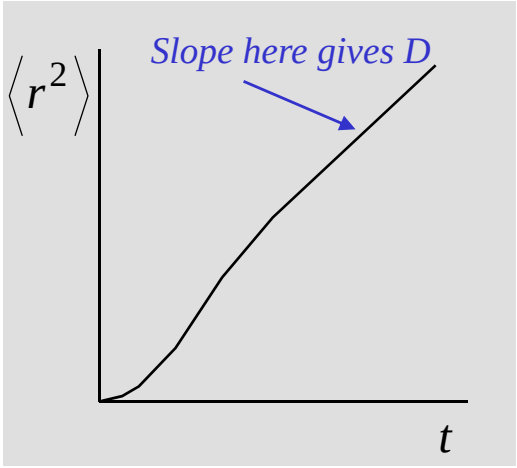
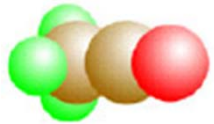
$$< r^2(t) >= \frac{1}{N} \sum (r_i(t))^2 = 2dDt$$



- ***Plot of t vs. square of traveled distance gives diffusion coefficient***
- ***In 3D –space, $<r^2>$ is mean square displacement (MSD)***

2. Properties Calculation in MD - Transport Properties



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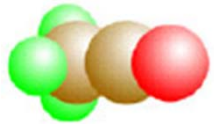
- An alternative formulation using velocity instead of particle position

$$\mathbf{r}_i(t) = \int_0^t \mathbf{v}(\tau) d\tau$$

$$\Rightarrow$$

$$\begin{aligned}
\left\langle r^2(t) \right\rangle &= \left\langle \int_0^t \mathbf{v}(\tau_1) d\tau_1 \cdot \int_0^t \mathbf{v}(\tau_2) d\tau_2 \right\rangle \\
&= \int_0^t d\tau_1 \int_0^t d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle \\
&= 2\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(\tau_2) \cdot \mathbf{v}(\tau_1) \right\rangle \\
&= 2\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau_1 - \tau_2) \right\rangle \\
&= 2\int_0^t d\tau_1 \int_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle \\
2dDt &= 2t\int_0^t d\tau \left\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \right\rangle
\end{aligned}$$

2. Properties Calculation in MD - Transport Properties



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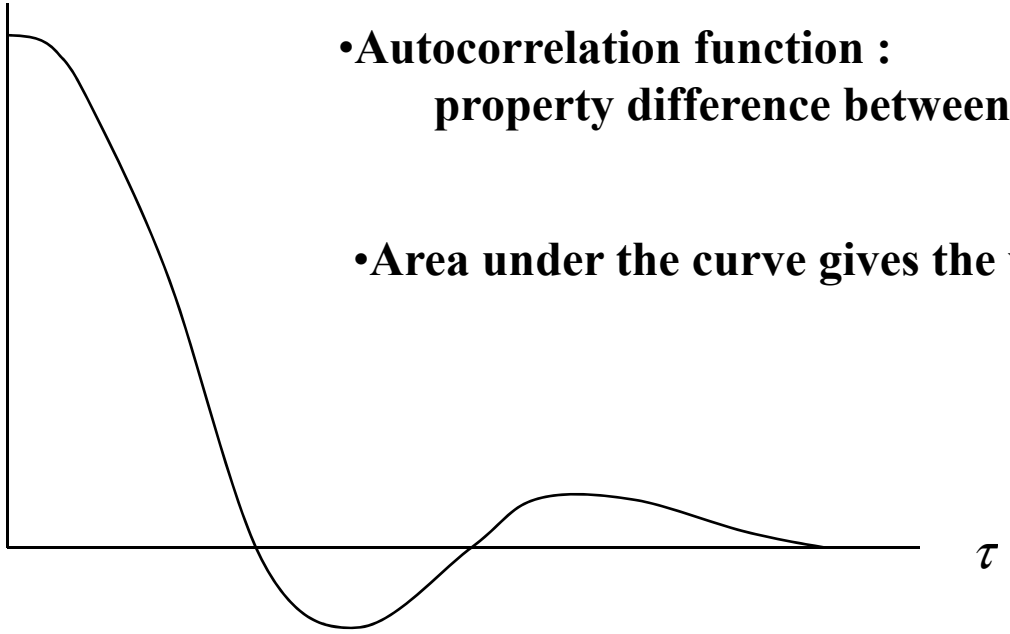
$$2dDt = 2t\int_0^t d\tau < \mathbf{v}(0)\mathbf{v}(\tau) > \xrightarrow{t \to \infty} D = \frac{1}{d}\int_0^\infty d\tau < \mathbf{v}(0)\mathbf{v}(\tau) >$$

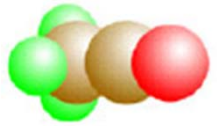
$< \mathbf{v}(0)\mathbf{v}(\tau) >$ $< \mathbf{v}(0)\mathbf{v}(\tau) >=< v(t')v(t'') >$



- **Autocorrelation function :**
  property difference between two adjacent time steps

- **Area under the curve gives the value of self-diffusion coefficient**

2. Properties Calculation in MD
- Evaluation of time correlation functions



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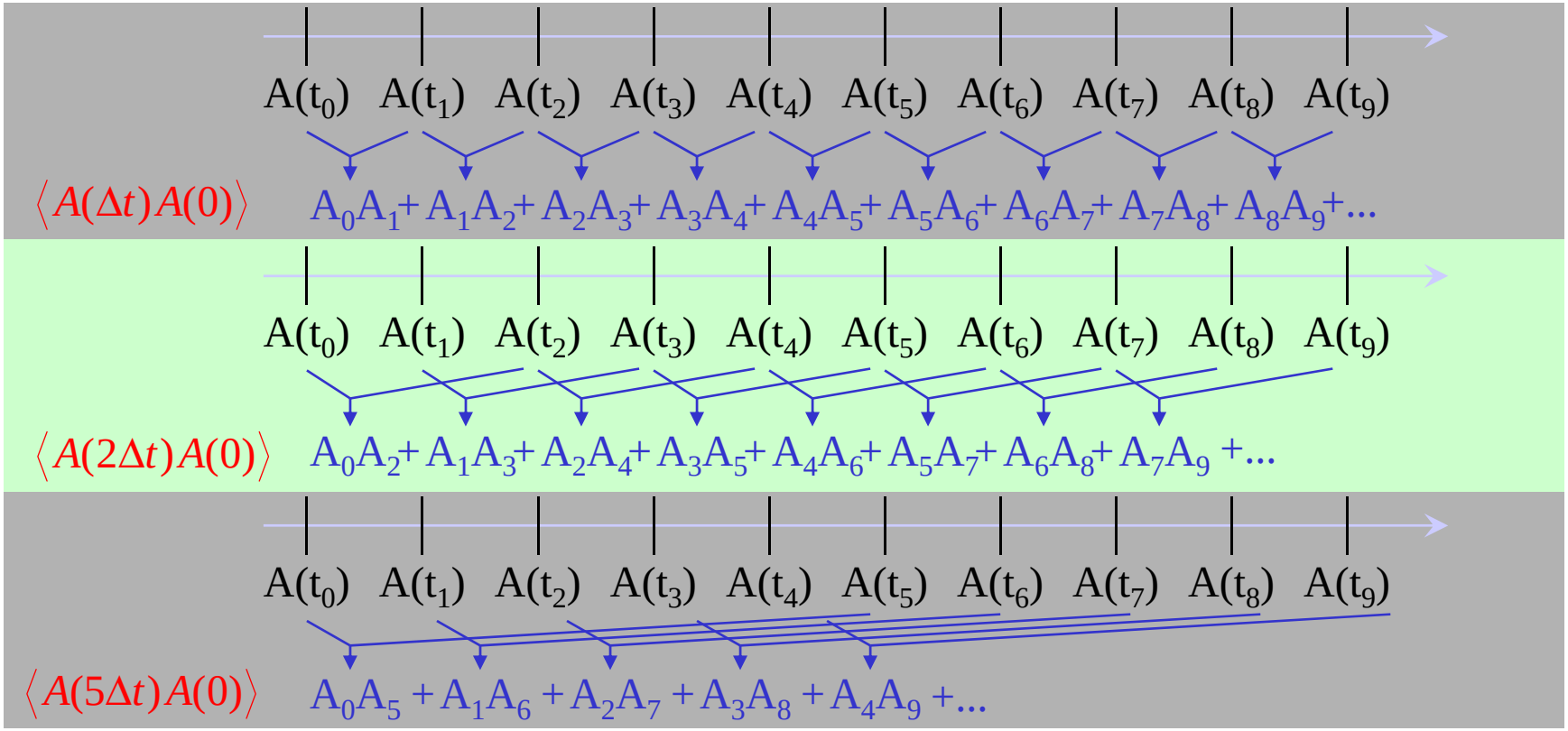
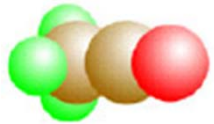
- Time consuming and require a lot of storage
  - Alternative method : FFT (Fast Fourier Transform), Coarse Graining method



2. Properties Calculation in MD - Transport Properties



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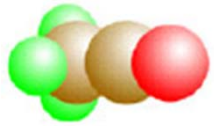
- Zero-shear viscosity

$$\eta = \frac{1}{VkT}\int_0^\infty d\tau < \sigma_{xy}(0)\sigma_{xy}(\tau) > \qquad \sigma_{xy} = \sum_i \left[m_i v_i^x v_i^y + \frac{1}{2}\sum_{i\neq j} x_{ij} f_y(r_{ij}) \right]$$

- Thermal Conductivity

$$\lambda_T = \frac{1}{VkT^2}\int_0^\infty d\tau < q(0)q(\tau) > \qquad q = \frac{d}{dT}\sum_i \left[m_i v_i^2 + \frac{1}{2}\sum_{i\neq j} u(r_{ij}) \right]$$

2. Properties Calculation in MD - Radial Distribution Function



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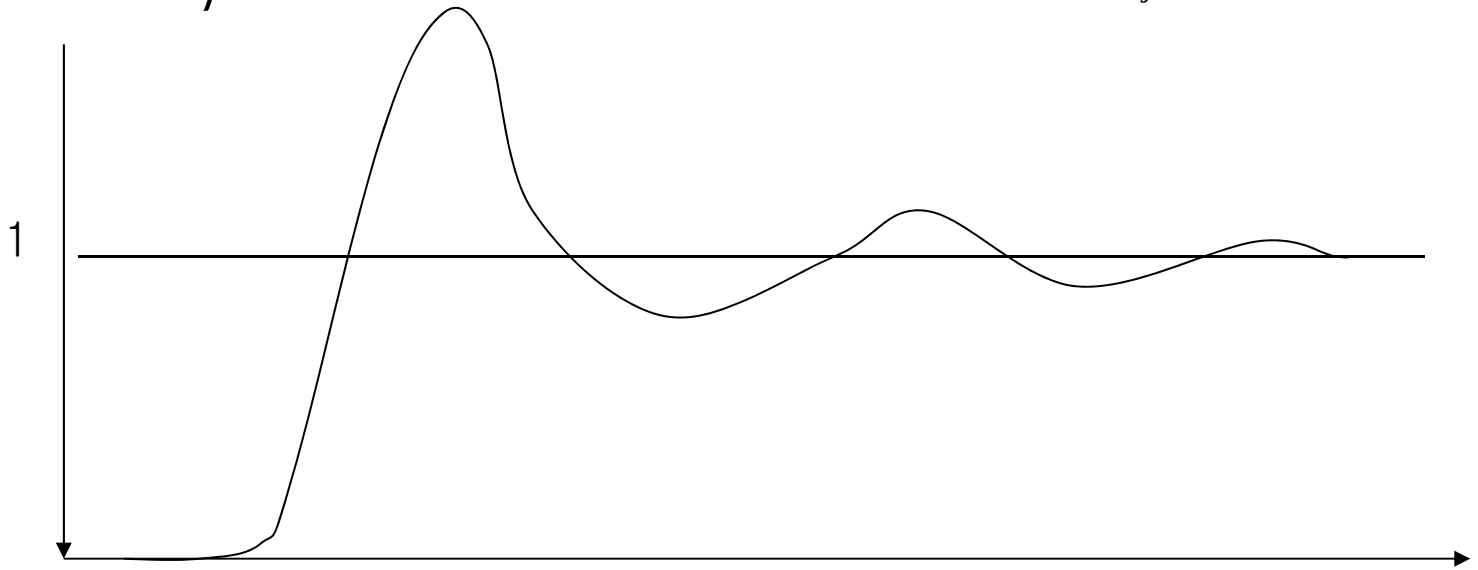
- Time averaged value of number density
- Ensemble averaged number density

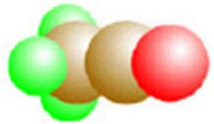
$$g(r) = \frac{\rho(r)}{\rho}$$

$$g(r) = \frac{V}{N} < \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) >$$



→ Just count the number of molecules within a range

3. MD in Other Ensembles - Constraints



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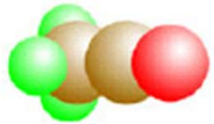
- With proper choice of *g(r)*, we can calculate useful thermodynamic properties
  - Internal energy $$U^c = 2\pi N\rho\int_0^\infty \phi(r)g(r)r^2dr$$
  - Pressure $$P = \rho kT - \frac{2\pi\rho^2}{3}\int_0^\infty \frac{d\phi(r)}{dr}g(r)r^3dr$$
  - Chemical Potential

$$\mu = kT\ln\left(\frac{\rho\Lambda^3}{q_{\text{int}}}\right) - \frac{2\pi}{3}\left\{\frac{\partial}{\partial N}\left[N^2\int_V^\infty \frac{dV'}{V'^2}\int_0^\infty \frac{d\phi(r)}{dr}g(r)r^3dr\right]\right\}$$

3. MD in Other Ensembles – Constraints



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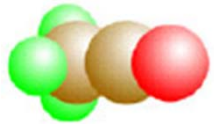
- Hamiltonian formulation
  - Conservation of kinetic + potential energy

    $H = K + U$
  - *(N,V,E)* ensemble
  - Cannot be applied to other ensemble
    - constant *T*, constant *P*, …
    - for example we can keep const *T* while *H* is constant
    - distribution of *K* and *U*
- Two types of constraints
  - Holonomic constraints : may be integrated out of equation of motion
  - Nonholonomic constraints : non-integrable (involves velocities)
    - Temperature, pressure, stress, …

3. MD in Other Ensembles – Constraints



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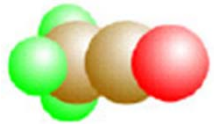
- Force momentum temperature to remain constant
- One (bad) approach
  - at each time step scale momenta to force K to desired value
    - advance positions and momenta
    - apply $p^{new} = \lambda p$ with λ chosen to satisfy
    - repeat
  - "equations of motion" are irreversible
    - "transition probabilities" cannot satisfy detailed balance
  - does not sample any well-defined ensemble

3. MD in Other Ensembles – Constraints



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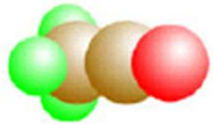
- "Gauss' principle of least constraints"
  - Gaussian constraints : perturbative force introduced into the equation of motion minimizes the deviation to classical trajectories of particles from their unperturbed trajectories
  - Consider a function f , a function of particle acceleration

$$f(\ddot{\mathbf{r}}_i) = \frac{1}{2}\sum_i m\left[\ddot{\mathbf{r}}_i - \frac{\mathbf{F}_i}{m_i}\right]^2$$

  - $f=0$: normal Newtonian equation of motion
  - otherwise, constrained non-Newtonian equation of motion
  - Gauss' principle : physical acceleration → f to be minimum

$$\frac{\partial}{\partial \ddot{\mathbf{r}}_i}\left(f(\ddot{\mathbf{r}}_i) - \zeta g(\ddot{\mathbf{r}}_i)\right) = 0 \qquad \zeta : \text{Lagrangin (Gauss) Multiplier}$$

3. MD in Other Ensembles – Constraints



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- Constant Temperature constraints

$$G(\dot{\mathbf{r}}_i, t) = \sum_i \frac{m_i \dot{\mathbf{r}}_i^2}{2} - \frac{3NkT}{2} = 0$$

$$g(\ddot{\mathbf{r}}_i, \dot{\mathbf{r}}_i, t) = \frac{dG}{dt} = \sum_i m\dot{\mathbf{r}}_i \bullet \ddot{\mathbf{r}}_i = 0$$

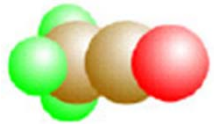
$$\frac{\partial}{\partial \ddot{\mathbf{r}}_i}\left(f(\ddot{\mathbf{r}}_i) - \zeta g(\ddot{\mathbf{r}}_i)\right) = 0$$

$$\frac{\partial}{\partial \ddot{\mathbf{r}}_i}\left[\frac{1}{2}\sum_j m\left(\ddot{\mathbf{r}}_i - \frac{\mathbf{F}_j}{m_j}\right)^2 - \sum_j m_j \dot{\mathbf{r}}_j \bullet \ddot{\mathbf{r}}_j\right] = 0$$

$$\underbrace{m\ddot{\mathbf{r}}_i}_{\text{Newtonian}} = \mathbf{F}_i - \zeta m_i \dot{\mathbf{r}}_i$$

Constraint force

3. MD in Other Ensembles – Constraints



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- Modified equation of motion

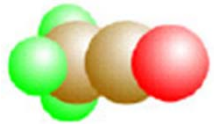
$$\mathbf{r}_i = \frac{\mathbf{p}_i}{m_i}$$

$$\mathbf{p}_i = \mathbf{F}_i - \zeta m_i \dot{\mathbf{r}}_i$$

$$\zeta = \frac{\sum_i \dot{\mathbf{r}}_i \cdot \mathbf{F}_i}{\sum_i m_i \dot{\mathbf{r}}_i^{\,2}}$$

→ one of good approach, but temperature is not specified !

3. MD in Other Ensembles – Nose Thermostat



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- Extended Lagrangian Equation of Motion

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

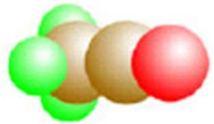
$$\mathbf{p}_i \equiv \frac{\partial L}{\partial \dot{\mathbf{r}}_i} = m_i s^2 \dot{\mathbf{r}}_i$$

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

$$U_s = -gkT \ln s$$

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

3. MD in Other Ensembles – Nose-Hoover Thermostat



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- Equations of motion

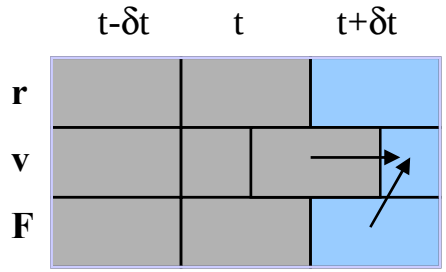
$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m_i}$$

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

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

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

- 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

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

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