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: $\mathcal{F} = C - \mathcal{P} + 2 = 2$

- Microcanonical ensemble: $E$ and $\rho$ specified
- Consider all systems with $N, V, E$ same
- For many-body system, many states consistent with specifications, number = degeneracy = $\Omega$
- $\Omega$ 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~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: $\mu, T$ ($V$ 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 $K$ & $U \sim \hbar \sim 10^{-34}$ J*s $<< k_B T \sim 10^{-21}$ J
- “Particle in a box” gives momentum part of partition function - translational part
- $Q=Q_{\text{trans}}[K(p^N)] Q_{\text{config}}[U(r^N)]$

$$Q_{\text{classical}} = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp\{- \beta U(\mathbf{r}^N)\}$$
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 $\mu$VT)
- Metropolis method: satisfy detailed balance
  
  \[ N(o)\pi(o \rightarrow n) = N(n)\pi(n \rightarrow o) \]

- Make moves randomly and acceptance probs = 

  \[
  \frac{\text{acc}(o \rightarrow n)}{\text{acc}(n \rightarrow o)} = \frac{N(n)}{N(o)} = \frac{\exp(-\beta U(r_n))}{\exp(-\beta U(r_o))} = \exp(-\beta[U(r_n) - U(r_o)])
  \]

- 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?

1. **Initialize and place particles**
2. **Sample Properties**
   - Select any particle at random
   - Calculate \( U(r^N) \)
   - Displace particle randomly by \( r' = r + \Delta \)
   - Calculate \( U(r'^N) \)
   - \[
   \text{acc}(r^N \rightarrow r'^N) = \min(1, \exp[-\beta(U(r'^N) - U(r^N))])
   \]
   - Randomly select \( \chi \in [0,1) \)
   - If \( \chi < \text{acc}(r^N \rightarrow r'^N) \), then YES; otherwise, NO
3. **Update positions, calculate properties**
4. **Repeat for NSTEPS**
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

START

Initialize positions and velocities

Calculate \( r(t-\Delta t) \) and \( r(t) \)

Calculate net force on each atom

Increment \( t \) by \( \Delta t \)

Update \( r \) of each particle using \( f \)

Update \( r(t-\Delta t) \)

At regular intervals sample properties

NSTEPS Complete? NO

YES

Output Results

STOP
Integrating Equations of Motion

- Need accurate integration for ~3N coordinates
- Balance computational speed, numerical accuracy, and conserving energy
- Standard method: Verlet algorithm
  \[
  r(t + \Delta t) \approx 2r(t) - r(t - \Delta t) + \frac{f(t)}{m} (\Delta t)^2
  \]
  \[
  v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}
  \]
- 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

\[ \mathcal{H} = \sum p_i^2 / 2m_i + \sum p_n^2 / 2m_n + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|r_{ij}|} + \frac{1}{2} \sum_{nn'} \frac{e^2}{|r_{nn'}|} - \sum \frac{Z_i e^2}{|r_{in}|} \]

- Mass (nuclei) >> mass(electrons), so make Born-Oppenheimer Approximation

\[ \mathcal{H}^\text{nuc} = \sum \left[ p_i^2 / 2m_i + V(r_i) \right] \quad \mathcal{H}^\text{el} \Phi(r_{el}; r_i) = V(r_i) \Phi(r_{el}; r_i) \]

\[ \mathcal{H}^\text{el} = \sum p_n^2 / 2m + \frac{1}{2} \sum_{ij} \frac{Z_i Z_j e^2}{|r_{ij}|} + \frac{1}{2} \sum_{nn'} \frac{e^2}{|r_{nn'}|} - \sum \frac{Z_i e^2}{|r_{in}|} \]

\text{H}_2-\text{H}_2 \text{ interactions from } \text{ab initio} \text{ calcs.}

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)**
  - \(<N>, \langle T \rangle, \langle E \rangle, \langle V \rangle, \langle P \rangle, \langle C_V \rangle\)
    - from instantaneous configurations
  - \(P\) from virial (depends on forces between particles)
  - \(C_V\) from fluctuations - \(<E^2>-<E>^2\)

- **Thermodynamic free energy parameters**
  - Cannot measure directly
  - Grand canonical simulations - equate to ideal gas (\(\mu\))

- **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
  \[ 2t\gamma = \left\langle (A(t) - A(0))^2 \right\rangle \]
- Autocorrelation function integration
  \[ \gamma = \int_0^\infty dt \left\langle \dot{A}(t) \dot{A}(0) \right\rangle \]
- 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
- Approximate corrections for truncation

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

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