

Configurational-Bias Monte Carlo

Thijs J.H. Vlugt

Professor and Chair Engineering Thermodynamics
Delft University of Technology
Delft, The Netherlands

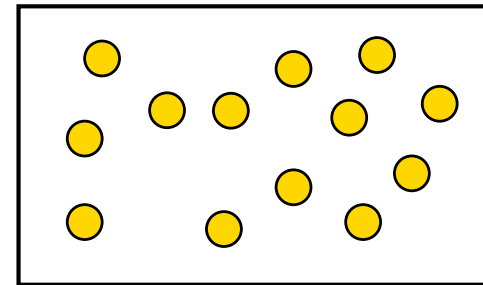
t.j.h.vlugt@tudelft.nl

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Random Sampling versus Metropolis Sampling (1)

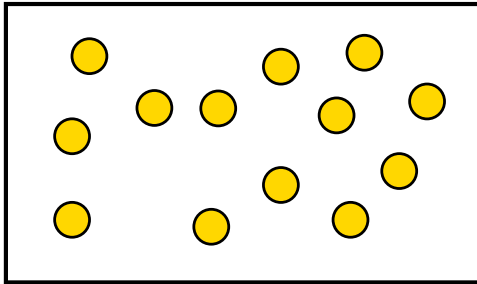
N interacting particles in volume V at temperature T



- 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 $\beta = 1/(k_B T)$

Random Sampling versus Metropolis Sampling (2)

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



$$U(\mathbf{r}^N) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N u(r_{ij}) = \sum_{i < j} u(r_{ij})$$

$$Q(N, V, T) = \frac{1}{\Lambda^{3N} N!} \int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]$$

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

Random Sampling versus Metropolis Sampling (3)

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

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

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

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

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

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

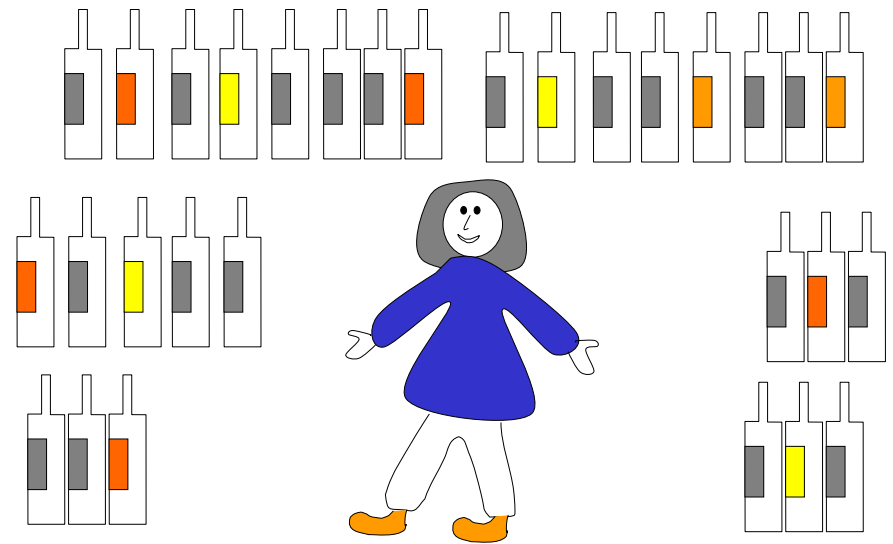
Simulation Technique (1)

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

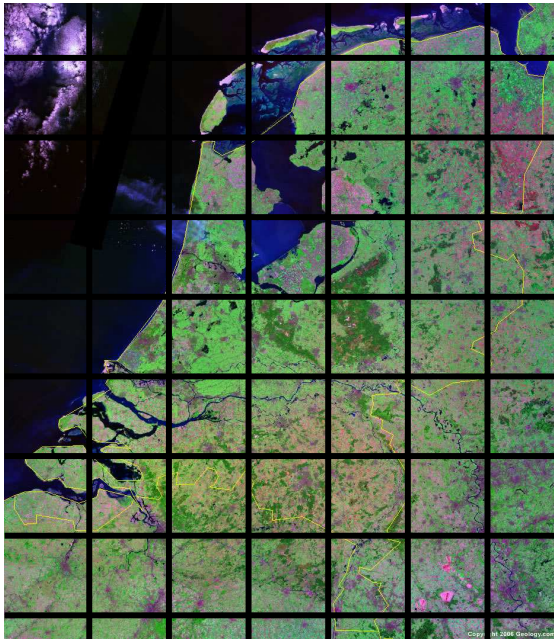


Simulation Technique (2)

Bottoms up



Simulation Technique (3)



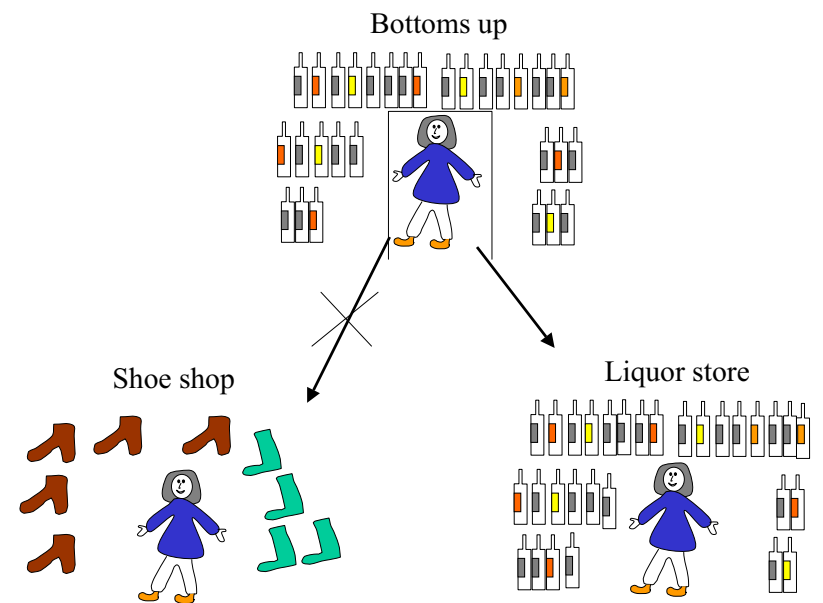
Simulation Technique (4)



Simulation Technique (5)



Simulation Technique (6)



Metropolis Monte Carlo (1)

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

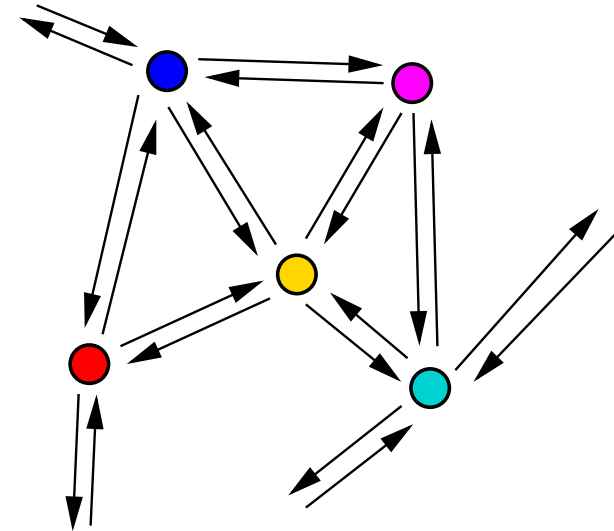


Nick Metropolis

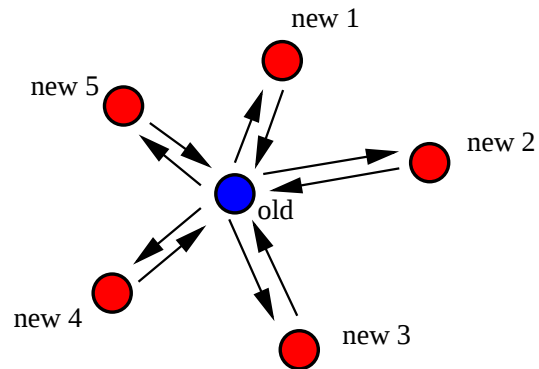
N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller and E. Teller, "Equation of State Calculations by Fast Computing Machines," J. Chem. Phys., 1953, 21, 1087-1092.

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



leaving state o = entering state o

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

$\mathcal{N}(i)$: 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

$\text{acc}(x \rightarrow y)$: probability to accept move from state x to state y

Detailed Balance (1)

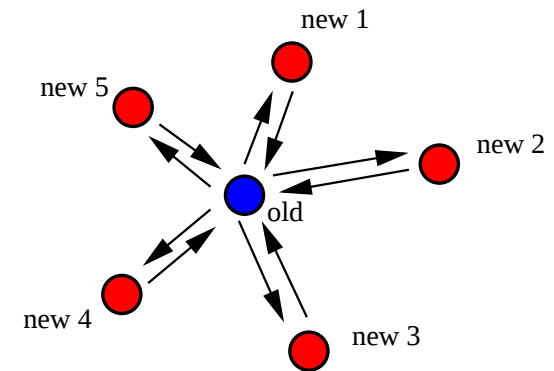
Requirement (balance):

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

Detailed balance: much stronger condition

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

for every pair o, n



Detailed Balance (2)

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

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

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

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

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

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

Metropolis Acceptance Rule

General:

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

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

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

Note that $\min(a, b) = a$ 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 $\text{acc}(o \rightarrow n)$

Monte Carlo Casino



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

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

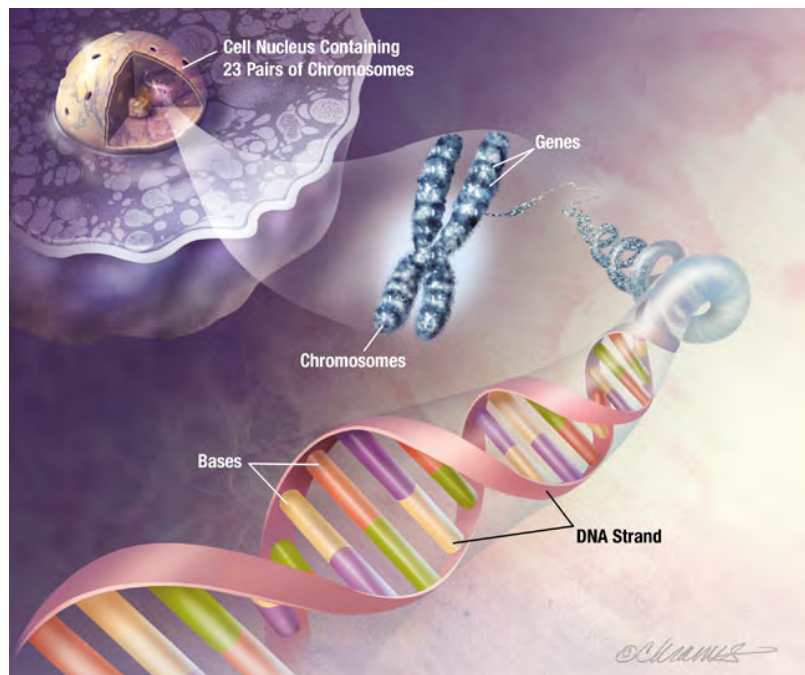
A : constant

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

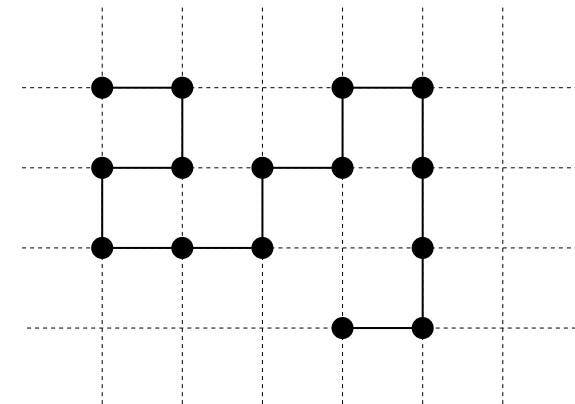
$$P(r_{\text{new}}) \sim \exp \left[-\frac{(r_{\text{new}} - (r_{\text{old}} + A \times F(o)))^2}{4A} \right]$$

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

Chain Molecules



Self-Avoiding Walk on a Cubic Lattice



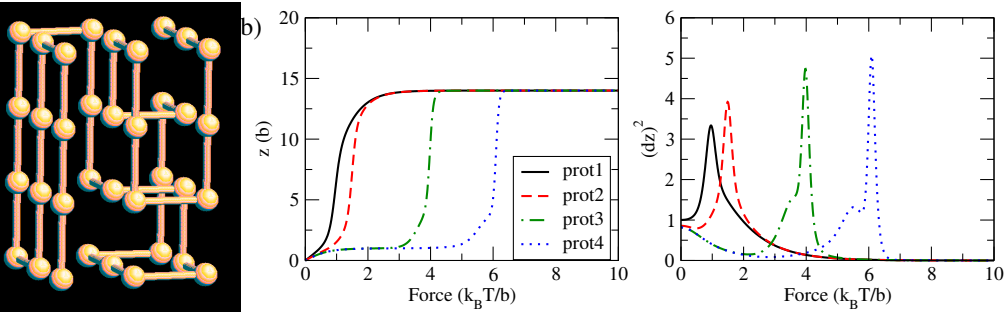
- 3D lattice; 6 lattice directions
- only 1 monomer per lattice site (otherwise $U = \infty$)
- interactions only when $|r_{ij}| = 1$ and $|i - j| > 1$

Simple Model for Protein Folding

20 by 20 interaction matrix Δ_{ij}

YPDLTKWHAMEAGKIRFSVPDACLNGEGIRQVTLN

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



Number of Configurations without Overlap

Random Chains:

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

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	...	...	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 ($j = 1, 2, \dots, k$) each with energy u_{ij}

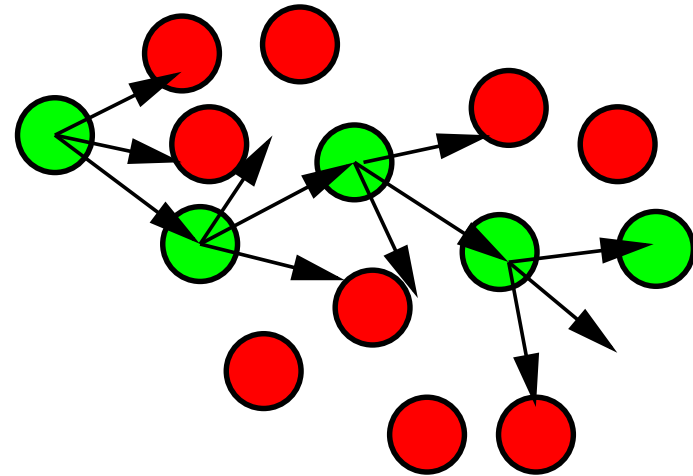
3. Select trial direction j^* with a probability

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

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

Rosenbluth Sampling (2)

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



Rosenbluth Sampling (3)

Probability to choose trial direction j^* for the i th monomer

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

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

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

Rosenbluth Sampling (4)

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

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

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

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

The unweighted distribution is called the Rosenbluth distribution:

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

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

Intermezzo: Ensemble Averages at Different Temperatures

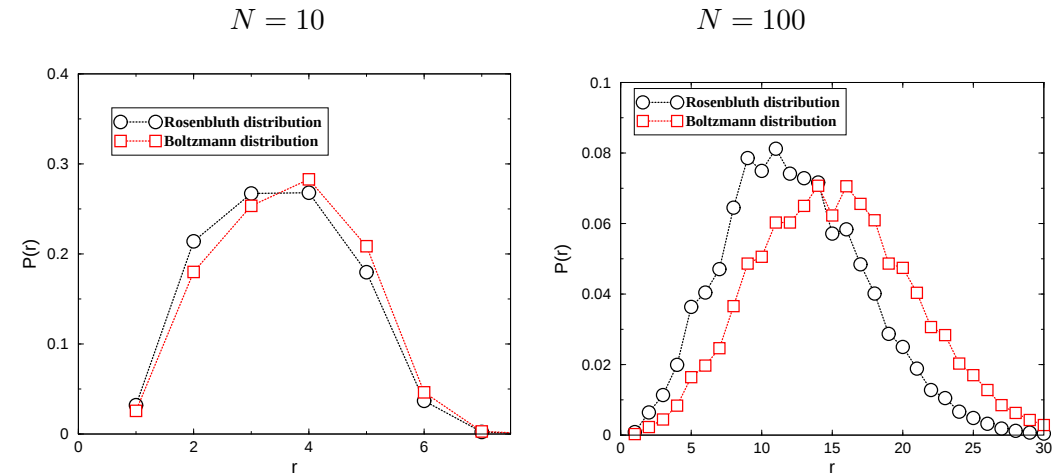
Ensemble averages at β^* can (in principle) be computed from simulations at β :

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

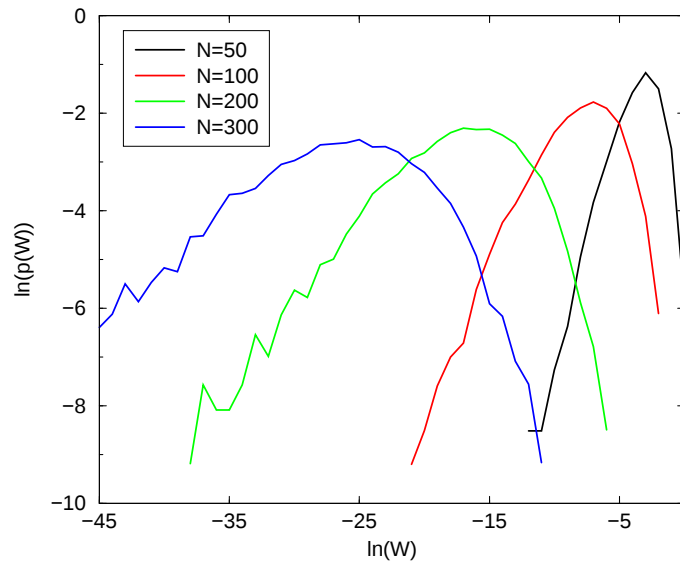
Useful or not???

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:

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

Two additional elements:

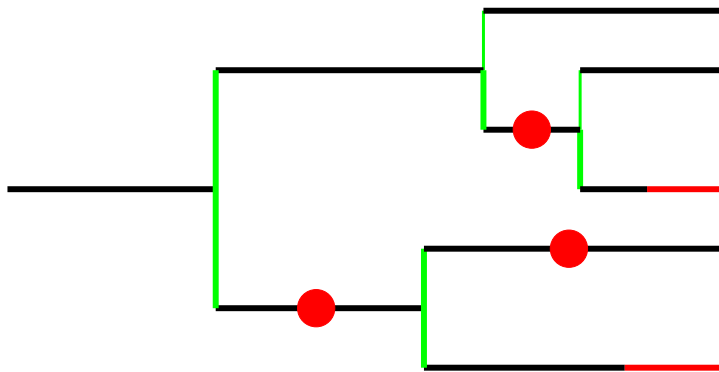
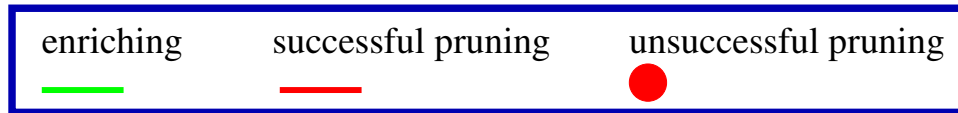
- **Enriching**

If $W > W_{\max}$ 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**

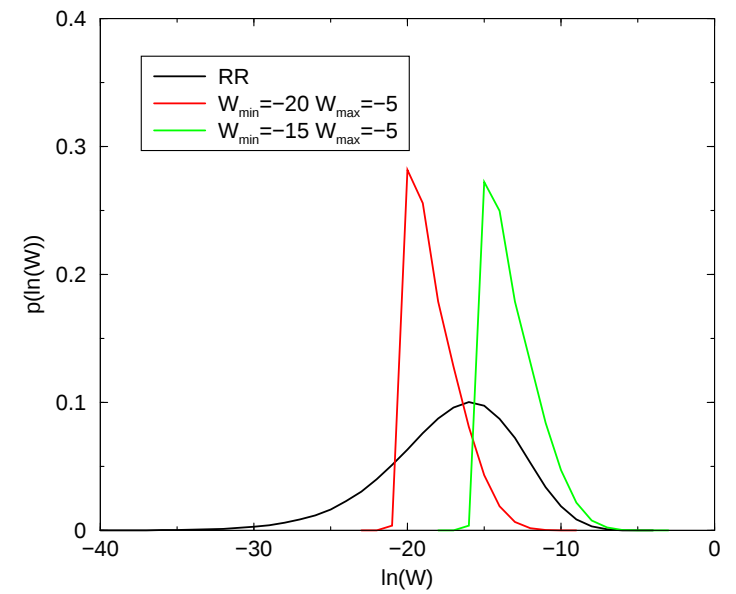
If $W < W_{\min}$ during the construction of a chain, with a probability of $1/2$ the chain is pruned resulting in $W = 0$. If the chain survives, the Rosenbluth weight is multiplied by 2 and the growth of the chain is continued.

Pruned-Enriched Rosenbluth Method (2)



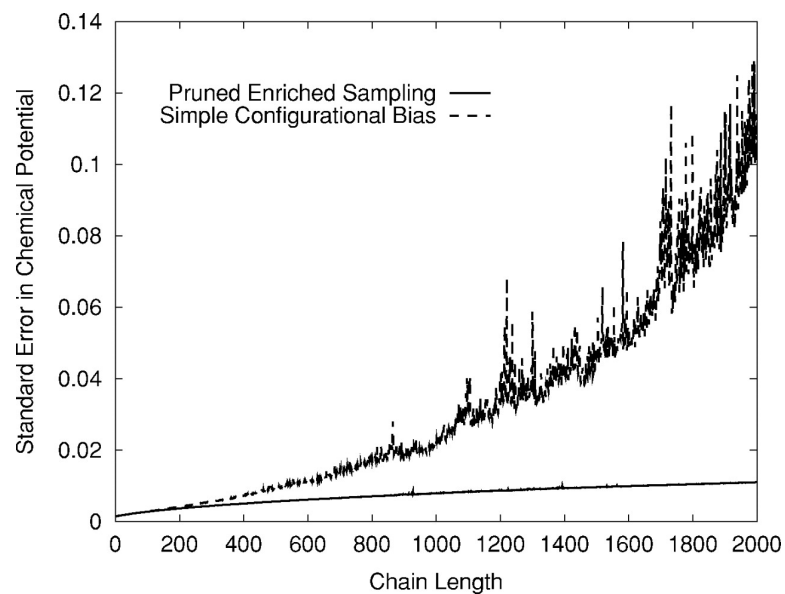
Pruned-Enriched Rosenbluth Method (3)

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**

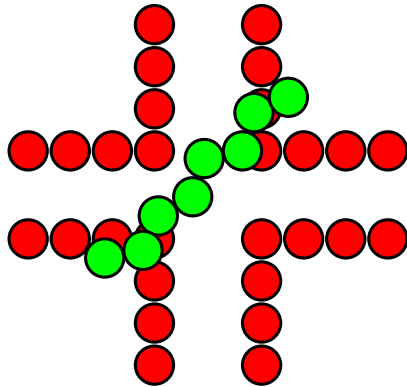
- create single chain conformations, and use correct weight factor (random insertion, Rosenbluth scheme, PERM) to compute single chain averages
- **single chain only; no Markov chain**

- **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)

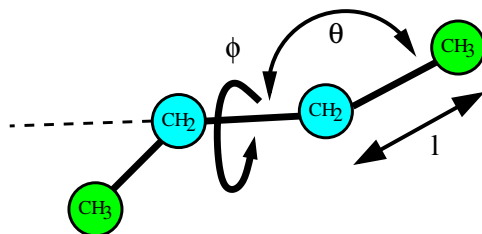
$$U_{\text{bonded}} = U_{\text{stretch}}(l) + U_{\text{bend}}(\theta) + U_{\text{tors}}(\phi)$$

$$P(l) \sim dl l^2 \exp[-\beta u(l)]$$

$$P(\theta) \sim d\theta \sin(\theta) \exp[-\beta u(\theta)]$$

$$P(\phi) \sim d\phi \exp[-\beta u(\phi)]$$

Generate Trial Configurations: Linear Alkane



$$u(l) = (k_l/2) (l - l_0)^2$$

$$u(\theta) = (k_\theta/2) (\theta - \theta_0)^2$$

$$u(\phi) = \sum_{i=0}^5 c_i \cos^i(\phi)$$

$$P(l) \sim dl l^2 \exp[-\beta u(l)]$$

$$P(\theta) \sim d\theta \sin(\theta) \exp[-\beta u(\theta)]$$

$$P(\phi) \sim d\phi \exp[-\beta u(\phi)]$$

Generate a Random Number from a Distribution (1)

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

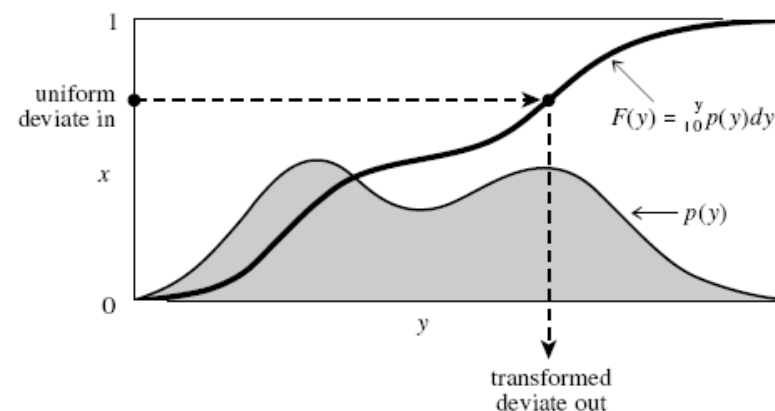


Figure 7.2.1. Transformation method for generating a random deviate y from a known probability distribution $p(y)$. The indefinite integral of $p(y)$ must be known and invertible. A uniform deviate x is chosen between 0 and 1. Its corresponding y on the definite-integral curve is the desired deviate.

Generate a Random Number from a Distribution (2)

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

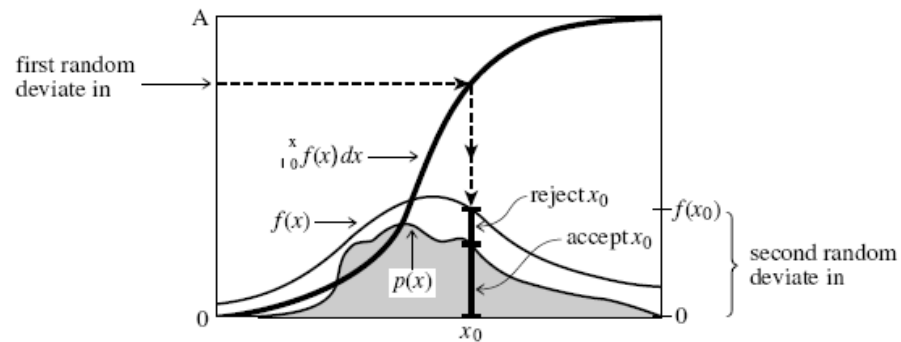


Figure 7.3.1. Rejection method for generating a random deviate x from a known probability distribution $p(x)$ that is everywhere less than some other function $f(x)$. The transformation method is first used to generate a random deviate x of the distribution f (compare Figure 7.2.1). A second uniform 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  $\theta$  and  $\phi$ 

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

$$P(\mathbf{b}) \sim \exp[-\beta u_{\text{bonded}}(\mathbf{b})]$$

- Compute non-bonded energy, select configuration i with a probability

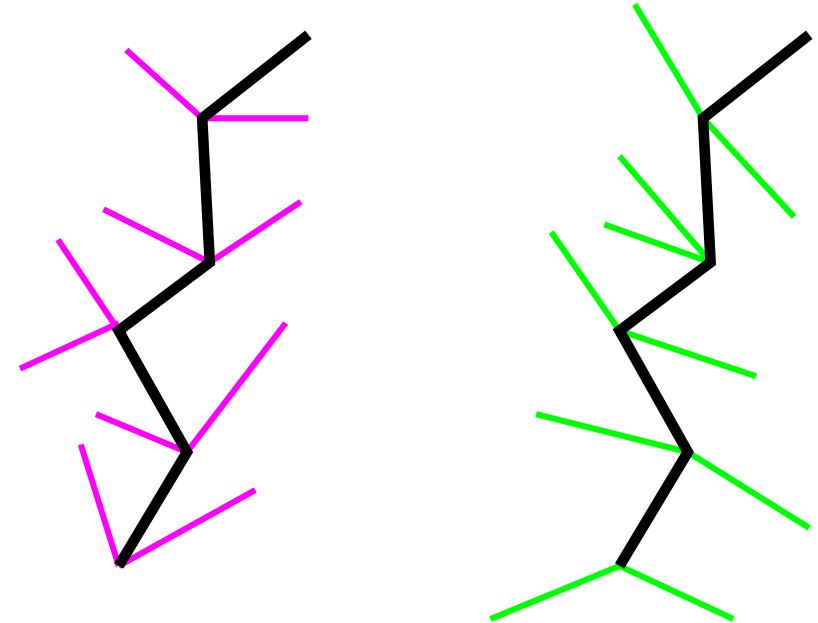
$$P(\mathbf{b}_i) = \frac{\exp[-\beta u_{\text{non-b}}(\mathbf{b}_i)]}{\sum_{j=1}^k \exp[-\beta u_{\text{non-b}}(\mathbf{b}_j)]} = \frac{\exp[-\beta u_{\text{non-b}}(\mathbf{b}_i)]}{w_i}$$

- 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

$$\text{acc}(o \rightarrow n) = \min(1, W(n)/W(o))$$

Super-Detailed Balance (1)

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



Super-Detailed Balance (2)

Flux of configurations

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

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

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 $\mathbf{b}_n \mathbf{b}_o$:

$$K(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) = N(o) \times \alpha(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o) \times \text{acc}(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o)$$

$$= \exp[-\beta U(o)] \times C \exp[-\beta u_{\text{bonded}}(n)] \times \frac{\exp[-\beta u_{\text{non-b}}(n)]}{W(n)} \times P(\mathbf{b}_n \mathbf{b}_o) \times \text{acc}(o \rightarrow n | \mathbf{b}_n \mathbf{b}_o)$$

$$K(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o) = \exp[-\beta U(n)] \times C \exp[-\beta u_{\text{bonded}}(o)] \times \frac{\exp[-\beta u_{\text{non-b}}(o)]}{W(o)} \times P(\mathbf{b}_n \mathbf{b}_o) \times \text{acc}(n \rightarrow o | \mathbf{b}_n \mathbf{b}_o)$$

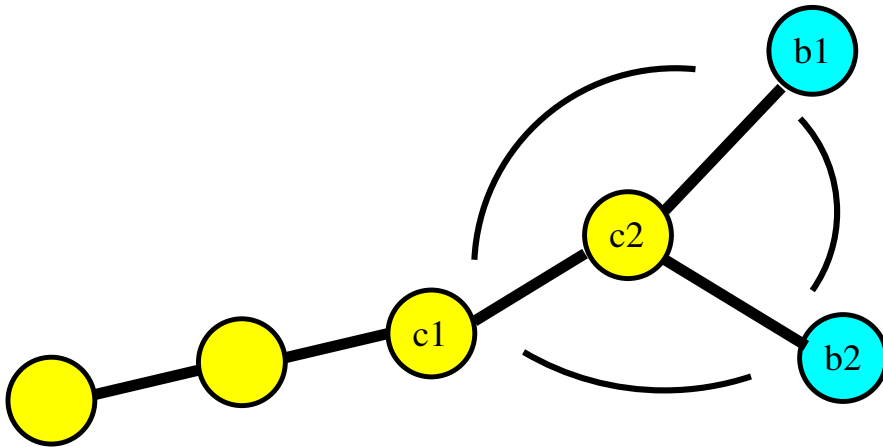
As

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

therefore

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

Branched Molecules (1)



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

Branched Molecules (2)

Use CBMC to generate internal configurations:

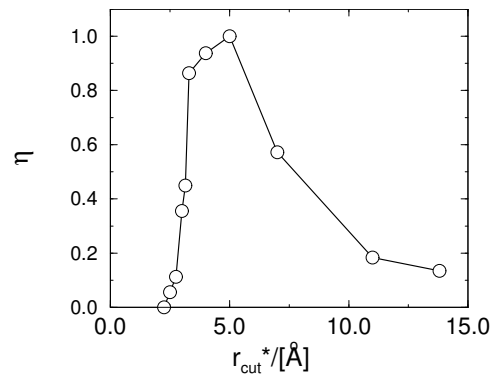
- Generate n_t *random* trial positions and select one (i) with a probability

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

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

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

Significant Speedup: Dual-Cutoff CBMC



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

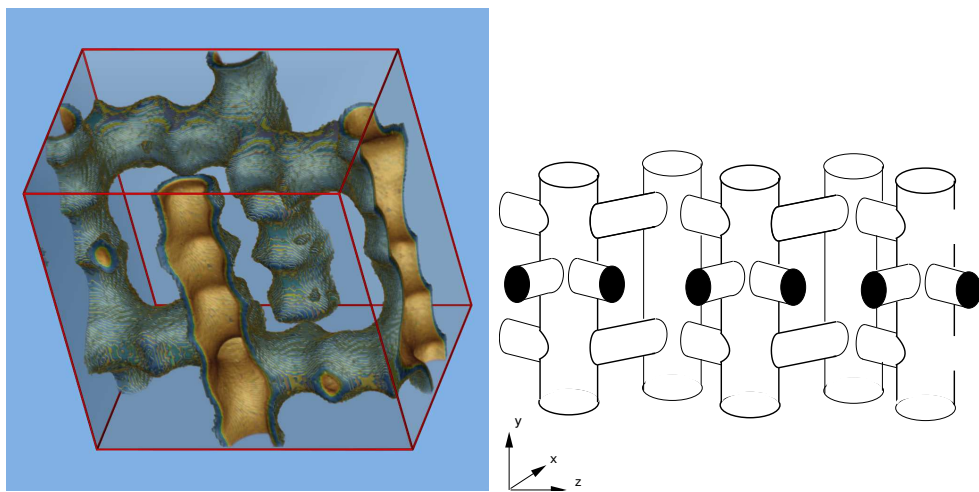
$$\text{acc}(o \rightarrow n) = \min \left(1, \frac{W^*(n)}{W^*(o)} \times \exp[-\beta[\delta u(n) - \delta u(o)]] \right)$$

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 Å
- synthetic and natural; >190 framework types

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

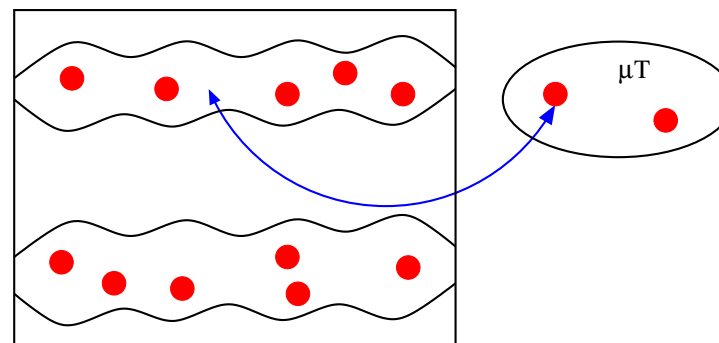


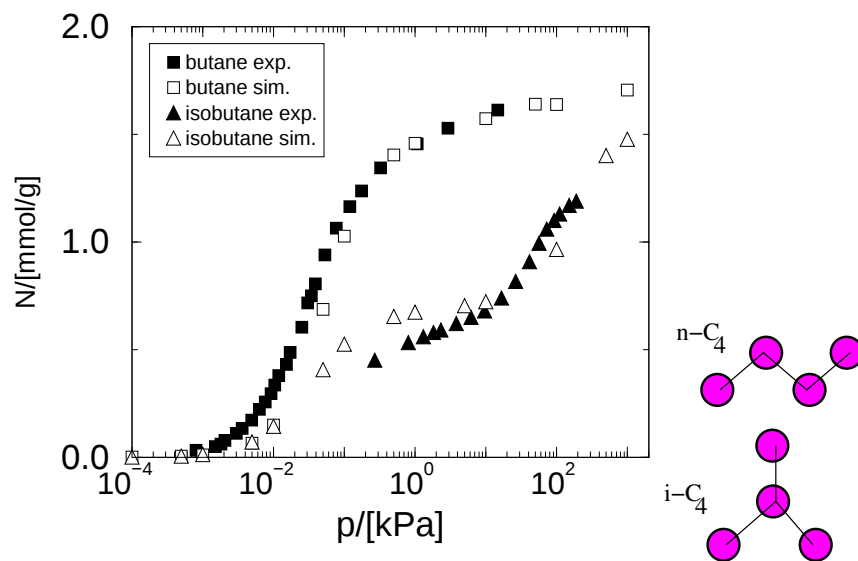
straight channels (y direction), zig-zag channels (xz plane) and intersections

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

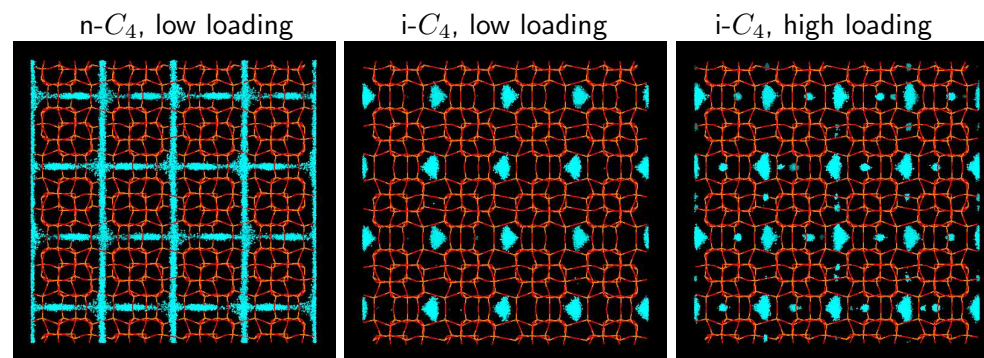
Grand-canonical (μVT) ensemble; number of particles (N) fluctuates

- system is coupled to particle reservoir at chemical potential μ and temperature T , statistical weight $\sim V^N \exp[\beta\mu N - \beta U(\mathbf{r}^N)] / (\Lambda^{3N} N!)$
- 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)

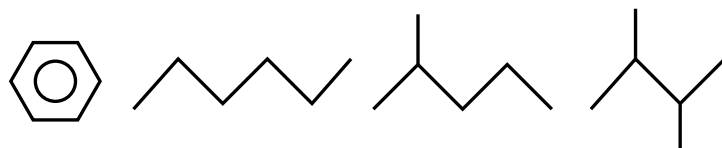
Vlugt et al, J. Am. Chem. Soc., 1998, 120, 5599

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

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

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

Research Octane Number (RON)



>100

25

73

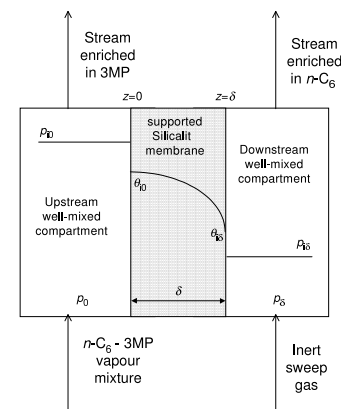
92



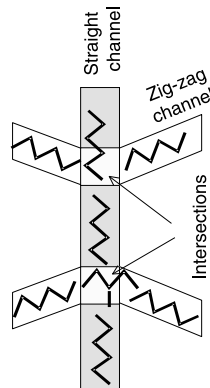
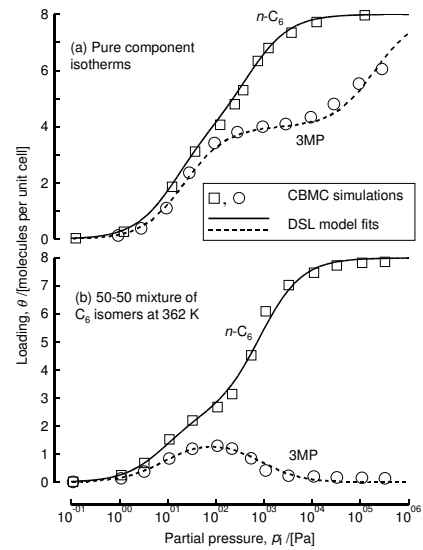
Application 1: Adsorption of Alkanes in MFI-type zeolite (7)

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

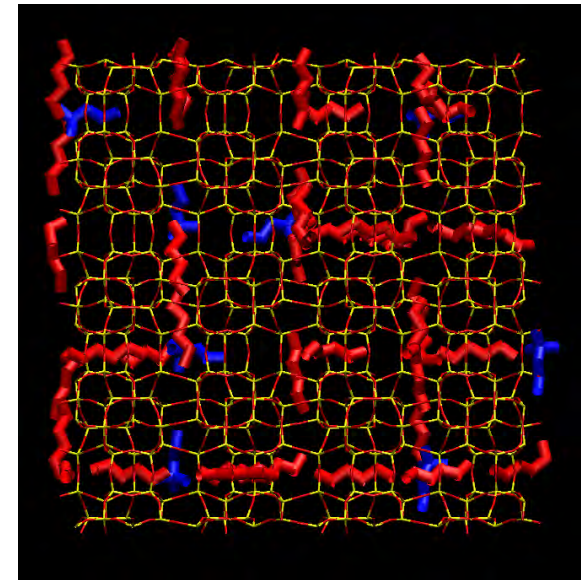


Application 1: Adsorption of Alkanes in MFI-type zeolite (8)

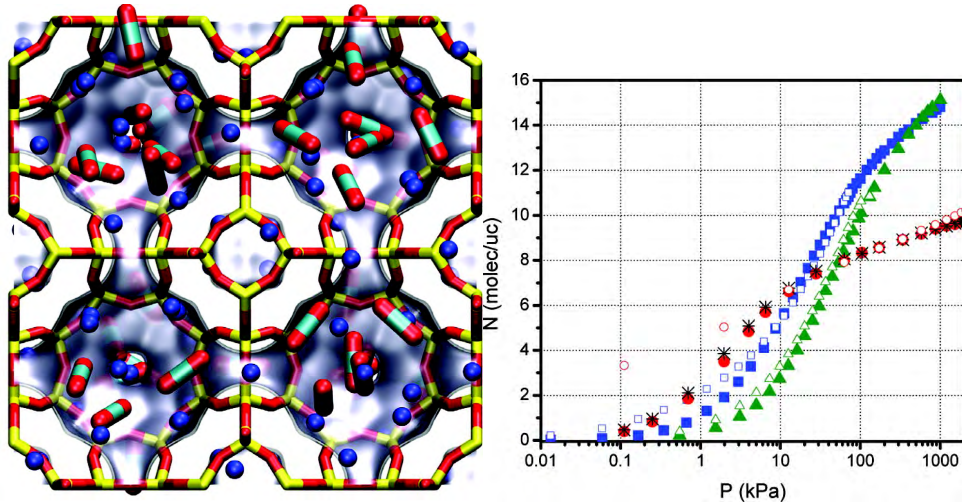


Application 1: Adsorption of Alkanes in MFI-type zeolite (9)

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

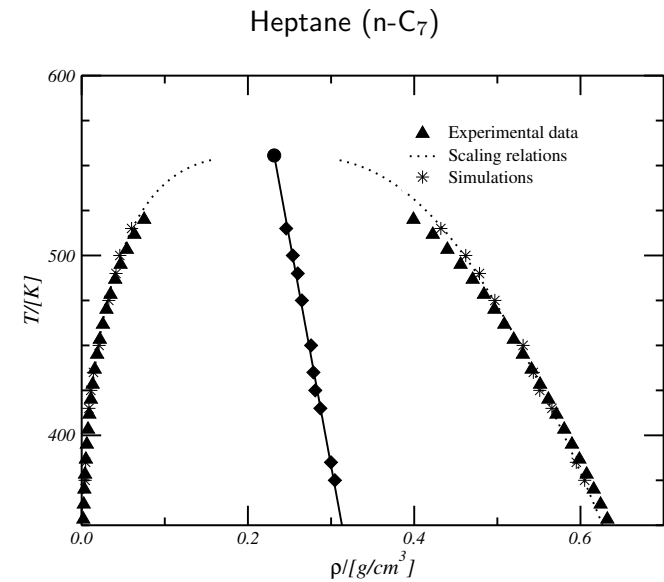


Application 2: Adsorption of CO_2 in Na^+ containing zeolites



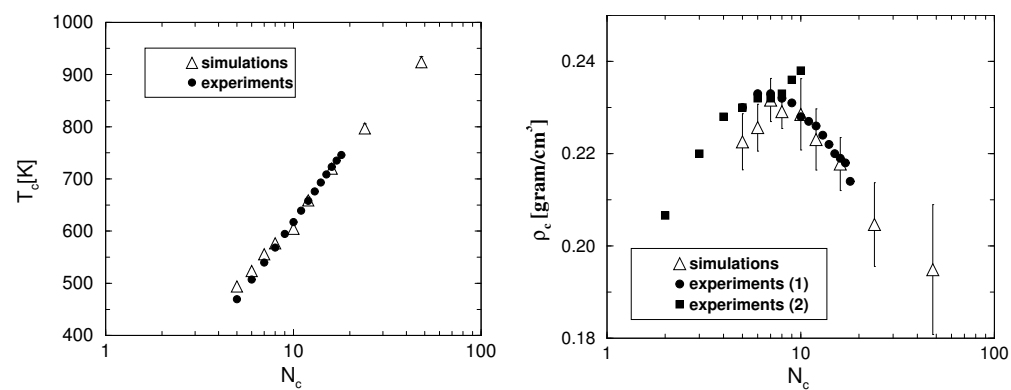
Sofia Calero et al., J. Phys. Chem. C, 2009, 113, 8814-8820

Application 3: Gibbs Ensemble Monte Carlo (1)



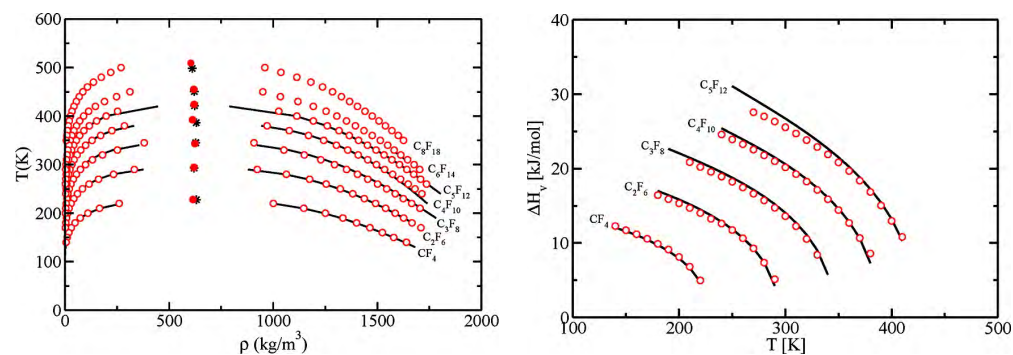
B. Smit, S. Karaborni, and J.I. Siepmann, J. Chem. Phys. 102, 2126 (1995)

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

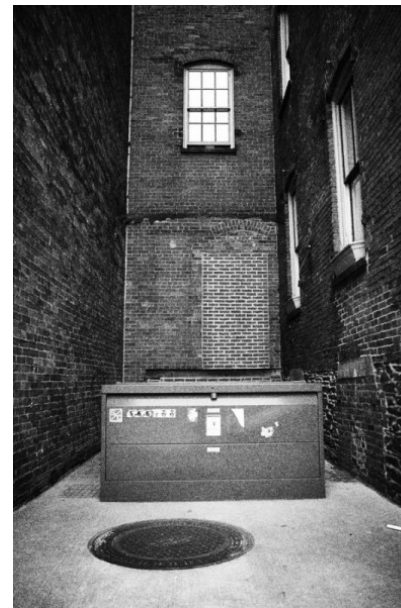
Efficiency of CBMC

- 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

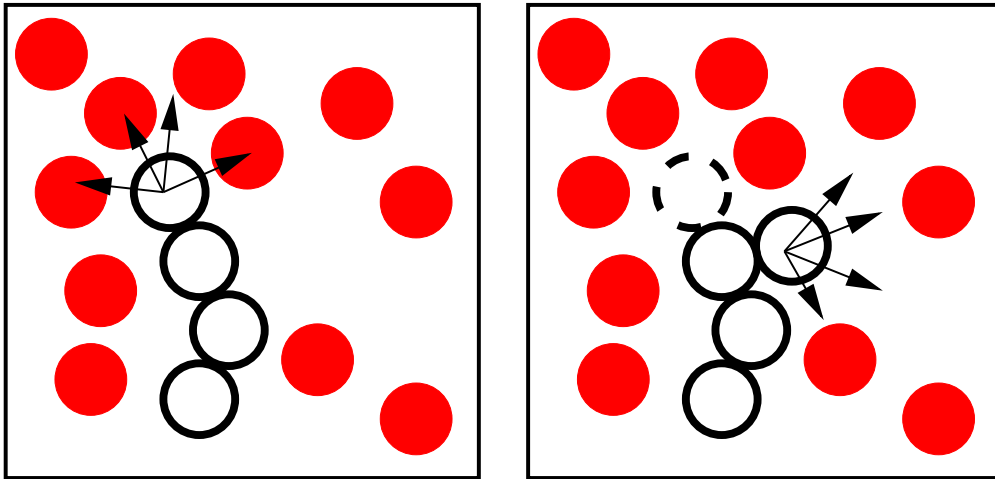
$$P_{\text{success}} = (1 - (1 - a)^k)^N = \exp[-cN]$$

- increasing k means increasing CPU time.

Dead-End Alley



Recoil Growth: Avoiding Dead-End Alley

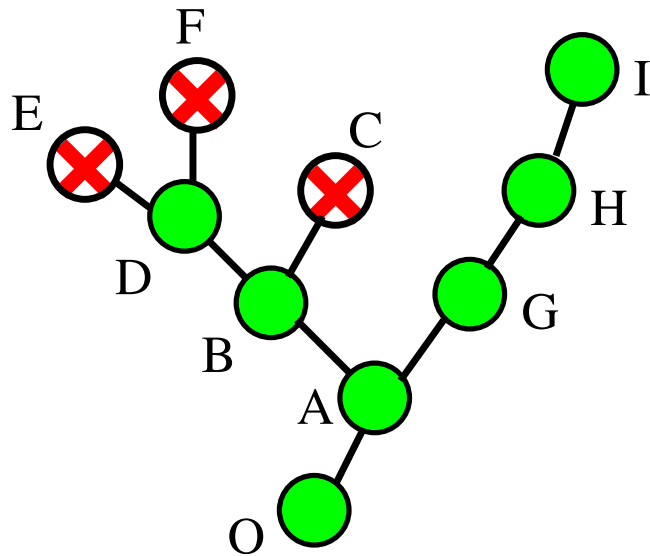


Recoil Growth Algorithm (1)

- 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: $l_{\text{max}} - l + 1$
- 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 $\text{acc}(o \rightarrow n) = \min(1, W(n)/W(o))$

Recoil Growth Algorithm (2)

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



Super Detailed Balance

In general,

$$N(o) \times \alpha(o \rightarrow n) \times \text{acc}(o \rightarrow n) = N(n) \times \alpha(n \rightarrow o) \times \text{acc}(n \rightarrow o)$$

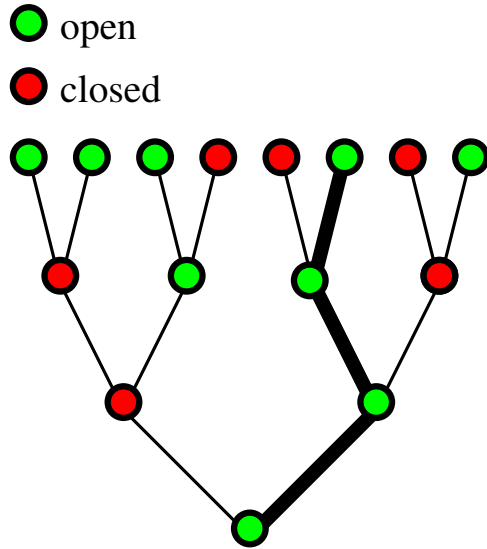
Therefore,

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

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

- 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

$$K(o \rightarrow n | t_n t_o O_n O_o) = K(n \rightarrow o | t_n t_o O_n O_o)$$

$$\alpha(o \rightarrow n | t_n t_o O_n O_o) = P(t_n) P(O_n | t_n) P(rw_n | t_n O_n) \times P(t_o | rw_o) P(O_o | t_o rw_o)$$

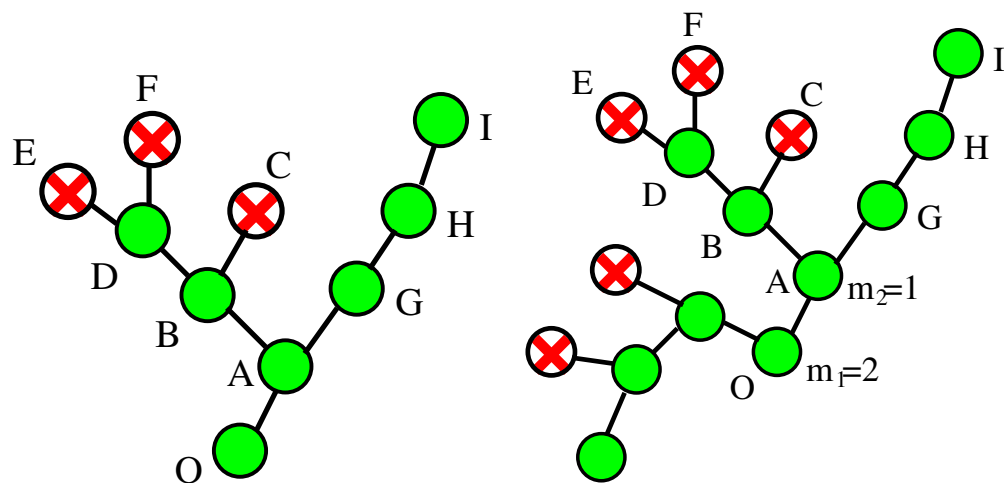
$$\alpha(n \rightarrow o | t_n t_o O_n O_o) = P(t_o) P(O_o | t_o) P(rw_o | t_o O_o) \times P(t_n | rw_n) P(O_n | t_n rw_n)$$

$$\frac{P(O_n | t_n)}{P(O_n | t_n rw_n)} = \prod_{i=1}^n p_i$$

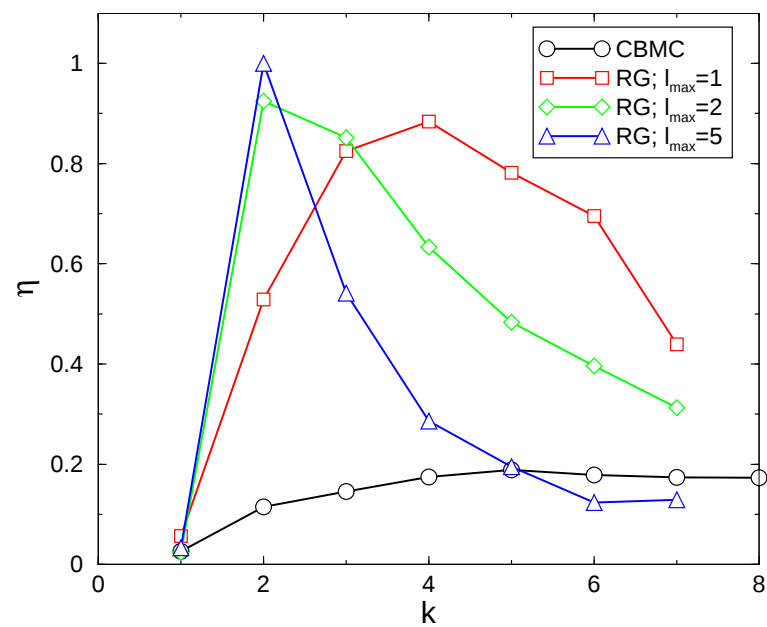
$$P(rw_n | t_n O_n) = \frac{1}{\prod_{i=1}^n m_i}$$

$$\text{acc}(o \rightarrow n) = \min \left(1, \exp[-\beta \Delta U] \times \frac{\prod_{i=1}^n \frac{m_i(n)}{p_i(n)}}{\prod_{i=1}^n \frac{m_i(o)}{p_i(o)}} \right)$$

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



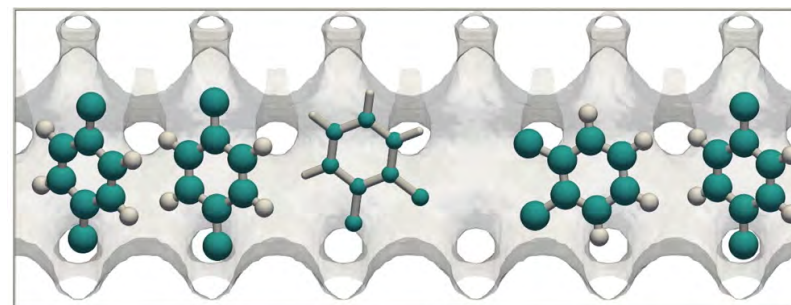
Efficiency of RG Compared to CBMC



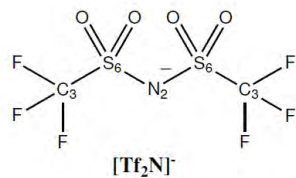
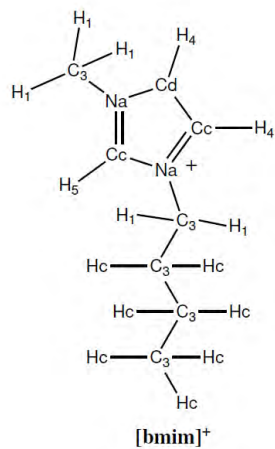
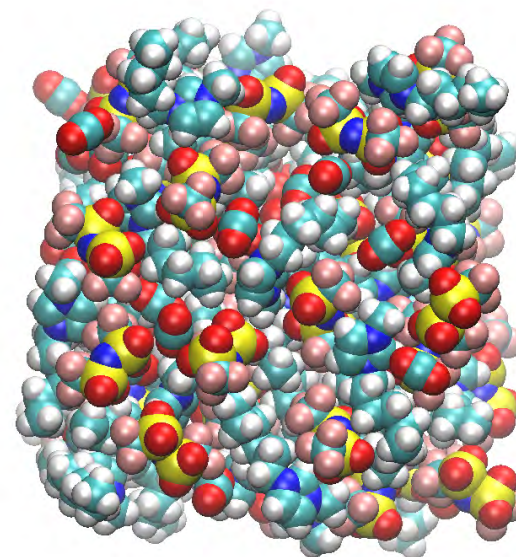
Other Methods

- 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

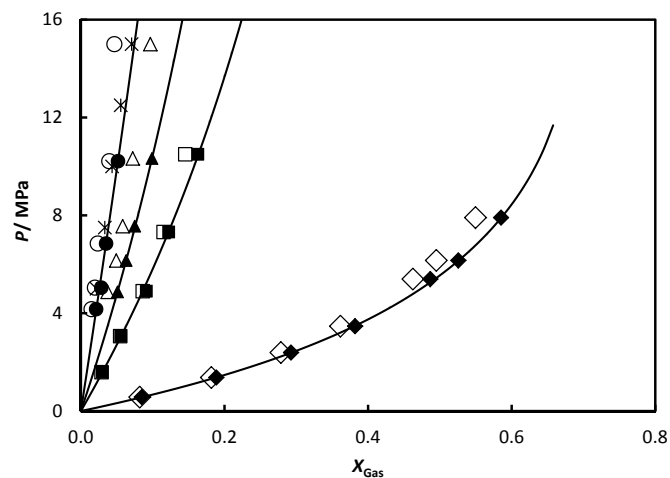
Continuous Fractional Component Monte Carlo



- 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][Tf2N]**

Solubility of precombustion gasses in [bmim][Tf₂N]



Solubility of CO₂, CH₄, CO, H₂ and N₂ in [bmim][Tf₂N] from MC simulations (open symbols) and experiments (filled symbols) at 333.15 K. CO₂ experiments (filled diamonds) and MC data (open diamonds); CH₄ experiments (filled squares) and MC data (open squares); CO experiments (filled triangles) and MC data (open triangles); H₂ experiments (filled circles) and MC data (open circles), and MC data of N₂ (stars). Lines: PR-EOS modeling

Henry constants of CO₂, CH₄, CO, H₂, N₂, and H₂S in Selexol and [bmim][Tf₂N] at 333.15 K

solute	$H_{\text{Selexol}}^{\text{exp.}}/\text{MPa}$	$H_{\text{IL}}^{\text{exp.}}/\text{MPa}$	$H_{\text{IL}}^{\text{sim.}}/\text{MPa}$	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 ₂ S (3S)	1.01 ^c	2.17	1.15	47.0
H ₂ S (4S)	1.01	2.17	1.16	46.5
H ₂ S (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

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

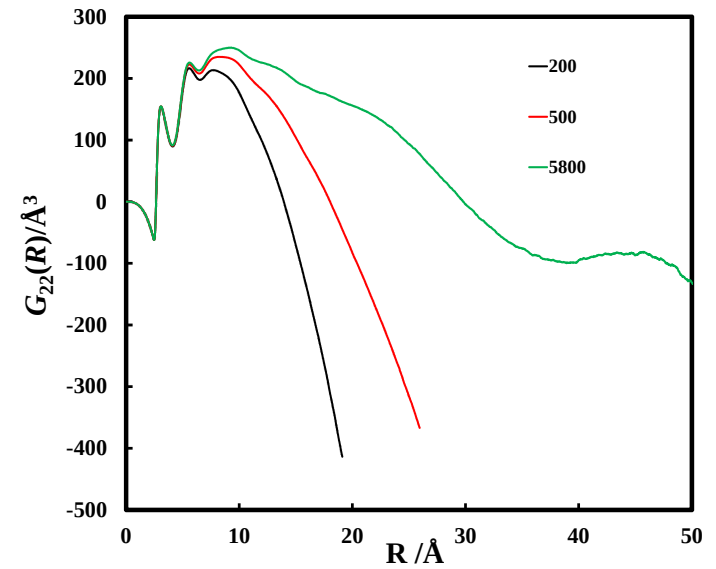
Using PCFs from MD:

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

Often used, but is it correct?

Kirkwood-Buff theory for finite systems (2)

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



Kirkwood-Buff theory for finite systems (3)

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

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

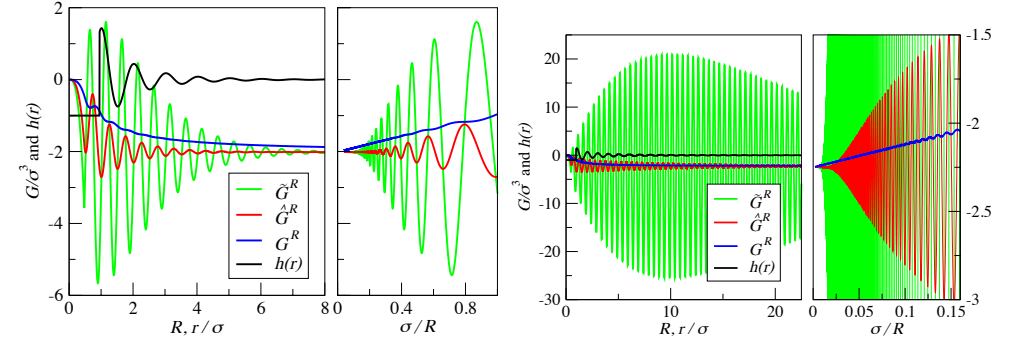
$$\begin{aligned} G_{\alpha\beta}^V &\equiv \frac{1}{V} \int_V \int_V (g_{\alpha\beta}^{NVT}(r_{12}) - 1) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 4\pi \int_0^{2R} (g_{\alpha\beta}^{NVT}(r) - 1) r^2 \left(1 - \frac{3r}{4R} + \frac{r^3}{16R^3}\right) dr \\ &\equiv G_{\alpha\beta}(R) \end{aligned}$$

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)



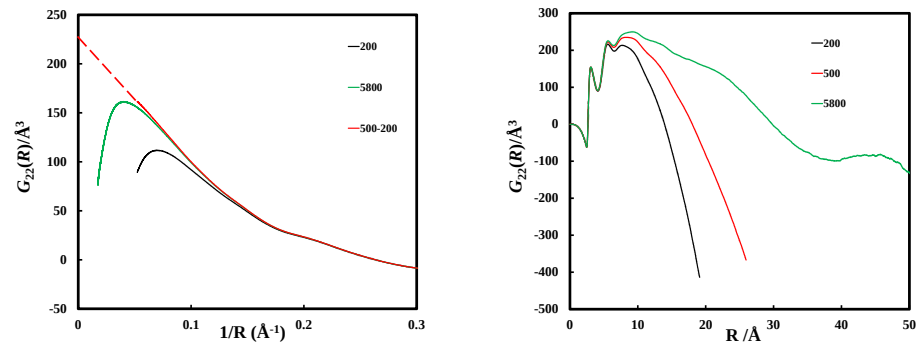
$$h(r) = g(r) - 1 = \begin{cases} \frac{3/2}{r/\sigma} \exp\left(\frac{1-r/\sigma}{\chi}\right) \cos\left[2\pi\left(\frac{r}{\sigma} - \frac{21}{20}\right)\right], & \frac{r}{\sigma} \geq \frac{19}{20} \\ -1, & r < \frac{19}{20}\sigma. \end{cases}$$

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 $g(r)$

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



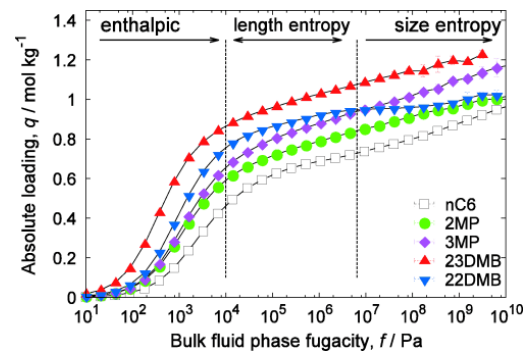
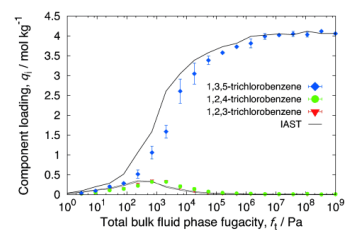
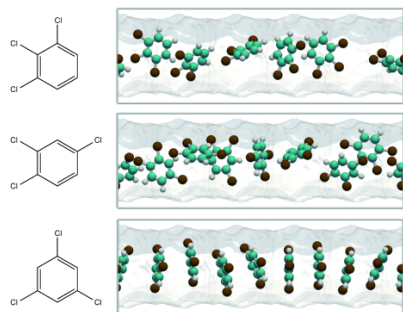
Equimolar mixture of methanol and acetone, LJ+electrostatics, 298K, 1atm

The End

Questions ??

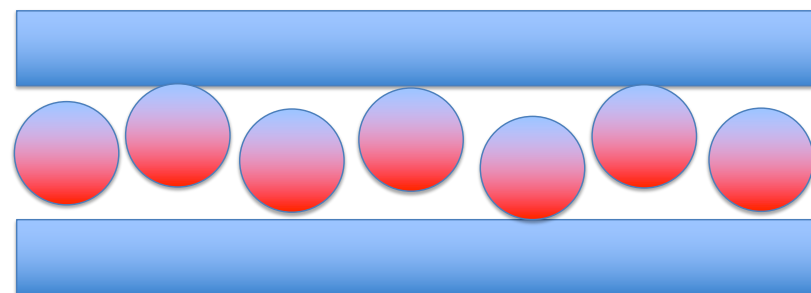


High loadings are relevant!

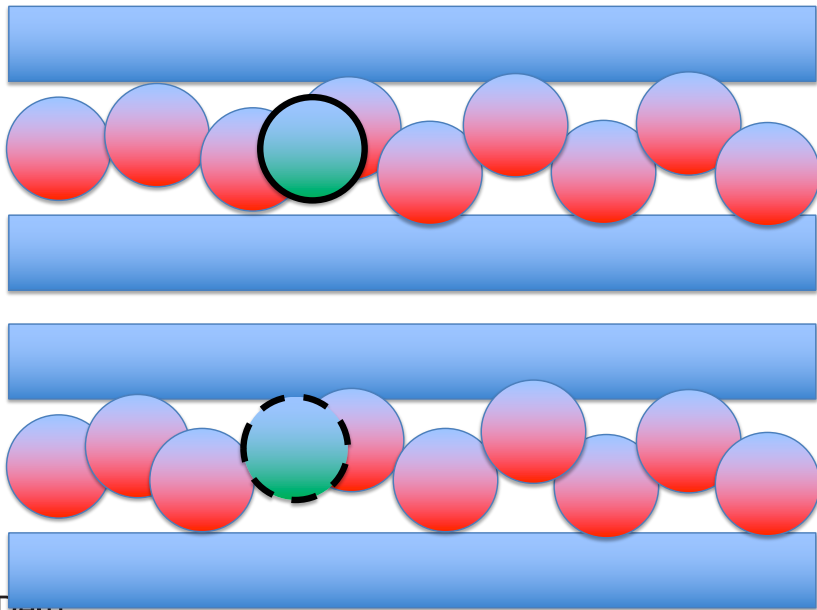


David Dubbeldam and co-workers
ChemPhysChem, 16 (3), 532-535
ChemPhysChem, 16 (10), 2046-2067

What is the maximum pore loading?



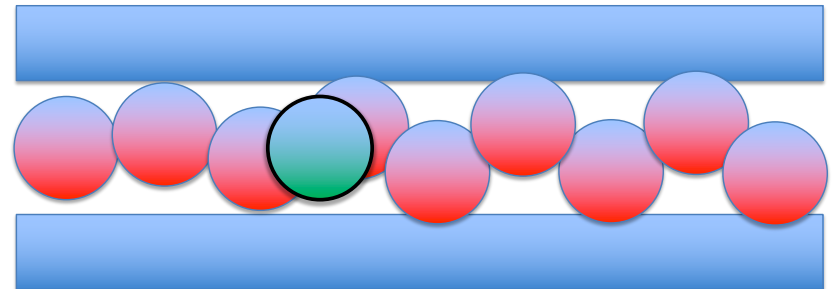
Insertion of a whole vs fractional molecule



3

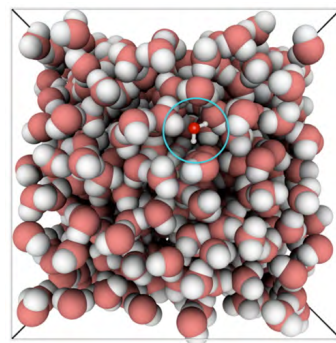
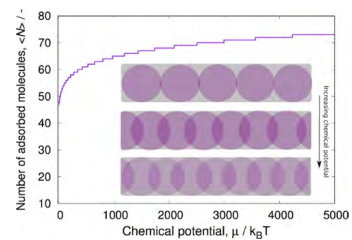
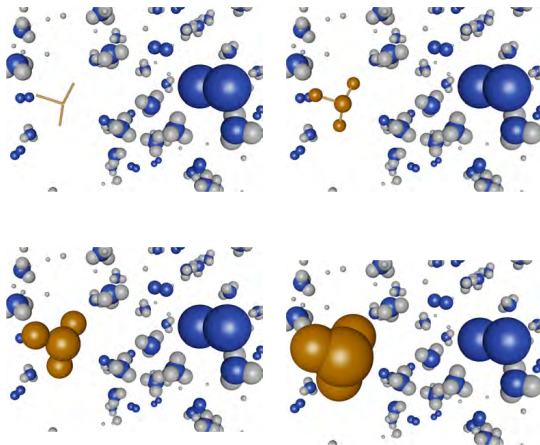
Zero times infinity problem → bad statistics

$$p(25M€) = (\text{\#wins})/(\text{\#tickets})$$



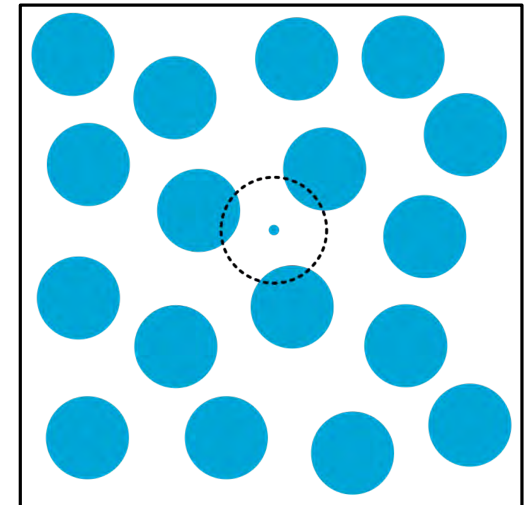
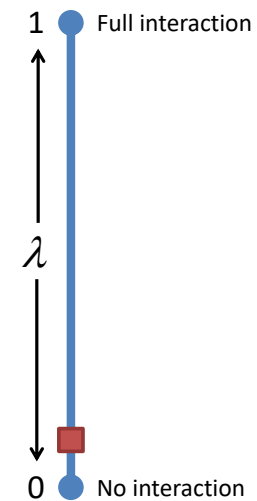
4

Insertions made easy using fractional molecules

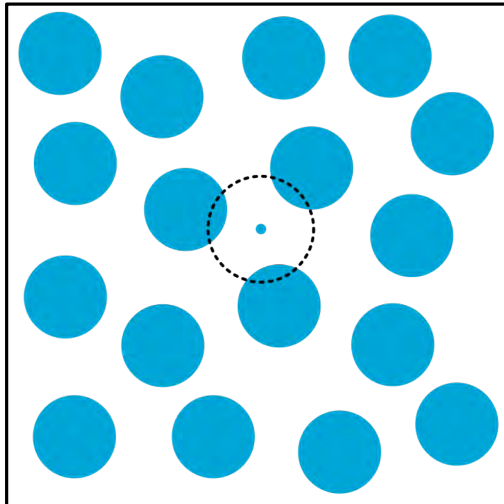
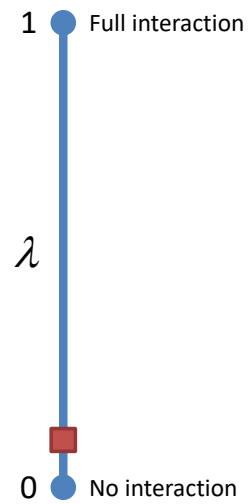


Shi & Maginn, *J. Chem. Theory Comput.*, 2007, 3, 1451–1463

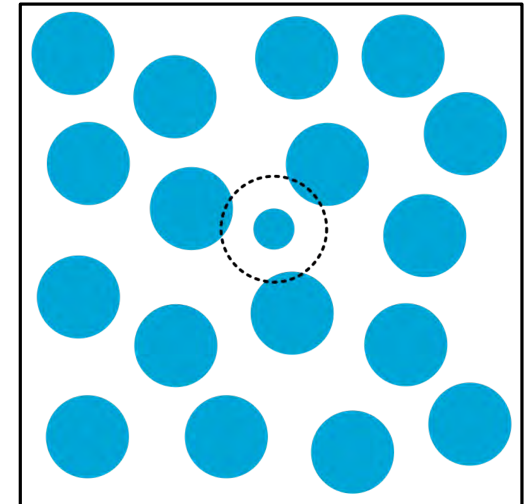
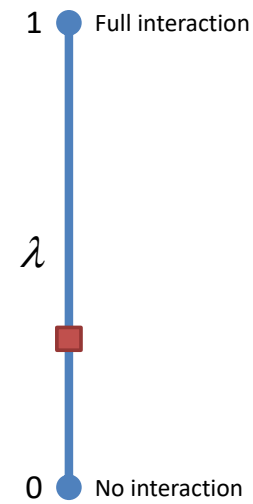
CFCMC



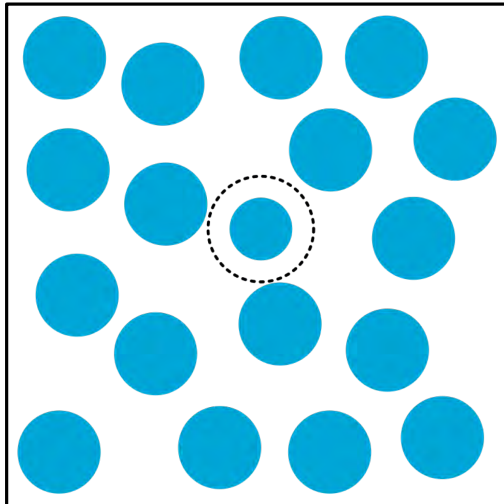
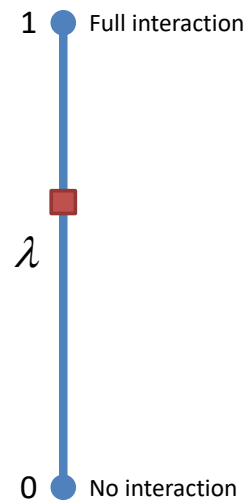
CFCMC



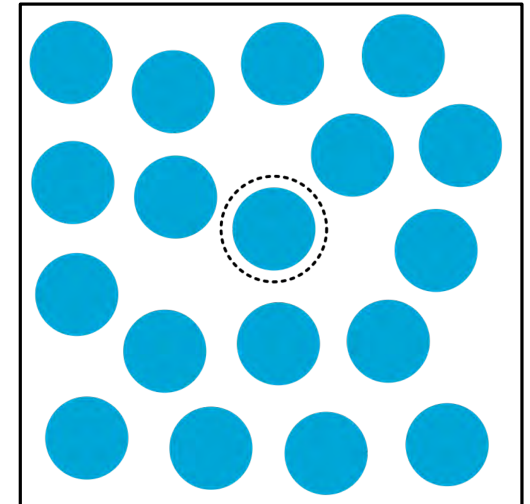
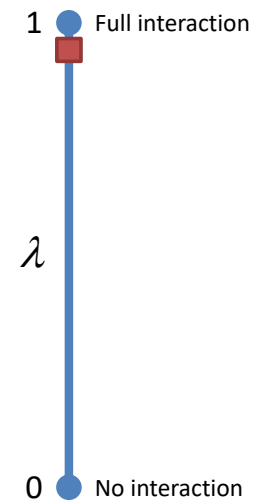
CFCMC



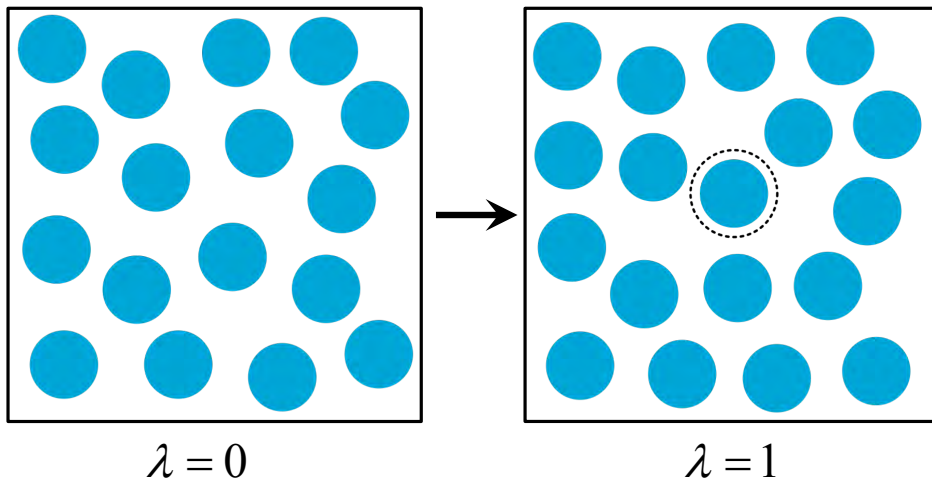
CFCMC



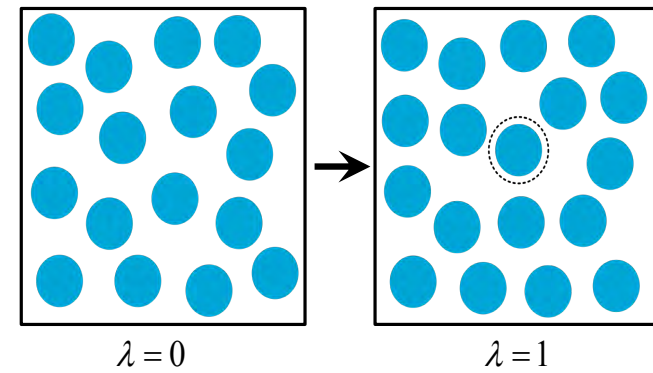
CFCMC



CFCMC



Avoid singularities



$$u_{IJ}(r) = \lambda 4e \left[\frac{1}{\left[\frac{1}{2}(1 - \lambda)^2 + \left(\frac{r}{\sigma} \right)^6 \right]^2} - \frac{1}{\left[\frac{1}{2}(1 - \lambda)^2 + \left(\frac{r}{\sigma} \right)^6 \right]} \right]$$

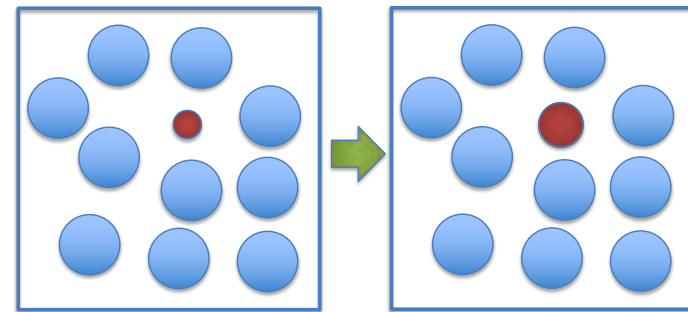
CFCMC in the grand-canonical ensemble

- N whole molecules, 1 fractional molecule
- Fractional molecule has scaled interactions (λ)
 - $\lambda=0$: no interactions with surrounding molecules
 - $\lambda=1$: full interactions with surrounding molecules
- Usual trial moves (translation, rotation, volume change, etc.)
- New types of trial moves:
 - Change value of λ
 - Identity change of the fractional molecule

Changes in lambda

- $\lambda(\text{new})$ between 0 and 1

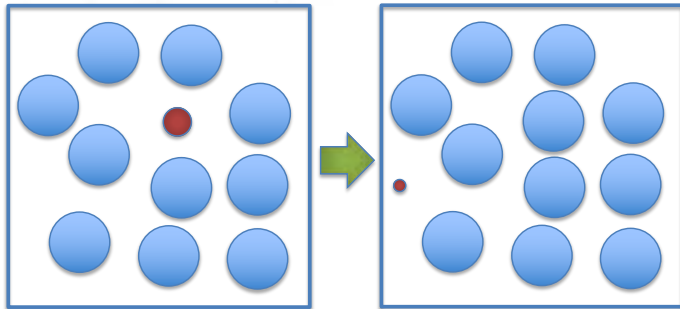
$$P_{\text{acc}} = \min(1, \exp[-\beta(U_{\text{inter}}(n) - U_{\text{inter}}(o)) + \eta(\lambda(n)) - \eta(\lambda(o))])$$



Changes in lambda

- $\lambda(\text{new})$ larger than 1: fractional becomes whole and insert new fractional with $\lambda(\text{new}) - 1$

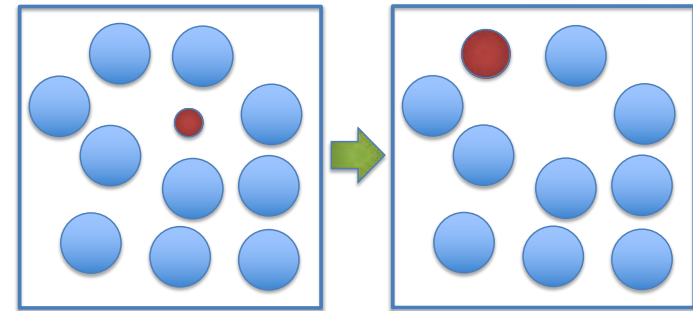
$$P_{\text{acc}}(N \rightarrow N + 1) = \min \left(1, \frac{f\beta V}{N + 1} \exp[\eta(\lambda(n)) - \eta(\lambda(o))] \exp[-\beta(U_{\text{inter}}(n) - U_{\text{inter}}(o))] \right)$$



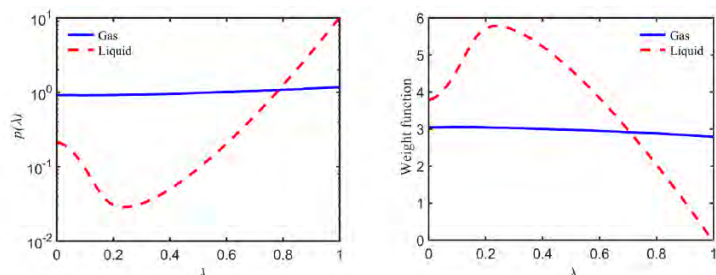
Changes in lambda

$\lambda(\text{new})$ smaller than 0: delete fractional molecule, pick random new whole molecule and turn it into a fractional one, and insert new fractional with lambda equals $1 + \lambda(\text{new})$

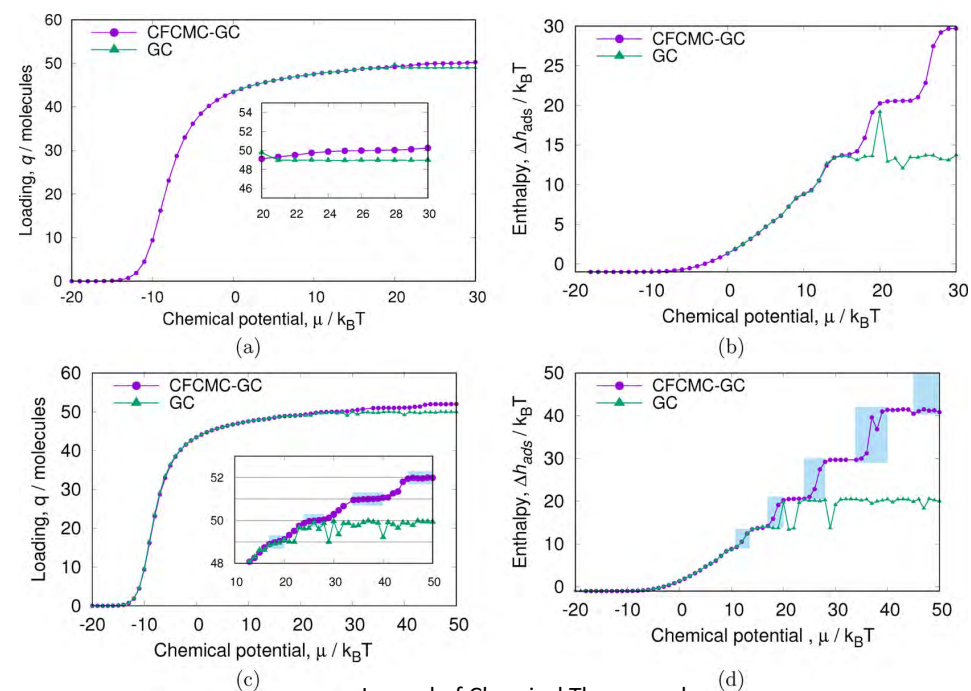
$$P_{\text{acc}}(N \rightarrow N - 1) = \min \left(1, \frac{N}{f\beta V} \exp[\eta(\lambda(n)) - \eta(\lambda(o))] \exp[-\beta(U_{\text{inter}}(n) - U_{\text{inter}}(o))] \right)$$



Add weight function $W(\lambda)$ (or $\eta(\lambda)$) for flat sampling of λ



- Avoid getting stuck in λ -space
- Add weight factor $\exp[W(\lambda)]$ to the partition function
- Choose $W(\lambda)$ such that the observed $p_{\text{obs}}(\lambda)$ is flat (e.g. using the Wang-Landau method, Phys. Rev. Lett., 2001, 86, 2050-2053)
- Obtain Boltzmann averages by multiplying with $\exp[-W(\lambda)]$ for each sampled configuration



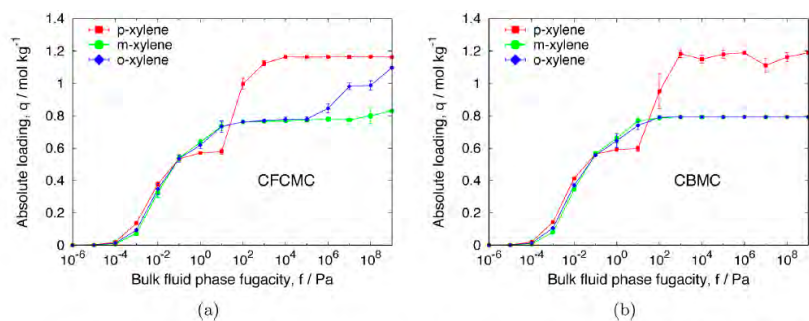


Figure 3. Pure component adsorption isotherms of xylenes isomers in MTW zeolite at 433 K calculated with (a) CFCMC and (b) CBMC.

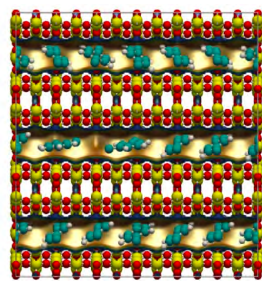
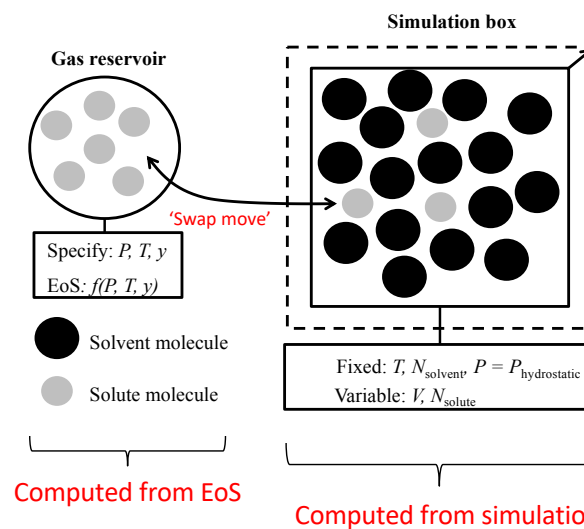


Figure 4. YZ view of MTW channels with an equimolar mixture of xylenes isomers at 10^8 Pa and 433 K. The channels are cut open and volume-rendered based on an energy grid probed with methane. Color code: carbon (cyan), hydrogen (white), oxygen (red), and silicon (yellow).

Osmotic Ensemble



MC moves at fixed T:

- Translation
- Rotation
- Swap move (solute)
- Volume change

Journal of Chemical Theory and
Computation, 2014, 10, 942-952.

CFCMC in the osmotic ensemble

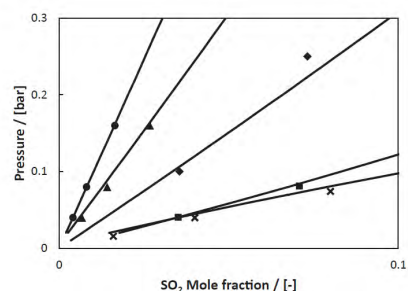
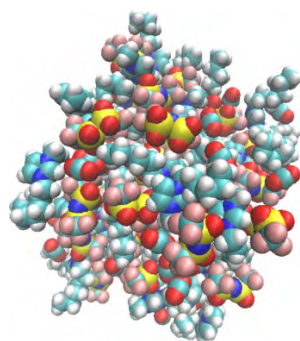


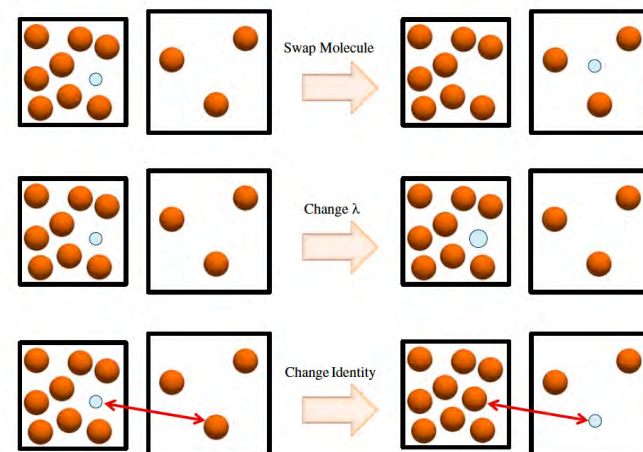
Fig. 3. Solubility of SO_2 in PC (closed circles), NMP (closed triangles), Selexol (closed squares), Rectisol (crosses), and [bmim][Tf_2N] (closed diamonds) molecules at 333.15 K (except Rectisol at 248.15 K). The lines are fitted to the PR EOS. The fitted parameters are available in Table S15 of the Supplementary Content.



J. Chem. Eng. Data, 2015, 60, 3039-3045.

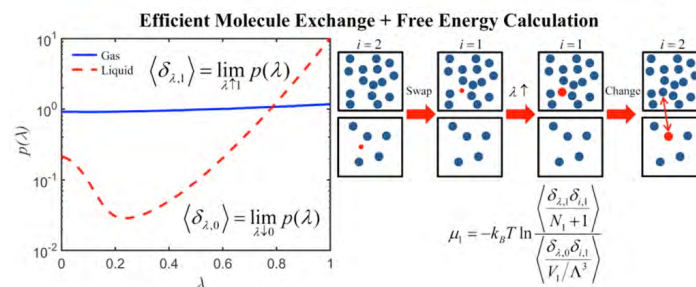
Henry coefficients (H_i /bar, Equation (1)) of the investigated solutes in PC, NMP, selexol, and the ionic liquid [bmim][Tf_2N] at 333.15 K and Rectisol at 248 K. The available experimental Henry coefficients are provided for comparison.

		PC	NMP	Selexol	Rectisol	[bmim][Tf_2N]
CS_2	Sim.	2.3	1.6	3.2	0.42	1.2
	Exp.	—	—	—	—	—
CH_3SH	Sim.	3.5	1.9	2.4	0.51	2.4
	Exp.	—	—	—	—	—
SO_2	Sim.	9.8	6.1	1.2	1.01	3.3
	Exp.	4.69 [47], 4.89 [48]	0.94 [48]	0.84 [49]	0.72 [50]	—
COS	Sim.	36.8	33.7	27.0	9.1	18.0
	Exp.	—	—	—	10.97 [5]	—
H_2S	Sim.	43.2	33.8	19.7	11.1	23.9
	Exp.	44.2 [47], 42.2 [51]	16.5 [52]	—	6.09 [5]	22.8 [53]
CO_2	Sim.	156	135	68.6	42.9	62
	Exp.	154 [47], 142.6 [52]	115 [52]	65 [54]	43.0 [55], 40.8 [56]	64.2 [57], 56.0 [58]
CH_4	Sim.	1500	1320	765	950	470
	Exp.	1340 [59], 1390 [60]	1100 [61]	394 [61]	840 [5], 990 [62]	522 [63]



New CFCMC formulation for the Gibbs Ensemble

Journal of Chemical Theory and Computation, 2016, 12, 1481-1490.



$$Q_{\text{CFCMC}} = \frac{1}{\Lambda^{3(N_T+1)} (N_T)!} \sum_{i=1}^2 \sum_{N_i=0}^{N_T} \int_0^1 d\lambda$$

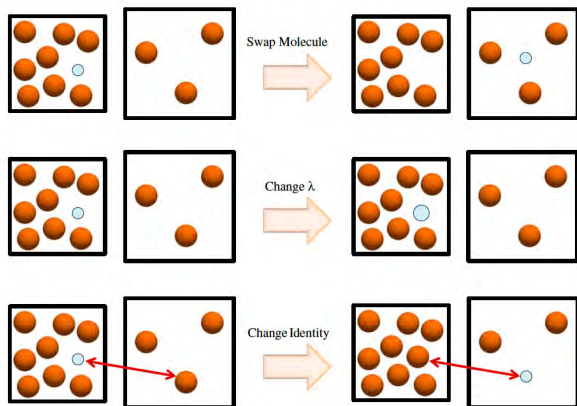
$$\times \int_0^{V_T} dV_1 V_1^{N_i+\delta_{i,1}} (V_T - V_1)^{N_T-N_i+\delta_{i,2}} \frac{(N_T)!}{(N_i)! (N_T - N_i)!}$$

$$\times \int ds^{N_i} \exp[-\beta U_{\text{int},1}(s^{N_i}, V_1)]$$

$$\times \int ds^{N_T-N_i} \exp[-\beta U_{\text{int},2}(s^{N_T-N_i}, V_T - V_1)]$$

$$\times \left(\delta_{i,1} \int ds_{\text{frac}}^1 \exp[-\beta U_{\text{frac},1}(s_{\text{frac}}^1, s^{N_i}, \lambda, V_1)] \right.$$

$$\left. + \delta_{i,2} \int ds_{\text{frac}}^2 \exp[-\beta U_{\text{frac},2}(s_{\text{frac}}^2, s^{N_T-N_i}, \lambda, V_T - V_1)] \right)$$



Trial moves:

- volume changes
- translation, rotation etc.
- change lambda
- swap molecule
- change identity

Compute the chemical potential "for free"

$$\mu_{i,\text{CFCGEMC}} = -k_B T \ln \left\langle \frac{V_i/\Lambda^3}{N_i + 1} \right\rangle - k_B T \ln \left\langle \frac{p_i(\lambda \uparrow 1)}{p_i(\lambda \downarrow 0)} \right\rangle$$

Journal of Chemical Theory and Computation, 2016, 12, 1481-1490.

Molecular Simulation, 2018, 44, 405-414

Molecular Simulation, 2017, 43, 189-195.

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Add weight function

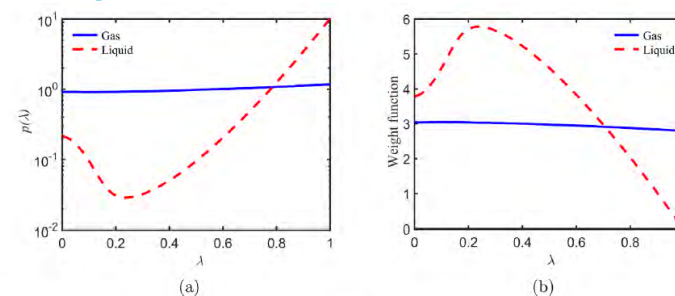
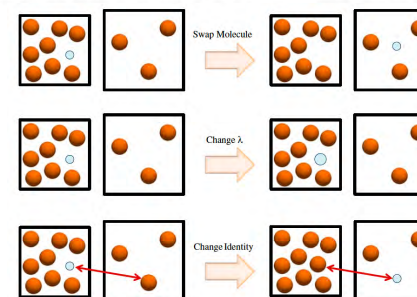


Figure 5. (a) Probability distribution of λ for the gas and the liquid phases as used in CFCMC GE of LJ particles at $T^* = 0.8$; (b) weight functions to flatten the corresponding probability distributions of λ (as in panel a) and to ensure that the fractional molecule is equally likely to be in both simulation boxes.



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Do not “count” fractional molecules

Table 1. Coexistence Densities and Chemical Potentials for Vapor–Liquid Equilibria of LJ Particles for Different System Sizes and Reduced Temperatures Computed with the Conventional GE and the Proposed CFCMC GE Methods^a

T	GE				CFCMC GE			
	ρ_l	ρ_g	μ_l	μ_g	ρ_l	ρ_g	μ_l	μ_g
$N_T = 256$								
0.7	0.788(2)	0.0074(1)	-3.52(1)	-3.51(1)	0.786(2)	0.0074(2)	-3.52(2)	-3.52(2)
0.8	0.731(1)	0.0198(2)	-3.34(1)	-3.34(1)	0.729(1)	0.0198(3)	-3.35(1)	-3.35(1)
0.9	0.664(1)	0.0450(3)	-3.20(1)	-3.20(1)	0.662(1)	0.0451(5)	-3.21(1)	-3.22(1)
0.95	0.623(1)	0.0659(8)	-3.14(1)	-3.14(1)	0.621(1)	0.0660(8)	-3.15(1)	-3.16(1)
$N_T = 512$								
0.7	0.788(2)	0.0074(1)	-3.52(1)	-3.52(1)	0.786(1)	0.0075(1)	-3.52(1)	-3.52(1)
0.8	0.731(1)	0.0199(1)	-3.34(1)	-3.33(1)	0.730(1)	0.0199(3)	-3.34(1)	-3.34(1)
0.9	0.664(1)	0.0451(2)	-3.20(1)	-3.20(1)	0.663(1)	0.0449(2)	-3.21(1)	-3.21(1)
0.95	0.624(1)	0.0661(6)	-3.14(1)	-3.14(1)	0.623(1)	0.0665(4)	-3.14(1)	-3.15(1)

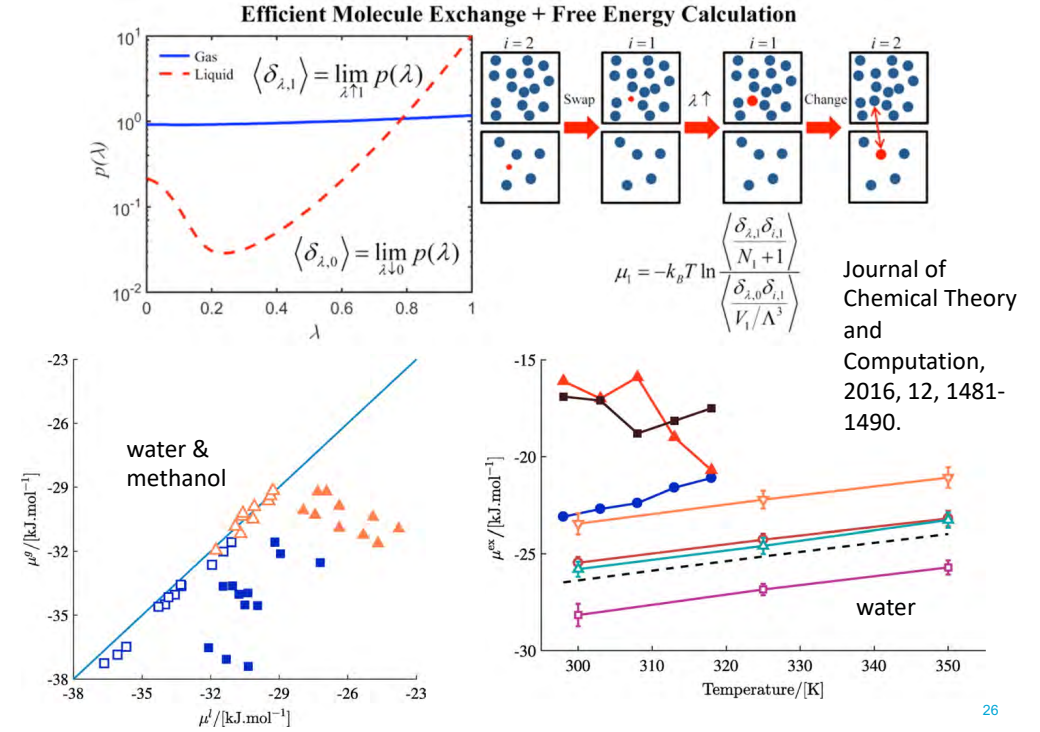
^aNumbers in brackets are uncertainties in the last digit, i.e., -3.52(1) means -3.52 ± 0.01 . A weight function was used in the CFCMC GE simulations to flatten the probability distribution of the coupling parameter λ and to ensure that the fractional molecule is equally likely to be in both simulation boxes. The total volume $V_T = 2 \times 8^3$ for $N_T = 256$ and 2×10^3 for $N_T = 512$.

Table 2. Acceptance Probabilities for the Molecule Exchange Trial Moves in the Conventional GE and the CFCMC GE Methods for Different Reduced Temperatures and System Sizes, For the Simulations Reported in Table 1 (LJ Particles)^a

T	$N_T = 256$		$N_T = 512$	
	$P_{acc}(swap)_{GE}$	$P_{acc}(change)_{CFCMC\ GE}$	$P_{acc}(swap)_{GE}$	$P_{acc}(change)_{CFCMC\ GE}$
0.7	8.93×10^{-4}	4.20×10^{-1}	9.12×10^{-4}	4.38×10^{-1}
0.8	3.59×10^{-3}	4.66×10^{-1}	3.60×10^{-3}	4.76×10^{-1}
0.9	1.18×10^{-2}	4.96×10^{-1}	1.17×10^{-2}	5.04×10^{-1}
0.95	2.07×10^{-2}	5.00×10^{-1}	2.04×10^{-2}	5.12×10^{-1}

^aThe acceptance probabilities of swap trial moves in the conventional GE are compared to the acceptance probabilities of exchanging the fractional molecule with a whole molecule in the other simulation box (Figure 3), using the proposed CFCMC GE method (eq 19). A weight function was used in the CFCMC GE simulations to flatten the probability distribution of the coupling parameter λ and to ensure that the fractional molecule is equally likely to be in both simulation boxes.

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Combining CFCMC and CBMC

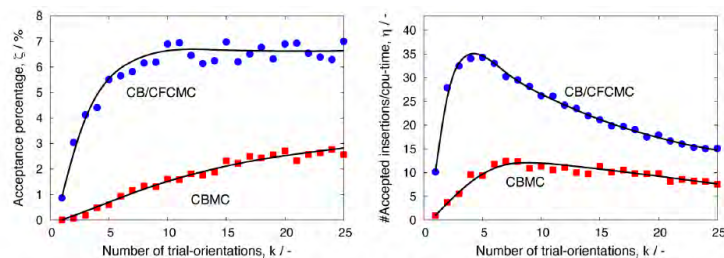


Figure 6. Efficiencies for CBMC, CFCMC, and CB/CFCMC algorithms for Lennard-Jones chains with eight beads. Total number of chain molecules $N = 200$, temperature $T^* = 1.887$, and total volume $V_t^* = 3456$. The number of MC production cycles = 50,000.

Journal of Chemical Theory and Computation, 2014, 10, 942-952

Molecular Simulation, 2015, 41, 1339-1347

Take home message

- Insertions/deletions become more difficult at high loading / low temperature
- Ensure that you have a sufficient number of accepted insertions/deletions
- Add identity changes for fractional molecules
- Do not “count” fractional molecules when computing the loading
- Use the biasing scheme that works for your molecule (if needed invent your own scheme)

Take home message

Molecular simulation software always provide “numbers”, but it is your task to check if these numbers actually make sense!

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