Incorporating configurational-bias Monte Carlo into the Wang-Landau algorithm for continuous molecular systems

Katie A. Maerzke,[1] Lili Gai,[1] Peter T. Cummings,[1,2] and Clare McCabe[1,3,a)]

[1]*Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, USA*
[2]*Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*
[3]*Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, USA*

Configurational-bias Monte Carlo has been incorporated into the Wang-Landau method. Although the Wang-Landau algorithm enables the calculation of the complete density of states, its applicability to continuous molecular systems has been limited to simple models. With the inclusion of more advanced sampling techniques, such as configurational-bias, the Wang-Landau method can be used to simulate complex chemical systems. The accuracy and efficiency of the method is assessed using as a test case systems of linear alkanes represented by a united-atom model. With strict convergence criteria, the density of states derived from the Wang-Landau algorithm yields the correct heat capacity when compared to conventional Boltzmann sampling simulations. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4766354]

I. INTRODUCTION

Monte Carlo (MC) simulations are a widely used tool for determining the structural and thermophysical properties of molecular systems. Simulations in the Gibbs ensemble[1,2] or grand canonical ensemble[3,4] with configurational-bias[5] (CBMC) enable the simulation of phase equilibria for complex molecular systems. In particular, MC simulations with configurational-bias have been used to calculate the phase equilibria of linear and branched alkanes[6–13] ring structures,[14–16] and other complex molecules with strong intramolecular potentials.[17–24] However, even with CBMC the simulations become challenging for very dense systems and/or very low temperatures, where adequately sampling phase space in a reasonable amount of simulation time is problematic. Numerous MC algorithms have been proposed to overcome this difficulty, including expanded ensemble,[25,26] parallel tempering,[27–30] umbrella sampling,[31] and multicanonical algorithms.[32,33]

A more recent method is the Wang-Landau algorithm,[34,35] which allows for the direct calculation of the density of states. The density of states, or degeneracy, can be used to calculate all thermodynamic properties at the conditions of interest, including the free energy, provided the relevant energy range has been sampled. To date, the Wang-Landau algorithm has been primarily used to study spin and lattice systems; however, some researchers have applied the method to continuous systems. For example, Yan *et al.*[36] and Shell *et al.*[37] used the Wang-Landau algorithm to calculate vapor-liquid coexistence curves for small systems of the Lennard-Jones (LJ) fluid. Faller *et al.*[38] studied a binary Lennard-Jones glass using the Wang-Landau method and Poulain *et al.* studied Lennard-Jones clusters.[39] Several

groups have used the Wang-Landau algorithm to study the collapse transition in fully flexible bead-spring and square well polymers,[40–45] for which adequate sampling can be obtained through single-bead displacements and other simple move types, and to study the folding of simple peptide models in vacuum or continuum solvent[39,46–48] where the conformational degrees of freedom are limited to the dihedral rotation of rigid side chains about the protein backbone. More recently, Yin and Landau have also studied the thermodynamics of water clusters using several different rigid water models.[49] For these systems with limited intra-molecular interactions, advanced moves, such as configurational-bias, are unnecessary.

In order for the Wang-Landau algorithm to be more broadly applicable to systems of chemical interest, the method must be able to sample the conformations of complex molecules with strong intramolecular potentials (i.e., bond stretching, angle bending, and/or torsional potentials). This can be done either through a modified Wang-Landau approach incorporating molecular dynamics[50,51] or through the addition of more advanced MC moves. Although several advanced MC algorithms for sampling the internal degrees of freedom of complex molecules exist, such as concerted rotation,[52] end bridging,[53] and pivot moves,[54] the most widely used is the CBMC method.[5] Since the off-lattice version of CBMC was first applied to linear chain systems,[6–8,55,56] we will also use linear alkanes as a test case for the applicability of CBMC to Wang-Landau simulations.

The remainder of this paper is organized as follows: we begin with a brief discussion of the Wang-Landau algorithm in Sec. II, followed by a more in-depth discussion of configurational-bias and its incorporation into a Wang-Landau simulation in Sec. III. The details of our simulations can be found in Sec. IV. We then discuss the importance of the appropriate choice of parameters in a Wang-Landau simulation in Sec. V A and the results of our simulations in

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a)Electronic mail: c.mccabe@vanderbilt.edu.

Sec. V B. The conclusions of this work can be found in Sec. VI.

II. WANG-LANDAU ALGORITHM

In a Wang-Landau simulation, configurations are sampled with a probability proportional to the reciprocal of the density of states,

$$P(U) \propto \frac{1}{\Omega(U)}, \qquad (1)$$

where Ω is the density of states or degeneracy. Obviously, the density of states is not known *a priori*; therefore, the simulation begins with a value of $\Omega(U) = 1$ for every U in the specified energy range. Although initially developed for spin systems with discrete energy levels, the algorithm can be applied to continuous systems by discretizing the energy. The simulation begins in a random configuration at an energy U_o (where $U_{min} \leq U_o \leq U_{max}$). A trial move generates a new state with energy U_n, which is accepted according to

$$\text{acc(o} \to \text{n)} = \min \left\{ 1, \frac{\Omega(U_o)}{\Omega(U_n)} \right\}. \qquad (2)$$

Note that the temperature no longer appears in the acceptance rule. This means that a single Wang-Landau simulation can be used to determine properties over a wide range of temperatures, provided that the relevant energy range is adequately sampled. After each move, the estimate of the density of states is updated with a modification factor, f,

$$\Omega(U) \to \Omega(U) \times f, \qquad (3)$$

where $f > 1$. Since the density of states spans many orders of magnitude, the natural logarithm of the density of states is typically calculated instead, such that

$$\ln \Omega(U) \to \ln \Omega(U) + \ln f. \qquad (4)$$

In addition to the density of states, a histogram (H) of visited states is also collected and incremented after each move

$$H(U) \to H(U) + 1. \qquad (5)$$

The simulation continues until the histogram is sufficiently "flat," that is, until each value of $H(U)$ is not less than a specified percentage of the average value of $H(U)$,

$$H(U) \geq p \times \langle H(U) \rangle, \qquad (6)$$

where p is the flatness criterion. When the histogram is "flat," the modification factor is reduced according to $f \to f^{1/2}$ or $\ln f \to \ln f/2$, the histogram entries are reset to zero, and the simulation is continued. Once the modification factor becomes less than some predetermined value, the simulation ends. We should note that since the density of states is continuously updated the Wang-Landau algorithm violates detailed balance; however, towards the end of the simulation the modification factor has become so small that detailed balance is essentially satisfied.

III. CONFIGURATIONAL-BIAS ALGORITHM

The CBMC algorithm is an extension of the self-avoiding random walk scheme proposed by Rosenbluth and Rosenbluth in 1955 for the simulation of lattice polymers.[57] In a CBMC move, an arbitrary number of segments, or beads, of the molecule are grown in a stepwise manner. Before a bead is grown a number of trial sites are generated and the Boltzmann weight of each trial site is computed. One of these trial sites is then selected based on its Boltzmann weight. Favorable configurations with large Boltzmann weights are chosen more often than unfavorable configurations with low Boltzmann weights. Since its development in 1990,[5] several variations of the CBMC algorithm have been proposed.[7, 12–14, 16, 20, 56, 58–60] For simplicity, the following discussion will focus on simple unbranched chains. For further details, the reader is referred to the overview in Frenkel and Smit[61] as well as the original papers.

When using CBMC, it is often convenient to split the potential energy into two parts, the internal, or bonded potential (U^{int}) and the external, or nonbonded potential (U^{ext}). The bonded potential, which may include the bending, stretching, and torsional potentials, is used to generate trial sites. The nonbonded potential is used to bias the selection of a trial site from the set of trial sites generated by the bonded potential. The way that the potential is separated into these two parts is completely arbitrary and may be adjusted for different applications in order to increase the efficiency of the method.

During a CBMC move, any portion of the chain, up to and including the entire chain, may be regrown. Let us consider the regrowth of a chain of s segments, or beads. Each segment l is grown consecutively until the chain is complete by first generating k trial orientations $\mathbf{b}_i$ according to the Boltzmann weight of the internal potential of the chain

$$P_{li}^{\text{generating}}(\mathbf{b}_i) d\mathbf{b} = \frac{e^{-\beta U_{li}^{int}} d\mathbf{b}}{\int e^{-\beta U_l^{int}} d\mathbf{b}} = C e^{-\beta U_{li}^{int}} d\mathbf{b}, \qquad (7)$$

where C is a constant of integration. One of the trial sites $\mathbf{b}_i$ for segment l is then selected according to the Boltzmann weight of its external potential

$$P_{li}^{\text{selecting}}(\mathbf{b}_i) = \frac{e^{-\beta U_{li}^{ext}}}{w_l(\text{n})}, \qquad (8)$$

where

$$w_l(\text{n}) = \sum_{j=1}^{k} e^{-\beta U_{lj}^{ext}} \qquad (9)$$

is the Rosenbluth weight of segment l. Once the entire chain of s segments has been grown, the Rosenbluth weight for the new configuration can be computed by multiplying the Rosenbluth weights of each segment

$$W(\text{n}) = \prod_{l=1}^{s} w_l(\text{n}) \qquad (10)$$

and the probability of making the transition from the old to the new configuration can be computed by multiplying the

probability of generating and selecting each segment

$$\alpha(\text{o} \to \text{n}) = \prod_{l=1}^{s} P_{li}^{\text{selecting}} P_{li}^{\text{generating}}, \qquad (11)$$

where i denotes the specific trial site that was selected. Substituting Eqs. (7) and (8) and recalling that $U = U^{\text{ext}} + U^{\text{int}}$ we find that

$$\alpha(\text{o} \to \text{n}) = \prod_{l=1}^{s} \frac{C e^{-\beta U(\text{n})}}{w_l(\text{n})}. \qquad (12)$$

In order to compute the acceptance probability for the new chain, the Rosenbluth weight W for the old configuration (o) must be computed. This is done in much the same way as for the new configuration, except that $k-1$ trial sites are generated and the kth orientation is the actual old configuration. Hence, the probability that each of the kth segments (that is, each of the segments in the old configuration) would have been generated is given by

$$P_{lk}^{\text{generating}}(\mathbf{b}_k)d\mathbf{b} = \frac{e^{-\beta U_{lk}^{\text{int}}}d\mathbf{b}}{\int e^{-\beta U_l^{\text{int}}}d\mathbf{b}} = C e^{-\beta U_{lk}^{\text{int}}}d\mathbf{b} \qquad (13)$$

and the probability of selecting each of the kth segments is

$$P_{lk}^{\text{selecting}}(\mathbf{b}_k) = \frac{e^{-\beta U_{lk}^{\text{ext}}}}{w_l(\text{o})}, \qquad (14)$$

where the Rosenbluth weight for segment l is given by

$$w_l(\text{o}) = \sum_{j=1}^{k-1} e^{\beta U_{lj}^{\text{ext}}} + e^{-\beta U_{lk}^{\text{ext}}}, \qquad (15)$$

where again $e^{-\beta U_{lk}^{\text{ext}}}$ is the actual external potential for the lth segment in the old configuration. The probability of making a transition to the old chain configuration starting from the new configuration is thus given by

$$\alpha(\text{n} \to \text{o}) = \prod_{l=1}^{s} \frac{C e^{-\beta U(\text{o})}}{w_l(\text{o})}. \qquad (16)$$

To derive the appropriate acceptance criteria, we must recall the condition of microscopic reversibility, which states that the number of moves to and from any given state i must be equal. In other words,

$$P(\text{o}) \alpha(\text{o} \to \text{n}) \text{acc}(\text{o} \to \text{n}) = P(\text{n}) \alpha(\text{n} \to \text{o}) \text{acc}(\text{n} \to \text{o}), \qquad (17)$$

where $P(i)$ is the probability of being in state i, $\alpha(i \to j)$ is the probability of proposing a move from state i to state j, and $\text{acc}(i \to j)$ is the probability of accepting the move. Unbiased moves, such as simple translations and rotations, are proposed with equal probability, and thus $\alpha(i \to j) = \alpha(j \to i)$. In a configurational-bias move, however, $\alpha(i \to j) \neq \alpha(j \to i)$.

A. Boltzmann sampling

In a conventional Metropolis-style simulation in the canonical ensemble, the probability of being in any given state i is

$$P(i) = \frac{e^{-\beta U_i}}{Q}, \qquad (18)$$

where Q is the canonical ensemble partition function and U_i denotes the potential energy of state i.[62] Now consider the growth of a single segment l. The probability of going from state o to state n is given by

$$P(\text{o}) \alpha(\text{o} \to \text{n}) \text{acc}(\text{o} \to \text{n}) = \frac{e^{-\beta U_{\text{o}}}}{Q} \frac{C e^{-\beta U_{\text{n}}}}{w_l(\text{n})} \text{acc}(\text{o} \to \text{n}) \qquad (19)$$

and the reverse probability is given by

$$P(\text{n}) \alpha(\text{n} \to \text{o}) \text{acc}(\text{n} \to \text{o}) = \frac{e^{-\beta U_{\text{n}}}}{Q} \frac{C e^{-\beta U_{\text{o}}}}{w_l(\text{o})} \text{acc}(\text{n} \to \text{o}). \qquad (20)$$

Imposing the condition of microscopic reversibility yields

$$\frac{\text{acc}(\text{o} \to \text{n}) w_l(\text{o})}{\text{acc}(\text{n} \to \text{o}) w_l(\text{n})} = 1 \qquad (21)$$

and hence the new segment is accepted with probability

$$\text{acc}(\text{o} \to \text{n}) = \min\left\{1, \frac{w_l(\text{n})}{w_l(\text{o})}\right\}. \qquad (22)$$

Notice that we do not need to know either the partition function or constant of integration. The acceptance probability for the entire chain of s segments is given by the product of the probabilities of the individual segments

$$\text{acc}(\text{o} \to \text{n}) = \min\left\{1, \prod_{l=1}^{s} \frac{w_l(\text{n})}{w_l(\text{o})}\right\} = \min\left\{1, \frac{W(\text{n})}{W(\text{o})}\right\}. \qquad (23)$$

B. Wang-Landau sampling

If instead we are performing a Wang-Landau simulation at constant density, from which we can calculate properties in the canonical ensemble, the probability of being in state i is given by

$$P(i) \propto \frac{1}{\Omega(U_i)}, \qquad (24)$$

where $\Omega(U)$ is the density of states or microcanonical ensemble partition function. For unbiased moves, the acceptance ratio is given by Eq. (2). For configurational-bias moves, we now have

$$P(\text{o}) \alpha(\text{o} \to \text{n}) \text{acc}(\text{o} \to \text{n}) = \frac{1}{\Omega(U_{\text{o}})} \frac{C e^{-\beta U_{\text{n}}}}{w_l(\text{n})} \text{acc}(\text{o} \to \text{n}) \qquad (25)$$

and

$$P(\text{n}) \alpha(\text{n} \to \text{o}) \text{acc}(\text{n} \to \text{o}) = \frac{1}{\Omega(U_{\text{n}})} \frac{C e^{-\beta U_{\text{o}}}}{w_l(\text{o})} \text{acc}(\text{n} \to \text{o}). \qquad (26)$$

Therefore, the appropriate acceptance probabilities are given by

$$\frac{\text{acc}(\text{o} \to \text{n})}{\text{acc}(\text{n} \to \text{o})} \frac{W(\text{o})}{W(\text{n})} \frac{\Omega(U_{\text{o}})}{\Omega(U_{\text{n}})} \frac{e^{-\beta U_{\text{o}}}}{e^{-\beta U_{\text{n}}}} = 1, \qquad (27)$$

or in other words,

$$\text{acc}(\text{o} \to \text{n}) = \min\left\{1, \frac{\Omega(U_{\text{o}})}{\Omega(U_{\text{n}})} \frac{W(\text{n})}{W(\text{o})} e^{\beta \Delta U}\right\}. \qquad (28)$$

The key point in this new acceptance rule is that temperature is now included – both in the Rosenbluth weights

and the energetic terms for the old and new configurations. In general, temperature is not specified in a Wang-Landau simulation, although alternate methods do include temperature explicitly.[63,64] Performing a simulation at an unspecified temperature is generally considered a strength of the algorithm. For instance, conventional MC simulations for a simple 3D lattice lipid model completely missed a second phase transition, which was easily identified using the Wang-Landau algorithm.[65] For lattice model simulations, one can employ a simplified version of CBMC in which the Rosenbluth weight is the ratio of available number of lattice sites to the total number of lattice sites, which eliminates the need for temperature;[65,66] however, simply counting available sites is not possible for continuous systems.

The simplest way to include temperature is to use the thermodynamic relationship

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} \tag{29}$$

since $S = \ln \Omega$ (to within a constant); however, there are several problems with this approach. First, we only have an accurate estimate of the density of states, and thus the temperature, towards the end of the simulation. Without a reliable value for the density of states, the temperature estimate fluctuates wildly, and can even become negative. Second, this relationship is only valid at constant density, which limits its applicability. Third, and most important, the old and new configurations may (and likely will) have different energies, which could lead to different temperatures. While one could adjust the acceptance rule to take into account a situation where $\beta_{\text{old}} \neq \beta_{\text{new}}$, this does not solve the problem. The configurational-bias regrowth proceeds bead-by-bead, which means we need to know both β_{old} and β_{new} at the start of the move. However, we do not know the energy of the new configuration, and thus also the new temperature, until the entire molecule is regrown.

Faller and de Pablo used a simple version of CBMC[66] to sample identity exchanges in a binary Lennard-Jones glass.[38] However, their acceptance rule did not include the factor of $e^{\beta \Delta U}$ derived in this work and in their calculation of the Rosenbluth weights it is unclear if they specify a fictitious temperature to calculate Boltzmann factors or use the density of states itself as a bias. Siretskiy *et al.* simulated semi-stiff polymer chains using a variant of CBMC which includes an extra term, called the "compaction factor."[67] If the compaction factor is set to 1, their acceptance rule is the same as that derived here; however, their study was limited to a single polymer chain with a fixed bond length. While more complex than fully flexible polymers, this semi-stiff chain is simpler than many molecular force fields which include additional intra-molecular potentials. Recently, Ngale *et al.* have incorporated CBMC into a variant of the Wang-Landau algorithm.[68] Although this work may initially appear similar to ours, their version of the Wang-Landau algorithm is significantly different from the more standard Wang-Landau method used here. Rather than calculate the density of states as a function of the energy ($\Omega(U)$), Ngale *et al.* calculate the canonical ensemble partition function ($Q(N, V, T)$) at a fixed number of molecules and temperature in order to calculate

the isobaric-isothermal partition function and thus determine points along the vapor-liquid coexistence curve. Since they are not performing a random walk in energy space, the CBMC acceptance rule is unchanged from that found in conventional simulations. Although this approach is useful for phase equilibria simulations, this version of the Wang-Landau algorithm loses much of its attractiveness at low temperatures.

Recently, Radhakrishna *et al.* have expanded on the work of Jain and de Pablo[66] and applied CBMC to a lattice system using a more complex biasing scheme, identical to that derived here, including the energetic factor and temperature.[69] They found that for simple lattice proteins they could specify a single "pseudo-temperature," which was used over the whole energy range. Although it is possible to perform Wang-Landau simulations for continuous systems with CBMC using a "pseudo-temperature," we find that the simulations are very inefficient and less accurate than simulations performed at a real temperature. Since the energy range is typically very large, a common way to increase the efficiency of a Wang-Landau simulation is to divide the system into multiple overlapping energy "windows," then patch together the resulting density of states in some *ad hoc* fashion. The efficiency of such a scheme depends on how evenly the workload of the windows is distributed. Finding the optimal division of the energy range is challenging, especially for systems with more complex MC moves.[70,71] Care must be taken when constructing the windows to ensure that each window has a sufficiently large range to sample all of the relevant configurations and prevent the system from becoming trapped in a metastable state.[37,45] Moreover, the best way of combining the results is unclear. Thus, we have taken an alternate approach and instead divide the system into multiple temperature windows with overlapping energies, where the specified energy range corresponds to the relevant energy range for the temperature of each window. We then use standard reweighting techniques[72,73] to combine the results in a systematic manner. We find that this results in more accurate and efficient simulations (see supplementary material[74]). Moreover, we find that the errors resulting from using a pseudo-temperature are increased as the chain length increases; thus, we anticipate that using a pseudo-temperature could lead to sampling problems for larger, more flexible molecules.

1. Temperature reweighting

To regain the ability to determine properties as a continuous function of temperature, we perform several simulations in the desired temperature range and then use histogram reweighting to join together the density of states. Although histogram reweighting is generally performed in the context of a grand canonical ensemble simulation,[75] the same technique can be applied in the canonical ensemble, where we reweight the energy distributions at several different temperatures. In the canonical (NVT) ensemble, the probability distribution function is $f(E)$, given by

$$f(E) = \frac{\Omega(N, V, E) \exp(-\beta E)}{Q(N, V, T)}, \tag{30}$$

where Q is the canonical ensemble partition function and Ω is the microcanonical ensemble partition function or density of states. By taking the natural logarithm of the above equation and rearranging the terms, we get

$$\ln \Omega = \ln f(E) + \beta E + C, \tag{31}$$

where C is a run-specific constant. In conventional simulations, one keeps track of a histogram $f(E)$, but in a Wang-Landau simulation we instead determine the density of states $\Omega(E)$.

If we perform simulations at several different temperatures with overlapping energy ranges, we can join the density of states (or histogram) data using the technique of Ferrenberg and Swendsen.[72,73] Say we have R overlapping histograms. The composite probability $\mathcal{P}(E; \beta)$ of observing the system at energy E for a specified temperature β is given by

$$\mathcal{P}(E; \beta) = \frac{\sum_{i=1}^{R} f_i(E) \exp(-\beta E)}{\sum_{i=1}^{R} K_i \exp(-\beta_i E - C_i)}, \tag{32}$$

where K_i is the total number of observations ($K_i = \sum_E f_i(E)$) for run i and C_i is a constant ("weight") for run i. The weights are obtained iteratively using the relationship

$$\exp(C_i) = \sum_E \mathcal{P}(E; \beta_i). \tag{33}$$

Once we know $\mathcal{P}$, we can calculate average thermodynamic properties, such as the potential energy

$$\langle U \rangle_\beta = \sum_E \mathcal{P}(E; \beta) E \tag{34}$$

as well as the square of the potential energy

$$\langle U^2 \rangle_\beta = \sum_E \mathcal{P}(E; \beta) E^2 \tag{35}$$

from which we can calculate the heat capacity as a continuous function of temperature using the standard fluctuation formula[76]

$$C_V(T) = \frac{\langle U^2 \rangle - \langle U \rangle^2}{k_B T^2}. \tag{36}$$

Note that we are neglecting the kinetic energy in this calculation and including both the intra- and intermolecular energy in U. While this means we cannot compare directly to experimental data, we can still compare the results from different MC methods, which is the primary focus of this work.

IV. SIMULATION DETAILS

Simulations were run for systems of linear alkanes, a relatively simple class of molecules that provide an excellent test case for configurational-bias moves.[6–8] We have deliberately chosen a simple molecular system in order to more easily compare the accuracy and efficiency of Wang-Landau and traditional Boltzmann sampling. The model used was the transferable potentials for phase equilibria – united atom (TraPPE–UA) force field.[10] For increased computational efficiency, the TraPPE–UA force field employs pseudoatoms for all CH_x groups (where $0 \le x \le 4$), which are located at the

TABLE I. TraPPE–UA parameters for linear alkanes.

Pseudo-atom	σ [Å]		ϵ/k_B [K]
CH_3	3.75		98.0
CH_2	3.95		46.0
Bond type	r_0 [Å]		
CH_x–CH_y	1.54		
Angle type	θ_{eq} [deg]		k_θ/k_B [K]
CH_x–CH_2–CH_y	114.0		62 500
Torsion type	c_0/k_B [K]	c_1/k_B [K]	c_2/k_B [K]	c_3/k_B[K]
CH_x–CH_2–CH_2–CH_y	0	335.03	-68.19	791.32

position of the carbon atom. The TraPPE–UA force field contains terms for bond stretching, angle bending, dihedral rotations, and nonbonded interactions. The bond lengths are fixed. The angle bending is represented using a harmonic potential

$$u_{bend}(\theta) = \frac{k_\theta}{2}(\theta - \theta_{eq})^2, \tag{37}$$

where θ is the bond angle, θ_{eq} is the equilibrium value for that angle, and k_θ is the force constant. Dihedral rotations are represented using a cosine series, which for the CH_x–CH_2–CH_2–CH_y torsion is given by

$$u_{tor}(\phi) = c_0 + c_1[1 + \cos(\phi)] + c_2[1 - \cos(2\phi)]$$
$$+ c_3[1 + \cos(3\phi)]. \tag{38}$$

Nonbonded interactions are described by pairwise-additive LJ interactions

$$u_{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], \tag{39}$$

where r_{ij}, ϵ_{ij}, and σ_{ij} are the separation, LJ potential well depth, and LJ diameter, respectively. The unlike LJ interactions are determined using the Lorentz-Berthelot combining rules[77]

$$\sigma_{ij} = \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \quad \text{and} \quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2}. \tag{40}$$

The TraPPE–UA parameters for linear alkanes can be found in Table I.

Simulations were run at constant density in the NVT ensemble with a simulation box length of 52 Å and 600 interaction sites, or 200 propane, 150 n-butane, 100 n-hexane, and 75 n-octane molecules. This results in a system with a constant density of approximately 0.1 g/mL which forms a dense vapor phase at high temperatures and a droplet at low temperatures. The phase transition temperature can be located by examining the heat capacity as a function of temperature. A spherical center-of-mass based cutoff of 14 Å with analytic tail corrections[78] was employed for the LJ interactions. The specific implementation of CBMC employed in this work is the coupled-decoupled dual-cutoff CBMC algorithm of Martin and Siepmann,[13] which has been used effectively with the TraPPE force field to simulate complex molecules.[18,19,21,23] The shorter cutoff for CBMC moves was 5 Å, and the number of trial sites k were $k_{LJ} = 10$, $k_{bend} = 1000$, and $k_{tor} = 100$ for LJ, bending, and torsional interactions, respectively. For further details on the specific

implementation of the algorithm, the reader is referred to the original paper.[13] For propane 20% of the moves were CBMC regrowths, whereas for the longer chains 1/3 of the moves were CBMC regrowths. The remaining moves were divided evenly between center-of-mass translations and rotations.

When performing a Wang-Landau simulation, one must carefully choose the parameters used to evaluate the convergence of the simulation; namely, the flatness criterion and the final modification factor. The flatness criterion controls when the modification factor will be updated, while the final modification factor controls when the simulation will end. It is important that these parameters are chosen to have values strict enough to produce reliable results, but that will also enable the simulation to finish in a reasonable amount of time. To this end, we have tested a variety of parameters for the propane system (see discussion below), which allowed us to determine that the modification factor should be updated when all the histogram entries are not less than 85% of the average and the simulation should end when the natural logarithm of the final modification factor is less than 10^{-6}. For all systems, an energy bin width of 200 K was used, resulting in 300–750 energy bins at each temperature, or 1300–2000 bins overall, where the number of bins increases as the chain length increases and as the critical temperature is approached. We found that the results were not strongly dependent on the size of the bin width, although for sizes much larger or smaller than 200 K the simulation time either increased (for smaller bins) or the accuracy decreased (for larger bins). The upper and lower bounds for the energy were determined from short conventional MC simulations over a 10 K interval. Since we were already performing conventional simulations for comparison (see below), this did not result in any extra effort on our part. However, in cases where traditional sampling is difficult, the energy ranges could be determined using the adaptive procedure of Tröster and Dellago.[79] Wang-Landau simulations were performed at 10 K intervals throughout the temperature range of interest, with a smaller interval of 5 K at temperatures below the critical point. We found that by using a smaller interval of 5 K below the critical point, where the energy distribution at each temperature is narrower, we could reduce the low temperature fluctuations in the heat capacity by a small amount (see supplementary material[74]). For higher statistical precision, four independent simulations were performed and the errors are reported as the standard deviation.

To validate our results, we performed additional simulations at select temperatures using conventional Boltzmann sampling, with the heat capacity calculated on-the-fly using the standard fluctuation equation (see Eq. (36)) where U is again the intra- and intermolecular potential energy. For these simulations, the reported results are the average of four independent 1×10^6 cycle runs.

V. RESULTS AND DISCUSSION

A. Parameterization

Using a relatively strict flatness criterion of $p = 80\%$, several values of the final modification factor were tested in order to find the optimal balance between efficiency and ac-
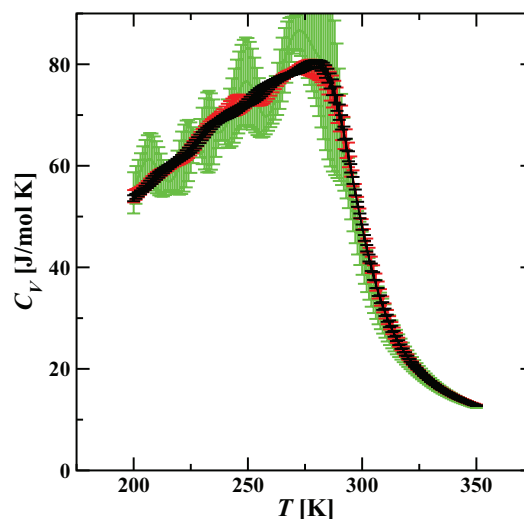

FIG. 1. Heat capacity curves for the propane system showing the effect of different final modification factors: final $\ln f = 10^{-8}$ (black), 10^{-6} (red), and 10^{-4} (green).

curacy. Although some researchers have used larger values of the final modification factor[37,38,47,48] (often accompanied by very strict flatness criteria), most recommend a value of 10^{-6} or smaller.[40,42–46,49] With a very large final $\ln f$ of 10^{-4}, the resulting heat capacity curve is found to be very noisy (see Figure 1). By decreasing the final $\ln f$ to 10^{-6}, much more satisfactory results are obtained, although the amount of simulation time required increases considerably (see Table II). By decreasing the final $\ln f$ even further to 10^{-8}, a heat capacity curve that is even smoother than the results with 10^{-6} is obtained, with even smaller error bars. However, the modest increase in precision does not compensate for the very large

TABLE II. Comparison of the efficiency of Wang-Landau convergence criteria for the propane system over a range of temperatures.

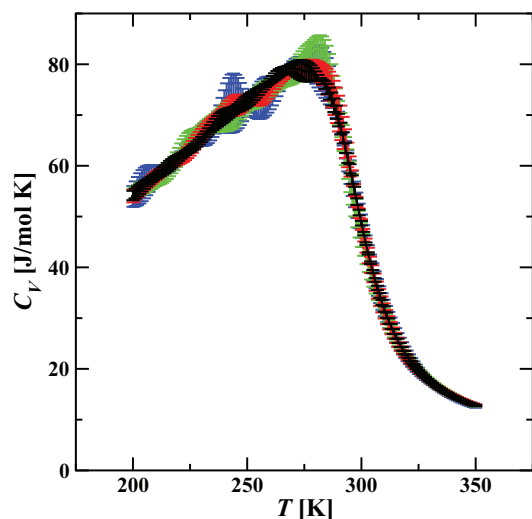| Flatness [%]	Final $\ln f$	T [K]	MC cycles
40	10^{-6}	200	$(6.4 \pm 1.2) \times 10^5$
		275	$(1.2 \pm 0.2) \times 10^5$
		350	$(3.6 \pm 1.7) \times 10^5$
60	10^{-6}	200	$(1.0 \pm 0.2) \times 10^6$
		275	$(2.2 \pm 0.5) \times 10^6$
		350	$(7.3 \pm 2.5) \times 10^5$
80	10^{-6}	200	$(3.3 \pm 0.9) \times 10^6$
		275	$(6.3 \pm 2.4) \times 10^6$
		350	$(1.0 \pm 0.3) \times 10^6$
85	10^{-6}	200	$(3.3 \pm 0.9) \times 10^6$
		275	$(8.7 \pm 1.9) \times 10^6$
		350	$(1.9 \pm 0.9) \times 10^6$
80	10^{-4}	200	$(3.7 \pm 0.6) \times 10^5$
		275	$(1.0 \pm 0.1) \times 10^6$
		350	$(2.3 \pm 0.2) \times 10^5$
80	10^{-6}	200	$(3.3 \pm 0.9) \times 10^6$
		275	$(6.3 \pm 2.4) \times 10^6$
		350	$(1.0 \pm 0.3) \times 10^6$
80	10^{-8}	200	$(9.1 \pm 2.1) \times 10^6$
		275	$(2.2 \pm 0.6) \times 10^7$
		350	$(3.3 \pm 1.3) \times 10^6$

FIG. 2. Heat capacity curves for the propane system showing the effect of different flatness criteria: $p = 85\%$ (black), 80% (red), 60% (green), and 40% (blue).
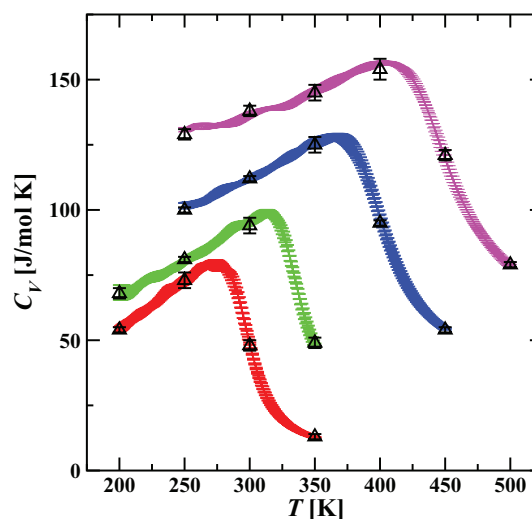

FIG. 3. Heat capacity curves for the propane (red), *n*-butane (green), *n*-hexane (blue), and *n*-octane (magenta) systems. Black triangles at select temperatures are the results from conventional Boltzmann sampling simulations.

increase in simulation time required for convergence. Thus, in agreement with previous work,[40, 42, 43, 45, 46] we find that a final value of $\ln f = 10^{-6}$ is a reasonable choice.

After determining the appropriate final modification factor, the effect of the flatness criterion on the results was tested. Although we began with a fairly strict value of 80%, we wanted to see if this value could be reduced in order to decrease the amount of simulation time required for convergence since many previous Wang-Landau simulations of continuous systems use very loose flatness criteria of 20%–40%[43–46] or only require each histogram entry to be visited a specified number of times;[37, 41] though others have determined that a stricter flatness criterion of 80%–90% is necessary.[38, 40, 47, 48] To determine an appropriate value for our systems, we tested flatness criteria of 40% and 60%, in addition to the 80% already used in determining the final modification factor. Reducing the flatness criterion does reduce the number of MC cycles required for convergence (see Table II); however, as can be seen in Figure 2, the resulting heat capacity curves are unsatisfactory, given the large fluctuations, especially for the system with $p = 40\%$. The heat capacity curve with a flatness of 80%, while smoother than the other curves, still had larger fluctuations than one might like. Thus, we ran an additional test with an even stricter flatness criterion of 85%. The resulting heat capacity curve has much smaller fluctuations with only a modest increase in the simulation time (see Table II). Thus, for the remaining simulations we have used a flatness criterion of 85% with a value of 10^{-6} for the final value of the natural logarithm of the modification factor.

B. Validation

To validate the proposed WL-CBMC method, additional simulations were performed for longer chains, namely, *n*-butane, *n*-hexane, and *n*-octane. From the results of these simulations, as shown in Figure 3, we find that our implementation of CBMC within a Wang-Landau simulation yields results for the heat capacity in excellent agreement with conventional Boltzmann sampling simulations. Each system

goes through a phase transition from a dense vapor phase ($\rho \approx 0.1$ g/mL) to a condensed droplet and the phase transition shifts to higher temperatures as the chain length increases. The heat capacity at each temperature increases as the chain length increases, in agreement with the findings of Bessières *et al.*[80]

Although both the Wang-Landau algorithm and conventional MC simulations yield the same results to approximately the same degree of accuracy, we also need to compare the efficiency of the two methods. Remembering that the Boltzmann sampling simulations were run for 10^6 MC cycles, it is easy to see from Table III that the Wang-Landau simulations require a larger amount of simulation time. Additionally, we find that the number of cycles required for convergence is strongly dependent on the initial conditions. Given that we do not know *a priori* which starting configuration will require the least (or most) cycles for convergence, it is difficult to predict exactly how many cycles will be required. Although the Wang-Landau algorithm does not offer any significant time-saving advantages for calculating the heat capacity of the systems examined here, it may be more attractive for low-temperature studies, such as supercooled liquids, glasses, and polymers, where conventional MC sampling is more problematic. To increase the efficiency of the algorithm, several researchers have proposed variants of the original Wang-Landau method.[39, 50, 63, 64, 81–85] The 1/*t* method of Belardinelli and Pereyra[85] has been shown to be particularly efficient for a variety of systems.[48, 86–88] Assessing the

TABLE III. Average number of MC cycles to convergence and average time (in s) for 10^6 MC cycles on a 2.26 GHz Intel Xeon Processor.

Molecule	T [K]	MC cycles	Time for 10^6 cycles [s]
Propane	275	$(8.7 \pm 1.9) \times 10^6$	1600 ± 300
Butane	315	$(5.1 \pm 0.9) \times 10^6$	4900 ± 400
Hexane	370	$(3.5 \pm 0.9) \times 10^6$	6900 ± 700
Octane	410	$(3.4 \pm 0.6) \times 10^6$	7300 ± 900

accuracy and efficiency of these different flavors of the Wang-Landau algorithm is beyond the scope of this work.

VI. CONCLUSIONS

Advanced Monte Carlo moves such as configurational-bias can be incorporated into the Wang-Landau algorithm by re-deriving the acceptance rule. For the CBMC move, this requires either a fictitious temperature for the entire energy range or specifying a real temperature with appropriate values for the upper and lower bound of the energy. We find that for continuous systems using a real temperature with reweighting results in greater accuracy and efficiency. Even so, conventional Boltzmann sampling simulations are more efficient than the Wang-Landau method for the systems studied in this work; however, the Wang-Landau algorithm may be more suited to low-temperature systems or other situations where conventional sampling becomes problematic. With the inclusion of CBMC, the Wang-Landau algorithm becomes applicable to more complex molecular systems.

ACKNOWLEDGMENTS

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[74]See supplementary material at http://dx.doi.org/10.1063/1.4766354 for four figures comparing the accuracy of using varying bin widths for propane (Figure S1) as well as real vs. pseudo-temperatures for propane (Figure S2), *n*-butane (Figure S3), *n*-hexane and *n*-octane (Figure S4), two tables comparing the efficiency varying bin widths for propane (Table SI)

and of real vs. pseudo-temperatures for all molecules studied (Table SII) and a figure showing the improved accuracy obtained by using smaller temperature intervals below the critical point (Figure S4).

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