

Freezing by Monte Carlo Phase Switch

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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 utilizes 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.

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Freezing is the archetypal phase transition, one of the prime examples of thermodynamics in action, and a topic of ongoing interest [1–3]. 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 *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 idealized reference state [6]. 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 [7,8].

This paper describes a different approach to the problem. We build on recent work [9], in which we showed that the disjoint configuration spaces associated with two phases of a many-body system can *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 *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 [9] 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 *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 *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 [4,8,13].

Consider N particles (hard spheres) confined to volume V , variable under a constant external effective pressure p [14], and subject to periodic boundary conditions. The configurational weight of a phase may be written as

$$Z_\gamma(N, p) = \int_0^\infty dV e^{-pV} Z_\gamma(N, V), \quad (1)$$

where γ (CS or F) labels the phase, while

$$Z_\gamma(N, V) = C_0 \prod_{i=1}^N \int_{V,\gamma} d\vec{r}_i e^{-E(\{\vec{r}\})}. \quad (2)$$

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 γ label on the integral stands for some *configurational constraint* that picks out configurations $\{\vec{r}\}$ that “belong” to phase γ . We choose to formulate that constraint as follows [15]. Let $\vec{R}_1^\gamma, \dots, \vec{R}_N^\gamma \equiv \{\vec{R}\}^\gamma$ denote some *representative configuration* of phase γ . Then the constraint may be regarded as picking out those configurations which can be reached from $\{\vec{R}\}^\gamma$ on the simulation time scale [16]. It is convenient to use the sites defined by $\{\vec{R}\}^\gamma$ 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 $E^\gamma(\{\vec{u}\}) \equiv E(\{\vec{R}^\gamma + \vec{u}\})$.

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

$$Z_F(N, V) = C_0 \prod_{i=1}^N \int_{V, \{\vec{R}\}^F} d\vec{u}_i e^{-E^F(\{\vec{u}\})}, \quad (3)$$

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 recognize that the complete CS configuration space actually comprises a number of distinct mutually inaccessible *fragments* [18] corresponding essentially to the different permutations of particles among lattice sites [19]. 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 *one* fragment includes *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

$$Z_{CS}(N, V) = C_0(N - 1)! \prod_{i=1}^N \int_{V, \{\vec{R}\}^{CS}} d\vec{u}_i e^{-E^{CS}(\{\vec{u}\})}. \quad (4)$$

The ratio of the configurational weights of the two phases (the ratio of their total *a priori* probabilities) follows by combining Eqs. (1), (3), and (4):

$$\begin{aligned} \mathcal{R}_{F,CS} &= \frac{P(F | N, p)}{P(CS | N, p)} = \frac{Z_F(N, p)}{Z_{CS}(N, p)} \\ &= \frac{[N!]^{-1} \int_0^\infty dV e^{-pV} \prod_{i=1}^N \int_{V, \{\vec{R}\}^F} d\vec{u}_i e^{-E^F(\{\vec{u}\})}}{[N!]^{-1} \int_0^\infty dV e^{-pV} \prod_{i=1}^N \int_{V, \{\vec{R}\}^{CS}} d\vec{u}_i e^{-E^{CS}(\{\vec{u}\})}} \end{aligned} \quad (5)$$

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

$$\Delta g \equiv g_{CS}(N, p) - g_F(N, p) \equiv \frac{1}{N} \ln \mathcal{R}_{F,CS}. \quad (6)$$

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 [20] one may regard the former as the familiar indistinguishability overcount correction appropriate for phases (fluids) of nonlocalized particles. But then one must recognize the existence of an analogous correction (the $1/N$) for the CS phase, in which particles are localized—but 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. (5)]. 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 ($\vec{R}_i^F \rightleftharpoons \vec{R}_i^{CS} \nabla i$), by continuity, *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 realized as a MC step, so that the phase label γ 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 θ is the step function. $T_i \equiv \alpha u_i$ measures the length of a notional tether connecting site i to its associated particle [21]. O_i measures the overlap (between particle i and its neighbors) which *would* be created by a phase switch. The parameter α controls the relative importance of T_i and O_i ; u_c controls the tether-length domain in which each contributes [22]. The equilibrium states of both phases are characterized 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 [23] 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 communal entropy barrier. We identify the gateway states as those which have $M = 0$ (i.e., $O_i = 0$ and $u_i < u_c, \forall i$). The constraint that $M = 0$ imposes on the overlap simply recognizes 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

$$\tilde{Z}(N, p, \{\eta\}) \equiv \sum_\gamma \int_0^\infty dV \prod_i \int_\gamma d\vec{u}_i e^{-\mathcal{H}^\gamma(\{\vec{u}\}, V)}, \quad (7)$$

where

$$\begin{aligned} \mathcal{H}^\gamma(\{\vec{u}\}, V) &= E^\gamma(\{\vec{u}\}) + pV + \eta_\gamma(M) \\ &\quad - \delta_{\gamma,CS} \ln(N - 1)!, \end{aligned}$$

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. (5)] follows by “marginalizing” M and V to give the *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 neighboring pressures, using histogram reweighting techniques [25].

We turn to the MC procedure required for efficient exploration of the space spanned by the configuration variables $\{\vec{u}\}$, V , and γ . It comprises four types of configuration update, each of which is accepted with a probability defined by a Metropolis rule [8] and reflects the associated change in the effective energy \mathcal{H} . The first two—particle position updates [26] and volume updates (implemented as dilations)—are effected in standard ways [8]. 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

$$\begin{aligned}\vec{u}_i &\rightarrow \vec{u}'_i \equiv \vec{u}_j + \vec{R}_j - \vec{R}_i \quad \text{and} \\ \vec{u}_j &\rightarrow \vec{u}'_j \equiv \vec{u}_i + \vec{R}_i - \vec{R}_j.\end{aligned}$$

This process can be thought of as an *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 [27]. 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, $\{\vec{R}\}^\gamma$ say, by the other, $\{\vec{R}\}^{\gamma'}$, with the volumes scaled appropriately and the displacement coordinates $\{\vec{u}\}$ held fixed [28].

Simulations have been performed using systems of $N = 32$, 108, and 256 particles [29]. Figure 1 shows the density distribution for the $N = 256$ system in the vicinity of the coexistence pressure. Coexistence [$\Delta g = 0$; Eq. (6)] 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 $1/N$ [30]. The results for $N = 108$ and $N = 256$ were obtained in the fashion just described; the associated uncertainties $\sigma[p]$ follow simply from Eq. (6) as $\sigma[p] = \sigma[\mathcal{R}]/(N|\Delta v|)$, where $\Delta v = [\bar{V}_F - \bar{V}_{CS}]/N$ 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 interphase 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

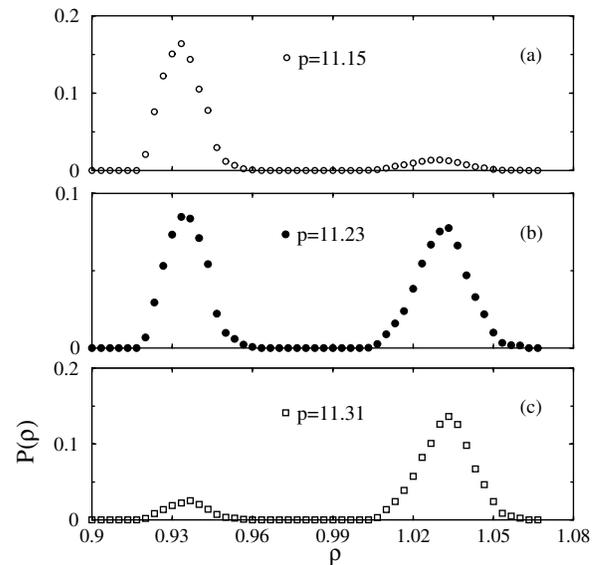


FIG. 1. The distribution of the density of the system of $N = 256$ particles at pressures (a) just below, (b) at, and (c) just above coexistence for this N . The mean single phase density averages are $\rho_F = 0.934(3)$ and $\rho_{CS} = 1.031(4)$ in accord with the coexistence parameters reported in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

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 [30]. The extrapolated prediction [$p = 11.49(9)$] is, within error, in accord with [4] and [13] (see Fig. 2 inset).

The lower set of data points shown in Fig. 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

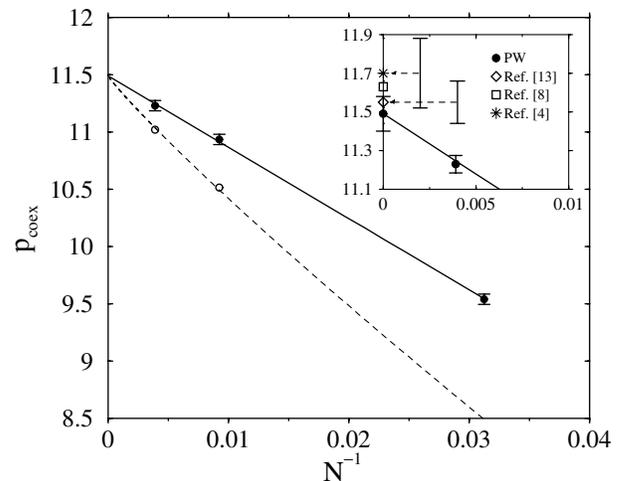


FIG. 2. The coexistence pressure for systems of different N using Eq. (5) both with (\bullet) and without (\circ) the $1/N$ prefactor in the CS configurational weight. The solid line is a fit to the former; the dashed line is lower by $\ln N/|N\Delta v|$. The inset compares our extrapolated value with the results of others, with error bars shifted for clarity.

$1/N$ correction in Eq. (5). The associated *overestimate* of the CS-configurational weight *lowers* the predicted coexistence pressure by an amount $([\ln N]/[N\Delta v])$, which is significant for systems of this size, and leads to values that are hard to reconcile (cf. the dashed line in Fig. 2) with the independent measurement at $N = 32$ [31]. While this correction vanishes in the $N \rightarrow \infty$ limit, its existence is potentially important for any systematic study of the finite-size scaling of free energies [32].

In summary, we have presented a method which allows one to locate liquid-solid coexistence parameters (and uncertainties) directly and transparently (Fig. 1) 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. [1]) that the limiting thermodynamic behavior can be identified with some confidence. The method can be readily generalized to systems with real (soft) potentials [3] and arbitrary geometries [2]. It can also be naturally combined with histogram reweighting techniques [25] to allow the full coexistence curve to be mapped efficiently.

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- [11] If the two phases share a common lattice (e.g., in spin models) the interface traverse by ES methods is both possible and physically illuminating: B. A. Berg, U. H. E. Hansmann, and T. Neuhaus, *Z. Phys. B* **90**, 229 (1993).
- [12] See, e.g., T.L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 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 , 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 time scale 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. (2)] the indices $1, \dots, N$ on the coordinates $\{\vec{r}\}$ are (can be only) *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 (Amsterdam)* **249A**, 266 (1998).
- [20] Note that the factor of C_0 has canceled in writing Eq. (5): the way one *views* the factors of N and $N!$ is thus a matter of taste.
- [21] Similar constructs have been used in the context of *solid* phases by other authors: see [13].
- [22] There is some license in setting the values of these parameters; we chose $u_c = D/2$ and $\alpha = 1.7$.
- [23] Given the convention adopted in [26] (below); but note the alternative possibilities described in [27].
- [24] Weights are customized to sample the full range of M space; some of the techniques are described in G. R. Smith and A. D. Bruce, *Phys. Rev. E* **53**, 6530 (1996).
- [25] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **61**, 2635 (1988); **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 association 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].
- [28] In the switch, the volume is scaled by $\alpha_v \equiv \bar{V}^{\gamma'}/\bar{V}^\gamma$, where \bar{V}_γ is the equilibrium volume of phase γ .
- [29] Sweeps of particle position updates, sweeps of association updates, and volume updates were performed with frequencies in the ratios 3:1:1. The data shown in Fig. 1 entailed some 350 CPU hours on a 433 MHz Dec Alpha workstation.
- [30] This choice of scaling variable is common—see e.g., [32]—but seems to lack a rigorous basis.
- [31] The inset of Fig. 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.
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