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The self-referential method for linear rigid bodies: Application to hard and Lennard-Jones dumbbells

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The self-referential (SR) method incorporating thermodynamic integration (TI) [Sweatman *et al.*, J. Chem. Phys. **128**, 064102 (2008)] is extended to treat systems of rigid linear bodies. The method is then applied to obtain the canonical ensemble Helmholtz free energy of the α-N_2 and plastic face centered cubic phases of systems of hard and Lennard-Jones dumbbells using Monte Carlo simulations. Generally good agreement with reference literature data is obtained, which indicates that the SR-TI method is potentially very general and robust. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Studies of crystal free energies are of great importance for crystal engineering and understanding fundamental phase behavior, and molecular simulation has become an increasingly popular technique in this context in recent decades.[1] This is especially the case for molecules, which usually have much more complex phase diagrams, including numerous crystal polymorphs than atomic (spherical) species.[2] The precise knowledge of a molecular crystal phase diagram can be of tremendous practical and economical interest, for instance, in the pharmaceutical industry, where the impact of crystal polymorph can be almost as important as the choice of chemical compound on its possible prescription as a drug.[3]

Probably the most popular method for calculating crystal free energies is based on the method of Frenkel and Ladd[4] (note also Ref. 5), which computes the free energy difference between the crystal of interest and the corresponding Einstein crystal. With this method the Einstein crystal free energy must also be calculated and for simple molecules, this is considered straightforward. The Frenkel–Ladd (FL) method, initially developed for particles having spherical symmetry such as atomic systems, has been both refined[6,7] and extended to systems composed of more complex particles[8] and, in particular, to rigid models of molecules.[9–12] The derivation and application of the FL method to molecular systems has been the subject of two recent reviews.[13,14]

In 2005, one of us (M.S.) introduced another technique for calculating crystal free energies via molecular simulation.[15] This technique, called the self-referential (SR) method, is expected to be very versatile and robust, and in an earlier publication it was also shown to be straightforward and relatively efficient when combined with a kind of thermodynamic integration (TI).[16] The SR method is founded on the central principle that at fixed pressure and temperature the Gibbs free energy scales linearly with system size. So, the absolute Gibbs free energy can be obtained by calculating the free energy difference between two systems with different numbers of particles. In a sense, the smaller of the two systems is the reference system, hence the name "SR," yet initially its absolute free energy is unknown.

The SR method consists of two stages; (i) a "replication" stage and (ii) a "relaxation" stage. According to the current implementation of the SR method replication calculates the free energy difference between a single-size system and a constrained double-size system which is a replica, to within a self-similarity constraint, of the single-size system. The relaxation stage calculates the free energy difference between the constrained self-similar double-size system and an ordinary, unconstrained, or relaxed double-size system. The relaxed double-size system has twice the Gibbs free energy of the initial single-size system. Because it utilizes states that only differ in their size, the SR-TI method has many advantages over earlier techniques.[17–20] With these other techniques one always has the problem of how to specify the path between the reference state (Einstein crystal, fluid state, etc.) and the state of interest. Different paths might be required for continuous or discontinuous interaction potentials or for confined crystals or if there are some other unusual features of the system. The only issue with the SR method is specification of the temperature path during the relaxation stage. Currently, a simple algorithm, described in Sec. III A, which automatically chooses the temperature path is found to be entirely adequate.

Until this work, the SR method has only been used for atomic systems, namely, hard-sphere (HS) and Lennard-Jones (LJ) fcc crystals.[15,16] This paper describes extension of the SR method, especially the version that incorporates thermodynamic integration (SR-TI), to systems of rigid linear molecules. This extension is important in demonstrating the versatility and generality of the SR-TI method because any molecular model can be considered as an assembly of spherical and rigid nonspherical bodies, linked by intramolecular bonds. Rigid models of molecules are also the starting point for understanding the relationship between molecular shape and phase behavior.[8,10–12,21–23] Particular attention has been paid to the case of linear di- and triatomic molecules, with studies of realistic models of nitrogen, carbon dioxide, and nitrous oxide.[9,24–29] There have also been many studies of primitive models such as hard and LJ dumbbells.[10,11,30–33] This provides us with valuable and reliable data sets of crystal free energies with which we can compare our results. As the purpose of this paper is mainly the validation of the SR-TI method, we choose to test it for two simple models: hard and LJ dumbbells in the α-N_2 and fcc plastic crystal (PC) structures for which data are available.[10,33]

The reminder of this paper is organized as follows. In Sec. II we describe in detail how the SR-TI method can be extended to treat a crystal of rigid linear bodies. As explained in the earlier paper,[16] it is convenient to perform calculations with the canonical rather than the isothermal-isobaric ensemble, and the theory is also developed in this way. Use of the canonical ensemble avoids the requirement for "volume scaling" Monte Carlo (MC) moves during the relaxation stage. Conversion from the canonical to the isothermal-isobaric ensemble is straightforward, and also accurate if the system is large enough. We then compare in Sec. III B the results obtained with both SR methods for hard and LJ dumbbells, with those previously published by Vega *et al.*[10] and Galbraith and Hall[33] finding good agreement. We conclude with a summary and a discussion about further generalization of the SR-TI method to more complex molecular crystals and confined crystals.

II. THE SR-TI METHOD FOR A SYSTEM OF RIGID LINEAR MOLECULES

We consider here a perfect crystalline solid consisting of three-dimensional rigid linear bodies, called molecules in the remaining of the paper, in the canonical ensemble. The position and orientation of a molecule, molecule i for instance, are labeled by $\mathbf{r}_i$ (usually taken as the molecule center of mass but other choices are possible, see Ref. 14) and $\boldsymbol{\Omega}_i = \{\theta_i, \phi_i\}$, which defines the orientation of the molecule with respect to space-fixed axes. θ is the polar angle formed by the symmetry axis of the molecule with the z-axis and ϕ is the azimuthal angle formed by projection of the symmetry axis on the x-y plane and the x-axis. Periodic boundaries are employed. The two stages, replication and relaxation, are described in turn.

A. Replication

The purpose of this stage is to find the free energy difference between a single-size system and a constrained, self-similar, double-size system. This difference is

$$\Delta(\beta F_{\mathrm{rep}}) = -\ln\left(\frac{\Phi_\alpha}{\Phi_s}\right), \tag{1}$$

where Φ_s and Φ_α are the partition functions of the single-size system and the constrained double-size system, respectively. Here, α represents the self-similarity, or relaxation, state of the double-size system, defined in more detail later in this section. The canonical ensemble partition function for N linear molecules in a crystal in the semiclassical approximation is given by

$$\Phi = \frac{\Lambda_t^{3N}\Lambda_r^{N}}{N}\int_{V'}\int_{V_\Omega} d\mathbf{r}^N d\Omega^N e^{-\beta H(\mathbf{r}^N,\Omega^N,V)}, \tag{2}$$

where $\Lambda_t = \sqrt{2\pi m k_B T/h^2}$ and $\Lambda_r = V_\Omega I k_B T/h^2$ are the translational and rotational contributions obtained by integrating over momenta, H is the configurational contribution to the Hamiltonian, and $\beta^{-1} = k_B T$ (k_B is Boltzmann's constant and T is temperature). The factor of N rather than $N!$ occurs because particles are not allowed to permute their positions; this constraint is indicated by the symbol V'. $V_\Omega = 4\pi/D$ is the integral of the orientational phase space, where D is a symmetry number with value 1 for linear bodies without inversion center (such as heteronuclear diatomic molecules) and 2 for bodies with an inversion center (such as homonuclear diatomic molecules, hard spherocylinders, or ellipsoids). Symmetry requires that θ is defined in $\{0, \pi/2\}$ when $D=2$, and in $\{0, \pi\}$ when $D=1$, while ϕ is always defined in $\{-\pi, \pi\}$ (or $\{0, 2\pi\}$ which is equivalent). Note that the momentum contribution to the free energy is not important here because it is the same for all phases. Only the configuration contribution is important in the context of phase behavior.

If we clamp particle 1 to a fixed position, then the single-size partition function for hard dumbbells can be written as

$$\Phi_s = \frac{V_s}{N_s}\int_{V'}\int_{V_\Omega} d\mathbf{r}^{N_s-1} d\omega^{N_s} d\phi^{N_s} e^{-\beta_s H_s(\mathbf{r}^{N_s},\Omega^{N_s},V_s)}, \tag{3}$$

where $\omega_i = \cos(\theta_i)$, V is the system volume and subscript s refers to the single-size system. Note that the momentum contribution terms have been omitted as they play no significant role in this study which concentrates on the configurational contribution.

For a double-size system $\boldsymbol{\Omega}_{i+N_s}$, for $i=1,\ldots,N_s$, is described relative to $\boldsymbol{\Omega}_i$ rather than space-fixed axes so that $\boldsymbol{\Omega}_{i+N_s} = \{\tau_i, \varphi_i\}$, where τ_i is the relative polar angle formed by the axes of molecule i and its partner molecule $i+N_s$, and φ_i is the relative azimuthal angle, ranging from 0 to 2π, defined via rotation matrices given later [Eqs. (26)–(29)].

The self-similarity constraint on the centers of mass of molecules $N_s+1\cdots 2N_s$ is expressed as $r_i = |\mathbf{r}_i - (\mathbf{r}_{i+N_S} - \mathbf{L}_x)| \le \hat{r}(\alpha)$, where $\mathbf{L}_x$ is a vector equal to half the double-size box length in the replication direction. Introducing a similar constraint on the cosine ξ_i of the angle τ_i, i.e., $1-\xi_i \le \hat{\eta}(\alpha)$, it follows that the partition function of the constrained double-size system is

$$\Phi_\alpha = \frac{2V_s}{2N_s}\int_{V'}\int_{V_\Omega} d\mathbf{r}^{2N_s-1} d\omega^{N_s} d\phi^{N_s} d\xi^{N_s} d\varphi^{N_s} \times e^{-\beta_\alpha H_\alpha(\mathbf{r}^{2N_s},\Omega^{2N_s},2V_s)}. \tag{4}$$

Here, α controls the self-similarity constraint for relative translational and orientational degrees of freedom simultaneously. When α is very small the double-size system is self-similar, i.e., both halves of the double-size system are almost identical to within a tolerance defined by the constraints $\hat{r}(\alpha)$ and $\hat{\eta}(\alpha)$. On the other hand, when α is very large these constraints have no significant effect and the double-size system is said to be fully relaxed. The temperature is also allowed to vary with α, and we denote $\beta_\alpha = \beta(\alpha)$. In the limit of very small initial self-similarity constraints for both translational and orientational degrees of freedom (when $\alpha = \alpha_1$), we can write $H_{\alpha_1} \approx 2H_s$, and therefore,

$$\Phi_{\alpha_1} \approx \frac{2V_s}{2N_s} \int_{V'} \int_{V_\Omega} d\mathbf{r}^{2N_s-1} d\omega^{N_s} d\phi^{N_s} d\xi^{N_s} d\varphi^{N_s} \times e^{-2\beta_{\alpha_1} H_s(\mathbf{r}^{N_s}, \Omega^{N_s}, V_s)}. \tag{5}$$

We are able to integrate Eq. (5) with respect to translational and orientational coordinates for particles $N_s+1 \cdots 2N_s$ because the Hamiltonian is now practically independent of these coordinates. By also choosing $\beta_{\alpha_1} = \beta_s/2$, we obtain

$$\Phi_{\alpha_1} \approx \frac{(V_{r_1} V_{\eta_1})^{N_s} V_s}{N_s} \int_{V'} \int_{V_\Omega} d\mathbf{r}^{N_s-1} d\omega^{N_s} d\phi^{N_s} \times e^{-\beta_s H_s(\mathbf{r}^{N_s}, \Omega^{N_s}, V_s)}, \tag{6}$$

where $V_{r_1} = 4\pi \hat{r}_1^3/3$ and $V_{\eta_1} = 2\pi \hat{\eta}_1$, in which we define $\hat{r}_1 = \hat{r}(\alpha_1)$ and $\hat{\eta}_1 = \hat{\eta}(\alpha_1)$. By substituting Eqs. (6) and (3) into Eq. (1) we obtain the configurational free energy difference for the replication stage,

$$\Delta(\beta F_{\text{rep}}) = -\ln\left(\frac{\Phi_{\alpha_1}}{\Phi_s}\right) \approx -N_s \ln\left(\frac{V_{r_1} V_{\eta_1}}{\lambda^3}\right), \tag{7}$$

where λ is a suitable arbitrary length scale. This relation, allowing a direct calculation of the replication free energy, is exact in the simultaneous limit $\hat{r}_1 \to 0$ and $\hat{\eta}_1 \to 0$, which is the same as taking the limit $\alpha_1 \to 0$ since we take both $\hat{r}$ and $\hat{\eta}$ to be proportional to a power of α (actually, we take $\hat{r} = \alpha$ and $\hat{\eta} = A_\eta \alpha^{B_\eta}$, where A_η and B_η are constants to be chosen). A similar technique was used in our earlier work[16] concerning hard and LJ particles, except of course the V_{η_1} term is absent in this earlier work concerning spherical particles. It allows calculation of the replication free energy difference immediately, without the requirement of a separate simulation, as is the case in Ref. 15.

B. Relaxation

The relaxation free energy can be expressed as

$$\Delta(\beta F_{\text{rel}}) = \int_{\alpha_1}^{\alpha_m} d\alpha \frac{d(\beta_\alpha F_\alpha)}{d\alpha}, \tag{8}$$

where α_m is chosen such that the self-similarity constraint is so large that it no longer has any influence on the system. To find $d(\beta_\alpha F_\alpha)/d\alpha$ we take into account that the Helmholtz free energy is related to the corresponding partition function via the relation $\beta F = -\ln \Phi$. Hence

$$d(\beta_\alpha F_\alpha) = -d(\ln(\Phi(\alpha))) = -\frac{d\Phi(\alpha)}{\Phi} = -\frac{1}{\Phi}\left(\left(\frac{\partial \Phi}{\partial \alpha}\right) d\alpha\right). \tag{9}$$

This relation can be re-expressed using Eq. (4) as

$$d(\beta_\alpha F_\alpha) = \left\langle \beta_\alpha \frac{\partial H_\alpha}{\partial \alpha} + H_\alpha \frac{\partial \beta_\alpha}{\partial \alpha} \right\rangle d\alpha. \tag{10}$$

So we have three contributions to $\Delta(\beta F_{\text{rel}})$: one due to changes in temperature,

$$\Delta(\beta F_T) = \int_{\beta_s/2}^{\beta_s} \langle H_\alpha \rangle d\beta_\alpha, \tag{11}$$

and two due to changes in the tolerance constraint α,

$$\Delta(\beta F_{\hat{r}}) = \int_{\alpha_1}^{\alpha_m} d\alpha \left\langle \beta_\alpha \left(\frac{\partial H_\alpha}{\partial \hat{r}}\right)\left(\frac{d\hat{r}}{d\alpha}\right) \right\rangle_\alpha = \int_{\hat{r}_1}^{\hat{r}_m} d\hat{r} \left\langle \beta_\alpha \left(\frac{\partial H_\alpha}{\partial \hat{r}}\right) \right\rangle_{\hat{r}}, \tag{12}$$

and

$$\Delta(\beta F_{\hat{\eta}}) = \int_{\alpha_1}^{\alpha_m} d\alpha \left\langle \beta_\alpha \left(\frac{\partial H_\alpha}{\partial \hat{\eta}}\right)\left(\frac{d\hat{\eta}}{d\alpha}\right) \right\rangle_\alpha = \int_{\hat{\eta}_1}^{\hat{\eta}_m} d\hat{\eta} \left\langle \beta_\alpha \left(\frac{\partial H_\alpha}{\partial \hat{\eta}}\right) \right\rangle_{\hat{\eta}}. \tag{13}$$

The first contribution, $\Delta(\beta F_T)$, can be evaluated using numerical quadrature. Contributions (12) and (13) must be determined by differentiating the Hamiltonian with respect to $\hat{r}$ and $\hat{\eta}$, respectively.

The Hamiltonian of the system, including the translational and orientational constraints, can be defined as

$$H_\alpha = H_d + \gamma \sum_{i=1}^{N_s} (\Theta(r_i - \hat{r})(r_i - \hat{r}) + \Theta(1 - \xi_i - \hat{\eta})(1 - \xi_i - \hat{\eta})), \tag{14}$$

where H_d is the Hamiltonian of an unconstrained double-size system, Θ is the Heaviside step function, and γ is an arbitrary constant. As defined, Eq. (14) describes a "soft" tolerance constraint, i.e., particles are allowed to violate the constraint with a probability that depends on γ. As γ increases the constraint becomes "harder" and fewer violations are allowed. Eventually we will take the limit $\gamma \to \infty$ corresponding to a perfectly hard constraint, but we prefer to work with the soft constraint when calculating the derivative of the Hamiltonian with respect to the tolerance constraint. These derivatives are

$$\frac{\partial H_\alpha}{\partial \hat{r}} = -\gamma \sum_{i=1}^{N_s} (\delta(r_i - \hat{r})(r_i - \hat{r}) + \Theta(r_i - \hat{r})), \tag{15}$$

and

$$\frac{\partial H_\alpha}{\partial \hat{\eta}} = -\gamma \sum_{i=1}^{N_s} (\delta(1 - \xi_i - \hat{\eta})(1 - \xi_i - \hat{\eta}) + \Theta(1 - \xi_i - \hat{\eta})). \tag{16}$$

Rather than repeating the derivation in our earlier paper[16] concerning the substitution of Eq. (15) into Eq. (12) in the limit $\gamma \to \infty$, we simply state here the result that the second contribution to $\Delta(\beta F_{\text{rel}})$ can be written as

$$\Delta(\beta F_{\hat{r}}) = -4\pi N_s \int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d\,\ln(\hat{r}) g_r(\hat{r},\hat{r})\hat{r}^3, \tag{17}$$

where

$$g_r(r,\hat{r}) = \left\langle \frac{1}{N_s}\sum_{i=1}^{N_s} \delta(r_i - r) \right\rangle_{\hat{r}}$$

is the probability distribution function for the reduced separation, r, when the tolerance constraint is $\hat{r}(\alpha)$.

However, we describe the derivation for orientational relaxation in full following a similar route to that used to derive Eq. (17). Substituting Eq. (16) in Eq. (13) gives

$$\Delta(\beta F_{\hat{\eta}}) = \int_{\hat{\eta}_1}^{\hat{\eta}_m} d\hat{\eta} \langle -\beta_\alpha(\hat{\eta})\gamma \sum_{i=1}^{N_s} (\delta(1-\xi_i-\hat{\eta}) \times (1-\xi_i-\hat{\eta}) + \Theta(1-\xi_i-\hat{\eta}))\rangle_{\hat{\eta}}. \tag{18}$$

The first term in brackets is always zero and the remainder can be written as

$$\Delta(\beta F_{\hat{\eta}}) = -\gamma N_s \int_{\hat{\eta}_1}^{\hat{\eta}_m} d\hat{\eta}\beta_\alpha(\hat{\eta}) \int_{\xi_{\min}}^{1} d\xi g_\xi(\xi,\hat{\eta})\Theta \times (1-\xi-\hat{\eta}), \tag{19}$$

where $\xi_{\min}=-1$ or 0 for a molecule with $D=1$ or 2, respectively, and

$$g_\xi(\xi,\hat{\eta}) = \left\langle \frac{1}{N_s}\sum_{i=1}^{N_s} \delta(\xi_i - \xi) \right\rangle_{\hat{\eta}}$$

is the probability distribution for ξ when the orientational constraint is $\hat{\eta}$. Taking into account the definition of the Heaviside step function we can write Eq. (19) as

$$\Delta(\beta F_{\hat{\eta}}) = -\gamma N_s \int_{\hat{\eta}_1}^{\hat{\eta}_m} d\hat{\eta}\beta_\alpha(\hat{\eta}) \int_{\xi_{\min}}^{1-\hat{\eta}} d\xi g_\xi(\xi,\hat{\eta}). \tag{20}$$

The pair distribution function for $\xi \leq 1-\hat{\eta}$ can be written exactly as

$$g_\xi(\xi,\hat{\eta}) = g_\xi(1-\hat{\eta},\hat{\eta})\exp(-\beta_\alpha\gamma(1-\xi-\hat{\eta}) + c_\xi(\xi,\hat{\eta}) - c_\xi(1-\hat{\eta},\hat{\eta})), \quad \xi \leq 1-\hat{\eta}, \tag{21}$$

where c_ξ represents the effective potential resulting from indirect interactions, or correlations, between a particle and its constrained partner. As $\gamma \to \infty$ the constraint potential dominates this expression because it becomes increasingly strong and short ranged. So as $\gamma \to \infty$, c_ξ becomes essentially constant over that part of g_ξ that is not effectively zero, and so we can write

$$g_\xi(\xi,\hat{\eta}) \approx g_\xi(1-\hat{\eta},\hat{\eta})\exp(-\beta_\alpha\gamma(1-\xi-\hat{\eta})), \quad \xi \leq 1-\hat{\eta}. \tag{22}$$

Placing Eq. (22) in Eq. (20) and taking the limit $\gamma \to \infty$, we get

$$\Delta(\beta F_{\hat{\eta}}) = -N_s \int_{\hat{\eta}_1}^{\hat{\eta}_m} d\hat{\eta} g_\xi(1-\hat{\eta},\hat{\eta}). \tag{23}$$

To archive greater numerical accuracy we can integrate Eq. (23) with respect to $\ln(\hat{\eta})$

$$\Delta(\beta F_{\hat{\eta}}) = -N_s \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d\,\ln(\hat{\eta})\hat{\eta} g_\xi(1-\hat{\eta},\hat{\eta}). \tag{24}$$

Putting Eqs. (7), (11), (17), and (24) together gives the final result for the configurational contribution to the Helmholtz free energy difference per particle

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{V_{r_1}V_{\eta_1}}{\lambda^3}\right) + \frac{1}{N_s}\int_{\beta_s/2}^{\beta_s} d\beta_\alpha \langle H_\alpha \rangle - 4\pi \int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d\,\ln(\hat{r}) g_r(\hat{r},\hat{r})\hat{r}^3 - \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d\,\ln(\hat{\eta}) g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta}, \tag{25}$$

which is exact in the limits $\alpha_1 \to 0$ and $\alpha_m \to \infty$ (noting that there is an upper limit of 0 or ln(2) for $\ln(\hat{\eta}_m)$ if $D=2$ or 1, respectively). This is our final result. Recall that a term $\ln(\lambda^3)$ has been added arbitrarily to Eq. (25) to provide a suitable reduced length scale, and that the same amount must be subtracted from the momentum contribution to the Helmholtz free energy difference for consistency. Also, note that to compare our results with literature values that use normalized orientational coordinates[14] we must simultaneously add $\ln(V_\Omega)$ to the right hand side of (25) and subtract the same amount from the momentum part of the Helmholtz free energy. The last three terms on the right hand side of Eq. (25) can be calculated via numerical quadrature from MC simulations of constrained double-size systems with a suitable range of $\hat{r}$ and $\hat{\eta}$. These simulations are described in Sec. III.

III. SIMULATIONS

A. Numerical and simulation details

We give here the numerical details of the SR-TI simulations of hard and LJ homonuclear dumbbells. For an easier comparison we adopt essentially the same definitions and units as Vega *et al.*[10] and Galbraith and Hall.[33] A dumbbell is made of two spheres of diameter σ (σ being either the hard-sphere diameter or the LJ length scale parameter) rigidly connected with a bond of length L, and we define a reduced bond length $L^*=L/\sigma$. Following Vega *et al.*,[10] for hard dumbbells we define a reduced density $\rho^*=\rho d^3$, where ρ is the system density ($\rho=N/V$) and d is the diameter of a sphere with the same volume as the dumbbell: $d^3=1+\frac{3}{2}L-\frac{1}{2}L^3$. On the other hand, following Galbraith and Hall, for LJ dumbbells we define the reduced density as $\rho^*=\rho\sigma^3$. For hard dumbbells we choose $\lambda=d$ in Eqs. (7) and (25), while for LJ dumbbells we set $\lambda=\sigma$, in line with Galbraith and Hall. The crystal structures considered in this work are the α-N_2 structure (fcc arrangement of the center of mass with dumbbell axes directed along the cube diagonals), and the fcc PC structure which is the orientationally disordered analog of the α-N_2 structure. Note that in the limit of zero bond length $L^*=0$ these two structures are identical to the stable fcc structure of hard spheres. Here, we consider systems with $N_s=108$ or 256 dumbbells in the single-size system at several reduced densities and bond lengths. We recognize that for studies of phase behavior a systematic study of finite-size effects should be performed by considering systems with a range of sizes. However, we choose these system sizes for comparison with reference data in literature. Note that for homonuclear dumbbells the symmetry parameter $D=2$, and hence $V_\Omega=2\pi$.

According to the previously introduced definition of orientations the Cartesian coordinates of the centers of the two spheres of dumbbell i are calculated using

$$\mathbf{r}_i^{(a)} = \mathbf{r}_i + L(1.5 - a)(\mathbf{A}_i \cdot \mathbf{i}_z), \tag{26}$$

where $a=1$ or 2, $\mathbf{i}_z$ is the unit vector along the z-axis (0,0,1), and $\mathbf{A}_i$ is the rotation matrix[34] for dumbbell i given by

$$\mathbf{A}_i = \begin{pmatrix} \omega_i \cos\phi_i & -\sin\phi_i & \sqrt{1-\omega_i^2}\cos\phi_i \\ \omega_i \sin\phi_i & \cos\phi_i & \sqrt{1-\omega_i^2}\sin\phi_i \\ -\sqrt{1-\omega_i^2} & 0 & \omega_i \end{pmatrix}. \tag{27}$$

Likewise, the Cartesian coordinates of the centers of the two spheres of dumbbell $i+N_s$ are

$$\mathbf{r}_{i+N_s}^{(a)} = \mathbf{r}_{i+N_s} + L(1.5 - a)(\mathbf{A}_i(\mathbf{A}_{i+N_s} \cdot \mathbf{i}_z)), \tag{28}$$

where $\mathbf{A}_{i+N_s}$ is the rotation matrix expressing the relative orientation of dumbbell $i+N_s$ with respect to dumbbell i,

$$\mathbf{A}_{i+N_s} = \begin{pmatrix} \xi_i \cos\varphi_i & -\sin\varphi_i & \sqrt{1-\xi_i^2}\cos\varphi_i \\ \xi_i \sin\varphi_i & \cos\varphi_i & \sqrt{1-\xi_i^2}\sin\varphi_i \\ -\sqrt{1-\xi_i^2} & 0 & \xi_i \end{pmatrix}. \tag{29}$$

To appreciate the role of these rotation matrices, imagine first that the director (symmetry axis) of molecule $i+N_s$ points in the direction of the z-axis. However, this molecule is defined to be at an angle $\mathbf{\Omega}_{i+N_s}=\{\tau_i,\varphi_i\}$ relative to molecule i. So the orientation of molecule $i+N_s$ with respect to molecule i is obtained by multiplication of $\mathbf{i}_z$ by the rotation matrix $\mathbf{A}_{i+N_s}$. Moreover, molecule i is defined to be at an angle $\mathbf{\Omega}_i=\{\theta_i,\phi_i\}$ with respect to the Cartesian coordinate axes. So we must multiply again by the rotation matrix $\mathbf{A}_i$ to obtain the orientation of particle $i+N_s$ with respect to these axes.

To improve sampling efficiency trial MC moves consist of compound moves similar to those in earlier work.[15,16] That is, trial moves are applied simultaneously to a randomly selected pair of molecules (i and its partner $i+N_s$). Compound trial moves consist of a random translation or rotation. A compound translation attempt consists of moving both molecules by $\boldsymbol{\delta}\mathbf{r}$ (within a sphere of radius $\delta r_{\max}$) and also translating one of the molecules, chosen randomly, an additional $\boldsymbol{\delta}\mathbf{r}'$ (within a sphere of radius $\min(\delta r_{\max},\hat{r})$. Likewise, a compound rotation consist of a random rotation $\{\delta\omega,\delta\phi\}$ of molecule i (with maximum step sizes $\{\delta\omega_{\max},\delta\phi_{\max}\}$) together with a random rotation $\{\delta\xi,\delta\varphi\}$ of the relative orientation of molecule $i+N_s$ with respect to molecule i (with maximum step sizes $\{\min(\delta\omega_{\max},\hat{\eta})\delta\phi_{\max}\}$). Recall that the center of mass of molecule 1 is clamped, which implies that $\boldsymbol{\delta}\mathbf{r}$ is always zero for molecules 1 and $1+N_s$. However, molecule $1+N_s$ can still be translated by $\boldsymbol{\delta}\mathbf{r}'$. Maximum displacements are chosen to ensure suitable acceptance rates,[34] translations and rotations are chosen with equal probability, and all these move attempts are accepted or rejected with the usual acceptance probability $\min(1,\exp(-\beta_\alpha\Delta H_\alpha))$, where ΔH_α is the change in the configurational energy caused by a trial move. Trial moves are, of course, automatically rejected if they violate the tolerance constraint.

To calculate the integrals in Eq. (25) n_α separate evaluations of $\langle H_\alpha\rangle$, $g_r(\hat{r},\hat{r})\hat{r}^3$, and $g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta}$, each corresponding to a different value of α, are performed via canonical MC simulations of constrained double-size systems. Recall that β_α, $\hat{r}$, and $\hat{\eta}$ are all functions of α, which controls the relaxation of the crystal from a highly constrained self-similar state to a fully relaxed state. The β-path adopted for LJ dumbbells (this path is irrelevant for hard dumbbells) is similar to the one used in previous work on LJ spheres. Changes in β_α are chosen according to

$$\beta_{\alpha_i} = \beta_{\alpha_{i-1}} + \begin{cases} \dfrac{\beta_s - \beta_{\alpha_{i-1}}}{n_\alpha - i}\min(k_E, n_\alpha - i), & 2 < i < n_\alpha \\ \beta_s - \beta_{\alpha_{i-1}}, & i = n_\alpha, \end{cases} \tag{30}$$

where i stands for the ith relaxation step and k_E is an integer which is zero initially, and is also set to zero when the average energy for a given value of α is $\langle H_\alpha\rangle < 2E_t$ (E_t being the average configurational energy of the unconstrained single-size system at inverse temperature β_s) or incremented by 1 (to a maximum of 3) otherwise. Each SR-TI simulation for a given value of α comprises 356 000 MC cycles (for $N_s=108$) or 164 000 MC cycles (for $N_s=256$), of which 100 000 are used to achieve equilibrium, where 1 cycle consists of $2N_s$ attempted compound translational or rotational moves. For each simulation we measure the distribution functions $g_r(r,\hat{r})\hat{r}^3$ and $g_\xi(\xi,\hat{\eta})\hat{\eta}$ by dividing them into n_b bins each. However, we are interested only in the values of these distribution functions at their "edges," i.e., right at the respective constraints, and so we determine $g_r(\hat{r},\hat{r})\hat{r}^3$ and $g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta}$ by linear extrapolation using the ensemble averages for bins n_b and n_{b-1}. Values for n_α and n_b are in the range of 10–100 and are specified later.

The SR-TI method introduces six sources of systematic error for rigid linear molecules specified by the choice of $\hat{r}_1$, $\hat{r}_m$, $\hat{\eta}_1$, $\hat{\eta}_m$, n_α, and n_b. Or equivalently, since $\hat{r}=\alpha$ and $\hat{\eta}=A_\eta\alpha^{B_\eta}$, the systematic error is specified by the choice of α_1, α_m, A_η, B_η, n_α, and n_b. These errors can be reduced below a given statistical error by decreasing α_1, and/or increasing α_m, n_α, and n_b (but $\hat{\eta}_m$ has a maximum of one for homonuclear dumbbells). It is also important that $\hat{r}_1$ and $\hat{\eta}_1$ are chosen small enough to ensure that Eq. (5) is accurate, i.e., that the Hamiltonian is essentially independent of the position $\mathbf{r}_i$ and orientation $\mathbf{\Omega}_i$ of the replicated molecules $1+N_s$ to $2N_s$ when the system is fully constrained. This occurs when the distribution functions are constant over their entire range, i.e., when

TABLE I. Results from the SR-TI method for an α-N_2 crystal consisting of 108 hard dumbbells with $L^*=0.6$ at the reduced density $\rho^*=1.225$. The integration limits are $\hat{r}_1^*=\hat{r}_1/\sigma=0.000\,42$, $\hat{r}_m^*=0.8$, $\hat{\eta}_1=0.000\,004\,8$, and $\hat{\eta}_m=1$. Standard errors are to two standard deviations.

n_α	n_b	$\Delta(\beta F)/N_s$
10	10	11.83 ± 0.03
10	20	11.73 ± 0.03
10	30	11.71 ± 0.04
10	40	11.70 ± 0.04
20	10	11.86 ± 0.02
20	20	11.75 ± 0.02
20	30	11.72 ± 0.02
20	40	11.73 ± 0.03
30	10	11.845 ± 0.012
30	20	11.77 ± 0.02
30	30	11.73 ± 0.02
30	40	11.71 ± 0.02
40	10	11.846 ± 0.012
40	20	11.750 ± 0.014
40	30	11.74 ± 0.02
40	40	11.73 ± 0.02

$$g'_{\hat{r}_1}(r) = 4\pi g_r(r,\hat{r}_1)\hat{r}_1^3 = 3, \tag{31}$$

and

$$g'_{\hat{\eta}_1}(\xi) = g_\xi(\xi,\hat{\eta}_1)\,\hat{\eta}_1 = 1. \tag{32}$$

Similarly, $\hat{r}_m$ and $\hat{\eta}_m$ must be chosen large enough such that

$$g'_{\hat{r}_m} = 4\pi g_r(\hat{r}_m,\hat{r}_m)\hat{r}_m^3 = 0, \tag{33}$$

and

$$g'_{\hat{\eta}_m} = g_\xi(1-\hat{\eta}_m,\hat{\eta}_m)\,\hat{\eta}_m = 0, \tag{34}$$

unless the crystal is orientationally disordered when $\hat{\eta}_m=1$ for homonuclear dumbbells. As in previous work[15] we choose a relaxation process of the form $\alpha_{i+1}=\chi\alpha_i$ so that we take equally spaced steps in $\ln(\alpha)$, and hence also in $\ln(\hat{r})$ and $\ln(\hat{\eta})$.

B. Results

The results below are all obtained using the SR-TI method. We have also extended the parameter hopping version of the SR method[15] to linear rigid bodies, and applied it to the hard dumbbell systems described below. We did not apply the parameter hopping technique to LJ dumbbells because it is very inefficient. In every case the parameter hopping method and SR-TI method agree to within statistical error, which adds a further degree of confidence to our methods and results. However, we do not describe this parameter hopping method here because it is not the focus of this paper, and in any case we cannot recommend its use because it is so inefficient. Its only advantage is that it has only one source of systematic error, namely, the choice of an upper relaxation limit defined here by α_m.

We first discuss the SR-TI results obtained for the α-N_2 and fcc PC structures composed of hard dumbbells, and compare them to those of Vega *et al.*[10,31] Recall that to obtain agreement with their results based on normalized orientational coordinates we must add $\ln(V_\Omega)=\ln(2\pi)$ to the right hand side of Eq. (25).

A crystal of 108 dumbbells of length $L^*=0.6$ in the α-N_2 structure at density $\rho^*=1.225$ is considered first. The canonical Helmholtz free energy per particle obtained by Vega *et al.*[10] using the FL method is 11.72 (no error estimate is given). Results obtained with the SR-TI method for the same system with several values for n_α and n_b are given in Table I. We see that all the results with $n_\alpha \geq 20$ and $n_b \geq 30$ are consistent with those obtained with the FL method (and the SR parameter hopping method, which yields 11.71 ± 0.03; see Table II). Results with $n_\alpha=10$ or $n_b \leq 20$ appear to have significant systematic error. Since there is very little efficiency penalty for increasing n_α at fixed overall number of MC trial moves (because an increase in the standard error of each simulation will be compensated by an increase in the number of simulations) we suggest always using a high value for this parameter provided sufficient trial moves are attempted for each α so that the standard error can be reliably estimated. However, with our simple linear extrapolation technique that only uses the last and next to last bins to perform the ex-

TABLE II. Results for the SR-TI and SR parameter hopping (SR-PH) methods for α-N_2 crystals and fcc PC structures of hard dumbbells and the fcc crystal of HSs. L^* is the reduced bond length, N_s is the number of dumbbells in the single-size system, and ρ^* is the reduced density. The integration limits for the SR-TI method are $\hat{r}_1^*=\hat{r}_1/\sigma=0.0005$, $\hat{r}_m^*=0.8$, $\hat{\eta}_1=0.000\,01$, and $\hat{\eta}_m=1$. Standard errors are to two standard deviations. Results obtained with the FL method are given for comparison (although no error estimates are available).

Lattice	L^*	N_s	ρ^*	$\Delta(\beta F)/N_s$ (SR-TI)	$\Delta(\beta F)/N_s$ (SR-PH)	$\beta F/N_s$ (FL)
α-N_2	0.6	108	1.225	11.70 ± 0.02	11.71 ± 0.03	11.72[a]
α-N_2	0.3	256	1.269	11.12 ± 0.03	11.08 ± 0.04	11.11[a]
PC	0.3	108	1.090	6.41 ± 0.02	6.42 ± 0.03	6.39[a]
PC	0.3	108	1.125	7.05 ± 0.02	7.06 ± 0.03	7.06[a]
PC	0.3	108	1.160	7.78 ± 0.02	7.81 ± 0.03	7.86[a]
PC	0.15	108	1.041	5.16 ± 0.02	5.13 ± 0.03	5.15[b]
PC	0.01	108	1.041	4.96 ± 0.02	4.96 ± 0.03	
HS	0	108	1.041	4.94 ± 0.02	4.94 ± 0.03	4.95[c]

[a] Vega *et al.* (Ref. 10) results.
[b] Vega *et al.* (Ref. 31) results.
[c] Frenkel and Ladd (Ref. 4) results.

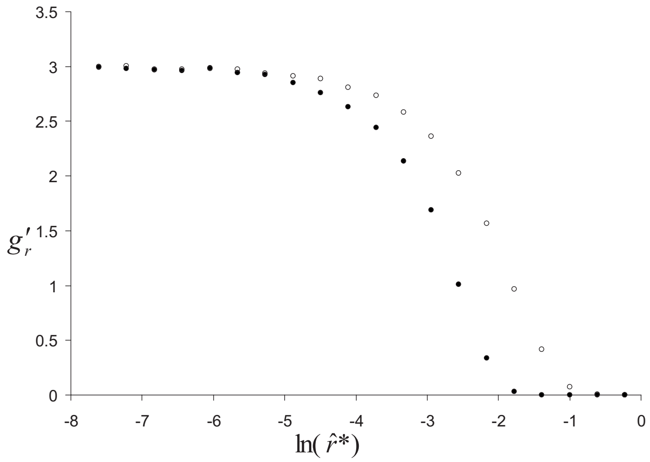

FIG. 1. The variation of g_r' (see text) with $\ln(\hat{r}^*)$, where $\hat{r}^*=\hat{r}/\sigma$, for hard dumbbells with the α-N_2 structure ($N_s=256$, $L^*=0.3$, $\rho^*=1.269$) (solid circles) and PC structure ($N_s=108$, $L^*=0.3$, $\rho^*=1.090$) (open circles). Error bars are smaller than symbol sizes.

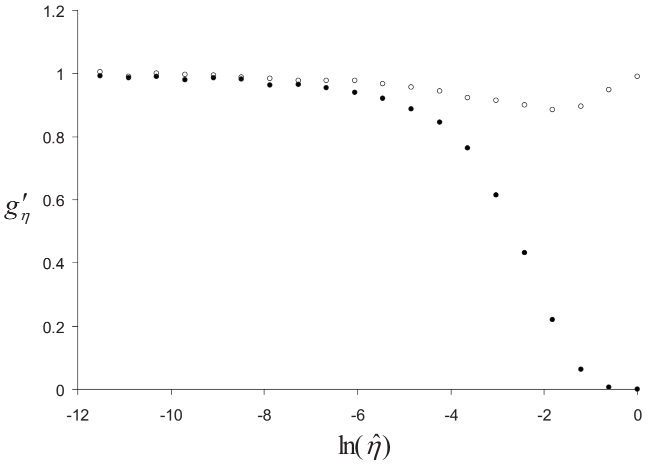

FIG. 2. The variation of g_η' with $\ln(\hat{\eta})$ for the same crystals as in Fig. 1.

trapolation for $g_r(\hat{r},\hat{r})\hat{r}^3$ and $g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta}$, increasing n_b will result in increasing statistical error in the free energy calculation if the overall number of MC trials is fixed. We aim to investigate improved extrapolation techniques in future work, but for the remainder of this paper we continue to use linear extrapolation with $n_\alpha=20$ and $n_b=30$.

Table II compares results obtained with the SR-TI and SR parameter hopping methods for the α-N_2 and PC structures for different system sizes, bond lengths, and densities. Comparison is also made with reference data obtained with the FL method.[4,10,31] Notice that all results show very good agreement at the level of two standard deviations in the standard error, except perhaps for the PC structure at $N_s=108$, $L^*=0.3$, and $\rho^*=1.160$, although Vega *et al.* did not provide standard error estimates. Note that the computational cost of the two SR methods is very different. While the SR-TI calculation of the $N_s=256$ α-N_2 crystal is achieved in a few hours, the CPU time needed to perform the same calculation (even with less accuracy as indicated by the error estimate) with the SR parameter hopping method is around three weeks.

We can also see from Table II that in the limit of zero bond length, the free energy per particle of a hard dumbbell system equals the HS fcc crystal at the same density. This is a consequence of using normalized orientational coordinates in line with Vega *et al.*

Finally, as a further validation of the SR-TI method, it is interesting to observe how $g_{\hat{r}}'=4\pi g_r(r=\hat{r},\hat{r})\hat{r}^3$ and $g_{\hat{\eta}}'=g_\xi(\xi=1-\hat{\eta},\hat{\eta})\hat{\eta}$ vary as the system relaxes to make sure that the limits applied are sufficient. Figures 1 and 2 show that the limits used are adequate because $g_{\hat{r}}'$ is very close to 3 at small $\hat{r}$ and very close to 0 at large $\hat{r}$, while $g_{\hat{\eta}}'$ is close to 1 for small $\hat{\eta}$, then approaches 0 and 1 at large $\hat{\eta}$ for the α-N_2 structure ($N_s=256$, $L^*=0.3$, $\rho^*=1.269$) and PC structure ($N_s=108$, $L^*=0.3$, $\rho^*=1.090$), respectively, in agreement with Eqs. (31)–(34).

We now move on to the results for systems of LJ dumbbells. We applied the SR-TI method to an α-fcc crystal composed of LJ dumbbell molecules and compare results obtained to those of Galbraith and Hall.[33] The LJ potential interaction between two LJ dumbbells is

$$u=4\varepsilon\sum_{a=1}^{2}\sum_{b=1}^{2}\left[\left(\frac{\sigma}{r_{ab}}\right)^{12}-\left(\frac{\sigma}{r_{ab}}\right)^{6}\right], \tag{35}$$

where $r_{ab}(r_{ij},\omega,\phi,\xi,\varphi)$ is the distance between atom a of dumbbell i and atom b of dumbbell j, and σ and ε are the LJ parameters. We performed simulations with $N_s=256$ using a cut-off radius of half the box length together with long-range corrections for the potential energy.[17] Once again, comparison with the Galbraith and Hall results can be carried out provided that we cancel a factor of $-\ln(2\pi)$ in the replication term on the right hand side of Eqs. (7) and (25), *and* if we reduce our free energy data with respect to the LJ energy parameter ε and not with respect to k_BT as stated in the Galbraith and Hall work. Results obtained with the SR-TI method for three different systems of LJ dumbbells are given in Table III. We see that excellent agreement with the results of Galbraith and Hall is found only for one (at $T^*=1.45$) of the three systems studied, although it is worth noting that Galbraith and Hall also did not provide standard error estimates. A second result (at $T^*=1.2$) is quite close but only agrees at the level of 6 standard deviations in the standard error, while agreement for the other result is very poor. It is not clear why the results are so different for the case when $T^*=1.4$, although it is shown in the work of Galbraith and Hall that their results are sensitive to the choice of spring constant used in the FL method, and this particular system has much higher energy than the other two cases. Figures 3 and 4 confirm that the limits for $\hat{r}$ and $\hat{\eta}$ used to numerically evaluate the integrals in Eq. (25) are adequate. Moreover, Fig. 5 shows how the temperature of each crystal is relaxed during these simulations, and that our temperature change algorithm is functioning correctly.

IV. DISCUSSION

We have shown how the SR-TI technique can be adapted to rigid linear molecules, and have validated this technique by comparison with literature data for the free energy of some α-N_2 and fcc PC structures of hard and LJ dumbbells.

TABLE III. Results from SR-TI method for α-fcc crystals of LJ dumbbells. $L^*=L/\sigma$ is the reduced bond length, $T^*=k_BT/\varepsilon$ is the reduced temperature, and ρ^* is the reduced density $\rho^*=\rho\sigma^3$. The integration limits for the SR-TI method are $\hat{r}_1^*=\hat{r}_1/\sigma=0.001$, $\hat{r}_m^*=0.3$, $\hat{\eta}_1=0.000\,01$, and $\hat{\eta}_m=0.3$. Standard errors are to two standard deviations. Results obtained with the FL method are given for comparison (although no error estimates are available).

L^*	T^*	ρ^*	$\Delta F/\varepsilon N_s$ (SR-TI)	$F/\varepsilon N_s$ [a]
0.67	1.45	0.8296	13.29 ± 0.03	13.2844
0.7292	1.40	0.85	23.56 ± 0.03	22.2768
0.505	1.20	0.85	-1.69 ± 0.03	-1.7728

[a] Galbraith and Hall (Ref. 33) results.

Based on the techniques developed in this work we expect that Eq. (25) can be generalized to arbitrary crystals to give a rather compact expression for the configurational Helmholtz free energy difference per particle,

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{\Psi_1}{\lambda^d}\right) + \frac{1}{N_s}\int_{\beta_s/2}^{\beta_s} d\beta_\alpha\langle H_\alpha\rangle - \sum_{i\prime}\int_{\ln(\hat{r}_{i1})}^{\ln(\hat{r}_{im})} d\ln(\hat{r}_i)\, g_{r_i}(r_i=\hat{r}_i,\hat{r}_i)\,\hat{r}_i \left.\frac{d\Psi}{d\hat{r}_i}\right|_{\hat{r}_i}, \qquad (36)$$

although further work would be useful to confirm this theoretical extrapolation for a range of cases. Here, r_i is an independent degree of freedom of the Hamiltonian, $\hat{r}_i$ is the tolerance constraint for this degree of freedom, and $\hat{r}_{i1}$ and $\hat{r}_{im}$ are the minimum and maximum values of this degree of freedom. Of course, these initial and final constraints must be chosen sufficiently small and large, respectively, such that altering them makes no significant difference to results. $\Psi=\Pi_i f_i(\hat{r}_i)$ is the phase space available to a single particle (which is just the product of the phase space functions $f_i(\hat{r}_i)$ for each degree of freedom), while $\Psi_1=\Pi_i f_i(\hat{r}_{i1})$ is the phase space available to each replicated particle when the system is fully constrained. Finally, λ is an (arbitrary) characteristic length of each particle, d is the dimension, and

$$g_{r_i}(r_i,\hat{r}_i) = \left\langle \frac{1}{N_s}\sum_{j=1}^{N_s}\delta(r_{ij}-r_i)\right\rangle_{\hat{r}_i}$$

is the relative distribution function for the ith degree of freedom when the tolerance constraint is $\hat{r}_i$. It is important to note that some degrees of freedom do not need to be constrained at all, and so are already fully relaxed at the replication stage. This is indicated by the symbol '$i\prime$' in the sum in Eq. (36). A clear example of this is the relative azimuthal degree of freedom for linear rigid molecules discussed in this work, which yields a factor of $-\ln(2\pi)$ at the replication stage. Likewise, the polar coordinates describing relative displacement degrees of freedom can be fully relaxed for any system, which yields the factor of $4\pi\hat{r}^2$ in Eqs. (17) and (25). Finally, we recognise that (36) cannot account, for example, for the residual entropy of water ice. The additional calculations required in this case are described by Vega *et al.*[14]

So, for example, the configurational free energy difference per particle for hard rods on a line is

$$\frac{\Delta(\beta F)}{N_s} = -\ln\left(\frac{2\hat{x}_1}{\lambda}\right) - \int_{\ln(\hat{x}_1)}^{\ln(\hat{x}_m)} d\ln(\hat{x})\, g_x(x=\hat{x},\hat{x})\,2\hat{x}, \qquad (37)$$

while for general nonlinear rigid molecules without any internal symmetry we have

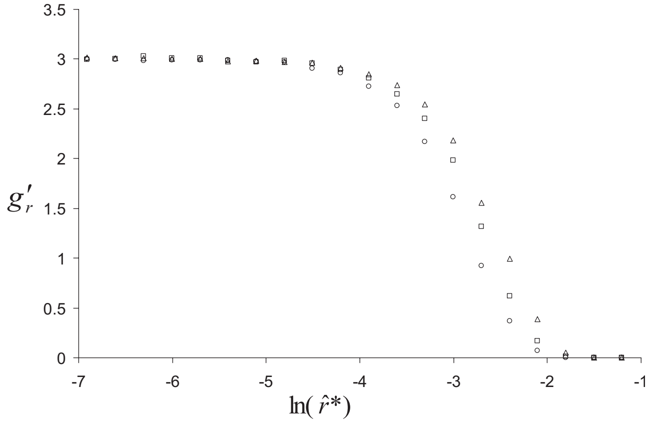

FIG. 3. The variation of g_r' with $\ln(\hat{r}^*)$, where $\hat{r}^*=\hat{r}/\sigma$, for the following α-fcc structures consisting of LJ dumbbells: squares for $L^*=0.67$, $\rho^*=0.8296$, $T^*=1.45$, circles for $L^*=0.7292$, $\rho^*=0.85$, $T^*=1.40$, and triangles for $L^*=0.505$, $\rho^*=0.85$, $T^*=1.20$. Error bars are smaller than symbol sizes.

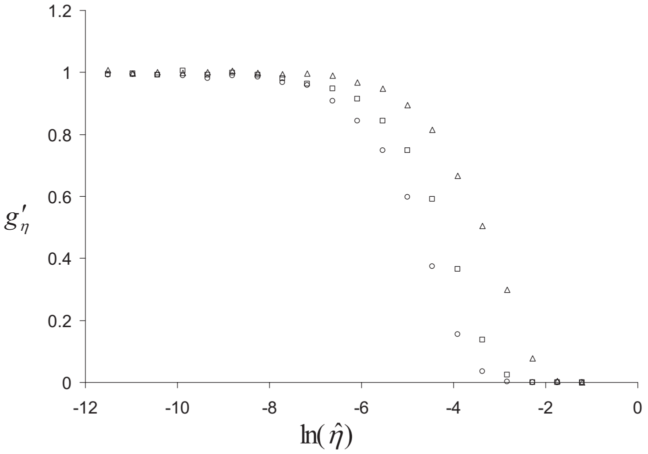

FIG. 4. The variation of g_η' with $\ln(\hat{\eta})$ for the same crystals as in Fig. 3.

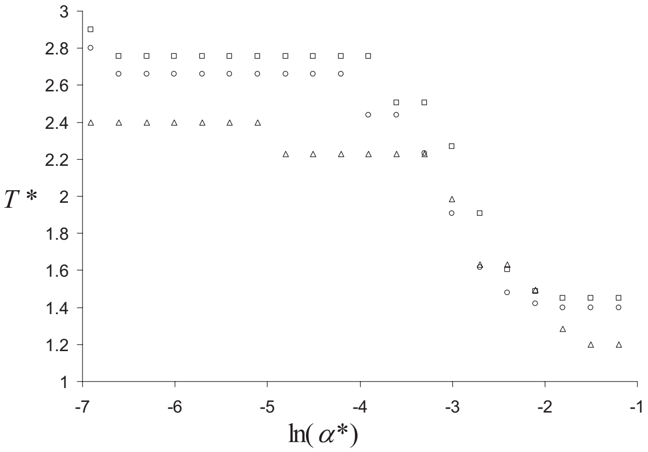

FIG. 5. Variation of temperature $T^*=k_BT/\varepsilon$ with $\ln(\alpha^*)$, where $\alpha^*=\alpha/\sigma$, for the same crystals as in Figs. 3 and 4.

$$\begin{aligned}\frac{\Delta(\beta F)}{N_s} = {} & -\ln\left(\frac{4\pi V_{r_1}\hat{\eta}_1\hat{\kappa}_1}{\lambda^3}\right) + \frac{1}{N_s}\int_{\beta_s/2}^{\beta_s} d\beta_\alpha\langle H_\alpha\rangle \\ & - 4\pi\int_{\ln(\hat{r}_1)}^{\ln(\hat{r}_m)} d\ln(\hat{r})g_r(\hat{r},\hat{r})\hat{r}^3 \\ & - \int_{\ln(\hat{\eta}_1)}^{\ln(\hat{\eta}_m)} d\ln(\hat{\eta})g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta} \\ & - \int_{\ln(\hat{\kappa}_1)}^{\ln(\hat{\kappa}_m)} d\ln(\hat{\kappa})g_\kappa(\hat{\kappa},\hat{\kappa})2\hat{\kappa}, \end{aligned} \tag{38}$$

where all terms are as above for hard dumbbells except now $0 \leq \eta \leq 2$ and $0 \leq |\kappa| \leq \pi$ is a degree of freedom describing relative internal molecular rotations about the major axis.

We have shown that the SR-TI technique can be applied to systems comprising hard-body or continuous interactions for ordered or plastic crystals. Because the technique is based on measuring relative distribution functions, such as $g_r(r,\hat{r})$, we also expect, without any change in the technique, that it can be applied to systems involving pairwise or higher body interactions, for bulk crystals and crystals confined in idealized pores (ideal slit pores for example), although once again further work is needed to confirm this. For isothermal-isobaric simulations all quantities become ensemble averaged with respect to volume fluctuations (see Ref. 16 for a detailed treatment of this matter for spherical particles). So we consider this technique to also be very versatile.

Of course, other methods are available for this purpose, and perhaps the most well known and used are those detailed in the book by Smit and Frenkel[17] related to the FL method. Future work will aim to optimize the SR-TI technique and compare its efficiency with other techniques including the FL method. Currently, we do not expect the SR-TI method to be optimal in terms of efficiency mainly because of our extrapolation technique for calculating $g_r(\hat{r},\hat{r})\hat{r}^3$ and $g_\xi(1-\hat{\eta},\hat{\eta})\hat{\eta}$ and our use of the trapezoidal rule to perform the integrals in Eq. (25). Our simple linear extrapolation technique essentially "throws away" most of each of these distribution functions since only the final two bins are used. Future work will assess better extrapolation and integration techniques, which should finally yield a SR-TI method which is very efficient.

We also consider the SR-TI method to be more straightforward than other methods. With the SR-TI approach the contribution of each degree of freedom, including rotational degrees of freedom, is explicit in the replication contribution, and no Einstein crystal free energy calculations are required. We also point out that the SR method does not require any center-of-mass corrections at all, which considering the complications that such corrections incur (indeed, entire papers[6] have been written solely on this matter) is, in our view, a significant advantage. To sum up then, the SR-TI method is accurate and relatively efficient (at least compared to the parameter hopping version of the method[15]), and in our view it is also straightforward and versatile.

ACKNOWLEDGMENTS

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