Freezing by Monte Carlo Phase-Switch

N.B. Wilding and A.D. Bruce

Department of Physics and Astronomy, The University of Edinburgh
Edinburgh, EH9 3JZ, Scotland, United Kingdom

We describe a Monte Carlo procedure which allows sampling of the disjoint configuration spaces associated with crystalline and fluid phases, within a single simulation. The method utilises biased sampling techniques to enhance the probabilities of gateway states (in each phase) which are such that a global switch (to the other phase) can be implemented. Equilibrium freezing-point parameters can be determined directly; statistical uncertainties prescribed transparently; and finite-size effects quantified systematically. The method is potentially quite general; we apply it to the freezing of hard spheres.

PACS numbers: 64.70Dv, 02.70.Lq
Freezing is the archetypal phase transition, one of the prime examples of thermodynamics in action, and a topic of ongoing interest \[9,10\]. It is therefore remarkable that the challenge it presents to computational science has yet to be satisfactorily met. The generic problem is to compute the location of the freezing transition (more generally the liquid-solid coexistence curve) on the basis of a particle-level model. The approach to this problem has evolved little since the pioneering work of Hoover and Ree \[4\]. The free energy of each phase (fluid (F) and crystalline solid (CS)) is computed for states of a range of densities, using integration methods which connect their thermodynamic properties with those of effectively single-particle reference states, whose free energies are known \textit{a priori}; the two branches of the free-energy are then matched to determine the freezing parameters. This approach has several drawbacks. The integration path may encounter singularities – both real and artificial \[5\]. Corrections may be needed to allow for the fact that the path does not quite reach the idealised reference state \[5\]. The implicit perspective adopted (that there are two separate calculations to be done – one for each phase) has meant that predictions for freezing parameters are often a synthesis of work done by different authors on different system-sizes, making it hard to quantify finite-size effects \[11\].

This paper describes a different approach to the problem. We build on recent work \[11\], in which we showed that the disjoint configuration spaces associated with two phases of a many-body system can \textit{both} be visited in a single Monte Carlo (MC) simulation, by harnessing extended-sampling (ES) methods \[10\] to facilitate a direct switch from one phase to the other; instead of traversing a region where both phases coexist \[11\] the method may be thought of as \textit{leaping} from one space to the other; the role of ES is to allow the system to find the ‘gateway’ states from which a leap will be accepted. The method was developed \[10\] to tackle the problem posed by two crystalline phases, where interfacial states are computationally problematic. The same is true of the CS-F problem. But significant extensions of the framework are needed to address the qualitatively different characters of the two configuration spaces. First, the \textit{communal entropy} of the fluid \[12\] provides a conceptually different form of barrier that has to be negotiated to reach the gateway states: we show how one can do this. Second, the \textit{distinct contributing configurations} have to be identified with care: in so doing we unearth a small but significant flaw, inherent (we think) in all previous simulation-studies of CS-phase free energies. The method we develop is general; we illustrate it here with a study of the entropically-driven freezing of hard spheres, where earlier studies provide useful benchmarks \[13\].

Consider \(N\) particles (hard spheres) confined to volume \(V\), variable under a constant external effective pressure \(p\) \[13\], and subject to periodic boundary conditions. The configurational weight of a phase may be written as

\[
Z_{\gamma}(N, p) = \int_0^\infty dV e^{-pV} Z_{\gamma}(N, V)
\]

where \(\gamma\) (CS or F) labels the phase, while

\[
Z_{\gamma}(N, V) = C_0 \prod_{i=1}^N \int_{V, \gamma} d\vec{r}_i e^{-E_i(\vec{r})}
\]

Here \(E\) is the hard sphere configurational energy \[14\]. The prefactor \(C_0\) is chosen according to whether the particles are regarded as ‘strictly classical’ \((C_0 = 1)\) or ‘classical but indistinguishable’ \((C_0 = \frac{1}{N!})\). The results for observables are independent of this choice. The \(\gamma\)-label on the integral stands for some \textit{configurational constraint} that picks out configurations \(\{\vec{r}\}\) that ‘belong’ to phase \(\gamma\). We choose to formulate that constraint as follows \[13\]. Let \(\vec{R}_1^\gamma \ldots \vec{R}_N^\gamma \equiv \{\vec{R}\}^\gamma\) denote some \textit{representative configuration} of phase \(\gamma\). Then the constraint may be regarded as picking out those configurations which can be reached from \(\{\vec{R}\}^\gamma\) on the simulation timescale \[16\]. It is convenient to use the sites defined by \(\{\vec{R}\}\) as the origins of the particle coordinates. Thus we define a set of displacement vectors \(\{\vec{u}\}\) by \(\vec{u}_i \equiv \vec{r}_i - \vec{R}_i^\gamma\) and write \(E^\gamma(\{\vec{u}\}) \equiv E(\{\vec{R}_i^\gamma + \vec{u}\})\).

In the case of the F-phase all contributing configurations are reachable from any one; we may write simply

\[
Z_F(N, V) = C_0 \prod_{i=1}^N \int_{V, \{\vec{R}\}^F} d\vec{u}_i e^{-E_i(\{\vec{u}\})}
\]

where \(\{\vec{R}\}^F\) is some specific but arbitrary fluid configuration, which can be selected at random in the course of MC exploration of the fluid phase. It is natural to choose \(\{\vec{R}\}^{CS}\) to define the sites of a lattice of the appropriate symmetry (here fcc) and scale \[17\]. But one must recognise that the complete CS configuration space actually comprises a number of distinct mutually inaccessible \textit{fragments} \[18\] corresponding essentially to the different permutations of particles amongst lattice sites \[9\]. By symmetry each fragment should contribute equally to the configurational weight; but MC simulation will visit (and thus count) only the states within the fragment in which it is initiated. The total configurational weight of the CS phase is given by multiplying the contribution of one fragment by the number of fragments. Since global translation (permitted by the boundary conditions) ensures that \textit{one} fragment includes \textit{all} possible locations of any chosen particle, the number of fragments is the number of ways of assigning the ‘other’ \(N - 1\) particles to \(N - 1\) Wigner-Seitz cells of some underlying notional fixed lattice. This number is not \(N!\) but \((N - 1)!\). Thus

\[
Z_{CS}(N, V) = C_0(N - 1)! \prod_{i=1}^N \int_{V, \{\vec{R}\}^{CS}} d\vec{u}_i e^{-E_i^{CS}(\{\vec{u}\})}
\]
The ratio of the configurational weights of the two phases (the ratio of their total \textit{a priori} probabilities) follows by combining Eqs. 1, 3 and 4:

\[
\mathcal{R}_{F,CS} = \frac{P(F|N,p)}{P(CS|N,p)} = \frac{Z_F(N,p)}{Z_{CS}(N,p)}
\]

\[
= \frac{[N]^{-1} \int_0^\infty dV e^{-pV} \prod_{i=1}^N \int V_i \{ \vec{R} \}_F d\vec{u}_i e^{-E_F(\{ \vec{u} \})}}{[N]^{-1} \int_0^\infty dV e^{-pV} \prod_{i=1}^N \int V_i \{ \vec{R} \}_{CS} d\vec{u}_i e^{-E_{CS}(\{ \vec{u} \})}}
\]

from which the Gibbs free-energy-density difference follows as

\[
\Delta g \equiv g_{CS}(N,p) - g_F(N,p) \equiv \frac{1}{N} \ln \mathcal{R}_{F,CS}
\]

In writing Eq. 5 we have chosen to split the fragment number \((N-1)!\) into separate factors of \(1/N!\) and \(1/N\). If one so wishes \([22]\) one may regard the former as the familiar indistinguishability overcount-correction appropriate for phases (fluids) of non-localised particles. But then one must recognise the existence of an analogous correction (the \(1/N\) for the CS phase, in which particles are localised—only relative to one another. It seems that this correction has been missed by other authors; we shall see that it contributes significantly to finite-size effects.

The relative stability of the two phases is determined by the ratio of the associated configurational weights (Eq. 6). To determine that ratio we need a MC procedure which visits both solid and fluid regions of configuration space. Since, by construction, the system may be transformed between the CS and F reference states simply by switching the representative vectors \((\vec{R}_i^F \rightleftharpoons \vec{R}_i^{CS} \forall i)\), by continuity, \textit{any} CS (F) configuration ‘sufficiently close’ to the representative one will also transform to a F (CS) state under this operation. This phase switch can itself be realised as a MC step, so that the phase label \(\gamma\) becomes a stochastic variable. The set of configurations for which the MC switch will be accepted will, however, constitute only a small fraction of the respective configuration spaces. To ensure effective two-phase sampling the MC procedure must be biased \([10]\) to enhance the probabilities with which these ‘gateway’ regions are visited. To that end we define an order parameter

\[
M = M_\gamma(\{ \vec{u} \}) = \sum_{i} \{ O_i [1 - \theta(u_i - u_c)] + T_i \theta(u_i - u_c) \}
\]

Here \(\theta\) is the step function. \(T_i \equiv \alpha u_i\) measures the length of a notional tether connecting site \(i\) to its associated particle \([20]\). \(O_i\) measures the overlap (between particle \(i\) and its neighbours) which would be created by a phase switch. The parameter \(\alpha\) controls the relative importance of \(T_i\) and \(O_i\); \(u_c\) controls the tether-length domain in which each contributes \([21]\). The equilibrium states of both phases are characterised by large \(M\) values. The ‘overlap’ term contributes in both phases: swapping the \(\{ \vec{R} \}\) vectors will (in general) produce a configuration of the ‘other’ phase in which spheres overlap. The ‘tether’ term contributes only in the F-phase \([22]\) where particles may drift arbitrarily far from the sites with which they are nominally associated; the tethers provide the means to ‘pull’ the fluid up the commensal entropy barrier. We identify the gateway states as those which have \(M = 0\) \(\text{(ie} O_i = 0 \text{and} u_i < u_c, \forall i\)\). The constraint that \(M = 0\) imposes on the overlap simply recognises that MC-switches which generate overlaps will necessarily be rejected. The constraint \((u_i < u_c)\) on the tether length is needed to ensure that switches from the fluid create only crystalline solid (not defective, glassy) configurations. The entire region of configuration space relevant to the problem can then be sampled in the multicanonical ensemble defined by

\[
\tilde{Z}(N,p,\{ \eta \}) \equiv \sum_{\gamma} \int_0^\infty dV \prod_{i=1}^N \int_{\gamma} d\vec{u}_i e^{-\mathcal{H}(\{ \vec{u} \}, V, \{ \eta \})}
\]

where

\[
\mathcal{H}(\{ \vec{u} \}, V, \{ \eta \}) = E^\gamma(\{ \vec{u} \}) + pV + \eta_\gamma(M) - \delta_{\gamma,CS} \ln (N-1)!
\]

while \(\{ \eta \}\) represents weights (defined on the M-macrostates) which have to be constructed so as to enhance, appropriately, the probabilities of the \(M = 0\) gateway states \([24]\). Simulation in this ensemble allows one to measure the multicanonical probability distribution \(P(M,V,\gamma|N,p,\{ \eta \})\) from which (unfolding the bias due to the weights) one may infer the true equilibrium distribution \(P(M,V,\gamma|N,p)\). The desired ratio of the phase probabilities (Eq. 6) follows by ‘marginalising’ \(M\) and \(V\) to give the \textit{a priori} probabilities of the phases. Having the underlying distribution of \(M\) and \(V\) allows one to determine, in addition, the value of \(\mathcal{R}_{F,CS}\) at neighbouring pressures, using histogram reweighting techniques \([22]\).

We turn to the MC procedure required for efficient exploration of the space spanned by the configuration variables \(\{ \vec{u} \}\), \(V\) and \(\gamma\). It comprises four types of configuration update, each of which is accepted with a probability defined by a Metropolis rule \([5]\) and reflects the associated change in the effective energy \(\mathcal{H}\). The first two—particle position updates \([21]\) and volume updates (implemented as dilations)—are effected in standard ways \([3]\). The third—like the first two—also preserves the phase label; but it is novel. In this process, we choose two sites at random \((i\ and\ j\ say)\) and identify the corresponding displacement vectors \(\vec{u}_i\) and \(\vec{u}_j\). The candidate configuration is defined by the replacements

\[
\vec{u}_i \rightarrow \vec{u}_i' \equiv \vec{u}_j + \vec{R}_j - \vec{R}_i \quad \text{and} \quad \vec{u}_j \rightarrow \vec{u}_j' \equiv \vec{u}_i + \vec{R}_i - \vec{R}_j
\]

This process can be thought of as an \textit{association} update: the particle initially associated with (‘tethered to’) site \(j\) is subsequently associated with site \(i\) (and vice
versa). It changes the representation of the configuration (the coordinates \{\vec{u}\}); but it leaves the physical configuration invariant. It is required in the fluid phase only \cite{22}. In the fluid phase the particles diffuse far from the sites with which they are initially associated; the members of \{\vec{u}\} become large and the tethers correspondingly so; association updates allow the tethers to respond efficiently to the influence of the tether contribution to \{\eta\}. Finally, the ‘phase update’ (the switch) entails replacing one set of representative vectors, \{\vec{R}\}’ say, by the other, \{\vec{R}\}′, with the volumes scaled appropriately and the displacement coordinates \{\vec{u}\} held fixed \cite{28}.

Simulations have been performed using systems of \(N = 32, 108\) and 256 particles. Figure 1 shows the density distribution for the \(N = 256\) system in the vicinity of the coexistence pressure. Coexistence (\(\Delta g = 0\); Eq. 1) is identified by the equality of the contributions associated with each phase (essentially the area under each peak).

Figure 2 shows the coexistence pressure for our three system sizes plotted as a function of \(1/N\) \cite{29}. The results for \(N = 108\) and \(N = 256\) were obtained in the fashion just described; the associated uncertainties \(\sigma[p]\) follow simply from Eq. 2 as \(\sigma[p] = \sigma[\mathcal{R}]/(N \mid \Delta \nu)\) where \(\Delta \nu = [V_F - V_{CS}]/N\) and \(\sigma[\mathcal{R}]\) is the uncertainty in the measured ratio of the peak-weights, which is controlled, at heart, by the statistics of the inter-phase switch. The result for \(N = 32\) was determined differently: this system is sufficiently small that transitions back and forth between F and CS phases occur spontaneously, over a range of pressures, and a density distribution (sampling both phases) can be determined –and a coexistence pressure inferred –without multicanonical weighting. The three points are consistent with the presumed scaling form \cite{29}. The extrapolated prediction \((p = 11.49(9))\) is, within error, in accord with \cite{11} and \cite{13} (see Fig. 3 inset).

The lower set of data points shown in figure 2 gives the values of the coexistence pressure implied by our measurements for \(N = 108\) and \(N = 256\) if one fails to fold in the \(1/N\) correction in Eq. 2. The associated overestimate of the CS-configurational weight lowers the predicted coexistence pressure by an amount \((\ln N)/[N\Delta \nu]\) which is significant for systems of this size, and leads to values which is hard to reconcile (cf the dashed line in Fig. 3) with the independent measurement at \(N = 32\) \cite{22}. While this correction vanishes in the \(N \to \infty\) limit, its existence is potentially important for any systematic study of the finite-size scaling of free energies \cite{33}.

We summarise. We have presented a method which allows one to locate liquid-solid coexistence parameters (and uncertainties) directly and transparently (Fig. 2) within a single simulation, conducted in the appropriate (constant pressure) ensemble. The method avoids the need to appeal to integration through to ‘distant’ reference states, double-tangent-constructions or off-the-shelf equations of state. It prescribes finite-size effects explicitly and handles systems sufficiently large (cf \cite{14}) that the limiting thermodynamic behaviour can be identified with some confidence. The method can be readily generalised to systems with real (soft) potentials \cite{15} and arbitrary geometries \cite{16}. It can also be naturally combined with histogram reweighting techniques \cite{17} to allow the full coexistence-curve to be mapped efficiently. 

\begin{thebibliography}{99}

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12. See eg T.L. Hill, Statistical Mechanics (McGraw-Hill, 1956).
13. R.J. Speedy, J.Phys: Condens. Matter, 9, 8591 (1997).
14. \(p, V\) and \(E\) are measured in units of \(kT/D^3\) and \(kT\) respectively, where \(D\) is the hard sphere diameter.
15. There are many ways of formulating such a constraint; this choice seems to reflect what MC studies actually do.
16. The timescale is presumed to be sufficiently long to explore ‘one phase’ but still short compared to (unaided) interphase traverses.
17. Both \(\{\vec{R}\}^{CS}\) and \(\{\vec{R}\}^{F}\) scale (by dilation) with the system volume.
18. At our starting point (Eq. 3) the indices \(1 \ldots N\) on the coordinates \(\vec{r}\) are (can only be) particle labels which confer distinguishability. Any ‘correction for indistinguishability’ is made post hoc through \(C_0\). With this perspective (there are alternatives), the ‘fragments’ are ‘distinct’.
19. One may think of freezing as breaking the permutation-
symmetry: S. Alexander, Physica A, 249, 266 (1998).

[20] Similar constructs have been used in the context of solid
phases by other authors: see [13].

[21] There is some licence in setting the values of these pa-
rameters; we chose \(u_c = D\) and \(\alpha = 1.7\).

[22] Given the convention adopted in [24] (below); but note
the alternative possibilities described in [27].

[23] Note that the factor of \(C_0\) has cancelled in writing Eq. 4;
the way one views the factors of \(N\) and \(N!\) is thus a
matter of taste.

[24] Weights are customized to sample the full range of
\(M\)-space; some of the techniques are described in G.R. Smith
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61, 2635 (1988); ibid 63, 1195 (1989).

[26] We chose to keep one particle fixed at its representative
site in each phase; this suppresses the global translation
mode in the CS phase and eliminates the need for associ-
ation updates in this phase; consequences for acceptance
probabilities have been accommodated.

[27] One may implement association updates in the CS phase
too: the simulation can then be thought of as exploring
different CS-phase fragments; the factor of \((N-1)!\) in
Eq. 4 is no longer needed and it is no longer necessary
to clamp one particle [26]. We have verified that our re-
results remain unchanged if these substantially less efficient
alternative strategies are adopted.

[28] In the switch, the volume is scaled by \(\alpha_v \equiv \bar{V}^{\gamma'}/\bar{V}^\gamma\)
where \(\bar{V}_\gamma\) is the equilibrium volume of phase \(\gamma\).

[29] This choice of scaling variable is common –see eg [31]–
but seems to lack a rigorous basis.

[30] The inset of 2 shows that our extrapolation lies below
the results of [4,8,13]. If there is a trend here the 1/N
correction is not the source: it has the opposite effect.
The differences may lie in residual finite size effects in
equations of state fitted to fluid simulation data.

[31] J.M. Polson et al, J. Chem. Phys., 112, 5339 (2000)

FIG. 1. The distribution of the density of the system of
\(N = 256\) particles at pressures (a) just below, (b) at and (c)
just above coexistence for this \(N\). The mean single phase
density averages are \(\rho_F = 0.934(3)\) and \(\rho_{CS} = 1.031(4)\) in
accord with the coexistence parameters reported in [13].

FIG. 2. The coexistence pressure for systems of different \(N\)
using Eq. 4 both with (•) and without (○) the \(1/N\) prefactor in
the CS configurational weight. The solid lines is a fit to the
former; the dashed line is lower by \(\ln N/|N\Delta v|\). The inset
compares our extrapolated value with the results of others,
with error bars shifted for clarity.