

MSE 620 Fall 2008

Quick Review of MC/MD for Exam 1

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Postulates of statistical mechanics

⊗ Equal *a priori* probabilities

- ☐ All configurations consistent with a given energy level occur with *equal probability*

⊗ Ergodic hypothesis

- ☐ Averaging over time = “ensemble averaging”
- ☐ Any configuration should be accessible from another

Microcanonical ensemble

- ⊗ Consider one component and one phase
- ⊗ Gibbs phase rule: $F = C - P + 2 = 2$
- ⊗ Microcanonical ensemble: E and ρ specified
- ⊗ Consider all systems with N, V, E same
- ⊗ For many-body system, many states consistent with specifications, number = degeneracy = Ω
- ⊗ Ω is microcanonical *partition function*
- ⊗ Probability of any configuration = $1/\Omega$

Canonical Ensemble

⊗ T and ρ specified (N, V, T)

⊗ Contact with large heat bath so that $E \sim \text{constant}$

⊗ Boltzmann distribution, probability of observing system with energy E_i :
$$P_i = \frac{\exp(-E_i/k_B T)}{Q}$$

⊗ Canonical partition coefficient: $Q = \sum_i \exp(-E_i/k_B T)$

⊗ Ensemble average of any property:

$$\langle A \rangle = \sum_i A_i P_i = \frac{\sum_i A_i \exp(-E_i/k_B T)}{\sum_i \exp(-E_i/k_B T)}$$

⊗ All thermodynamic properties derivable from Q

Grand Canonical Ensemble

⊗ Specifications: μ, T (V specified for simulation)

⊗ N, E are variable - probability of N and E_i :

$$P_i(N; \mu, V, T) = \frac{\exp(-E_i(N, V)/k_B T) \exp(N\mu/k_B T)}{\Xi}$$

⊗ Grand partition function

$$\Xi(\mu, V, T) = \sum_{N=1}^{\infty} \sum_i \exp(-E_i/k_B T) \exp(N\mu/k_B T)$$

⊗ Averaging

$$\langle A \rangle = \sum_{i, N} A_i(N) P_{i, N} = \frac{\sum_{i, N} A_i(N) \exp(-E_i/k_B T) \exp(\mu N/k_B T)}{\Xi}$$

Classical Statistical Mechanics

- ⊗ Only for quantum systems is coupling between momenta and positions important for energy
- ⊗ Commutator between K & $U \sim h \sim 10^{-34} \text{ J*s} \ll k_B T \sim 10^{-21} \text{ J}$
- ⊗ “Particle in a box” gives momentum part of partition function - translational part
- ⊗ $Q = Q_{\text{trans}} [K(\mathbf{p}^N)] Q_{\text{config}} [U(\mathbf{r}^N)]$

$$Q_{\text{classical}} = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp\{-\beta U(\mathbf{r}^N)\}$$

Molecular Simulations

⊗ Idea: use detailed models of interatomic interactions to derive macroscopic properties

⊗ Components

- ▢ Sample configuration space

- ▢ Measure properties

- ▢ Limitation: only small systems, short times
(be careful of statistics!)

Monte Carlo Simulations

- ⊗ Sample configurations according to Boltzmann distribution of energies (+ V for NPT, N for μVT)
- ⊗ Metropolis method: satisfy detailed balance

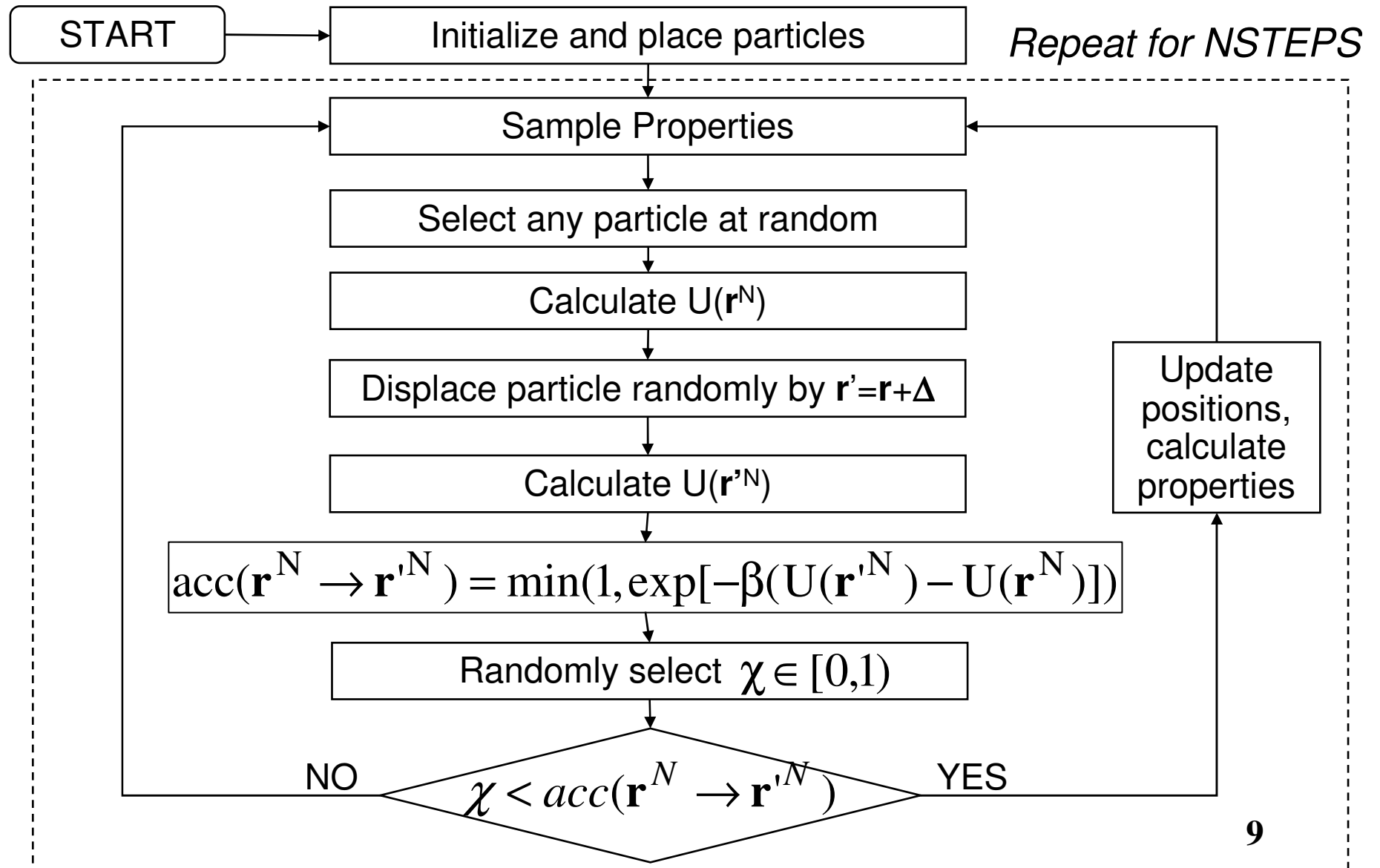
$$N(o)\pi(o \rightarrow n) = N(n)\pi(n \rightarrow o)$$

- ⊗ Make moves randomly and acceptance probs =
$$\frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)} = \frac{\exp(-\beta U(\mathbf{r}_n))}{\exp(-\beta U(\mathbf{r}_o))} = \exp(-\beta[U(\mathbf{r}_n) - U(\mathbf{r}_o)])$$

- ⊗ One way to satisfy: Metropolis

$$\text{acc}(o \rightarrow n) = \begin{cases} \exp(-\beta\Delta U) & \text{if } \Delta U > 0 \\ 1 & \text{if } \Delta U \leq 0 \end{cases}$$

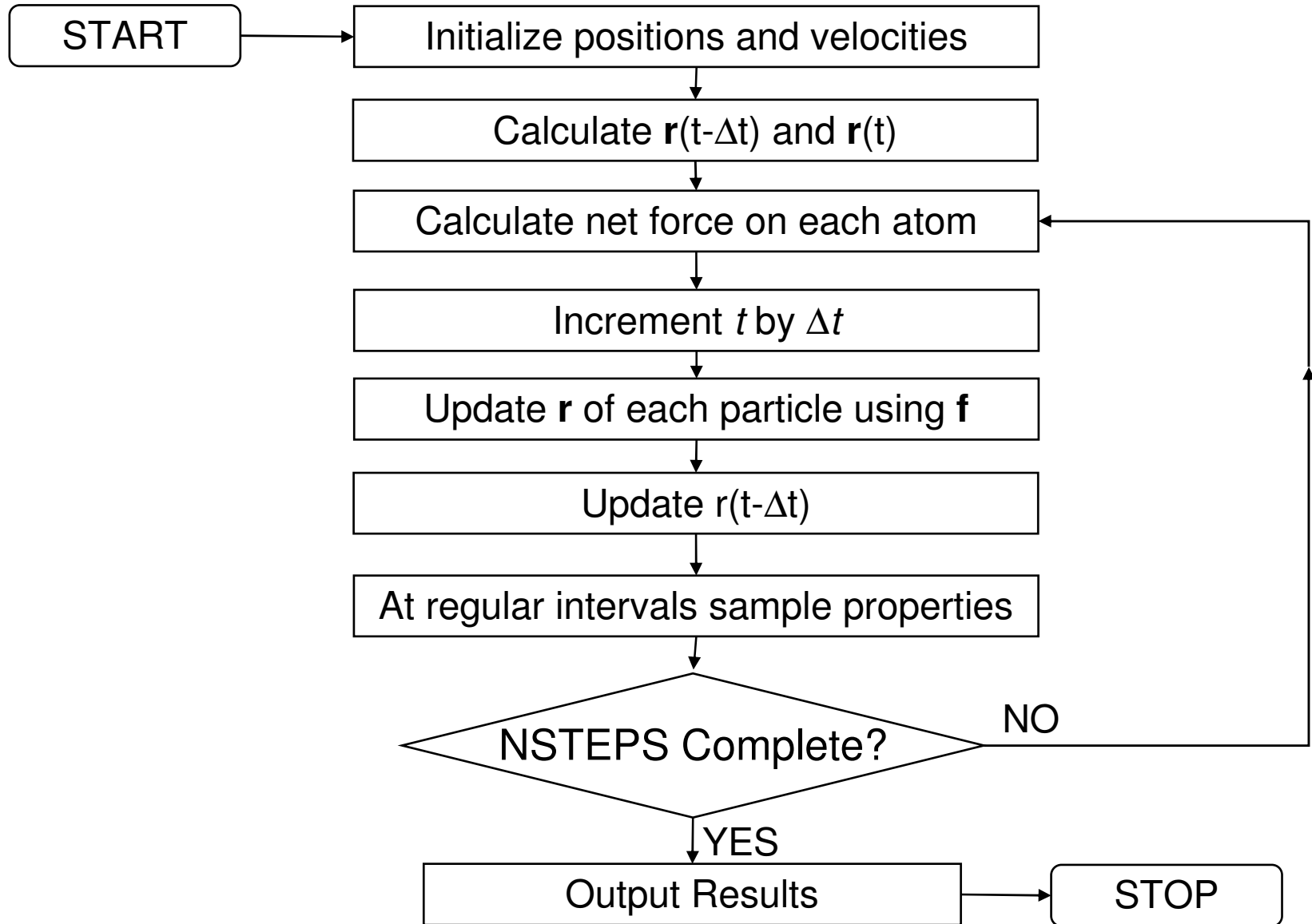
How does MC really work?



Molecular Dynamics Simulation

- ⊗ We have classical potential functions -
Let's try integrating equations of motion!
- ⊗ Like experiments - mix and see what happens
- ⊗ Must set up (initialize) correctly (velocities match average kinetic energy)
- ⊗ Must ensure that equilibrium reached
- ⊗ Must time-average observables [= $f(p,q)$]

MD Algorithm



Integrating Equations of Motion

- ⊗ Need accurate integration for $\sim 3N$ coordinates
- ⊗ Balance computational speed, numerical accuracy, and conserving energy
- ⊗ Standard method: Verlet algorithm

$$r(t + \Delta t) \approx 2r(t) - r(t - \Delta t) + \frac{f(t)}{m}(\Delta t)^2 \quad v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}$$

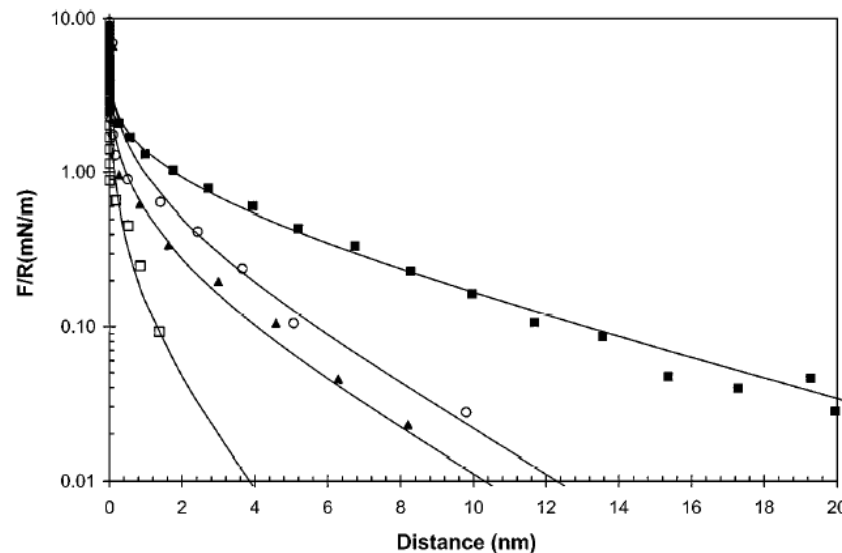
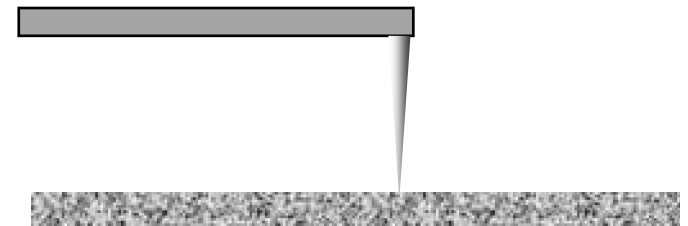
- ⊗ Variants increase accuracy, esp. of velocity
- ⊗ More efficient numerical schemes dangerous (energy not conserved!)

Revisiting Potential Functions

⊗ Where do functions and parameters come from?

☰ Direct measurement

- Atomic Force Microscopy
- Surface Force Apparatus (mostly colloidal and modified surfaces)



Calculation of Potentials

$$\mathcal{H} = \sum p_i^2 / 2m_i + \sum p_n^2 / 2m_n + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|\mathbf{r}_{ij}|} + \frac{1}{2} \sum_{nn'} \frac{e^2}{|\mathbf{r}_{nn'}|} - \sum_{in} \frac{Z_i e^2}{|\mathbf{r}_{in}|}$$

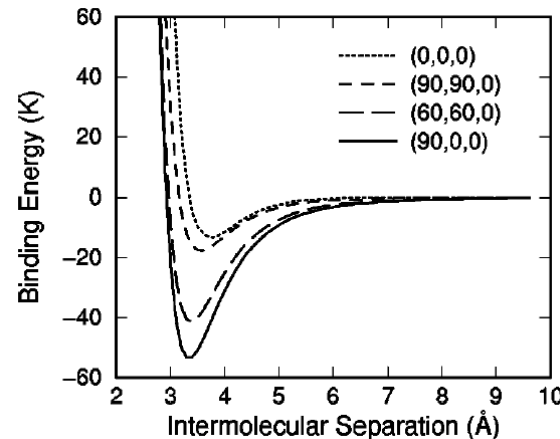
⊗ Mass (nuclei) \gg mass(electrons), so make Born-Oppenheimer Approximation

$$\mathcal{H}^{\text{nuc}} = \sum \left[p_i^2 / 2m_i + V(\mathbf{r}_i) \right] \quad \mathcal{H}^{\text{el}} \Phi(\mathbf{r}_{\text{el}}; \mathbf{r}_i) = V(\mathbf{r}_i) \Phi(\mathbf{r}_{\text{el}}; \mathbf{r}_i)$$

$$\mathcal{H}^{\text{el}} = \sum p_n^2 / 2m + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|\mathbf{r}_{ij}|} + \frac{1}{2} \sum_{nn'} \frac{e^2}{|\mathbf{r}_{nn'}|} - \sum_{in} \frac{Z_i e^2}{|\mathbf{r}_{in}|}$$

H₂-H₂ interactions
from *ab initio* calcs.

P. Diep and J.K.
Johnson, *J. Chem.*
Phys. **2000** 112:4465.



Bulk properties \rightarrow potential function

⊗ Less direct, but still effective, methods for $u(r)$

- ▮ X-ray, neutron, molecular beam scattering - $g(r)$
- ▮ Spectroscopy (vibrational) of associated molecules
- ▮ Second virial coefficient (temperature dependence)
- ▮ Solid-state properties (e.g. lattice parameters)

⊗ Yet less direct methods

- ▮ Comparison/fitting of predictions of simulations / theories using classical potentials (vapor-liquid coexistence, equation of state)
- ▮ Phase change enthalpies, heat capacities, other thermodynamic properties (simulation in between?)

Properties to Measure

⊗ Thermodynamic (depend on specifications)

- ▮ $\langle N \rangle$, $\langle T \rangle$, $\langle E \rangle$, $\langle V \rangle$, $\langle P \rangle$, $\langle C_V \rangle$

- from instantaneous configurations

- ▮ P from virial (depends on forces between particles)

- ▮ C_V from fluctuations - $\langle E^2 \rangle - \langle E \rangle^2$

⊗ Thermodynamic free energy parameters

- ▮ Cannot measure directly

- ▮ Grand canonical simulations - equate to ideal gas (μ)

⊗ Structural properties

- ▮ Radial distribution function (RDF)

- ▮ Averages of configurational properties from RDF

Dynamic Properties

⊗ Only directly available from MD

⊗ Einstein relations based on mean-square change in property

$$2t\gamma = \langle (A(t) - A(0))^2 \rangle$$

⊗ Autocorrelation function integration

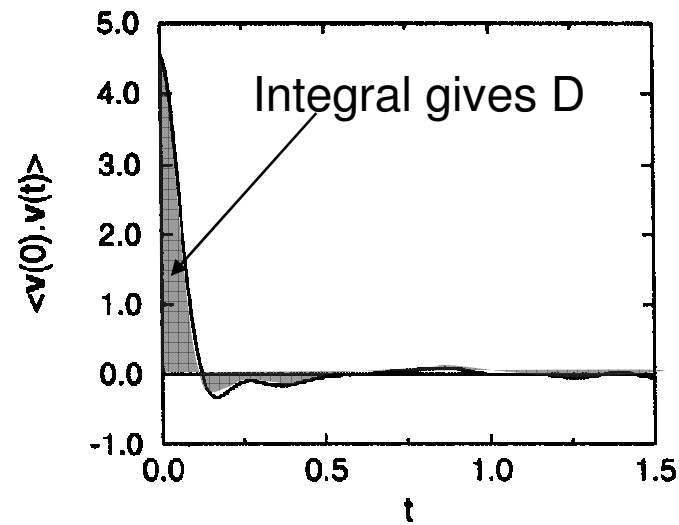
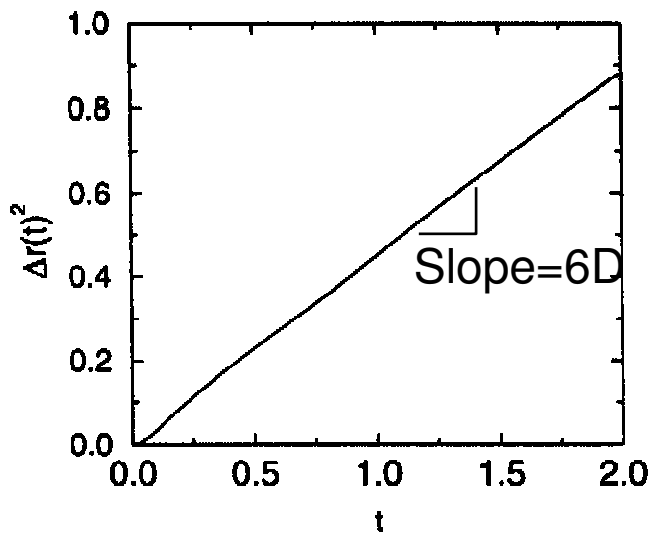
$$\gamma = \int_0^\infty dt \langle \dot{A}(t) \dot{A}(0) \rangle$$

⊗ Statistics

- ▮ Closely spaced points are artificially correlated
- ▮ Lump together data to minimize artificial correlation
- ▮ Increase size of lumping until statistics constant

MD Case Study 5: Diffusion

- ⊗ Dynamic property: diffusion
- ⊗ Measure mean-square displacement and velocity autocorrelation function



- ⊗ Estimate D at various t - look for plateau

Speeding up Calculations

- ⊗ Periodic boundaries
approximate large system
- ⊗ Potential truncation speeds
potential & force calculations

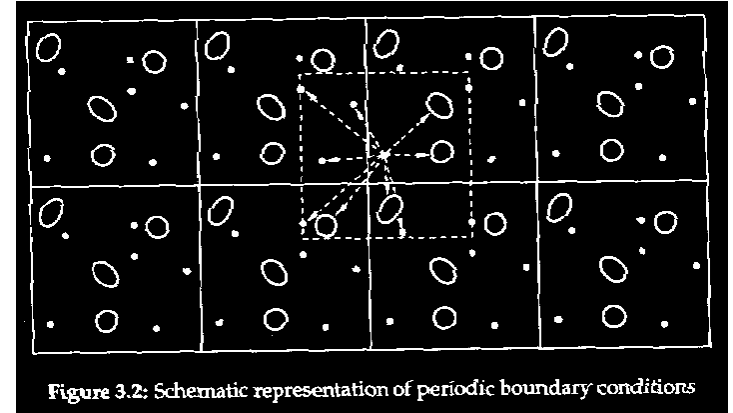


Figure 3.2: Schematic representation of periodic boundary conditions

- ⊗ Approximate corrections for truncation

$$u_{\text{tail}} = (1/2) \int_{r_c}^{\infty} dr 4\pi r^2 \rho(r) u(r) = \frac{8}{3} \pi \rho \epsilon \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right]$$

- ⊗ Carefully sample internal degrees of freedom by
MC (will talk about MD with constraints later)
- ⊗ MC most efficient when acceptance $\sim 20\%$
- ⊗ MD time step chosen to keep stable