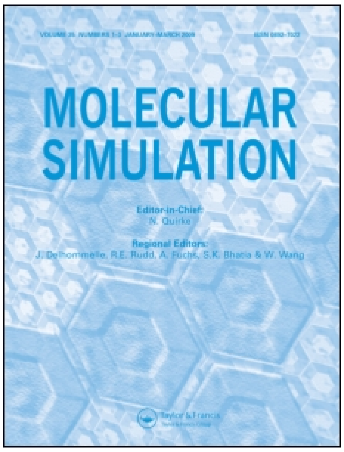

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Monte Carlo simulation of branched alkanes and long chain n -alkanes with anisotropic united atoms intermolecular potential

Emeric Bourasseau[a,b]; Philippe Ungerer[a,b]; Anne Boutin[a]; Alain H. Fuchs[a]
[a] Laboratoire de Chimie Physique, UMR 8000 CNRS, Université Paris-Sub, Orsay Cedex, France [b] Institut Français du Pétrole, Rueil-Malmaison Cedex, France

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MONTE CARLO SIMULATION OF BRANCHED ALKANES AND LONG CHAIN *N*-ALKANES WITH ANISOTROPIC UNITED ATOMS INTERMOLECULAR POTENTIAL

EMERIC BOURASSEAU[a,b] *, PHILIPPE UNGERER[a,b], ANNE BOUTIN[a] and ALAIN H. FUCHS[a]

[a]*Laboratoire de Chimie Physique, UMR 8000 CNRS, Université Paris-Sub,*
bâtiment 349, 91405 Orsay Cedex, France; [b]*Institut Français du Pétrole,*
1–4 Avenue de Bois Préau, 92852 Rueil-Malmaison Cedex, France

The anisotropic united atoms potential for linear alkanes proposed by Ungerer (*J. Chem. Phys.*, **112**, 5499, 2000), called AUA4, has been used to predict several equilibrium properties (vapour pressure, vaporisation enthalpies, and liquid densities) of alkanes by Gibbs ensemble Monte Carlo simulation. In order to extend the potential to branched alkanes, potential parameters for the CH group have been determined by optimisation on the basis of equilibrium properties of isobutane, keeping the same parameters as AUA4 for the CH_3 groups. The resulting CH parameters form a regular sequence with those previously determined for CH_3 and CH_2 groups, so that a physically consistent parameter set is obtained.

Simulations have been performed at temperatures ranging from 450 to 800 K for long *n*-alkanes (C20, C25 and C30) and from 350 to 450 K for four heptane isomers (*n*-heptane, 2-methylhexane, 2,4-dimethylpentane and 2-ethylpentane). In order to achieve internal relaxation of long chains with a good efficiency, a specific Monte Carlo move was used in which a united atom is rotated around its nearest neighbours. Equilibrium properties of long chain alkanes are well predicted, and small differences between heptane isomers are represented with a good accuracy. It is concluded that the AUA4 potential shows an interesting degree of transferability.

Keywords: Gibbs ensemble Monte Carlo simulations; Anisotropic united atoms potential; Long linear alkanes; Branched alkanes

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*Corresponding author.

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INTRODUCTION

Efficient modelling of fluid properties by molecular simulation for industrial needs mainly requires two important items: first, a reliable theoretical framework, given by statistical mechanics, and second, realistic and efficient potential models to describe intermolecular and intramolecular interactions in complex fluids. The present work is aimed at improving the second item, which is often found to be the limiting factor of prediction accuracy. It is dedicated to linear and branched alkanes, which are abundant molecular types in crude oils and manufactured products. As thermodynamic properties are poorly known in the case of heavy compounds in these families, there is a particular need for prediction methods.

At present, the limited capacity of computers prevents us from efficiently using all atoms descriptions (AA potential), in which each atom is represented by a separate Lennard–Jones force centre (for instance carbon and hydrogen atoms in the case of alkanes). Consequently, several authors have proposed United Atom (UA) potentials, where a group like CH_2 or CH_3 is represented by a single force centre. Such potentials represent equilibrium properties with a good accuracy, especially for *n*-alkanes [1–4] and branched alkanes [5,6].

Nevertheless, a step has been made in the realism of such potentials with the use of the Anisotropic United Atom (AUA) description proposed by Toxvaerd [7,8] for *n*-alkanes. While each force centre is located on the carbon in the more classic United Atoms potentials, the force centre is shifted in the AUA potential, so that it is placed between the carbon and hydrogen atoms of the related group. Furthermore, it appeared possible to optimize simultaneously the CH_2 and CH_3 Lennard–Jones parameters, in order to describe differently those two types of force centres in AUA potential. The resulting potential, called AUA4 [9], has permitted equilibrium properties of short *n*-alkanes (from ethane to dodecane) to be predicted with a good accuracy on the basis of a unique set of parameters. It also appeared that long chain *n*-alkanes such as *n*-eicosane were not so well described, presumably because the Monte Carlo algorithm was not achieving a sufficient internal relaxation of the chain.

In view of industrial applications of molecular simulation, it is very important that the same potential applies to numerous different molecules containing the same groups, i.e. that its transferability is acceptable. If transferability is not satisfied, time-consuming parameter calibration would be required if a well-documented compound is investigated, and extrapolation capability would be poor in the case of poorly documented compounds. In the present work, it is proposed to test AUA4 transferability by applying it to molecules other than those used to optimise the potential, without modifying any of its parameters. In the present work, we try to describe first long chains *n*-alkanes, and then branched alkanes. In reference [9], AUA4 has been tested for the *n*-eicosane (*n*-C20). As mentioned above, results were not satisfactory, probably because of an insufficient relaxation of long chains. In the present work, we implement a Monte Carlo move to relax internal configuration of chains containing more than ten carbon atoms. This improvement allows us to perform long simulations with important systems of long chains *n*-alkanes, and to test the adequacy of AUA4 potential with these systems. In order to extend the potential to branched alkanes, we use iso-butane to optimise AUA4 parameters of the CH group, using a similar fitting procedure as for CH_2 and CH_3 groups [9]. The transferability of this potential is then evaluated on the basis of results obtained for three isomers of *n*-heptane: 2-methylhexane, 2,4-dimethylpentane and 3-ethylpentane. Including theoretical discussions about the sequence formed by the parameters of the three groups, we perform test simulations, to predict equilibrium properties of selected branched alkanes.

These tests allow a large range of conditions to be investigated. On the one hand, long chain alkanes exhibit liquid densities close to those of polymers mixtures, and provide a severe test of the AUA4 potential in dense fluids. On the other hand, modelling heptane isomers allows the capacities of the AUA4 potential in predicting subtle property differences to be tested, since the boiling points of the investigated compounds lie within a 20–K range.

METHODS

Gibbs Ensemble Monte Carlo

To compute phase equilibria, we have mainly used the Gibbs ensemble Monte Carlo method (GEMC) at constant global volume introduced by Panagiotopoulos [10]. Details about algorithms, and configurational bias methods, used can be found elsewhere ([2], [11], and [12]), especially with regard to insertion bias, which is particularly important in the case of long molecules.

To perform simulations of long chain alkanes, we used a high transfer frequency (more than 0.745), due to the difficulty of inserting a molecule of 20 to 30 carbon atoms in a dense phase. In order to avoid simulations that were too long, we used a total number of 100 molecules per system.

The simulations of branched alkanes were performed with 200 molecules. The occurrences of the various moves were as detailed for *n*-alkanes in reference [9], i.e. 0.695 for transfers, 0.1 for translations, rotations and regrowth, and 0.005 for volume changes.

A cut-off radius of 10Å was used, using standard long range corrections [13]. The simulations lengths were of $5-12 \times 10^6$ iterations for the long chains alkanes, with a stabilisation of $5 \times 10^5-4 \times 10^6$ iterations, and of $2 \times 7-7 \times 10^6$ iterations for the branched alkanes, with a stabilisation of $4 \times 10^5-4 \times 10^6$ iterations.

The desired equilibrium properties (vapour pressure, molar vaporisation enthalpy and average liquid density) were computed by averaging after the stabilisation period. Vapour pressure was taken as the average pressure in the vapour simulation box. The molar vaporisation enthalpy was computed as the difference between the average molar enthalpies of liquid and vapour 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 favourable reduced temperature range for the Gibbs ensemble method, i.e. for $0.6 < \mathrm{T}/\mathrm{T}_\mathrm{c} < 0.95$. In the case of branched alkanes, the critical temperature was obtained by fitting the critical scaling law $\rho_\mathrm{l} - \rho_\mathrm{g} = \lambda(\mathrm{T}_\mathrm{c} - \mathrm{T})^{0.325}$. The law of rectilinear diameters was used to estimate the critical densities.

Thermodynamic Integration

As mentioned above, increasing the number of atoms in a molecule lowers the efficiency of transfer moves. In the same way, when temperature decreases, the Gibbs ensemble method becomes poorly efficient, particularly when reduced temperature is lower than 0.6. In order to extend the computation of vapour pressure to lower temperatures, we have integrated the Clapeyron equation as proposed by Kofke [14], using an integration scheme of second order with regularly spaced 1/T values [9]:

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

The molar vaporization enthalpy was then estimated from a single monophasic simulation at constant pressure according to:

$$\Delta H_{\mathrm{vap}} \approx -E_{\mathrm{liq}} + RT \tag{2}$$

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

The reasons of implementing this scheme can be found in reference [9].

Implementation of the Anisotropic United Atom Potential

To describe with AUA model a CH group linked with three carbon atoms C_1, C_2 and C_3, we place the force centre on the vector $\overrightarrow{T} = \overrightarrow{CC_1} + \overrightarrow{CC_2} + \overrightarrow{CC_3}$, as proposed in reference [15]. We could have placed the force centre on the normal of the plane formed by C_1, C_2 and C_3, but it would have appeared an uncertainty when the four carbon atoms are in the same plane.

The Lennard–Jones parameters of the AUA4 potential are shown in Table I, and other parameters in Table II. Parameters of CH_2 and CH_3 groups have been taken from reference [9], and parameters of the CH group have been optimised in this work as described later.

In accordance with reference [9], the carbon–carbon distance has been set to 1.535Å. The usual expression for the bending potential $U_{\mathrm{bend}}/k = (1/2)k_{\mathrm{bend}}(\theta - \theta_0)^2$ has been modified, in order to use an expression including

TABLE I Lennard–Jones parameters of AUA4 potential. CH_2 and CH_3 parameters are taken from reference [9], and CH parameters from this work. The carbon to carbon distance is set to 1.535Å

	σ (Å)	ϵk (K)	δ (Å)
CH	3.3625	50.98	0.64599
CH2	3.4612	86.29	0.38405
CH3	3.6072	120.15	0.21584

TABLE II AUA4 potential parameters for molecular weight, carbon to carbon distance, bending potential and torsion potential.

Molecular Weight (g/mol)	CH_3		15.03
	CH_2		14.03
	CH		13.03
C–C distance (Å)			1.535
Bending	C–CH_2–C	θ_0(deg)	114
		K_{bend}(K)	74900
	C–CH–C	θ_0(deg)	112
		K_{bend}(K)	72700
Torsion	C–CH2–CH2–C*	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
	C–CH2–CH–C†	c_1(K)	355.03
		c_2(K)	−68.19
		c_3(K)	791.35

* Reference [7].
† Reference [3].

$\cos(\theta)$ which is easier for computer calculations [7,8]. Consequently, we used $U'_{\mathrm{bend}}/k = (1/2)k'_{\mathrm{bend}}(\cos(\theta) - \cos(\theta_0))^2$ 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 for the standard value $k_{\mathrm{bend}} = 62500\,\mathrm{K}$. The resulting values are $k'_{\mathrm{bend}} = 74900\,\mathrm{K}$ for a bending angle centred on a CH_2 group and $k'_{\mathrm{bend}} = 72700\,\mathrm{K}$ for a bending angle centred on a CH group. This makes bond angles somewhat more rigid than in earlier work [7–9]. However, we did not detect any significant change in equilibrium properties.

The general expression for the torsion potential $U_{\mathrm{tors}}/k = \sum_{\mathrm{j}=0}^{8} \mathrm{a_j}(\cos\Phi)^{\mathrm{j}}$ has been taken identical to Toxvaerd [8], and the same parameters $\mathrm{a_j}$ were used for the dihedral angle composed of only binary carbon atoms. For the dihedral angles composed of at least one ternary carbon atom, the parameters $\mathrm{a_j}$ were determined so that the potential is identical to the expression $U_{\mathrm{tors}}/k = \mathrm{c}_1(1 + \cos\Phi) + \mathrm{c}_2(1 - \cos 2\Phi) + \mathrm{c}_3(1 + \cos 3\Phi)$ used by Martin and Siepmann [5].

Internal Relaxation of Carbon Atoms of Long Chains

The configurational bias method of Smit *et al.* [2] allows regrowth of a part of a chain, relaxing several force centres in just one move. However, we show in Fig. 1 that for the *n*-eicosane molecule, only six carbon atoms located in an end-segment can be efficiently relaxed by this technique. This means that for this

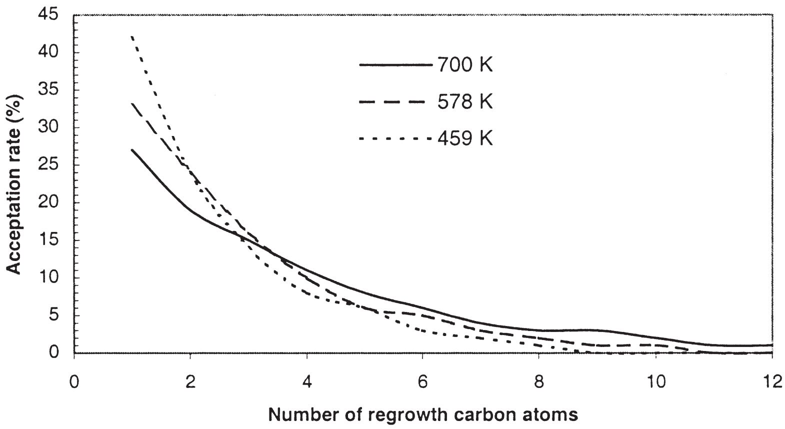

FIGURE 1 Acceptance ratio of classical configurational bias method as described in reference [2], vs. number of regrowth carbon atoms, for the *n*-eicosane molecule, and for 10 000 MC moves. Six insertion trials have been performed for every new centre in the growth process.

molecule, the innermost eight carbon atoms never change through regrowth, and are relaxed only by transfers. This problem worsens with increasing chain length since for *n*-pentatriacontane (35 carbon atoms), 23 force centres keep their internal configuration without transfer.

It is thus necessary to introduce an additional Monte Carlo move. In order to implement innermost atoms relaxation, Dodd [16] has proposed a concerted move of several force centres, applying a rotation around a dihedral angle. This implementation appeared quite successful, but needs a mathematical development that increases simulation time. Consequently, we choose to implement a simpler move. It consists of applying a rotation on one randomly chosen force centre around the axis formed by it neighbours.

In the first implementation, the rotation angle is chosen randomly between -0.5 and +0.5 radian, and the algorithm realises the move in a single step, which gives the acceptance probability as:

$$P_{\mathrm{acc}}(\mathrm{old} \rightarrow \mathrm{new}) = \min(1, \exp(-\beta(U^{\mathrm{new}} - U^{\mathrm{old}}))) \qquad (3)$$

where U^{new} is the new configuration energy, and U^{old} is the old configuration energy.

It is important to note that even if just one carbon atom is rotated, three AUA force centres are changed. So the acceptance probability is different with AUA and UA potential.

The width of the rotation angle interval must be selected with care. The smaller the bounds of the domain are, the higher the acceptance ratio is. However, if the interval is too small, the configuration space is not explored efficiently. In Fig. 2, we show that despite the maximum rotation angle of 0.5 radian, the whole spectrum of rotation angles is explored by the algorithm at two temperatures (350 and 700 K) representative of prospect applications. The resulting angle distribution is comparable with experimental distributions (see [8] and[18]) and exhibits the same dependence with temperature, i.e. an increasing proportion of cis configurations.

In a second implementation, we have tried to use a configurational bias technique [2]. It consists of generating a few configurations on the basis of their internal energy, and introducing intermolecular energy at the selection stage. This avoids the expensive determination of intermolecular energy for unrealistic configurations. Nevertheless, the algorithm introduced in this way needs three steps, and the resulting acceptance probability is quite different:

- In a first step, we generate k trial internal rotations. The set of k trial rotations are denoted $\{a\}_k = a_1, a_2, \ldots a_k$. The probability to generate each internal rotation is a function of the internal energy calculated with the more simple UA

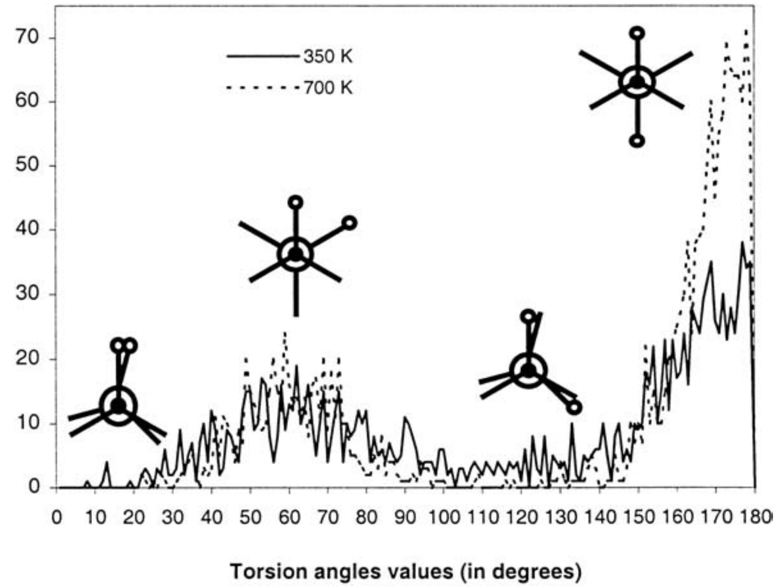

FIGURE 2 Angles distribution in a simulation of *n*-eicosane, composed of 100 molecules (1700 torsion angles), at two temperatures: 350 K and 700 K.

potential:

$$p^{\text{int}}(a_i) = \frac{\exp\left(-\beta u^{\text{int}(UA)}(a_i)\right)}{C} \tag{4}$$

• For each of these trials rotations the external energy is calculated with the UA potential, and we select one of these k configurations with probability

$$p^{\text{ext}}(a_i) = \frac{\exp\left(-\beta u^{\text{ext(UA)}}(a_i)\right)}{W^{\text{new}}} \tag{5}$$

where the Rosenbluth factor of the new configuration is:

$$W^{\text{new}} = \sum_{j=1}^{k} \exp\left(-\beta u^{\text{ext(UA)}}(a_j)\right) \tag{6}$$

• The Rosenbluth factor of the old configuration is determined in the same way, generating $(k-1)$ trials internal rotations denoted $\{b\}_k = b_1, b_2, \ldots, b_{k-1}$ (see reference[2])

$$W^{\text{old}} = \sum_{\text{j}=1}^{\text{k}-1} \exp\left(-\beta u^{\text{ext}(UA)}(b_j)\right) + \exp\left(-\beta u^{\text{ext}(UA)}(\text{old})\right) \tag{7}$$

and finally, according to Metropolis algorithm [17], the acceptance probability is taken as:

$$P_{\mathrm{acc}}(\mathrm{old} \rightarrow \mathrm{new}) = \min\left(1, \frac{W^{\mathrm{new}}}{W^{\mathrm{old}}} \exp\left(-\beta\left(\delta U^{\mathrm{new}} - \delta U^{\mathrm{old}}\right)\right)\right) \qquad (8)$$

where $\delta U = (u^{\mathrm{ext(AUA)}} + u^{\mathrm{int(AUA)}}) - (u^{\mathrm{ext(UA)}} + u^{\mathrm{int(UA)}})$ is the energy difference between the UA potential used in the configurational bias and the desired AUA potential.

Both implementations of the internal rotation have been tested, yielding the same distributions. It appears that the first one is clearly faster for long chains alkanes (see the simulations length in Results). As a consequence, the simulations related in this article have been made with the first implementation.

Parameters Determination, Optimisation Method

The reference component used to define the parameters of CH group is the isobutane for which the CH group represents 25% of the force centres in the molecule. Consequently, no torsion potential is needed. The Lennard–Jones parameters of the CH_3 group have been taken to be equal to those of the AUA4 potential taken from reference [9].

As described in reference [9], we introduce vaporization enthalpies, vapour pressures and liquid densities of reference component at three temperatures (180 K, 261.4 K and 340 K) as reference data. These properties have been taken from the Dortmund Data Bank correlations, after having checked that they were consistent with known properties such as normal boiling temperature and standard liquid density.

The lower temperature requires monophasic simulation in the NPT ensemble (T/T_c=0.44) to introduce liquid density and vaporization enthalpy, while simulation can be performed in the Gibbs ensemble for the two other temperatures. Finally, eight reference data are used and compared with the simulation results.

We used the optimisation method proposed in reference [9], i.e. we determined the parameters of the CH group by minimizing the following dimensionless error criterion:

$$\mathrm{F} = \frac{1}{n}\sum_{i=1}^{n} \frac{\left(X_i^{mod} - X_i^{\exp}\right)^2}{S_i^2}$$

where s_{i} is the estimated statistical uncertainty on the computed variable $X_{\mathrm{i}}^{\mathrm{mod}}$, while $X_{\mathrm{i}}^{\mathrm{exp}}$ is the associated experimental measurement (either $\ln(P_{\mathrm{sat}})$, ΔH_{vap}, or ρ_{l}). F is considered as a function of the three parameters to optimise, namely the interaction energy parameter ϵ_{CH}, the molecular diameter $\sigma\mathrm{CH}$, and the carbon to centre distance δ_{CH}. This definition of the error criterion is a way to obtain the maximum likelihood optimum.

In a first step we used an estimated set of parameters ($\epsilon_{\mathrm{CH}}/k = 55\,\mathrm{K}$, $\sigma_{\mathrm{CH}} = 3.36\mathrm{\AA}$ and $\delta_{\mathrm{CH}} = 0.5\mathrm{\AA}$), resulting in an error criterion of $\mathrm{F}^{1/2} = 3.05$. With the optimized set of parameters (Table I) the error criterion was reduced to $\mathrm{F}^{1/2} = 1.12$. The evolution of the ϵ parameter with the sequence CH_4, CH_3, CH_2, CH shown in Fig. 3 appears logical and regular. In the case of σ, the decreasing sequence shown in Fig. 4 for the AUA potential indicates a better physical meaning than the UA potentials, for which σ_{CH3} is greater than σ_{CH4}. Indeed σ should represent an average molecular diameter, logically greater for groups with more hydrogen atoms. Also, we can notice that the carbon-to-centre of force distance (0. 646Å) corresponds to an intermediate position of the force centre between the carbon and the hydrogen atom, as was expected.

RESULTS AND DISCUSSION

Long Chain Alkanes

The efficiency of the new method to describe long chain alkanes has been compared with results obtained in reference [9] on *n*-eicosane at the same temperatures (459–700 K). Table III shows the average errors on vapour pressures, vaporization enthalphy and liquid density. With the new method, the

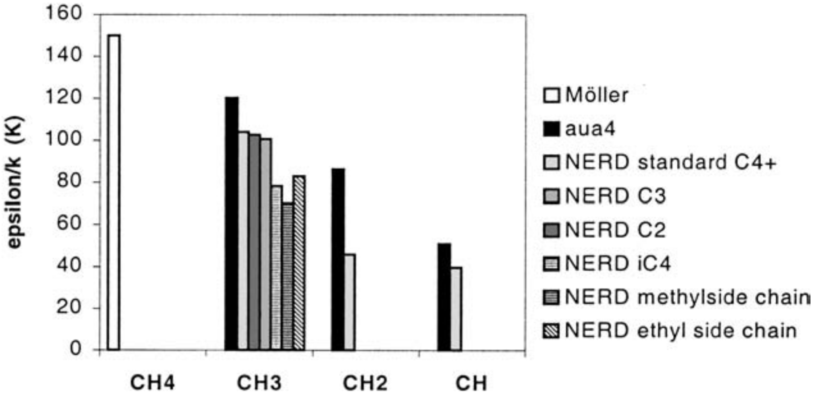

FIGURE 3 Energetic parameter for Lennard–Jones potential ϵ/k, of CH_2, CH_3 and CH groups, used in AUA4 potential ([9]and this work), and in NERD potential ([4]and[6]).

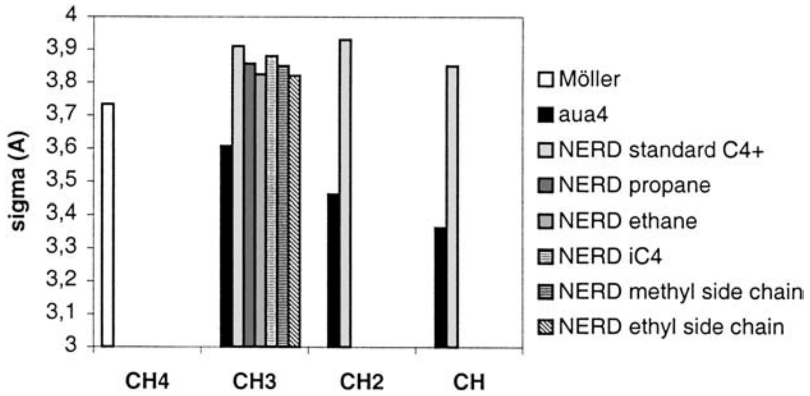

FIGURE 4 Lennard–Jones diameter σ of CH_2, CH_3 and CH groups, used in AUA4 potential ([9] and this work), and in NERD potential ([4]and[6]).

average errors on liquid density and vaporization enthalpy are divided by 4 and 2 respectively. A slight loss of precision on vapour pressure is observed, however smaller than statistical errors. As it was conjectured in reference [9], the somewhat disappointing results found on *n*-eicosane were not due to a poor extrapolation of the AUA4 potential to higher carbon numbers, but to the insufficient exploration of internal chain configurations.

In order to test the applicability of the method to predict equilibrium properties of long chain linear alkanes, GEMC and NPT monophasic simulations were performed with several systems: *n*-eicosane ($C_{20}H_{42}$), *n*-pentacosane ($C_{25}H_{52}$), *n*-triacontane ($C_{30}H_{62}$), and *n*-pentatriacontane ($C_{35}H_{72}$). For the first three hydrocarbons, Gibbs ensemble simulations have been performed at two different temperatures, and liquid simulations in the NPT ensemble at four different temperatures. In the case of *n*-pentatriacontane, we performed only two Gibbs simulations. The total computing time required for this optimisation has been about 3500 h of a single processor on a SGI 02000 computer. Numeric results are shown in Table IV. Graphic results are presented on Fig. 5 for liquid densities, Fig. 6 for molar vaporization enthalpies, and Fig. 7 for vapour pressures.

TABLE III Compared average errors for the three equilibrium properties taken as data between this work and a precedent work without internal relaxation [9]. The averages have been calculated on the basis of six values for each property, from 450 to 700 K, with a system of 200 molecules of *n*-eicosane.

Average error	Reference [9]	*This work*	(*statistical error*)
Liquid density	4.11 %	1.15 %	(0.5 %)
Vaporisation enthalpy	4.98 %	2.45 %	(1 %)
Vapor pressure*	2.68 %	3.38 %	(5 %)

* error based on ln(Psat)

TABLE IV Application of the AUA4 potential with the internal relaxation move. Vapour pressures (Psat) are expressed in kPA, vaporization enthalpies (ΔH_{vap}) in kJ/mol, and liquid densities (ρ_l) in kg/m^3.

	T(K)	*Simulation*	*Properties*	*Calculated values*
n-eicosane	700	Gibbs	Psat	526
(*n*-C20)			ΔH_{vap}	41.0
			ρ_l	445
	633.58	Gibbs	Psat	168
			ΔH_{vap}	55.0
			ρ_l	518
	578.67	NPT	ΔH_{vap}	62.1
		Monophasic	ρ_l	573
	532.52	NPT	ΔH_{vap}	67.8
		Monophasic	ρ_l	612
	493.18	NPT	ΔH_{vap}	73.4
		Monophasic	ρ_l	651
	459.26	NPT	ΔH_{vap}	76.2
		Monophasic	ρ_l	672
n-pentacosane	750	Gibbs	Psat	404
			ΔH_{vap}	43.
(*n*-C25)			ρ_l	404
	680	Gibbs	Psat	156.5
			ΔH_{vap}	62.83
			ρ_l	516.8
	622	NPT	ΔH_{vap}	65.67
		Monophasic	ρ_l	543
	573.12	NPT	ΔH_{vap}	76.6
		Monophasic	ρ_l	584.6
	531.32	NPT	ΔH_{vap}	82.2
		Monophasic	ρ_l	618
	495.21	NPT	ΔH_{vap}	87.3
		Monophasic	ρ_l	651
n-triacontane	780	Gibbs	Psat	295
(*n*-C30)			ΔH_{vap}	50.8
			ρ_l	423.8
	710	Gibbs	Psat	85
			ΔHvap	72.1
			ρ_l	496
	651.53	NPT	ΔHvap	78.7
		Monophasic	ρ_l	521
	601.95	NPT	ΔHvap	88.4
		Monophasic	ρ_l	579
	559.39	NPT	ΔHvap	97.2
		Monophasic	ρ_l	623
	522.45	NPT	ΔHvap	100
		Monophasic	ρ_l	635.2
n-pentatriacontane	810	Gibbs	Psat	918*
(*n*-C35)			ΔHvap	–
			ρ_l	456*
	750	Gibbs	Psat	94.2*
			ΔHvap	74.2*
			ρ_l	477.8*

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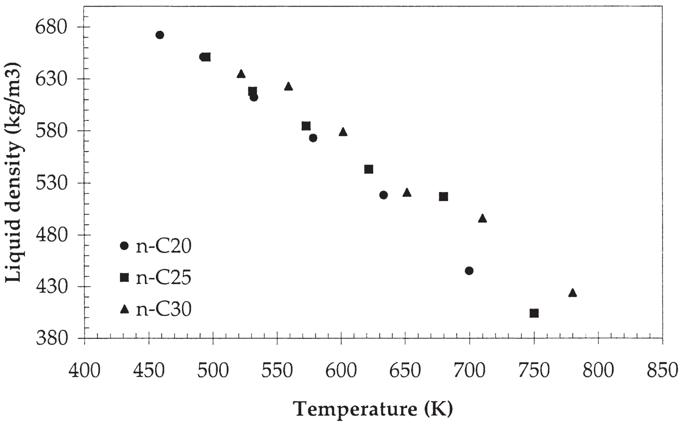

FIGURE 5 Liquid densities obtained by simulations for three linear alkanes studied in this work.

Figure 6 shows a regular evolution in regard with temperature, and also a consistent evolution with the increase of carbon number. Indeed, the longer the molecule is, the higher the vaporization enthalpy will be, as has already been proved for smaller linear alkanes (see Ungerer [9] and Errington [19] for simulations results and Piacente [20,21] for experimental studies).

Figure 7 also shows a good compatibility with Piacente's experimental results [21].

Figure 5 presents a more complicated evolution. Nevertheless, we note that liquid density increases when molecules become longer at high temperatures,

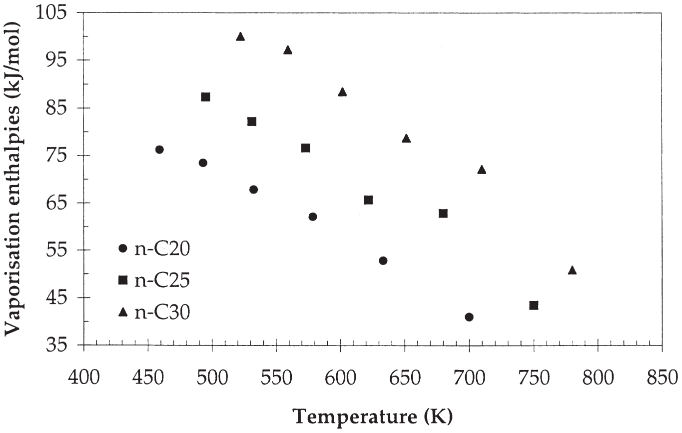

FIGURE 6 Vaporisation enthalpies obtained by simulations for three linear alkanes studied in this work.

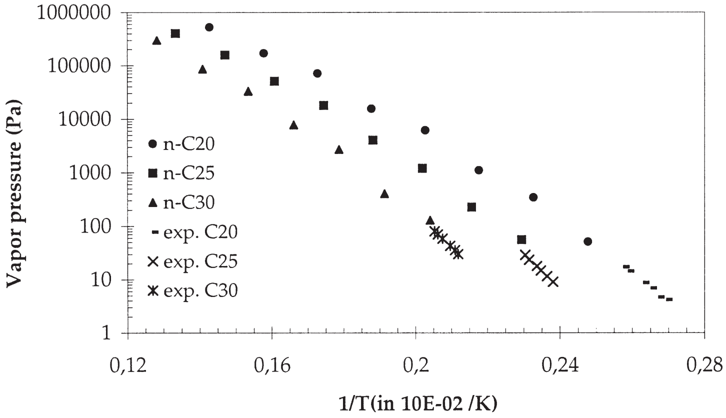

FIGURE 7 Vapour pressures obtained by simulations for three linear alkanes studied in this work, compared with experimental datas from Piacente *et al.* [20–22].

which seems reasonable. At lower temperatures, we predict a convergence of the densities of the different systems. This is consistent with the normal evolution of liquid density with carbon number, as shown in several experimental reference data [20–25].

As these results present a very satisfactory prediction of equilibrium properties where experimental data are available without parameter fitting, there is a high probability that our simulation results are correct in conditions where experimental data are not yet available. This is the case for instance at high temperatures for long chain *n*-alkanes.

Branched Alkanes

In order to test the new parameters of CH group, GEMC and NPT monophasic simulations have been performed for several C_7 isomers. The total computing time required for this optimisation has been about 1000 h of a single processor on a SGI O2000 computer. Results are shown in Tables V–VII and in Figs. 8–10. The average errors are 6.6% for vapour pressures generally underestimated, 1.0% for liquid densities and 2.7% for vaporisation molar enthalpies globally overestimated. The observed error on vapour pressure is moderate, since it corresponds to a discrepancy of temperature of about 2.5 K near to the boiling point, and of about 6 K near to the critical point.

The critical temperatures and liquid densities for *n*-heptane and 2-methylhexane have been calculated on the basis of simulations results (Table VIII). It appears that the CH group parameters allow a realistic prediction of these critical properties.

TABLE V Application of the AUA4 potential with the CH group parameters. Vapour pressures (Psat) are expressed in kPA. The experimental data are taken from the Dortmund Data Bank [27].

	T (K)	*P_{sat} experimental values*	*P_{sat} simulation values*	*Calculated error*
$n\mathrm{C}_7$	371.60	100	86	0.140
	400.00	218	207	0.050
	425.00	390	386	0.010
	450.00	647	685	0.059
	475.00	1016	1049	0.032
	500.00	1524	1578	0.035
2-methylhexane	363.20	100	87	0.130
	400.00	271	241	0.111
	435.00	576	499	0.134
	465.00	999	925	0.074
	490.00	1505	1390	0.076
3-ethylpentane	366.60	100	95	0.050
2.4-dimethylpentane	353.95	100	93	0.070
	375.00	185	165	0.108
	400.00	341	337	0.012
	425.00	579	570	0.016
	450.00	926	928	0.002
			Average error	0.065

TABLE VI Application of the AUA4 potential with the CH group parameters. Vaporization enthalpies (ΔH_{vap}) are expressed in kJ/mol. The experimental datas are taken from the Dortmund Data Bank [27].

	T (K)	*ΔH_{vap} experimental values*	*ΔH_{vap} simulation values*	*Calculated error*
$n\mathrm{C}_7$	371.60	31.77	31.98	0.007
	400.00	29.64	29.93	0.010
	425.00	27.46	28.16	0.025
	450.00	24.98	25.36	0.015
	475.00	22.02	22.70	0.031
	500.00	18.25	18.74	0.027
2-methylhexane	363.20	30.75	31.53	0.025
	400.00	28.05	28.91	0.031
	435.00	24.99	25.93	0.038
	465.00	21.74	22.75	0.046
	490.00	18.19	19.51	0.073
3-ethylpentane	366.60	31.00	31.44	0.014
2.4-dimethylpentane	353.95	29.62	29.96	0.011
	375.00	28.11	28.33	0.008
	400.00	26.13	26.59	0.018
	425.00	23.87	24.69	0.034
	450.00	21.21	22.10	0.042
			Average error	0.027

TABLE VII Application of the AUA4 potential with the CH group parameters. Liquid densities (ρ_{liq}) are expressed in kg/m^3. The experimental data are taken from the Dortmund Data Bank [27].

	T (K)	ρ_{liq} *experimental values*	ρ_{liq} *simulation values*	*Calculated error*
$n\mathrm{C}_7$	371.60	614.6	617.6	0.005
	400.00	585.3	588.3	0.005
	425.00	557.2	562.4	0.009
	450.00	526.0	535.0	0.017
	475.00	490.1	492.2	0.004
	500.00	446.2	447.5	0.003
2-methylhexane	363.20	615.4	625.3	0.016
	400.00	577.1	587.6	0.018
	435.00	535.9	542.3	0.012
	465.00	494.1	502.6	0.017
	490.00	450.7	452.0	0.003
3-ethylpentane	366.60	631.0	640.8	0.016
2.4-dimethylpentane	353.95	618.3	620.3	0.003
	375.00	597.7	593.5	0.007
	400.00	571.1	573.8	0.005
	425.00	541.6	547.5	0.011
	450.00	507.7	513.3	0.015
			Average error	0.010

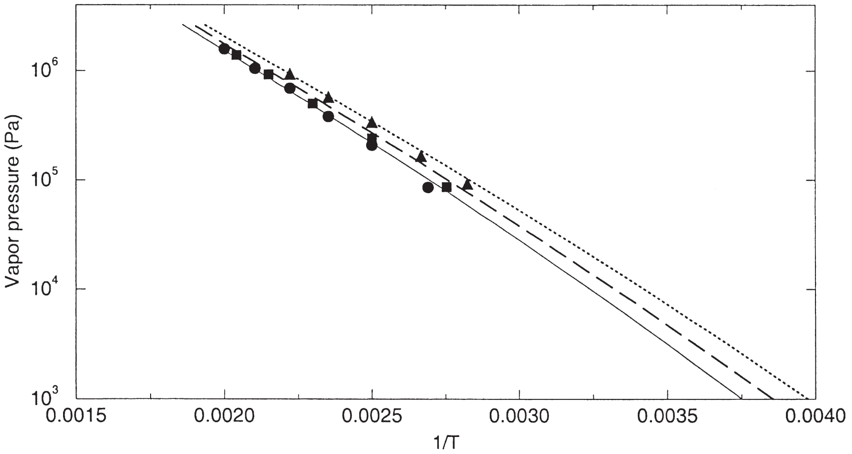

FIGURE 8 Vapour pressures obtained by simulations for three branched (2,4-dimethylpentane, *n*-heptane, and 2-methylhexane) studied in this work (triangle, circle and square, respectively), compared with experimental datas from the Dortmund Data Bank (DDB) [27] (dotted line, full line, and dashed line, respectively).

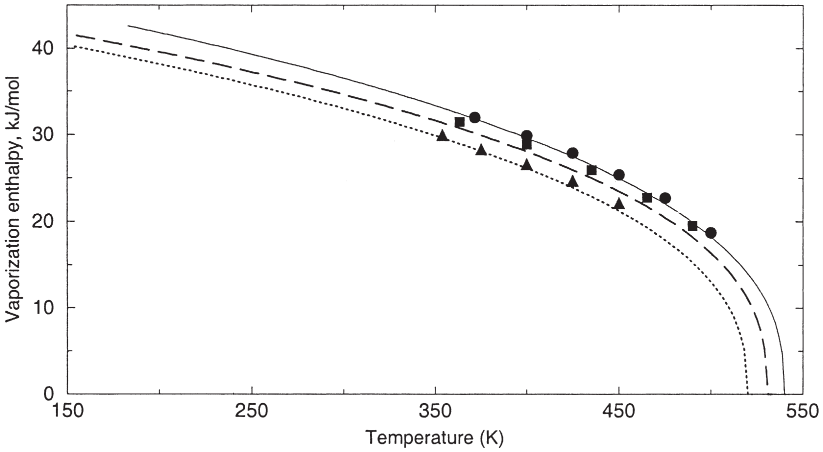

FIGURE 9 Vaporisation enthalpies obtained by simulations for three branched alkanes (2,4-dimethylpentane, *n*-heptane, and 2-methylhexane) studied in this work (triangle, circle and square, respectively), compared with experimental datas from the Dortmund Data Bank (DDB) [27] (dotted line, full line, and dashed line, respectively).

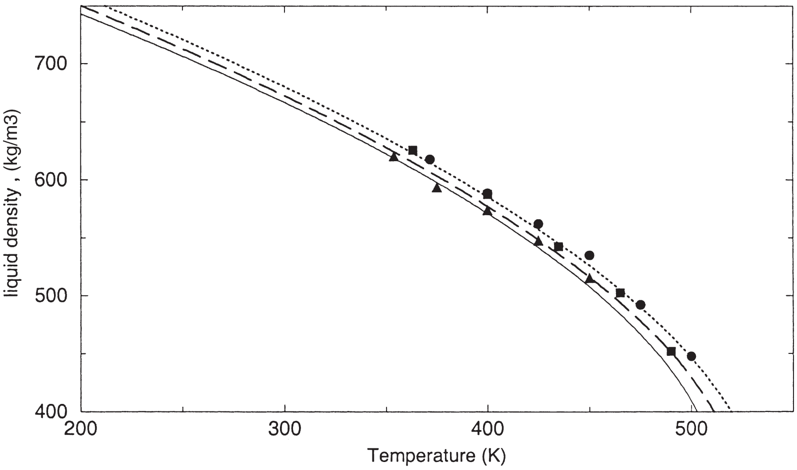

FIGURE 10 Liquid densities obtained by simulations for three branched alkanes (2,4-dimethylpentane, *n*-heptane, and 2-methylhexane) studied in this work (triangle, circle and square, respectively), compared with experimental datas from the Dortmund Data Bank (DDB) [27] (full line, dotted line, and dashed line, respectively).

TABLE VIII Critical temperatures and liquid densities calculated on the basis of simulations results. Experimental datas are taken from reference [28].

	Experimental values		*Simulation*	
	T_c *(K)*	ρ_c *(kg/m³)*	T_c *(K)*	ρ_c *(kg/m³)*
n-heptane	540.3	232	546.8	231
2-methylhexane	530.4	227	537.2	238

The AUA4 potential allows thus efficient prediction of the equilibrium properties of the C_7 isomers, in spite of the fact that it has been optimised on the basis of other alkanes.

Moreover, only one set of parameters for each group is used in AUA4 potential for different molecules, which is different from most UA potential. For instance, the NERD potential needs different values for the same force centre in two different molecules. In contrast with classical United Atoms potentials [3,4], no modification of group parameters was needed in order to predict small differences in properties between the different isomers.

CONCLUSION

The AUA4 potential is now efficient in predicting thermodynamic properties of alkanes. This work has shown that the optimisation method proposed by Ungerer allows determination of parameters that offer a good consistency, and a real physical meaning. The evolution noted between the Lennard–Jones parameters ϵ and σ is more regular than the same observations performed with UA potentials [4]. As the position of the force centres is consistent with molecular structure, i.e. intermediate between carbon and hydrogens, we may say that the AUA4 force field is probably the first to propose Lennard–Jones diameters that really correspond to average group diameters in alkanes.

Moreover, this work has shown that this kind of potential can be considered as transferable potential. Although only three linear alkanes and one branched alkane have been used to optimise it, we could have predict several equilibrium properties for different linear alkanes from ethane to pentatriacontane, and for different isomers of heptane. This work has also shown that AUA4 potential permits small differences in properties between isomers to be predicted.

All this contributes to proving that the shift of force centre used in Anisotropic United Atoms potential allows a significant improvement of potential transferability. This agrees with the conclusions of Delhommelle [26], who has used successfully the AUA4 parameters of CH_2 and CH_3 groups to propose an intermolecular potential for several polar components (organic sulfides and thiols).

Favourable perspectives for AUA4 potential could be the transferability to other types of molecules as isoalkanes with a quaternary carbon, cyclic alkanes, olefins, etc. Its use to predict transport properties is also an interesting challenge that might involve optimisation of the bending and torsion potential. The improvement of transport properties prediction in dense liquids, while maintaining a satisfactory representation of thermodynamic properties, would provide a transferable model particularly useful for industrial applications.

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