A comparison of some variational formulas for the free energy as applied to hard-sphere crystals

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We examine several variational methods for determining bounds on the free energy of model crystalline phases, as applied to hard spheres in one and three dimensions. Cell- and harmonic-based reference systems are considered. Methods that provide the tightest bounds on the free energy are similar in form to free-energy perturbation, and are prone to inaccuracy from inadequate sampling. Gibbs–Bogoliubov formulas are reliable but weaker. For hard potentials they can give only a lower bound, indicating that their ability to provide upper bounds for other potentials is limited. Nevertheless, bounds given by Gibbs–Bogoliubov when applied with the optimal harmonic system prescribed by Morris and Ho [Phys. Rev. Lett. **74**, 940 (1995)] yields impressive results; for hard spheres at higher density it is, within confidence limits, equal to the exact hard-sphere free energy. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1516592]

I. INTRODUCTION

Many solid-phase behaviors can be understood through the analysis or calculation of the free energy. Phenomena of interest include polymorphic transitions, melting, response to stress, miscibility and compound formation, design of alloys, influence of defects, and so on. The free energy of solids is problematic to compute by molecular simulation, in part because (unlike the situation for fluid phases) there exists no particle-insertion-based method for its calculation.[1,2] The most successful and reliable method for calculating solid-phase free energies is thermodynamic integration.[3–5] The disadvantage of this approach is that it is computationally expensive, involving the simulation of systems or conditions that often are not of intrinsic interest; moreover, there can be problems arising in practice, such as when a phase transition lies on the path of integration (although this problem can be mitigated with judicious selection of the reference system).

Analytical methods include cell models,[6–8] density functional theory,[9–13] and harmonic-based approaches such as lattice dynamics,[14] self-consistent phonon theory,[15,16] and others.[17] The literature on all of these topics is vast.[1,18]

In the present work we consider variational methods, which might be considered as intermediate between molecular simulation and analytic approaches. These methods provide only bounds on the free energy, not the free energy itself, but sometimes the bound can narrow the range of values sufficiently well for practical applications. We consider these methods used in conjunction with molecular simulation to provide quantities needed for their application. However, unlike rigorous free-energy calculation methods, these techniques provide their result in a single simulation of the system of interest, perhaps supplemented by a simulation of the reference system to obtain the complementary free-energy bound.

We consider applications to hard-sphere systems. The hard-sphere potential is highly relevant to solid-phase behavior, and it may be argued that the qualitative features of real potentials responsible for their formation of crystals is captured by the hard-sphere model. The ability of a method to characterize hard-sphere solid-phase free energies is an indicator of its general capacity to describe this feature in other systems, particularly at conditions approaching the melting point. We believe, for example, that the inability of lattice-dynamics approaches to satisfactorily describe solids at high temperatures[19] is not unrelated to their complete inapplicability to the hard-sphere potential. We also consider one-dimensional systems of hard rods. Hard rods do not exhibit a freezing transition, but because the rods are ordered we can unambiguously associate each one with a lattice position, so it can be considered a crystal from this point of view. They are of interest because exact analytic expressions can be developed for most of their properties.[20,21]

This paper is organized as follows. In the next section, we introduce the reference systems used as a basis for the variational calculations. Then in Sec. III we provide details of the variational methods we examine. In Sec. IV we present our results, and we conclude in Sec. V.

II. REFERENCE SYSTEMS

The variational formulas considered here describe bounds on free-energy differences. To apply them to a target system, it is necessary to identify a reference of known free energy, and the variational bound then describes the difference in free energy from that of the reference. We consider two choices of reference in this work: a system of coupled harmonic oscillators, and a system of noninteracting particles confined to cells.

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A. Harmonic reference

The configurational potential energy of a system of N particles interacting harmonically with force constant ω is

$$U(\boldsymbol{\gamma}^N)=\sum_{i=1}^{N}\sum_{j=nbrs}\frac{\omega}{2}[\boldsymbol{\gamma}_i-\boldsymbol{\gamma}_j]^2, \tag{1}$$

where $\boldsymbol{\gamma}_i$ is the Cartesian position vector of particle i relative to a reference (lattice site) position. Normally, we consider systems in which only nearest neighbors interact. As is well known,[14] the free energy A_H of this model can be written analytically in terms of the DN eigenvalues of the force-constant matrix implied by Eq. (1); thus

$$e^{-\beta A_H}=\prod_{m=1}^{DN}\left(\frac{2\pi}{\omega\lambda_m}\right)^{1/2}. \tag{2}$$

For a periodic one-dimensional system, the eigenvalues are

$$\lambda_m=2\left(1-\cos\frac{2\pi m}{N}\right). \tag{3}$$

Singer[22] gives a corresponding result for the eigenvalues of such a system on a three-dimensional fcc lattice. Alternatively, the eigenvalues can be evaluated numerically using standard methods.[23]

In our study we examine the effect of the choice of harmonic force constant ω on the performance of the variational calculation. Because hard-sphere potentials have no characteristic energy that can be used to select or scale the harmonic value, we employ a different, albeit arbitrary, scale. At the density and temperature of interest, we consider the energy of a system of equally spaced particles interacting with the inverse-12 potential $u(r)=kT(\sigma/r)^{12}$, where σ is the hard-particle diameter. We expand this form to second order in the particle separations, and use the terms that arise as the basis for defining the harmonic reference system. We then consider a range of harmonic reference systems obtained by multiplying each term in the quadratic expansion by the same "force-factor", F, which has the effect of loosening or tightening the range of motion of the reference system. The adoption of this scale is a matter of convenience for the discussion, and has no impact on the performance of the calculation.

B. Noninteracting particles in single-occupancy cells

We also consider a system of particles each confined to a cell centered on the particle's reference lattice site. Each cell pertains to only a single particle—particles are influenced only by the cell centered on their reference lattice site. There is, in general, no single-occupancy restriction, although for sufficiently small cells this outcome is affected. The free energy of this cell-constrained (CC) system is

$$e^{-\beta A_{\mathrm{SOC}}}=\nu_{\mathrm{cell}}^N, \tag{4}$$

where ν_{cell} is the volume of each cell. We consider spherical cells and examine the performance of the calculation as a function of the cell radius.

III. VARIATIONAL FORMULAS

Variational formulas describe bounds on free-energy differences. In this section we summarize the ones examined in this work. We use the subscript "0" to describe the reference system, and "1" to refer to the system of interest, or target system. We ignore momentum contributions to the free energy in all that follows.

The Gibbs–Bogoliubov relation is perhaps the first and most widely known variational free-energy formula.[24] It may be used in either of two ways to obtain upper and lower bounds to the free energy system of interest. The upper bound is

$$A_1\leqslant A_0+\langle U_1-U_0\rangle_0. \tag{5}$$

The angle brackets indicate an ensemble average, with configurations weighted according to the system indicated by the subscript (here, the reference system); U is the configurational energy of the reference system, and the angled brackets represent the average of the term inside them. By switching all subscripts, the lower bound is obtained,

$$A_1\geqslant A_0-\langle U_1-U_0\rangle_1, \tag{6}$$

which now indicates an average over the target system. Here and below we present the equations in the general form, not exploiting the fact that $\langle U_1\rangle_1=0$ for a hard-sphere target system.

For a hard-sphere target system and the harmonic reference, only the lower bound provides useful information. The average indicated by the upper bound is infinite, because any harmonic reference system will have some nonzero probability of a configuration in which overlap occurs in the target, contributing infinity to the average. For the CC reference, Eq. (5) can be used if the cell radius is sufficiently small such that spheres confined to their cells cannot overlap. Correspondingly, Eq. (6) can be applied only if the cells are large enough to ensure that each interacting sphere does not depart from its cell.

Morris and Ho[25] have proposed a method for determining an optimum harmonic reference for use in a Gibbs–Bogoliubov inequality. They do not constrain the harmonic system to nearest-neighbor interactions of the uniform force constant. Instead, they apply pair potentials between all atoms such that the determinant of a matrix of displacement covariances $C_{ij}=\langle\gamma_i\gamma_j\rangle-\langle\gamma_i\rangle\langle\gamma_j\rangle$ is the same in the harmonic as measured in the target system. The lower bound on the free energy is then given by Eq. (6). For the hard-rod system, the covariances can be evaluated analytically,[21]

$$C_{ij}=\left(\frac{L-N\sigma}{N+1}\right)^2\frac{i(N+1-j)}{N+2},\quad j\geqslant i. \tag{7}$$

Frenkel[26] derived an expression for bounds on the free energy of hard potentials giving narrower limits, where the upper bound is

$$A_1\leqslant A_0-2kT\ln\left\langle\exp\left[-\frac{\beta}{2}(U_1-U_0)\right]\right\rangle_0, \tag{8}$$

and the lower bound is

$$A_1 \geqslant A_0 + 2kT \ln\left\langle \exp\left[+\frac{\beta}{2}(U_1 - U_0)\right]\right\rangle_1 . \quad (9)$$

These formulas may both be applied for harmonic or CC reference systems.

Finally, we consider the performance of an exact free-energy perturbation (FEP) between the target system and a harmonic reference, measured in the target system,[27,28]

$$\beta A_1 = \beta A_0 + \ln\langle \exp[+\beta(U_1 - U_0)]\rangle_1 . \quad (10)$$

IV. RESULTS AND DISCUSSION

We calculate the bounds given by these inequalities using both harmonic and cell reference systems applied to systems of 100 hard rods (in one dimension) and 108 spheres (in three dimensions). We compare to the analytic expression for the free energy of hard rods:

$$e^{-\beta A_{\mathrm{HR}}} = \frac{(L - N\sigma)^N}{N!}, \quad (11)$$

where $L = N/\rho$ is the length (volume) of a system of number density ρ. For hard spheres, we compare to the free energy obtained by integrating the equation of state of Hall,[29] with the reference free energy given by the results of Frenkel and Ladd.[3] Results were obtained by Monte Carlo simulations sampling 10^6 cycles for $N = 100$ hard rods (where a cycle is one attempted displacement, on average, for each particle), and 10^5 cycles for $N = 108$ hard spheres. Standard Metropolis Monte Carlo was used, except when simulating the reference systems, which could be sampled by directly generating independent configurations at random (i.e., without relying on a Markov chain).

Figures 1 and 2 show the results for a system of hard rods at densities $N\sigma/L$ of 0.95 and 0.70. The results are plotted as a function of the dimensionless force factor F on the bottom axis for simulations using the harmonic reference, or as a function of one-half the cell width across the top axis for simulations using the cell reference system.

The performance of all methods depends strongly on the selection of the reference system. Each method provides a tight bound over only a narrow range of the spring constant. In comparing the behaviors at different densities, we observe that the optimal bounds move to larger spring constant when the target moves to higher density. This behavior is as one would expect, because a tighter spring constant permits less freedom of motion of the harmonic system, bringing it into better correspondence with a higher-density target system.

The cell reference system provides the least useful bound. The upper bound is finite for only a very small range of cell sizes, and the lower bound is not very tight.

Gibbs–Bogoliubov using a harmonic reference is much better than the cell reference, and at its nearest point it provides a much tighter limit on the free energy. The related method of Morris and Ho coincides with this optimum bound (its placement along the abscissa is arbitrary for this plot, and it is presented at the optimum to emphasize the relation). One would expect the method to provide a result at least as good as the Gibbs–Bogoliubov with a nearest-neighbor reference, and it is of interest to see that it does no better. This

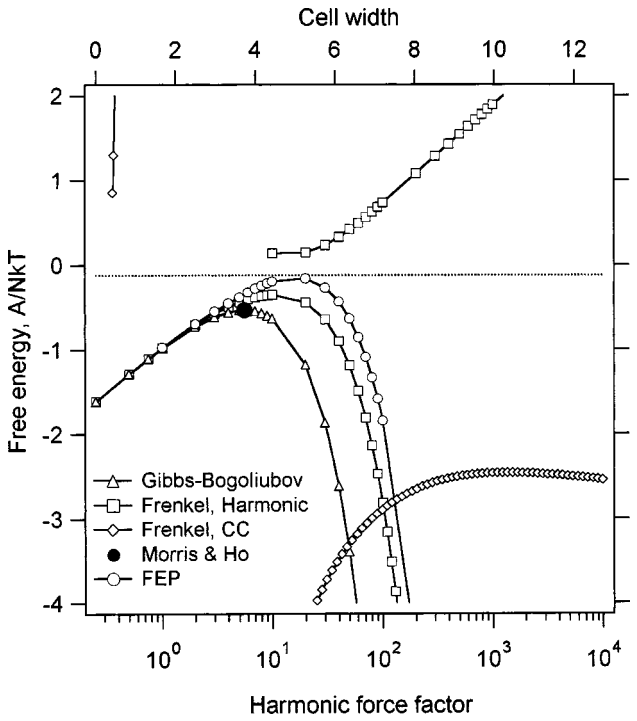

FIG. 1. Free-energy results of various methods for a system of 100 hard rods at a density $N\sigma/L = 0.7$. Triangles show the lower bound given by the Gibbs–Bogoliubov inequality, Eq. (6), using a harmonic reference with a force constant given by the factor on the bottom axis. Squares show upper [Eq. (8)] and lower [Eq. (9)] bounds from the Frenkel inequality, using a harmonic reference indicated by the bottom axis. Diamonds show the Frenkel inequality using a constraining cell of size, as indicated by the top axis (given in units of the hard-rod diameter, σ). Open circles are results from free-energy perturbation, Eq. (10), to the harmonic reference (bottom axis). The single large filled circle is the lower bound given by the Gibbs–Bogoliubov inequality with the harmonic reference of Morris and Ho (placement along the abscissa is arbitrary). The correct value of the free energy is indicated by the horizontal dashed line.

outcome is most likely related to the close correspondence of the hard-rod displacement covariances and those of a system of nearest-neighbor harmonic oscillators: we showed previously[21] that these second-order correlations are identical in both systems. Thus the simple nearest-neighbor harmonic system at its maximum bound is automatically satisfying the optimization criterion of Morris and Ho. Since both are otherwise based on Gibbs–Bololiubov, we can understand why they produce the same free-energy bound.

The Frenkel inequality and FEP are very sensitive to the ability of the simulation to sample relevant configurations of both systems. When state parameters and the reference-potential parameters are such that the two systems do not have a sufficiently large overlap in configuration space, the methods yield a zero average and the free-energy bound diverges. Thus, if sampling the harmonic or cell systems, if the force constant is too small, or the cell width too large, all generated configurations perturb into a system having overlap of at least one hard rod. The curves are truncated at the point in which this occurs. The cell must be quite narrow to prevent this, and very few points in the range considered provided a finite bound.

The Frenkel inquality (harmonic reference) and FEP provide results very similar to each other, with curves nearly

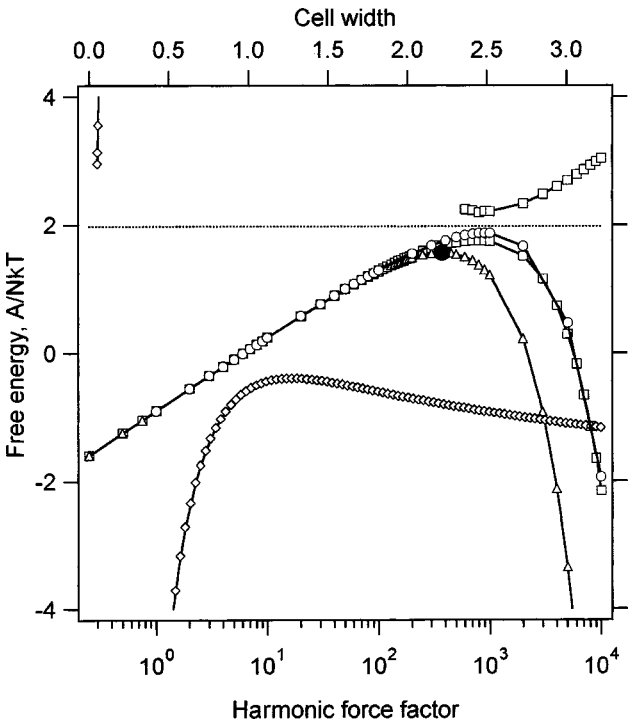

FIG. 2. The same as Fig. 1, but for a density of 0.95.

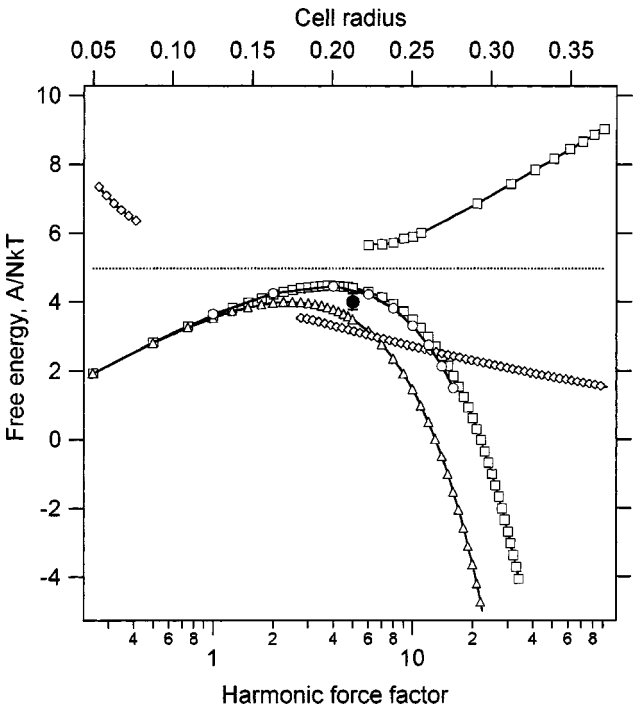

FIG. 3. The same as Fig. 1, but for a system of 108 hard spheres at the melting density $N\sigma^3/V=1.041$. The error bar on the Morris–Ho result represents a 67% confidence limit.

coinciding over the entire range of reference spring constants. This is interesting because FEP is, in principle, an exact equality, and should produce a horizontal line coinciding with the exact free energy for all reference systems. Of course, it does not for the reason just discussed. The difference between FEP and the exact result represents a problem in sampling. The simulations are not providing accurate ensemble averages. The fact that the Frenkel inequality tracks this behavior is an indication that it too is affected by sampling limitations, and it is not yielding the true bound derived from the ensemble averages in Eqs. (8) and (9). Nevertheless, the results from the Frenkel inequality (harmonic reference) are quite good.

Figures 3 and 4 show the results for a system of hard spheres at densities $N\sigma^3/V$ of 1.3 and 1.04 (melting density), respectively. The behavior of the methods is qualitatively the same as that seen in application to the hard-rod system, with the exception of the Morris–Ho inequality at the higher density. The exact result for the correlation matrix is not available for the three-dimensional system, so the inequality was tested by calculating the matrix in Monte Carlo simulations of 108 hard spheres. Seven independent runs of 50 000 cycles each were performed, and the variance in the data was used to generate the confidence limits given in the figure. At high density, the inequality gives a result that, within the error estimate, is equal to the exact free energy. The quality of the result at the melting density is not as good, but it still gives a bound that is comparable to the best of the other methods.

V. CONCLUSIONS

A proper selection of the reference system is the key to the successful application of these variational methods. Even within a given class of systems (harmonic or cell), only a narrow range of parameter values yield bounds that are of any use, and in the case of the cell reference, the bounds are worthless for all values of the cell size. Regarding methods, the better approaches among those studied are prone to inaccuracy when the simulation does not sample well the con-

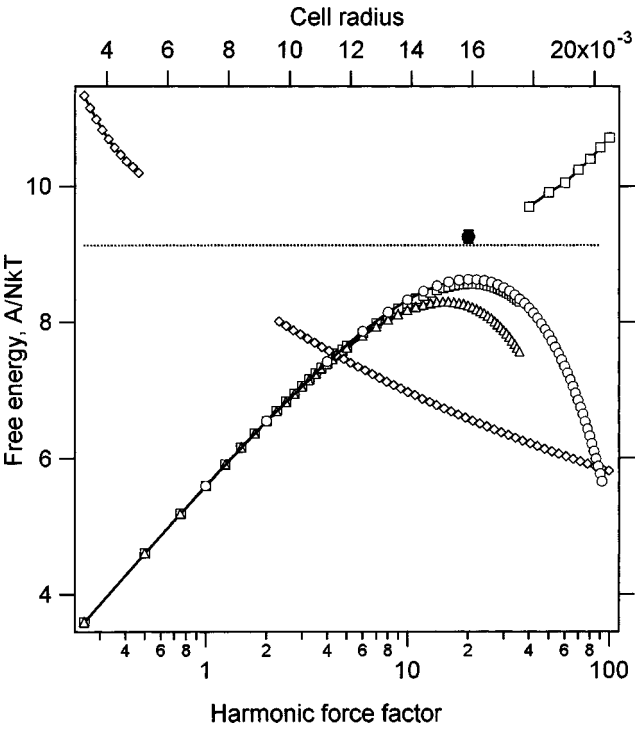

FIG. 4. The same as Fig. 3, but for a density of 1.3. The error bar on the Morris–Ho result is about equal to the size of the symbol.

figurations important to both the target and reference system. Nevertheless, in the applications considered here, they provide useful bounds to the free energy. Gibbs–Bololiubov methods are more reliable (less prone to inaccuracy), but weaker. Their inability to provide upper bounds for hard spheres indicates that upper bounds given by them for realistic systems are not likely to be useful.

In all cases it is important to select an optimal reference system to achieve a good bound on the free energy. The method of Morris and Ho provides an easy and effective prescription for this optimization. It loses effectiveness when approaching the melting point, so it is likely to see its best application in studying polymorphic transitions.

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[1] P. A. Monson and D. A. Kofke, Adv. Chem. Phys. **115**, 113 (2000).
[2] C. D. Barnes and D. A. Kofke, Phys. Rev. E **65**, 036709 (2002).
[3] D. Frenkel and A. J. C. Ladd, J. Chem. Phys. **81**, 3188 (1984).
[4] D. A. Kofke, in *Monte Carlo Methods in Chemistry*, edited by D. M. Ferguson, J. I. Siepmann, and D. G. Truhlar (J. Wiley, New York, 1998), Vol. 105.
[5] J. Henning and D. A. Kofke, in *Molecular Dynamics*, edited by P. B. Balbuena and J. Seminario (Elsevier, Amsterdam, 1999).
[6] J. A. Barker, *Lattice Theories of the Liquid State* (Macmillan, New York, 1963).
[7] D. A. Young, J. Chem. Phys. **58**, 1647 (1973).
[8] X. Cottin and P. A. Monson, J. Chem. Phys. **99**, 8914 (1993).
[9] T. V. Ramakrishnan and M. Yussouff, Phys. Rev. B **19**, 2775 (1979).
[10] P. Tarazona, Phys. Rev. A **31**, 2672 (1985).
[11] P. Tarazona, U. M. B. Marconi, and R. Evans, Mol. Phys. **60**, 573 (1987).
[12] J. L. Barrat, M. Baus, and J. P. Hansen, Phys. Rev. Lett. **56**, 1063 (1986).
[13] J. L. Barrat, M. Baus, and J. P. Hansen, J. Phys. C **20**, 1413 (1987).
[14] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).
[15] N. S. Gillis, N. R. Werthamer, and T. R. Koehler, Phys. Rev. **165**, 951 (1968).
[16] J. R. Morris and R. J. Gooding, Phys. Rev. B **46**, 8733 (1992).
[17] R. C. Shukla and D. J. Lacks, J. Chem. Phys. **107**, 7409 (1997).
[18] D. Frenkel and J. P. McTague, Annu. Rev. Phys. Chem. **31**, 491 (1980).
[19] M. L. Klein and W. G. Hoover, Phys. Rev. B **4**, 539 (1971).
[20] L. Tonks, Phys. Rev. **50**, 955 (1936).
[21] C. D. Barnes and D. A. Kofke, J. Chem. Phys. **110**, 11390 (1999).
[22] S. Singer, Comput. Phys. Commun. **59**, 463 (1990).
[23] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, *Numerical Recipes: The Art of Scientific Computing*, 2nd ed. (Cambridge University, Cambridge, 1992).
[24] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).
[25] J. R. Morris and K. M. Ho, Phys. Rev. Lett. **74**, 940 (1995).
[26] D. Frenkel, in *Proceedings of the Como School on Monte Carlo and Molecular Dynamics Simulation*, edited by K. Binder and G. Ciccotti (SIF, Bologna, 1996), pp. 4–42.
[27] R. W. Zwanzig, J. Chem. Phys. **22**, 1420 (1954).
[28] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic, New York, 1996).
[29] K. R. Hall, J. Chem. Phys. **57**, 2252 (1972).