

Prediction of Equilibrium Properties of Cyclic Alkanes by Monte Carlo Simulation—New Anisotropic United Atoms Intermolecular Potential—New Transfer Bias Method

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To predict equilibrium properties of cyclic alkanes using the Gibbs ensemble Monte Carlo method (GEMC), a new transfer move is proposed to sample the configuration space with efficiency. This new method, called reservoir bias Monte Carlo, consists of adapting the reservoir bias insertion in the grand canonical ensemble, proposed by Errington (Errington, *J. Chem. Phys.* **1999**, *111*, 9731), to the Gibbs ensemble. It is coupled with a preinsertion bias to favor transfer in the dense phase. Its application appears more efficient than the adaptation of the configurational bias Monte Carlo in the case of cyclic alkanes (Neubauer; et al. *Mol. Phys.* **1999**, *6*, 769). The anisotropic united atoms potential for linear alkanes proposed by Ungerer (*J. Chem. Phys.*, **2000**, *112*, 5499) has been partially optimized to describe the CH₂ group of cyclopentane and cyclohexane. The resulting parameters are close to those previously determined for linear alkanes. Simulations have been performed at temperatures ranging from 250 to 600 K for cyclopentane, cyclohexane, and cyclooctane. Equilibrium properties are quite well predicted, and critical properties can be evaluated with a good accuracy. It is concluded that the AUA potential, because of a relevant physical meaning, can be transferred to a large range of cyclic alkanes with good success.

Introduction

Prediction by molecular simulations is planned to be a serious complement to experimental measurements soon, to describe properly thermodynamic properties of pure compounds and mixtures. Monte Carlo methods or molecular dynamics have already been used to predict thermodynamic behavior, especially when the desired range of temperature or pressure is not easy to access and when the study of pure compounds is expensive.

Efficient modeling of fluid properties requires mainly two important items. On the one hand, the use of statistical mechanics with computers of limited capacity imposes the development of efficient algorithms. On the other hand, accuracy of predictions requires realistic and efficient potentials in order to describe properly intermolecular and intramolecular interactions. The aim of the present work is to improve both items in order to handle the special case of Monte Carlo simulations of liquid vapor equilibrium of cyclic alkanes in the Gibbs ensemble. Several efficient potentials and molecular insertion/deletion algorithms have been developed to represent the equilibrium properties of linear and branched paraffins.^{1–11} The parameters obtained thus from equilibrium data are similar to those obtained previously from second virial coefficient.¹² Light cyclic alkanes (from cyclopentane to cycloheptane) are also abundant molecular types in petroleum and natural gas.¹³ However, only few potentials and algorithms are available to describe such molecules in phase equilibrium.^{14,15} Yet, this represents an interesting challenge for many disciplines: first, the petroleum industry, second, biological chemistry, as cyclohexane ring represents the backbone for many sugars, terpenes, and steroids, and finally,

organic chemistry, because such cycles form part of many marketed compounds.

In the first part of this work, we implement a new algorithm to transfer a ring from one phase to another in the Gibbs ensemble. Indeed, the classical configurational bias method, proposed by Smit³ to transfer a linear or branched alkane from one phase to another and extended by Escobedo and al.,¹⁶ is poorly efficient, because closing the cycle puts hard constraints on the regrowth of the carbon chain. To solve this problem, a first solution could be to use rebridging techniques as proposed by Dodd et al.¹⁷ and Uhlherr.¹⁸ However, it is likely that rebridging methods will be poorly efficient for small cycles such as five- or six-membered rings, because the reconstructed segments would not be flexible enough. As an alternative strategy, we propose to transfer the complete cycle in a given conformation, taking care that statistically representative internal conformations are used. Such a method has been proposed by Errington¹⁵ in order to simulate cyclohexane and benzene in the grand canonical ensemble. This method, based on the use of a reservoir of relaxed conformations of cycles, is here adapted to transfer cyclic molecules from one phase to the other in the Gibbs ensemble. To favor the insertion of the transferred molecule in dense liquid phase, we add a preinsertion bias, aimed at finding “holes” in the liquid structure by several test insertions of a single force center of suitable size. This bias could be compared with the “cavity bias” developed by Mezei.¹⁹

In view of industrial applications of this work, it is also important that the potential used to describe interactions between cyclic molecules applies to numerous different molecules containing the same CH₂ group. More precisely, it is important that the same set of parameters can be used for several molecules. Existing potential parameters for cyclic alkanes are available only within the united atom (UA) model.^{14,15} In the second part of this work, we propose to use the anisotropic

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united atom (AUA)^{2,4} model because it should be a good compromise between calculation time, structural relevance, and transferability. Indeed, in this model, the CH₂ group is represented with only one force center located near the geometric center of the three atoms. Compared with all atoms potentials, this implies a significant reduction of calculation time (which depends on the square of the total number of force centers). Compared with united atoms potentials, the AUA model allows a more realistic description of molecules. Moreover, it has already been shown that the same set of Lennard-Jones parameters of the AUA potential allows the determination of several thermodynamic properties of short linear and branched alkanes, long linear alkanes, and also different mixtures of alkanes.^{10,20}

Ideally, Lennard-Jones AUA parameters of the CH₂ group for linear and branched alkanes should be directly transferable to cyclic alkanes. However, there are significant reasons that this ideal approach is not successful. Indeed, cycle closure produces specific torsion and bending constraints, which result in slightly different C–C–C and H–C–H average angles.²¹ It is thus likely that at least part of the Lennard-Jones parameters of the CH₂ group have to be modified. The second part of this work is thus dedicated to the optimization of a new set of parameters for the AUA Lennard-Jones model of the CH₂ group in all-cyclic alkanes. Two cyclic alkanes were chosen to perform the optimization: cyclopentane and cyclohexane.

Finally, in a third part, we present the evaluation of the optimized potential on the basis of a larger amount of data. We perform Gibbs ensemble^{22,23} and NPT ensemble²⁴ simulations of cyclopentane, cyclohexane, and cyclooctane in a large range of temperatures from 250 to 600 K. Several equilibrium properties as well as critical properties have been calculated (liquid densities, vaporization enthalpies, vapor pressures, critical density, and critical temperatures) and compared with previous results obtained with united atom potentials on Lennard-Jones or Buckingham exponential-6 descriptions.^{14,15} It is important to notice that only the experimental data from cyclopentane and cyclohexane were used to parametrize the new AUA potential. Consequently, cyclooctane simulation results constitute pure predictions.

Algorithm Development

Monte Carlo simulations are based on sampling the configuration space by generation of random configurations via elementary moves.²⁵ When describing liquid vapor equilibrium with the Gibbs ensemble,^{22,23} the key Monte Carlo move is the transfer of molecules from one phase to another. This allows getting the equality of chemical potentials between two phases without representing explicitly the interface. Nevertheless, the insertion of a large molecule in a dense phase requires efficient algorithms, because low energy location of a molecule is hardly found by generating strictly randomly molecular positions. Consequently, the simulation of large molecules needs statistical bias methods.

To predict equilibrium properties of linear and branched alkanes, the usual method is the configurational bias Monte Carlo method (CBMC)³. It consists of a stepwise regrowth of the chain, which takes into account the bending and torsional energy. Although cyclic alkanes exhibit the same kind of flexibility, they cannot be treated efficiently by the CBMC method. Indeed, the algorithm must include constraints during the regrowth to allow the closure of the molecule. This implies an increase of calculation time and a decrease of the acceptance rate of transfer moves. This is why in this work we

implement a new algorithm to transfer cyclic alkanes. This algorithm comprises two stages. The first stage (preinsertion bias) can be used for rigid molecules, and the second stage (reservoir bias) takes into account the fact that cycles are flexible molecules. Descriptions of those two biases are presented in the following paragraphs. Theoretical aspects and speed-up of the complete transfer move are presented later.

Preinsertion Bias. The aim of this first part of the transfer move is to find favorable places for insertion in the liquid structure. Consequently, in this paragraph, we consider a cycle as a rigid molecule, fixed in a particular internal conformation. Thus, the acceptance rate of transfer is limited only by the density of receiver phase; that is, the transfer occurs only if the insertion is attempted in a free space (a “hole” where insertion is possible with a low energy). To favor the discovery of a low energy location, we use a statistical bias. It consists of choosing randomly several places in the receiver phase and picking one on the basis of external energy of the molecule in this place. The bias could be realized with the real molecule, but energy calculation directly depends on the number of force centers on the molecule. As several molecular locations must be tested, calculation time becomes rapidly important. Consequently, during this step, we use a simplified potential composed of only one Lennard-Jones force center, located on the center of mass of the molecule, to approximate the interactions between the molecule and its environment. Thus, for a cyclohexane molecule in a phase containing 200 molecules, the number of distances that have to be calculated decreases from 7200 to 1200. Calculation time is divided by a factor equal to the number of force centers in the molecule. The optimal Lennard-Jones parameters of the simplified potential have to be determined by a specific study, as will be discussed later.

We can imagine two other improvements of the preinsertion bias. The first consists of using the same simplified description to represent all of the molecules in the receiver phase during the preinsertion bias. However, preliminary tests with cyclohexane have proved that this strategy was unefficient, and it has been therefore abandoned. The second improvement consists of using a reduced cutoff distance to evaluate the simplified potential in the receiver phase. The reduced cutoff is set to $(2)^{1/2}\sigma$ where σ is the Lennard-Jones diameter of the simplified potential, so that only the interactions with the nearest force centers are considered. As this procedure provides a moderate but significant speed-up, it has been used throughout this study.

Reservoir Bias. The second step of the transfer bias consists of inserting the entire molecule in the place found by the preinsertion bias, in an internal conformation randomly chosen. As mentioned before, it is impossible to construct with efficiency a cycle in a few steps in a dense phase, even if the insertion place in the dense phase is favorable. Consequently, one way to spend less time in the insertion is to pick up a conformation in a reservoir previously built for this purpose. We propose to adapt to the Gibbs ensemble the insertion method proposed by Errington in the grand canonical ensemble.¹⁵ To increase the success probability, we choose several conformations in the reservoir, and we select one on the basis of the total interaction energy with the environment.

To build an appropriate reservoir, a first problem is that it is impossible to store the infinity of internal conformations of a cyclic alkane. Indeed, the Metropolis algorithm,²⁶ which allows us to consider the Markov chain as a representation of the configuration space, requires that any internal conformation can be chosen. This can be solved by a periodic update of the reservoir.¹⁵ Thus, a reservoir containing N conformations,

updated X times during the run, is a trick to represent a larger reservoir of NX conformations.

A second problem is to select the most adapted probability distribution of the reservoir. There are two possibilities to insert a molecule in a realistic conformation. The first way is to use a reservoir with a uniform probability distribution. Then we could pick a conformation randomly in the reservoir and accept it with its Boltzmann probability at temperature T . The second way is to construct with a Monte Carlo procedure a reservoir where each conformation appears with its Boltzmann probability. We choose to implement the second method, as Errington did, because it avoids construction and storage of numerous unlikely conformations. Also, it allows controlling reservoir validity through the energy distribution and through the occurrence of the various conformers.

Theoretical Aspects. This section is dedicated to the theoretical development of the acceptance probability of reservoir bias transfer moves. To follow the Metropolis algorithm, microreversibility must be respected. It means that to establish the Markov chain with the desired probability density ρ the probability π_{ab} of changing from state a to state b is given by

$$\rho_a \pi_{ab} = \rho_b \pi_{ba}$$

In the case of an unbiased scheme with the use of the Metropolis criterion, the following expression can be applied:

$$\pi_{ab} = \frac{1}{\Omega} P_{\text{acc}}(a \rightarrow b)$$

where Ω is the number of accessible states and the acceptance probability expresses as

$$P_{\text{acc}}(a \rightarrow b) = \min\left(1, \frac{\rho_b}{\rho_a}\right)$$

When a biased Metropolis scheme is used, the transition probability includes the fact that the probability to generate a configuration is not equal for all configurations. Consequently

$$\pi_{ab} = \frac{P_{\text{gen}}(a \rightarrow b)}{\Omega} P_{\text{acc}}(a \rightarrow b)$$

and the acceptance probability satisfying microscopic reversibility is

$$P_{\text{acc}}(a \rightarrow b) = \min\left(1, \frac{P_{\text{gen}}(b \rightarrow a)\rho_b}{P_{\text{gen}}(a \rightarrow b)\rho_a}\right)$$

where P_{gen} is the ratio of the probability of generating the move in the biased ensemble to the probability of generating it in the unbiased ensemble. For configurations favored by the bias, $P_{\text{gen}} > 1$.

It imposes that the acceptance probability of such a transfer move follows the expression

$$P_{\text{acc}}(\text{new}) = \left[\frac{P_{\text{gen}}(\text{old}) * \rho(\text{new})}{P_{\text{gen}}(\text{new}) * \rho(\text{old})} \right] \times \left(\frac{N(\text{donor})V(\text{receiver})}{(N(\text{receiver}) + 1)V(\text{donor})} \right) \quad (1)$$

where $P_{\text{gen}}(\text{old})$ is the ratio between the probability to generate the old configuration with bias and without bias, $P_{\text{gen}}(\text{new})$ is the ratio between the probability to generate the new configuration with bias and without bias, V and N respectively are the

volume and the number of molecules in each box before the transfer, and

$$\rho(\text{new}) = \exp\{-\beta[U_{\text{elec}}(\text{new}) + U_{\text{LJ}}(\text{new}) + U_{\text{ind}}(\text{new}) + U_{\text{corr}}(\text{new}) + U_{\text{int}}(\text{new})]\} \quad (2)$$

$$\rho(\text{old}) = \exp\{-\beta[U_{\text{elec}}(\text{old}) + U_{\text{LJ}}(\text{old}) + U_{\text{ind}}(\text{old}) + U_{\text{corr}}(\text{old}) + U_{\text{int}}(\text{old})]\} \quad (3)$$

U_{elec} is the electrostatic energy, U_{LJ} is the Lennard-Jones interaction energy, U_{ind} is the induction energy, U_{corr} is the tail correction energy, and U_{int} is the internal energy of a configuration (new or old), i.e., the ensemble of the two boxes. It is important to notice that, in the particular case of pure cycloalkanes simulations, neither electrostatic nor induction interactions are taken into account.

Although a single Rosenbluth factor appears in the expression of the acceptance probability of classical bias procedures,²⁵ every bias introduces its own Rosenbluth factor in our algorithm. Moreover, the fact that $P_{\text{gen}}(\text{old})$ and $P_{\text{gen}}(\text{new})$ are not equal implies that their evaluation is critical. It requires considering the transfer algorithm in several steps, to establish the expression of $P_{\text{acc}}(\text{new})$.

(1) First, in the old configuration, we randomly choose and delete one molecule in one of the two phases. The molecule will be called the transferred molecule, and the phase it comes from, the donor phase (in opposition with the receiver phase).

(2) In the receiver phase, we randomly pick up k positions. For each position i , the intermolecular energy $\bar{U}_{\text{LJ}}(i)$ is calculated with the simplified potential. That represents the interaction between the provisional Lennard-Jones force center and the molecules located near the randomly chosen position.

One of these positions is chosen on the basis of the probability:

$$P_1(n) = \frac{\exp[-\beta\bar{U}_{\text{LJ}}(n)]}{W_1^{\text{new}}} \quad (4)$$

with

$$W_1^{\text{new}} = \sum_{i=1}^k \exp[-\beta\bar{U}_{\text{LJ}}(i)] \quad (5)$$

This position is called n .

(3) On this position n , in the receiver phase, we try to insert k' conformations randomly taken in the reservoir. For each conformation, the external energy $U_{\text{ext}}(j) = U_{\text{LJ}}(j) + U_{\text{elec}}(j)$ is calculated. In this step, all force centers are taken in account, and U is calculated with the real potential.

One of these conformations is chosen on the basis of the following expression:

$$P_2(N) = \frac{\exp[-\beta U_{\text{ext}}(N)]}{W_2^{\text{new}}} \quad (6)$$

with

$$W_2^{\text{new}} = \sum_{j=1}^{k'} \exp[-\beta U_{\text{ext}}(j)] \quad (7)$$

This conformation is called N . The probability to generate the

new configuration is given by

$$P_{\text{gen}}(\text{new}) = P_1(n) P_2(N) P_{\text{res}}(N) \quad (8)$$

where $P_{\text{res}}(N) = \exp[-\beta U_{\text{int}}(N)]/C$ is the probability density of the conformation N in the reservoir, $U_{\text{int}}(N)$ is the internal energy of conformation N , and $C = \sum_{i=1}^{\mathcal{N}} \exp[-\beta U_{\text{int}}(i)]$, where \mathcal{N} is the total number of conformations in the reservoir.

So,

$$P_{\text{gen}}(\text{new}) = \frac{1}{W_1^{\text{new}} W_2^{\text{new}} C} \exp\{-\beta[\bar{U}_{\text{LJ}}(n) + U_{\text{ext}}(N) + U_{\text{int}}(N)]\} \quad (9)$$

(4) To evaluate $P_{\text{gen}}(\text{old})$, we first generate in the donor phase $k - 1$ positions. The probability to choose the position of the transferred molecule (the old position, called o) is

$$P_1(o) = \frac{\exp[-\beta \bar{U}_{\text{LJ}}(o)]}{W_1^{\text{old}}} \quad (10)$$

with

$$W_1^{\text{old}} = \sum_{i=1}^k \exp[-\beta \bar{U}_{\text{LJ}}(i)] \quad (11)$$

(5) On this position o , in the donor phase, we try to insert $k' - 1$ conformations randomly taken in the reservoir. The probability to pick up the conformation of the transferred molecule (the old conformation called O) is

$$P_2(O) = \frac{\exp[-\beta U_{\text{ext}}(O)]}{W_2^{\text{old}}} \quad (12)$$

with

$$W_2^{\text{old}} = \sum_{j=1}^{k'} \exp[-\beta U_{\text{ext}}(j)] \quad (13)$$

Finally, the probability to generate in the same way the old configuration is

$$P_{\text{gen}}(\text{old}) = P_1(o) P_2(O) P_{\text{res}}(O) \quad (14)$$

where $P_{\text{res}}(O)$ is the probability density of conformation O in the reservoir

$$P_{\text{gen}}(\text{old}) = \frac{1}{W_1^{\text{old}} W_2^{\text{old}} C} \exp\{-\beta[\bar{U}_{\text{LJ}}(o) + U_{\text{ext}}(O) + U_{\text{int}}(O)]\} \quad (15)$$

It is important to note that the factor C defined here must include $U_{\text{int}}(O)$. To realize a theoretically correct transfer move, this imposes that either the old conformation O is included in the reservoir, or the real factor C taken in expressions (9) and (15) is $C = C' + \exp[-\beta U_{\text{int}}(O)]$, with $C' = \sum_{i=1}^{\mathcal{N}} \exp[-\beta U_{\text{int}}(i)]$. In those two ways, it appears that the factor C does not need to be evaluated.

As $U_{\text{int}}(\text{new}) - U_{\text{int}}(\text{old}) = U_{\text{int}}(N) - U_{\text{int}}(O)$ and $U_{\text{ext}}(\text{new}) - U_{\text{ext}}(\text{old}) = U_{\text{ext}}(N) - U_{\text{ext}}(O)$, it is now possible to evaluate

the acceptance probability:

$$P_{\text{acc}}(\text{new}) = \min\left(1, \left[\frac{W_1^{\text{new}} W_2^{\text{new}}}{W_1^{\text{old}} W_2^{\text{old}}} \exp\{-\beta[U_{\text{ind}}(\text{new}) + U_{\text{corr}}(\text{new}) - \bar{U}_{\text{LJ}}(\text{new}) - U_{\text{corr}}(\text{old}) - U_{\text{ind}}(\text{old}) + \bar{U}_{\text{LJ}}(\text{old})]\} \right] \frac{N(\text{donor})V(\text{receiver})}{(N(\text{receiver}) + 1)V(\text{donor})} \right) \quad (16)$$

Optimal Parameters and Resulting Speed-Up. During the preinsertion step, the transferred molecule is represented as a single Lennard-Jones force center, and thus, two parameters have to be defined. The values of those parameters are directly linked with the nature of the molecule. From systematic tests with cyclohexane, it has appeared that the energetic parameter ϵ_{LJ} does not have a significant influence. On the contrary, the diameter parameter σ_{LJ} represents the global volume of the molecule, and its influence is more important. Indeed, the higher the value of σ_{LJ} is, the larger the chosen places are. Consequently, the insertion is easier, and the rate of accepted transfers increases with the value of σ_{LJ} . Nevertheless, the selection of an excessive value for σ is not so good. It appears that, if σ_{LJ} represents a sphere greater than the molecule, the system cannot easily converge toward equilibrium. Indeed, if molecules are transferred only in large free places, other moves such as translations and rotations are needed to reach the equilibrium density. As a consequence, σ_{LJ} should be chosen approximately as the smallest dimension of the molecule. For rings from five to eight carbon atoms, the value of σ_{LJ} was optimized to 5.0 Å.

The number of attempted positions k and k' have been set to 10 in all of our simulations. No attempt has been made to optimize these parameters.

The reservoir of ring conformations is initialized at the beginning of the simulation and composed of 5000 different conformations. To perform internal relaxation of cycles, we used the internal rotation move described in ref 20. The initial reservoir is built as follows. A first conformation is constructed applying 20 internal rotations to a planar cycle; the second is constructed applying 20 internal rotations to the first conformation, etc. Then, the reservoir is updated every 20 000 Monte Carlo moves by applying 20 internal rotations on each conformation. This way of building the reservoir allows for the obtaining of the equilibrium distribution of conformations at a given temperature. The energy distribution shows for example that the chair conformation is more abundant than the boat and twisted conformation in the well-known case of cyclohexane.

Using the reservoir bias transfer algorithm, the acceptance rate increases by an order of magnitude compared with the CBMC method of Neubauer.¹⁴ For instance, in a simulation of phase equilibrium of cyclohexane at 450 K, this method increases the acceptance rate from 0.5% (CBMC) to 5.5%. Although a transfer attempt requires more computing time with the reservoir bias algorithm than with configurational bias, the computer time needed to accept 1000 transfers is divided by approximately a factor 3 with the reservoir bias. As the extent of probing the configuration space is primarily controlled by the number of accepted transfers, it is a good indicator of simulation accuracy. Thus, we can state that the overall speed-up provided by the new algorithm is approximately a factor three at constant accuracy.

It is also important to note that the algorithm developed here can be used not only for cyclic molecules but also whenever configurational bias is useless. Indeed, the reservoir bias transfer can be used for any rigid or poorly flexible molecule because

its two-stage procedure provides efficient selection of favorable places in the liquid and testing of various molecular orientations. This is for instance the case of rigid polar molecules such as water, CO₂, and H₂S, for which reservoir bias transfer is analogous to the algorithm of Cracknell et al.²⁷ More generally, the reservoir bias transfer is likely to be efficient with linear or branched molecules, provided their shape is sufficiently condensed and they present a moderate number of different conformations. In practice, this should be particularly the case of small size molecules with a skeleton of two, three, or four carbon atoms bearing functional groups. Thus the method is applicable to a large variety of olefins, alcohols, ketones, etc.

Potential Optimization

Optimization Method. An optimization of a special set of AUA parameters for “cyclic CH₂” (it means CH₂ group of cyclic alkanes) could appear unnecessary considering the transferability of parameters for “linear CH₂” already optimized.¹⁰ Indeed, it has already been shown that the same parameters could predict with accuracy equilibrium properties of short, long and branched alkanes.²⁰

As a consequence, we have first tried to predict equilibrium properties of cyclohexane with CH₂ parameters for linear alkanes. Although low temperature densities are reasonably reproduced, the representation of equilibrium properties is poor on average. More precisely, the simulated coexistence curve with this set of parameters is shifted by approximately 50 K toward lower temperatures compared with the experimental curve. The optimization of a new set of parameters for cyclic CH₂ appears thus necessary.

Nevertheless, from a chemical point of view, the CH₂ group of cyclic alkanes is quite similar to the CH₂ group of linear alkanes. We can infer that a small modification of the AUA force center parameters should be sufficient. Thus, we practice a partial optimization of the potential, keeping the diameter parameter σ constant, to compare the two types of force centers.

Using the optimization method proposed by Ungerer,¹⁰ we determine the energy parameter ϵ and the carbon to center of force distance δ , on the basis of three equilibrium properties: liquid density, vaporization enthalpy, and saturation pressure. As cyclopentane and cyclohexane are much more abundant in industrial fluids than cyclic alkanes with more than six carbon atoms, we optimize the selected parameters on the basis of experimental data of those two molecules at two different temperatures. As described in ref 10, we perform GEMC simulations of cyclopentane at 400 K and cyclohexane at 450 K and NPT simulations of cyclopentane at 300 K and cyclohexane at 346.15 K in order to define the following dimensionless error criterion:

$$F = -\frac{1}{n} \sum_{i=1}^n \frac{(X_i^{\text{mod}} - X_i^{\text{exp}})^2}{s_i^2}$$

where X_i^{exp} is the reference experimental measurement²⁸ (either $\ln(P_{\text{sat}})$, ΔH_{vap} , or ρ_l) and s_i is the estimated statistical uncertainty on the computed variable X_i^{mod} ($s_i = 0.1$ for $\ln(P_{\text{sat}})$, $s_i = 0.5$ kJ/mol for ΔH_{vap} , and $s_i = 10$ kg/m³ for ρ_{liq}). F is considered as a function of the two parameters to optimize, namely, the interaction energy parameter ϵ_{CH_2} and the carbon to center distance δ_{CH_2} . This definition of the error criterion is a way to obtain the maximum likelihood optimum.

Simulation Details. Every phase in the system is represented by a cubic simulation box using periodic boundary conditions

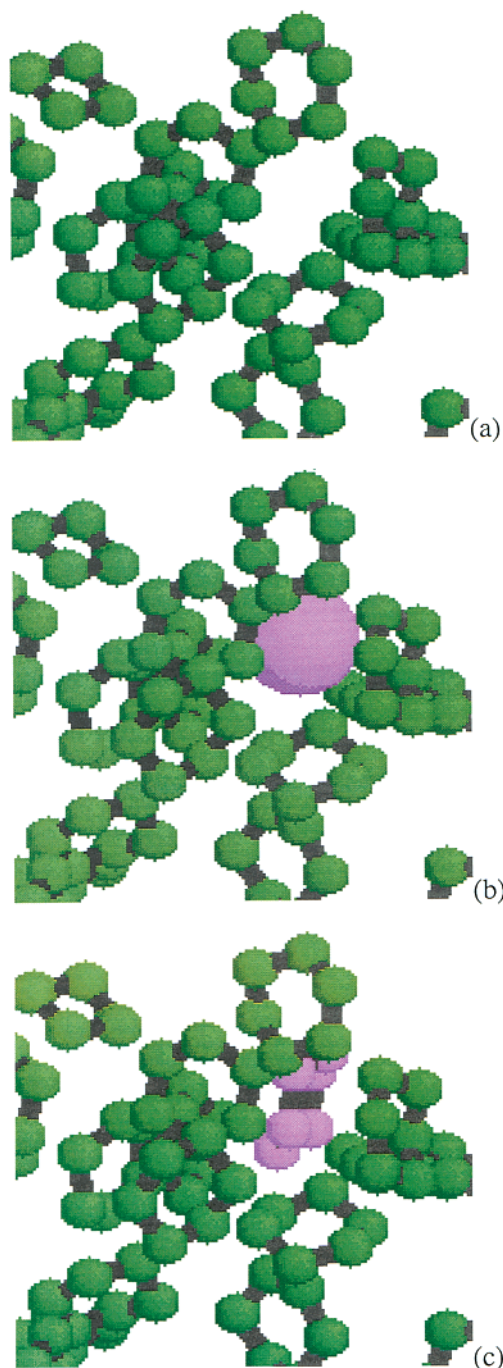


Figure 1. Snapshot of a simulation box (receiver phase) before transfer move (a), during preinsertion bias (b), and during reservoir bias (c). This is a simulation of cyclohexane at 500 K.

to avoid boundary effects. The thermal equilibrium in a box is assured by three types of random Monte Carlo moves, which comprise translation and rotation to change position and orientation of the molecules, and internal relaxation to change conformation of cycles. The latter consists of a single rotation of an atom in a cycle, as described in a previous work for long linear alkanes.²⁰ Both ensembles (NPT ensemble and Gibbs ensemble) require volume change moves, with a constraint for the Gibbs ensemble by the fact that the global volume of the two boxes must stay constant. Simulations in the Gibbs ensemble make use of the reservoir bias transfer move as described in the first section. The occurrences of the various moves are the same as those used for alkanes in ref 20, i.e., 0.695 for transfers, 0.1 for translations, rotations, and internal

TABLE 1: Lennard-Jones Parameters of the CH₂ Group for Linear¹⁰ and Cyclic Alkanes (This Work)

	σ (Å)	ϵ/k (K)	δ (Å)
CH ₂ (linear alkanes)	3.461	86.29	0.384
CH ₂ (cyclic alkanes)	3.461	90.09	0.336
LJ center for preinsertion bias	5.0	10.0	

TABLE 2: Parameters for Molecular Weight, Carbon to Carbon Distance, Bending Potential, and Torsion Potential

MW (g/mol)	CH ₂		14.03
C–C distance (Å)			1.535
bending	C–CH ₂ –C	θ_0 (deg)	114
		k_{bend} (K)	74900
torsion	C–CH ₂ –CH ₂ –C ^a	a_0 (K)	1001.35
		a_1 (K)	2129.52
		a_2 (K)	–303.06
		a_3 (K)	–3612.27
		a_4 (K)	2226.71
		a_5 (K)	1965.93
		a_6 (K)	–4489.34
		a_7 (K)	–1736.22
		a_8 (K)	2817.37

^a Reference 4.

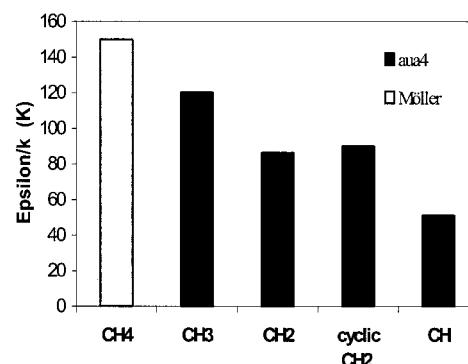
relaxations, and 0.005 for volume changes. With the exception of the simplified potential used in the preinsertion bias, a cutoff radius of 10 Å was used, using standard long-range corrections.²⁵ We chose a system size of about 200 molecules.

The intermolecular interactions were modeled via a 6–12 Lennard-Jones potential U_{LJ} with parameters optimized in this work and presented in Table 1. We used the same model to describe interactions between nonbonded atoms in cyclooctane (i.e., atoms separated by more than three bonds). As usual in the AUA approach, the force centers are located on the external bisector of the angle formed by the neighboring bonds.

The bonded interactions between force centers are then given by two terms. The usual expression for the bending potential $U_{\text{bend}}/k = 1/2 k_{\text{bend}}(\theta - \theta_0)^2$ has been modified, to use an expression including $\cos(\theta)$ easier for computer calculations.^{2,4} Consequently, we used $U'_{\text{bend}}/k = 1/2 k'_{\text{bend}}[\cos(\theta) - \cos(\theta_0)]^2$ for the bending potential. We determined the parameters k'_{bend} so that the second expression is identical to the usual one within second-order approximation with the standard value $k_{\text{bend}} = 62\,500$ K. The resulting values is $k'_{\text{bend}} = 74\,900$ K. The general expression for the torsion potential $U_{\text{tors}}/k = \sum_{j=0}^8 a_j (\cos \Phi)^j$ has been taken identical to Toxvaerd,⁴ where Φ is the torsion angle with reference to the most stable conformation (i.e., $\Phi = 0$ in the trans position). The same parameters a_j were unchanged (see also Table 2).

In accordance with ref 10, the carbon–carbon distance has been set to 1.535 Å.

The desired equilibrium properties (vapor pressure, molar vaporization enthalpy, and saturated liquid density) were computed by averaging after the stabilization period. Vapor pressure was taken as the average pressure in the vapor simulation box. The molar vaporization enthalpy was computed as the difference between the average molar enthalpies of liquid and vapor simulation boxes. The average liquid density was determined directly as the ratio of the average mass of the liquid simulation box and its volume. These three properties were generally determined with a statistical uncertainty of respectively 5%, 1%, and 0.5% in the favorable reduced temperature range for Gibbs ensemble method, i.e., for $0.6 < T/T_c < 0.95$. The critical temperature was obtained by fitting the critical scaling law $\rho_l - \rho_g = \lambda(T_c - T)^{0.325}$. The law of rectilinear diameters was used to estimate the critical densities.

**Figure 2.** Energetic parameter for the Lennard-Jones potential ϵ/k of the CH₂ group for cyclic alkanes and CH₂, CH₃, and CH groups for linear and branched alkanes used in the AUA4 potential.^{10,20} (CH₄ parameter taken from ref 30.)

To extend the computation of vapor pressure to lower temperatures, we have integrated the Clapeyron equation as proposed by Kofke,²⁹ using a second order integration scheme with regularly spaced $1/T$ values:

$$\ln P_{\text{sat}}^{(n+1)} = \ln P_{\text{sat}}^{(n-1)} - \frac{\Delta H_{\text{vap}}^{(n)}}{R} \left(\frac{1}{T^{(n+1)}} - \frac{1}{T^{(n-1)}} \right) \quad (17)$$

For reduced temperatures lower than 0.6, the molar vaporization enthalpy was estimated from a single monophasic simulation at constant pressure according to

$$\Delta H_{\text{vap}} \approx -E_{\text{liq}} + RT \quad (18)$$

where E_{liq} is the average molar intermolecular potential energy of the liquid simulation box.

The reasons for implementing this scheme and more simulation details can be found in refs 10 and 20. As equilibrium pressures are known to be lower than 100 kPa, for reduced temperatures lower than 0.6, we have performed the NPT simulations at $P = 0$. Indeed, the influence of this approximation is negligible compared with statistical uncertainties for pure liquids in such conditions.

Optimization Results. The optimization method allows us to minimize the error function from $F = 7.9$ with the set of parameters given by the CH₂ group of linear alkanes, to $F = 1.52$ with the new set of parameters presented in Table 1. We can note that the energetic parameter is changed by less than 5% (Figure 2), which supports the physical relevance of the AUA model. In the same way, the δ parameter is changed only by 0.048 Å compared with linear alkanes (Figure 3). The small decrease of δ can be explained by the main difference between cyclic and linear alkanes: the tension of cycle. Indeed, this tension implies a modification of the C–C–C angles. This modification induces a similar change on the H–C–H angle, which is directly linked with the δ parameter, if we consider that the AUA force center is expected to be close to the geometrical center of the three atoms. For instance, the H–C–H angle changes from 114° on a linear CH₂ group, to 106° on cyclopentane and 107.5° on cyclohexane.²¹ So the decrease of δ can be explained qualitatively from these geometrical considerations.

Prediction of Cyclic Alkane Properties

To test the accuracy of the new set of parameters and the efficiency of the new reservoir bias transfer move, we have performed simulations of cyclopentane, cyclohexane, and cy-

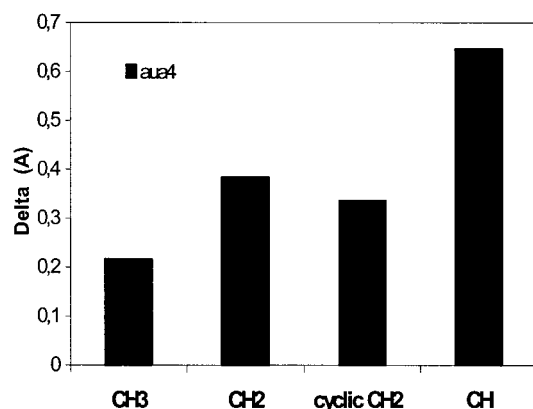


Figure 3. Carbon to center distance δ of the CH₂ group for cyclic alkanes and CH₂, CH₃, and CH groups, used in the AUA4 potential.^{10,20}

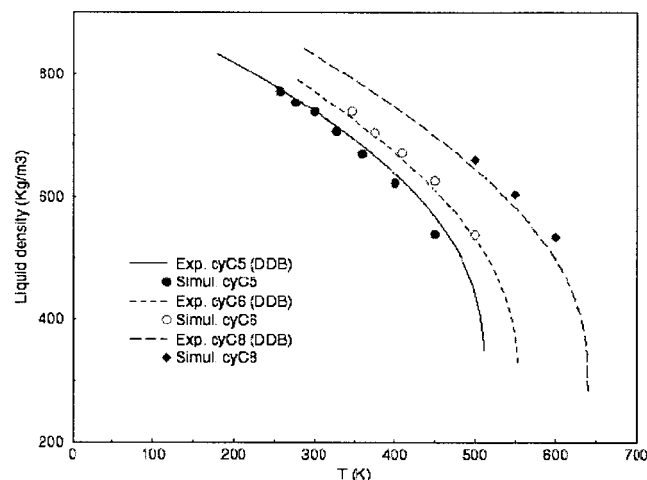


Figure 4. Saturated liquid densities obtained by simulation for the three cyclic alkanes studied in this work, compared with experimental data from the Dortmund Data Bank.²⁸

cyclooctane in a large temperature range. The study of small cyclic alkanes with less than seven carbon atoms presents a real interest in industrial applications, because they frequently appear in heavy molecules such as alkyl-cycloalkanes, Decalin, naphtho-aromatic compounds, terpenoids, steroids, etc. The interest of larger cyclic alkanes is more academic, because they are less abundant in natural fluids. Nevertheless, the prediction of equilibrium properties of cyclooctane allows the validation of the potential for larger cyclic alkanes.

Figures 4–6 show the calculated values respectively of liquid densities, molar vaporization enthalpies, and vapor pressures for cyclopentane, cyclohexane, and cyclooctane, compared with experimental data from Dortmund Data Bank correlations.²⁸ Table 3 presents calculated and experimental properties as well. For each compound, the three higher temperatures have been simulated in the Gibbs ensemble, whereas lower temperatures have been simulated in the NPT ensemble. In Figure 5, vapor pressures corresponding to lower temperatures have been calculated by thermodynamic integration.

We can note that simulation results are in good agreement with experimental data. Saturation pressures, which usually represent the most difficult properties to simulate, are predicted with an average error under 5%. The liquid density is a little underestimated in the case of cyclopentane, whereas it is overestimated for cyclohexane. Nevertheless, the estimated average error is not higher than 2%. The vaporization enthalpy is also well described. The slight underestimation obtained for

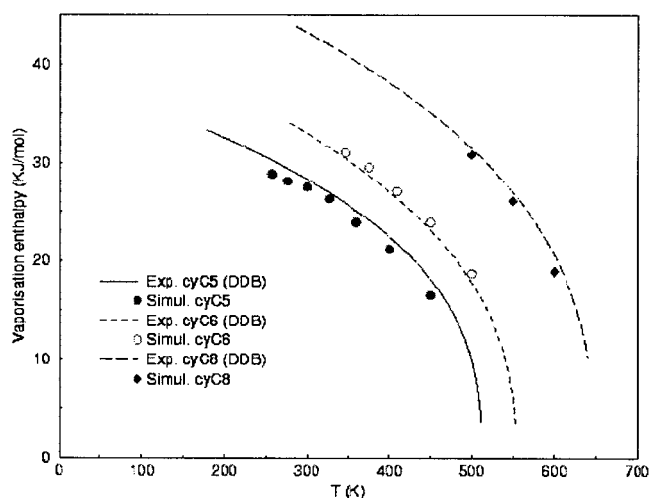


Figure 5. Vaporization enthalpies obtained by simulation for the three cyclic alkanes studied in this work, compared with experimental data from the Dortmund Data Bank.²⁸

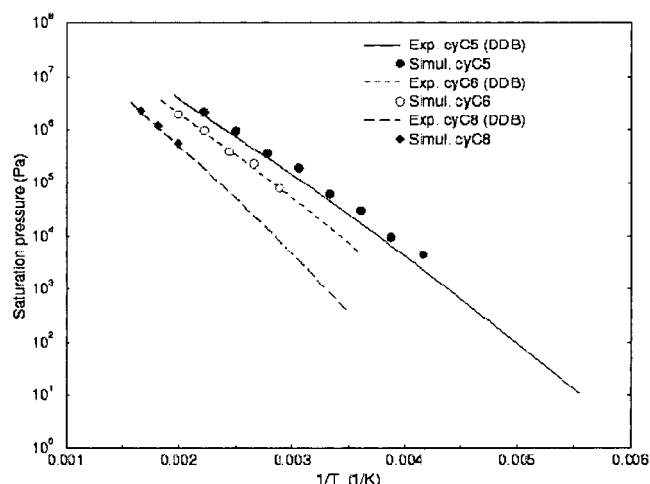


Figure 6. Vapor pressures obtained by simulation for the three cyclic alkanes studied in this work, compared with experimental data from the Dortmund Data Bank.²⁸

cyclopentane and cyclooctane, and the overestimation obtained for cyclohexane can be linked with the cycle constraint strength. Indeed, cyclopentane and cyclooctane have a high tension of cycle, whereas in cyclohexane, the cycle is almost not constrained. Because the optimization process has been performed using both a constrained and a nonconstrained cycle (i.e., cyclopentane and cyclohexane), the resulting parameters lead to a compromise. Consequently, the same trend, i.e., underestimation of vaporization enthalpy, is observed for the two constrained cycles.

This work provides a more accurate method to describe critical properties of cyclic alkanes than previous literature work. Indeed, critical temperatures are predicted with an average relative error of about 1%, and critical densities are predicted with an average relative error of less than 4% (Table 4). This corresponds to a shift of 3–5 K of the simulated coexistence curve compared with the experimental curve, underestimated for cyclopentane and overestimated for cyclohexane and cyclooctane.

We have compared results of this work with other recent results for cyclic alkanes. Compared with the United Atoms potential of Neubauer et al.,¹⁴ the AUA potential allows a major improvement as illustrated by the critical properties in Table 4. Errington and al.¹⁵ have used a Buckingham exponential-6

TABLE 3: Simulation Results Obtained with New Potential and New Transfer Bias for Cyclopentane, Cyclohexane, and Cyclooctane^a

<i>T</i> (K)	simulation	properties	calculated values	expt values
Cyclopentane				
450	Gibbs	P_{sat}	2160	1814
		ΔH_{vap}	16.5	18.1
		ρ_l	539.9	567.6
400 ^b	Gibbs	P_{sat}	944	741
		ΔH_{vap}	21.2	22.4
		ρ_l	622.3	638.2
360	Gibbs	P_{sat}	355	300
		ΔH_{vap}	23.9	25
		ρ_l	669.6	682.9
327.27	NPT	ΔH_{vap}	26.3	26.9
	monophasic $P=0$	ρ_l	707.4	715
300 ^b	NPT	ΔH_{vap}	27.5	28.3
	monophasic $P=0$	ρ_l	738.2	739.7
276.97	NPT	ΔH_{vap}	28.1	29.3
	monophasic $P=0$	ρ_l	753.4	759.2
257.22	NPT	ΔH_{vap}	28.8	30.2
	monophasic $P=0$	ρ_l	771.6	775
Cyclohexane				
500	Gibbs	P_{sat}	1950	2020
		ΔH_{vap}	18.7	17.8
		ρ_l	538.8	532.2
450 ^b	Gibbs	P_{sat}	975	913
		ΔH_{vap}	23.9	23.1
		ρ_l	626.1	610.8
409.09	Gibbs	P_{sat}	387	411
		ΔH_{vap}	27.1	26.4
		ρ_l	671.8	661.7
375	NPT	ΔH_{vap}	29.5	28.7
	monophasic $P=0$	ρ_l	705.1	699
346.15 ^b	NPT	ΔH_{vap}	31	30.4
	monophasic $P=0$	ρ_l	739	728.3
Cyclooctane				
600	Gibbs	P_{sat}	2320	2117
		ΔH_{vap}	18.9	20.6
		ρ_l	535	498.2
550	Gibbs	P_{sat}	1190	1082
		ΔH_{vap}	26.1	26.9
		ρ_l	604	582.5
500	Gibbs	P_{sat}	556	493
		ΔH_{vap}	30.8	31.4
		ρ_l	660	645.5

^a Saturated liquid densities (ρ_{liq}) are expressed in kg m⁻³, vaporization enthalpies (ΔH_{vap}) are expressed in kJ mol⁻¹, and vapor pressures (P_{sat}) are expressed in kPa. The experimental data are taken from the Dortmund Data Bank.²⁸ ^b Reference points used for the optimization of the potential parameters are related to the cyclic CH₂ group.

TABLE 4: Critical Temperatures and Critical Densities Calculated on the Basis of Simulations Results Compared with Experimental Data Taken from Reference 28 and Previous Simulation Results Obtained by Neubauer and al.¹⁴

	<i>T_c</i> (K)			ρ_c (kg/m ³)		
	this work	expt (DDB)	previous work	this work	expt (DDB)	previous work
cyclopentane	507 ± 5	511.8	477	275 ± 10	271.3	268
cyclohexane	559 ± 5	553.6	532	271 ± 10	272.7	309
cyclooctane	647 ± 5	640	607	303 ± 10	282.8	324

potential, optimized on the basis of experimental data of cyclohexane. Critical properties and liquid densities of cyclohexane are better predicted by Errington's simulations, with deviations less than 0.5 K. However, these parameters have not been tested for other cyclic alkanes. Moreover, it appears that cyclohexane vaporization enthalpies and saturation pressures are predicted with a comparable accuracy in this work and in ref 15.

Conclusion

While our previous work^{10,20} on the anisotropic united atom potential was dedicated to linear and branched alkanes, the present study has extended this kind of potential to cyclic alkanes. Its main achievements are a general set of parameters for cyclic alkanes and a new transfer bias algorithm (called reservoir bias transfer) in order to perform efficient gibbs ensemble simulations with such molecules.

The new algorithm allows a very significant improvement, because it increases the acceptance probability of GEMC transfers by a factor of 10 compared with our previous configurational bias procedure. As a result, the net speed-up on the whole simulation time is approximately a factor three at constant accuracy. The proposed algorithm developed here is not applicable only to cyclic molecules but also to many rigid or poorly flexible molecules. This for instance the case of polar molecules such as H₂O, CO₂, and H₂S and small organic molecules with a limited number of possible conformations.

On the basis of cyclopentane and cyclohexane, the optimization of the cyclic CH₂ potential parameters has led to a good agreement with experimental data for these compounds. Small parameter changes have been found compared with linear alkanes, which supports the physical relevance of the anisotropic united atoms model. The agreement between our simulated properties and experimental data is similar to the Buckingham exp-6 model of Errington,¹⁵ which is specific for cyclohexane. Simulation results are also in good agreement with experimental data in the case of cyclooctane, which was not considered in the optimization procedure. As a result, the new potential performs much better than the united atoms potential of Neubauer et al.¹⁴ for the three molecules tested so far. This is an interesting perspective for future industrial applications in which predictions are desired on more complicated molecules. An extension of this work will be thus the test with larger rings, with alkyl substituted cyclic alkanes, and the prediction of properties of industrial fluids composed of several different saturated hydrocarbons.

This perspective will require the optimization of quaternary carbon parameters, which is the last missing step to provide a complete set of transferable parameters for saturated hydrocarbons within the anisotropic united atoms potential. A further perspective will be the optimization of functional alkanes (alcohols, ethers, ketones, etc.) and other cyclic compounds (aromatics, thiophenes, etc.).

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