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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR.865 - 3

WORKSHOP ON
COMPUTATIONAL METHODS IN
MATERIALS SCIENCE AND ENGINEERING

"Monte Carlo Calculations in Materials Science"

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MONTE CARLO CALCULATIONS IN MATERIALS SCIENCE

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OVERVIEW

Lecture I

- Introduction
- Hit-and-Miss Integration
- Importance Sampling - Metropolis MC
- Ensembles
  - canonical
  - microcanonical
  - isobaric-isothermal
  - grand canonical
  - Gibbs
- Free Energy Calculations
  - particle insertion / removal
  - (umbrella sampling
  - thermodynamic integration)

Lecture II

- Finite-Size Corrections
- (Force-Bias MC)
- Configurational-Bias MC

Lecture III Applications

- Self-Assembled Monolayer
- Vapor-Liquid Equilibria
- Confined Fluids
- Conclusions

MOLECULAR DYNAMICS

configurations are sampled following the natural time-evolution by solving Newton's classical equations of motion

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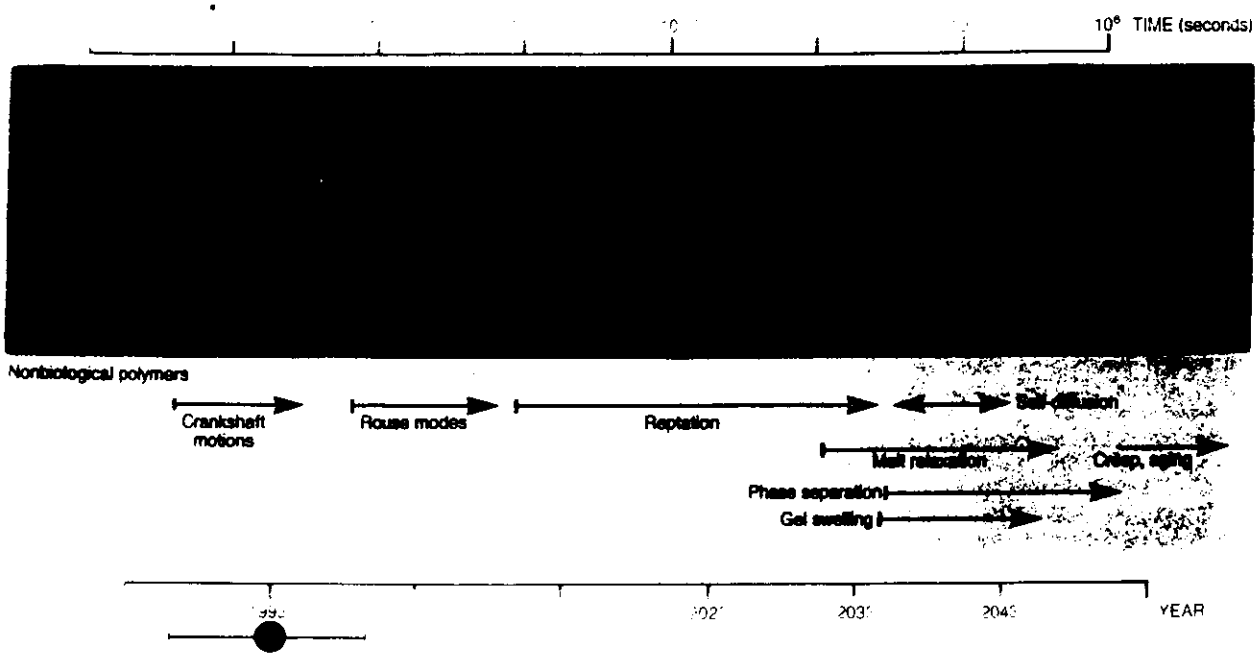
MONTE CARLO

involves the generation of a series of configurations (Markov chain) using RANDOM moves that obey RULES which ensure that CORRECT statistical-mechanical ensemble is sampled

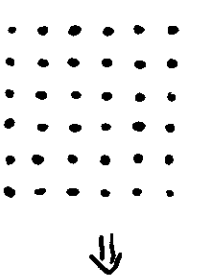
A.P. [illegible] Physics Today 2/93



Time scales for various motions [illegible] nonbiological polymers (blue). The year scale [illegible] process is the accessible to force-field simulation on [illegible] computers assuming [illegible] speed increases at about the rate of [illegible] years and [illegible] breakthroughs. At current capabilities, a given allotment [illegible] few hundred picoseconds for a small protein in a [illegible] to explore a thousand processes that have relaxation [illegible] indicates the error bar below the year scale. **Figure 5**

Advantages of the Monte Carlo method

- unphysical moves (smart moves) to sample different kinds of motion with same computational efficiency
  - reliable mechanical properties



nature : 10^{9} s
MD : 10^{24} s
MC : 10 s

... but unphysical moves are rather difficult to implement for complex fluids (in particular for off-lattice sim.)

- ensembles with fluctuating particle #
  - reliable thermal properties

... but random insertions of complex molecules have a rather low acceptance probability

STAT. MECH. BASICS

- the canonical partition function of a quantum-mechanical system with N accessible states is given by

$$Q = \sum_{n=1}^{N} \exp(-\beta E_n)$$

where $\beta = (k_B T)^{-1}$

- the probability P_i of finding the system in a particular state is

$$P_i = \frac{\exp(-\beta E_i)}{Q}$$

- the characteristic thermodynamic function of the canonical ensemble is the Helmholtz free energy

$$A = -k_B T \ln Q$$

CLASSICAL STAT. MECH.

- the volume of phase space that can be accessed by a classical system consisting of N particles in the canonical ensemble is given by its partition function

$$Q_{class} = C \int d\bar{p}^N \, d\bar{q}^N \exp[-\beta H(\bar{q}^N, \bar{p}^N)]$$

where C is a constant of proportionality which ensures the equality of the quantum-mechanical sum over states (in the classical limit) and the classical partition function;
for a system of N identical atoms

$$C = (h^{DN} N!)^{-1}$$

where D is the dimensionality

- the canonical-ensemble average of an observable X is

$$\langle X \rangle = \frac{\int d\bar{p}^N d\bar{q}^N \, X(\bar{p}^N, \bar{q}^N) \exp[-\beta H(\bar{p}^N, \bar{q}^N)]}{\int d\bar{p}^N d\bar{q}^N \exp[-\beta H(\bar{p}^N, \bar{q}^N)]}$$

- the Hamiltonian can be divided into kinetic and potential energy parts

$$H = K + U$$

- since X is a quadratic function of the momenta, the integration over momenta can be carried out analytically
- to solve the multi-dimensional configuration integral over $\bar{q}^N$ is the main application of the Monte Carlo method

$$Q_c = C \int d\bar{q}^N \exp[-\beta U(\bar{q}^N)]$$

HIT-AND-MISS INTEGRATION

- consider system of N hard disks in a defined area (X, Y)
- construct a configuration by random generation of N x- and y-coordinates
- check for overlap
- calculate properties as average of all allowed configurations

NUMERICAL QUADRATURE

- evaluate the integrand on a mesh of m^{DN} points in configuration space
- take $m = 10$ $\quad D = 2$ $\quad N = 100$

[Is function smooth over distances corresponding to the mesh size ???]

CONFIGURATIONAL PHASE SPACE

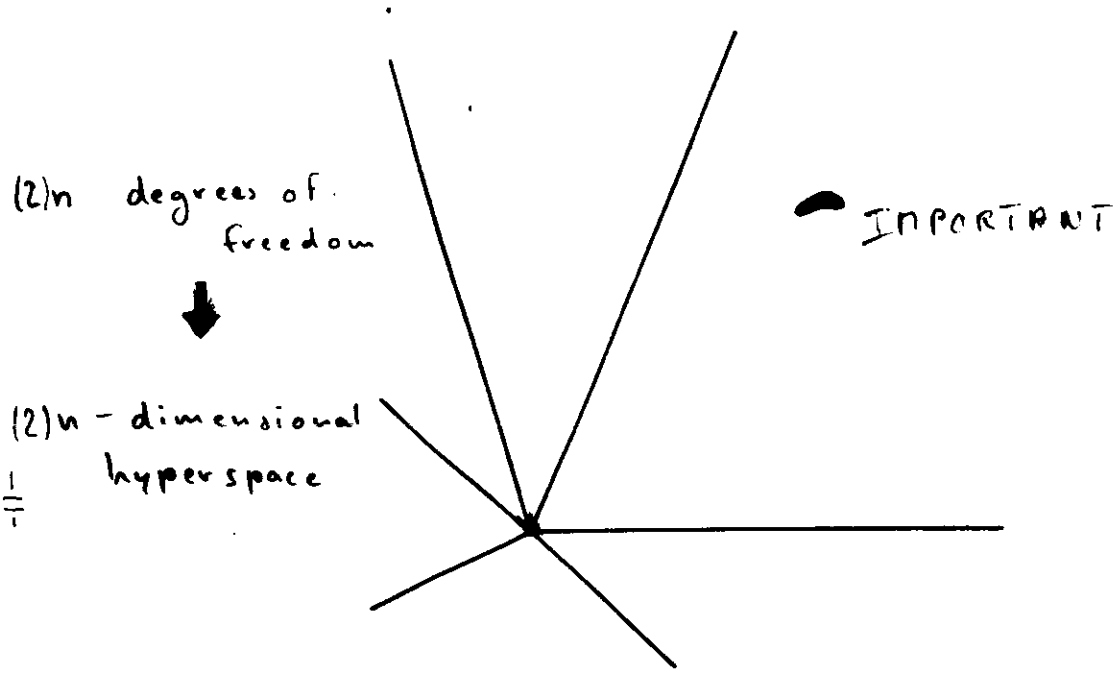


Figure 1: Schematic diagram of configurational hyperspace. At substantial densities only a tiny subvolume is usually of importance to statistical-mechanical integrals, as suggested here.

[Valleau]

METROPOLIS IMPORTANCE SAMPLING

- "instead of choosing configurations randomly, then weighting them with $\exp(-U/kT)$ (their Boltzmann factor), we choose configurations with a probability $\exp(-U/kT)$ and weight them evenly" (Metropolis et al., 1953)

- acceptance rule:

$$\text{random}[0,1] < \exp(-\Delta U/kT)$$

$$\Delta U = U_{new} - U_{old}$$

MARKOV CHAIN

- a Markov chain is a sequence of trials in which the outcome of each trial is one of a set of states (the configurational space) and depends only on the state that immediately precedes it
- two states m and n are linked by a transition probability π_{mn} which is an element of a stochastic matrix Π
- the probability distribution $\bar{p}(t)$ after t steps starting from an arbitrary initial distribution is

$$\bar{p}(t) = \Pi^{t} \bar{p}(0)$$

- there exists a limiting distribution

$$\lim_{t \to \infty} \Pi^{t} \bar{p}(0)$$

- this leads to an eigenvalue equation with an eigenvalue unity (steady-state)

$$\Pi \bar{P} = \bar{P}$$

- if there exists only ONE eigenvalue of unity, there exists only ONE limiting distribution independent of initial state

[non-zero, multi-step transition probability]

- thus the stochastic matrix Π must NOT destroy the limiting distribution once it is reached

MICROSCOPIC REVERSIBILITY
"detailed balance"

- this much stronger condition implies

$$\rho_m \pi_{mn} = \rho_n \pi_{nm}$$

- in a Monte Carlo simulation a move consists of two parts:
  - perform trial move
  - accept / reject trial move

$$\pi_{mn} = \alpha_{mn} P_{mn}$$

where α is the underlying matrix of the Markov chain and P is the acceptance probability

- if α is symmetric, then

$$\rho_m P_{mn} = \rho_n P_{nm}$$

or

$$P_{mn} / P_{nm} = \rho_n / \rho_m$$

- in the canonical ensemble the limiting probability ρ_m is given by

$$\rho_m = \frac{\exp(-\beta U_m)}{Q_c}$$

- hence

$$\rho_n / \rho_m = \exp[-\beta (U_n - U_m)]$$

- the Metropolis acceptance probability is an asymmetrical one

$$\left.\begin{aligned} P_{mn} &= \rho_n / \rho_m \\ P_{nm} &= 1 \end{aligned}\right\} \quad \text{for } \rho_n < \rho_m$$

- to summarize

$$\pi_{mn} = \alpha_{mn} \quad \text{for } \rho_n \geq \rho_m$$

$$\pi_{mn} = \alpha_{mn} (\rho_n / \rho_m) \quad \text{for } \rho_n < \rho_m$$

$$\pi_{mm} = 1 - \sum_{n \neq m} \pi_{mn}$$

TYPES OF TRIAL MOVES

- in the canonical ensemble we can make use of two different classes of trial moves
  - Glauber-like excitations which change a single-site property
  - Kawasaki-like excitations which are caused by a two-site exchange of a single site property
- combinations of different moves of the same class or of different classes in one simulation are allowed, but to guarantee the symmetry of the underlying Markov chain the choice of move at a particular instance during has to be a stochastic (random) choice

Monte Carlo for complex fluids consisting of molecules with many different degrees of freedom has to make use of different types of moves:

- translations
- rotations
- <u>conformational changes</u>
- <u>particle (or identity) swaps</u>

TRANSLATIONAL MOVE

1.) select particle at <u>random</u>

2.) select COM ✓ coordinate at random

3.) displace coordinate using

$$x_i \rightarrow x_i + \delta x_{max} (2R - 1)$$

where δx_{max} is an adjustable maximum displacement and R is a random number uniformly distributed between 0 and 1

ROTATIONAL MOVE [Barker & Watts]

1.) select particle at <u>random</u>

2.) select space-fixed axis at random

3.) determine rotational displacement

$$\delta \zeta_x = \delta x_{max} (2R - 1)$$

4.) generate trial coordinates for a site by rotating the vector from a given origin (COM, <u>pre-specified</u>, random) to the site using a set of rotational matrices

$$A_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\delta\zeta_x & \sin\delta\zeta_x \\ 0 & -\sin\delta\zeta_x & \cos\delta\zeta_x \end{pmatrix}$$

CONFORMATIONAL MOVE

- completely flexible molecule: perform translational moves of individual beads of the molecule
- stiff, but flexible molecule with strong intramolecular potentials:
  - introduce holonomic constraints
  - introduce certain fixed bond length and angles

"The technique of choice is constrained dynamics..."

[Allen & Tildesley, 1987]

"... I cannot recommend the use of the Monte Carlo technique for any but the smallest flexible molecules with internal constraints."

[Frenkel, 1990]

MICROCANONICAL MC

[Creutz, 1983; Frenkel, 1990]

- microcanonical MC uses NO random numbers to determine the acceptance of a move
- introduce an energy demon for every quadratic term in the kinetic energy

1.) attempt translational, rotational, etc. move

2.) select demon at random

3.) accept move if demon can pay for it
   - and update system coordinates and energy of demon

ISOBARIC - ISOTHERMAL MC

[Wood 1968 ; McDonald, 1972]

- the canonical partition function of a system of N identical atoms is given by

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} \int_0^L \cdots \int_0^L d\bar{q}^N \exp(-\beta U(\bar{q}^N))$$

- use scaled coordinates (cubic box)

$$\bar{s} = V^{-1/3} \bar{q}$$

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 \cdots \int_0^1 d\bar{s}^N \exp[-\beta U(\bar{s}^N; L)]$$

- the Helmholtz free energy is

$$A(N,V,T) = k_B T \ln Q$$

$$= k_B T \ln\left(\frac{V^N}{\Lambda^{3N} N!}\right) - k_B T \ln \int d\bar{s}^N \exp[-\beta U(\bar{s}^N; L)]$$

$$= A_{id}(N,V,T) + A_{ex}(N,V,T)$$

- bring system into contact with ideal gas reservoir of pressure P :

total volume: $V_0 = V + (V_0 - V)$

total # particles: $N_0 = N + M$

$$Q(N,M,V,V_0,T) = \frac{V^N (V_0 - V)^M}{\Lambda^{3N_0} N! M!} \int d\bar{s}^M \int d\bar{s}^N \exp[-\beta U(\bar{s}^N; L)]$$

- if the system and the reservoir can exchange volume, then the most probable value of V is the one which minimizes the free energy of the combined system

$$\mathcal{P}(V) = \frac{V^N (V_0 - V)^M \int d\bar{s}^N \exp[-\beta U(\bar{s}^N; L)]}{\int_0^{V_0} dV\, V^N (V_0 - V)^M \int d\bar{s}^N \exp[-\beta U(\bar{s}^N; L)]}$$

- consider the limit

$$V_0 \to \infty \qquad N_0 \to \infty \qquad \Rightarrow \quad N / V_0 \to \rho$$

$$(V_0 - V)^N = V_0^N \left(1 - \frac{V}{V_0}\right)^N \to V_0^N \exp\left(-\frac{NV}{V_0}\right)$$

$$\| \qquad\qquad \| \qquad\qquad \| \qquad\qquad \|$$

$$V_0^N \exp(-\beta P V) = V_0^N \exp(-\rho V)$$

- thus our probability distribution can be rewritten as

$$P(V) = \frac{V^N \exp(-\beta P V) \int d\vec{s}^N \exp[-\beta U(\vec{s}^N; L)]}{\int_0^{V_0} dV\, V^N \exp(-\beta P V) \int d\vec{s}^N \exp[-\beta U(\vec{s}^N; L)]}$$

- the Gibbs free energy is the difference in free energy between the combined system and the ideal gas system in V_0

$$\exp(-\beta \Delta A) = \frac{1}{V_0} \int_0^{V_0} dV \frac{V^N \exp(-\beta P V)}{\Lambda^{3N} N!} \int d\vec{s}^N \exp[-\beta U(\vec{s}^N; L)]$$

- the corresponding probability distribution is

$$\rho(\vec{s}, V) = \frac{\exp\left[-\beta \left\{U(\vec{s}^N, V) + PV - N\beta^{-1} \ln V\right\}\right]}{\Delta}$$

- besides normal translational and rotational moves on (reduced) coordinates, we have to attempt trial moves that change the volume

- the Metropolis acceptance rule for a volume move is $V \to V'$

$$R < \min\left[1 ; \exp\left\{ U(\vec{s}^N, V') - U(\vec{s}^N, V) + P(V' - V) - N\beta^{-1} \ln \frac{V'}{V} \right\}\right]$$

* for LJ: $U_n = \varepsilon \left(\frac{\sigma}{r_{ij}}\right)^n \Rightarrow U_n(L') = \left(\frac{L}{L'}\right)^n U_n(L)$

* if tail-corrections are used, these have to be re-evaluated and included in U

[Norman & Filinov, 1969]

GRAND CANONICAL MC

- following an analogous path as for the isobaric - isothermal ensemble, we can define a partition function for a combined system

$$\Omega(N_0, V, V_0, T) = \sum_{N=0}^{N_0} \frac{V^N (V_0 - V)^{N_0}}{\Lambda^{3N_0} N! (N_0 - N)!}$$

$$\times \int d\vec{s}^{\,N} \int d\vec{s}^{\,N_0} \exp(-\beta U(\vec{s}^{\,N}))$$

- besides conventional trial moves, we have to attempt partical additions (insertions) or removals

$$P_{N \to N+1} = \frac{V}{N+1} \Lambda^{-3} \exp(\beta\mu) \exp\left[-\beta \left\{U(\vec{s}^{\,N+1}) - U(\vec{s}^{\,N})\right\}\right]$$

$$P_{N+1 \to N} = \frac{N+1}{V} \Lambda^{3} \exp(-\beta\mu) \exp\left[-\beta \left\{U(\vec{s}^{\,N}) - U(\vec{s}^{\,N+1})\right\}\right]$$

[Panagiotopoulos, 1987]

GIBBS ENSEMBLE MC

- consider combined system with

$$N_0 = N_1 + N_2 \qquad V_0 = V_1 + V_2$$

- acceptance rate for particle swap move from box 2 into box 1

$$P_{b_2 \to b_1} = \frac{V_1 N_2}{V_2 (N_1 + 1)} \exp\Big[-\beta \big\{U_1(\vec{s}^{\,N_1+1}; V_1) - U_1(\vec{s}^{\,N_1}; V_1)$$

$$+ U_2(\vec{s}^{\,N_2-1}; V_2) - U_2(\vec{s}^{\,N_2}; V_2)\big\}\Big]$$

- acceptance rate for volume exchange

$$P(V_1 \to V_1 + \Delta V, \; V_2 \to V_2 - \Delta V) =$$

$$\exp\Big[-\beta \big\{U_1(\vec{s}^{\,N_1}; V_1 + \Delta V) - U_1(\vec{s}^{\,N_1}; V_1)$$

$$+ U_2(\vec{s}^{\,N_2}; V_2 - \Delta V) - U_2(\vec{s}^{\,N_2}; V_2)\big\}\Big]$$

$$\times \exp\Big[N_1 \ln\Big(\frac{V_1 + \Delta V}{V_1}\Big) + N_2 \ln\Big(\frac{V_2 - \Delta V}{V_2}\Big)\Big]$$

WIDOM'S PARTICLE INSERTION METHOD

- scheme to calculate the chemical potential μ via virtual moves
- thermodynamic definition of μ

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V,T}$$

where we consider only one-component systems

- thus for sufficiently large N the chemical potential can be expressed as a ratio of partition functions

$$\mu = -k_B T \ln\left(\frac{Q_{N+1}}{Q_N}\right)$$

$$= -k_B T \ln\left(\frac{V}{\Lambda^3 (N+1)}\right) - k_B T \ln\left[\frac{\int d\bar{s}^{N+1} \exp[-\beta U(\bar{s}^{N+1})]}{\int d\bar{s}^{N} \exp[-\beta U(\bar{s}^{N})]}\right]$$

$$= \mu_{id}(V) - k_B T \ln\left[\frac{\int d\bar{s}^{N} d\bar{s}_{N+1} \exp(-\beta \Delta U) \exp[-\beta U(\bar{s}^{N})]}{\int d\bar{s}^{N} \exp[-\beta U(\bar{s}^{N})]}\right]$$

$$\mu_{ex} = -k_B T \ln \left\langle \int d\bar{s}_{N+1} \exp(-\beta \Delta U) \right\rangle_{N,V,T}$$

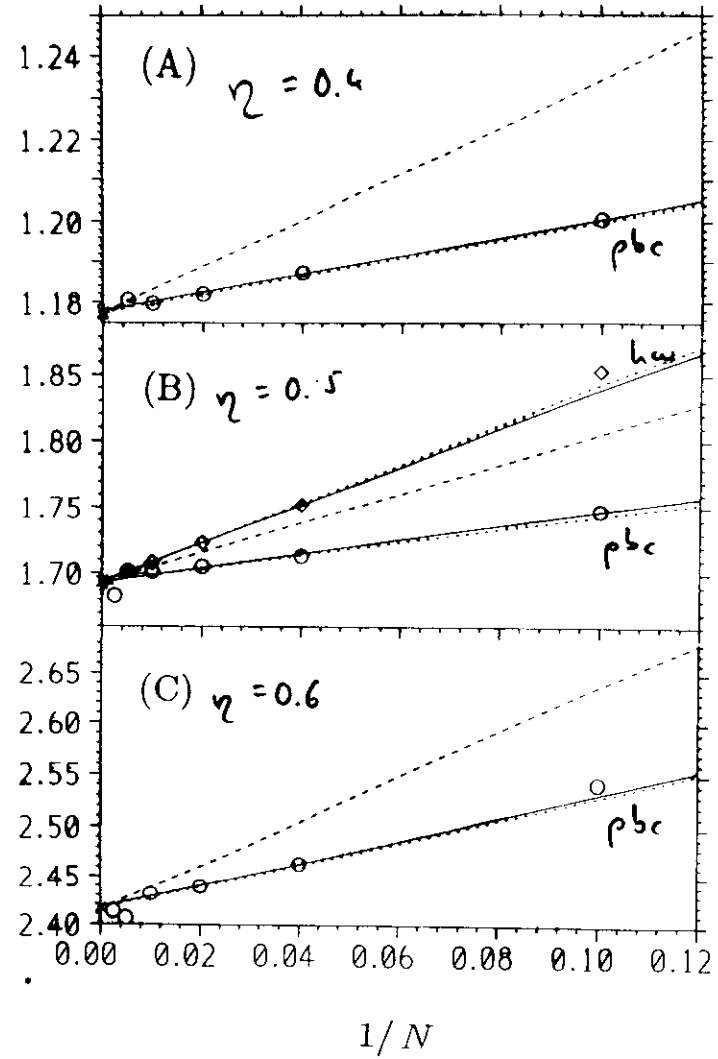
where $\Delta U \equiv U(\bar{s}^{N+1}) - U(\bar{s}^{N})$

- calculate $\int d\bar{s}_{N+1} \exp(-\beta \Delta U)$ by unweighted Monte Carlo sampling
- this is the canonical average of the Boltzmann factor associated with the random insertion of an additional particle
- but the virtual move is never carried out
- isobaric - isothermal ensemble

$$\mu_{ex}(P) = -k_B T \ln \left\langle \frac{\beta P V}{N+1} \int d\bar{s}_{N+1} \exp(-\beta \Delta U) \right\rangle_{N,P,T}$$

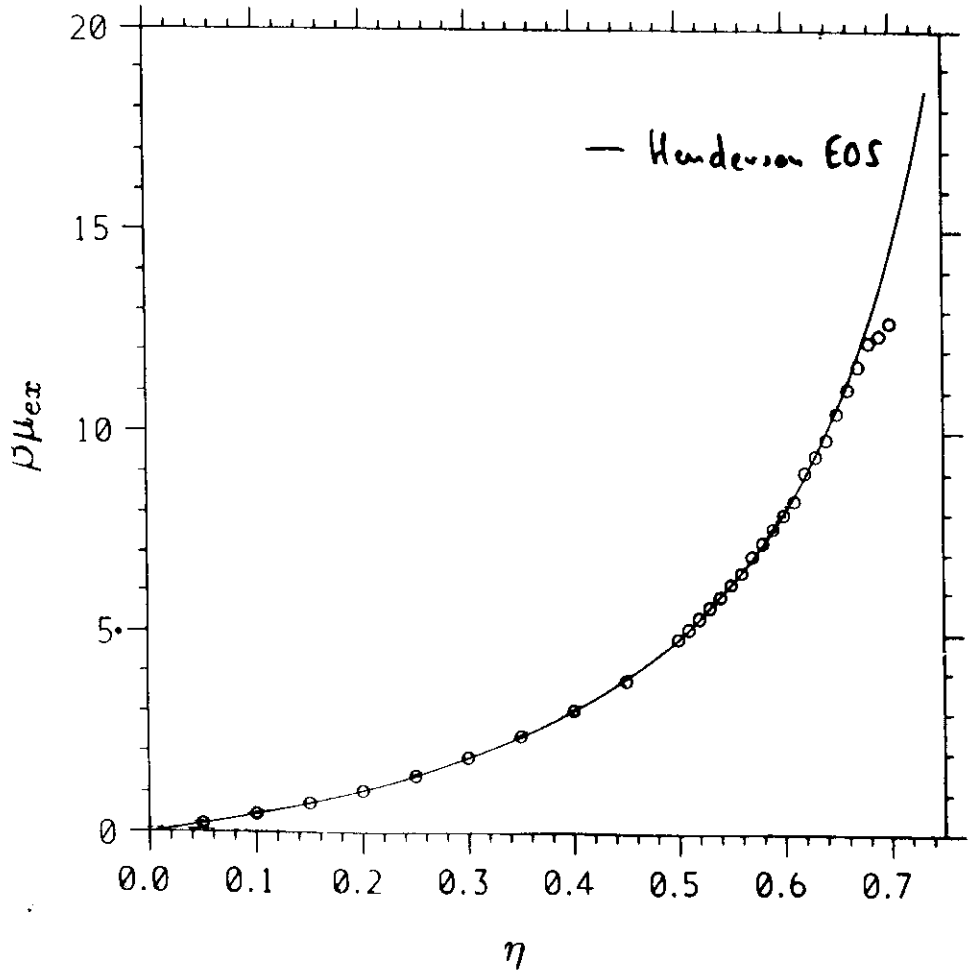
- microcanonical ensemble

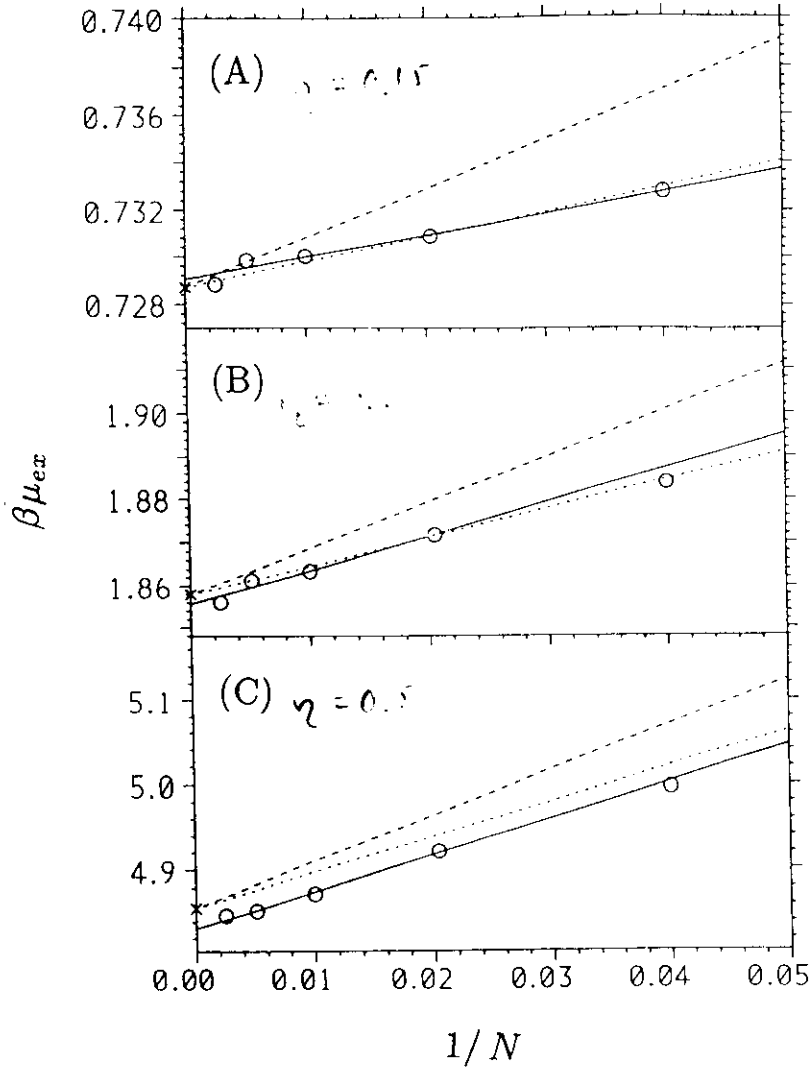
$$\mu_{ex}(E) = k_B T \ln \left\{ \frac{\langle T^{3/2} \exp(-\beta \Delta U) \rangle_{N,V,E}}{\langle T \rangle^{3/2}_{N,V,E}} \right\}$$



Tonks gas

100 - particle hard disk system





hard disk

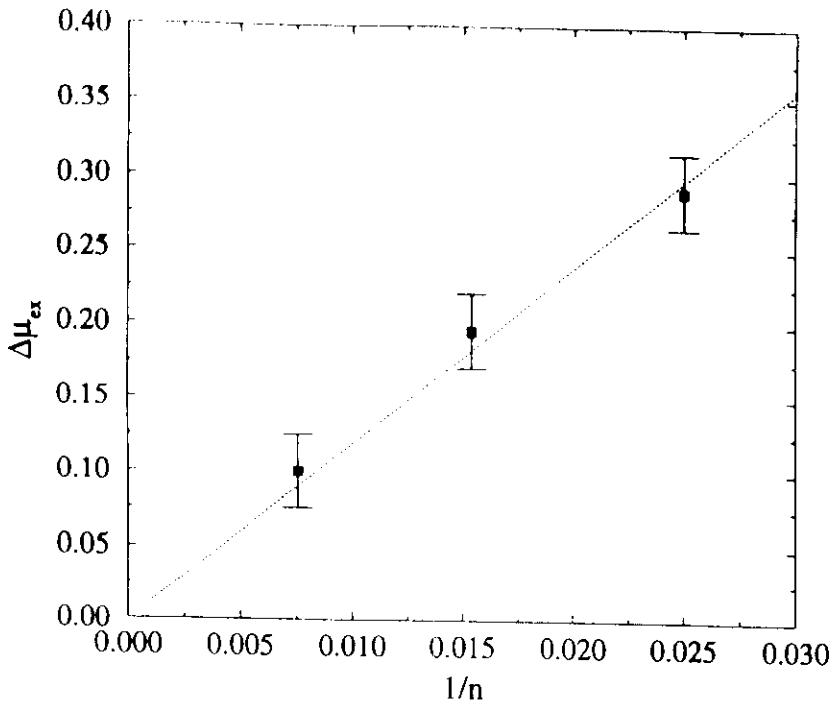


FIG. 6. The measured value of the chemical potential for a system of athermal polymers of chain length $N=40$ at volume fraction $\rho=0.2$ for system sizes $L=40$, 47, and 60. A constant corresponding to the infinite volume estimate $\mu_{ex}=19.50$ has been subtracted from the data. Also shown (broken curve) is the predicted finite-size dependence of μ_{ex} following from Eq. (16) utilizing predetermined equation of state data (Ref. 12).

FINITE SIZE CORRECTIONS

- consider reversible work required to insert tagged particle into volume V in contact with a reservoir at chemical potential μ

$$\beta w_{rev} = -\ln\left[\sum_{N=0}^{\infty} \frac{\exp(\beta\mu N) f(T)^N}{N!\,V} \int d\bar{q}^{N+1} \exp[-\beta U(\bar{q}^N)] \times \exp[-\beta\Delta U] \times \left(\sum_{N=0}^{\infty} \frac{\exp(\beta\mu N) f(T)^N}{N!} \int d\bar{q}^N \exp[-\beta U(\bar{q}^N)]\right)^{-1}\right]$$

where $f(T)$ is the momenta contribution

- replace $f(T)\exp(\beta U) \equiv z$

$$\beta w_{rev} = -\ln\left[(zV)^{-1} \frac{\sum \frac{(N+1) z^{N+1}}{(N+1)!} \int d\bar{q}^{N+1} \exp(-\beta U)}{\sum \frac{z^N}{N!} \int d\bar{q}^N \exp(-\beta U(\bar{q}^N))}\right]$$

$$= -\ln\left(\frac{\langle N\rangle}{zV}\right)$$

$$w_{rev} = \mu - \mu_{id}(\langle N\rangle/V) \equiv \mu_{ex}(\langle N\rangle/V)$$

- for the infinite-system chemical potential we obtain

$$\beta \mu_{ex}^{\infty} = -\ln \left[\sum \frac{z^N Q_N}{N!} \langle \exp(-\beta \Delta U) \rangle_{N,V,T} \Big/ \sum \frac{z^N Q_N}{N!} \right]$$

- using some thermodynamic relations

$$\Delta \mu_{ex}^{N} \equiv \beta \mu_{ex}^{id}(\langle N \rangle, V, T) - \mu_{ex}^{\infty}$$

$$= \frac{1}{2N} \left(\frac{\partial p}{\partial \rho} \right) \left[1 - k_B T \left(\frac{\partial^2 p}{\partial \rho^2} \right) - \rho k_B T \frac{(\partial^2 p / \partial \rho^2)}{(\partial p / \partial \rho)^2} \right]$$

$$+ O(N^{-2})$$

The new MC trial move

It should change the conformation of a chain molecule or part of it directly into a very different conformation.

Analogous to the force-bias MC scheme the attempted move should be biased towards conformations that are more likely, *i.e.* have a higher statistical weight.

The trial conformation has to be generated in a smart way, *i.e.* avoiding itself and other molecules in the system (taking all inter- and intramolecular potential terms into account).

CONFIGURATIONAL-BIAS MONTE CARLO

dual purpose:

- change conformation of flexible molecule
  ↳ mechanical properties
- insert / remove flexible molecule
  ↳ thermal properties

underlying idea:

- generate trial conformation / ghost molecule segment-by-segment
- search for "convenient" positions
  ↳ introduces awful bias

Rosenbluth's self-avoiding random walk

JCP 23, 356 (1955)

* initial weight of unity: $W_1 = 1$

* links added step-by-step

* one of the available nearest-neighbour sites is picked at random and the weight is propagated according to

$$W_{m+1} = \left(\frac{n'}{n}\right) W_m$$

* process repeated until desired length is reached

* properties of SAW calculated as weighted average

$$\langle F \rangle = \frac{\sum_{k=1}^{N} F_k W_k}{\sum_{k=1}^{N} W_k}$$

Rosenbluth sampling for insertion probabilities μ_{ex}

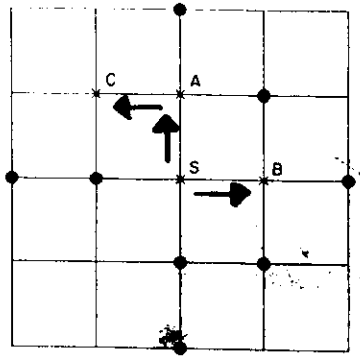
Mol. Phys. 70, 1145

Example illustrating the insertion of a three-unit 'polymer' into a system of random obstacles on a two-dimensional square lattice:

$$T_{tot} = T_3 \cdot W_3 = \frac{1}{12}$$

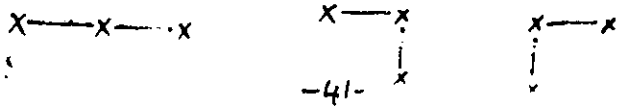
$W_2 = \frac{2}{4}$
$T_2 = \frac{1}{2}$

$W_3 = \frac{2}{4} \cdot \frac{1}{3} = \frac{1}{6}$
$T_3 = \frac{1}{2} \cdot 1 = \frac{1}{2}$



$W_2 = \frac{2}{4}$
$T_2 = \frac{1}{2}$

three possible conformations for 'polymer'



General

- probability of generating conformation Γ

$$P(\Gamma) = \prod_{m=2}^{\ell} \left(\frac{\mathcal{B}_{m,i}}{\sum_{i=1}^{n} \mathcal{B}_{m,i}} \right)$$

with $\mathcal{B}_{m,i} = \exp^{-\beta U_{m,i}}$

- Rosenbluth weight

$$W(\Gamma) = \prod_{m=2}^{\ell} \left(\sum_{i=1}^{n} \frac{\mathcal{B}_{m,i}}{n} \right) \cdot \mathcal{B}_1$$

- mean insertion probability into system

$$\bar{I}(Q) = \frac{1}{n^{\ell-1}} \langle \exp^{-\beta U_\Gamma} \rangle_\Gamma$$

$$\langle \bar{I}(Q) \rangle = \frac{\sum_Q \langle \exp^{-\beta U_\Gamma} \rangle_\Gamma \exp^{-\beta U(Q)}}{\sum_Q n^{\ell-1} \exp^{-\beta U(Q)}}$$

$$\equiv \frac{\mathcal{Z}_{\text{system + ghost}}}{\mathcal{Z}_{\text{system + ideal polymer}}}$$

How can we perform MC with Rosenbluth?

(i.e. smart move to change conformation of polymer)

Propose: $P_{acc}(r \to r') = \min\left\{1, \frac{W(r')}{W(r)}\right\}$

Detailed balance condition:

$$K(r \to r') = K(r' \to r)$$

with $K(r \to r') = e^{-\beta U_r} \cdot P(r \to r') \cdot P_{acc}(r \to r')$

Remember definitions of $P(r)$ and $W(r)$:

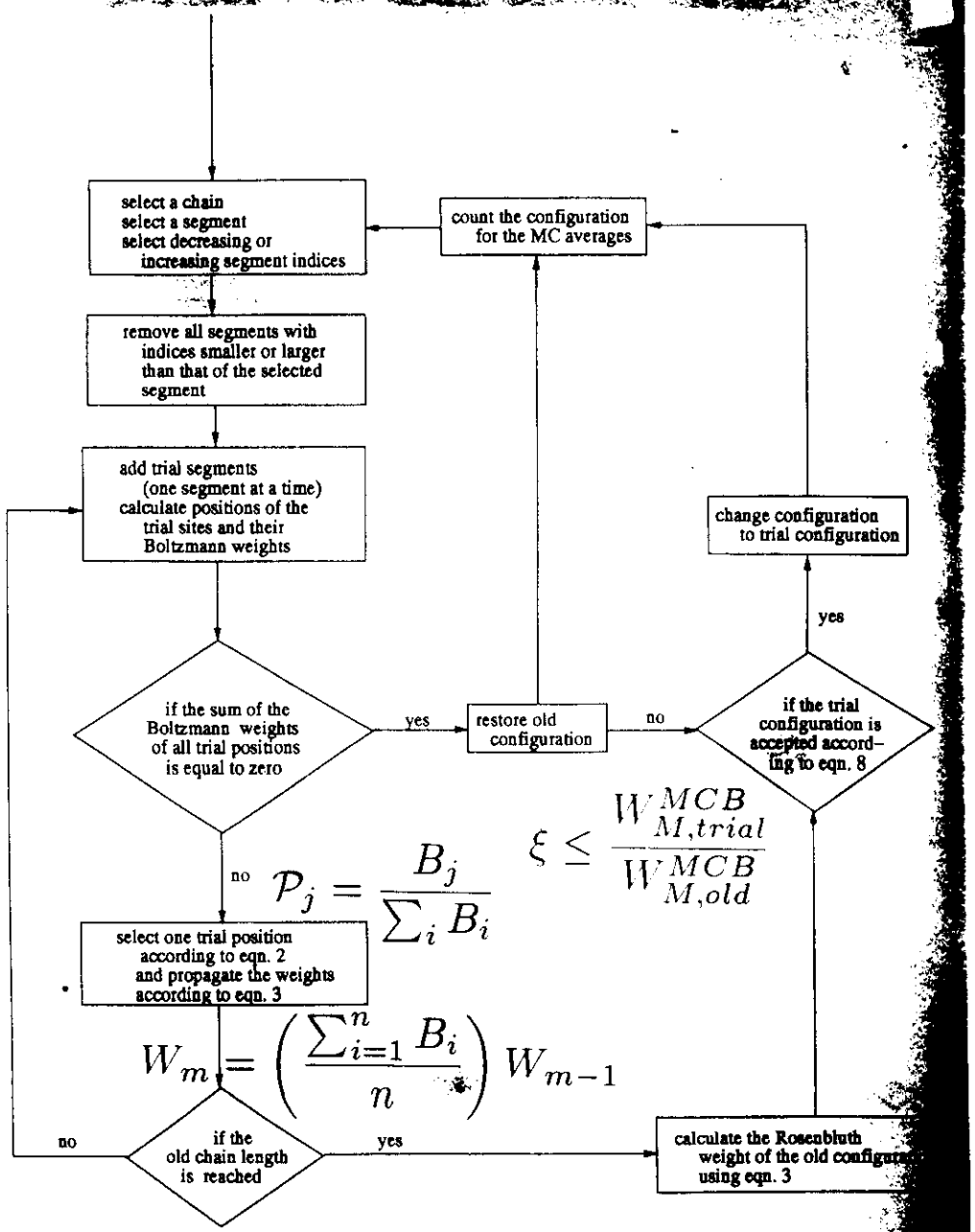
$$W(r) = \frac{\prod_i^n B_j(r)}{n^l P(r)}$$

$$\Rightarrow \frac{n^l W(r')}{n^l W(r)} = \frac{e^{-\beta U_{r'}}}{P(r')} \cdot \frac{P(r)}{e^{-\beta U_r}} \quad \overset{?}{=} \quad 0$$

general "Metropolis" rule for smart MC

ERGODIC!

General flow diagram for CBMC



Growth of trial conformation

- arbitrary multi-chain system with N chains of lengths $L(N)$ (chains can differ in length) in continuous space
- random selections of chain molecule (I) and segment (S)
- discard
  - entire molecule, if $S = 1$ or $S = L(I)$
  - or a part thereof (random choice whether to rearrange units with indices larger or smaller than S)
- call first trial segment A (where $A = S \pm 1$), and last trial segment B (where $B = 1$ or $B = L(I)$)
- draw trial segment from set of, say, n trial sites (chosen in a suitable way) with probability $\mathcal{P}_j$

$$\mathcal{P}_{m,j} = \frac{\mathcal{B}_{m,j}}{\sum_{i=1}^{n} \mathcal{B}_{m,i}} \tag{1}$$

where $\mathcal{B}_{m,j} = \exp(-\beta U_{m,j})$ and denominator includes j

  - in calculation of $\mathcal{B}_{m,j}$ the contributions of segments of chain I with indices ranging from m to B are excluded, so total energy of conformation Γ consisting of the segments from A to B is given by $U_\Gamma = \sum_{m=A}^{B} U_{m,j}$
  - define "overlap" for site i (set $B_{m,i} = 0$) when actual Boltzmann weight is very small, then growth resulting in trial conformation with very low statistical weight can be terminated if $\sum_{i=1}^{n} \mathcal{B}_{m,i} = 0$ at any given step
- probability of generating conformation Γ

$$\mathcal{P}_\Gamma = \prod_{m=A}^{B} \mathcal{P}_{m,j} \tag{2}$$

- define Rosenbluth weight factor of Γ as

$$\mathcal{W}_\Gamma = \prod_{m=A}^{B} \frac{\sum_{i=1}^{n} \mathcal{B}_{m,i}}{n} \tag{3}$$

Compute set of suitable trial sites

- simple where molecules have only finite number of conformations, as for lattice models and for rotational-isomeric-state (RIS) model, because positions of trial sites can be computed by geometric rules
  - with certain choice of CBMC parameter n all possible conformations can be explored and Rosenbluth weights can be calculated exactly
- for continuously deformable molecules only possible to sample a random subset of the accessible conformations and there is added task of constructing suitable set of n trial sites at each step
- distribution of trial sites need not be uniform, and in practice, internal potentials (for which energy can be readily computed), should be used to guide selection of trial-site positions

(i) compute random vector on surface of unit sphere

(ii) internal potential energy and corresponding Boltzmann weight for bond directed along this vector are calculated

(iii) vector is accepted or rejected according to standard Metropolis criterion (if rejected, we return to step (i); if accepted, we proceed to the next step)

(iv) position of trial site is determined by scaling vector to required bond length (if bond length is also flexible, pick at random from correct distribution)

- since statistical weights associated with internal potentials are already taken account of in creation of trial sites, Boltzmann factors in eqn. 1 (selection of trial site i) and eqn. 3 (propagation of Rosenbluth weights) are based only on the remaining contributions to the potential energy (in most cases inter- and intramolecular Lennard-Jones terms)

Re-growth of old conformation

- compute corresponding Rosenbluth weight of old conformation $\mathcal{W}_{\Gamma'}$ while tracing 'actual' path starting at segment A and ending at segment B (set of n sites chosen such that it always contains 'actual' site as one member)
  - choice of sets of trial sites used to calculate $\mathcal{W}_{\Gamma'}$ is not entirely free (also true for reverse move changing from Γ' to Γ)

    $\Rightarrow$ super-detailed balance
- accept move if

$$\xi \leq \frac{\mathcal{W}_{\Gamma}}{\mathcal{W}_{\Gamma'}} \tag{4}$$

where ξ is a random number uniformly distributed between 0 and 1

Detailed balance

- detailed balance implies that a configuration Γ is transformed into another configuration Γ' at the same rate $\mathcal{K}_{(\Gamma\rightarrow\Gamma')}$ as opposite transformation

$$\mathcal{K}_{(\Gamma\rightarrow\Gamma')} = \mathcal{K}_{(\Gamma'\rightarrow\Gamma)} \tag{5}$$

- for any arbitrary MC move rate $\mathcal{K}_{(\Gamma\rightarrow\mathcal{Y})}$ is given by

$$\mathcal{K}_{(\Gamma\rightarrow\Gamma')} = \rho_{\Gamma}\ \alpha_{(\Gamma\rightarrow\Gamma')} \tag{6}$$

where ρ_{Γ} denotes probability density to find system in configuration Γ, and $\alpha_{(\mathcal{X}\rightarrow\Gamma')}$ is transition probability for move from Γ to Γ' which is product of the probability $\tau_{\Gamma'}$ to generate Γ' and the probability $\mathrm{acc}_{(\Gamma\rightarrow\Gamma')}$ to accept the move

- for MC sampling of Boltzmann distribution, we can, by substitution of eqn. 6 into detailed-balance conditon (eqn. 5), obtain the following equation which determines acceptance rules

$$\frac{\alpha_{(\Gamma\to\Gamma')}}{\alpha_{(\Gamma'-\Gamma)}} = \frac{\rho_{\Gamma'}}{\rho_{\Gamma}} = \frac{\exp(-\beta U_{\Gamma'})}{\exp(-\beta U_{\Gamma})} \tag{7}$$

- usual, and most convenient, choice for acceptance rules is the Metropolis form

$$\mathrm{acc}_{(\Gamma\to\Gamma')} = \min\left(1\,,\,\frac{\tau_{\Gamma}\,\exp(-\beta U_{\Gamma'})}{\tau_{\Gamma'}\,\exp(-\beta U_{\Gamma})}\right) \tag{8}$$

- for CBMC scheme, the probability $\tau_{\Gamma'}$ to generate a particular configuration Γ' for the trial segments is given by eqn. 2, and we can rewrite corresponding Rosenbluth weight factor (eqn. 3) in a form where $\mathcal{P}$ appears in denominator

$$\mathcal{W}_{\Gamma'} = \frac{\prod_{m=A}^{B}\mathcal{B}_{m,j}}{n^{|A-B|}\,\mathcal{P}_{\Gamma'}} \tag{9}$$

- the product in nominator is the relevant Boltzmann weight of configuration Γ', this means that as $U_{\Gamma'} = \sum_{m=A}^{B} U_{m,j}$ eqn. 9 is equivalent to

$$n^{|A-B|}\mathcal{W}_{\Gamma'} = \frac{\exp(-\beta U_{\Gamma'})}{\mathcal{P}_{\Gamma'}} \tag{10}$$

and the same holds for configuration Γ

- substitution of left-hand side of eqn. 10 and its equivalent for configuration Γ into eqn. 8 (which leads to a cancellation of prefactors $n^{|A-B|}$) shows indeed that CBMC acceptance rule given in eqn. 4 satisfies the detailed-balance requirement

Configurational-bias Insertion (CBI)

- the chemical potential, a thermal property, is usually calculated by the so-called "Widom's particle-insertion method which relates excess chemical potential, μ^{ex} to canonical average of the probability of inserting a 'ghost' particle (or, test particle) at a random position into the system

$$\mu^{ex} = -\beta^{-1} \ln\langle \exp(-\beta U_{test}) \rangle \tag{11}$$

where U_{test} denotes interaction energy of test particle with all other particles which, however, are not affected by the presence of the 'ghost'

- in the course of a CBI, first bead of the 'ghost'-chain is inserted at a random position, and all other segments of chain are generated by step-wise configurational-bias approach

- Rosenbluth weight for insertion

$$\mathcal{W}_\Gamma = \mathcal{B}_1 \prod_{m=2}^{L} \frac{\sum_{i=1}^{n} \mathcal{B}_{m,i}}{n} \tag{12}$$

- show that canonical average of Rosenbluth weights of 'ghost' chains is related in a simple way to excess chemical potential

- for a particular configuration of the system, $\mathbf{Q}$, we can compute a mean Rosenbluth insertion probability as unweighted average over all 'ghost' conformations sampled

$$\overline{\mathcal{I}}_L(\mathbf{Q}) \equiv \langle \mathcal{P}_\Gamma(\mathbf{Q}) \mathcal{W}_\Gamma(\mathbf{Q}) \rangle_\Gamma \tag{13}$$

- inserting the right-hand sides of eqns. 2 and 12 into eqn. 13 we obtain

$$\overline{\mathcal{I}}_L(\mathbf{Q}) = \frac{1}{n^{L-1}} \langle \exp[-\beta U_\Gamma(\mathbf{Q})] \rangle_\Gamma \tag{14}$$

- the canonical average of $\overline{\mathcal{I}}_L(\mathbf{Q})$ is given by

$$\langle \overline{\mathcal{I}}_L(\mathbf{Q}) \rangle \equiv \frac{\sum_{\mathbf{Q}} \langle \exp[-\beta U_\Gamma(\mathbf{Q})] \rangle_\Gamma \exp[-\beta U(\mathbf{Q})]}{\sum_{\mathbf{Q}} n^{L-1} \exp[-\beta U(\mathbf{Q})]} \tag{15}$$

where $\exp[-\beta U(\mathbf{Q})]$ is the Boltzmann factor of the system with configuration $\mathbf{Q}$; the denominator of this equation is equal to the partition function of the system plus an ideal polymer, and the numerator is equal to the partition function of the system plus an additional 'ghost' polymer

- replace eqn. 11 by

$$\mu^{ex} = -\beta^{-1} \ln\langle \overline{\mathcal{I}}_L(\mathbf{Q}) \rangle \tag{16}$$

CBMC in the Gibbs' ensemble

- a Monte Carlo trial to exchange a particle between the two boxes is performed in the following way:

(i) a chain is selected at random

(ii) using step-by-step configurational-bias scheme the Rosenbluth weights of the selected chain are calculated for a trial insertion in the new box ($\mathcal{W}_I$) and for the removal of the existing conformation in the old box ($\mathcal{W}_R$)

(iii) the biased exchange trial is accepted at the following acceptance rate

$$\xi \leq \frac{\mathcal{W}_I}{\mathcal{W}_R} \frac{n_R(V - v_R)}{(N - n_R + 1)v_R} \qquad (17)$$

where N and V are combined number of particles and combined volume of the two simulations boxes, respectively; and n_R and v_R are thenumber of particles and volume of the box in which the trial particle was located before the trial move

Energy minimization of LJ polymer

Chem. Phys. Lett. 199, 220 ('92)

- Method: Configurational-bias MC
- Model: 61 freely-jointed beads connected by bonds of fixed length B (2-dimensional)
- Potentials: $\sigma_i = (1 + (Ai/N))\,\sigma_0$ and $\sigma_{ij} = 0.5\,(\sigma_i + \sigma_j)$

$$T^* = 0.02\,k_B\,T/\epsilon$$

$A = 0.$, $B = 2^{1/6}\,\sigma_0$ $\qquad$ $nn = 96.$, $v = -110\,\epsilon$

$A = 0.1$, $B = \sigma_0$ $\qquad$ $nn = 91.$, $v = -114\,\epsilon$