Configurational-Bias Monte Carlo

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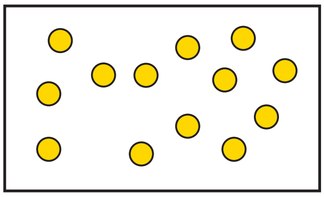
Random Sampling versus Metropolis Sampling (1)

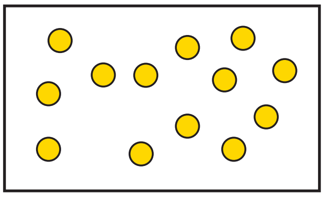
N interacting particles in volume V at temperature T



- vector representing positions of all particles in the system: $\mathbf{r}^N$
- total energy: $U(\mathbf{r}^N)$
- statistical weight of configuration $\mathbf{r}^N$ is $\exp[-\beta U(\mathbf{r}^N)]$ with $\beta = 1/(k_BT)$

Random Sampling versus Metropolis Sampling (2)

N interacting particles in volume V at temperature T
pair interactions $u(r_{ij})$



$$\begin{aligned} U(\mathbf{r}^N) &= \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} u(r_{ij}) = \sum_{i<j} u(r_{ij}) \\ Q(N,V,T) &= \frac{1}{\Lambda^{3N}N!}\int d\mathbf{r}^N \exp\left[-\beta U(\mathbf{r}^N)\right] \\ F(N,V,T) &= -k_BT\ln Q(N,V,T) \end{aligned}$$

Random Sampling versus Metropolis Sampling (3)

Computing the ensemble average $\langle \cdots \rangle$ of a certain quantity $A(\mathbf{r}^N)$

- Random Sampling of $\mathbf{r}^N$:

$$\langle A \rangle = \lim_{n\to\infty} \frac{\sum_{i=1}^{n} A(\mathbf{r}_i^N)\exp\left[-\beta U(\mathbf{r}_i^N)\right]}{\sum_{i=1}^{n}\exp\left[-\beta U(\mathbf{r}_i^N)\right]}$$

Usually this leads to $\langle A \rangle =$ “0” / “0” $=$???

- Metropolis sampling; generate n configurations $\mathbf{r}^N$ with probability proportional to $\exp\left[-\beta U(\mathbf{r}_i^N)\right]$, therefore:

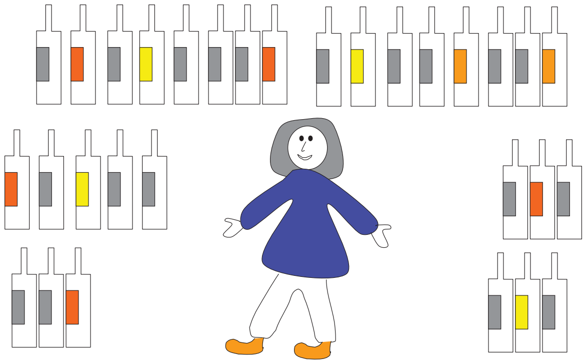
$$\langle A \rangle = \lim_{n\to\infty} \frac{\sum_{i=1}^{n} A(\mathbf{r}_i^N)}{n}$$

Simulation Technique (1)

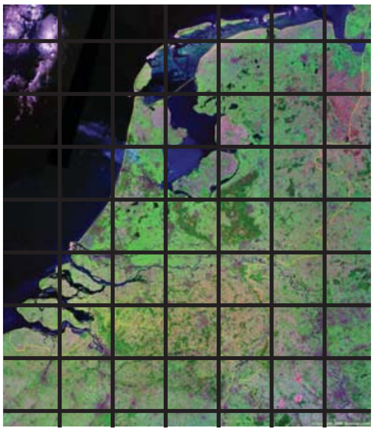
What is the ratio of red wine/white wine in the Netherlands?

Simulation Technique (2)

Bottoms up



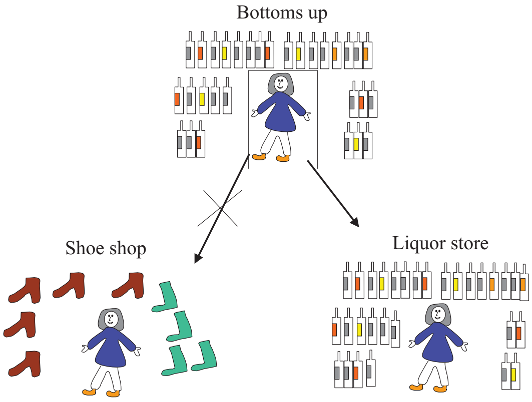
Simulation Technique (3)



Simulation Technique (4)

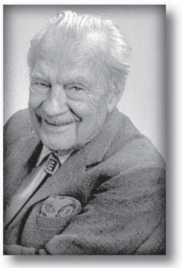
Simulation Technique (5)

Simulation Technique (6)



Metropolis Monte Carlo (1)

How to generate configurations $\mathbf{r}_i$ with a probability proportional to $\mathcal{N}(\mathbf{r}_i) = \exp[-\beta U(\mathbf{r}_i)]$???

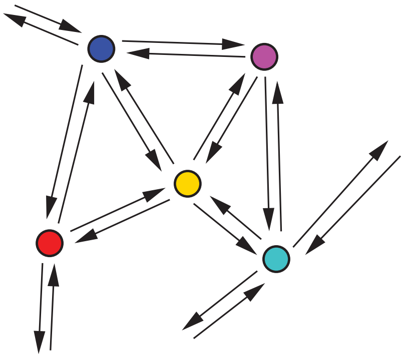


Nick Metropolis

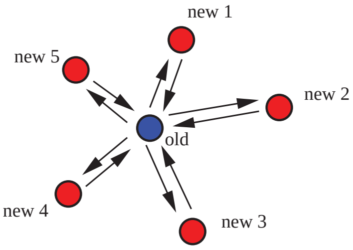
N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth. A.H. Teller and E. Teller, "Equation of State Calculations by Fast Computing Machines," J. Chem. Phys., 1953, 21, 1087-1092.

Metropolis Monte Carlo (2)

Whatever our rule is to move from one state to the next, the equilibrium distribution should not be destroyed



Move from the old state (o) to a new state (n) and back



$$\begin{array}{rcl} \text{leaving state o} & = & \text{entering state o} \\ \mathcal{N}(o)\sum_n\left[\alpha(o\rightarrow n)\mathrm{acc}(o\rightarrow n)\right] & = & \sum_n\left[\mathcal{N}(n)\alpha(n\rightarrow o)\mathrm{acc}(n\rightarrow o)\right] \end{array}$$

$\mathcal{N}(i)$: probability to be in state i (here: proportional to $\exp[-\beta U(\mathbf{r}_i)]$)
$\alpha(x\rightarrow y)$: probability to attempt move from state x to state y
$\mathrm{acc}(x\rightarrow y)$: probability to accept move from state x to state y

Detailed Balance (1)

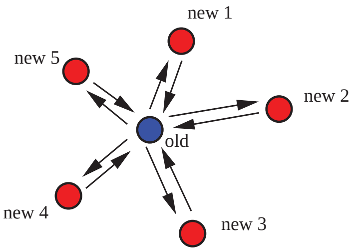
Requirement (balance):

$$\mathcal{N}(o)\sum_n\left[\alpha(o\rightarrow n)\mathrm{acc}(o\rightarrow n)\right]=\sum_n\left[\mathcal{N}(n)\alpha(n\rightarrow o)\mathrm{acc}(n\rightarrow o)\right]$$

Detailed balance: much stronger condition

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

for every pair o,n



Detailed Balance (2)

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

- $\alpha(x\rightarrow y)$; probability to select move from x to y
- $\mathrm{acc}(x\rightarrow y)$; probability to accept move from x to y
- often (but not always); $\alpha(o\rightarrow n)=\alpha(n\rightarrow o)$

Therefore (note that $\Delta U=U(n)-U(o)$):

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

In case that $\alpha(o\rightarrow n)=\alpha(n\rightarrow o)$

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

Metropolis Acceptance Rule

General:

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

Choice made by Metropolis (note: infinite number of other possibilities)

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

Note than $\min(a,b)=a$ if $a<b$ and b otherwise

- always accept when $X\geq 1$
- when $X<1$, generate uniformly distributed random number between 0 and 1 and accept or reject according to $\mathrm{acc}(o\rightarrow n)$

Monte Carlo Casino

Smart Monte Carlo: $\alpha(o \to n) \neq \alpha(n \to o)$

Not a random displacement Δr uniformly from $[-\delta, \delta]$, but instead

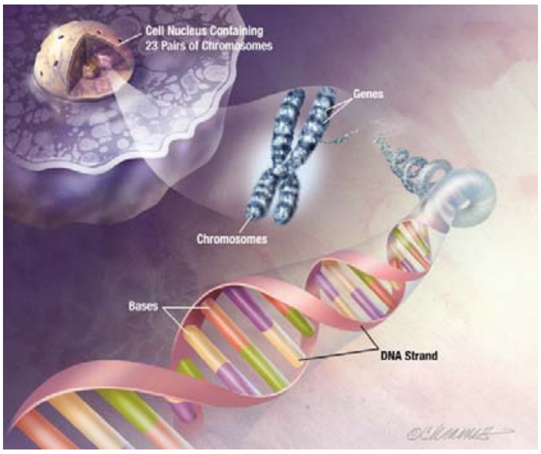
$$\Delta r = r(\text{new}) - r(\text{old}) = A \times F + \delta r$$

F : force on particle
A : constant
δr : taken from Gaussian distribution with width $2A$
so $P(\delta r) \sim \exp[-(\delta r^2)/4A]$

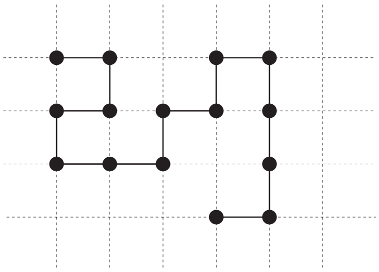
$$P(r_{\text{new}}) \sim \exp\left[-\frac{(r_{\text{new}} - (r_{\text{old}} + A \times F(o)))^2}{4A}\right]$$

$$\frac{\alpha(o \to n)}{\alpha(n \to o)} = \frac{\exp\left[-\frac{(\Delta r - A \times F(o))^2}{4A}\right]}{\exp\left[-\frac{(\Delta r + A \times F(n))^2}{4A}\right]}$$

Chain Molecules



Self-Avoiding Walk on a Cubic Lattice



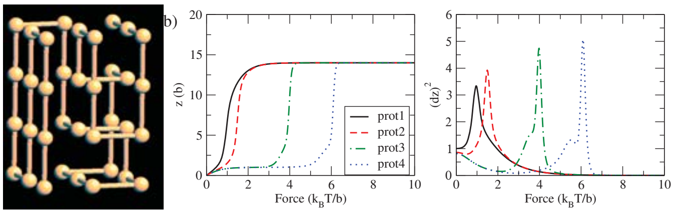
- 3D lattice; 6 lattice directions
- only 1 monomer per lattice site (otherwise $U = \infty$)
- interactions only when $|r_{ij}| = 1$ and $|i - j| > 1$

Simple Model for Protein Folding

20 by 20 interaction matrix Δ_{ij}

YPDLTKWHAMEAGKIRFSVPDACLNGEGIRQVTLSN

(E. Jarkova, T.J.H. Vlugt, N.K. Lee, J. Chem. Phys., 2005, 122, 114904)



Number of Configurations without Overlap

Random Chains:

$$\langle R \rangle = \lim_{n \to \infty} \frac{\sum_{i=1}^{n} R_i \exp[-\beta U_i]}{\sum_{i=1}^{n} \exp[-\beta U_i]}$$

Fraction of chains without overlap decreases exponentially as a function of chainlength (N)

N	total $(= 6^{N-1})$	without overlap	fraction no overlap
2	6	6	1
6	7776	3534	0.454
8	279936	81390	0.290
10	10077696	1853886	0.183
12	362797056	41934150	0.115
13	2176782336	198842742	0.091
14	13060694016	943974510	0.072
15	78364164096	4468911678	0.057
16	470184984576	21175146054	0.045
50	$\cdots$	$\cdots$	1.3×10^{-5}

Rosenbluth Sampling (1)

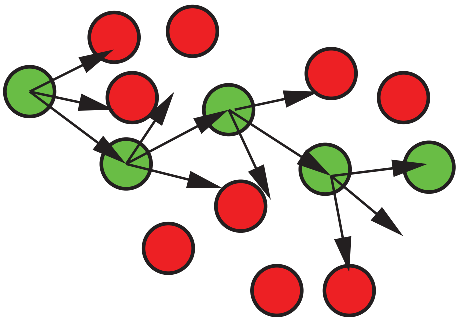
1. Place first monomer at a random position
2. For the next monomer (i), generate k trial directions $(j = 1, 2, \cdots, k)$ each with energy u_{ij}
3. Select trial direction $j^\star$ with a probability

$$P_{j^\star} = \frac{\exp[-\beta u_{ij^\star}]}{\sum_{j=1}^{k} \exp[-\beta u_{ij}]}$$

4. Continue with step 2 until the complete chain is grown (N monomers)

Rosenbluth Sampling (2)

$$P_{j^\star} = \frac{\exp[-\beta u_{ij^\star}]}{\sum_{j=1}^{k} \exp[-\beta u_{ij}]}$$



Rosenbluth Sampling (3)

Probability to choose trial direction $j^\star$ for the i th monomer

$$P_{j^\star} = \frac{\exp[-\beta u_{ij^\star}]}{\sum_{j=1}^{k} \exp[-\beta u_{ij}]}$$

Probability to grow this chain (N monomers, k trial directions)

$$P_{\text{chain}} = \prod_{i=1}^{N} P_{j^\star(i)} = \frac{\prod_{i=1}^{N} \exp[-\beta u_{ij^\star(i)}]}{\prod_{i=1}^{N} \sum_{j=1}^{k} \exp[-\beta u_{ij}]} = \frac{\exp[-\beta U_{\text{chain}}]}{W_{\text{chain}}}$$

Rosenbluth Sampling (4)

Probability to grow this chain (N monomers, k trial directions)

$$P_{\text{chain}} = \frac{\prod_{i=1}^{N} \exp[-\beta u_{ij^\star(i)}]}{\prod_{i=1}^{N} \sum_{j=1}^{k} \exp[-\beta u_{ij}]} = \frac{\exp[-\beta U_{\text{chain}}]}{W_{\text{chain}}}$$

Therefore, weightfactor for each chain i is the Rosenbluth factor W_i:

$$\langle R \rangle_{\text{Boltzmann}} = \lim_{n \to \infty} \frac{\sum_{i=1}^{n} W_i \times R_i}{\sum_{i=1}^{n} W_i}$$

The unweighted distribution is called the Rosenbluth distribution:

$$\langle R \rangle_{\text{Rosenbluth}} = \lim_{n \to \infty} \frac{\sum_{i=1}^{n} R_i}{n}$$

Of course: $\langle R \rangle_{\text{Rosenbluth}} \neq \langle R \rangle_{\text{Boltzmann}}$

Intermezzo: Ensemble Averages at Different Temperatures

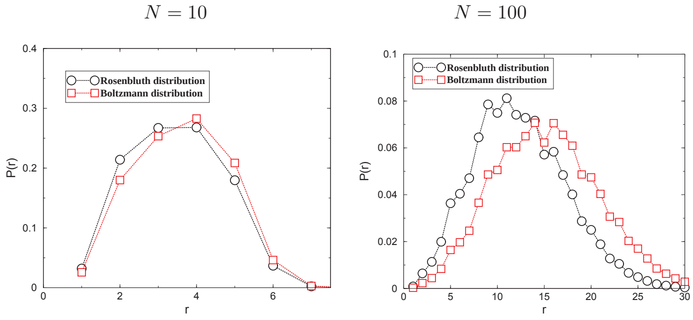
Ensemble averages at $\beta^\star$ can (in principle) be computed from simulations at β:

$$\begin{aligned}
\langle U \rangle_\beta &= \frac{\int d\mathbf{r}^N U(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \\
&= \frac{\int d\mathbf{r}^N U(\mathbf{r}^N) \exp[-\beta^\star U(\mathbf{r}^N)] \exp[(\beta^\star - \beta) \times U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta^\star U(\mathbf{r}^N)] \exp[(\beta^\star - \beta) \times U(\mathbf{r}^N)]} \\
&= \frac{\left\langle U(\mathbf{r}^N) \exp[(\beta^\star - \beta) \times U(\mathbf{r}^N)] \right\rangle_{\beta^\star}}{\langle \exp[(\beta^\star - \beta) \times U(\mathbf{r}^N)] \rangle_{\beta^\star}} \\
&= \frac{\left\langle U(\mathbf{r}^N) \exp[\Delta\beta \times U(\mathbf{r}^N)] \right\rangle_{\beta^\star}}{\langle \exp[\Delta\beta \times U(\mathbf{r}^N)] \rangle_{\beta^\star}}
\end{aligned}$$

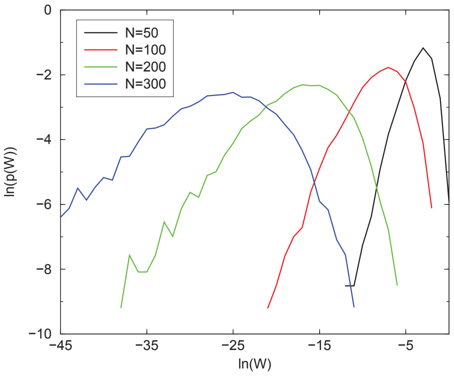
Useful or not???

Rosenbluth Distribution Differs from Boltzmann Distribution

Probability distribution for the *end-to-end distance* r



Distribution of Rosenbluth Weights



Of course, $\text{Probability}(W = 0) \neq 0$ (not shown in this figure)

Pruned-Enriched Rosenbluth Method (1)

Grassberger (1997); grow chains using Rosenbluth Method:

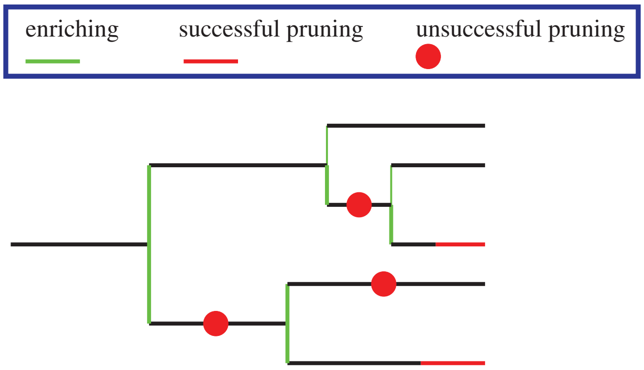
$$W = \sum_{j=1}^{6} \frac{\exp\left[-\beta u_{2j}\right]}{6} \times \prod_{i=3}^{N} \sum_{j=1}^{5} \frac{\exp\left[-\beta u_{ij}\right]}{5} = \prod_{i=3}^{N} \sum_{j=1}^{5} \frac{\exp\left[-\beta u_{ij}\right]}{5}$$

Two additional elements:

- **Enriching**
  If $W > W_{\text{max}}$ during the construction of the chain, k copies of the chain are generated, each with a weight of W/k. This is a deterministic process. The growth of those k chains is continued.

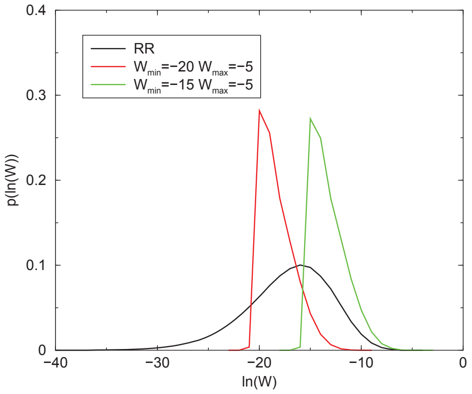
- **Pruning**
  If $W < W_{\text{min}}$ during the construction of a chain, with a probability of $1/2$ the chain is pruned resulting in $W = 0$. If the chain survives, the Rosenbluth weight is multiplied by 2 and the growth of the chain is continued.

Pruned-Enriched Rosenbluth Method (2)



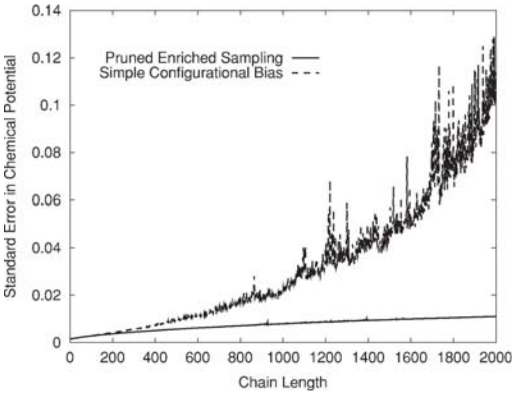
Pruned-Enriched Rosenbluth Method (3)

Example: $N = 200,\ k = 2,\ \beta\mu_{\text{ex}} = -\ln\langle W\rangle = -12.14$



Pruned-Enriched Rosenbluth Method (4)

$\beta\mu_{\text{ex}} = -\ln\langle W\rangle$, Ann. Rev. of Phys. Chem. 1999, 50, 377-411

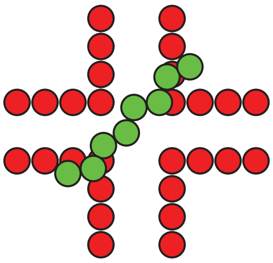


Static versus Dynamic Monte Carlo

- **Static Monte Carlo**
  - create single chain conformations, and use correct weight factor (random insertion, Rosenbluth scheme, PERM) to compute single chain averages
  - **single chain only; no Markov chain**
- **Dynamic Monte Carlo**
  - create Markov chain, accept/reject new configuration, acceptance rules should obey detailed balance
  - **multi-chain system, usable for all ensembles (e.g. Gibbs, μVT)**
  - Configurational-Bias Monte Carlo (CBMC), Recoil Growth (RG), Dynamic PERM (DPERM)

Random Insertion of Chains is Useless

Chain Length	Probability without overlaps
1	10^{-2}
2	10^{-4}
3	10^{-6}
…	…
8	10^{-16}



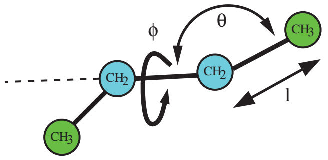
Configurational-Bias Monte Carlo

- Generate configurations using the Rosenbluth scheme
- Accept/Reject these configurations in such a way that detailed balance is obeyed
- Split potential energy into "**bonded**" (bond-stretching, bending, torsion) and "**non-bonded**" (i.e. Lennard-Jones and/or Coulombic) interactions
- Generate (k) trial positions according to **bonded** interactions (unbranched chain: l, θ, ϕ are independent)

$$U_{\text{bonded}} = U_{\text{stretch}}(l) + U_{\text{bend}}(\theta) + U_{\text{tors}}(\phi)$$

$$\begin{aligned} P(l) &\sim dl\, l^2 \exp[-\beta u(l)] \\ P(\theta) &\sim d\theta\, \sin(\theta) \exp[-\beta u(\theta)] \\ P(\phi) &\sim d\phi\, \exp[-\beta u(\phi)] \end{aligned}$$

Generate Trial Configurations: Linear Alkane



$$
\begin{aligned}
u(l) &= (k_l/2)\,(l-l_0)^2 \\
u(\theta) &= (k_\theta/2)\,(\theta-\theta_0)^2 \\
u(\phi) &= \sum_{i=0}^{5} c_i \cos^i(\phi)
\end{aligned}
$$

$$
\begin{aligned}
P(l) &\sim dl\, l^2 \exp[-\beta u(l)] \\
P(\theta) &\sim d\theta\, \sin(\theta) \exp[-\beta u(\theta)] \\
P(\phi) &\sim d\phi\, \exp[-\beta u(\phi)]
\end{aligned}
$$

Generate a Random Number from a Distribution (1)

$$F(y) = \int_0^y p(y')dy'$$

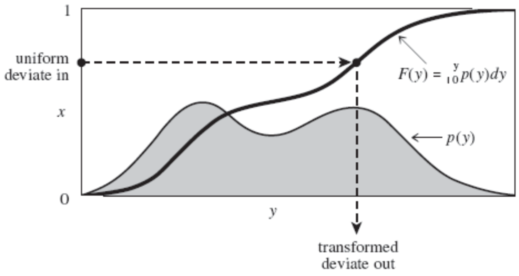


Figure 7.2.1. Transformation method for generating a random deviate y from a known probability distribution $p(y)$. The indefinite integral of $p(y)$ must be known and invertible. A uniform deviate x is chosen between 0 and 1. Its corresponding y on the definite-integral curve is the desired deviate.

Generate a Random Number from a Distribution (2)

$$F(y) = \int_0^y f(y')dy' \qquad f(x) > p(x)$$

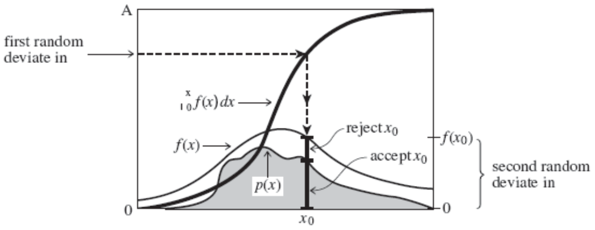


Figure 7.3.1. Rejection method for generating a random deviate x from a known probability distribution $p(x)$ that is everywhere less than some other function $f(x)$. The transformation method is first used to generate a random deviate x of the distribution f (compare Figure 7.2.1). A second uniform deviate is used to decide whether to accept or reject that x. If it is rejected, a new deviate of f is found; and so on. The ratio of accepted to rejected points is the ratio of the area under p to the area between p and f.

Generate a Random Number from a Distribution (3)

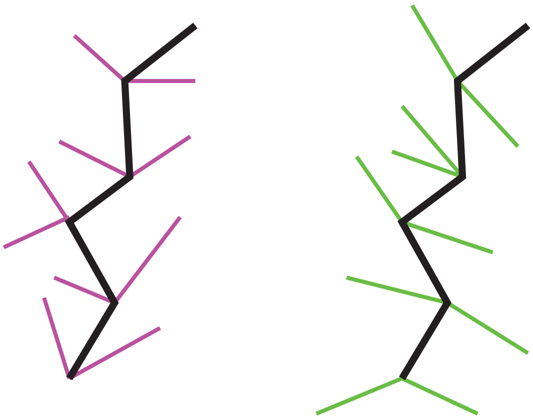
```
subroutine bend-tors                           generate appropriate θ and ϕ

lready=.false
do while (.not.lready)
  call ransphere(dx,dy,dz)                     random vector on unit sphere
  x = xold + dx                                monomer position
  y = yold + dy
  z = zold + dz
  call bend(ubend,x,y,z)                       bending energy
  call tors(utors,x,y,z)                       torsion energy
  if(ranf().lt.exp(-beta*(ubend+utors)))       accept or reject
 +  lready=.true
enddo
```

CBMC Algorithm

- Generate a trial configuration using the Rosenbluth scheme. k trial segments $\{\mathbf{b}\}_k = \{\mathbf{b}_1 \cdots \mathbf{b}_k\}$, each trial segment is generated according to
$$P(\mathbf{b}) \sim \exp[-\beta u_{\mathrm{bonded}}(\mathbf{b})]$$
- Compute non-bonded energy, select configuration i with a probability
$$P(\mathbf{b}_i) = \frac{\exp[-\beta u_{\mathrm{non-b}}(\mathbf{b}_i)]}{\sum_{j=1}^{k} \exp[-\beta u_{\mathrm{non-b}}(\mathbf{b}_j)]} = \frac{\exp[-\beta u_{\mathrm{non-b}}(\mathbf{b}_i)]}{w_l}$$
- Continue until chain is grown, $W(n) = \prod_{l=1}^{n} w_l$
- Similar procedure for old configuration, generate $k-1$ trial positions (trial position 1 is the old configuration itself), leading to $W(o)$
- Accept/reject according to
$$\mathrm{acc}(o \rightarrow n) = \min(1, W(n)/W(o))$$

Super-Detailed Balance (1)

Same chain can be grow for different sets of trial directions...



Super-Detailed Balance (2)

Flux of configurations

$$\begin{aligned} K(o \rightarrow n) &= \sum_{\mathbf{b}_n \mathbf{b}_o} K(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) \\ K(n \rightarrow o) &= \sum_{\mathbf{b}_n \mathbf{b}_o} K(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o) \end{aligned}$$

Detailed balance requires

$$K(o \rightarrow n) = K(n \rightarrow o)$$

Possible solution (**super-detailed balance**):

$$K(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) = K(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o)$$

for each $\mathbf{b}_n \mathbf{b}_o$.

Super-Detailed Balance (3)

Detailed balance for each set $\mathbf{b}_n \mathbf{b}_o$:

$$\begin{aligned} K(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) &= N(o) \times \alpha(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) \times \mathrm{acc}(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) \\ &= \exp[-\beta U(o)] \times C \exp[-\beta u_{\mathrm{bonded}}(n)] \times \\ &\quad \frac{\exp[-\beta u_{\mathrm{non-b}}(n)]}{W(n)} \times P(\mathbf{b}_n \mathbf{b}_o) \times \mathrm{acc}(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) \\ K(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o) &= \exp[-\beta U(n)] \times C \exp[-\beta u_{\mathrm{bonded}}(o)] \times \\ &\quad \frac{\exp[-\beta u_{\mathrm{non-b}}(o)]}{W(o)} \times P(\mathbf{b}_n \mathbf{b}_o) \times \mathrm{acc}(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o) \end{aligned}$$

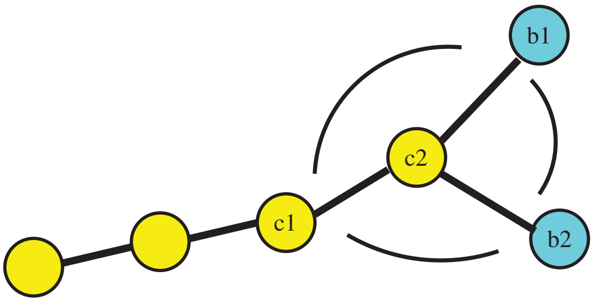
As

$$U = u_{\mathrm{non-b}} + u_{\mathrm{bonded}}$$

therefore

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

Branched Molecules (1)



$$P(\mathbf{b}_1,\mathbf{b}_2) \sim \exp[-\beta[u_{\rm bend}(\mathbf{c}_1,\mathbf{c}_2,\mathbf{b}_1)] + u_{\rm bend}(\mathbf{c}_1,\mathbf{c}_2,\mathbf{b}_2)] + u_{\rm bend}(\mathbf{b}_1,\mathbf{c}_2,\mathbf{b}_2)]]$$

Branched Molecules (2)

Use CBMC to generate internal configurations:

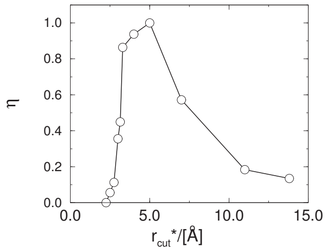
- Generate n_t *random* trial positions and select one (i) with a probability

$$P^{\rm int}(i) = \frac{\exp[-\beta U_{\rm bonded}(i)]}{\sum_{j=1}^{n_t} \exp[-\beta U_{\rm bonded}(j)]} = \frac{\exp[-\beta U_{\rm bonded}(i)]}{W^{\rm int}(n)}$$

- Repeat until k trial orientations are found; these are fed into CBMC leading to $W(n)$
- Repeat procedure for old configuration, leading to $W^{\rm int}(o)$ and $W(o)$.
- Accept or reject according to

$$\mathrm{acc}(o \to n) = \min\left(1, \frac{W(n) \times W^{\rm int}(n)}{W(o) \times W^{\rm int}(o)}\right)$$

Significant Speedup: Dual-Cutoff CBMC



- Grow chain with approximate (cheaper) potential; $W^\star$
- Correct for difference later
  (δu, difference real and approximate potential for *selected* configuration)

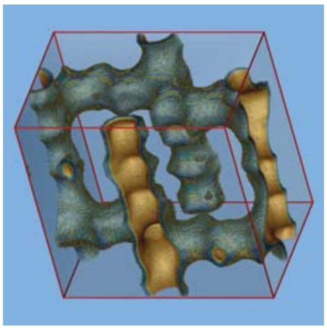
$$\mathrm{acc}(o \to n) = \min\left(1, \frac{W^\star(n)}{W^\star(o)} \times \exp[-\beta[\delta u(n) - \delta u(o)]]\right)$$

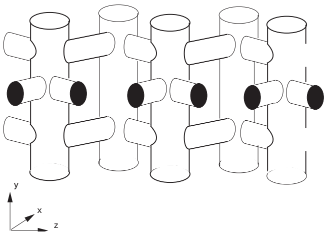
Application 1: Adsorption of Alkanes in MFI-type zeolite (1)

Zeolites:

- microporous channel structure
- crystalline, SiO_2 building blocks
- substitution of Si^{4+} by Al^{3+} and a cation $(Na^+$ or $H^+)$
- typical poresize: $4-12\AA$
- synthetic and natural; >190 framework types

Application 1: Adsorption of Alkanes in MFI-type zeolite (2)





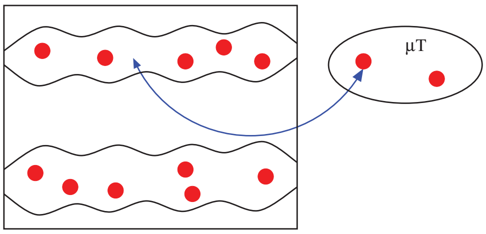
straight channels (y direction), zig-zag channels (xz plane) and intersections

---

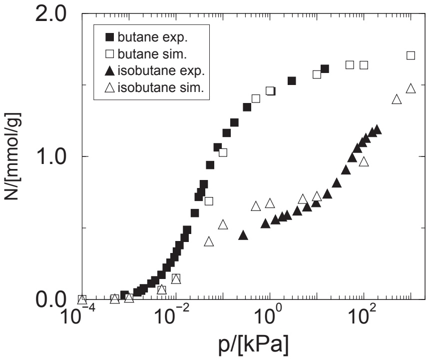
Application 1: Adsorption of Alkanes in MFI-type zeolite (3)

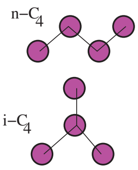
Grand-canonical (μVT) ensemble; number of particles (N) fluctuates

- system is coupled to particle reservoir at chemical potential μ and temperature T, statistical weight $\sim V^N \exp[\beta\mu N - \beta U(\mathbf{r}^N)]/\left(\Lambda^{3N} N!\right)$
- trial moves to exchange particles between zeolite and reservoir (using CBMC)
- equilibrium: $\mu_{\text{gas}} = \mu_{\text{zeolite}}$; measure average $\langle N \rangle$ for given μ and β



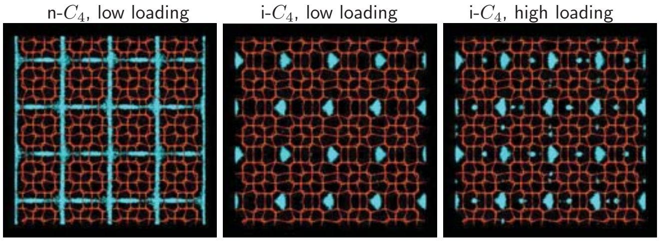
Application 1: Adsorption of Alkanes in MFI-type zeolite (4)





Vlugt et al, J. Am. Chem. Soc., 1998, 120, 5599

Application 1: Adsorption of Alkanes in MFI-type zeolite (5)



n-C_4, low loading

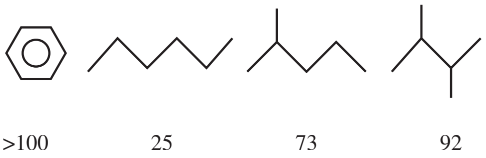
i-C_4, low loading

i-C_4, high loading

Vlugt et al, J. Am. Chem. Soc., 1998, 120, 5599

Application 1: Adsorption of Alkanes in MFI-type zeolite (6)

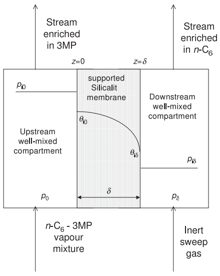
Research Octane Number (RON)



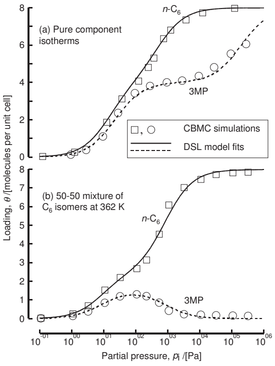
Application 1: Adsorption of Alkanes in MFI-type zeolite (7)

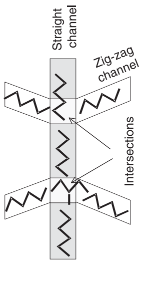
Flux	$n - C_6$	$i - C_6$	selectivity
pure	179	136	1.3
50%-50%	46	1.9	24

Experiments by J. Falconer, Univ. Colorado



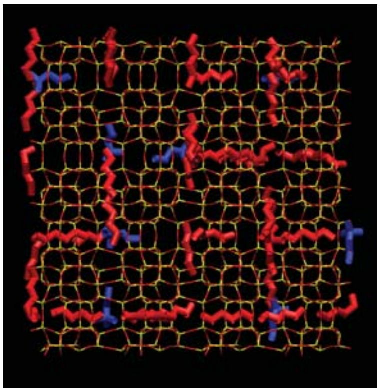
Application 1: Adsorption of Alkanes in MFI-type zeolite (8)



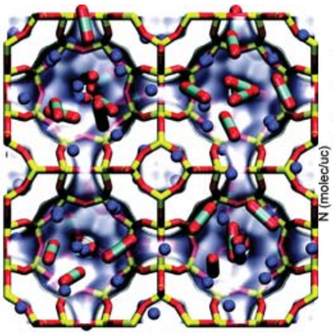


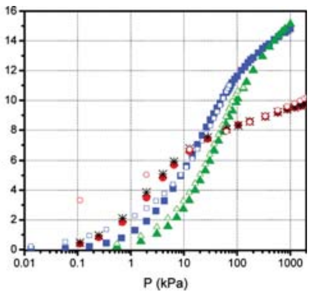
Application 1: Adsorption of Alkanes in MFI-type zeolite (9)

blue = branched (i-C_6) red = linear (n-C_6)



Application 2: Adsorption of CO_2 in Na^+ containing zeolites

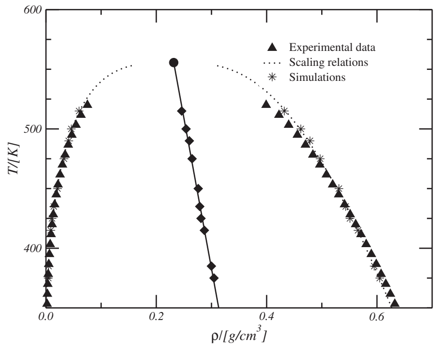




Sofia Calero et al., J. Phys. Chem. C, 2009, 113, 8814-8820

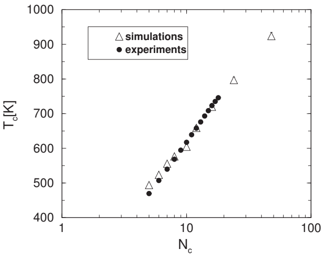
Application 3: Gibbs Ensemble Monte Carlo (1)

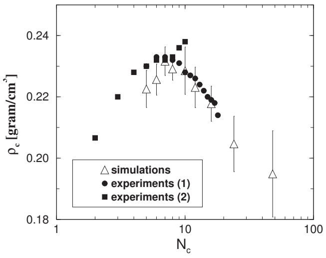
Heptane (n-C_7)



B. Smit, S. Karaborni, and J.I. Siepmann, J. Chem. Phys. 102, 2126 (1995)

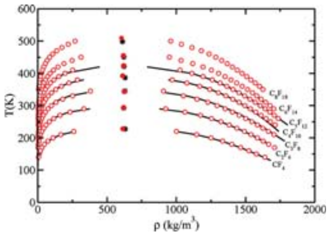
Application 3: Gibbs Ensemble Monte Carlo (2)

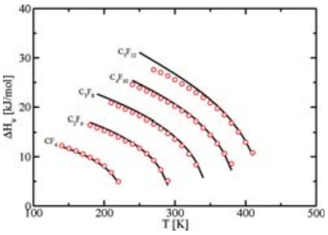




B. Smit, S. Karaborni, and J.I. Siepmann, J. Chem. Phys. 102, 2126 (1995)

Application 4: GCMC Histogram Reweighting





J.J. Potoff et al., J. Phys. Chem. B, 2009, 113, pp 14725-14731

Efficiency of CBMC

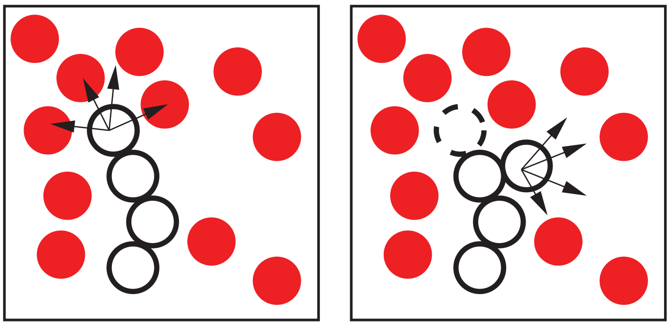
- k: number of trial directions
- a: probability that trial direction has a “favorable” energy
- growth can continue as long as at least 1 trial direction is “favorable”
- generate chain of length N successfully

$$P_{\text{success}} = (1 - (1-a)^k)^N = \exp[-cN]$$

- increasing k means increasing CPU time.

Dead-End Alley

Recoil Growth: Avoiding Dead-End Alley

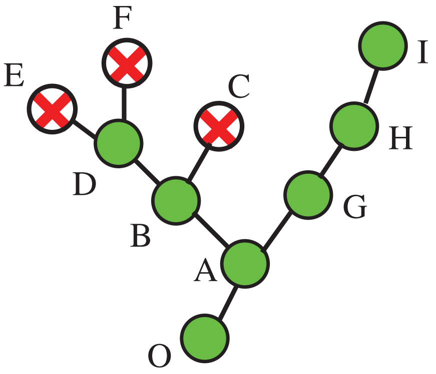


Recoil Growth Algorithm (1)

- Place first bead at random position
- Position (i) can be “open” or closed” depending on the environment (energy u_i); here we use $p_{\text{open}} = \min(1, \exp[-\beta u_i])$ and toss a coin.
- If “open”, continue with next segment
- If “closed”, try another trial direction up to a maximum of k
- If all k directions are closed, retract by one step
- Maximum retraction length: $l_{\max} - l + 1$
- l: recoil length, $l_{\max}$: maximum length obtained during the growth of the chain
- Computed weight $W(n)$ and repeat procedure for old configuration
- Accept or reject using $\text{acc}(o \to n) = \min(1, W(n)/W(o))$

Recoil Growth Algorithm (2)

Example for $k = 2$ and $l = 3$



Super Detailed Balance

In general,

$$N(o) \times \alpha(o \to n) \times \mathrm{acc}(o \to n) = N(n) \times \alpha(n \to o) \times \mathrm{acc}(n \to o)$$

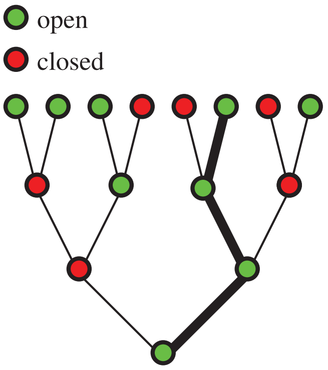
Therefore,

$$\mathrm{acc}(o \to n) = \min\left(1, \exp[-\beta \Delta U] \times \frac{\alpha(n \to o)}{\alpha(o \to n)}\right)$$

What about $\alpha(o \to n)$?

- Generate a tree t_n.
- Decide which parts of the tree are “open” or “closed” (O_n).
- Make a random walk on the tree (rw_n)

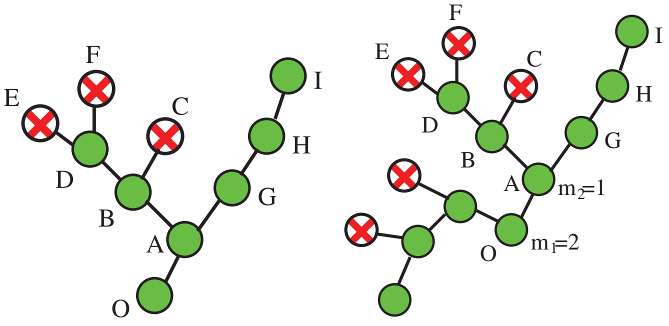
Random Walk on a Tree ($k = 2$, $l = 3$)



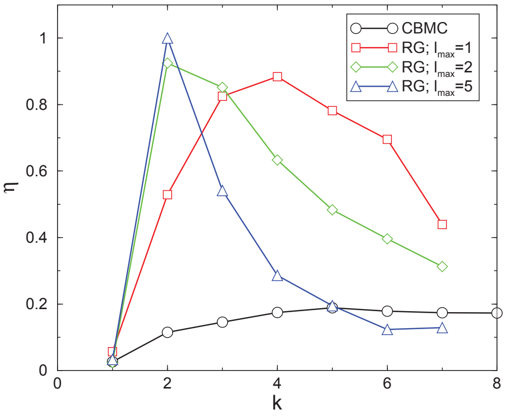
Super-Detailed Balance

$$\begin{aligned}
K(o \to n | t_n t_o O_n O_o) &= K(n \to o | t_n t_o O_n O_o) \\
\alpha(o \to n | t_n t_o O_n O_o) &= P(t_n) P(O_n | t_n) P(rw_n | t_n O_n) \times \\
&\quad P(t_o | rw_o) P(O_o | t_o rw_o) \\
\alpha(n \to o | t_n t_o O_n O_o) &= P(t_o) P(O_o | t_o) P(rw_o | t_o O_o) \times \\
&\quad P(t_n | rw_n) P(O_n | t_n rw_n) \\
\frac{P(O_n | t_n)}{P(O_n | t_n rw_n)} &= \prod_{i=1}^{n} p_i \\
P(rw_n | t_n O_n) &= \frac{1}{\prod_{i=1}^{n} m_i} \\
\mathrm{acc}(o \to n) &= \min\left(1, \exp[-\beta \Delta U] \times \frac{\prod_{i=1}^{n} \frac{m_i(n)}{p_i(n)}}{\prod_{i=1}^{n} \frac{m_i(o)}{p_i(o)}}\right)
\end{aligned}$$

Computing the Weight ($k = 2$, $l = 3$)



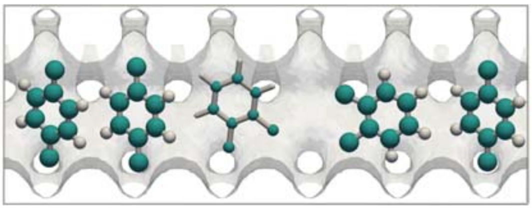
Efficiency of RG Compared to CBMC



Other Methods

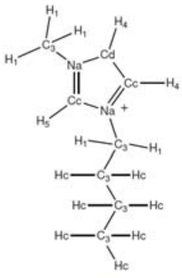
- Continuous Fractional Component Monte Carlo
  - system contains N molecules and one “fractional” molecule
  - interactions of the fractional molecule are described by order parameter λ
  - include trial-moves to change λ
  - “fractional” molecule can become a “real” molecule or disappear
  - Maginn, J. Chem. Theory Comput., 2007, 3, 451-1463
- Wormhole move
  - create an artificial “hole” in the system
  - use reptation steps to gradually insert the chain
  - accept/reject individual reptation steps
  - move is completed when the whole chain is transferred through the hole
  - Houdayer, Journal of Chemical Physics, 2002, 116, 1783-1787

Continuous Fractional Component Monte Carlo

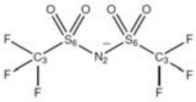


- Not inserting whole molecules, but step by step
- Slowly switching on/off interactions of a “ghost molecule”
- Maginn and co-workers; Dubbeldam, Vlugt et al., Journal of Chemical Theory and Computation, 2014, 10, 942-952.

[bmim][Tf2N]

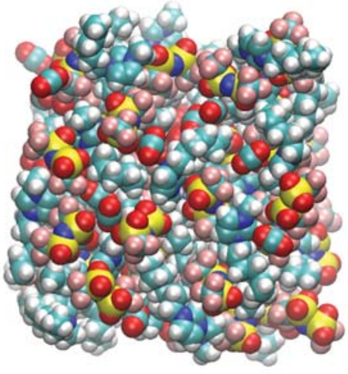


[bmim]$^+$

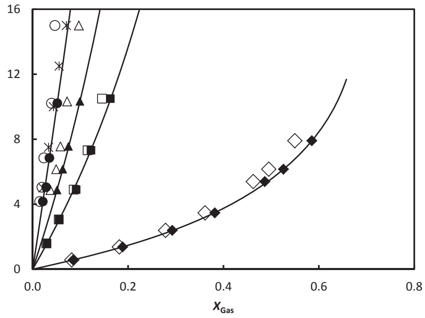


[Tf$_2$N]$^-$

[bmim][Tf2N]



Solubility of precombustion gasses in [bmim][Tf2N]



Solubility of CO_2, CH_4, CO, H_2 and N_2 in [bmim][Tf_2N] from MC simulations (open symbols) and experiments (filled symbols) at 333.15 K. CO_2 experiments (filled diamonds) and MC data (open diamonds); CH_4 experiments (filled squares) and MC data (open squares); CO experiments (filled triangles) and MC data (open triangles); H_2 experiments (filled circles) and MC data (open circles), and MC data of N_2 (stars). Lines: PR-EOS modeling

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Henry constants of CO_2, CH_4, CO, H_2, N_2, and H_2S in Selexol and [bmim][Tf_2N] at 333.15 K

solute	$H^{\text{exp.}}_{\text{Selexol}}$/MPa	$H^{\text{exp.}}_{\text{IL}}$/MPa	$H^{\text{sim.}}_{\text{IL}}$/MPa	difference/%
CO_2	6.81[a]	6.56	7.10	8.2
CH_4	40.13[a]	52.4	53.7	2.5
CO	-	95	125.9	33.0
H_2	193[b]	199	271.7	36.3
N_2	151[b]	-	225.7	-
H_2S (3S)	1.01[c]	2.17	1.15	47.0
H_2S (4S)	1.01	2.17	1.16	46.5
H_2S (5S)	1.01	2.17	1.17	46.1

[a] Taken from Rayer *et al.*[b] Calculated from Gainar *et al.* [c] Taken from Xu *et al.*

Kirkwood-Buff theory for finite systems (1)

Integrals of pair correlation functions (PCFs) are related to fluctuations in the grand-canonical ensemble

$$\begin{aligned} G_{\alpha\beta}^{V} &\equiv 4\pi \int_0^\infty (g_{\alpha\beta}^{\mu VT}(r)-1)r^2 \mathrm{d}r \\ &= V\frac{\langle N_\alpha N_\beta\rangle - \langle N_\alpha\rangle\langle N_\beta\rangle}{\langle N_\alpha\rangle\langle N_\beta\rangle} - \frac{V\delta_{\alpha\beta}}{\langle N_\alpha\rangle} \end{aligned}$$

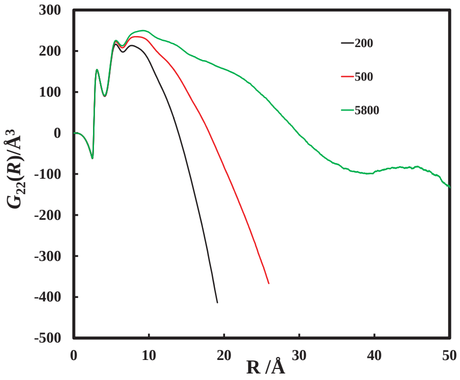
Using PCFs from MD:

$$G_{\alpha\beta}^{V} \approx \hat{G}_{\alpha\beta}(R) = 4\pi \int_0^R (g_{\alpha\beta}^{NVT}(r)-1)r^2 \mathrm{d}r$$

Often used, but is it correct?

Kirkwood-Buff theory for finite systems (2)

$$\hat{G}_{\alpha\beta}(R) = 4\pi \int_0^R (g_{\alpha\beta}^{NVT}(r)-1)r^2 \mathrm{d}r$$



Kirkwood-Buff theory for finite systems (3)

$$\hat{G}_{\alpha\beta}(R) = 4\pi \int_0^R (g_{\alpha\beta}^{NVT}(r)-1)r^2 \mathrm{d}r$$

$\hat{G}_{\alpha\beta}(R)$ is not a valid approximation for the KB coefficient. For finite volumes, the exact expression is:

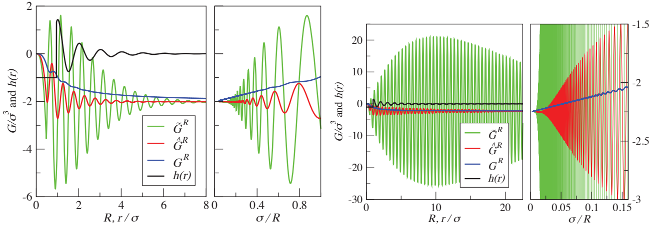
$$\begin{aligned} G_{\alpha\beta}^{V} &\equiv \frac{1}{V}\int_V\int_V (g_{\alpha\beta}^{NVT}(r_{12})-1)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ &= 4\pi\int_0^{2R}(g_{\alpha\beta}^{NVT}(r)-1)r^2\left(1-\frac{3r}{4R}+\frac{r^3}{16R^3}\right)\mathrm{d}r \\ &\equiv G_{\alpha\beta}(R) \end{aligned}$$

One can rigorously show that $G_{\alpha\beta}(R)$ scales as $1/R$.

P. Krüger, S.K. Schnell, D. Bedeaux, S. Kjelstrup, T.J.H. Vlugt, J.M. Simon
J. Phys. Chem. Lett., 2013, 4, 235-238.

Kirkwood-Buff theory for finite systems (4)

$\chi = 2$ (left) and $\chi = 20$ (right)



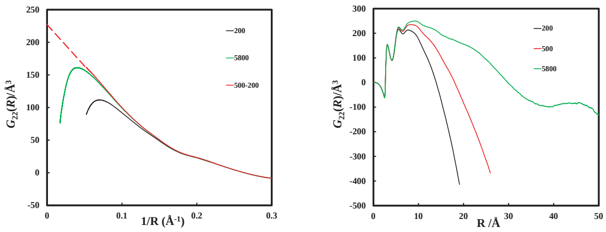
$$h(r) = g(r) - 1 = \begin{cases} \frac{3/2}{r/\sigma}\exp\left(\frac{1-r/\sigma}{\chi}\right)\cos\left[2\pi(\frac{r}{\sigma}-\frac{21}{20})\right], & \frac{r}{\sigma} \geq \frac{19}{20} \\ -1, \ r < \frac{19}{20}\sigma. \end{cases}$$

P. Krüger, S.K. Schnell, D. Bedeaux, S. Kjelstrup, T.J.H. Vlugt, J.M. Simon
J. Phys. Chem. Lett., 2013, 4, 235-238.

Kirkwood-Buff theory for finite systems (5)

MD simulations: beware of the finite-size effect of $g(r)$

$$g^{\infty}_{\alpha\beta}(r) \approx g^{N}_{\alpha\beta}(r) + \frac{c(r)}{N}$$



Equimolar mixture of methanol and acetone, LJ+electrostatics, 298K, 1atm

The End

Questions ??

Continuous Fractional Component Monte Carlo

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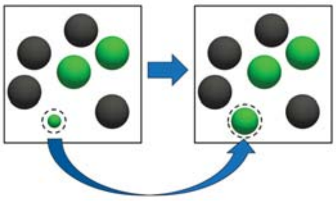
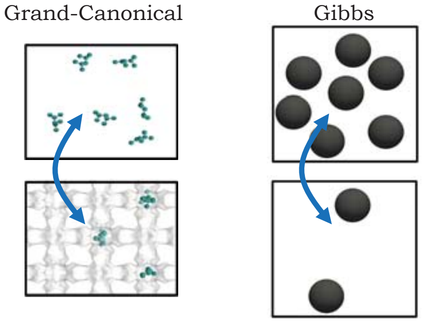
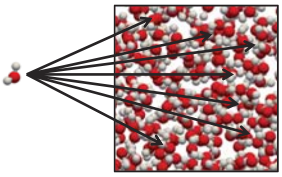


Grand-Canonical and Gibbs Ensembles Critically Rely on Molecule Transfer



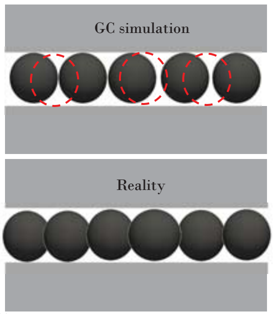
Insertion/Deletion of Molecules

- Very low acceptance probability at high densities
  - Problem: Molecules inserted in one MC step
  - Problem: Depends on occurrence of spontaneous cavities
  - Dense liquids: water at room temperature
  - Deletion: Molecule has very favourable interactions



Adsorption in a nearly full pore

- At high loadings acceptance probability is almost zero
- Sampled configurations are not representative of real configurations
- No spontaneous cavity is formed
- Same problem with Widom Test particle insertion (zero * ∞ problem)



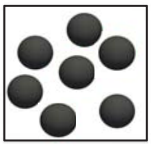
Probability of wining 1 M Euro in Lottery

$$P(\text{Winning}) = \frac{\#\text{Won}}{\#\text{Entered}}$$

Expanded Ensembles

- Conventional (NVT)

$$Q(N,V,T) = \frac{V^N}{\Lambda^{3N} N!}\int dr^N \exp[-\beta u(r^N)]$$



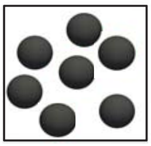
- Expanded ensemble
  - Ensemble is expanded by number of parameters

$$Q_{\text{Ex}}(N,V,T,x,y,z,\ldots) = \ldots$$

Escobedo, et. al., J. Chem. Phys., 1995, 7, 2703–2710

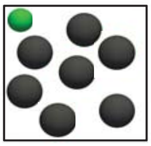
Continuous Fractional Component Mote Carlo

- Conventional (NVT)



$$Q(N,V,T)=\frac{V^N}{\Lambda^{3N}N!}\int dr^N \exp[-\beta u(r^N)]$$

- CFCMC
  - 1 molecule with interactions scaled with Additional parameter λ



$$Q_{\text{CFCMC}}(N,V,T,\lambda)=\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int_0^1 d\lambda\int dr^N \exp[-\beta u(r^N)]$$
$$\int dr_{\text{F}} \exp[-\beta u_F(r^N,r_{\text{F}},\lambda)]$$

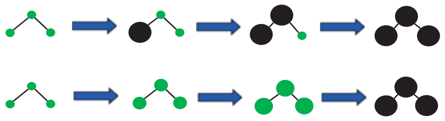
Shi, et. al., J. Chem. Theo. Comp., 2007, 4, 1451–1463

CFCMC

- Interactions of fractional molecule with whole molecules are scaled with scaling parameter λ

$$u_{\text{LJ}}(r,\lambda)=\lambda 4\varepsilon\left(\frac{1}{\left[\frac{1}{2}(1-\lambda)^2+\left(\frac{r}{\sigma}\right)^6\right]^2}-\frac{1}{\left[\frac{1}{2}(1-\lambda)^2+\left(\frac{r}{\sigma}\right)^6\right]}\right)$$

  - When $\lambda = 0$ ➡ Ideal gas Molecule
  - When $\lambda = 1$ ➡ Whole Molecule



CFCMC

$$Q_{\text{CFCMC}}(N,V,T,\lambda)=\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int_0^1 d\lambda\int dr^N \exp(-\beta u(r^N))\int dr_{\text{F}} \exp[-\beta u_F(r^N,r_{\text{F}},\lambda)]$$

- Additional trial move: changing the value of λ
- Acceptance rule

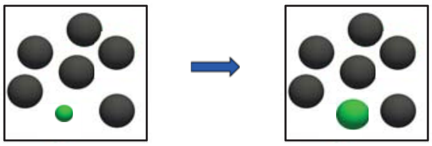
$$\text{acc}(\text{o}\rightarrow\text{n})=\frac{p(\text{n})}{p(\text{o})}$$

$$\mathcal{N}(\text{o})=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\exp[-\beta U_{\text{o}}(r^N,r_{\text{F}},\lambda_{\text{o}})]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$

$$\mathcal{N}(\text{n})=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\exp[-\beta U_{\text{n}}(r^N,r_{\text{F}},\lambda_{\text{n}})]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$

➡

$$\text{acc}(\text{o}\rightarrow\text{n})=\min\left[1,\exp[-\beta\Delta U]\right]$$



Chemical Potential

$$p(\lambda=1)=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int dr^N \exp[-\beta u(r^N)]\int dr_{\text{F}} \exp[-\beta u_F(r^N,r_{\text{F}},\lambda=1)]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$
$$=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int dr^{N+1} \exp[-\beta u(r^{N+1})]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$

$$p(\lambda=0)=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int dr^N \exp[-\beta u(r^N)]\int dr_{\text{F}} \exp[-\beta u_F(r^N,r_{\text{F}},\lambda=0)]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$
$$=\frac{\frac{V^{N+1}}{\Lambda^{3(N+1)}N!}\int dr^N \exp[-\beta u(r^N)]}{Q_{\text{CFCMC}}(N,V,T,\lambda)}$$

$$\frac{p(\lambda=1)}{p(\lambda=0)}=\frac{\int dr^{N+1} \exp[-\beta u(r^{N+1})]}{\int dr^N \exp[-\beta u(r^N)]}$$

CFCMC

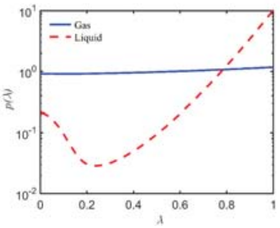
- Chemical Potential

$$\mu_{\text{ex}} = -k_B T \ln\left[\frac{\int dr^{N+1} \exp[-\beta u(r^{N+1})]}{\int dr^{N} \exp[-\beta u(r^{N})]}\right] = -k_B T \ln\left[\frac{p(\lambda=1)}{p(\lambda=0)}\right]$$

$$\mu = -k_B T \ln\left[\frac{Q(N+1,V,T)}{Q(N,V,T)}\right] \Rightarrow \mu = \underbrace{-k_B T \ln\left[\frac{V/\Lambda^3}{N+1}\right]}_{\mu_{\text{id}}} \underbrace{-k_B T \ln\left[\frac{\int dr^{N+1} \exp[-\beta u(r^{N+1})]}{\int dr^{N} \exp[-\beta u(r^{N})]}\right]}_{\mu_{\text{ex}}}$$

CFCMC

- Flat probability distribution of λ is preferred
- Biasing functions are used to make the observed probability distribution flat



CFCMC

Modified Ensemble:

$$Q_{\text{Modified}} = \frac{V^{N+1}}{\Lambda^{3(N+1)} N!}\int_0^1 d\lambda \int dr^N \exp[-\beta u(r^N)]$$

$$\int dr_{\text{F}} \exp[-\beta u_{\text{F}}(r_{\text{F}}, r^N, \lambda)] \exp[W(\lambda)]$$

- Using biasing function, we are not computing Boltzmann averages anymore
- To obtain the correct Boltzmann averages of observable X

$$\langle X \rangle_{\text{Modified}} = \frac{\langle X \exp[-W(\lambda)]\rangle_{\text{Modified}}}{\langle \exp[-W(\lambda)]\rangle_{\text{Modified}}}$$

Wang-Landau Algorithm

- Initially Histogram and Weight Function are set to zero

$$H(\lambda) = 0 \textbf{ and } W(\lambda) = 0$$

- When certain λ is visited

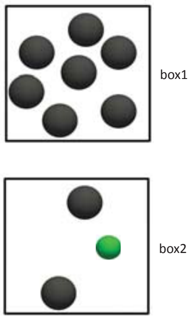
$$H(\lambda) = H(\lambda) + 1 \quad \textbf{and} \quad W(\lambda) = W(\lambda) - F$$

- F is the modification factor
- When Histogram ($H(\lambda)$) is flat enough the value of F is reduced and the $H(\lambda)$ is set to zero and $W(\lambda)$ is kept
- Iterate until $W(\lambda)$ converges
- Note: detailed balance is violated

Wang et. al., Phys. Rev. Lett., 2001, 86, 2050 - 2053

Formulation of CFCMC GE

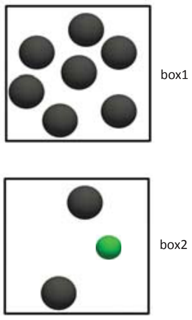
- One fractional molecule per component
- Fractional molecule can be in either of the simulation boxes
- Three additional trial moves to facilitate particle exchange



Partition function CFCMC Gibbs Ensemble

$$Q_{\mathrm{CFCMC}} = \frac{1}{\Lambda^{3(N_T+1)}(N_T)!}\sum_{i=1}^{2}\sum_{N_1=0}^{N_T}\int_0^1 d\lambda \int_0^{V_T} dV_1 V_1^{N_1+\delta_{i,1}}(V_T - V_1)^{N_T-N_1+\delta_{i,2}}$$
$$\frac{(N_T)!}{(N_1)!(N_T-N_1)!}\times\int ds^{N_1}\exp[-\beta U_{\mathrm{int},1}(s^{N_1})]$$
$$\int ds^{N_T-N_1}\exp[-\beta U_{\mathrm{int},2}(s^{N_T-N_1})]\times$$
$$\begin{pmatrix} \delta_{i,1}\int ds^1_{\mathrm{frac}}\exp[-\beta U_{\mathrm{frac},1}(s^1_{\mathrm{frac}}, s^{N_1}, \lambda)] + \\ \delta_{i,2}\int ds^2_{\mathrm{frac}}\exp[-\beta U_{\mathrm{frac},2}(s^2_{\mathrm{frac}}, s^{N_T-N_1}, \lambda)] \end{pmatrix}$$

- where $\delta_{i,1} = 1$ when the fractional molecule is in box 1 and otherwise $\delta_{i,1} = 0$



Poursaeidesfahani, et. al., J. Chem. Theo. Comp., 2016, 12, 1481–1490

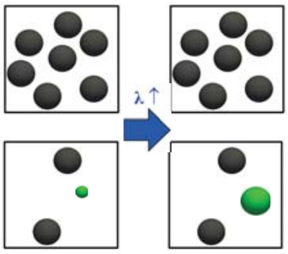
Changing the Strength of Interactions between the Fractional Molecule and Whole Molecules

- Acceptance rule

$$\mathrm{acc}(o \to n) = \min\left(1, \exp\left[-\beta\Delta U\right]\right)$$

- Rejected when

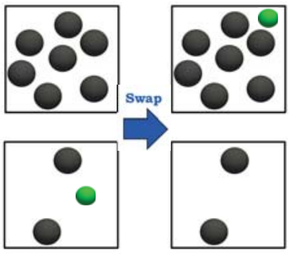
$$\lambda \notin \langle 0,1 \rangle$$



Swapping the Fractional Molecule to the Other Box

- Very efficient at low values of λ
- Acceptance rule

$$\mathrm{acc}(o \to n) = \min\left(1, \frac{V_T - V_1}{V_1}\exp\left[-\beta\Delta U\right]\right)$$

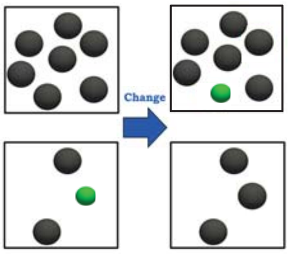


Changing the identity of the Fractional Molecule with a Whole Molecule in the other Box

- Very efficient at high values of λ

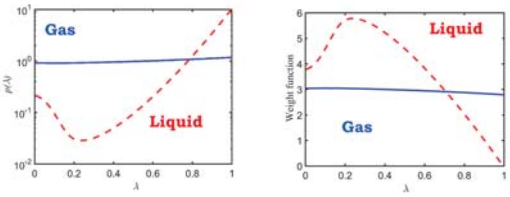
- Acceptance rule

$$\mathrm{acc}(o \to n) = \min\left(1, \frac{N_T - N_1}{N_1 + 1} \exp\left[-\beta \Delta U\right]\right)$$



Chemical Potential

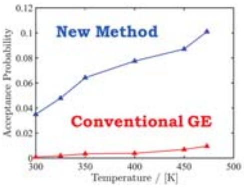
$$\mu_j \approx -k_B T \ln \left\langle \frac{V_1 / \Lambda^3}{N_1 + 1} \right\rangle - k_B T \ln\left(\frac{p_1(\lambda \uparrow 1)}{p_1(\lambda \downarrow 0)} \right)$$



Performance

- Excellent agreement in densities and chemical potentials for TiP3P-EW water model

- **30 times higher** acceptance for molecule exchange at low temperatures



GE					
T /[K]	ρ_l /[kg m^{-3}]	ρ_g /[kg m^{-3}]	μ_l /[kJ mol^{-1}]	μ_g /[kJ mol^{-1}]	$P_{acc}(Swap)_{GE}$
400	882 (2)	1.7 (1)	-32 (2)	-33.1 (1)	2.86×10^{-3}
450	798 (2)	6.8 (1)	-32.2 (8)	-32.9 (2)	6.83×10^{-3}
473	754 (5)	12.2 (5)	-32.4 (7)	-33.0 (3)	9.52×10^{-3}

CFCMC GE					
T /[K]	ρ_l /[kg m^{-3}]	ρ_g /[kg m^{-3}]	μ_l /[kJ mol^{-1}]	μ_g /[kJ mol^{-1}]	$P_{acc}(Change)_{CFCMCGE}$
400	882 (2)	1.7 (1)	-33.2 (6)	-33.0 (1)	7.75×10^{-2}
450	798 (2)	6.7 (1)	-33.3 (5)	-32.8 (1)	8.71×10^{-2}
473	753 (2)	12.2 (2)	-33.4 (5)	-32.9 (1)	1.01×10^{-1}

Chemical Potential

- Widom insertion method fails to compute the correct chemical potential of the liquid phase

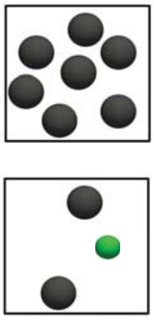
$$\mu_j \approx -k_B T \ln \left\langle \frac{V_1 / \Lambda^3}{N_1 + 1} \right\rangle - k_B T \ln\left(\frac{p_1(\lambda \uparrow 1)}{p_1(\lambda \downarrow 0)} \right)$$

T=350K	New Method		Widom	
	μ_l /[kJ mol^{-1}]	μ_g /[kJ mol^{-1}]	μ_l /[kJ mol^{-1}]	μ_g /[kJ mol^{-1}]
SPC	-33.3(4)	-33.6(1)	-31(2)	-33.6(1)
TiP3P-EW	-33.3(4)	-33.6(1)	-31(2)	-36.6(1)
TiP4P-EW	-35.6(4)	-36.5(2)	-32(1)	-36.5(1)
TiP5P-EW	-31.1(5)	-31.5(1)	-29(1)	-31.5(1)

- New method does not rely on occurrence of spontaneous cavities in liquid

Today's Exercise

- Simulate the VLE of LJ particles using CFCMC GE algorithm
  - – Calculate the chemical potential of the two phases
  - – How Wang-Landau algorithm works?
  - – Importance of using an appropriate weight function
  - – Effect of the density on acceptance probabilities
  - – Comparison of conventional GE / CFCMC GE in terms of results/efficiency



Questions

References:

- Poursaeidesfahani, A., et al. J. Chem. Theo. Comp. 2017, 13, 4452-4466.
- Poursaeidesfahani, A., et al. J. Mol. Sim. Comp. 2017, 43.3, 189-195.
- Poursaeidesfahani, A., et al. J. Chem. Theo. Comp. 2016, 12, 1481-1490.

Gibbs Ensemble

- Vapour-Liquid Equilibria (VLE) is vary important for many processes
- Simulations in the Gibbs Ensemble are widely used to study VLE
- Fixed temperature ➡ $T_1 = T_2$
- Volume exchange ➡ $P_1 = P_2$
- Molecule exchange ➡ $\mu_1 = \mu_2$
- Very low number of molecule exchange at low temperatures (high liquid density)

$$\mu_1 \overset{?}{=} \mu_2$$