Computational Nanoscience NSE C242 & Phys C203 Spring, 2008

Lecture 9:
Hard Sphere Monte Carlo:
In-Class Simulation
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One of the advantages of MC is that it permits to study systems characterized by non-analytical interaction potentials.

The first application of the Metropolis Monte Carlo method that we will consider is to a system of classical identical particles of mass m interacting via the so-called *hard-sphere* interaction potential:

$$v(r) = +c$$
 if $r \le \sigma$ and 0 otherwise

where c is just the "height" of the potential core.

The Metropolis algorithm was first applied to such a system, which is of great theoretical interest despite its apparent artificiality.

Its treatment by molecular dynamics is rendered complicated by the nonanalyticity of the interaction potential.

MD simulation is possible, but it requires the exact treatment of particle collisions, which in turn involves some changes of the algorithm (no use of the Verlet algorithm is possible).

On the other hand, a Monte Carlo simulation is straightforward. The simplest way to do it is to use the Metropolis algorithm with single-particle moves.

One simply attempts to move one particle at a time, and update the total potential energy by counting the number of particles whose radii overlap with the radius of the particle being moved at the current and proposed new position.

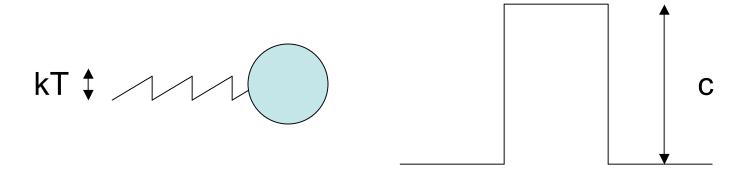
The acceptance/rejection test is performed as explained previously.

Note that the relevant parameter of the simulation is βc ; if the temperature is very high, then $\beta c \rightarrow 0$ and the acceptance becomes large. The system behaves more and more like a free-particle system, which is expected of any system at sufficiently high temperature.

On the other hand, as the temperature is lowered, then $\beta c \rightarrow \infty$, and the presence of the core becomes more and more important. Moves that would result in particles overlapping are inevitably rejected.

Note that, on lowering sufficiently the temperature, any core will become important enough, and in the limit $\beta \rightarrow \infty$ the system will behave as if the core were infinitely high, and the density determines all thermodynamic properties.

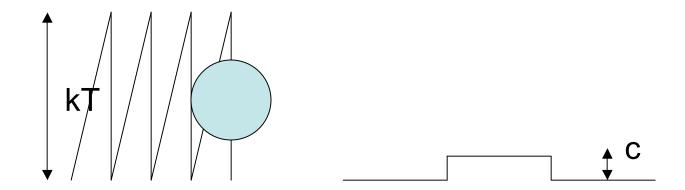
(Think about marbles -- they cannot penetrate each other.)



thermal energy much lower than barrier height -- barrier becomes inpenetrable

^{*} See, e.g., J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, Academic Press (1969).

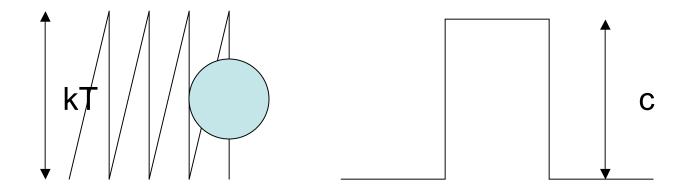
Conversely, if c→0 then the system behaves in the same way at any temperature, and again the density is the relevant quantity.



thermal energy much larger than barrier height -- particle does not "see" the barrier

^{*} See, e.g., J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, Academic Press (1969).

At intermediate temperatures, the thermal energy is comparable to the barrier height. Thermal effects are important here.



thermal energy comparable to barrier height -- system can "play"

^{*} See, e.g., J. P. Hansen and I. R. McDonald, Theory of Simple Liquids, Academic Press (1969).

One of the most interesting problems in theoretical physics consists of determining whether the hard-sphere system, which lacks a transition comparable to liquid-gas due to the absence of attractive forces, can nonetheless display a melting-freezing transition at sufficiently low temperatures, upon varying the density.

This problem cannot be tackled convincingly analytically, due to the discontinuity of the potential, particularly in the limit $c \rightarrow \infty$, and arguably represents the earliest success of computational many-body physics.*

Ok, let's do a few MC simulations.

We'll use the code "HSMC" (Hard-Sphere Monte Carlo), which yet again has been given an absolutely stupendous web interface on the NanoHUB.

We'll need to enter some input information:

- The dimension for your simulation
- The number of particles
- The density
- The scaled temperature (kT/c)
- The maximum displacement of a single particle in Metropolis
- The total length of the simulation (1 sweep means that a move is attempted for all particles).

Output is simpler (or less) than in MD since the momentum/velocity part is gone and there is no temperature monitoring.

Let's do the following here in class:

We will start in the low temperature limit.

Start with a system in 2 or 3 dimensions, 64 particles, a scaled temperature of 0.05 and a density of 0.5 -- is this a high or low density??

Does the temperature of 0.05 correspond to a high or low potential barrier?

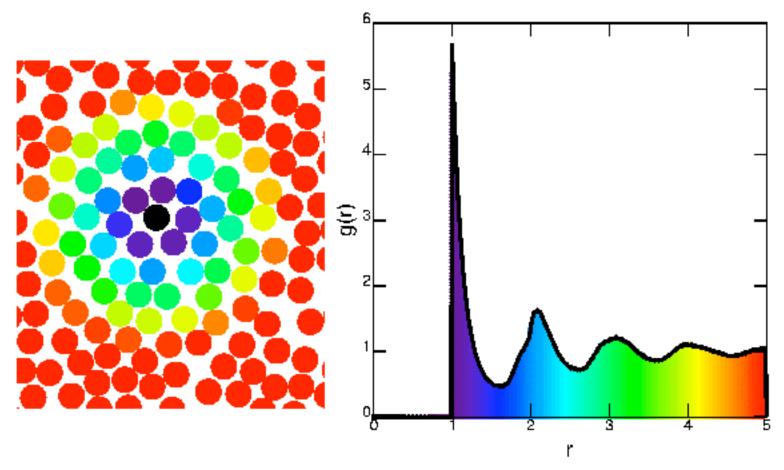
Now observe how the pair distribution functions change with density? What can we say about them? Can you find an ordering transition? What might be the order parameter for the transition?

What happens to the transition when we go to higher temperature? Does the transition exist in 1 or 2 dimensional systems?

WARNING: For each of your simulations, make sure your choice for (a) the number of metropolis sweeps and (b) the metropolis step size are reasonable! The system should be equilibrated by the end, and you should have reasonable acceptance ratios whenever possible.

A Hint

from http://www.physics.emory.edu/~weeks/idl/gofr.html



What can you tell about the short-range order? Long-range order?

In Closing ...

The hard sphere system, although not new by any means, is still the subject of research.

For example, it has been used recently to explore the nature of the glass transition.



News and Views

Nature 405, 521-523 (1 June 2000) | doi:10.1038/35014711

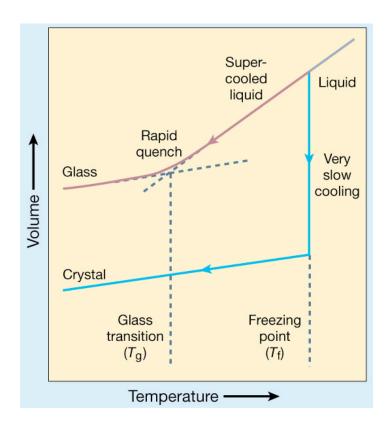
Glass transition: Hard knock for thermodynamics

Salvatore Torquato

It was once thought that relatively few materials could be prepared as amorphous (or disordered) solids. It is now widely believed that the amorphous state is a universal property of condensed matter, whether ceramic, polymeric or metallic. The amorphous solid known as a 'glass' can be achieved by quenching (cooling) a liquid sufficiently rapidly to below its glass transition temperature, $T_{\rm g}$, to avoid crystallization (Fig. 1). Roughly speaking, a glass is a material that is out of equilibrium, having the disordered molecular structure of a liquid and the rigidity of a solid. But the underlying physics of the glass transition remains one of the most fascinating open questions in materials science and condensed-matter physics. A hotly debated issue is whether the glass transition involves an underlying thermodynamic (static) or kinetic (dynamic) phase transition. On page 550 of this issue, Santen and Krauth provide further evidence that the glass transition is not thermodynamic in origin.

In Closing ...

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An underlying thermodynamic phase transition would be reflected in a discontinuous change in certain thermodynamic properties in crossing this density. In doing these calculations, one must ensure that all of the phase space is sampled without bias (that is, sampling is ergodic). But standard Monte Carlo techniques are known to be non-ergodic when the dynamics slow down near phase transitions. To circumvent this problem, Santen and Krauth use a 'cluster' Monte Carlo algorithm — a method originally introduced to study so-called spin systems near their critical points $\frac{9,\ 10}{2}$. In particular, by a non-local swapping of large clusters of disks, they avoid the problems that conventional Monte Carlo methods have near critical points and find no evidence for a thermodynamic glass transition. Although the specific case studied here does not settle the issue once and for all (for example, other realistic models for glass formation might behave differently), it is another piece of evidence that adherents of the thermodynamic phase-transition theory will find difficult to discount.