The continuous configurational Boltzmann biased direct Monte Carlo method for free energy properties of polymer chains

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We develop here a highly efficient variant of the Monte Carlo method for direct evaluation of the partition function, free energy, and other configurational dependent physical properties for long polymer chains. This method (CC–BB) combines continuous configurational biased sampling with Boltzmann factor biased enrichment. To illustrate the efficiency and to validate the bias correction for weighting the torsion and chain enrichments, we applied this model to isolated single chains using a united atom force field. For a 50 monomer polymer chain CC–BB with 400 chains leads to an accuracy of 0.1% in the free energy whereas simple sampling direct Monte Carlo requires about 10^9 chains for this accuracy. This leads to cost savings by a factor of about 350 000. CC–BB is easily extended to multichain systems, to the condensed state, to more realistic force fields, and to evaluating the mixing free energy for polymer blends. © *1997 American Institute of Physics.* [S0021-9606(97)51016-6]

I. INTRODUCTION

Atomistic simulations using chemically realistic models are becoming quite important in characterizing the structural, mechanical, and polarization properties[1–3] of macromolecules. However, practical applications to polymer technology require evaluation of the free energy as a function of temperature. This requires expensive thermodynamic integrations, and despite the advances in Metropolis Monte Carlo and molecular dynamics (MD) methods, there are few realistic simulations for the free energy function even for system as simple as long polymer chains.

The direct method for estimating the free energy function is simple sampling direct Monte Carlo (SS–DMC) in which the whole phase space is sampled uniformly by randomly generating a large number of possible configurations. The partition function is calculated as the average Boltzmann factor for all the sampled configurations. For polymer systems described with rigid constraints on bond lengths and angles, SS–DMC is preceded by a random sampling of the complete set of torsion angles. SS–DMC has been extensively used for self-avoiding walk studies on a lattice.[4] However, because of drastic sampling attrition, SS–DMC is not applicable to long polymer chains, even for lattice systems.

Many methods have been proposed to remedy the inefficiency of SS–DMC. Most widely used is the biased sampling (inversely restricted sampling) proposed by Rosenbluth and Rosenbluth[5] in 1955. In the Rosenbluth procedure for a self-avoiding lattice walk, all nearest-neighbor sites are checked at each step and pre-occupied sites are excluded from the sample. The sampling bias is then corrected to give the proper statistical average value.

This biasing idea has been developed and modified by many others.[6,7] An excellent such method is the the scanning method of Meirovitch.[7] This method uses step-by-step growth with the torsion angle sampling based on a transition probability function (TPF) determined by scanning for possible future continuation of the whole chain. The applicability of the TPF method to evaluation of the entropy has been well demonstrated for relatively long chains on a lattice.[6,7] However, for off-lattice systems building the TPF is too expensive because it requires evaluation of an enormous number of nonbonded interactions. Consequently, application of TPF sampling to realistic systems has been limited to very short chains, often with future scanning of only a few steps.

Another workable extension of biasing methods is the continuous configurational biased (CCB) sampling developed by Frenkel *et al.*[8] which extends the Rosenbluth method to the continuous space suitable for dense systems. Frenkel used the Metropolis procedure in developing the CCB method but modified the transition probability by introducing a weighting on the energies for the next-step configuration. In this case, the dynamic nature of the method prevents direct evaluation of the free energy function.

Another efficient modification of SS–DMC is the enrichment method first developed by Wall and Erpenbeck[9] in 1959. This method dramatically reduces sampling attrition by using successfully generated short chains more than once. Lax and Gill[10] used this method for an extensive study of the Domb–Joyce model of random walks on a simple cubic lattice.[11] However, its application is still limited to self-avoiding walk problems on lattice systems.

Orland, *et al.*[12] and Grassberger, *et al.*[13] successfully extended the enrichment method to off-lattice systems. Their method is based on the replication–deletion procedure (RDP), in which the chain is replicated or deleted by a factor proportional to the Boltzmann factor increment per added
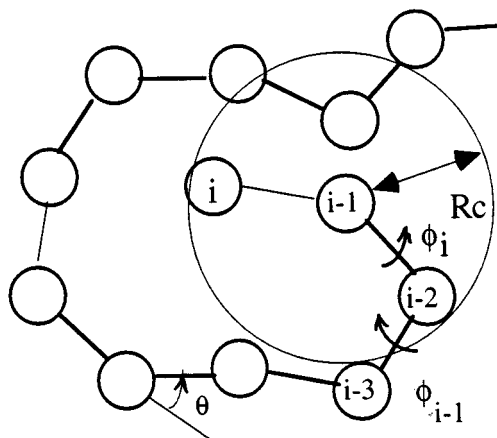

FIG. 1. Definition of geometric parameters θ, ϕ_i, and R_c.

monomer throughout chain growth. For real polymers with long-range interactions the calculation time for inserting a monomer is proportional to the chain length. For long polymers, most chains are deleted after the expensive procedure of calculating the energy because they often encounter high energy nonbonding overlaps. For realistic systems this limits the application of the RDP to relatively short chains. The other drawback of RDP is that it tends to replicate burst numbers of chains unless suitable population controls are established. Unfortunately there is no general method to assign the population control factor; it requires trial and error adjustments.

In this paper we present two improved MC sampling methods for off-lattice polymer chains:

(i) The CCB–DMC method is the extension of the continuous configurational biased (CCB) method to direct MC sampling, using a fast algorithm for evaluating the torsion sampling weighting function.

(ii) The Boltzmann factor biased (BFB) method is an improved enrichment method, which introduces a configurational-dependent enrichment procedure with correct bias correction and automatic population control.

Combining CCB and BFB (denoted CCBB) dramatically accelerates the convergence of direct Monte Carlo sampling. This leads to efficient direct calculations of the free energy function for long polymer chain systems. Herein we describe the algorithm in detail, demonstrate the sampling efficiency, and validate the bias correction through applications to predicting free energy dependent properties of polyethylene (PE) polymers.

II. THE POLYMER MODEL

As a prototype we will consider isolated single polyethylene chains with N carbon atoms using the united atom model defined by Ryckaert–Bellmans (UA/RB).[14] The new methods are quite suitable for polymers containing side chains, but the emphasis here is on the method. In the (UA/RB) model each atom i in the chain (Fig. 1) is characterized

by a Lennard-Jones 12-6 potential as

$$E_{LJ}(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right] \quad |i-j| \geqslant 4, \tag{1}$$

where $\epsilon/k_B = 72$ K, $\sigma = 0.3923$ nm, and r_{ij} is the distance between ith and jth atoms.

In addition, the torsion potential in Eq. (2) is included

$$\frac{E_t(\phi_i)}{k_B} = \sum_{n=0}^{5} a_n (\cos \phi_i)^n, \tag{2a}$$

where

$$a_0 = 1.157, \quad a_1 = 1.515, \quad a_2 = -1.636,$$
$$a_3 = -0.382, \quad a_4 = 3.271, \quad \text{and} \quad a_5 = -3.927. \tag{2b}$$

Here ϕ_i is ith torsion angle, and the geometry properties are taken as[14]

bond length: $l = 0.153$ nm,

bond angle: $\vartheta = 70.53°$, (3)

as defined in Fig. 1 (this corresponds to a CCC angle of 109.47°).

The total Hamiltonian has the form

$$H[\{\phi_i\}] = \sum_{i=5}^{N} \sum_{j=1}^{i-4} E_{LJ}[r_{ij}(\{\phi_i\})] + \sum_{i=4}^{N} E_t(\phi_i), \tag{4}$$

and we will quote the results in terms of a reduced temperature

$$T_r = \frac{k_B T}{\epsilon}. \tag{5}$$

III. THE THERMODYNAMIC FUNCTIONS

The configurational partition function for the model polyethylene chain consisting of N carbon atoms is defined as

$$Z_N = \int_0^{2\pi} \int_0^{2\pi} \exp[-\beta H(\{\phi_i\})] d\phi_4 \cdots d\phi_N, \tag{6}$$

where $\beta = 1/kT$. (Here ϕ_i is the torsion specifying the position of atom i with respect to atoms $i - 3$, $i - 2$, and $i - 1$.)

The Helmholtz free energy A, the potential energy E, and the entropy S, are given by

$$A_N = -\beta \ln Z_N,$$

$$E_N = \int_0^{2\pi} \int_0^{2\pi} H(\{\phi_i\}) \exp[-\beta H(\{\phi_i\})] d\phi_4 \cdots d\phi_N,$$
$$\tag{7}$$
$$S_N = \frac{(E_N - F_N)}{T}.$$

A. Simple sampling

In the conventional direct Monte Carlo (DMC) method, polymer chains are generated by random step-by-step sampling of torsion angles. A complete N-mer chain is constructed in sequence, where the ith step samples the ith tor-

sion to construct an i-mer chain. Then a new chain is setup and sampled again from scratch. This is referred to as simple sampling (SS). The partition function is evaluated by

$$Z_N = N_c^{-1}(2\pi)^{N-3}\sum_1^{N_c} \exp[-\beta H(\{\phi_i\})]. \tag{8}$$

Here N_c is total number of chains generated.

The average value $\langle f \rangle$ of a physical property, $f = f(\{\phi_i\})$, is calculated as

$$\langle f \rangle = \frac{\Sigma_1^{N_c} f(\{\phi_i\})\exp[-\beta H(\{\phi_i\})]}{\Sigma_1^{N_c} \exp[-\beta H(\{\phi_i\})]}. \tag{9}$$

B. Independent rotational sampling

The sampling efficiency of SS–DMC is improved by applying rotationally biased sampling, in which torsions are sampled using a weighting function based on the Boltzmann factor of the torsion energy. We denote this as independent rotational sampling (IRS). For IRS the normalized torsion weighting function (TWF), W_{IRS} is defined as

$$W_{\text{IRS}}(\phi) = \frac{g_{\text{IRS}}(\phi)}{z_{\text{IRS}}}, \tag{10a}$$

where

$$z_{\text{IRS}} = \int_0^{2\pi} g_{\text{IRS}}(\phi)d\phi, \tag{10b}$$

$$g_{\text{IRS}}(\phi) = \exp[-\beta E_t(\phi)]. \tag{10c}$$

Torsion angles are generated in accordance with Eq. (10a). The partition function for IRS after bias correction is evaluated by

$$Z_N = N_c^{-1}(z_{\text{IRS}})^{N-3}\sum_1^{N_c} \exp\left[-\beta\sum_{i-5}^{N}\sum_{j=1}^{i-4} E_{\text{LJ}}(r_{ij})\right]. \tag{11}$$

W_{IRS} need be calculated only once so that computational work involved in evaluating the partition function involves just the Boltzmann factor for the nonbonding energy. With IRS the use of W_{IRS} effectively excludes high torsion energies throughout the MC sampling. However, spatial overlaps between nonbonding atoms are inevitable, leading to high configurational energies. In order to exclude these overlaps, information about the spatial environment in the vicinity of the growing chain end should be introduced into the TWF. The resulting form of the TWF, W^*, is given by

$$W^*(\phi_i; \phi_4,...,\phi_{i-1}) = \frac{g^*(\phi; \phi_4,...,\phi_{i-1})}{z^*(\phi_4,...,\phi_{i-1})}, \tag{12a}$$

where

$$z^*(\phi_4,...,\phi_{i-1}) = \int_0^{2\pi} g^*(\phi_i; \phi_4,...,\phi_{i-1})d\phi_i, \tag{12b}$$

$$g^*(\phi_i; \phi_4,...,\phi_{i-1}) = g_{\text{IRS}}(\phi_i)\exp\left[-\beta\sum_{j=1}^{i-4} E_{\text{LJ}}(r_{ij})\right]. \tag{12c}$$

The form of the partition function after bias correction becomes

$$Z_N = N_c^{-1} z_{\text{IRS}}\sum_1^{N_c} \left\{\prod_{i=5}^{N} z^*(\phi_4,...,\phi_{i-1})\right\}. \tag{13}$$

W^* must be calculated at every step since it depends on all previous steps. The computation time for this TWF is approximately proportional to the step number, i; therefore, this sampling method becomes too expensive for systems containing a large number of atoms.

C. Continuous configurational biased (CCB) direct Monte Carlo

To remedy the above problem with rotational sampling, we implemented the continuous configurational biased (CCB) direct Monte Carlo method, an efficient alternative sampling method. In CCB–DMC, a cutoff length for non-bonding interactions is introduced into the TWF calculation. On constructing the TWF for the ith torsion, we define a sphere of radius R_c, centered at the $(i-1)$th atom position, as shown in Fig. 1. The length of R_c should be taken larger than $l + \sigma$ in order to ensure that all possible atomic overlaps are checked. Boltzmann factors for the nonbonding energy between ith atom and all other atoms inside the cutoff sphere are included in TWF, W_{CCB}, as

$$W_{\text{CCB}}(\phi_i; \phi_4,...,\phi_i) = \frac{g_{\text{CCB}}(\phi_i; \phi_4,...,\phi_{i-1})}{z_{\text{CCB}}(\phi_4,...,\phi_{i-1})}, \tag{14a}$$

where

$$z_{\text{CCB}}(\phi_4,...,\phi_{i-1}) = \int_0^{2\pi} g_{\text{CCB}}(\phi_i; \phi_4,...,\phi_{i-1})d\phi_i, \tag{14b}$$

$$g_{\text{CCB}}(\phi_i; \phi_4,...,\phi_{i-1})$$
$$= g_{\text{IRS}}(\phi_i)\exp\left[-\beta\sum_{j=1}^{i-4} \Theta(R_C - r_{ij})E_{\text{LJ}}(r_{ij})\right], \tag{14c}$$

and $\Theta(R)$ is the Heavyside step function

$$\Theta(R) = 0 \quad \text{if } R < 0 = 1 \quad \text{if } R \geq 0. \tag{15}$$

The computation time for W_{CCB} is almost independent of i because the only nonbonding atoms considered are those in the local vicinity of a growing chain end. In addition, the list of atoms inside the cutoff circle for the ith atom is automatically available since all the necessary atomic distances were calculated to obtain the energy at the just previous step. The bias-corrected partition function has the form of Eq. (16), which includes the calculation of those nonbonding energies that did not appear in the TWF calculation of

$$Z_N = N_c^{-1} z_{\text{IRS}}\sum_1^{N_c} \left\{\prod_{i=5}^{N} z_{\text{CCB}}(\phi_4,...,\phi_{i-1})\right\}$$
$$\times \exp\left[-\beta\sum_{i=5}^{N}\sum_{j=1}^{i-4} \Theta(r_{ij} - R_C)E_{\text{LJ}}(r_{ij})\right]. \tag{16}$$

Orland *et al.*[15] proposed introducing a weighting function. However, they implemented the weight only for the valence part of energy and did not suggest practical methods for treating nonbonding interaction.

D. The continuous configuration Boltzmann biased (CC–BB) method

In the enrichment method for self-avoiding walks on a lattice, once a walk of $i-1$ steps is successfully generated by the SS method, this chain continues to be grown up to step i in m_{i-1} different ways. In order to avoid bias the enrichment factor m_{i-1} is always fixed *ahead* of the MC simulation. The total chain multiplicity M_i for step i is defined as

$$M_i = \prod_{j=1}^{i-1} m_j. \qquad (17)$$

In the enrichment method the chains obtained from a particular first monomer are not statistically independent. Hence the set of all chains using the same seed as the first monomer are collected together and denoted as a *cluster*. Each cluster is given the same weight.

In RDP for a continuous space, chain enrichment is used to achieve a Boltzmann population for the collected chains. Here M_i is determined at every step as statistically proportional to the ratio of the Boltzmann factor of step $(i-1)$ to that of step $(i-2)$, where m_i is not integer. This leads to a high frequency of sampling chains with high energy (caused by nonbonding overlap) which are subsequently deleted in the course of sampling. The partition function is evaluated from the ratio of the total number of generated chains to the number of seeds. To avoid replicating chains too often, a scaling factor p is multiplied by Boltzmann factor. Since the suitable choice of scaling factors is unknown and strongly dependent on chain size and temperature, one determines them in trial and error manner prior to the MC simulation. These scaling factors should be fixed ahead of MC simulation.

In CCB–DMC we can exclude almost all high energy chains having nonbonding overlaps; thus we delete chains very seldom in comparison with RDP. However, the sampling distribution is not Boltzmann; low energy chains in the collection can be included with too high a contribution to the partition function. Thus we extended the chain enrichment to control sampling so that all collected chains make a nearly equal contribution to the partition function (although we do not intend to achieve a Boltzmann distributed collection of chains). In our new method the multiplicity M_i is determined at every step as proportional to the ratio of the Boltzmann factor of a just-sampled chain to that of the running average value for the chain with same length. The partition function is explicitly calculated as the average of the weighting-bias-corrected Boltzmann factor divided by the chain multiplicity. We denote this as the continuous configuration Boltzmann biased (CCBB) method.

We rewrite Eq. (16) in terms of a sum over K clusters as

$$Z_N(K) = K^{-1} \sum_{C=1}^{K} \zeta_N(C). \qquad (18)$$

Denoting $L_n(C)$ as the total number of chains generated for cluster C cluster by using an arbitrary choice for the enrichment factor, the partition function (18) is calculated by

$$\zeta_N(C) = \sum_{n=1}^{L_N(C)} \frac{\zeta_N^n(C)}{M_N^n(C)}, \qquad (19)$$

$$M_N^n(C) = \prod_{i=1}^{N-1} m_i^n(C), \qquad (20)$$

$$L_N(C) = \sum_{n=1}^{L_{N-1}} m_{N-1}^n(C). \qquad (21)$$

In CCBB, the chain multiplicity, $M_i^n(C)$, is determined as proportional to the ratio of $\zeta_{i-1}^n(C)$ to $Z_{i-1}(C-1)$:

$$Q_i^n(C) = \frac{p \cdot \zeta_{i-1}^n(C)}{Z_{i-1}(C-1)}, \qquad (22)$$

$$M_i^n(C) = \mathrm{INT}[Q_i^n(C)] \quad \text{if } Q_i^n(C) > 1$$
$$= 1 \quad \text{if } Q_i^n(C) \leq 1. \qquad (23)$$

The enrichment factor m_{i-1}^n is evaluated from the ratio of M_i^n to M_{i-1}^n. This procedure always keeps the chain multiplicity approximately proportional to the Boltzmann factor of the chain at the just-previous step:

$$P_i^n(C) = \frac{M_i^n(C)}{M_{i-1}^n(C)}, \qquad (24a)$$

$$m_{i-1}^n(C) = \mathrm{INT}[P_i^n(C)] \quad \text{if } P_i^n(C) > 1$$
$$= 1 \quad \text{if } P_i^n(C) \leq 1. \qquad (24b)$$

For $i < 5$ the Boltzmann population of the chain collection is completely satisfied in CCB. Therefore, we set the chain multiplicity to unity

$$M_0^n = M_1^n = \cdots = M_4^n = 1. \qquad (24c)$$

The choice of p in Eq. (22) is arbitrary. Too large a value of p could lead to an exploding number of samples of highly correlated configurations. Too small a value might lead to too few chains per cluster. For the PE example considered here, we used $p=1$ since it results in enriched chains having nearly equal contribution to the partition function.

To obtain an initial guess for the partition function, $Z_i(0)$, a short non-BFB run is performed. (For this study we sampled 200 chains prior to BFB sampling.) If the partition function used in the initial guess is too small, an extraordinarily large enrichment factor might occur for clusters just after beginning the BFB sampling and ruin the MC sampling. To avoid this we can introduce an upper limit for the enrichment factor (arbitrarily without any additional bias). For the example reported here no special controls of the enrichment factor were needed. Equation (24) gave automatic control of the number of chains generated by BFB sampling. The average number of generated chains per seed atom

tended to become large at low temperature. It ranged from 3.5 at the highest temperature to 11.2 at lowest one for $N = 400$.

IV. PROCEDURE

A. CCB sampling

Prior to the chain sampling, the torsion energy was calculated for a fixed number of grid points (in this study we used 200 equally separated grid points from 0 to 2π). W_{IRS}, the normalized TWF for IRS, is then evaluated using numerical integration for z_{IRS} as in Eq. (10b). This uses the auxiliary distribution $P_{\mathrm{IRS}}(\phi)$ in

$$P_{\mathrm{IRS}}(\phi) = \int_0^\phi W_{\mathrm{IRS}}(\phi') d\phi'. \tag{25}$$

We define a local Cartesian reference frame for each bond of the chain.[16] The axial transformation matrix t_i is

$$t_i = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\phi_i & -\cos\theta\sin\phi_i & \sin\phi_i \\ \sin\theta\sin\phi_i & -\cos\theta\sin\phi_i & -\cos\phi_i \end{bmatrix}. \tag{26a}$$

The first atom is set at origin and t_2 and t_3 are set as

$$t_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

$$t_3 = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta & -\cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{26b}$$

The position vector, R_i, of atom i is calculated as

$$\mathbf{R}_i = \mathbf{R}_{i-1} + \mathbf{T}_i \cdot \mathbf{b},$$

$$\mathbf{T}_i = \sum_{k=2}^i \mathbf{t}_k, \tag{26c}$$

$$\mathbf{b}^t = (l, 0, 0).$$

Here $\mathbf{b}$ is the bond vector and $\mathbf{T}_j$ is the transformation matrix from the local reference frame on the jth bond to the original reference frame. A random number ξ, uniformly distributed in the interval [0, 1), is drawn and the fourth torsion angle ϕ_4 is obtained by requiring

$$P_{\mathrm{IRS}}(\phi_4) = \xi. \tag{27}$$

For $i > 4$ after sampling the $(i-1)$th torsion, all nonbond distances are calculated to evaluate the energy and also to define an atom group $\{k\}_i$, whose elements consist of the neighbors of the $(i-1)$th atom

$$\{k\}_i = \{k \mid |\mathbf{R}_{i-1} - \mathbf{R}_k| < R_c ; 1 \le k < i-5\}. \tag{28}$$

The coordinates of all atoms in the list $\{k\}_i$ are transformed into the local reference frame on the $(i-1)$th bond by using the inverse matrix $(\mathbf{T}_{i-1})^{-1} = T_{i-1}^t$,

$$\mathbf{R}_k' = (\mathbf{T}_{i-1})^{-1} \cdot \mathbf{R}_k = \mathbf{T}_{i-1}^t \cdot \mathbf{R}_k. \tag{29}$$

In the local reference frame the coordinates of atom i for a trial move at the qth grid point ϕ_i^q is

$$\mathbf{r}_q^t = (l\cos\theta, l\sin\theta\cos\phi_i^q, l\sin\theta\sin\phi_i^q), \tag{30}$$

which is independent of i if the same type of grid is used for all torsions. $g_{\mathrm{CCB}}(\phi_i)$ is evaluated as

$$g_{\mathrm{CCB}}(\phi_i^q; \phi_4, \dots, \phi_{i-1})$$

$$= g_{\mathrm{IRS}}(\phi_i^q) \exp\left[-\beta \sum_{\{k\}_i} E_{\mathrm{LJ}}(|\mathbf{R}_k' - \mathbf{r}_q|) \right]. \tag{31}$$

Then z_{CCB} and W_{CCB} are evaluated by using the above expressions of g_{CCB}. The auxiliary distribution P_{CCB} is obtained by

$$P_{\mathrm{CCB}}(\phi_i) = \int_0^{\phi_i} W_{\mathrm{CCB}}(\phi; \phi_4, \dots, \phi_{i-1}) d\phi. \tag{32}$$

B. BFB sampling

In the BFB method we cannot foresee how many chains will be generated in a cluster. Thus we cannot know how much memory is needed to store the information for all growing branches of the chains in a cluster. Consequently we use a memory-saving algorithm, in which just one chain is grown at a time.
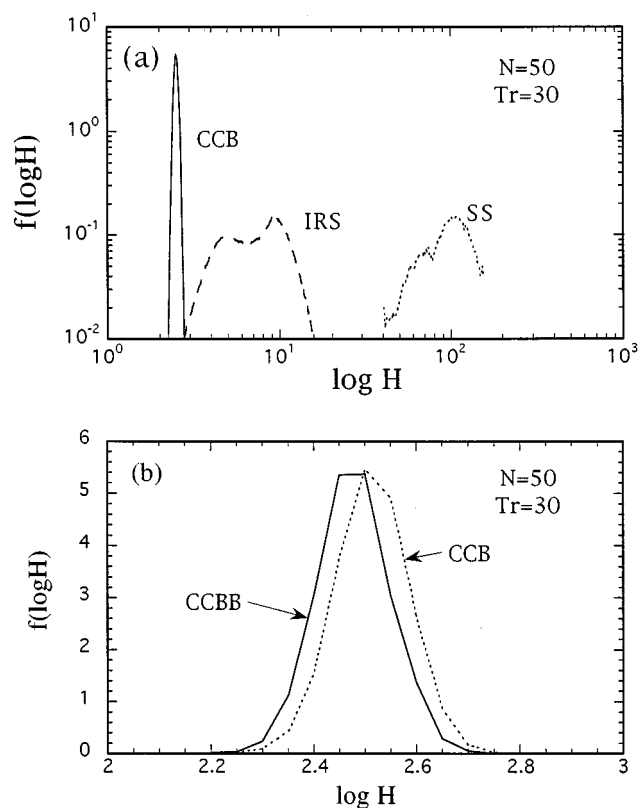

FIG. 2. Frequency distribution of the logarithmic potential energy at $T_r = 30$ for $N = 50$. (a) CCB (solid line), IRS (broken line), and SS (dotted line). (b) CCB (dotted line) and CCBB (solid line). Note that (b) is for just the range of log H from 2 to 3.
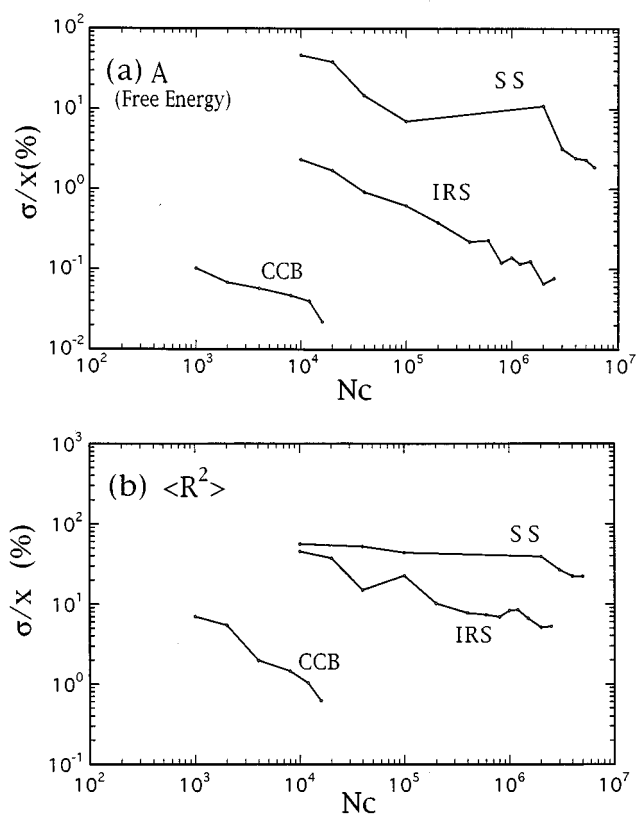
FIG. 3. Convergence of CCB, IRS, and SS simulations for $N=50$, $T_r=30$. (a) Free energy (A) and (b) squared end-to-end distance ($\langle R^2 \rangle$). Plotted is the ratio of the standard deviation to the average value for each property vs the total number of sample chains N_c.
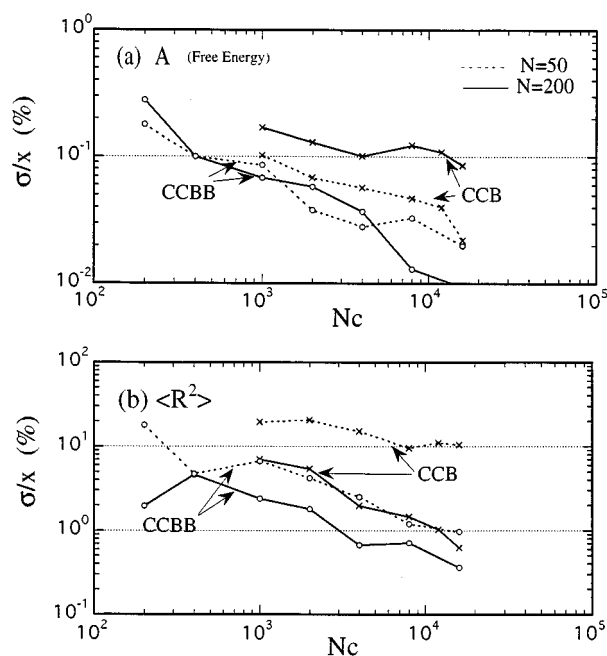
TABLE I. Estimated N_c and computer times[a] for convergence of the free energy to 0.1% ($N=50, T_r=301$).

	N_c	Time/chain ms	Total time s	Ratio to CCBB
SS	10^9	6.4	6.4×10^6	350 000
IRS	1.7×10^6	6.6	1.1×10^4	600
CCB	10^3	90	90	5
CCBB	4×10^2	45	18	1

[a]Using the IRIS CRIMSON of Silicon Graphics Inc.

For BFB sampling we simply complete construction of one chain at a time. For cluster $k+1$, the i index starts at $i=4$ and increases to $i=N$. For each such i we consider each i' from i to N. First we determine the enrichment factor $m_{i'}$, using Eq. (22) and evaluate the running average of the partition function, $Z_{i'}(k+1)$. For each step i' the chain generation counter $F_{i'}$ is then defined and set to $F_{i'}=m_{i'}$. After calculating F_i from $i'=i$ to $i'=N$, we then start at $i''=N$ and work from N back to i. Each $F_{i''}$ is checked to determine if it is greater than unity. When $F_{i''}>1$ for $i''>i-1$, the i''th torsion is sampled once more and $F_{i''}$ is reduced by

FIG. 4. Convergence of the CCB and CCBB methods for $N=50$ (broken line) and $N=200$ (solid line) at $T_r=30$. (a) Free energy and (b) squared end-to-end distance.
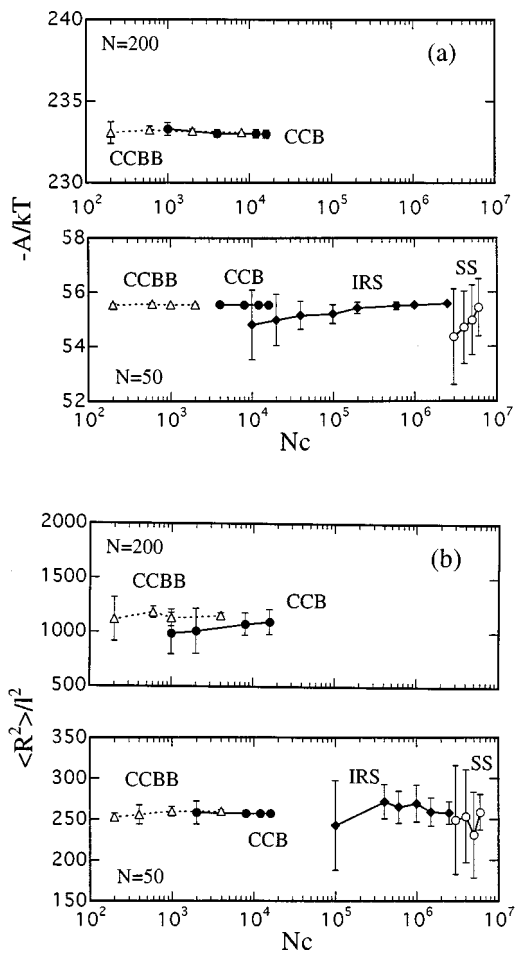

FIG. 5. Comparison of properties for $T_r=30$ and $N=50$. (a) Free energy and (b) end-to-end distance. Error bars show the standard deviations: SS (open circle), IRS (filled circle), CCB (triangle), and CCBB (open square).

unity. A new chain is grown from step i'' to N and a new value of $m_{i''}$ is evaluated for each step. The same procedure is repeated until there is no $F_{i''}$ larger than unity. At this point the $(k+1)$th cluster is completed, and the $(k+2)$th cluster can be started. The flow chart is shown in the Appendix.

V. EFFICIENCY

To compare the effectiveness of these various methods, we analyzed the distribution of sampled energies. In Fig. 2(a) the distributions of the logarithmic energy, $f(\log H)$, are compared for SS, IRS, and CCB. Here simulations were performed for a polymer with $N=50$ at $T_r=30$ (which corresponds to the Θ temperature). $f(\log H)$ is defined as the normalized occurrence rate of the total potential energy between $\log H$ and $\log H + d\log H$ during the course of a simulation. Figure 2 shows that CCB and CCBB place nearly all sampling points in the range ($H=10^{2.25}-10^{2.7}$) which contributes significantly to the Boltzmann factor. In contrast IRS leads to a maximum in the distribution function at $H=10^{10}$ (with only 0.1% of the points below $H=10^{2.7}$). SS leads to a

maximum in the distribution function at $H=10^{100}$ (with only 0.001% of the points below $H=10^{2.7}$). This shows clearly the high efficiency of CCBB sampling.

Figure 3 shows the rates of convergence for the Helmholtz free energy A and for the squared end-to-end distance $\langle R^2 \rangle$. These are evaluated from 10 independent runs for each method to obtain the standard deviation σ from the average value. The simulation conditions were the same as in Fig. 2. For an 0.1% level of uncertainty in A and $\langle R^2 \rangle$, IRS requires a factor of 400 fewer chains than SS while CCB requires a factor of 1300 fewer chains than IRS. Thus CCB requires a factor of 520 000 fewer chains than SS.

In Fig. 2(b) the $f(\log H)$ distributions are compared for CCB and for CCBB. Introduction of BFB into CCB shifts the peak of $f(\log H)$ lower by about 10% in $\log H$. As shown in Fig. 4, the convergence of A was accelerated by about 5 times for $N=50$ and 30 times for $N=200$. We see that BFB accelerates the convergence of $\langle R^2 \rangle$ by a factor of about 30 for $N=50$ and about 5 for $N=200$.

Extrapolating the results in Fig. 3, we estimate (see Table I) that to obtain an accuracy of 0.1% in A (for $N=50$) the number of chains required (N_c) is about 10^9 for SS, 1.7×10^6 for IRS, 10^3 for CCB, and 400 for CCBB.

Figure 5 shows the absolute values of the running average of A and $\langle R^2 \rangle$ for each method. Also shown are the
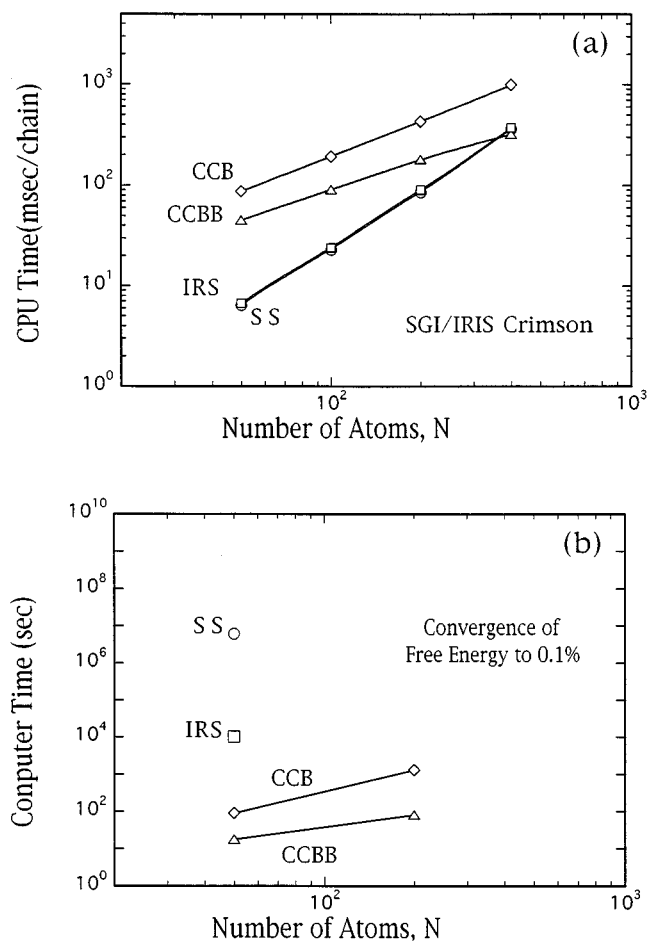

FIG. 6. Computation time for SS, IRS, CCB, and CCBB at $T_r=30$ (on the SGI IRIS CRIMSON). (a) The time per sample chain vs the number of atoms in a chain. (b) The time to obtain an accuracy of 0.1% in the free energy.
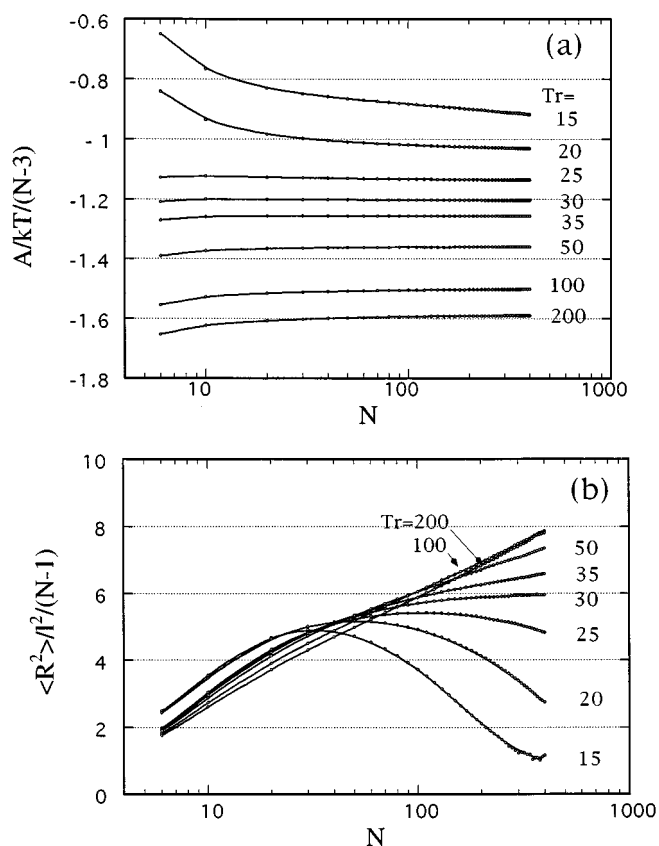

FIG. 7. Properties for various temperatures of isolated polyethylene chains as a function of the number of atoms. (a) Free energy, and (b) squared end-to-end distance. This indicates that the Θ temperature is about $T_r=30$.
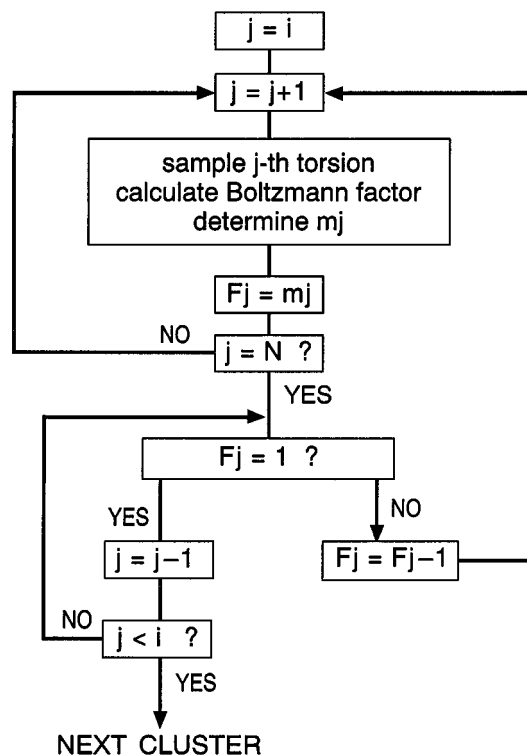
FIG. 8. The flow of BFB sampling.

We validated the bias correction for weighting the torsion and chain enrichments. Combining these two types of samplings (CCBB) dramatically improves MC convergence. This CCBB method provides the first practical approach for direct evaluation of the partition function for long polymer chains. It also allows evaluation of any configurational dependent physical properties simultaneously with the free energy.

This paper considered the simple model of an isolated single chain with a united atom force field. However, CCBB is easily extended to multichain systems, to more realistic force fields, and to the condensed state. For example, we have applied this method to evaluating the mixing free energy for polymer blends.[17]

APPENDIX

The flow of BFB sampling. (See Fig. 8.)

Initialize: Construct $\bar{Z}_i(0)$ $i=4,\ldots,N$. Denote as cluster $k=0$.

Start cluster $k=k+1$ with $i=4$.

uncertainties. The converged results coincide with each other, validating the bias correction for each method.

Figure 6 compares the dependence of the computation time per chain on the number of atoms, N. Table I uses these numbers to estimate the real time to converge A to 0.1% for $N=50$ and $T_r=30$. Introducing BFB into CCB reduces the computation time per chain dramatically since the chains are not all independent. In this case the average number of chains belonging to the same cluster is about ten. The result is that compared with a unit time for CCBB, CCB requires about 5 for the same 0.1% accuracy, while IRS requires about 600, and SS requires about 350 000. For larger systems the efficiency of CCBB increases relative to IRS or SS.

Figure 7 illustrates the results of evaluating A and $\langle R^2 \rangle$ using CCBB for a wide temperature range. From the proportionality of A and $\langle R^2 \rangle$ to the number of chain N, we expect the theta temperature of the model to be around $T_r=30$. Reference 13 reported similar plots for a simpler model of a continuous system. With CCBB we are able to treat a much longer chain at temperatures much further below the theta temperature, finding good convergence for both properties.

VI. CONCLUSION

This paper develops two highly efficient variants of the direct Monte Carlo method:

(i)   Continuous configurational biased (CCB) sampling and
(ii) Boltzmann factor biasing (BFB).

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