Structural Phase Behaviour...

...via Monte Carlo Techniques

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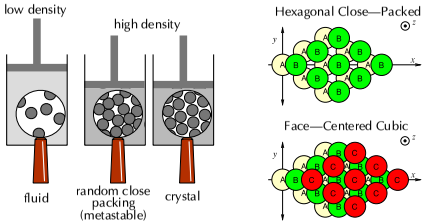
Introduction

Predicting crystal structure remains a challenge, even for our simplest models of matter. This work concerns a new technique, *Lattice—Switch Monte Carlo* [1,2], which allows different structures to be compared directly.

The Hard Sphere Solid

As the density of a system of hard-spheres is increased, the system undergoes an entropy-driven first-order phase transition from a fluid to an ordered crystalline phase.

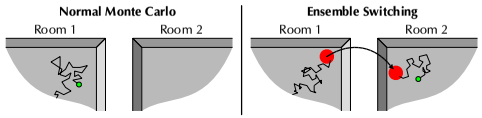


Is the equilibrium crystal structure face-centered cubic or hexagonal close-packed? To find out, we must calculate the entropy difference between these two structures.

Ensemble Switching

Calculating which structure has the greatest entropy via a Monte Carlo simulation is analogous to using a random walker to determine which of two rooms is the larger.

A normal Monte Carlo simulation will get stuck in one room, and so can tell you nothing about the relative sizes of the rooms.



An ensemble switch would allow the walker to switch ('teleport') back and forth between the Room 1 and Room 2 ensembles, via a 'gateway' in each room. The larger room is then simply the room that the walker spends the most time in.

A lattice-switch is an ensemble switch which allows a Monte Carlo simulation to visit the ensembles associated with two different crystalline structures. The structure with the greatest entropy is the one the simulation spends the most time in (the most probable phase).

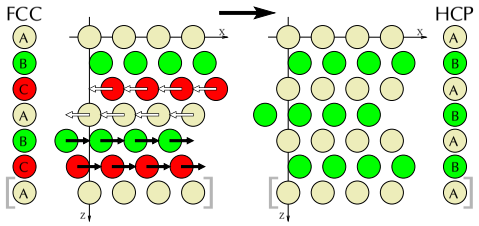
Lattice—Switch Monte Carlo

We need to design a mechanism by which a Monte Carlo simulation may switch between the *fcc* and *hcp* ensembles.

We first re-express the position of each sphere in terms of a lattice-site vector, and a displacement from that site:

$$\vec{r}_i = \vec{R}_i + \vec{u}_i$$

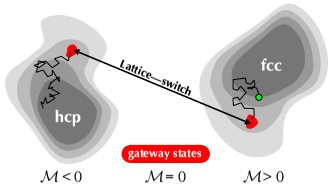
We can now define the lattice-switch as a Monte Carlo move where we attempt to swap one set of lattice site vectors ($\vec{R}_i$) for another, while keeping the displacements from those sites ($\vec{u}_i$) fixed. There are a large number of possible lattice-site mappings. The mapping illustrated below, translating pairs of planes together, was chosen due to it's simplicity and efficiency.



The lattice-switch move is usually rejected (as it would cause spheres to overlap). To overcome this problem, we first characterize the route between the phases via an order parameter $\mathcal{M}$:

$$\mathcal{M} = \left[\text{the 'cost' of switching to } hcp\right] - \left[\text{the 'cost' of switching to } fcc\right]$$

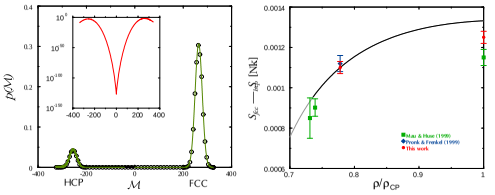
The 'cost' of the switch can be measured in terms of the number of overlaps that it would create. Thus, while the simulation is in *fcc*, $\mathcal{M}$ is positive, and while in *hcp* it is negative. The switch can only be performed when $\mathcal{M} = 0$ (i.e. in the gateway states).



The simulation is then biassed so that the entire range of $\mathcal{M}$ is visited. We measure the biassed probability distribution of $\mathcal{M}$, and remove the bias to recover the true P($\mathcal{M}$). The phase with the greatest entropy will have the largest of the two peaks in the P($\mathcal{M}$) distribution, and the entropy difference can be calculated from the ratio of the weights of the two peaks.

Hard—Sphere Results

The first graph shows the measured P($\mathcal{M}$) for a system of 1728 hard spheres (at 77.78% of the maximum close-packed density). The *fcc* peak is clearly larger, and so *fcc* has the greater entropy.



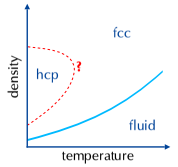
Combining our results[2] with those of others[3,4], we find that the entropy difference favours *fcc* for all densities up to close-packing (where $S_{fcc} - S_{hcp} = 125(3)\times10^{-5}\,Nk_B$).

Simulations have also been performed in the constant-pressure ensemble, and have shown that the Gibbs free-energy difference between the structures is numerically equal to the entropy difference to within the (high) accuracy of our results.

Various different lattice-site mappings have been investigated, as well as the nature of the gateway states. This has lead to a clearer picture of how the algorithm works, and how to get the best performance from it.

The Lennard—Jones Solid

The position of the *fluid—fcc* melting line has been calculated[5], and by evaluating ground-state energies one can determine which is the preferred structure along the T = 0°K isotherm. However, the behaviour between these two extremes is still unclear.



The lattice-switch technique has been extended to soft potentials, and simulation work has begun, with the aim of identifying the position of the *fcc—hcp* coexistence curve.

It should be possible to compare these results with experimental findings for rare gas solids, and so clarify the crossover from classical to quantum-mechanical behaviour.

References

[1] *AD Bruce, NB Wilding & GJ Ackland, Phys. Rev. Lett.* **79**, p3002 (1997).
[2] *AD Bruce, AN Jackson, GJ Ackland & NB Wilding, [to be published].*
[3] *S Pronk & D Frenkel, J. Chem. Phys.* **110**, p4589 (1999).
[4] *RJ Speedy, J. Phys: Condensed Matter* **10**, p4387 (1998).
[5] *Y Choi, T Ree & FH Ree, J. Chem. Phys* **99**, p9917 (1993).

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