Lecture 7

The Monte Carlo Simulation Method
Part II

Suggested reading:
Leach Chapter 8
Frenkel and Smit Chapter 3

Class stuff

- Lab assignment 6 now due 11/8.
- Proposal project now due 11/28.
- No class next week.

Proposal Project

The "proposal project" (25% of final grade) will involve the writing of a ***three page*** proposal to a fictitious group leader, project manager, agency program director, etc. to perform a detailed simulation study of a problem important to nanoscience and nanotechnology. Each student will choose a problem of interest to them, describe its important and relevance, and discuss the open questions they wish to address with simulation. He/she will then describe which simulation methods they propose to use to address the problem and why, how they will be implemented, and what the limitations, challenges, and possibilities, pros and cons are to using these methods to address the problem(s) of interest. The student will describe what will be learned from such a simulation study, and what the importance of that knowledge or understanding is in the context of the problem. The student will be graded on the depth of their understanding of the problem and the simulation approach, the appropriateness of the proposed method(s) for the problem described, the thoroughness of the project description, and how convincing his/her proposal is.

Outline for proposal

- Problem to be studied, specific questions to be addressed, importance and relevance of those questions
- Simulation methods to be used - why those methods, how implemented, limitations/challenges of method, pros & cons of method for this problem, how will you check your results?
- Outcomes - what will you learn from simulations, why important in the context of the problem?

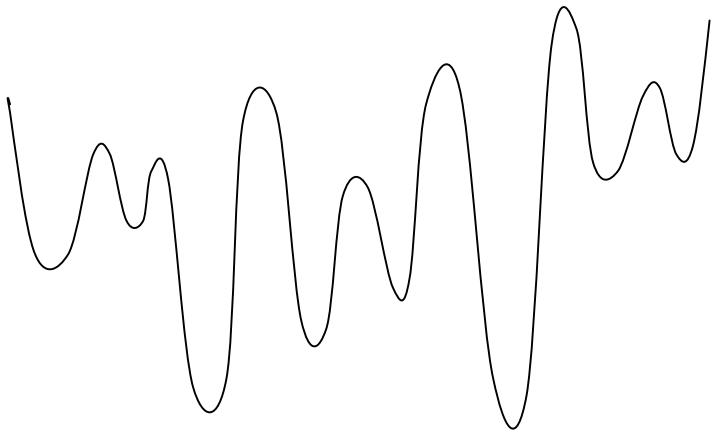
Monte Carlo vs. Molecular Dynamics

- The main goal of any simulation method is to explore efficiently those regions of phase space (position-momentum space) that are most likely to be physically realized.
  - Monte Carlo explores phase space by generating new configurations that satisfy certain energetic criteria that ensure the states visited by the method are indeed physically realizable states.
  - MD only generates states allowed by Newton's laws, which will always be physically realizable.

Monte Carlo vs. Molecular Dynamics

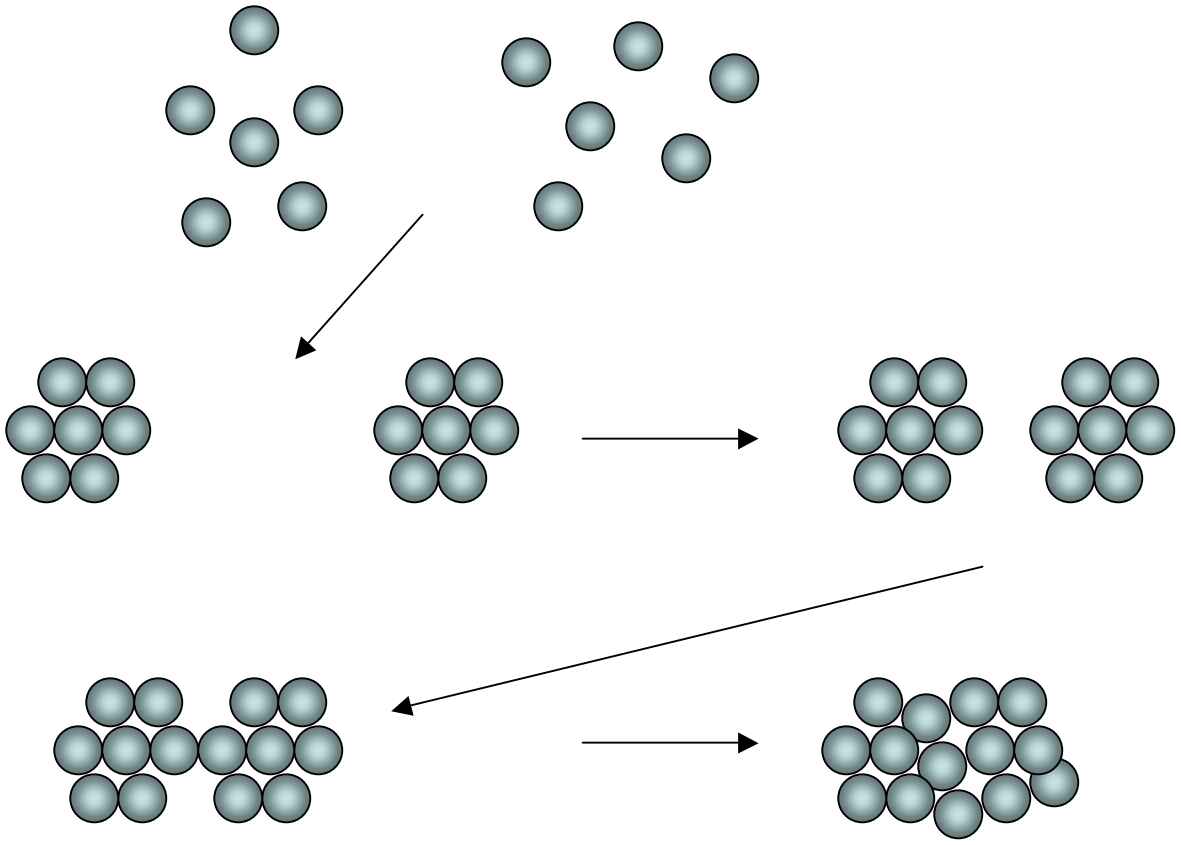
- When the system of interest is such that local moves are difficult to make (e.g. in dense liquids, polymer gels, etc.), MD generally will be more efficient than MC due to the low acceptance ratio of MC moves in those situations, since with MD everybody always moves a little.

- When the system of interest is such that there are many *local minima* in which the system can become "trapped", MC can help the system escape such traps by attempting "non-local" moves not possible with MD.



Advantages of Monte Carlo Methods

E.g. Cluster moves



Be careful to allow cluster breakage!

- As long as detailed balance is maintained, *any* trial moves may be attempted.

Monte Carlo vs. Molecular Dynamics

- For "particle-based" simulation studies (i.e. studies of materials with atomic, molecular, macromolecular or nanoparticle resolution), either method may be appropriate depending on the specific problem.
- When dynamics are required (e.g. transport coefficients like diffusivity and viscosity), MD must be used.
  - For some problems, MC may be used to study aspects of dynamics, in particular when dynamics are diffusive. Generally, this is only done for obtaining scaling relations (e.g. in phase separation by spinodal decomposition, the domain size $R \sim t^{1/3}$).
  - For specific time dependence, a mapping must be made between real time and one MC step (e.g. one MC step for glycerol may equal 12.4 fs, while one MC step for a 50 nanometer PMMA nanoparticle may equal 3.5 ns).

Monte Carlo vs. Molecular Dynamics

- MD is clearly the choice for exploring the NVE ensemble, but (depending on the problem) MC may be superior for exploring other ensembles due to some inaccuracies in thermostatting and barostatting.
- For lattice models, MC is always used since MD is awkward in discretized space.
- The two methods differ in their ability to explore phase space.
  - In some cases (e.g. isolated molecules or clusters), MC may give more rapid convergence of thermodynamic properties due to high acceptance ratios or ability to escape local minima through nonlocal (or non-physical) moves.
  - In some cases (e.g. large macromolecules with complex configurations), MC may explore phase space too slowly due to the need for small steps to keep acceptance ratio acceptable.

Monte Carlo vs. Molecular Dynamics

- Generally speaking,
  - Molecular dynamics advances the positions and velocities of all particles simultaneously and can be very useful for exploration of the *local* phase space.
  - Monte Carlo methods may be more effective for conformational or configurational changes in which the system "jumps" to a completely different area of phase space; that is, for exploration of the *global* phase space.

Monte Carlo vs. Molecular Dynamics

- Since the two methods complement each other in their ability to explore phase space, they are sometimes combined in a single simulation study.
  - E.g. force-biased MC
- They can also be combined more explicitly: by using each technique for the most appropriate part of the simulation.
  - E.g. Simulation of a solvated protein, DNA or nanotube. Equilibration is performed in a series of stages.
    - First, solute is kept fixed while solvent molecules and ions are allowed to move under the influence of the solute using MC.
    - Second, the solute itself is equilibrated using MD.

Monte Carlo vs. Molecular Dynamics

- *Hybrid MD/MC methods* exist in which the simulation algorithm alternates between MD and MC.
  - *Goal: achieve better sampling of phase space and consequently more rapid convergence of equilibrium thermodynamic and structural properties.*
- In one implementation, each MD step is followed by a MC step, where the velocities calculated in MD are unaffected by the acceptance or rejection of the MC move.

Hybrid MC/MD Methods

- In another implementation, a series of MD steps is used to generate a new state, which is then accepted or rejected on the basis of the *total* energy using the Metropolis criterion. If the new coordinates are rejected, the original coordinates are restored and MD is run again, but with new velocities chosen from a Gaussian distribution.
  - Similar to the stochastic collisions method for T control in MD, but with the addition of a MC step.
  - This hybrid algorithm samples from the canonical ensemble and has been shown to be more effective than conventional MD or MC for exploring the phase space of both simple systems and proteins.

MC vs. MD

- Given the same force field, MD is no more computationally intensive on a per particle, per timestep basis than MC.
- Generally speaking, all other things being equal, MD is the preferred method over MC, unless:
  - There is no natural dynamics for what is being studied.
    - E.g. Simulating phase equilibria to determine coexistence curves and chemical potentials can be best done with GEMC for small molecule systems, GEMD for chain molecules, unless biased MC methods used.
  - The force calculations are too burdensome (e.g. with many-body force fields).
  - A lattice model is employed.
  - MD is too slow to simulate the phenomena of interest.
    - Usually because there's lots of "ground" to cover.
    - Then MC can be used to perform unphysical moves that speed up the exploration of phase space and are essential for equilibration.

Monte Carlo Sampling from Other Ensembles

- Traditional MC samples from NVT (canonical) ensemble.
- Other ensembles may be sampled, including, e.g. NPT and μVT.
- To perform a MC simulation in the NPT ensemble, we must have a scheme for changing the volume of the simulation box to keep the pressure constant, as in MD.
  - This is done by combining random displacements of the particles with *random changes in the system volume*. The size of each volume change is governed by the maximum volume change, δV_{max}. A new volume is generated from the old volume as follows:

$$V_{new} = V_{old} + \delta V_{max}(2\xi - 1)$$

  - As usual, ξ is a random number between 0 and 1.

Monte Carlo Sampling from Other Ensembles

- NPT MC continued….
  - When V is changed, it is necessary to recalculate the interaction energy of the entire system, not just the interactions involving the one atom or molecule being displaced. (For atomic systems with simple interaction potentials only, this can be done rapidly through the use of *scaled coordinates*.)
  - It is advisable to change the volume relatively infrequently compared to the rate at which the particles are moved since energy computation is expensive.

Monte Carlo Sampling from Other Ensembles

- NPT MC continued….
  - The *acceptance criterion* used for NPT is different than for NVT. In NPT, we must consider the change in *enthalpy* H between the new and old configurations, not just potential energy U:

$$\Delta H(\mathbf{r}^N) = U_{new}(\mathbf{r}^N) - U_{old}(\mathbf{r}^N) + P(V_{new} - V_{old}) - Nk_BT\ln\left(\frac{V_{new}}{V_{old}}\right)$$

  - If ΔH is negative, then the move is accepted; otherwise $\exp(-\Delta H/k_BT)$ is compared to a random number between 0 and 1 and the move is accepted according to $\text{rand}(0,1) \leq \exp(-\Delta H/k_BT)$.

  - To check that an NPT simulation is working properly, the pressure can be calculated from the virial. This value should equal the target input pressure in the equation above.

Monte Carlo Sampling from Other Ensembles

- Grand Canonical MC
  - In the *grand canonical μVT ensemble*, the volume, temperature and chemical potential are held constant.
  - It can be more convenient to perform the simulation at constant *activity*, z, rather than constant μ. The activity is related to the chemical potential by $\mu = k_B T \ln(\Lambda^3 z)$, where Λ is the de Broglie wavelength: $\Lambda = \mathrm{sqrt}(h^2/2\pi m k_B T)$, where h is Planck's constant.
  - Key feature of GCMC: the number of particles may change during the simulation.
  - There are *three basic moves* in a GCMC simulation:
    - A particle is displaced, using the usual Metropolis method.
    - A particle is destroyed.
    - A particle is created in a random position.

Monte Carlo Sampling from Other Ensembles

- Grand Canonical MC continued….
  - The probability of creating a particle should be equal to the probability of destroying a particle. To determine whether to accept a destruction move the following change in the Gibbs free energy is calculated:

$$\Delta G_D = \frac{U_{new}(\mathbf{r}^N) - U_{old}(\mathbf{r}^N)}{k_B T} - \ln \frac{N}{zV}$$

  - For a creation step the equivalent quantity is:

$$\Delta G_C = \frac{U_{new}(\mathbf{r}^N) - U_{old}(\mathbf{r}^N)}{k_B T} - \ln \frac{zV}{N+1}$$

  - If ΔG_D or ΔG_C is negative then the move is accepted; if positive, then the exponential $\exp(-\Delta G_D/k_B T)$ or $\exp(-\Delta G_C/k_B T)$ as appropriate is calculated and compared with a random number between 0 and 1 in the usual way.

Monte Carlo Sampling from Other Ensembles

- Grand Canonical MC continued….
  - Important: the probability of creating a particle equals the probability of destroying one.
  - The ratio of *particle creation/destruction moves* to translation moves can vary, but the most rapid convergence is often achieved if all types of moves occur with approximately equal frequency.
  - GCMC is difficult to use efficiently for many systems where it is difficult to insert or destroy particles with a reasonable acceptance ratio. In those cases, *configurational bias MC methods* can help.

Monte Carlo Sampling from Other Ensembles

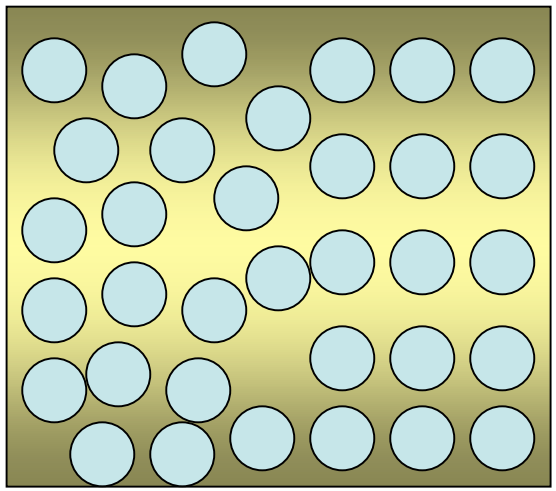
- Calculating chemical potential in NVT molecular simulation
  - To determine how *chemical potential* varies during a simulation, one uses the *Widom particle insertion method*, in which a test particle is inserted into the system and the resulting change in potential energy is calculated. *This can be used with both MC and MD*.
  - The *excess chemical potential* in the NVT ensemble (the difference between the actual value and that of the equivalent ideal gas system), is given by:

$$\mu_{excess} = -k_B T \ln\left\langle \exp\left[-U(\mathbf{r}^{test})/k_B T\right]\right\rangle$$

  - The test particle does not remain in the system. Many insertions typically required for statistically significant results.
  - Again, for many systems where particle insertion is difficult, additional techniques may be required.

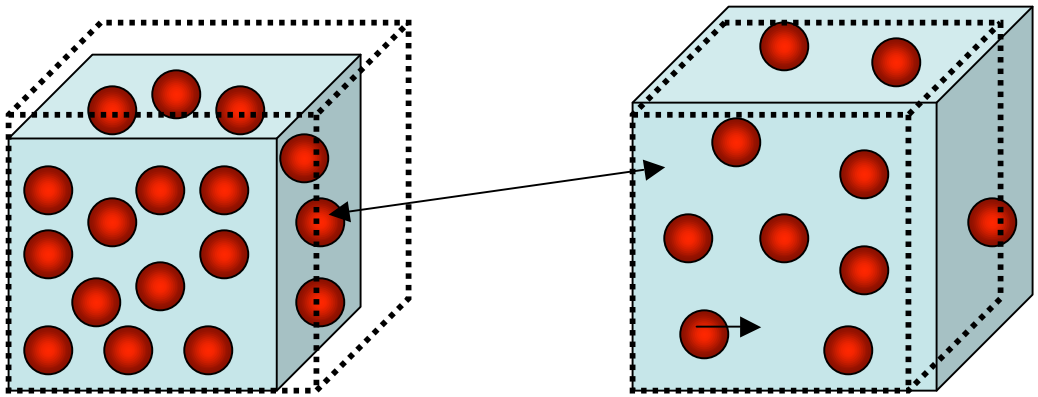
Monte Carlo Sampling from Other Ensembles

- Gibbs Ensemble Monte Carlo (Panagiotopoulis, 1987)
  - This method is used to simulate *phase equilibria*.
  - Calculations of conditions for phase equilibria is difficult with traditional methods due to presence of interface between phases, which can be comprised of a large fraction of molecules depending on system size.
  - GEMC requires only small systems.



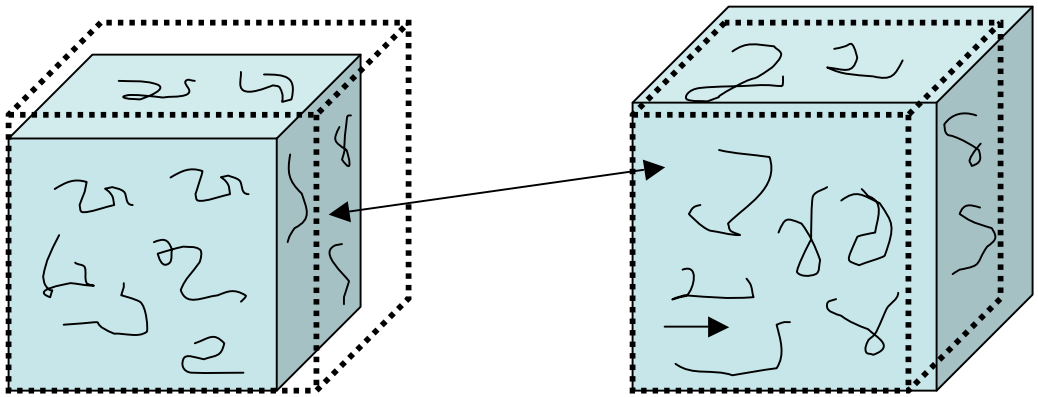
Monte Carlo Sampling from Other Ensembles

- Gibbs Ensemble Monte Carlo continued…
  - Rather than trying to form both phases and the interface within one simulation box, *use two boxes*, each representing one of the phases.
    - Boxes are subject to periodic boundary conditions.
    - Three types of move are possible:
      - Particle displacement
      - Volume change (by equal and opposite amounts).
      - Particle transfer between boxes.
    - Moves usually performed in strict order, but may be randomized.



Monte Carlo Sampling from Other Ensembles

- Gibbs Ensemble Monte Carlo continued…
  - From particle insertion, potential energies of the test particle are calculated so chemical potential may be calculated as in Widom insertion method.
  - GEMC may be used in conjunction with configurational bias MC to construct phase diagrams of complex, long-chain molecules.
    - Important prediction: that the critical density for alkanes increases with increasing chain length up to octane, but then decreases. Later verified experimentally.
  - GEMC available in Cerius2.



Random Number Generators in MC

- Random number generators produce “random” numbers.

- For a MC algorithm to work properly, the RNG must produce, over and over again, random numbers that are uncorrelated from each other and uncorrelated from the algorithm that is using them.
  - That is, if generating random numbers between 0 and 1, ALL numbers generated must be uniformly distributed between 0 and 1.

- For MC simulations of materials for which a very large (billions) of MC steps are required (e.g. long “times” needed, and/or system contains many atoms or molecules, and/or many independent samples needed), “cheap” RNGs may begin to produce strings of numbers that are correlated, and these correlations will contaminate the simulation, rendering the results unphysical.

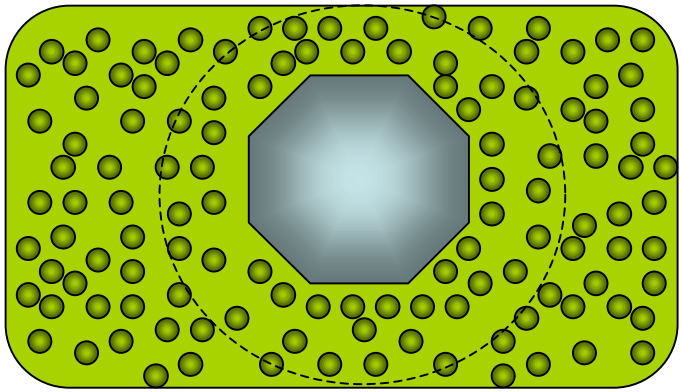
- Robust RNGs have been developed - use them!
  http://sources.redhat.com/gsl/ref/gsl-ref_17.html

Biased MC Methods

- In many instances, we are primarily interested in *part* of a system.
  - E.g. When studying *directed assembly* of nanoparticles or micelles in solvent, we are not interested in the details of the solvent per se, except insofar as they affect the dynamics of, or interactions between, the solute.
  - E.g. In proteins folding in aqueous solutions, we are uninterested in the solvent except for those solvent molecules affecting the folding process.

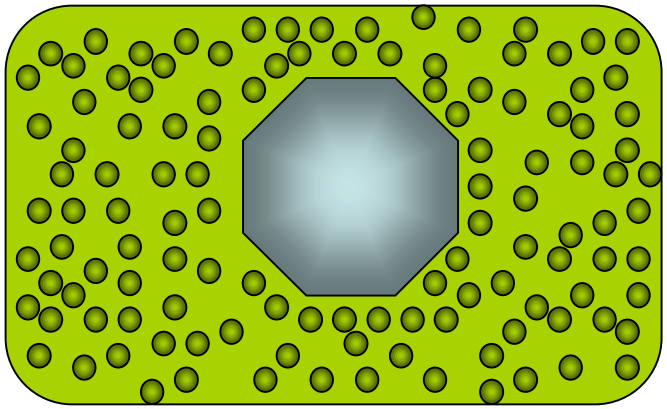
Biased MC Methods

- Preferential sampling - cutoff method
  - The molecules in the vicinity of the solute are moved more often than those farther away.
  - This can be done by defining a cutoff region around the solute. Molecules inside the region move more frequently than those outside it as determined by a probability parameter p, that can be tuned as necessary.



Biased MC Methods

- Preferential sampling - distance method
  - Instead of using a cutoff region, the probability of choosing a solvent particle to move can be related to its distance from the solute, usually by some inverse power of distance: $p \propto r^{-a}$.
  - Must follow correct procedures for accepting or rejecting moves to be consistent with detailed balance and microscopic reversibility, since out $\rightarrow$ in $\neq$ in $\rightarrow$ out.



Biased MC Methods

- Force-bias Monte Carlo (Pangali, 1978; Rao and Berne, 1979)
  - *Biases the move according to the direction of the forces acting on the particle or group of particles*.
    - A molecule is chosen at random, and the forces acting on are calculated as in MD.
    - The random displacement by which the molecule attempts to move is chosen from a probability distribution peaked in the direction of the force.

Biased MC Methods

- Smart Monte Carlo (Rossky, et al 1978)
  - Another force-bias-type algorithm. Also requires the forces acting on the molecule to be calculated as in MD.
  - The displacement of a molecule has two parts: the force, and a random vector δr^G such that:

$$\delta \mathbf{r}_i = \frac{A\mathbf{f}_i}{k_B T} + \delta \mathbf{r}_i^G$$

  - The random displacement δr^G is chosen from a normal distribution with zero mean and variance equal to 2A.

Biased MC Methods

- Force-biased vs. smart Monte Carlo
  - SMC imposes no limit on the displacement an atom may undergo.
  - FBMC limits the displacement to a cube centered on the atom.
  - In practice the two methods are very similar and can be used interchangeably.
  - In some cases they can be much more efficient at exploring phase space than traditional MC and can avoid traps in phase space better than conventional Metropolis.
  - FBMC and SMC significantly *enhance the acceptance rate* of trial moves, thereby enabling larger moves to be made as well as simultaneous moves of more than one particle.
  - The need to calculate the forces makes the methods more cpu-intensive.

Biased MC Methods

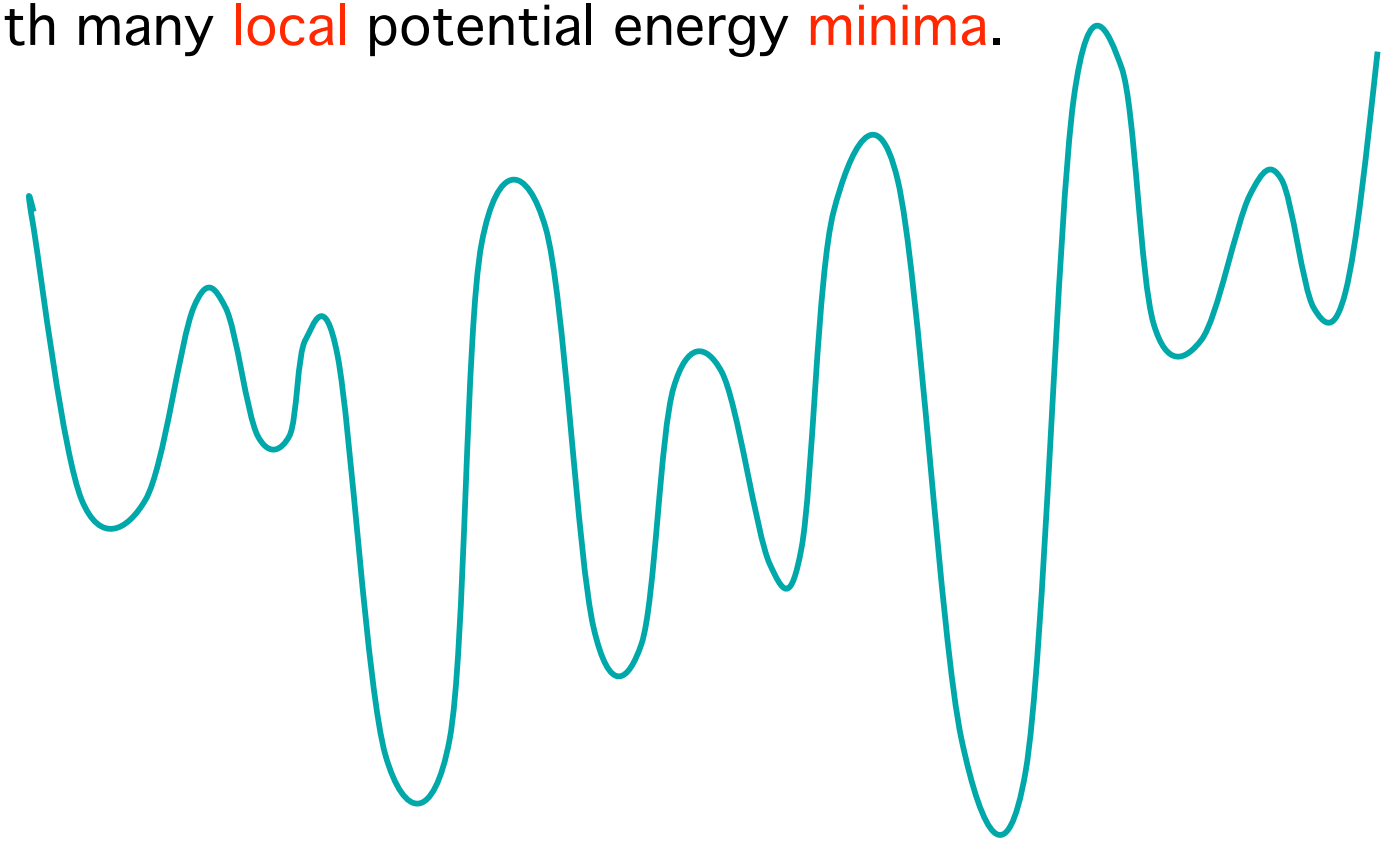
- Configurational biased MC (Rosenbluth & Rosenbluth, 1955; Siepmann 1990)
  - Developed originally with application towards macromolecules, but can be applied to any situation where acceptance ratio is low due to high energy overlaps.
  - Used for sampling equilibrium conformations of macromolecular materials, which is usually time-consuming because the natural dynamics of polymers are dominated by topological constraints.
  - In CBMC, a molecule is preferentially directed (biased) towards acceptable structures. The effects of these biases can be removed by modifying the acceptance rules.
    - E.g., non-physical moves involving the regrowing of chains are performed to accelerate the sampling of phase space.

  - *Read extended discussions in Leach and FS on configurational biased MC.*

Accelerating Equilibration with MC

"Parallel Tempering" Methods

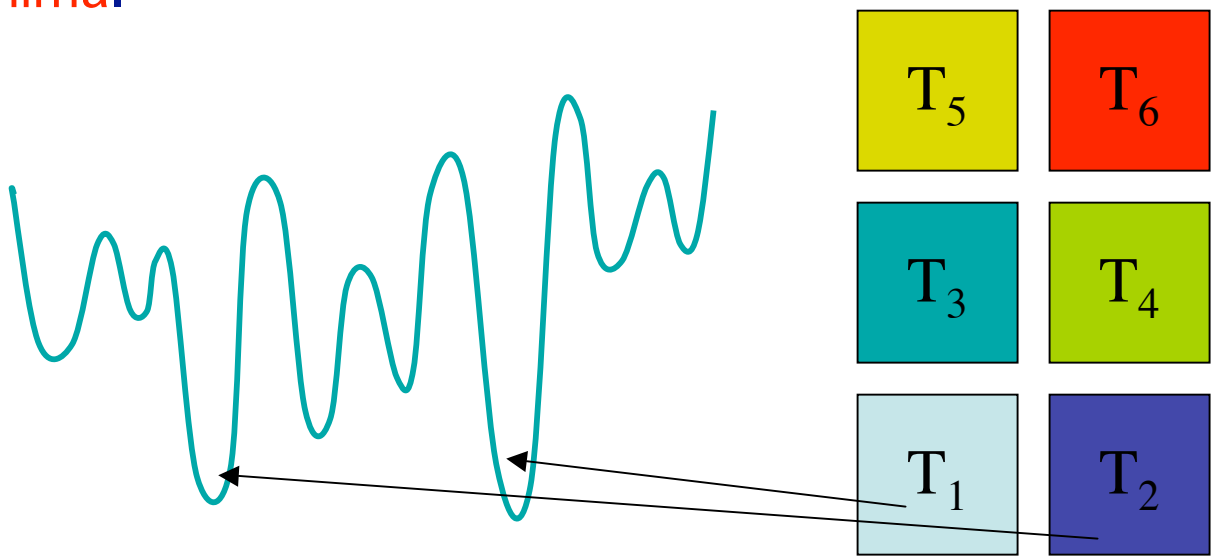
- The method of *parallel tempering* is a MC scheme developed to aid in exploring phase space for systems with many local potential energy minima.



Accelerating Equilibration

Parallel Tempering Methods

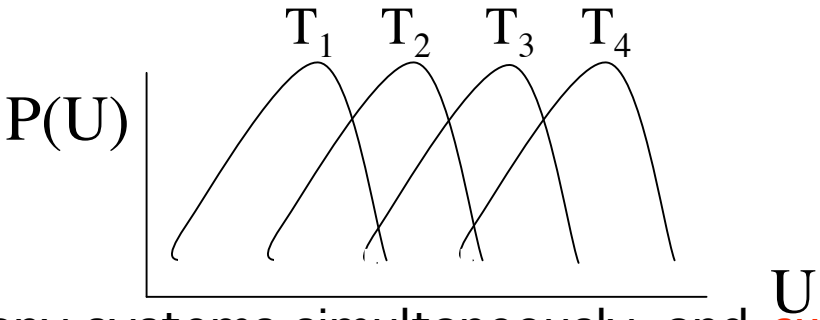
- In parallel tempering, many systems are *simulated simultaneously*, each at a different state point.
- Usually states differ in T, but can differ in P, μ, etc.
- Those states at sufficiently high T pass easily over energy barriers, while those at low T don't, and become trapped in local minima.



Accelerating Equilibration

Parallel Tempering Methods

- In parallel tempering, one includes MC moves that attempt to swap systems belonging to *different* thermodynamic states.
  - E.g. attempt to swap a configuration from a high T run with one in a low T run, using the Boltzmann factor.
  - If ΔT is very large, the swap probability will be very low.
  - Instead, take many smaller steps by using intermediate temperatures. Must use enough that their *density of states overlap* with each other.



  - Simulate many systems simultaneously, and *swap between those runs with a small ΔT*.

Accelerating Equilibration

Parallel Tempering Methods

- The swap moves do not disturb the Boltzmann distribution corresponding to a particular ensemble (state point), since the moves only *accelerate the sampling of the wings of the distribution*. This more quickly generates low probability moves that kick the system out of its local minima.

- Parallel tempering may be used in conjunction with traditional MC or MD.

- *Essentially gives many state points in parallel faster than one at a time.* Good if using many individual processors anyway.

- Parallel tempering has been used for dense liquids and glasses, polymers melts and gels, proteins, etc. *Any systems plagued by quasi-ergodicity are good candidates for parallel tempering*.