Statistical Thermodynamics and Monte-Carlo

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Preliminaries

Learning Goals

- From Micro to Macro
- Statistical Mechanics (Statistical Thermodynamics)
- Monte-Carlo Method
- Polymers
  - Lattice Model and Random Walk

References

- P. W. Atkins, *Physical Chemistry*.
- A. R. Leach, *Molecular Modelling: Principles and Applications*.
- I. Beichl, F. Sullivan, *The Metropolis algorithm*, Comp. Sci. Eng. 2000, v. 2, N 1, p. 65-69 (The Ten 10 Algorithms).

On-line Resources

- D. Kofke, Molecular Simulation, www.cheme.buffalo.edu/courses/ce530/Text/text.html
  - A survey of statistical mechanics as it pertains to molecular simulation
  - Markov processes
  - Monte Carlo simulation
  - Simple biasing methods

From Micro to Macro

Macro Properties

- Pressure, Diffusion coefficient, Average energy, Temperature
  - Atomic effects are smeared.

Micro Properties

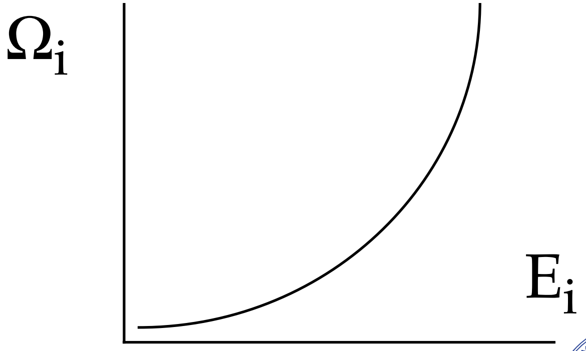
Classical Mechanics:

- Positions and velocities/ momenta of the atoms

Quantum Mechanics / Quantum Chemistry:

- Energy is quantized

- Energies of system states and their degeneracies $\{E_i, \Omega_i\}$
  - Energies and a number of eigenstates depend on volume.
  - For a system with a large number of particles Ω_i is huge and the energy levels are very close.



From Micro to Macro

Two Approaches

Molecular Dynamics - Time average:

- Classical Atomic Force, Classical Particle Mechanics - Newton mechanics
- Integrating transient Schrödinger equation

Statistical Mechanics - Ensemble average:

- No time, net effect of many particles
- Introduces temperature and entropy.
- Classical and quantum statistics
  - Classical statistics leads to paradoxes: need quantum statistics to solve them.
  - It is easier to derive statistical mechanics from quantum statistics.
  - In practice: quasi-classical approach.
- Gives rise to Monte-Carlo method.

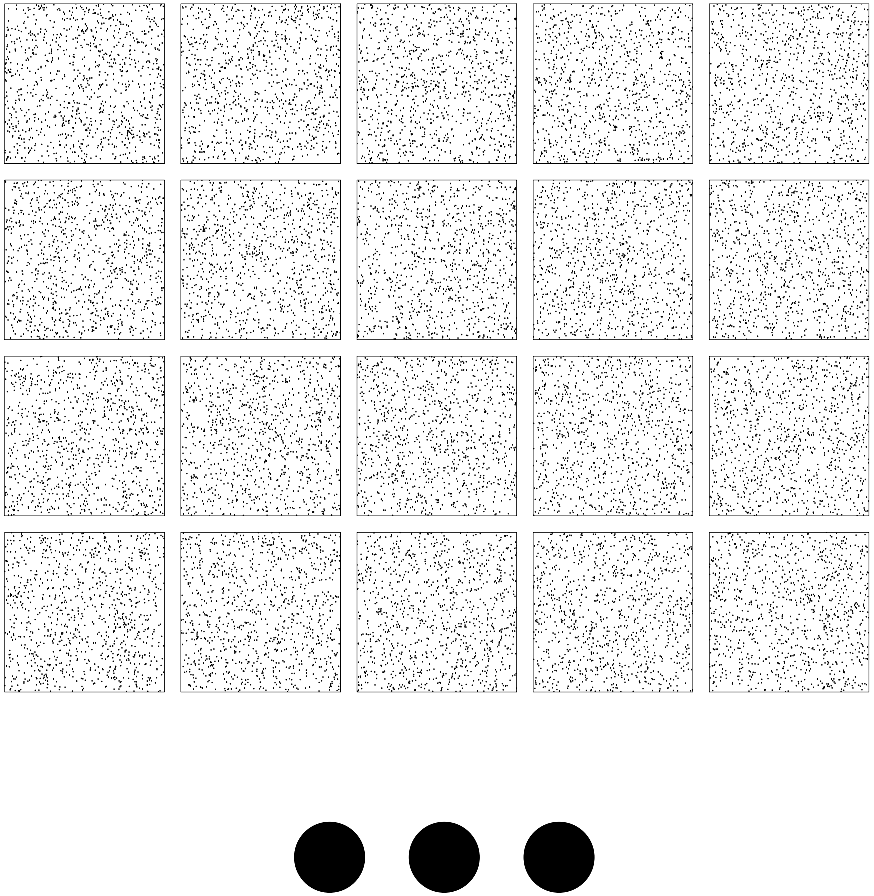
Overview

- Ensemble
- Microcanonical Ensemble
  - Basic Postulate
  - Ergodic Hypothesis
  - Non-ergodic system
- Canonical Ensemble
  - Definition
  - Temperature
  - Boltzmann Distribution
  - Partition Function
  - Classical Statistics
- Other Ensembles
- Classical vs. Quantum
- Closed-Form Solutions

Ensemble

- Macro properties are the same.
- Micro properties are different.
- Each micro state has some probability.
- Distribution function describes everything.
- Ensemble average for property D (P is the probability)
  - quantum $\langle D\rangle = \sum_i D_i P_i$
  - classical:

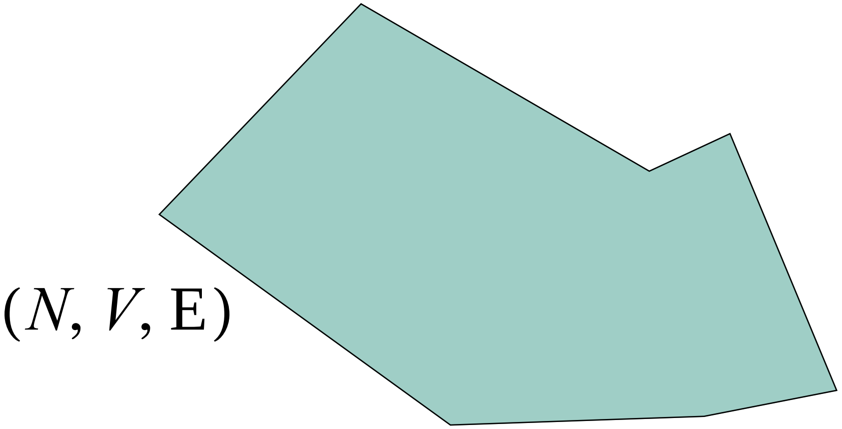
$$\langle D\rangle = \int P(\boldsymbol{p}^N, \boldsymbol{r}^N) D(\boldsymbol{p}^N, \boldsymbol{r}^N) d\boldsymbol{p}^N d\boldsymbol{r}^N$$



Microcanonical Ensemble

Basic Postulate

- Energy, volume and a number of particles are constant.



Quantum statistics

- $\Omega(N, V, E)$: Number of eigenstates of energy E for system with N particles in volume V.
- **Basic Postulate**: System with fixed (N, V, E) likely to be in any state.
- Probability

$$P_i(N, V, E) = \frac{1}{\Omega(N, V, E)}$$

- Collection of all such states is the **Microcanonical Ensemble**.

Microcanonical Ensemble

Ergodic Hypothesis

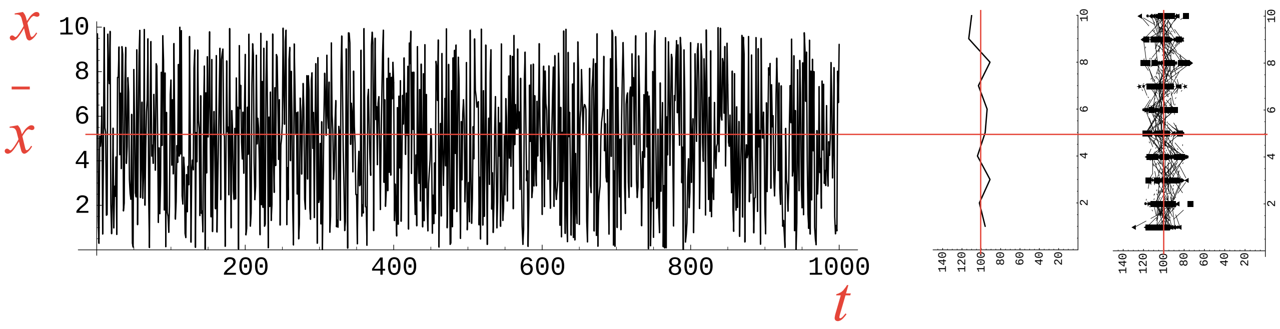
- Time average of N, V, E:

$$\overline{D} = \lim_{t \to \infty} \frac{1}{t} \int_0^t D(t')dt'.$$

- Initial conditions:

$$D(t') = D[\boldsymbol{r}^N(t'), \boldsymbol{p}^N(t'), \boldsymbol{r}_0^N, \boldsymbol{p}_0^N]$$

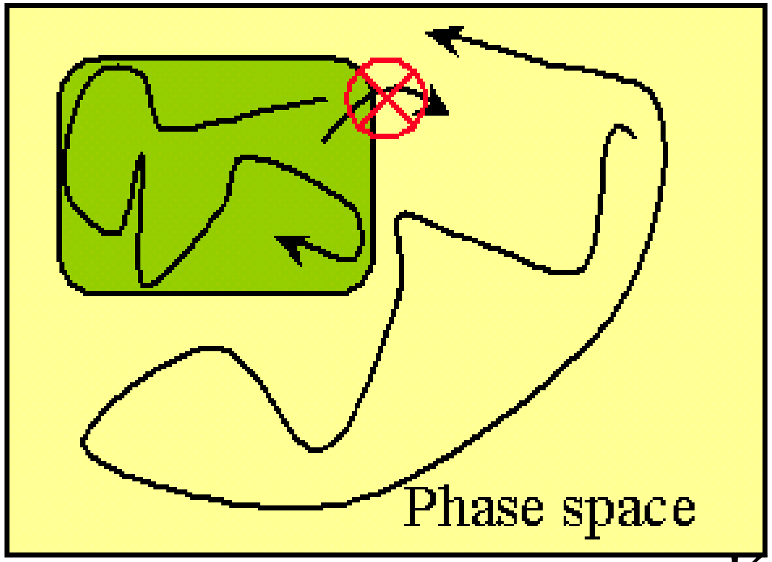
- Time averages should not depend on **initial conditions**.
- Ensemble average is equal to the time average $\overline{D} = \langle D \rangle$
- Time average: Molecular Dynamics
- Ensemble average: Monte-Carlo



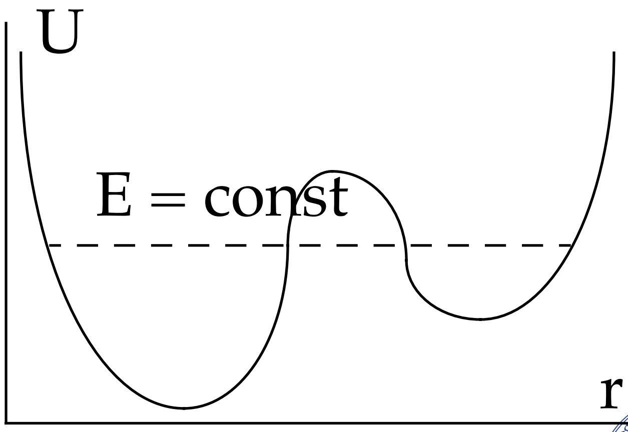
Time Averaging

Non-ergodic System

- If a time average does not give complete representation of full ensemble, system is non-ergodic.
  - Truly nonergodic: no way there from here.
  - Practically nonergodic: very hard to find route from here to there.



Kofka

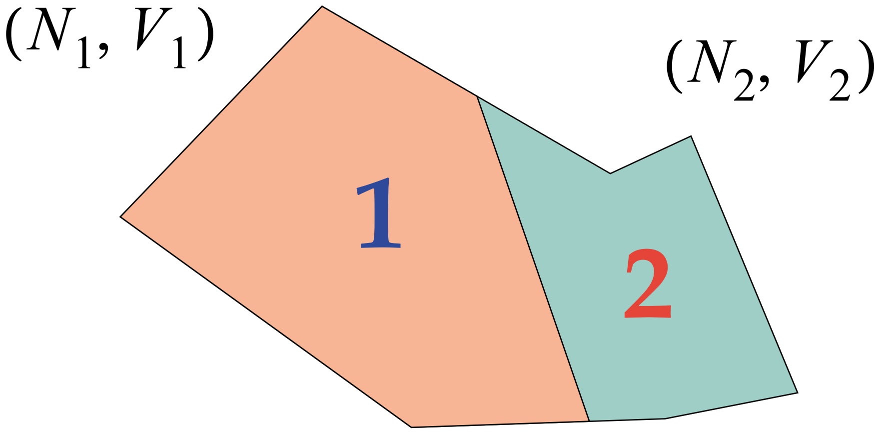


Canonical Ensemble

Definition

- Volume and a number of particles are constant.
- Systems within the ensemble can exchange energy, but the total energy is constant.

$$E_1 + E_2 = \text{const}$$



- After Bolzmann: take $L \to \infty$ similar systems.
- After Gibbs: put attention on a particular system, all others are surrounding.
- The most probable distribution function.
- Temperature is introduced during the treatment.
- At the end we can say, that temperature, volume and a number of particles are constant: $T, N, V = const.$

Canonical Ensemble

Temperature

- Energy E is **extensive** property: $E = E_1 + E_2$ over subsystems.
  - The system interaction is neglected: energy is additive.
- Number of states is multiplicative:
  $\Omega(E) = \Omega_1(E_1) \times \Omega_2(E - E_1)$
  - Better use $\ln[\Omega(E)]$.

$$\ln[\Omega(E_1, E - E_1)] =$$

$$\ln[\Omega_1(E_1)] + \ln[\Omega_2(E - E_1)]$$

- Most likely distribution of energy:

$$\left(\frac{\partial \ln \Omega(E_1, E - E_1)}{\partial E_1}\right)_{N, V, E} = 0$$

- **Temperature:**

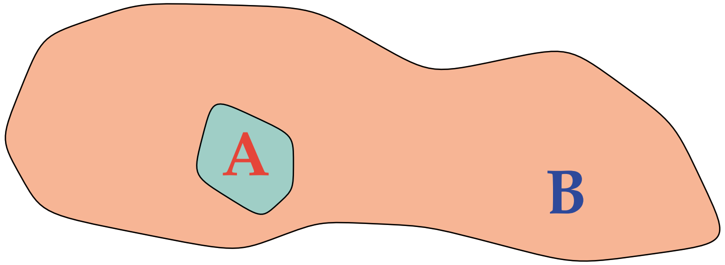
$$\left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{N, V} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{N, V} =$$

$$\beta = \frac{1}{k_B T}$$

- **Entropy:**
  $S(N, V, E) = k_B \ln \Omega(N, V, E)$

Canonical Ensemble

Boltzmann Distribution



- Small **A** in contact with large heat bath **B:** $E = E_A + E_B$.
- **A** in state *i* with energy E_i (no degeneracy). **Probability** is

defined by $P_i = \dfrac{\Omega_B(E - E_i)}{\sum_j \Omega_B(E - E_j)}$

- **Taylor** expansion about $E_i = 0$

$$\ln[\Omega_B(E - E_i)] = \ln[\Omega_B(E)] - E_i\left(\frac{\partial \ln \Omega_B(E)}{\partial E}\right)$$

- Substitute *T* and insert into probability

$$P_i = \frac{\exp[-E_i / k_B T]}{\sum_j \exp[-E_j / k_B T]}$$

Canonical Ensemble

Partition Function

- $Q = \sum_j \exp[-\mathrm{E}_j / k_B T]$
- Average energy

$$\langle E \rangle = \sum_i \mathrm{E}_i P_i = \frac{\sum_i E_i \exp[-\mathrm{E}_i / k_B T]}{\sum_i \exp[-\mathrm{E}_i / k_B T]} = \left(-\frac{\partial \ln[Q]}{\partial (1/k_B T)} \right)$$

- **Helmholtz Energy**

$$\mathrm{E} = \frac{\partial (\mathrm{F}/T)}{\partial (1/T)}$$

- Then

$$F = -k_B T \ln[Q]$$

- $F(T, V)$ is a potential function

and from it one can determine all other equilibria properties.

Caution

- Energy is given up to an arbitrary constant.
- It is impossible to determine a numerical value for the absolute energy, and Helmholtz energy.
- It is better

$$Q = \sum_j \exp[-(\mathrm{E}_j - \mathrm{E}_o)/k_B T]$$

$$F = \mathrm{E}_o - k_B T \ln[Q]$$

Canonical Ensemble

Classical Statistics

- Energy $E(\boldsymbol{p}, \boldsymbol{r}) = \sum_{i}^{N} \frac{p_i^2}{2m_i} + \mathrm{U}(\boldsymbol{r}^N)$
- Partition function becomes an integral

$$Q = \frac{1}{h^{3N}N!}\int \exp\{-\beta E\}\, d\boldsymbol{p}^N d\boldsymbol{r}^N .$$

- h is the least action. h^{3N} makes Z dimensionless.
- Particles are indistinguishable, hence $N!$.
- Average (Starting point for Monte-Carlo)

$$\langle D \rangle = \frac{\int \exp\{-\beta E\} D(\boldsymbol{p}^N, \boldsymbol{r}^N)\, d\boldsymbol{p}^N d\boldsymbol{r}^N}{\int \exp\{-\beta E\}\, d\boldsymbol{p}^N d\boldsymbol{r}^N}$$

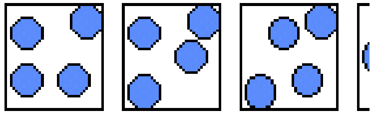
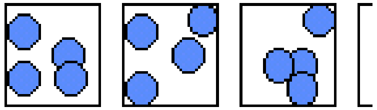
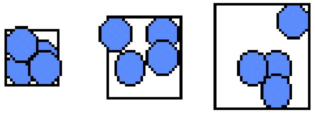
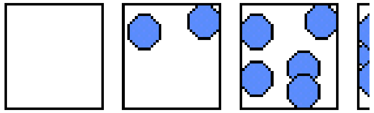
- Integral over kinetic energy can be taken analytically

$$Q = \frac{1}{N!}\left(\frac{2\pi m k T}{h^2}\right)^{3N} \int \exp\{-\beta U\}\, d\boldsymbol{r}^N$$

- Configuration integral
- Average becomes
- $\langle D \rangle = \dfrac{\int \exp\{-\beta U\} D(\boldsymbol{r}^N)\, d\boldsymbol{r}^N}{\int \exp\{-\beta U\}\, d\boldsymbol{r}^N}$

Other Ensembles, I

- From Kofka

Name	All states of:	Probability distribution	Schematic
Microcanonical (EVN)	given EVN	$\pi_i = \frac{1}{\Omega}$	
Canonical (TVN)	all energies	$\pi(E_i) = \frac{1}{Q} e^{-\beta E_i}$	
Isothermal-isobaric (TPN)	all energies and volumes	$\pi(E_i, V_i) = \frac{1}{\Delta} e^{-\beta(E_i + PV_i)}$	
Grand-canonical (TVμ)	all energies and molecule numbers	$\pi(E_i, N_i) = \frac{1}{\Xi} e^{-\beta(E_i + \mu N_i)}$	

Other Ensembles, II

- From Kofka

Ensemble	Thermodynamic Potential	Partition Function	Bridge Equation
Microcanonical	Entropy, S	$\Omega = \sum 1$	$S/k = \ln \Omega(E,V,N)$
Canonical	Helmholtz, A	$Q = \sum e^{-\beta E_i}$	$-\beta A = \ln Q(T,V,N)$
Isothermal-isobaric	Gibbs, G	$\Delta = \sum e^{-\beta(E_i + PV_i)}$	$-\beta G = \ln \Delta(T,P,N)$
Grand-canonical	Hill, L = –PV	$\Xi = \sum e^{-\beta(E_i + \mu N_i)}$	$\beta PV = \ln \Xi(T,V,\mu)$

Classical vs. Quantum

- Electron - always a quantum particle.
- Transitional movement of molecules - always classical:
  - Enormous number of states (300 K - about 10^{30}).
- Rotational movement of molecules - typically classical.
  - Quantum statistics might required at low temperatures.
- Vibrations - depends on temperature and the wave number.
  - At 300 K classical approach for v< 100 sm^{-1}.

Closed-Form Solutions

- Atomic ideal gas
  - Configuration integral is equal to volume.
- Molecular ideal gas
  - $E_{tot} = E_{transl} + E_{rot} + E_{vib}$
  - Rigid rotator and harmonic oscillator
- Dense gases: estimates for virial coefficients.
- Ideal crystal: Einstein and Debye approximations
  - For a real crystal it is necessary to know the phonon spectra
- A variety of theories for liquids
  - None of them is really successful.

Overview

- Basic Metropolis Algorithm
- Random Sampling
- Importance Sampling
- Markov Chain
- Metropolis Method
- Limits of Metropolis method

Basic Metropolis Algorithm

- Goal is to evaluate

$$\langle D\rangle = \frac{\int \exp\{-\beta[\mathrm{U}(\boldsymbol{r}^N)]\}D(\boldsymbol{r}^N)d\boldsymbol{r}^N}{\int \exp\{-\beta[\mathrm{U}(\boldsymbol{r}^N)]\}d\boldsymbol{r}^N}$$

- For each Monte Carlo cycle:
    - Select particle i at random.
    - Compute particle energy $\mathrm{U}_i(\boldsymbol{r})$.
    - Give particle i random displacement based on the uniform distribution $\boldsymbol{r}_i{}' = \boldsymbol{r}_i + \Delta\boldsymbol{r}$.
    - Compute new energy $\mathrm{U}_i(\boldsymbol{r}')$.
    - Accept transition from $\boldsymbol{r}$ to $\boldsymbol{r}'$ based on probability

$$\mathrm{accept}(\boldsymbol{r} \rightarrow \boldsymbol{r}') = \min(1, \exp[-\beta\{\mathrm{U}_i(\boldsymbol{r}') - \mathrm{U}_i(\boldsymbol{r})\}])\ '$$

$$\beta = 1/k_B T.$$

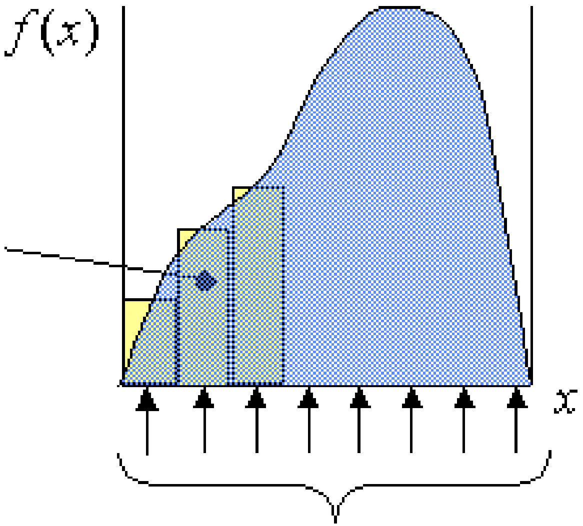
- Estimate is

$$\langle D\rangle \approx \frac{1}{L}\sum_{i=1}^{L} n_i D(\boldsymbol{r}^N{}_i)$$

Monte-Carlo Method

Random Sampling

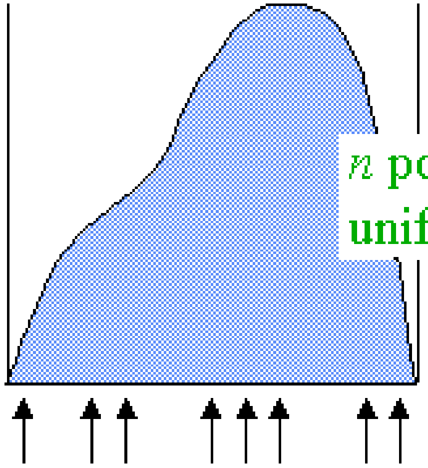
- Evaluating $I = \int_a^b f[x]dx$.
- Methodical approach



n uniformly separated points

- Stochastic approach

from Kofka



n points selected from uniform distribution $\pi(x)$

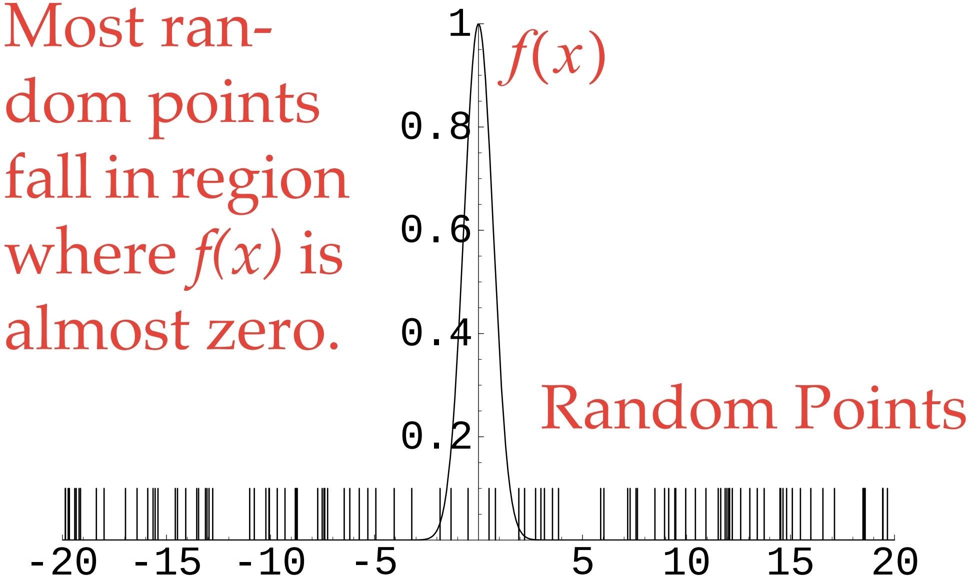
$$I \approx \frac{b-a}{n}\sum_{i=1}^{n} f(x_i)$$

- Error
  - Methodical $\delta I \sim n^{-2/d}$
  - Monte Carlo $\delta I \sim n^{-1/2}$

Monte-Carlo Method

Importance Sampling

Most random points fall in region where $f(x)$ is almost zero.



- $I = \int_a^b f[x]dx\,.$
- $I = (b-a)\langle f[x]\rangle.$
- $I = \int_a^b \frac{f[x]}{w[x]} w(x)dx$, e.g.
- $I = \int_0^1 \frac{f[x(u)]}{w[x(u)]} du\,.$
- $I \approx \frac{1}{L}\sum_{i=1}^{L} \frac{f[x(u_i)]}{w[x(u_i)]}\,.$
- $\sigma_I^2 = \frac{1}{L}[\langle (f/w)^2\rangle - \langle f/w\rangle^2]\,.$

If f/w is constant, variance vanishes

Monte-Carlo Method

Markov Chain

Stochastic process

- Movement through a series of well-defined states in a way that involves some element of randomness.
- For our purposes,“states” are microstates in the governing ensemble.

Markov process

- Stochastic process that has no memory.
- Selection of next state depends only on current state, and not on prior states.
- Process is fully defined by a set of transition probabilities π_{ij}.
- π_{ij} is probability of selecting state *j* next, given that presently in state *i*.
- Transition-probability matrix Π collects all π_{ij}.
- Limiting probability does not depend on the initial distribution $P = P\Pi$.

Metropolis Method

- At limiting distribution, detailed balance or the principle of microscopic reversibility:

$$\mathrm{N}(o)\pi(o \rightarrow n) = \mathrm{N}(n)\pi(n \rightarrow o)$$

- Use any convenient underlying transition matrix but not accept every step.
- Rather accept a step with such a probability to satisfy the detailed balance.
- Metropolis suggested

$$\pi(o \rightarrow n) = \alpha(o \rightarrow n)\mathrm{acc}(o \rightarrow n)$$

  - $\alpha(o \rightarrow n)$ is underlying probability to move (uniform distribution)
  - $\mathrm{acc}(o \rightarrow n)$ is the acceptance probability
- If $\mathrm{N}(n) < \mathrm{N}(o)$ then

$$\mathrm{acc}(o \rightarrow n) = \exp\{-\beta[\mathrm{U}(n) - \mathrm{U}(o)]\}$$

- If $\mathrm{N}(n) > \mathrm{N}(o)$ then

$$\mathrm{acc}(o \rightarrow n) = 1$$

- It is possible to prove that this leads to the detailed balance.

Limits of Metropolis method

- Can not estimate the configuration integral

  $Q_{conf} = \int \exp\{-\beta U\} d\boldsymbol{r}^N$ (or partition function).
- Metropolis algorithm can estimate only

$$\langle D \rangle = \frac{\int \exp\{-\beta[\mathrm{U}(\boldsymbol{r}^N)]\} D(\boldsymbol{r}^N) d\boldsymbol{r}^N}{\int \exp\{-\beta[\mathrm{U}(\boldsymbol{r}^N)]\} d\boldsymbol{r}^N}$$

- Trick $1 = \exp\{-\beta U\}\exp\{\beta U\}$
- Then we can write

$$\frac{V}{Q_{conf}} = \frac{\int \exp\{-\beta U\}\exp\{\beta U\} d\boldsymbol{r}^N}{\int \exp\{-\beta U\} d\boldsymbol{r}^N}$$

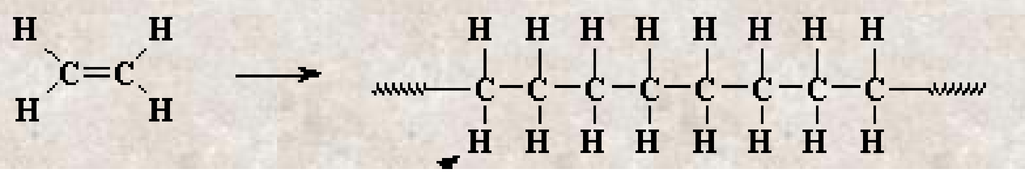
where $D = \exp\{\beta U\}$

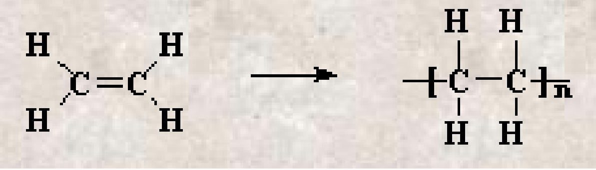
- Does not help: it is necessary to sample high energy regions.
- Special tricks are required to estimate the free energy and entropy.

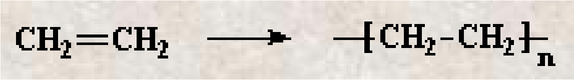
Polymers

Overview

- Monomer, repeat unit and polymer







$CH_2{=}CH_2 \longrightarrow -\!\!\left[CH_2\text{-}CH_2\right]\!\!-_n$

http://www.Psrc.Usm.Edu/macrog/index.htm

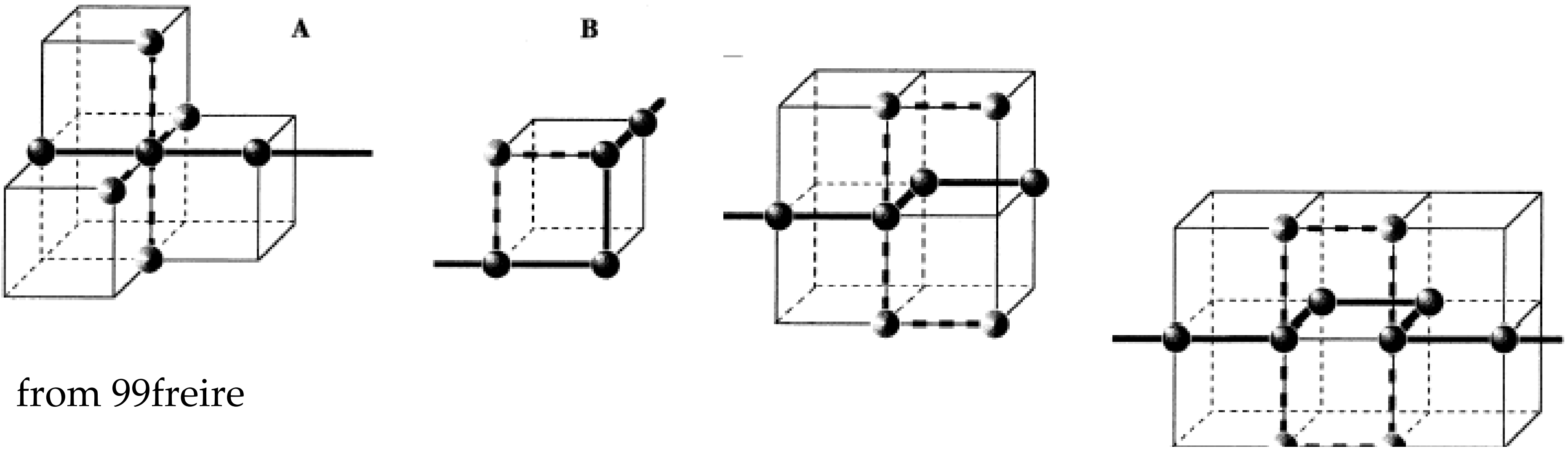
- End-to-end distance $\langle R_n^2\rangle_o$, from statistics nl^2
- Radius of gyration

  $$\langle S\rangle_o^2 = \langle \Sigma_i(\mathbf{r}-\mathbf{r}_o)^2/N\rangle$$
- Backbone chain

- Two extreme case for simulation:
  - dilute solution of a polymer and polymer melt.
- Full atomistic model is a challenge to simulate.

Lattice Model and Random Walk

- Lattices (two and three dimensional), bent and crankshaft



from 99freire

- Random walks
  - On and off lattice
  - Self-cross and self-avoiding
- Demo from Atkins

Summary

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