PHYSICAL REVIEW E VOLUME 54, NUMBER 6 DECEMBER 1996

Multiensemble sampling: An alternative efficient Monte Carlo technique

Kyu-Kwang Han
Department of Physics, Pai-Chai University, Taejon 302-735, Korea

(Received 26 July 1996)

We present a general recipe for the successful non-Boltzmann sampling simulation from which data including the free energy of a system over a moderately wide range of thermodynamic states can be obtained. A universal form of the non-Boltzmann weighting function W is derived by a functional minimization so that a most favorable condition for the simultaneous investigation of several states with uniform accuracy is satisfied. The realization of the method is simple and systemic. The accuracy of the method is demonstrated by comparison with reliable earlier results for a Lennard-Jones fluid. [S1063-651X(96)07112-7]

PACS number(s): 02.70.Lq, 05.20.Gg, 64.70.Fx

I. INTRODUCTION

Monte Carlo (MC) simulation is now a popular tool for the investigation of various statistical mechanical problems. Although the recent development of supercomputing power has made it possible to study larger and more complicated systems, improving the efficiency of the MC simulation is still an important matter of concern.

From a MC simulation, one usually obtains averages of thermodynamic quantities at a single thermodynamic state. Various efforts to remove this limitation and obtain information over a range of states have been made [1–7]. The simplest approach in this direction may be the one of Ferrenberg and Swendsen [3]. They used the information of configuration distribution obtained from a single conventional MC simulation to study the entire scaling region near a phase transition. However, in general, the parts of configuration space sampled from a conventional MC simulation are not broad enough to cover the parts relevant to more distant neighborhoods of the state at which the simulation was performed and it is hard to extract information over a wider range of states. In order to surmount this difficulty, one has to sample configurations upon a non-Boltzmann distribution function W with adequate coverage of the relevant parts of configuration space for every state. But the problem is what the recipe for W is. In previous works [4–6] of the non-Boltzmann sampling approach, there was no general *a priori* recipe for W. In the previous technique, an *ad hoc* form of W should be chosen for a given system and adjusted by trial and error with monitoring the sampled distribution until the distribution is as wide and uniform as possible, forming an ‘‘umbrella’’ over relevant regions of configuration space. In this sense the technique has been named ‘‘umbrella sampling’’ [4]. A few years ago, we developed a non-Boltzmann sampling method with a general recipe of W [7] for estimating the free-energy difference between two systems and demonstrated its accuracy and efficiency.

In this paper we present a generalized version of our previous method [7]. A universal form of W is derived by a functional minimization so that a most favorable condition for the simultaneous investigation of several systems or states with uniform accuracy is satisfied. The resulting form is a nonlinear superposition of Boltzmann distributions for the systems or states to be investigated. The realization of the method is simple and systemic. We demonstrate the reliability of this method by a comparison with reliable early results for a Lennard-Jones fluid. We demonstrate its efficiency by obtaining the data including the free energy of the fluid on a density over an almost infinite temperature range of gas phase from a single simulation and the data on an isotherm across the liquid-gas coexistence region from six simulations.

II. THEORY

A. Non-Boltzmann sampling scheme

For the sake of a logical argument, we begin by reviewing the basic theory of non-Boltzmann sampling scheme [4–6,8] for the general case. Suppose that one is going to investigate n similar N-particle systems with potential energies U_l and volumes V_l at temperatures T_l, $l=1,\ldots,n$. If all the U_l are identical, the problem reduces to investigating n states of a system. Their dimensionless canonical configuration integrals Z_l are

$$Z_l=V_l^{-N}Q_l=V_l^{-N}\int \exp[-U_l(\mathbf{q}^N)/kT_l]d^N\mathbf{q}, \tag{1}$$

where k is the Boltzmann constant, $\mathbf{q}^N$ and $d^N\mathbf{q}$ represent the N-particle configuration and corresponding volume element, and Q_l are the canonical configuration integrals. By introducing scaled position vectors $\mathbf{s}_i=V_l^{-1/3}\mathbf{q}_i$ for ith particle, Z_l is rewritten as

$$Z_l=\int \exp\{-\Phi_l[(V_l^{1/3}\mathbf{s})^N,T_l]\}d^N\mathbf{s}, \tag{2}$$

where $\Phi_l=U_l/kT_l$. The canonical ensemble average of a physical quantity X for system l is

$$\langle X\rangle_l=Z_l^{-1}\int X[(V_l^{1/3}\mathbf{s})^N]\exp\{-\Phi_l[(V_l^{1/3}\mathbf{s})^N,T_l]\}d^N\mathbf{s}. \tag{3}$$

It is impossible, in general, to obtain data of other $n-1$ systems from a conventional MC simulation for a single system since the parts of configuration space sampled upon the Boltzmann distribution for a system are not broad enough to cover all the parts of configuration space relevant to the other systems. For the successful simultaneous investigation, configurations should be sampled upon a general distribution W that covers the relevant parts of configuration space for every system adequately.

Assume that configurations are sampled on an arbitrary distribution function $W(\mathbf{s}^N)$. The probability density of configurations $\rho_l(\mathbf{s}^N)$ for system l is related with the probability density of sampled configurations $\rho_W(\mathbf{s}^N)$ by

$$\rho_l(\mathbf{s}^N)=\frac{\exp(-\Phi_l)/\int W(\mathbf{s}^N)d^N\mathbf{s}}{\int \exp(-\Phi_l)d^N\mathbf{s}/\int W(\mathbf{s}^N)d^N\mathbf{s}} \\ =\rho_W(\mathbf{s}^N)W^{-1}\exp(-\Phi_l)/\langle W^{-1}\exp(-\Phi_l)\rangle_W, \tag{4}$$

where $\langle\ \rangle_W$ denotes an average over sampled configurations. The canonical ensemble average of a physical quantity X is calculated by

$$\langle X\rangle_l=\int X[(V_l^{1/3}\mathbf{s})^N]\rho_l(\mathbf{s}^N)d^N\mathbf{s} \\ =\langle XW^{-1}\exp(-\Phi_l)\rangle_W/\langle W^{-1}\exp(-\Phi_l)\rangle_W. \tag{5}$$

Another advantage of this approach is that the reduced free-energy difference between system l and system m,

$$\frac{A_m}{kT_m}-\frac{A_l}{kT_l}=\ln\left(\frac{V_lZ_l}{V_mZ_m}\right), \tag{6}$$

can be obtained directly from calculating

$$Z_l/Z_m=\langle W^{-1}\exp(-\Phi_l)\rangle_W/\langle W^{-1}\exp(-\Phi_m)\rangle_W. \tag{7}$$

Thus, if the free energy of a system was known, free energies of others are immediately given. The chemical potential can be obtained, in turn, by

$$\mu_l=A_l/N+p_lV_l/N, \tag{8}$$

with the pressure p_l calculated by

$$p_l=\frac{NkT_l}{V_l}\left[1-\frac{1}{3N}\left\langle\sum_{i=1}^{N}W^{-1}\mathbf{s}_i\cdot\boldsymbol{\nabla}_i\Phi_l\right\rangle_W\Bigg/ \\ \times\langle W^{-1}\exp(-\Phi_l)\rangle_W\right]. \tag{9}$$

With an appropriate choice of W, in principle, one would be able to investigate several systems at a time. But, the problem is how to choose W appropriately. The efficiency of the non-Boltzmann sampling simulation is determined by the choice of W. The job without an *a priori* recipe for W is uncertain.

B. Multiensemble sampling

A most favorable form of W, which can be used universally, is obtained by the manner of least-squares fitting as follows. For an adequate simultaneous investigation of several systems, configurations should be sampled so that the estimate of $\rho_l(\mathbf{s}^N)$ is equally accurate for every system. That is, the error in the estimate of the denominator $\langle W^{-1}\exp(-\Phi_l)\rangle_W$ in Eq. (4) should be small and balanced for every l. This condition is optimally satisfied when W is chosen so that the sum of the squares of expected relative errors in $\langle W^{-1}\exp(-\Phi_l)\rangle_W$ is minimum, which is proportional to

$$\sum_l\frac{\langle W^{-2}\exp(-2\Phi_l)\rangle_W}{\langle W^{-1}\exp(-\Phi_l)\rangle_W^2} \\ =\int W\,d^N\mathbf{s}\int W^{-1}\sum_l[Z_l^{-2}\exp(-2\Phi_l)]d^N\mathbf{s} \tag{10}$$

for sufficiently large sample sizes. By setting the functional derivative with respect to W equal to zero and solving for it, we obtain a nontrivial solution of the W function

$$W=\text{const}\left[\sum_l Z_l^{-2}\exp(-2\Phi_l)\right]^{1/2}. \tag{11}$$

This is just the generalized form of our previous formula [7] of W; for $n=2$, the former becomes identical to the latter. Substituting Eq. (11) into Eqs. (4), (5), and (7) yields

$$\rho_l=\rho_WF_l/\langle F_l\rangle_W, \tag{12}$$

$$\langle X\rangle_l=\langle XF_l\rangle_W/\langle F_l\rangle_W, \tag{13}$$

and

$$Z_l/Z_m=\exp(C_{lm})\langle F_l\rangle_W/\langle F_m\rangle_W, \tag{14}$$

where

$$F_l=Z_l^{-1}W^{-1}\exp(-\Phi_l)=\left\{\sum_m\exp[2(C_{lm}+\Delta\Phi_{lm})]\right\}^{-1/2}, \tag{15}$$

$$C_{lm}=\ln(Z_l/Z_m), \tag{16}$$

and $\Delta\Phi_{lm}=\Phi_l-\Phi_m$. Equations (12)–(14) are true for any sets of values of shift constants C_{lm}, but the set satisfying the self-consistent condition of Eq. (16) optimizes the simulation result. The self-consistency of C_{lm} can be achieved easily by preliminary runs of simulation in which iterative adjustments are made by evaluating Eqs. (14) and (16). In this work, starting with the initial values of zeros, we obtained almost self-consistent values of C_{lm} with a few short preliminary runs.

The Markov chain of configurations is generated by accepting the trial move from configurational state i to configurational state j with the probability

$$\frac{\rho_W(j)}{\rho_W(i)}=\left[\frac{\sum_l Z_l^{-2}\exp[-2\Phi_l(j)]}{\sum_m Z_m^{-2}\exp[-2\Phi_m(i)]}\right]^{1/2} \\ =\left[\sum_l\frac{F_l(i)^2}{\exp(2\delta\Phi_l)}\right]^{1/2}, \tag{17}$$

where $\delta\Phi_l=\Phi_l(j)-\Phi_l(i)$. When $\rho_W(j)/\rho_W(i)>1$, the new configuration is always accepted.

TABLE I. Results of the constant density $\rho\sigma^3=0.02$. Values in ( ) are the results of Hansen and Verlet [9].

kT/ϵ	$\langle F_l \rangle$	$p/\rho kT$	A^c/NkT	μ^c/kT
∞	0.199±0.015	1.000	−4.912	−3.91
100.00	0.187±0.009	1.019	−4.893	−3.87
50.00	0.190±0.007	1.021	−4.891	−3.87
25.00	0.194±0.007	1.023	−4.890	−3.87
12.50	0.185±0.008	1.022	−4.892	−3.87
6.25	0.195±0.008	1.015	−4.898	−3.88
3.00	0.192±0.009	0.996	−4.917	−3.92
1.15	0.200±0.010	0.917 (0.918)	−4.994 (−5.00)	−4.08
0.75	0.203±0.018	0.823 (0.829)	−5.087 (−5.08)	−4.26

III. APPLICATIONS

As a test we applied the present method to investigate the phase transition of a Lennard-Jones 12-6 fluid for which there are reliable earlier results. For the system with 108 particles the investigations were carried out in two stages: on constant gas density $0.02\sigma^{-3}$ and isotherm $1.15\epsilon/k$. Here σ is the ''hard-core'' radius of the particle and ϵ is the depth of the potential well. In the case of the isotherm, it is important to apply the long-range corrections [8] to the calculated instantaneous energies and pressures during the course of simulations, since they will not be the same for different densities. In the general case, the calculation of $\Delta\Phi_{lm}$ for the difference of densities is computationally expensive. Fortunately, for a simple potential such as the Lennard-Jones potential, $\Delta\Phi_{lm}$ can be easily calculated by scaling. For the Lennard-Jones potential it can be done by dividing up the potential into its repulsive and attractive components and multiplying them by corresponding scaling factors [8].

A. Constant density

For the fluid on density $0.02\sigma^{-3}$, nine temperatures from $Kt/\epsilon=0.75$ to ∞ were investigated at a time. At $T=\infty$, the fluid is identical to the ideal gas and the free energy is analytically calculated. The *absolute* values of the free energy at finite temperatures can be obtained by adding the free energy of the ideal gas to our observed values relative to $T=\infty$. The quantity of interest in this work is the configurational free energy A^c, defined by

$$A^c/kT=-\ln(Q\sigma^{-3N}/N!). \tag{18}$$

The reduced configurational free energy per particle of the ideal gas at density $0.02\sigma^{-3}$ is $A^c_\infty/NkT=-4.912$.

Two preliminary 5×10^5 step runs were performed for the simultaneous adjustment of shift constants. In the first run the values of the shift constants C_{lm} were set to zero initially and updated iteratively during the run. The iterative update was made by evaluating Eqs. (14) and (16) every interval of 5×10^4 steps. It appears that the updated values of each shift constant converge very quickly and oscillate about its self-consistent value after 2.5×10^5 steps. In the second run the shift constants were adjusted once more by taking averages in Eq. (14) over the whole run. In the final run 10^6 configurations were generated and $\langle F_l \rangle$, energy, pressure, free energy, and chemical potential were calculated.

Table I lists the results and shows that the present method agrees well with an earlier investigation [9]. The almost identical estimates of $\langle F_l \rangle$, shown in Table I, indicate that the self-consistency of C_{lm} has been achieved very closely. The errors in $\langle F_l \rangle$ were estimated, taking account of the statistical inefficiency [8]. As shown in Table I, the relative errors are less than 5%, except for edge temperatures. The extra error at the edge temperature is due to the relatively inaccurate sampling for tails of configuration distribution, which always occurs in the important sampling scheme. From Eqs. (6) and (14) it easy to show that the error in the estimate of A^c_l/kT_l is the sum of the relative errors in the estimates of $\langle F_l \rangle$ and $\langle F_\infty \rangle$. It turns out that only the last digit is uncertain in the estimated values of A^c/NkT by less than 2; the relative errors are less than 0.05%. This was confirmed by the comparison with the results obtained from simulations with different initial configurations.

In order to see if the sampling has been performed as we expected in the theory, the energy density of sampled con-

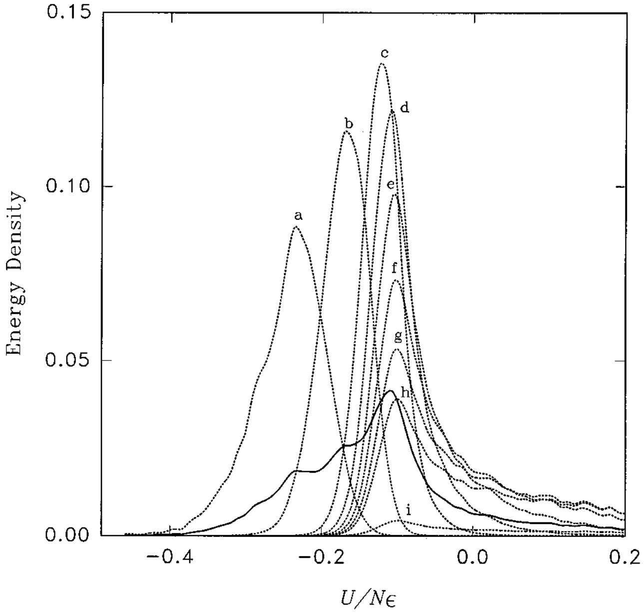

FIG. 1. Plot of energy densities. The solid line is the energy density of configurations sampled by the present method and the dotted lines are the energy densities for individual temperatures obtained from Eq. (12); $k\mathrm{T}/\epsilon=0.75$ (a), 1.15 (b), 3.00 (c), 6.25 (d), 12.50 (e), 25.00 (f), 50.00 (g), 100.00 (h), and ∞ (i).

TABLE II. Multiensemble simulations on the isotherm $kT/\epsilon = 1.15$. Here N_c is the length of the Markov chain.

Density range	Investigated densities	N_c
0.015–0.100	0.015, 0.020, 0.030, 0.040, 0.050, 0.060, 0.070, 0.080, 0.090, 0.100	4.5×10^6
0.100–0.190	0.100, 0.110, 0.120, 0.130, 0.140, 0.150, 0.160, 0.170, 0.180, 0.190	4.5×10^6
0.190–0.320	0.190, 0.200, 0.215, 0.230, 0.245, 0.260, 0.275, 0.290, 0.300, 0.320	6×10^6
0.320–0.500	0.320, 0.340, 0.360, 0.380, 0.400, 0.420, 0.440, 0.460, 0.480, 0.500	6×10^6
0.500–0.725	0.500, 0.525, 0.550, 0.575, 0.600, 0.625, 0.650, 0.675, 0.700, 0.725	9×10^6
0.725–0.920	0.725, 0.750, 0.775, 0.800, 0.825, 0.850, 0.875, 0.900, 0.920	9×10^6

figurations was evaluated as shown in Fig. 1. The energy densities for individual temperatures were obtained from Eq. (12). The results shown in Fig. 1 and Table I verify that the present method samples a superposition of the ensembles of interest and allows an investigation of several nearby states with uniform accuracy for every states.

B. Isotherm

For the fluid on the isotherm, $kT/\epsilon = 1.15$, six consecutive subranges of density from $0.015\sigma^{-3}$ to $0.92\sigma^{-3}$ were investigated with six independent parallel simulations. For each density range, 9–10 densities were investigated. Table II lists the nominal density ranges and densities. Since our six simulations overlapped at their edge densities, they immediately give the relative free energy over the whole range of investigated densities. Furthermore, since the free energy at density $0.02\sigma^{-3}$ is known from the previous stage, the values of the free energy for other densities are immediately obtained.

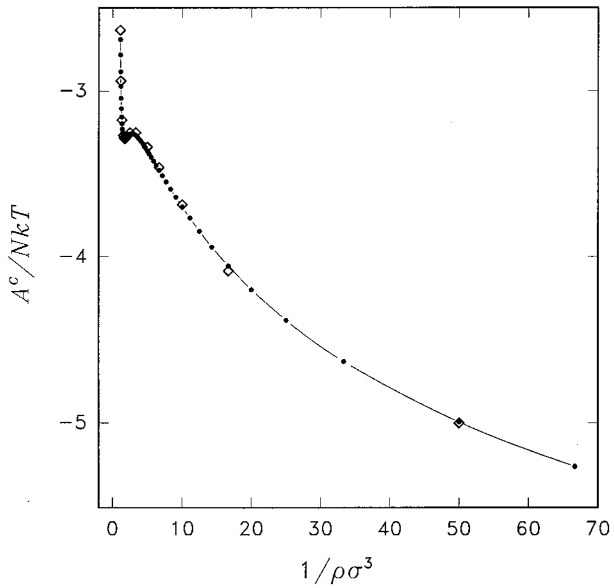

FIG. 3. Temperature-scaled configurational free energy per particle versus the inverse of the reduced density for the results of the present method (●), compared with the results of Hansen and Verlet [9] (◇).

The simultaneous adjustment of C_{lm} was carried out as done in the previous stage, varying the size of the updating interval up to 2×10^5 steps. Except for first two low-density ranges, however, the values of shift constants did not converge well. It appears that the result depends on the initial configuration. This indicates that the density range is so wide and/or the parts of configuration space relevant to individual nominal densities are relatively localized. For the successful

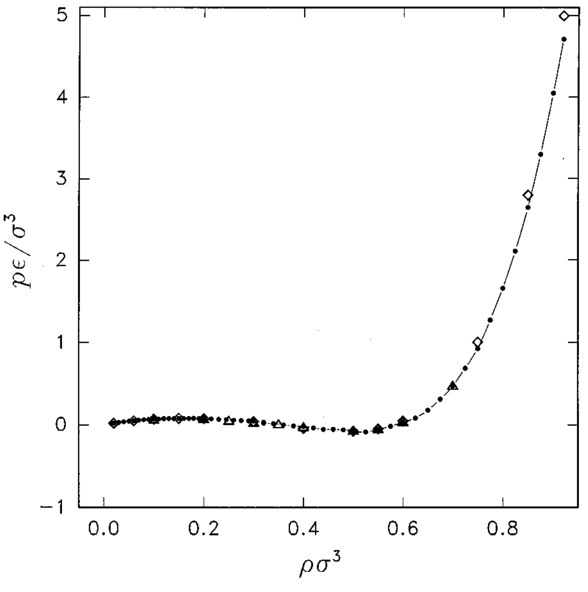

FIG. 2. Reduced pressure versus reduced density for the results of the present method (●), compared with the results of Hansen and Verlet [9] (◇) and Powles, Evans, and Quirke [10] (△).

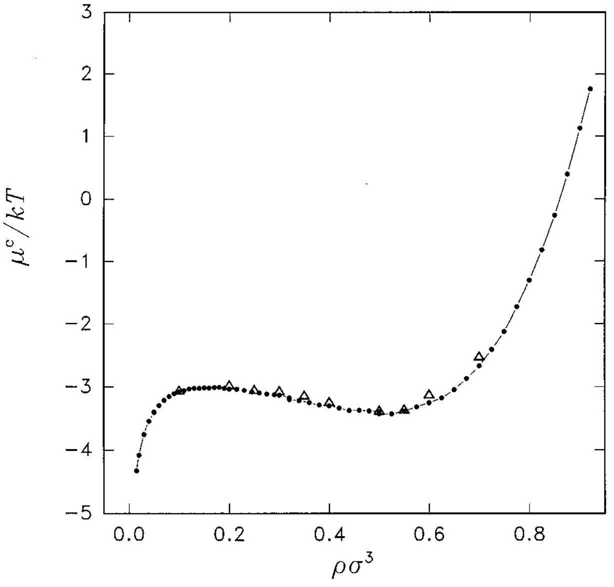

FIG. 4. Temperature-scaled configurational chemical potential versus the reduced density for the results of the present method (●), compared with the results of Powles, Evans, and Quirke [10] (△).

TABLE III. Liquid-gas transition properties of the Lennard-Jones fluid at $kT/\epsilon=1.15$. L is the latent heat of vaporization.

Source	$p\epsilon/\sigma^3$	$\rho_{\rm gas}\sigma^3$	$\rho_{\rm liq}\sigma^3$	L/ϵ
present method	0.0591	0.071	0.610	4.33
previous work (Ref. [9])	0.0597	0.073	0.606	4.34

simultaneous adjustment of shift constants with such short interval lengths, narrower density ranges should be taken and/or more densities should be included in the investigation over a density range. Instead of doing this, however, one can obtain a preliminary set of shift constants from short runs of two-ensemble sampling for $n-1$ pairs of nearest densities, from which $n-1$ self-consistent shift constants are determined independently. In our previous work [7] of two-ensemble simulations, it has been demonstrated that the value of the shift constant converges to its self-consistent value very quickly if the overlap of two distributions is not too poor. The complete set of shift constants is obtained in turn by the relations between the shift constants

$$C_{lm}=-C_{ml}\,, \quad C_{lm}=C_{lk}+C_{km}\,. \tag{19}$$

In the two-ensemble simulation the value of shift constant was set to zero initially and updated by two runs of 10^5 steps. After this, a preliminary n-ensemble sampling run of 10^6 steps was performed for each density range and the values of shift constants were updated once more, simultaneously. In the final runs, $(4.5–9)\times10^6$ configurations were generated and the internal energy, pressure, free energy, and chemical potential were calculated. Figures 2–4 plot the results of early Monte Carlo results [9,10] and show that they agree very well.

In Table III listed are the liquid-gas transition properties obtained by constructing the double tangent on the curve in Fig. 3. A few data near each of transition points are fitted by a polynomial. The double-tangent line on two curves of polynomials is obtained by solving two simultaneous equations. The latent heat of vaporization is calculated by

$$L=T\Delta_t S=\Delta_t(U-A), \tag{20}$$

where S is the entropy and Δ_t represents the change of a quantity upon vaporization.

IV. SUMMARY

We have shown that the present method is accurate, efficient, and greatly useful in the study of phase transitions. The theoretical derivation of the form of W guarantees the accuracy and universality of the method. The existence of the self-consistent condition Eq. (16), which should be satisfied by parameters in W for the optimal simulation result, simplifies the realization of the method; there is no need to monitor the sampled distribution for the adjustment of W, which is essential in the earlier technique [5,6] where an *ad hoc* form of W is taken. The universality and simplicity of the present technique make it powerful and efficient, especially in the study of systems with unknown behavior. The method is easily applied to other kinds of ensembles such as isobaric or grand canonical MC. Finally, we note that continuous thermodynamic functions over the range of investigated states can also be generated, using a technique like that of Ferrenberg and Swendsen [3].

ACKNOWLEDGMENTS

This work was supported in part by the Basic Science Research Institute Program, Ministry of Education under Contract No. BSRI-94-2436, by Korea Science Foundation under Contract No. KOSEF-941-0200-037-1, and by a Central Research Fund from Pai Chai University.

---

[1] G. Bhanot, S. Black, P. Cater, and R. Salvador, Phys. Lett. B **183**, 331 (1987).
[2] K.-C. Lee, J. Phys. A **23**, 2087 (1990).
[3] M. Ferrenberg and R. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988).
[4] G. M. Torrie and J. P. Valleau, J. Comput. Phys. **23**, 187 (1977).
[5] I. S. Graham and J. P. Valleau, J. Phys. Chem. **94**, 7894 (1990).
[6] J. P. Valleau, J. Comput. Phys. **96**, 193 (1991); J. Chem. Phys. **99**, 4718 (1993).
[7] K.-K. Han, Phys. Lett. A **165**, 28 (1992).
[8] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989); see pp. 64–65 for the long-range correction, p. 125 for the calculation of the potential energy by scaling the volume, and pp. 191–1913 for the estimation of errors.
[9] J. P. Hansen and L. Verlet, Phys. Rev. **184**, 151 (1969).
[10] J. G. Powles, W. A. B. Evans, and N. Quirke, Mol. Phys. **46**, 1347 (1982).