Free Energy of Crystalline Solids: A Lattice-Switch Monte Carlo Method

A. D. Bruce, N. B. Wilding, and G. J. Ackland

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

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We present a Monte Carlo method for evaluating the difference between the free energies of two crystal structures. The method uses a biased sampling of atomic displacements to favor configurations of one structure that can be replaced by corresponding configurations of the other through a Monte Carlo switch of the lattice. The configurations of both structures can be sampled in a single process, and the difference between their free energies evaluated from their measured probabilities. The method is applied to the free energies of the fcc and hcp phases of hard spheres. [S0031-9007(97)04322-6]

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One of the fundamental tasks of theoretical condensed matter physics is to understand the observed structures of crystalline materials in terms of microscopic models of the atomic interactions. The principles involved are well known: one needs to evaluate which of the candidate structures has the lowest free energy for given (model and thermodynamic) parameters. In practice the task is rather less straightforward. Conventional Boltzmann importance sampling Monte Carlo (MC) methods do not yield the free energy [1]. It is therefore customary to resort to integration methods (IM) which determine free energies by integrating free-energy *derivatives* measured at intervals along a parameter-space path connecting the system of interest to a reference system whose free energy is already known. This procedure has been used widely, and with ingenuity [2]. Nevertheless it leaves much to be desired. In particular, to determine the *difference* between the free energies of two phases one has to relate *each* of them separately to some reference system, with uncertainties which are not always transparent, and which can be significant on the scale of the free-energy difference of interest. Clearly, one would prefer a method which focuses more directly on this difference. The elements of such a strategy are to be found in the umbrella-sampling techniques pioneered by Torrie and Valleau [3], and recently revitalized in the multicanonical method of Berg and Neuhaus [4]. The key concept underlying this method is that of a configuration-space path comprising the macrostates of some chosen macroscopic property $\mathcal{M}$. The method utilizes a sampling distribution customized (biased) to even out the probabilities of different $\mathcal{M}$ macrostates. In principle, it allows one to sample along a path (whose canonical probability is generally extremely small) chosen to connect the distinct regions of configuration space associated with two phases; the difference between the free energies of the two phases can then be obtained directly from the ratio of the probabilities with which the system is found in each of the two regions. This idea has been applied in the investigation of the phase behavior of ferromagnets [4], fluids [5], and lattice gauge theories [6]. However, its application to *structural* phase behavior faces a distinctive problem: finding a path that links the regions of configuration space associated with two different crystal structures [7], *without* traversing regions of noncrystalline order, which present problems [8] for even multicanonical MC studies. We show here that this problem can be elegantly solved by combining *biased sampling along an appropriate path* with a suitable *global coordinate transformation.* The resulting ("lattice-switch MC") method allows direct high-precision measurement of free-energy differences of crystal structures.

The idea is simple; we describe it first in general and qualitative terms. The atomic position coordinates are written, in the traditions of lattice dynamics, as the sum of a lattice vector [9], and a displacement vector. The configurations associated with a particular structure are explored by MC sampling of the displacements. Given any configuration of one structure one may identify a configuration of the other, by *switching* one set of lattice vectors for the other, while keeping the displacement vectors *fixed.* Such lattice switches can be incorporated into the MC procedure by regarding the lattice type as a stochastic variable. Lattice switches have an intrinsically low acceptance probability, since typically they entail a large energy cost. But the multicanonical method can be used to draw the system along a path comprising the macrostates of this "energy cost," and thence into a region of displacement space in which the energy cost is low, and the lattice switch can be implemented. The net result is a MC procedure which visits both structures in the course of a single simulation, while never moving out of the space of crystalline configurations. The method is potentially very general. As an illustration we use it to determine the difference between the free energies of the two close-packed structures (fcc and hcp) of a system of hard spheres. This problem has a long history [10]. The difference between the free energies (effectively, the *entropies*) is extremely small, and recent IM studies have disagreed on its value [11,12]. It thus provides an exacting and topical testing ground for our method [13].

We consider a system of N particles [14] with spatial coordinates $\{\vec{r}\}$. In common with previous studies we work at constant volume, V, with periodic boundary

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conditions; generalization to the constant pressure ensemble is straightforward. We make the decomposition

$$\vec{r}_i = \vec{R}_i + \vec{u}_i\,, \tag{1}$$

where the vectors $\vec{R}_i, i = 1 \ldots N \equiv \{\vec{R}\}_\alpha$ define the sites of a lattice of type α (here, either fcc or hcp). Clearly there are many transformations that will map one set of vectors into the other; the mapping we have chosen is explained in Figs. 1(a) and 1(b): it exploits the fact that the two structures differ only in the stacking pattern of the close-packed planes.

We define a partition function (and free energy) associated with the structure α by [15]

$$\begin{aligned} Z(N,V,T,\alpha) &= \int_{\{\vec{u}\}\in\alpha} \prod_i [d\vec{u}_i] \exp[-\Phi(\{\vec{u}\},\alpha)] \\ &\equiv \exp[-F_\alpha(N,V,T)/kT]\,, \end{aligned} \tag{2}$$

where Φ represents the dimensionless configurational energy. In the present context

$$\Phi(\{\vec{u}\},\alpha) \equiv \Phi(\{\vec{r}\}) = \begin{cases} 0, & |\,\vec{r}_i - \vec{r}_j\,| > \sigma \quad \forall\, i,j\,, \\ \infty, & \text{otherwise,} \end{cases} \tag{3}$$

where σ is the hard-sphere diameter. The α label attached to the integral in Eq. (2) signifies that it must include only contributions from configurations within the subspace associated with the structure α [16].

Consider now the canonical ensemble with probability distribution

$$P(\{\vec{u}\},\alpha \mid N,V,T) = \frac{\exp[-\Phi(\{\vec{u}\},\alpha)]}{Z(N,V,T)}\,, \tag{4}$$

where $Z(N,V,T) \equiv \sum_\alpha Z(N,V,T,\alpha)$. The probability that the system will be found to have structure α provides a measure of the associated partition function,

$$\begin{aligned} P(\alpha \mid N,V,T) &\equiv \int_{\{\vec{u}\}\in\alpha} \prod_i [d\vec{u}_i] P(\{\vec{u}\},\alpha \mid N,V,T) \\ &= \frac{Z(N,V,T,\alpha)}{Z(N,V,T)}\,. \end{aligned} \tag{5}$$

The difference between the free energies of the two structures may thus be expressed as

$$F_{\rm hcp}(N,V,T) - F_{\rm fcc}(N,V,T) \equiv NkT\Delta f = kT \ln \mathcal{R}\,, \tag{6}$$

where

$$\mathcal{R} = \frac{Z(N,V,T,\text{fcc})}{Z(N,V,T,\text{hcp})} = \frac{P(\text{fcc} \mid N,V,T)}{P(\text{hcp} \mid N,V,T)}\,. \tag{7}$$

This identification is useful *only* if one can devise a MC procedure that will actually visit the configurations $\{\vec{u}\},\alpha$ with the probabilities prescribed by Eq. (4). To do so one must deal with the ergodic block against lattice switches ("updates" of the lattice label, α): almost invariably such a switch maps an accessible configuration of one structure onto an inaccessible configuration of the other [one which violates the hard-sphere constraint implied by Eq. (3)]. Figure 1(b) provides an example. The resolution is to *bias* the sampling procedure so as to favor the occurrence of configurations which transform *without* violating this constraint. To do so we define an *overlap order parameter*

$$\mathcal{M}(\{\vec{u}\}) \equiv M(\{\vec{u}\},\text{hcp}) - M(\{\vec{u}\},\text{fcc})\,, \tag{8}$$

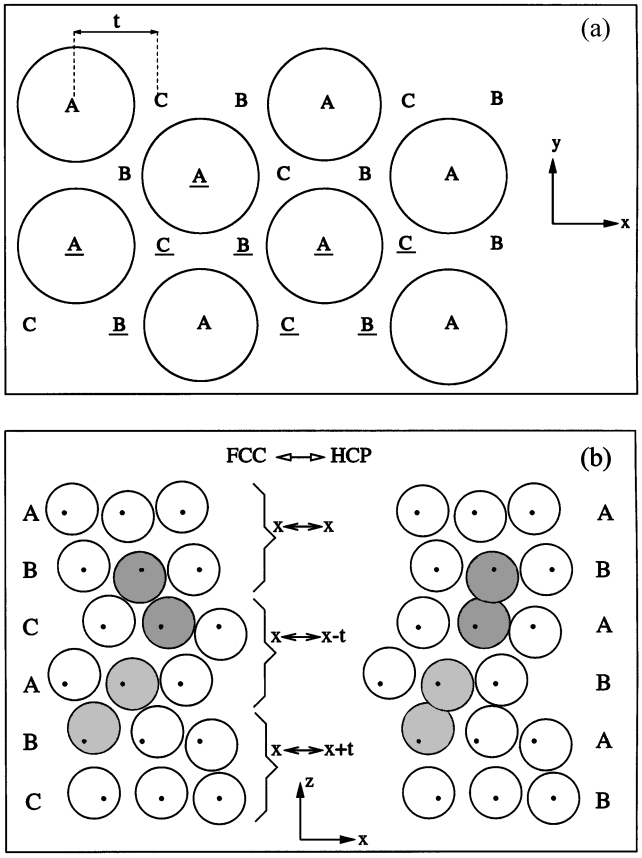

FIG. 1. Schematic representation of the close-packed structures. The points marked A show the positions of the sites in one close-packed (xy) layer; the circles show the boundaries of spheres occupying these sites in an ideal (zero-displacement) structure. The points marked B and C show the projections of sites in other layers (stacked along the z axis) onto the xy plane; the fcc and hcp structures entail sequences of type $ABCA\ldots$ and $ABAB\ldots$, respectively. The *lattice switch* from fcc to hcp entails *translations* of the close-packed planes, as detailed in (b). [(b), left side] The positions of the spheres in an arbitrary configuration of the fcc structure, projected onto the xz plane. We show 6 layers, with 3 spheres in each; the sites in the top 3 layers (A,B,C) correspond to those marked (and underlined) A,B,C in (a). [(b), center] The action of the lattice switch: reading from the top, the first two layers (A,B) of the fcc structure are invariant; the next two (C,A) layers are translated along the x direction by $-t$; and the final two (B,C) layers are translated by $+t$, where t is identified in (a). [(b), right side] Projections of the spheres in the resulting hcp arrangement. Here, the displacements $\{\vec{u}\}$, realizable in the fcc structure, give two overlapping pairs of spheres (shaded) in the hcp structure so that $\mathcal{M}(\{\vec{u}\}) = 2$ in this case. Note that the picture is *schematic:* in particular, the density shown here is much lower than that chosen for the present study.

where $M(\{\vec{u}\},\alpha)$ counts the number of pairs of overlapping spheres associated with the configuration $\{\vec{u}\},\alpha$ [again, see Fig. 1(b)]. Since $M(\{\vec{u}\},\alpha)$ will necessarily be zero for any set of displacements $\{\vec{u}\}$ *actually visited* when the system has lattice α, the order parameter $\mathcal{M}$ is necessarily ≥ 0 (≤ 0) for realizable configurations of the fcc (hcp) structure. The displacement configurations with $\mathcal{M} = 0$ are accessible in *both* structures and thus offer no barrier against lattice switches. Accordingly the set of $\mathcal{M}$ macrostates provides us with the required "path" connecting the two phases, through a lattice switch at $\mathcal{M} = 0$. To pick out this path we must sample from the biased configuration distribution

$$P(\{\vec{u}\},\alpha \mid N,V,T,\{\eta\}) \propto P(\{\vec{u}\},\alpha \mid N,V,T)e^{\eta(\mathcal{M}(\{\vec{u}\}))}, \tag{9}$$

where $\{\eta\} \equiv \eta(\mathcal{M}), \mathcal{M} = 0, \pm 1, \pm 2, \ldots$ define a set of multicanonical weights [4], which have to be determined such that configurations of all relevant $\mathcal{M}$ values are sampled. Once this is done, one can measure the weighted distribution of $\mathcal{M}$ values, and reweight (unfold the bias) to determine the true canonical form of this distribution,

$$P(\mathcal{M} \mid N,V,T) \propto P(\mathcal{M} \mid N,V,T,\{\eta\})e^{-\eta(\mathcal{M})}. \tag{10}$$

Finally, the difference between the free energies of the two structures may be read from this distribution through the identification [cf. Eqs. (6) and (7)] $\Delta f = N^{-1}\ln\mathcal{R}$, with

$$\mathcal{R} = \frac{\sum_{\mathcal{M}>0} P(\mathcal{M} \mid N,V,T)}{\sum_{\mathcal{M}<0} P(\mathcal{M} \mid N,V,T)}. \tag{11}$$

We have implemented this procedure to study systems of $N = 216$, 1728, and 5832 hard spheres (forming, respectively, 6, 12, or 18 close-packed layers). The volume V was chosen such that the fraction of space filled, ρ, satisfies $\rho/\rho_{\rm cp} = 0.7778$ [17], where $\rho_{\rm cp} \equiv 0.7404$ is the space filling fraction in the closest packing limit. The MC procedure entails sampling the displacement variables $\{\vec{u}\}$ and the lattice label α. The variables $\{\vec{u}\}$ were updated by drawing new values from a top-hat distribution [18] and accepting them provided they satisfy the hard-sphere constraint; the lattice switches were attempted (and accepted with probability 1/2) only when the system is in the $\mathcal{M} = 0$ macrostate. The weights (which enable the system to reach this special macrostate) were obtained using methods explained elsewhere [7]. We allowed typically 2×10^4 sweeps for equilibration and up to 5×10^7 sweeps for final sampling runs on the largest system size. The simulations were conducted on DEC ALPHA workstations using overall some 800 hours CPU time.

Figure 2 shows the measured overlap distribution for the $N = 1728$ system; the inset shows the probability on a logarithmic scale, exposing the enormity of the entropic "barrier" (probability "trough") that the multicanonical weighting enables us to negotiate. The difference between the free energies of the two structures is identifiable immediately and transparently from the ratio of the integrated weights of the two essentially Gaussian peaks.

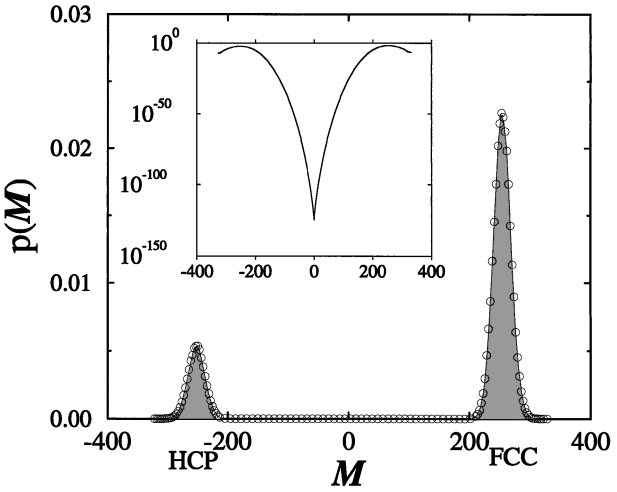

FIG. 2. The distribution of the overlap parameter $\mathcal{M}$ for a system of $N = 1728$ spheres; the inset shows the distribution on a logarithmic scale. The statistical uncertainties are smaller than the symbol size. The free-energy difference Δf is identified from the logarithm of the ratio $\mathcal{R}$ of the weights of the two peaks [Eq. (11)]. The smallness of Δf allows both peaks to be displayed on one linear scale in this case.

Our results (for a range of N values) are summarized in Table I, along with those of other authors. It is apparent that the present work greatly refines the largely inconclusive results of the original IM study [2]. Our results are consistent with—though substantially more precise than—very recent IM studies [12]. They are inconsistent with the result reported by Woodcock [11], given that Δf is believed to *decrease* as the density is reduced, towards melting [19]. While we have not attempted an explicit analysis of the finite-size behavior, the close agreement between our results for $N = 1728$ and $N = 5832$ indicates that the latter should provide an extremely good estimate of the thermodynamic limit, confirming the stability of the fcc structure at this density.

TABLE I. Results for the difference between the free energy of hcp and fcc structures, as defined in Eq. (6) with associated uncertainties in parentheses. Results attributed to Ref. [2] were deduced by combining the separate results for fcc and hcp given there. PW signifies the present work. The PW error bounds were computed from the statistical uncertainties in the weights of the peaks in $P(\mathcal{M})$ [21].

$\rho/\rho_{\rm cp}$	N	$\Delta f \times 10^5$		Ref.
0.7360	216	90	(135)	[2]
0.7360	12 000	500	(100)	[11]
0.7360	12 906	90	(20)	[12]
0.7778	1152	−120	(180)	[2]
0.7778	216	101	(4)	PW
0.7778	1728	83	(3)	PW
0.7778	5832	86	(3)	PW

Our principal concern here, however, is with the *general* lessons that can be learned about the method introduced in this work. The precision we have achieved with this method is self-evidently a significant advance on that of IM studies. Admittedly, this level of precision has entailed substantial processing *time*, principally because of the relative slowness of the diffusive exploration of the multicanonically weighted configuration space. But the point is that the procedure is *practicable* [20], with a computational strategy that is, we suggest, less complex and more transparent than that of IM. Thus, for example, the method described in [2] involves integration (of a mean-square displacement) along a parameter-space path connecting each structure to a reference system, comprising an Einstein model of the same structure; the MC integral then has to be combined with the known free energy of the Einstein model, a virial correction, and a correction to the virial correction, before taking the difference between the results for the two structures. The uncertainties in all the contributions have to be assessed separately. By contrast, the present method focuses directly on the quantity of interest (the relative weights of the peaks in Fig. 2); and the precision with which it is prescribed is defined by standard MC sampling theory [21].

More generally we note that, for systems other than hard spheres, the role of the overlap order parameter is played by the *energy barrier* encountered in the lattice switch; the generalization of the weighting procedure should be straightforward. The formulation of the lattice switch, however, will generally require some thought: in the present case one can readily identify a lattice-to-lattice mapping which *guarantees* no overlaps (high-energy-cost interactions) among subsets of the atoms (those lying within the *same* close-packed plane); the optimal form of mapping may not always be so evident. On the other hand, it seems that few problems will require the level of precision needed here, where the two phases are so finely balanced.

We summarize and, in so doing, set this paper in a wider context. We have presented a method for dealing with a general class of problem in which the task is to compare the statistical weights of two regions of configuration space (here, those of two crystal structures) such that a configuration belonging to one region can be mapped onto a configuration of the other by a global coordinate transformation (here, the lattice switch). Biased sampling within one region is used to enhance the probability of acceptance of a Monte Carlo switch to the other. We have seen that this method provides a transparent way of dealing with the crystal-structure problem. Its utility may, we speculate, extend to other problems including the (Bayesian) comparison of many-parameter models [22], and the comparison of conformations or mutations of complex molecules [23].

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[7] G. R. Smith and A. D. Bruce, Phys. Rev. E **53**, 6530 (1996), apply multicanonical methods to a structural phase transition which involves *no change of symmetry*, where an appropriate path is identified simply by $\mathcal{M} = \rho$.

[8] For example, the ergodic block associated with recrystallization.

[9] We use the term "lattice vector" a little loosely: we mean the set of vectors identified by the orthodox crystallographic lattice, convolved with the orthodox basis.

[10] B. J. Alder, B. P. Carter, and D. A. Young, Phys. Rev. **183**, 831 (1969).

[11] L. V. Woodcock, Nature (London) **384**, 141 (1997).

[12] P. G. Bolhuis and D. Frenkel (unpublished).

[13] The hard-sphere system has a wider significance. Y. Choi *et al.*, J. Chem. Phys. **99**, 9917 (1993), show that predictions for the phase diagram of a Lennard Jones solid depend extremely sensitively on the hard-sphere free-energy difference Δf computed here.

[14] N is fixed: we ignore contributions of vacancies.

[15] We use a general notation; formally the properties of the hard-sphere system are independent of T.

[16] In the MC context the configurations *associated* with a given structure are identified as the set which is actually *accessed* in a simulation initialized within the set.

[17] This value of ρ was chosen to coincide with one of those studied in Ref. [2].

[18] This choice of sampling procedure ensures that the center of mass is effectively fixed. For consistency the width of the top-hat distribution must be large compared to the range of displacements actually *accepted.*

[19] This follows from studies of the pressure in the two structures: B. J. Alder *et al.*, J. Comput. Phys. **7**, 361 (1971).

[20] The time required is measured on a scale of hours rather than the eons required if one were to attempt such a "direct" method *without* the multicanonical strategy provided here: recall the scale in the inset of Fig. 2.

[21] The full simulation run is divided into bins, each long on the scale of the autocorrelation time. Each bin provides an essentially independent estimate of the probability ratio; error bounds follow from their variance.

[22] See, e.g., R. E. Kass and A. E. Raftery, J. Am. Stat. Assoc. **90**, 773 (1995).

[23] See, e.g., M. Karplus and G. A. Petsko Nature (London) **347**, 631 (1990).