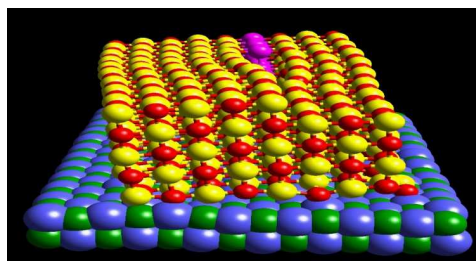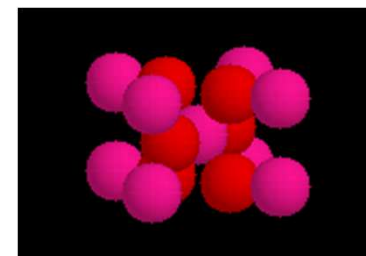# Molecular Simulations and Software Training Antofagasta Chile 2019

Monte Carlo

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Monte Carlo

Ulam reinvented the method while working on the nuclear weapons project in 1946. This required a code name, which was taken from the Monte Carlo Casino where Ulam's uncle gambled.

Overview

Monte Carlo is a stochastic molecular simulation technique

Sampling can be biased towards regions of specific interest

NOT constrained by natural timescales (in marked contrast with molecular dynamics)
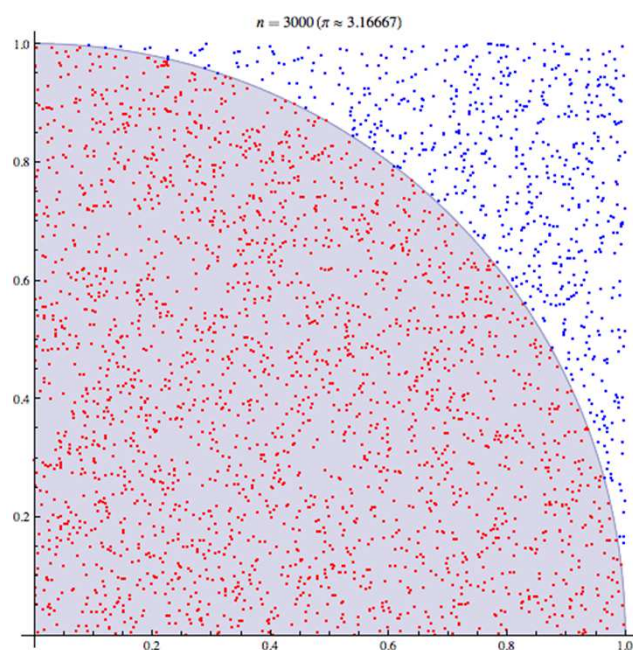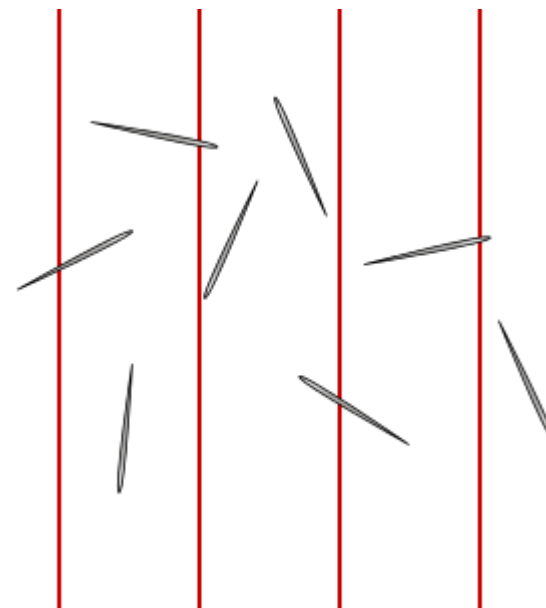
Straightforward to work at constant pressure (NPT) and can easily cope with fluctuating numbers of particles (via the grand canonical ensemble)

No (physical) dynamic foundation

Finding π the Monte Carlo way

~~Buffon's Needle~~

$n = 3000$ ($\pi \approx 3.16667$)

"Pi 30K" by CaitlinJo - Own work. This mathematical image was created with Mathematica. Licensed under CC BY 3.0 via Commons - https://commons.wikimedia.org/wiki/File:Pi_30K.gif#/media/File:Pi_30K.gif

Thermodynamic Monte Carlo

Unlike energy minimization, in Monte Carlo, configurations are generated by making random changes to the positions of the atoms or molecules present. As the calculation proceeds statistical averages are calculated to obtain the thermodynamic properties of the system.

In both Monte Carlo and molecular dynamics a box is set up containing the atoms or molecules of interest (can be up to up to 10^6 using modern computers). To simulate a liquid or solid the box is usually surrounded with replicas of the original box, avoiding an unwanted interface at the sides, i.e., we use *periodic boundary conditions.* Whenever a particle leaves the box through one of its faces, its image arrives through the opposite face so that the total number of particles remains constant.

Periodic boundary conditions
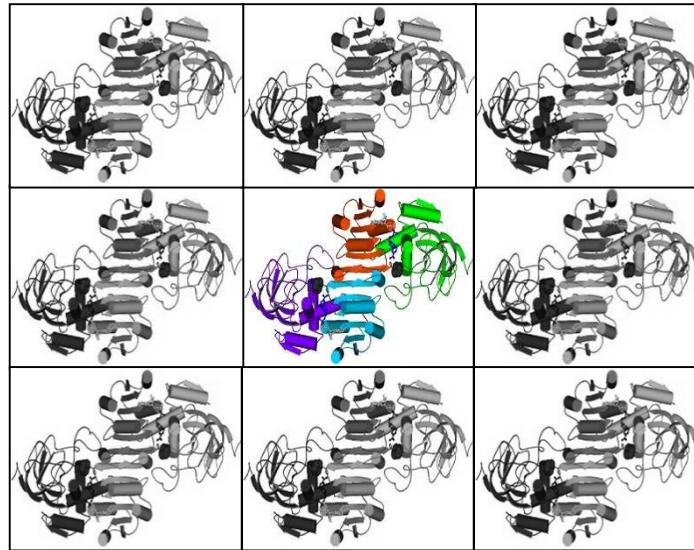
• If we wish to calculate a particular property *Q* of a system with a constant number of particles, temperature and volume (the canonical ensemble – usually referred to as NVT) the average value of that property *<Q>* is

$$< Q > = \int Q(Z)P(Z)\,\mathrm{d}Z$$

Boltzmann weighted probability

$$P(Z) = \frac{\exp(-U(Z)/kT)}{\int \exp(-U(Z)/kT)\,\mathrm{d}Z}$$

U(Z) internal energy associated with state of the system Z

The Metropolis algorithm

• Usually use the famous Metropolis algorithm - biases generation of configurations towards those that make the most significant contribution.

• So Monte Carlo method generates configurations randomly and uses the Metropolis scheme to decide whether or not to accept each new configuration. These criteria ensure that the probability of obtaining a given configuration is equal to its Boltzmann factor $\exp(-U(Z)/kT)$.

• *U(Z)* calculated almost always using interatomic or intermolecular potentials. Configurations with low energy generated with a higher probability than high energy ones. At each step calculate values of the desired properties - as simulation proceeds, the averages of these properties are obtained by simply averaging over the number *M* of values calculated.

$$< X > = \sum_{i=1}^{M} X(Z)$$

Each new configuration may be generated by randomly moving a single atom or molecule, or new configurations obtained by moving several atoms or molecules, or by rotating about one of more bonds.

$U(Z)$ calculated for new configuration.

If energy of new configuration *lower* than the energy of its predecessor then *accept* new configuration.

If energy of new configuration *higher* then its predecessor then calculate the *Boltzmann factor of the energy difference*.

A random number between 0 and 1 is then generated and compared with this Boltzmann factor. If this random number *higher* than the Boltzmann factor then move is *rejected* and original configuration kept for the next step. If this random number is *lower,* then move is *accepted* and new configuration becomes the next state.

Thus *some* moves are to states of higher energy.

The smaller the uphill move, the greater the chance the move will be accepted.

A bit more theory – why it works

If we don't know the value of the partition function and we can't easily calculate it, are we stuck?

$$p_i = \frac{e^{-\beta U(Z)}}{Q} \qquad Q(T,V,N) = \sum_i e^{-\beta U(Z)}$$

How do we choose states with probability $p(U(Z))$?

It turns out we can do it without knowing the partition function! We use a Markov Chain.

We choose a set of states for the sum to work out the thermodynamic averages. We do this by generating a set of states one after the other – the Markov Chain. Suppose we take a state i and make some change, usually small, to create a new state j (e.g., move one of the atoms a little, or swap two atoms). The choice of the new state is determined by probabilities – by a set of transition probabilities T_{ij}. T_{ij} gives the probability of changing from i to j.

If we choose T_{ij} appropriately we can ensure that the probability of visiting any particular state on any step of the Markov Chain is exactly the Boltmann probability $p(U(Z))$ so that when we take many steps the set of states through which we move is a correct sample of our Boltzmann distribution.

Then if we are interested in a quantity X all we have to do is measure the value in each state and take the average.

$$< X > = \sum_{i=1}^{M} X(Z)$$

Why it works (3)

The secret of the Markov Chain method is to choose the T_{ij} such that

$$\frac{T_{ij}}{T_{ji}} = \frac{p(U_j)}{p(U_i)} = \frac{e^{-\beta U_j}/Q}{e^{-\beta U_i}/Q} = e^{-\beta(U_j - U_i)}$$

And wonderfully the partition function Q cancels out of this equation!

Why it works (4)

So under the Metropolis scheme if the proposed move will decrease the energy of the system or keep it the same then we definitely accept it . If the proposed move will increase the energy then we may still accept it – with probability $e^{-\beta(U_j-U_i)}$. The probability of making a move from *i* to *j* is the probability that we choose that move out of all possibilities, which is $1/R$ if there are *R* possibilities, multiplied by the probability that we accept the move. So if for instance $U_j > U_i$

$$T_{ij} = \frac{1}{M} \times e^{-\beta(U_j-U_i)} \text{ and } T_{ji} = \frac{1}{M} \times 1 \text{ and the ratio } \frac{T_{ij}}{T_{ji}} = e^{-\beta(U_j-U_i)}$$

as required.

It is possible to prove that if we wait long enough the distribution of states in the Markov chain will always converge to the Boltzmann distribution; the important point is that if we start off the system in a any random state and run the Markov chain for long enough the distribution of states will converge to the Boltzmann distribution.

Monte Carlo in other ensembles

Can also carry out Monte Carlo simulations with a constant number of particles, temperature and pressure (the NPT ensemble). In such simulations, in addition to random moves of the atoms or molecules, also attempt random changes in the volume of the simulation cell. In Metropolis step $U(Z)+PV$ replaces $U(Z)$.

Monte Carlo calculations, both NVT and NPT, have been extremely useful in establishing equations of state.
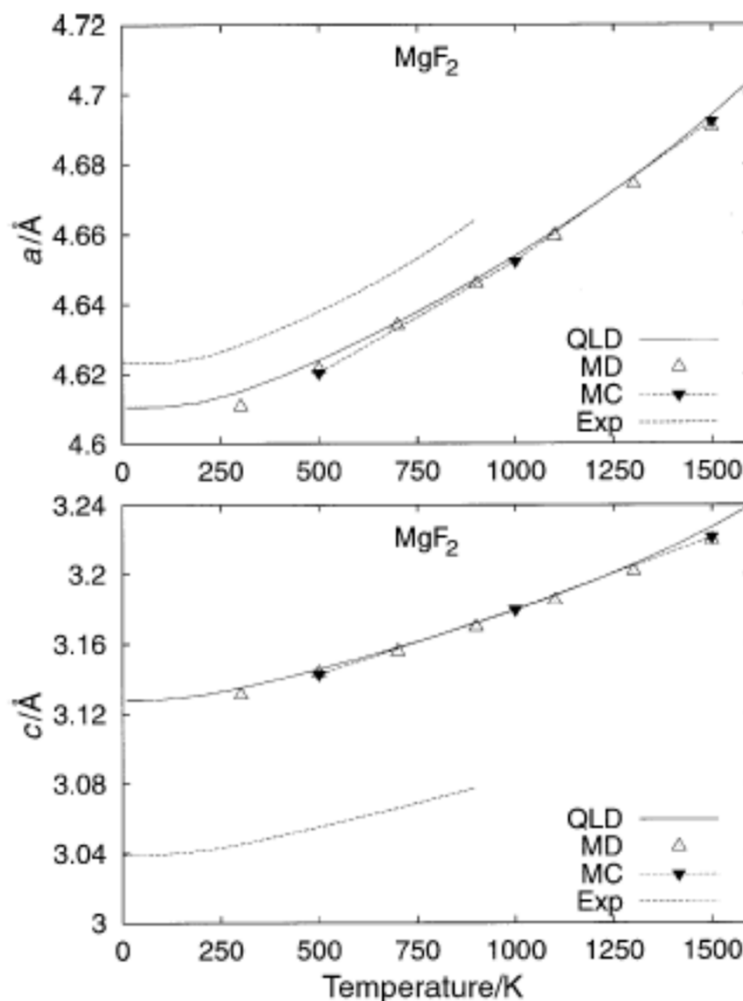
MgF_2 – calculated lattice parameters vs. T.

MC Monte Carlo

MD Molecular dynamics

QLD Direct free energy minimisation using Quasiharmonic Lattice Dynamics.

Other Monte Carlo Simulations

Monte Carlo simulations also useful for the study of alloys and solid solutions, calculating enthalpies of mixing and detailed information about the structure of such solutions.
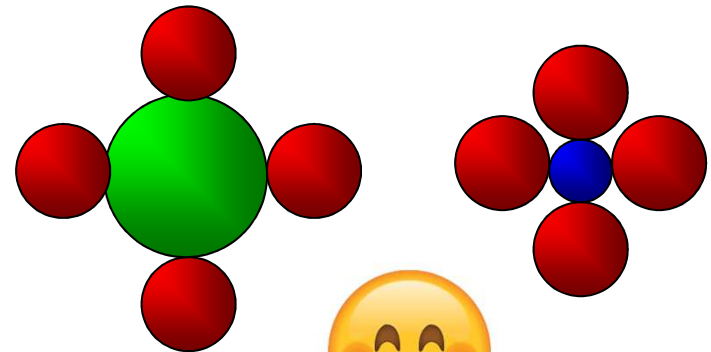
In these explicit exchanges of the different types of atoms present in the alloy are attempted, thus sampling many different configurations or atomic arrangements. Beyond mean field theory!
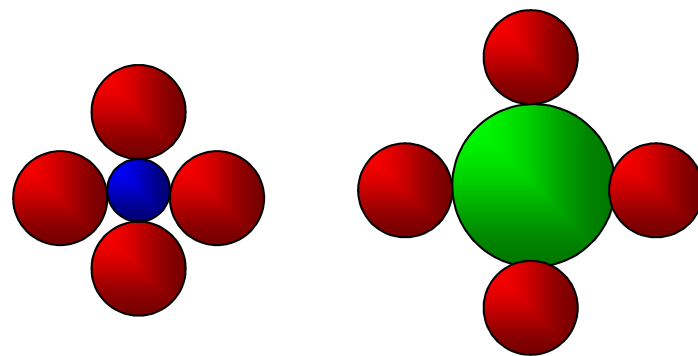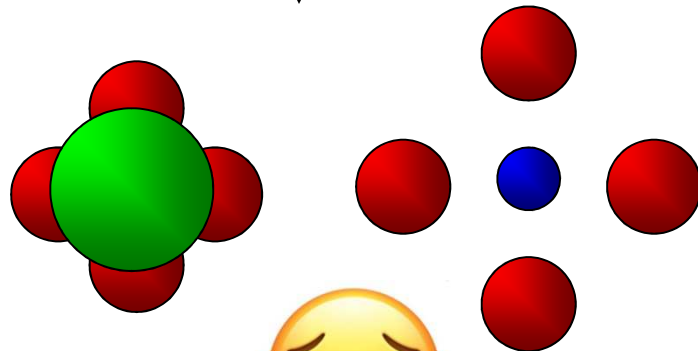
When looking at solid solutions of oxides or halides (or more generally in grossly non-stoichiometric materials) need to be able to take account of local *structural* relaxation, and clustering, particularly important when ions have different sizes and/or charges.

Swap

Relax

In Monte Carlo Exchange simulations any step may attempt a movement of an atom, or a change in size of the simulation box or an explicit exchange of two different cations.
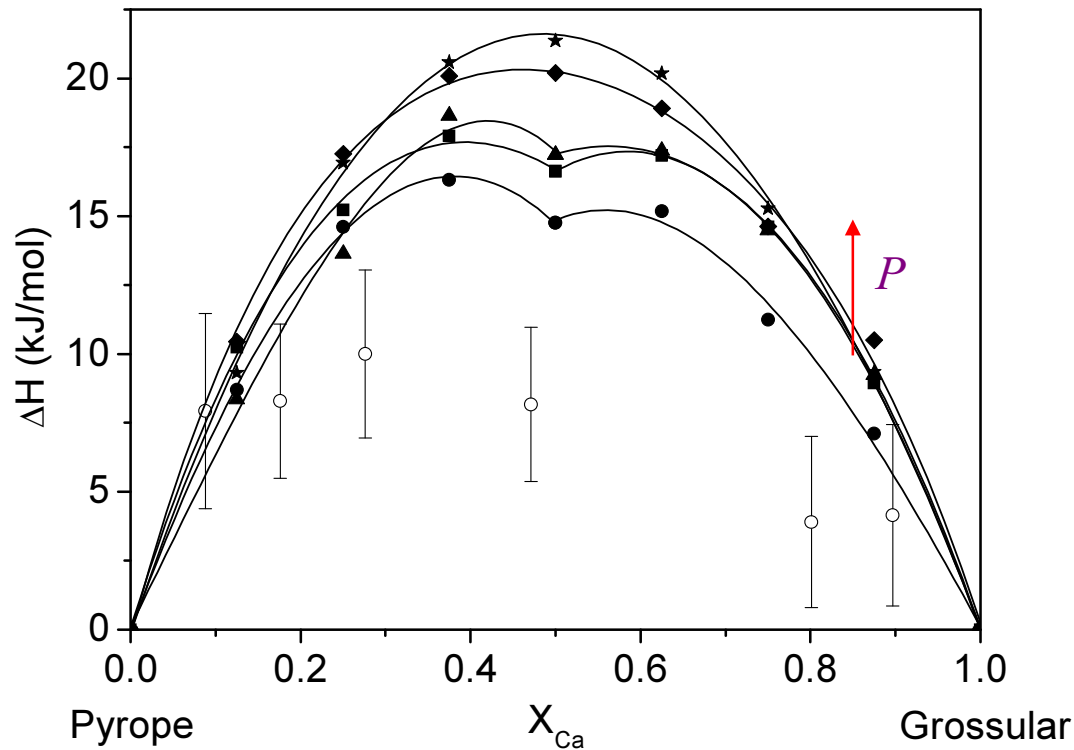

Calculated enthalpy of mixing (Exchange Monte Carlo) of pyrope (Mg) – grossular (Ca) garnets at different pressures. Experiment - empty circles.

PS Mean field a disaster!

These simulations also revealed an intriguing local ordering of the Ca and Mg ions such that third nearest cation neighbours of the same type are avoided at low temperatures. This has some intriguing consequences for the incorporation of other trace elements in the solid solution – these are more soluble than in either end member, i.e., pure pyrope or pure grossular. Also under certain circumstances large cations may preferentially substitute for Mg rather than Ca even on side grounds the reverse would be expected. Anti-Goldschmidt behaviour.

Case study - Spinel

AB_2O_4: contains both *tetrahedral* and *octahedral* cation sites.
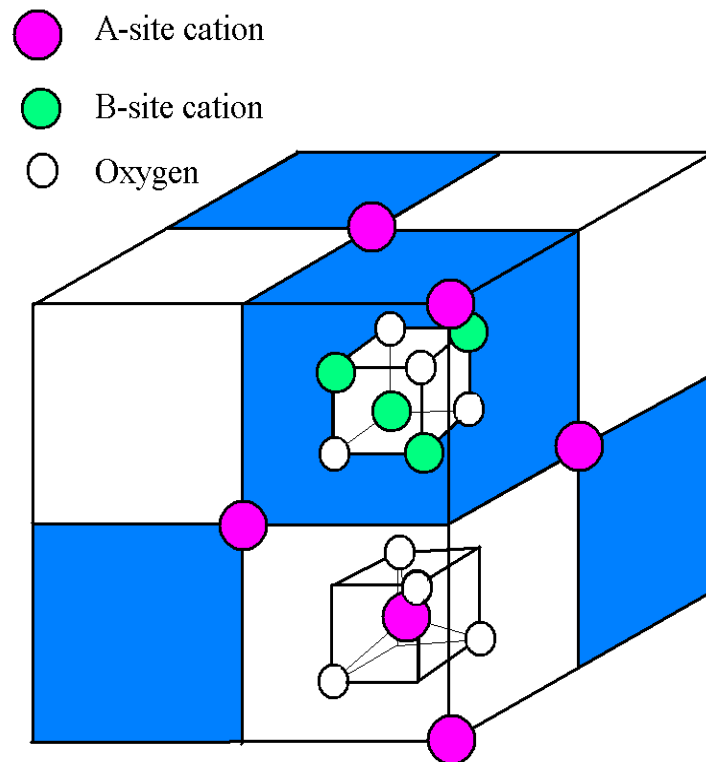
Normal spinel: A-type cations occupy *only* tetrahedral sites, while B-type cations occupy *only* octahedral sites.

Inverse spinel: tetrahedral sites occupied by B *only.* Octahedral sites occupied by *both* A and B.

In **real** systems, distribution of cations between the sites more complicated and varies with *T*.

- ⬤ A-site cation
- ⬤ B-site cation
- ◯ Oxygen

Order parameter Q for MgAl$_2$O$_4$

$(A_{1-x}B_x)_{Tet}(B_{2-x}A_x)_{Oct}O_4$
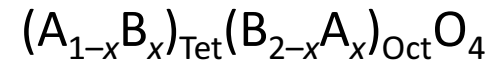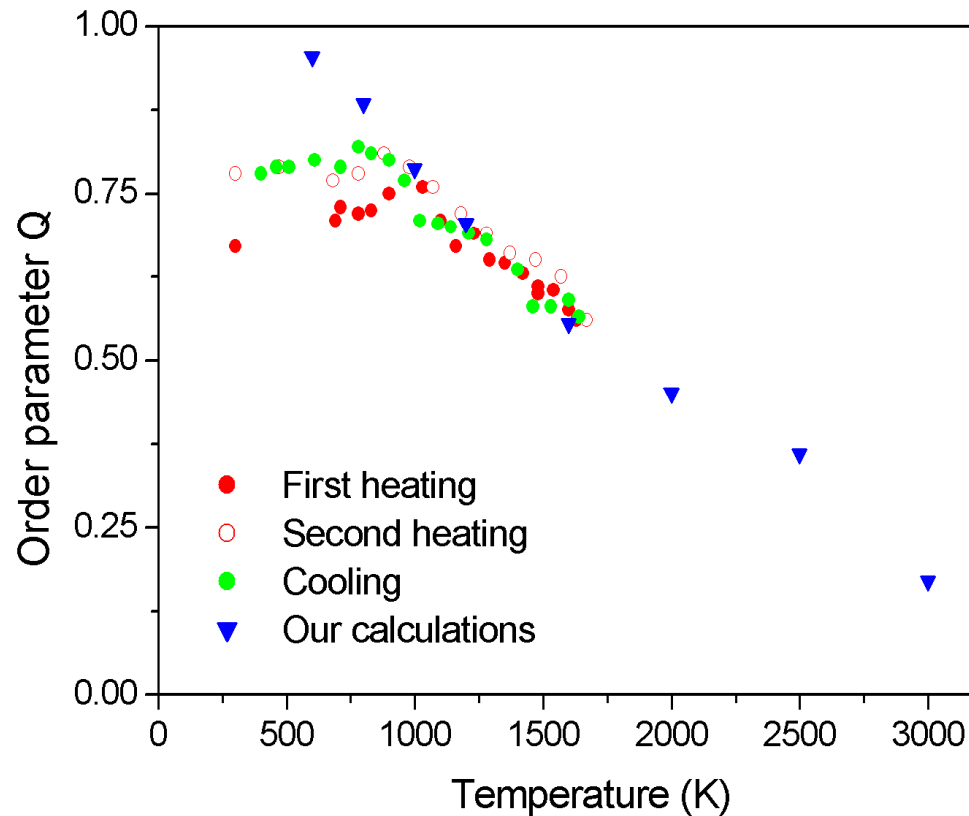
Define order parameter Q = 1-3x/2

   Q = 1 $\Rightarrow$ fully ordered normal spinel

  Q = -0.5 $\Rightarrow$ inverse

  Random distribution $\Rightarrow$ Q = 0

All calculations Monte Carlo Exchange

Kinetics vs. thermodynamics: very important

Other Monte Carlo Simulations

Many Monte Carlo simulations of magnetic ordering and its variation with temperature. Such models assume a particular form for the magnetic interactions, e.g, the Ising or Heisenberg Hamiltonian.

Monte Carlo simulations have had important roles in developing an understanding of behaviour approaching critical points, and in establishing the fundamental physics responsible for the values of critical exponents.

Other Monte Carlo Simulations (2)

- Problems involving adsorption can be tackled using grand-canonical Monte Carlo. Here the chemical potential, V and T are kept constant; the number of particles may change during the simulation.

Xe in silicalite
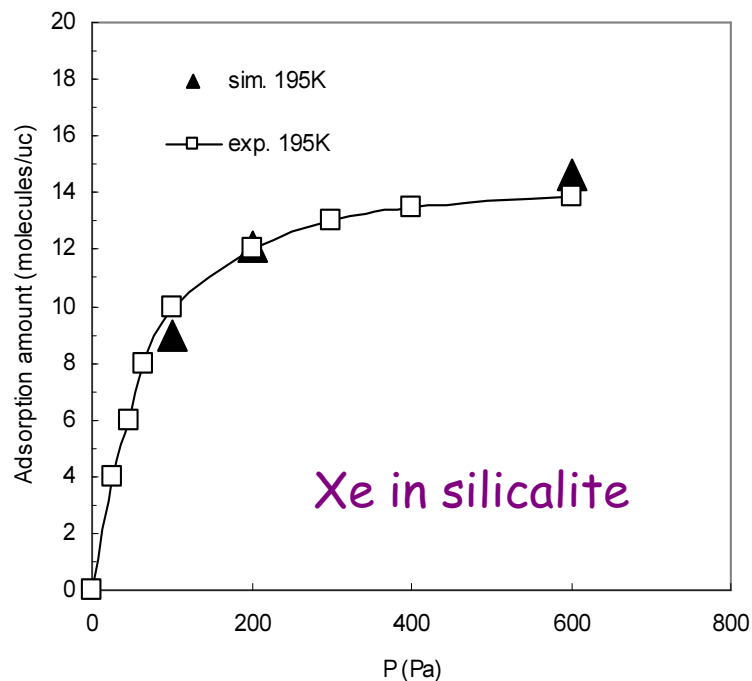
- 3 basic moves - attempts to move an atom, to destroy a particle, and to create a particle at a random position.

- Useful for calculating isotherms for adsorption of noble gases and hydrocarbons in zeolites - pressure can be directly calculated from the input chemical potential. Also examine the atomic mechanisms responsible for selectivity of a given zeolite.

Grand-Canonical Monte Carlo

In the grand canonical ensemble, the control variables are the chemical potential μ

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

the volume V and the temperature T. The total particle number N is therefore allowed to fluctuate.

It is related to the canonical ensemble by a Legendre transformation with respect to the particle number N (Statistical Mechanics Lecture)

Grand Canonical Partition function

$$\mathbb{Q}(V,T,\mu) = \sum_N Q(N,V,T)e^{\mu N/kT}$$

Closely represents the conditions under which experiments are often performed.

Grand-Canonical Monte Carlo

In a simulation one first chooses at random whether to attempt a trial particle deletion or insertion.

If insertion is chosen a particle is placed at a randomly chosen site inside the system.

If deletion is chosen, then one of the particles already present is chosen at random to be deleted. The trial move is then accepted or rejected according to the usual Monte Carlo Metropolis criterion.

Often there can be very low particle insertion and deletion probabilities, and we resort to a technique such as the configurational bias grand canonical technique to force such events. This is beyond this course!

Why not just use molecular dynamics?

Monte Carlo can sample from ensembles that go beyond molecular dynamics.

Monte Carlo is not restricted to local moves:

• Grand Canonical -> Insert/remove particles

• Swap particles -> Avoids local energy barriers

• Semi Grand-Canonical -> Trial swaps -> Free energy differences and phase diagrams

Modern Monte Carlo

Many other modern developments. Hybrid Monte Carlo/ molecular dynamics methods. Sophisticated methods have been developed to address sampling and phase problems:
• Free energy methods to improve sampling
• Lattice switch methods to sample from competing methods

See Smit and Frenkel, Understanding Molecular Simulation: From Algorithms to Applications, 2nd edition (2001)

On the inner workings of Monte Carlo codes,
Dubbeldam, Torres-Knoop and Walton, Molecular Simulation, 1253-1292 (2013)