Statistical Mechanics

Molecular Dynamics Simulation

Statistical Mechanics

- Systems with many degrees of freedom
- Classical: dof commute
- Huge phase space, e.g. $3\times3\times10^{24}\approx 10^{25}$
- Interested on time averages
- Also

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T} \int_0^T A(t)\,dt$$

Law of large numbers

- Instantaneous measurements would be very close to the time average of the quantity due to the Law of large numbers
  - Quantity is composed of N uncorrelated contributions
  - Fluctuations are of order $1/\sqrt{N}$
- Typical macroscopic physical quantities
  - N ~10^{24}
  - Fluctuations ~10^{-12} if we neglect correlations
  - If correlations extend over ~100 particles
  - Uncorrelated contribution is ~$10^{24}/10^{2}=10^{22}$

MD simulations

- Simulation time is of the order 10^{-9}-10^{-6} s
- Far below time in which most measuring devices sample physical quantities
- Results representative only if:
  - Spatial correlations extend over ranges smaller than the system size
  - Correlation time of the system is smaller than the simulation time

Ensembles

- Constant Energy: Microcanonical
- Constant Temperature: Canonical
- Other ensembles: grand canonical, …

Postulate: Ergodicity

- All states accesible to the system and having a prescribed energy, volume and number of particles are equally likely to be visited in the course of time $\bar{A}$ A
- Identification of the time average $\langle A \rangle$ of the physical quantity with a uniform average

$$\langle A \rangle = \frac{\sum_{\{X|E\}} A(X)}{\sum_{\{X|E\}}} = \frac{\sum_X A(x)\delta\left[H(X)-E\right]}{\sum_X \delta\left[H(X)-E\right]} = \bar{A}$$

Microcanonical

- Constant Energy
- Number of states with energy E is given by

$$\Omega(N,V,E) = \frac{1}{N!}\sum_{X}\delta[H(X)-E]$$

- The entropy

$$S(N,V,E) = k_B \ln\Omega(N,V,E)$$

Canonical

- Constant temperature $\beta = \frac{1}{k_B T}$
- Partition function

$$Z(N,V,T) = \frac{1}{N!} \sum_X \exp\left[-\beta H(X)\right]$$

- Free energy

$$F(N,V,T) = -k_B T \log Z(N,V,T)$$

Canonical

$$\langle A \rangle_{(N,V,T)} = \frac{1}{N!Z} \sum_{X} A(k) \exp\left[-\beta H(X)\right]$$

- In equilibrium F is minumum

Averages in Simulations

- Necessary for Molecular Dynamics and Monte Carlo
- Standard deviation
- Time correlations
- Data blocking

Data blocking

- Values recorded in a file
- Data sequence is chopped into a number of equal-size blocks
- Blocks have to be larger than the correlation time
- We calculate averages of A within block
- For blocks of size m, the jth block average is:

$$\overline{A}_j = \frac{1}{m} \sum_{k=mj+1}^{m(j+1)} A_k$$