Algorithm for constant-pressure Monte Carlo simulation of crystalline solids

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We describe an alternative method for performing isothermal-isobaric Monte Carlo simulations of crystalline solids. This method uses thermodynamics to estimate appropriate scaling of coordinates relative to their nominal lattice sites in order to increase the probability of acceptance of volume changes. We test this coordinate scaling with three systems: hard spheres, Lennard-Jones spheres, and hard dumbbells. In all cases, we find that the move allows for both a larger step size and faster convergence of calculated properties, in comparison to the conventional algorithm. The improvement is more dramatic for hard potentials, where compressing the system using the conventional algorithm (even a small amount) will almost always cause an overlap.

I. INTRODUCTION

Molecular simulation of model systems at constant pressure has long been studied via Metropolis Monte Carlo simulations using the algorithm developed by McDonald [1]. The algorithm has been applied to fluids and solids for various models [2–4] and it is also required when used in connection with phase-equilibrium calculations such as the Gibbs ensemble [5], Gibbs-Duhem integration [6,7], and the *NPT* plus test particle method [8]. A variation of the method that is important in application to solid phases is the allowance of changes in box shape (developed by Parrinello and Rahman for molecular dynamics [9]), which may be needed to relieve shear stresses in the crystal [4,10]. The *NPT* Monte Carlo methods have also been used in searching for stable crystal structures [11] and finding the densest packing of polyhedra [12,13]. Apart from these extensions and applications, the basic approach has not changed much from its initial implementation, notwithstanding an occasional prescription to take steps in $\ln V$ instead of the volume V itself [14] and perhaps the use of a virial bias [15].

An unfortunate side effect of the volume changes proposed during the *NPT* Monte Carlo simulations is that the configuration encountered after a trial volume change tends to be far from typical for the new volume. When attempting to decrease the volume, molecules tend to end up too close to one another and conversely, after a volume increase, they tend to be too far apart. The net effect is that trial volume changes must be relatively small or be rarely accepted. However, the nature of solids, specifically, the existence of a nominal position for each atom (or nominal values for molecular coordinates in multiatomic molecules), provides some guidance on how to transform the molecular coordinates during a volume scaling. By scaling the atom coordinates back toward the lattice site upon compression we can put the system in a configuration that is more appropriate for the higher density and thereby increase the likelihood of accepting the move. What remains is then to determine the appropriate amount of coordinate scaling when changing the volume.

The approach we take to this question is to assume that the total change in phase-space volume associated with the volume perturbation can be equally distributed among the molecular degrees of freedom, each defined with respect to a perfect lattice. To determine the change in phase-space volume, we relate it back to the partition function and use thermodynamics to express how the partition function changes with volume, in terms of the lattice energy and pressure. Although the method is formulated using an assumption about the connection between phase-space volume and molecular degrees of freedom, the algorithm is rigorous because the Monte Carlo acceptance criteria account for any deviation from those assumptions.

The remainder of this paper is divided into three sections. In Sec. II we describe the thermodynamics that allows us to relate the pressure to the coordinate scaling and how these relate to proposed Monte Carlo trials and acceptance criteria. In Sec. III we describe the results of applying this Monte Carlo move in isothermal-isobaric simulations of hard spheres, Lennard-Jones spheres, and hard dumbbells. Finally, in Sec. IV, we end with some conclusions.

II. FORMALISM AND METHOD

A. Monte Carlo trial

In order to improve the coordinate scaling in a volume-change trial, we first consider how the volume of phase space accessed by the system, Θ, depends on the system volume V. We define phase-space volume to be the integral

$$\Theta \equiv \frac{1}{\Lambda^{DN}} \int e^{-\beta(U-U_{\text{lat}})} d\mathbf{r}^N, \qquad (1)$$

where U is the configurational energy, U_{lat} is the lattice energy, Λ is the de Broglie wavelength, N is the number of molecules, and D is the spatial dimension. We use coordinates $\mathbf{r}$ that are each defined with respect to a nominal position on a perfect lattice, with each integrating over V.

We can relate the phase-space volume directly to the canonical-ensemble partition function Q,

$$\Theta = Q/e^{-\beta U_{\text{lat}}}. \qquad (2)$$

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The volume dependence of the partition function is known in terms of the pressure

$$P = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}. \tag{3}$$

We are interested only in the small perturbations in volume that are attempted in Monte Carlo trials; for such small changes we can ignore variation of the pressure when integrating Eq. (3) to yield

$$\beta P V + C = \ln Q, \tag{4}$$

where $\beta = 1/kT$ and C is a constant of integration. Rearranging, we can identify the general dependence of Q on volume

$$Q \propto e^{\beta P V}. \tag{5}$$

We can now substitute back into Eq. (2), yielding

$$\Theta \propto e^{\beta (P V + U_{\text{lat}})}. \tag{6}$$

From this expression we can estimate the change in the phase-space volume resulting from a volume-change Monte Carlo trial. We consider Θ to be composed of contributions from D center-of-mass (c.m.) motions ($\Theta_{\text{c.m.}} = V$) and $ND - D$ motions with fixed center of mass. We can then write

$$\Theta_{\text{fixed}} = \frac{1}{V} \Theta. \tag{7}$$

We assume that the change in Θ_{fixed} is distributed equally to the $ND - D$ configuration-space dimensions, meaning that the range of values sampled by a coordinate at the new V is increased or decreased in proportion to $(\Theta_{\text{fixed,new}}/\Theta_{\text{fixed,old}})^{1/(ND-D)}$. This can be recognized by introducing a reduced coordinate $\mathbf{s}$ in terms of the deviation from the lattice site $\mathbf{r}$, normalized by $\Theta_{\text{fixed}}^{1/(ND-D)}$,

$$\mathbf{r} = \left(\frac{1}{V} e^{\beta (P V + U_{\text{lat}})} \right)^{1/(ND-D)} \mathbf{s}, \tag{8}$$

and performing volume-change trials keeping all $\mathbf{s}$ unchanged. In this context we should mention that the placement of the lattice sites proceeds from specification of the volume and thus the lattice expands and contracts in proportion to V, independently of any issues of scaling of $\mathbf{r}$.

We note that this same prescription Eq. (8) could be arrived at by appeal to any number of noninteracting cell models (e.g., Einstein crystal). The approach we have used here is simply based on the degrees of freedom and assumes that changes to the phase-space volume are distributed equally to all of them. Arguably, this is more general than a derivation based on a specific cell model. If there is reason to expect significant disparity in the scaling of different degrees of freedom, it might be worthwhile to modify the approach to reflect this behavior.

Within an *NPT* simulation, we can take P to be the set pressure. While this value will not provide the optimal scaling for some densities seen within an *NPT* simulation, it provides a good estimate in the absence of other information. The lattice energy must be computed for each density, but can be computed easily for power-law pair potentials and interpolated between precomputed values for other potentials.

B. Monte Carlo acceptance criteria

The probability density in the isothermal-isobaric (*NPT*) ensemble is (for fixed c.m.)

$$\pi(V, \mathbf{r}^N) = \frac{1}{\Delta} e^{-\beta U(\mathbf{r}^N) - \beta P V} \delta(\Sigma \mathbf{r}), \tag{9}$$

where Δ is a normalization constant and δ is the Dirac delta function, which enforces the c.m. constraint. In the conventional approach to conducting Monte Carlo simulations in the *NPT* ensemble, the coordinates are scaled by the simulation box length $L = V^{1/3}$ (assuming a cubic box), which can be interpreted as defining the ensemble in terms of the coordinates V and $\boldsymbol{\sigma}$ such that $\mathbf{r} = \boldsymbol{\sigma} L$. Moreover, it is sometimes decided to use $\ln V$ rather than V as the volume variable. In terms of these quantities, the probability density is

$$\pi(\ln V, \boldsymbol{\sigma}^N) = \frac{1}{\Delta} e^{-\beta U(\boldsymbol{\sigma}^N, V) - \beta P V} V^N \delta(\Sigma \boldsymbol{\sigma}), \tag{10}$$

where we have used $\delta(\Sigma \mathbf{r}) = \frac{1}{V} \delta(\Sigma \boldsymbol{\sigma})$. Then, in the Metropolis algorithm sampling on these variables, the acceptance probability for a change from V^{old} to V^{new} is

$$p_{\text{acc}} = \min[1, \chi], \tag{11}$$

where

$$\chi = \exp[-\beta(\Delta U + P \Delta V) + N \ln(V^{\text{new}}/V^{\text{old}})] \tag{12}$$

and Δ here indicates the change in the quantity from the old to the new configuration.

In the context of the new Monte Carlo trial, we scale $\mathbf{r}$ in terms of $\mathbf{s}$ as defined in Eq. (8); the new limiting distribution is

$$\begin{aligned}
\pi \left(\ln V, \mathbf{s}^N \right) &= \frac{1}{\Delta} e^{-\beta U(\mathbf{s}^N, V) - \beta P V} \\
&\quad \times \left[\left(\frac{1}{V} e^{\beta [P V + U_{\text{lat}}(V)]} \right)^{1/(ND-D)} \right]^{(ND-D)} \\
&\quad \times V \delta(\Sigma \mathbf{s}) \\
&= \frac{1}{\Delta} e^{-\beta U(\mathbf{s}^N, V) - \beta P V} e^{\beta [P V + U_{\text{lat}}(V)]} \delta(\Sigma \mathbf{s}) \\
&= \frac{1}{\Delta} e^{-\beta [U(\mathbf{s}^N, V) - U_{\text{lat}}(V)]} \delta(\Sigma \mathbf{s}). \tag{13}
\end{aligned}$$

Accordingly, the acceptance parameter in Eq. (11) for a Monte Carlo volume trial is

$$\chi = e^{-\beta(\Delta U - \Delta U_{\text{lat}})}. \tag{14}$$

Remarkably, pressure no longer enters in the acceptance decision, as its influence has been made in the rescaling of the coordinates. Additionally, for any athermal potential, we will be able to accept any trial that would not cause any overlap.

To summarize, a volume-change move in the proposed algorithm proceeds as follows.

(i) A trial value of V is selected as $\ln V_{\text{new}} = \ln V_{\text{old}} + q(\delta \ln V)_{\text{max}}$, where q is a random value selected uniformly on $(-1, 1)$ and $(\delta \ln V)_{\text{max}}$ is tuned to achieve a target acceptance rate, typically 50%.

(ii) All lattice-site positions $\mathbf{r}_0$ are scaled from their current values as done in a conventional *NPT* algorithm, i.e.,

$\mathbf{r}_{i,0,\text{new}} = \mathbf{r}_{i,0,\text{old}}(V_{\text{new}}/V_{\text{old}})^{1/D}$; the corresponding change in the lattice energy is ΔU_{lat}.

(iii) All distances $\mathbf{r}$ from the lattice sites (as given in the pretrial configuration) are scaled as indicated by Eq. (8), so $\mathbf{r}_{i,\text{new}} = \mathbf{r}_{i,\text{old}}(\frac{V_{\text{old}}}{V_{\text{new}}}e^{\beta(P\Delta V + \Delta U_{\text{lat}})})^{1/(ND-D)}$.

(iv) Each molecule i is placed in a new position $\mathbf{r}_{i,0,\text{new}} + \mathbf{r}_{i,\text{new}}$; the change in the configurational energy ΔU from the original to this new trial configuration is computed.

(v) The new volume is accepted with probability given by Eqs. (11) and (14).

C. Simulation details

We have tested the volume-change move in three systems. First, we consider a fcc system of hard spheres. Second, we consider a fcc system of Lennard-Jones spheres to test applicability to soft vs hard potentials. Finally, we consider hard-dumbbell close-packed structures [16–19] in order to test the move's ability to handle orientation as an additional degree of freedom when scaling coordinates.

For the system of hard spheres (of diameter σ), we consider a system size of $N = 256$. We performed NPT simulations using either the conventional volume-change move or the new volume-change move, all at a pressure $P\sigma^3/kT = 23.3$, which yields a density close to $\rho\sigma^3 = 1.2$. Atomic displacement moves were chosen with N times greater likelihood than volume changes. In order to keep the center of mass fixed, we moved two atoms (chosen randomly) with each atomic displacement, applying the opposite translation to the second molecule. To better understand the behavior of the volume changes, we have also performed NVT simulations at densities $\rho\sigma^3$ ranging from 1.15 to 1.25 at intervals of 0.01. During the NVT simulations, we monitored the mean-square displacement of atoms from their lattice sites as well as the maximum amount of compression that could applied to the system (with a traditional volume-change move) without causing overlap.

For the system of Lennard-Jones spheres (with size and energy parameters σ and ϵ, respectively), we considered a system of size $N = 500$ with potential interactions calculated using neighbor lists truncated at $r_c = 0.46L$. The neighbor lists are constructed at the beginning of the simulation and are not updated during the simulation (no diffusion occurs). No other truncation of the potential is applied (the potential is calculated for atom pairs that are neighbors and not calculated for atom pairs that are not neighbors, regardless of separation distance). We have used a long-range correction equal to $U_{\text{lat}} - U_{\text{lat},r_c}$, where U_{lat} is

$$U_{\text{lat}}/\epsilon N = c_2(\rho\sigma^3)^2 + c_4(\rho\sigma^3)^4, \qquad (15)$$

with $c_2 = -14.453\,920\,93$ and $c_4 = 6.065\,940\,096$ [20]. For the purpose of the U_{lat,r_c}, we use Eq. (15) again, but with constants refit for the truncated potential, $c_2 = -14.298\,500\,64$ and $c_4 = 6.065\,922\,568$. We conducted the NPT simulation at $kT/\epsilon = 1.0$ and a pressure $P\sigma^3/\epsilon = 20.4$, which yields a density close to 1.2. We performed additional NVT simulations at densities from 1.15 to 1.25 to measure the mean-square displacement of atoms from their lattice sites.

The third system we have considered is a hard-dumbbell crystal (each molecule formed as two hard spheres of diameter σ and separated by a rigid bond length ℓ), which can adopt various periodic and aperiodic structures, depending on the packing of the atomic layers (fcc vs hcp) and the orientations of the dumbbells. Vega *et al.* found that the various close-packed ordered structures had indistinguishable properties [16] and so for this study we have chosen to examine the so-called CP2 structure, which has the dumbbell atoms arranged $ABAB$ hexagonal layers and all dumbbells having the same orientation. The unit cell is defined by vectors $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ where the atomic hexagonal layers exist in the $\mathbf{a}$-$\mathbf{b}$ plane and $\|\mathbf{a}\| = \sqrt{3}\|\mathbf{b}\|$, while $c_x/\sigma = [(\ell/\sigma)^2 - 1]/\sqrt{3}$ and $c_z/\sigma = (\ell/\sigma)\sqrt{1 - (\ell/\sigma)^2/3} + \sqrt{2/3}$. We have set the bond length to $\ell/\sigma = 0.6$ and have conducted simulations of 144 dumbbells at $Pd^3/kT = 45$, where d is the diameter of a sphere having a volume equal to the dimer ($d/\sigma = 1.792$ for $\ell/\sigma = 0.6$) and also $Pd^3/kT = 100$. At the close-packed density, the molecules lie in the xz plane with an angle of $\theta_0 = \sin^{-1}(\ell/3\sigma)$ from the z axis, pointing toward the positive x direction. We have employed two rotation moves, one that varies the angle from the z axis, taking steps in $\cos\theta$. The second move changes the second angle ϕ, defined as the angle of rotation around the z axis from the nominal orientation, by rotating the molecule around the z axis with a step size proportional to $\sin\theta$.

We have found that the molecules within a plane can rotate together such that ϕ averaged within the plane is some multiple of 60°. These rotations correspond to planar defects that would be unstable in a bulk crystal. Accordingly, we prevent the molecules in a plane from rotating together by adopting a constraint that prevents the value of ϕ averaged within a plane from exceeding 30°.

We perform three types of moves related to the size and shape of the simulation box during the simulation of the hard dumbbells. First, we use an isotropic volume change that takes steps in $\ln V$. In order to allow the box shape to change, we have also included a move that takes a step in $\ln\|a\|$ that is also applied to $\ln\|b\|$ so that the ratio $\|a\|/\|b\|$ remains fixed; $\|c\|$ is also adjusted so that the volume is constant. In the third move, steps in $\ln c_x$ are taken in order to allow the box angle to vary without changing the volume. When using the improved scaling in the moves, we apply the scaling to both translation and rotation in the isotropic move [now distributing the scaling to $N(D + 2) - D$ degrees of freedom]. For rotation, we apply the scaling to $\cos\theta$ and $\phi/\sin\theta$. For the shape-change moves, we do not apply any scaling. While we might apply scaling for the the first shape-change move based on its tendency to decrease vibrations in one dimension while increasing them in another direction, thermodynamics does not provide the type of guidance we have for the isotropic move. Additionally, several different approaches to perform the scaling did not significantly increase the step size and the fluctuation of $\|a\|/\|c\|$ is relatively small.

For all systems, we have conducted simulations of 10^9 steps, taking data every N steps, grouping the data into 100 blocks for error analysis. We have optimized the Monte Carlo move maximum step sizes so that 50% of the trials are accepted.

TABLE I. Results from *NPT* simulation of hard spheres.

Quantity	Standard move	Improved move
	$N = 256$, $P\sigma^3/kT = 23.3$	
$\langle\rho\sigma^3\rangle$	1.1997(3)	1.200042(11)
max step size	0.000336	0.0127
σ_V/V	0.00547	0.00549
	$N = 864$, $P\sigma^3/kT = 23.3$	
$\langle\rho\sigma^3\rangle$	1.2004(7)	1.199641(12)
max step size	0.000100	0.00538
σ_V/V	0.00323	0.00300
	$N = 256$, $P\sigma^3/kT = 47.6$	
$\langle\rho\sigma^3\rangle$	1.30015(18)	1.299894(5)
max step size	0.000175	0.00803
σ_V/V	0.00292	0.00288

TABLE II. Result from *NPT* simulation of 500 Lennard-Jones spheres at $P\sigma^3/\epsilon = 19.9$.

Quantity	Standard move	Improved move
$\langle\rho\sigma^3\rangle$	1.199894(12)	1.199894(7)
max step size	0.0104	0.0113
σ_V/V	0.00386	0.00388

III. RESULTS AND DISCUSSION

A. Hard spheres

The results of *NPT* simulations of hard spheres at a pressure $P\sigma^3/kT = 23.3$ are reported in Table I. The densities from the two approaches agree within uncertainty limits with the uncertainty limit from the simulation using the conventional Monte Carlo move being about 30 times larger. This is partly explained by the difference in Monte Carlo step sizes (in terms of $\ln V$) used for each move. The step size for the move using coordinate scaling was 38 times larger than the step size for the conventional move and more than 2 times larger than even the standard deviation of $\ln V$, σ_V/V. This indicates that the move is able to easily jump within the full range of volumes appropriate for the set pressure. The step size for the standard move was much smaller because every configuration tends to have at least two atoms that are very close. The system can be compressed only a small amount before those atoms would

overlap. We also examine a larger system of $N = 864$ atoms and find that the performance of the standard move decreases considerably, with the uncertainty of the density more than doubling. The uncertainty obtained using the improved move also increases, but only marginally. Finally, we also consider a system at $P\sigma^3/kT = 47.6$ with $N = 256$, which yields $\rho\sigma^3 \approx 1.3$. We find that the improved move's uncertainty is 34 times lower than the standard move, which is slightly higher than the ratio of uncertainties obtained for the lower pressure.

Although the larger step size of the new move helps to improve the precision of the average density measurement, it does not fully explain the improvement. The remaining difference is then due to a longer correlation time within the simulation using the traditional move. To better understand this, we have conducted *NVT* simulations, examining the root-mean-square distance of atoms from their lattice sites d,

$$d = \langle(\mathbf{r} - \mathbf{r}_0)^2\rangle^{1/2}. \qquad (16)$$

In Fig. 1 we present $d(\rho\sigma^3)/d(\rho\sigma^3 = 1.2)$ vs $\rho\sigma^3$. We also consider starting from $\rho\sigma^3 = 1.2$ and proposing a Monte Carlo volume change trial and plot the value of $d(\rho_{\text{new}}\sigma^3)/d(\rho\sigma^3 = 1.2)$ using both the standard and improved scaling. While the standard deviation of the density is only 0.0066, we have extended the range of the x axis to illustrate the performance of the scaling even out to relatively large fluctuations in the volume. The standard scaling is described by $d(\rho\sigma^3)/d(\rho_0\sigma^3) = (\rho_0\sigma^3/\rho\sigma^3)^{1/3}$ while the improved scaling is described by Eq. (8). We can see that the standard scaling provides only a small fraction of the total amount of scaling
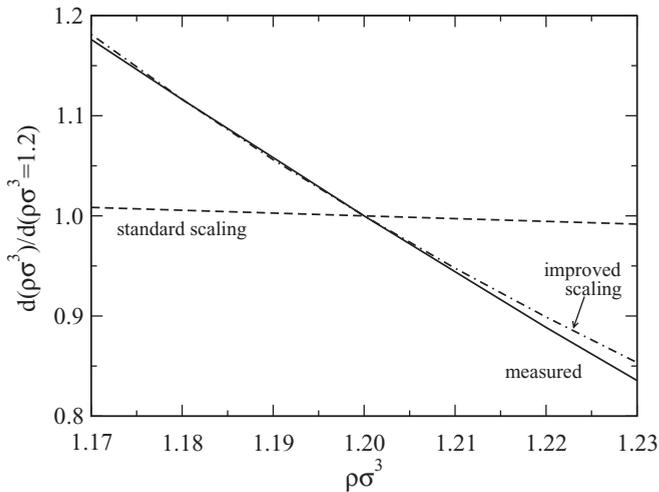

FIG. 1. Normalized root-mean-square (rms) deviation of atoms from their lattice sites as a function of density for a system of hard spheres. The solid curve corresponds to the measured rms deviation at different densities, while the dashed and dot-dashed curves show the rms deviation expected to result from scaling of the displacements from those encountered at a density of 1.2, as prescribed by standard and improved moves, respectively.
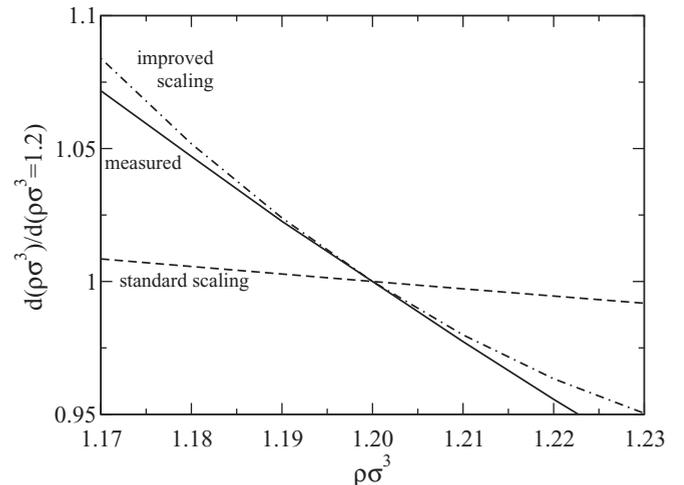

FIG. 2. Same as Fig. 1, but for a system of Lennard-Jones spheres.

TABLE III. Results from the *NPT* simulation of 144 hard dumbbells in the CP2 crystal.

Quantity	Standard move	Improved move	Standard move	Improved move
Pd^3/kT	45	45	100	100
$\langle \rho d^3 \rangle$	1.2827(4)	1.28329(12)	1.39643(19)	1.39613(3)
max step size	0.000325	0.00188	0.000156	0.00136
σ_V/V	0.00569	0.00557	0.00254	0.00258

that is needed to arrive in a configuration with the atoms at an appropriate distance from the lattice sites. Once a move is accepted, many steps of displacement moves must occur before the configuration can reach a system with typical atomic displacements. On the other hand, the improved scaling results in configurations with a much more appropriate amount of scaling of the atoms from their lattice sites. The result is that the improved move puts atoms at distances appropriate for the new density and additional re-equilibration is unnecessary.

B. Lennard-Jones spheres

The results of *NPT* simulations of Lennard-Jones spheres at a pressure $P\sigma^3/\epsilon = 19.9$ are reported in Table II. The densities from the two approaches agree within uncertainty limits, with the improvement in uncertainty limit being 68%. While still a substantial improvement, this is much less than what we found for hard spheres. Likewise, the Monte Carlo step size (in terms of $\ln V$) used in the improved volume change was only 10% larger than the step size used for the standard move; both step sizes are nearly 3 times larger than the standard deviation in $\ln V$.

We have again measured the deviation of the atoms from their lattice sites and present this plotted against density in Fig. 2. As in Fig 1, we have added curves for the scaling using the standard and improved scaling. As with hard spheres,

FIG. 3. Same as Fig. 1, but for a system of hard dumbbells. Also displayed are rms deviations for orientational coordinates (where θ is the inclination angle and ϕ is the azimuth angle, both with respect to the average orientation). The standard scaling for rotation is horizontal because the standard move does not alter the orientations of molecules. A single line represents the effect of the improved scaling method on translational and orientational deviations.

we find that the improved coordinate scaling matches the measured deviations very well. However, we also note that the scaling is somewhat flatter than what we found for hard spheres, which means that the standard scaling is closer to the appropriate scaling.

C. Hard dumbbells

The results of *NPT* simulations of hard-sphere dumbbells at pressures $Pd^3/kT = 45$ and 100 are reported in Table III. As in the previous cases, we see that the improved move yields the same densities as the standard move, but with improved precision (about 3 times better for $Pd^3/kT = 45$ and 6 times better for $Pd^3/kT = 100$). The average density at $Pd^3/kT = 45$ also matches the $\langle \rho d^3 \rangle = 1.279(13)$ reported in Ref. [16]. As we saw with hard spheres, the maximum step size (in $\ln V$) is 17 times smaller than σ_V/V for the standard move. The improved move is again able to take larger steps, although the improvement is less dramatic for hard dumbbells, and the resulting step size is still 2–3 times smaller than σ_V/V.

In Fig. 3 we plot the root-mean-square deviation of the hard dumbbells from their lattice coordinates as a function of density. For the purposes of scaling, we have taken $\langle \rho d^3 \rangle = 1.283$ as the nominal density to scale from. The standard scaling for the translational motion is the same as before for the spherical models, but the standard move does not scale the rotation at all. The improved move applies the same scaling to translation and rotation. We see that the measured translation matches the scaling used by the improved move while $\phi \sin(\theta)$ varies more and $\cos(\theta)$ varies less than predicted by the scaling. This signals a breakdown of our assumption that the change in phase-space volume is evenly distributed. We attempted additional *NPT* simulations where we distributed the scaling unevenly in order to match the measured variations, but the results were not significantly better than our results with the evenly distributed scaling.

IV. CONCLUSIONS

We have presented an improved method for performing Monte Carlo simulation of crystals in the isothermal-isobaric ensemble. The technique is simple and computationally inexpensive to implement, yet very effective. The approach is most advantageous in application to hard potentials and the improvement it offers over the conventional algorithm increases with the size and density of the simulated system. The performance in application to molecules with molecular flexibility is yet to be determined. Still, given its simplicity and effectiveness, the present method is worthwhile to consider when conducting *NPT* simulations of any crystalline phase.
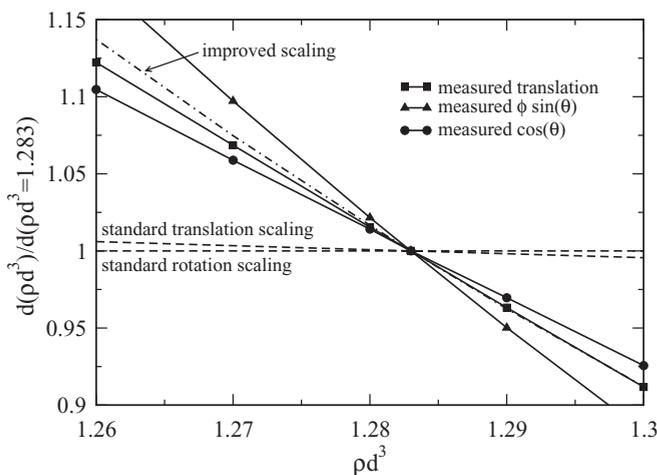
The sampling strategy presented in this work could find application in other contexts involving system perturbations in ordered phases. The general scheme is to estimate the effect of the perturbation on the accessible phase-space volume in an equilibrated system and to translate that change into a rescaling of appropriate degrees of freedom from their nominal values (e.g., distance from a lattice site in a crystal and rotation from a director in a liquid crystal). The strategy might also help in amorphous solids where the nominal coordinate could be taken as an average coordinate rather than a lattice site. However, the strategy might be less effective in amorphous solids since the coordinates will be qualitatively different from each other so that distributing the scaling equally to all of them is less likely to be appropriate. In addition to the application to ensemble sampling presented here, the general approach could also find use in perturbation- or work-based free-energy calculation methods. A closely related technique for free-energy temperature perturbations in crystals was presented recently [21,22], where it too was found to be very effective in trial applications.

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