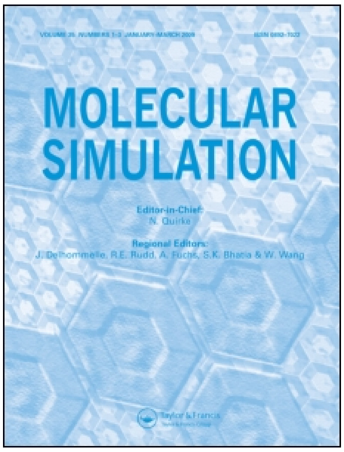

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Vapour-Liquid Phase Equilibria Predictions of Methane-Alkane Mixtures by Monte Carlo Simulation

Allan D. Mackie[a][b]; Bernard Tavitian[a]; Anne Boutin[c]; Alain H. Fuchs[c]
[a] Department of Applied Physical-Chemistry and Analysis, Institut Francais du Pétrole, Rueil-Malmaison Cedex, France [b] Departament d'Enginyeria Química, Escola Tècnica Superior d'Enginyeria Quimica, Universitat Rovira i Virgili, Tarragona, Spain [c] Department of Physical Chemistry, Chimie-Physique des Matériaux Amorphes, Bt, Orsay, France

To cite this Article Mackie, Allan D. , Tavitian, Bernard , Boutin, Anne and Fuchs, Alain H.(1997) 'Vapour-Liquid Phase Equilibria Predictions of Methane-Alkane Mixtures by Monte Carlo Simulation', Molecular Simulation, 19: 1, 1 — 15
To link to this Article: DOI: 10.1080/08927029708024135
URL: http://dx.doi.org/10.1080/08927029708024135

Molecular Simulation, 1997, Vol. 19, pp. 1–15
Reprints available directly from the publisher
Photocopying permitted by license only

VAPOUR-LIQUID PHASE EQUILIBRIA PREDICTIONS OF METHANE–ALKANE MIXTURES BY MONTE CARLO SIMULATION

ALLAN D. MACKIE[a,*], BERNARD TAVITIAN[a],
ANNE BOUTIN[b,†] and ALAIN H. FUCHS[b]

[a]*Department of Applied Physical-Chemistry and Analysis,*
Institut Français du Pétrole, 1 et 4 Avenue de Bois Préau,
BP 311, 92506 Rueil-Malmaison Cedex, France;
[b]*Department of Physical Chemistry, Chimie-Physique des*
Matériaux Amorphes, Bât. 490, Université de Paris Sud,
91405 Orsay, France

(Received October 1996; accepted October 1996)

We report molecular simulations of methane–alkane mixtures using the Gibbs ensemble technique combined with the configurational-bias Monte Carlo method. The intermolecular interactions are modeled using both the united atom model with parameters proposed by Smit *et al.* and the anisotropic united atom model by Toxvaerd. Liquid-vapour phase diagrams are calculated for methane–*n*-pentane and methane–*n*-dodecane mixtures using these two potential models and compared with experimental results.

Keywords: Gibbs ensemble Monte Carlo simulations; liquid-vapour equilibria; alkane mixtures

1. INTRODUCTION

Since alkanes are the basis of the petrochemical industry it is not surprising that the experimental determination and modeling of their behaviour has received a substantial amount of interest. Although the physical properties have in general been well studied, certain areas remain extremely difficult to

---

[*] Present address: Departament d'Enginyeria Químíca, Escola Tècnica Superior d'Enginyeria Químíca, Universitat Rovira i Virgili, Carretera de Salou, s/n, 43006 Tarragona, Spain.
[†] Author to whom correspondance should be addressed.

access by experimentation. These include systems under high pressure and temperature as well as molecules for which pure samples may not be readily available. However, because of the existence of oil-fields where precisely these conditions are found, there is a great deal of interest in studying these systems. The reservoir models that are used to help produce these fields require knowledge of the phase behaviour and dynamics of these systems. The use of computer simulations, which are not in principle limited by extreme conditions, is thus of increasing interest as a means to accurately predict the behaviour of these alkane mixtures.

Several different models for alkanes have been proposed for use in computer simulations. These models attempt to strike a balance between simplicity, in order to make the calculations possible, and enough complexity to quantitatively predict the behaviour of interest. The most successful approach has been to reduce the complexity of the alkane by introducing a united atom approximation. In this way groups of atoms are represented by one interaction site. For instance in alkanes, CH_3 and CH_2 groups are typically reduced to single sites.

These site-site interaction models have been applied with good results to pure systems of alkanes. Smit *et al.* [1,2,3] have fitted parameters that allow them to predict the vapour-liquid phase equilibria and critical points for a wide range of pure linear alkanes from *n*-pentane (C_5) up to *n*-octatetracontane (C_{48}). Experimental determination of alkanes longer than decane (C_{10}) becomes extremely difficult due to the instability of alkanes at high temperatures. Over the range obtainable by experiment the simulations results have been shown to be in good agreement with experimental values. These simulations thus provide a means to access an area which has thus far been inaccessible by experimental means.

The lack of explicit hydrogens becomes significant if systems at high pressures are considered where the alkanes start to pack together. Full atom models are an obvious solution to this problem, however this entails a large increase in computer time since the number of interactions goes as the square of the number of interaction sites. A useful compromise has been proposed by Toxvaerd [4,5] whereby the interaction site is moved from being located directly on the original carbon atom site to the geometrical centre of the atoms that have been united together. More generally, these displacements can be viewed as additional fitting parameters. This anisotropic united atom model has been shown to perform better for high pressure conditions [4]. In another related work, de Pablo *et al.* [6] were able to obtain good agreement with experimental values for several pure alkanes and methane-alkane mixtures by using density dependent potentials.

In this work we are interested in observing how well these models perform for the phase behaviour of mixtures of alkanes at reservoir conditions (high temperature and pressure). We are interested in finding the simplest model that will give a reasonable quantitative prediction of the phase behaviour and hence we prefer not to use density dependent potentials with the extra parameters that these models require. Instead we have investigated the united atom model by Smit *et al.* (UA) [1] and the anisotropic united atom model by Toxvaerd [4] (AUA) and in the following section details of these two models are given. The simulation techniques are described in section 4, namely the Gibbs-ensemble technique [7, 8, 9] combined with the configurational-bias Monte Carlo method [10, 11, 12]. In this work we include an additional bias that helps to place the first bead in a favourable position and we present the modifications necessary to the acceptance probability needed to keep detailed balance satisfied. In section 5 we present the simulation results for these models as applied to two systems, namely methane–*n*-pentane and methane–*n*-dodecane, and compare these predicted phase diagrams to experimental values. We finish in section 6 with the main conclusions from this work.

2. MODELS

The united atom models used to describe alkanes consist of two parts: a part to describe the intermolecular interactions and a part for the intramolecular interactions. In general the intermolecular interactions are described by a Lennard-Jones type potential,

$$u^{\mathrm{LJ}}(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

where ε_{ij} is the energy parameter of the interaction σ_{ij} is the size parameter and r_{ij} is the distance between interactions sites i and j. In this work we calculate the unlike interaction parameters by using a geometric combining rule for the energy $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$, and an arithmetic combining rule for the size, $\sigma_{ij} = (\sigma_i + \sigma_j)/2$. The values used for the Lennard-Jones potential are in fact effective two-body parameters which are fitted to take into account three and higher-body interactions in an approximate manner. The total intermolecular energy is calculated by summing over the interactions between all the different interaction sites i and j which belong to different molecules. For both models we use the same values for methane (CH_4) namely an energy parameter, $\varepsilon_{CH_4} = 149.92$ K and a size parameter, $\sigma_{CH_4} = 3.7327$ Å [13].

The intramolecular interactions are divided into three parts: (1) bond bending interactions between groups of three consecutively joined sites, (2) torsional interactions between groups of four consecutively joined atoms, and (3) non-bonded interactions between united atoms on the same molecule which are more than four sites apart. Bond lengths are kept fixed as this has been shown not to affect the system pressure [4]. The bending interaction used by Smit *et al.* takes the following form,

$$u^{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \tag{2}$$

where θ is the angle between the three united atoms, k_θ is the bending constant, and θ_0 is equilibrium angle. For his part, Toxvaerd proposed a slightly different form:

$$u^{\text{bend}}(\theta) = \frac{1}{2}k_\theta(\cos\theta - \cos\theta_0)^2 \tag{3}$$

with a different set of parameters. Both forms were tested in this work. No significant differences were found using expression (2) or (3) when the same values are taken for the equilibrium angle and the bending constant. The torsional potential is a function of the dihedral angle between three consecutive bonds and since different forms have been used for the two models they will be given in their respective sections. Finally, the non-bonded interactions are calculated using the same Lennard Jones form as given in Eq. (1) with the same parameters as are used in the intermolecular interactions.

2.1. United Atom (UA) Model

In the model developed by Smit *et al.* [1] the atom is represented by a united atom model with interaction sites located on each carbon atom. The Lennard-Jones energy parameters are: $\varepsilon_{CH_2} = 47.0$ K and $\varepsilon_{CH_3} = 114$ K. Both groups are given the same size parameter, $\sigma_{CH_2} = \sigma_{CH_3} = 3.93$ Å. The potential is truncated at 13.8 Å with tail corrections applied [14]. The bond bending potential is as is given in Eq. (2) with $k_\theta = 62500$ K rad^{-2} and an equilibrium angle $\theta_0 = 114\,\mathrm{deg}$. For the torsion, the Jorgensen potential [15] is used,

$$u^{\mathrm{tors}}(\phi) = c_0 + 0.5c_1(1+\cos\phi) + 0.5c_2(1-\cos 2\phi) + 0.5c_3(1+\cos 3\phi) \quad (4)$$

where ϕ is the dihedral angle, $c_1 = 355\,\mathrm{K}$, $c_2 = -68.19\,\mathrm{K}$, $c_3 = 791.3\,\mathrm{K}$. The C—C bond length is taken to be 1.54 Å.

2.2. Anisotropic United Atom (AUA) Model

In the model introduced by Toxvaerd [4], the interaction sites are positioned at the geometrical centre of each united atom instead of at the carbon atom site. The displacements away from the carbon atom sites are: $d_1(\mathrm{CH_3}) = 0.275\,\text{Å}$ and $d_2(\mathrm{CH_2}) = 0.37\,\text{Å}$. The interaction sites have the following Lennard Jones energy parameters: $\varepsilon_{\mathrm{CH_2}} = 80$ K and $\varepsilon_{\mathrm{CH_2}} = 120\,\mathrm{K}$. The size parameters are, $\sigma_{\mathrm{CH_2}} = \sigma_{\mathrm{CH_3}} = 3.527\,\text{Å}$ and the potential is truncated at 12.0 Å with tail corrections added. Note that the potential cut-off distance is different from that used in the UA model. It is known that the cut-off distance affects the phase behaviour and so should be the same as the one used to fit the potential parameters. In his work, Toxvaerd uses a cut-off distance which is a function of the sigma or size Lennard-Jones parameter instead of using a fixed distance. When there is more than one sigma parameter in the system this leads to several possible choices for the cut-off distance. Instead we follow the work by Smit *et al.* and use a constant cut-off distance of 12.0 Å. For the bond bending Eq. (3) is used with $k_\theta = 62500\,\mathrm{K\ rad^{-2}}$ and $\theta_0 = 113.3\,\mathrm{deg}$. The torsional potential is represented by the following equation,

$$u^{\mathrm{tors}}(\phi) = \sum_{k=0}^{5} c_k \cos^k(\phi) \quad (5)$$

where ϕ is the dihedral angle, $c_0 = 1037.76\,\mathrm{K}$, $c_1 = 2426.07\,\mathrm{K}$, $c_2 = 81.64\,\mathrm{K}$, $c_3 = -3129.46\,\mathrm{K}$, $c_4 = -163.28\,\mathrm{K}$, $c_5 = -252.73\,\mathrm{K}$. In the original work by Toxvaerd [4, 5], the values of the equilibrium bending angle and C—C bond length are allowed to change according to the length of the alkane, the values being taken from experimental evidence. The approach followed by Smit *et al.* [1] is to fix the internal parameters to be independent of chain length in order to have the model with the least number of parameters. In this work in the case of *n*-pentane we follow Toxvaerd's original scheme and use a C—C bond length of 1.533 Å. For n-dodecane, the experimental value was not available and so we chose the same C—C distance as specified by Smit *et al.* for all the alkanes, namely 1.539 Å. We have found that a change in the third decimal place for the bond length gives a small but significant shift in the phase equilibrium.

3. SIMULATION TECHNIQUES

The simulations in this work have been carried out using the Gibbs ensemble technique [7,8,9]. The Gibbs ensemble is a simulation technique developed specifically for the study of phase equilibria. A separate simulation cell is used to represent each phase and thermodynamic equilibrium is obtained by Monte Carlo moves which transfer particles between the cells and change the cell volumes to equilibrate the chemical potentials and pressure respectively. Moves are also carried out within each cell.

For pure component phase equilibria we are restricted to using the constant volume version of the Gibbs ensemble in which the sum of the volumes of the simulation cells is fixed. In the case of mixtures, the extra degrees of freedom from having more than one component allow the use of the constant pressure Gibbs-ensemble. In this version each cell is allowed to fluctuate independently against some given pressure. This is useful when we are interested in the phase behaviour at a fixed temperature and pressure and is thus the version used in this work.

The probability of inserting a chain during a transfer step into a dense phase can be greatly increased through the use of the configurational-bias Monte Carlo scheme [10, 11, 12]. We follow the procedure given by Smit *et al.* [1] for the two models. In addition we apply a bias for the insertion of the first bead of the chain. In the original scheme, the first bead of the chain is placed in a position chosen at random. Here we attempt to increase the probability of accepting the move by biasing the insertion of the first bead.

We generate m positions at random within the cell where the chain is to be placed which we denote by the set $\{\mathscr{A}\}$. We then calculate the following factor for this set,

$$w_1(n) = \sum_{i=1}^{m} \exp[-\beta U_1(\mathscr{A}_i)] \tag{6}$$

where $U_1(\mathscr{A}_i)$ is the energy of placing the first united atom at site $\mathscr{A}_i$ and $w_1(n)$ is the weight of the new configuration. One of these sites is picked with probabilities based on the Boltzmann weights of these energies,

$$P_i = \frac{\exp[-\beta U_1(\mathscr{A}_i)]}{w_1(n)} \tag{7}$$

where P_i is the probability of picking site $\mathscr{A}_i$. The weight of the old configuration, $w_1(o)$ is calculated in a similar manner,

$$w_1(o) = \sum_{i=1}^{m} \exp[-\beta U_1(\mathscr{B}_i)] \tag{8}$$

where the set of positions, $\{\mathscr{B}\}$ is now composed of $(m-1)$ random positions in the cell from which the chain is being taken from plus the original first site of the old configuration.

These weights, $w_1(n)$ and $w_1(o)$, are used to modify the acceptance criterion as is shown in Smit *et al.* [1] and take the place of the weight given there for the first bead. Otherwise the calculation of the probability of acceptance of this move follows exactly as given by Smit *et al.* [1] for the two models.

Note that when $m = 1$ these weights reduce to the case of random insertion of the first bead. This additional bias can be applied equally to mixtures or pure components. Another possibility for mixtures is to use a particle interchange step to insert a larger component in place of a smaller one [16]. This move was not implemented in this work.

The Monte Carlo moves were picked at random with fixed probabilities and were: (1) displacement of a random molecule, (2) rotation of a random molecule around its centre of mass, (3) rotation of one end of a random molecule about a randomly chosen united atom (pivot algorithm), (4) regrowth of part of a random molecule using the configurational-bias scheme (5) transfer of a random molecule between the simulation cells (6) a change in volume of one of the cells. Note that moves (3) and (4) both change the internal configuration of a molecule and can be used separately. For the number of trial orientations we used from 6 to 12 depending on the density and chain length and for the number of sites for the insertion of the first bead we used from 32 to 128. The program was tested by comparing against results from the work of Smit *et al.* [1] for pure systems of *n*-pentane and *n*-dodecane with reasonable agreement for both models.

4. RESULTS

In this section we present the results from calculating the phase behaviour of the UA and AUA models for mixtures of methane with *n*-pentane and *n*-dodecane at approximately the same temperature ($\approx 100°C$) for various pressures up to the critical point. The simulations were carried out using the NPT-Gibbs ensemble with configurational-bias for the regrowth of the chains with the additional bias for the first bead as has already been discussed in the previous section.

4.1. Methane-n-Pentane

The simulations were carried out at 104.4°C, the results for the phase behaviour for both models are given in Table I and are compared against experimental values [6, 17, 18, 19] for the compositions and the densities in Figures 1 and 2 respectively. Simulations were started with two equivalent simulation cells containing 100 molecules with 35 and 45% of methane. A system with 400 molecules was used for the AUA model for pressures of 10.34 and 12.0 MPa. Equilibrium was typically reached after 500 000 moves, and a further million moves were performed to average quantities. The transfer move acceptance probabilities were found to lie between 10 and 20% when using 50 random sites for the first bead insertion and 6 trial orientations at each insertion step. As can be seen, both models give reasonable quantitative predictions for the densities of the liquid and vapour phases as compared to experimental values though the UA model slightly overestimates the liquid density. For the prediction of the compositions we observe that both models are in agreement with experiment for the liquid, or *n*-pentane rich, phase. For the vapour phase we find that the UA model significantly overpredicts the fraction of methane while the AUA model continues to predict the experimental value.

TABLE I Simulation results for the UA and AUA models: methane-*n*-pentane system at 104.4°C, x and y represent the methane mole fractions in the liquid and vapour phases respectively. Densities are given as moles per cubic cm and P_{acc}, the insertion acceptance probability, is for the pentane

	UA model					*AUA model*				
Press. (*MPa*)	x_{CH_4} (*mol*)	y_{CH_4} (*mol*)	ρ_{liq} (*mol/cm*^{3})	ρ_{vap} (*mol/cm*^{3})	P_{acc} (%)	x_{CH_4} (*mol*)	y_{CH_4} (*mol*)	ρ_{liq} (*mol/cm*^{3})	ρ_{vap} (*mol/cm*^{3})	P_{acc} (%)
2.56						0.092_1	0.64_1	0.00755_1	0.00098_{10}	12.0
4.14	0.13_3	0.84_5	0.00824_{10}	0.00138_5	9.0	0.15_1	0.75_1	0.00752_5	0.00158_3	14.3
5.52	0.16_2	0.85_2	0.00829_5	0.00193_1	11.0	0.19_2	0.76_5	0.00793_6	0.00205_9	16.2
6.89	0.24_2	0.89_2	0.00851_5	0.00245_2	12.8	0.25_4	0.79_1	0.00783_4	0.00252_{10}	20.5
8.62	0.32_2	0.92_2	0.00863_{10}	0.00301_{30}	14.8	0.35_1	0.77_2	0.00803_4	0.00348_{10}	21.0
10.34						0.42_3	0.77_6	0.00820_3	0.00420_5	22.2
12.00						0.47_2	0.74_6	0.00819_2	0.00492_{52}	22.2

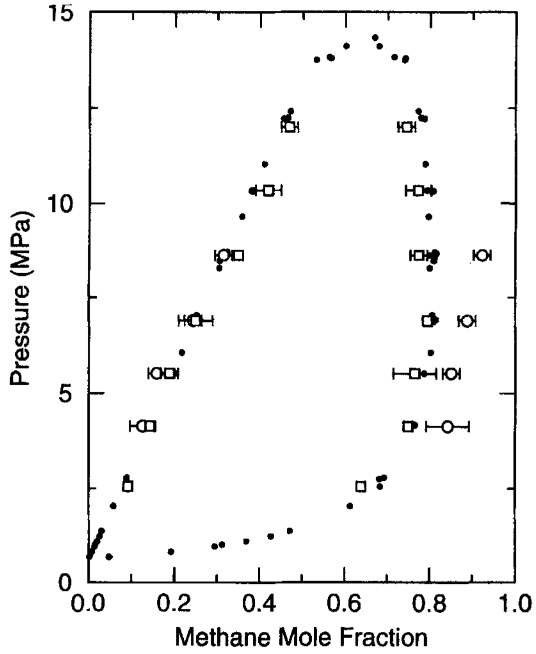

FIGURE 1 Pressure-composition coexistence behaviour for the methane–*n*-pentane system, (●) experimental data [6, 17, 18, 19] (○) UA model, (□) AUA model.

4.2. Methane–n-Dodecane

The simulation results for a system at 100.9°C are given in Table II and the phase behaviour of the composition and density are compared against experimental values [20] in Figures 3 and 4 respectively.

The simulations contained 100 *n*-dodecane molecules and enough methane to obtain roughly equivalent simulation cell dimensions for the liquid and vapour phases (from 200 to 800 methane molecules). The sampling for these systems was observed to be significantly more difficult than was found for the pure dodecane system due to the presence of the methane which greatly lowers the probability of accepting a chain insertion. Much longer equilibration and averaging runs were thus required, typically in the region of 2 million to equilibrate the system and 4 million to obtain averages.

Another difficulty found was due to the very low concentration of *n*-dodecane in the vapour phase especially at the lower pressures. This resulted in a small number of *n*-dodecane molecules being present at any one time and thus gave poor statistics for the vapour composition. The use of the additional bias for the first bead was found to significantly increase the

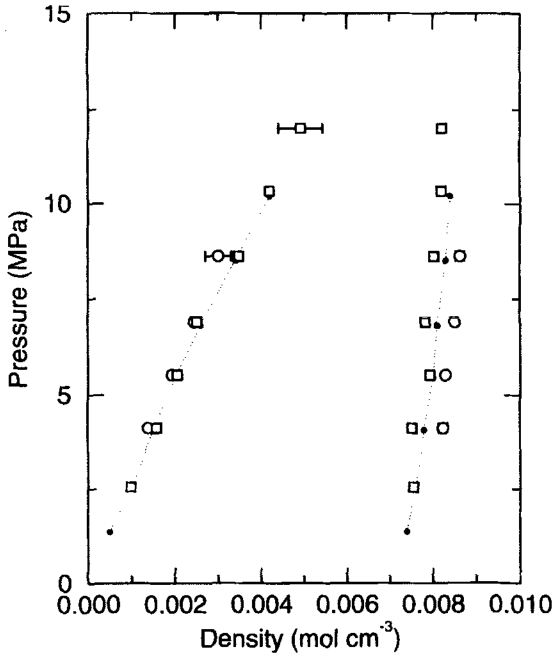

FIGURE 2 Pressure-density coexistence behaviour for the methane–*n*-pentane system (●) experimental data [6] (○) UA model, (□) AUA model. The dotted line connects the experimental values and is used as a guide for the eye.

TABLE II Simulation results for the UA and AUA models: methane–*n*-dodecane system at 100.9°C, x and y represent the methane mass fractions in the liquid and vapour phases respectively. Densities are given as grammes per cubic cm and P_{acc}, the insertion acceptance probability, is for the dodecane.

	UA model					*AUA model*				
Press. (*MPa*)	x_{CH_4} (*mass*)	y_{CH_4} (*mass*)	ρ_{liq} (*g/cm*^{3})	ρ_{vap} (*g.cm*^{3})	P_{acc} (%)	x_{CH_4} (*mass*)	y_{CH_4} (*mass*)	ρ_{liq} (*g/cm*^{3})	ρ_{vap} (*g/cm*^{3})	P_{acc} (%)
10	0.049_5	0.98_2	0.648_{15}	0.055_3	0.05	0.068_5	0.89_6	0.609_{11}	0.062_5	0.3
15	0.076_{11}	0.98_1	0.626_{23}	0.085_3	0.2	0.107_4	0.81_5	0.575_8	0.087_4	0.3
20	0.106_{11}	0.96_2	0.599_{20}	0.113_3	0.3	0.139_9	0.81_5	0.554_{20}	0.139_9	0.4
25	0.126_6	0.94_1	0.588_{12}	0.141_5	0.3	0.16_1	0.73_5	0.548_{20}	0.16_1	0.3
30	0.141_{11}	0.90_3	0.584_{17}	0.171_8	0.3	0.24_2	0.76_5	0.489_{26}	0.24_2	0.3
35	0.189_{14}	0.78_5	0.550_{20}	0.221_{15}	0.3					

probability of accepting a chain insertion. We typically found increases in the acceptance of the order of 10 to 20 times for an increase in cpu time of about 50%. These details are clearly both system and platform dependent.

The results for the UA model show quantitative agreement with experimental values for the liquid and vapour densities as well as the liquid

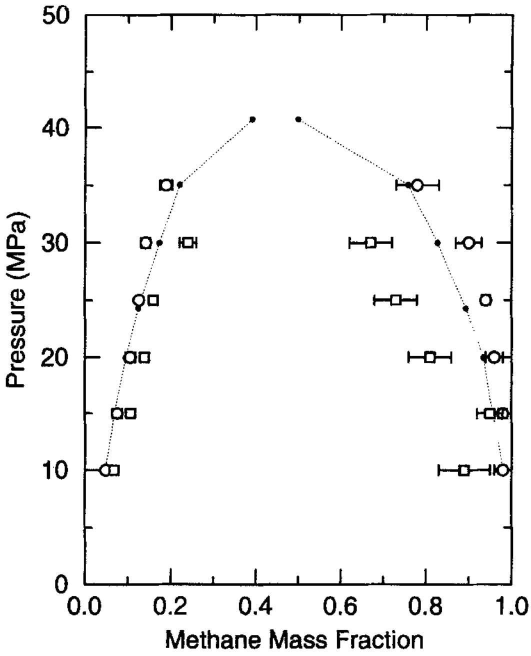

FIGURE 3 Pressure-composition coexistence behaviour for the methane–*n*-dodecane system (●) experimental data [20] (○) UA model, (□) AUA model. The dotted line connects the experimental values and is used as a guide for the eye.

composition but a slight overprediction of the proportion of methane in the vapour. In contrast, the AUA model clearly underpredicts the critical point for this system and both the densities and compositions for both phases are significantly different from experiment.

5. DISCUSSION

The UA model has been shown to be able to predict the phase behaviour of pure *n*-alkanes from C_5 up to C_{48} in good agreement with experiment up to the experimental limit [1]. This is remarkable for a model that includes a small number of "adjustable" parameters, namely the Lennard Jones energy parameter ε and size parameter σ for each united atom, and which has a simple united atom description of the molecules. It is of interest to observe if the same model can be equally successful when applied to mixtures of the same molecules. Our results from the two systems suggest that such an approach can provide a reasonable but not perfect solution. For the pentane

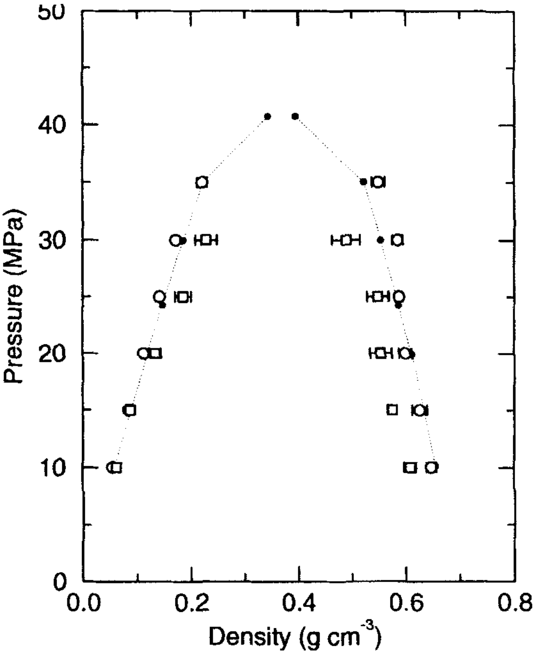

FIGURE 4 Pressure-density coexistence behaviour for the methane–*n*-dodecane system (●) experimental data [20] (○) UA model, (□) AUA model. The dotted line connects the experimental values and is used as a guide for the eye.

system it is not surprising that the UA model overpredicts the critical point since this is also the case for the pure *n*-pentane system. Different parameters than are used for the long alkanes would be needed for the short alkanes if better agreement for the phase behaviour is required. Even so, the model does reasonably well except that it overestimates the liquid density and the methane composition in the vapour phase. For the *n*-dodecane system the pure component phase diagram is in good agreement with experimental results and the model is in excellent quantitative agreement for the vapour and liquid densities. However, as for the *n*-pentane, it also shows a systematic though perhaps slighter tendency to overestimate the methane composition in the vapour phase. Here the poorer statistics make it more difficult to observe.

In contrast, the AUA model performs very well for the methane-*n*-pentane system in predicting correctly both the densities and compositions of the vapour and liquid phases. Since we use a shorter CC bond length than used by Smit to be more in keeping with Toxvaerd's original work, the pure pentane phase diagram will be different from that presented by Smit [1]. By decreasing the bond length we expect the phase behaviour to be closer to experiments. For the methane–*n*-dodecane system, however, the model significantly underpredicts the critical point. This is principally due to the fact that the pure component phase diagram for *n*-dodecane significantly underpredicts the critical point. For a better comparison between the two models it would be necessary for both models to give a good prediction of the same pure component phase behaviour. Unfortunately, in the case of the *n*-pentane the UA model overpredicts the critical point and for the *n*-dodecane the AUA model, used by Smit *et al.* significantly underestimates the critical point.

It is interesting to note that while the UA model predicts the phase behaviour of the pure *n*-dodecane system very well, it still appears to slightly overpredict the composition of methane in the vapour phase for the methane-dodecane mixture. It is possible that the UA model needs merely to be even better tuned for the pure systems in order to get better agreement for the mixtures. It is also possible that there may be more fundamental problems involved. Several approximations have been made in applying the model including the use of effective two-body interaction potentials as well as the approximate combining rules for the interaction between unlike united atoms. There may also be problems with the methane potential but we have experimented with different potentials ($\varepsilon_{CH_4} = 148.2\,K$ and $\sigma_{CH_4} = 3.817\,\mathring{A}$ [21]) without noticing any significant change. Another possibility is that the increase of density due to the presence of the methane may make the way in which the chains pack be of importance. The UA model is thought to have problems under such conditions [4]. The AUA model, which has been designed specifically with the packing of chains at high density in mind, appears to do well for the densities and compositions of both phases for the methane-pentane system. Further work on the AUA model would be required to confirm this.

6. CONCLUSIONS

In this work, we have simulated two methane-alkane mixtures using two model potentials designed for pure hydrocarbons with a simple combining rule. No readjustments of the potential parameters were made. In general a reasonable agreement was found with experiments however neither the UA nor the AUA model were able to reproduce quantitatively the vapour-liquid equilibrium behaviour for both short and long chain alkane systems. This result is not surprising since both models have deficiencies for the phase equilibria of pure systems and the problems for the mixtures more or less follow those of the pure systems. In a future work, we shall carefully test all the hypothesis made when designing such model potentials, both in pure systems and more particularly in mixtures. A study of specific influence of parameters such as the cut-off radius and the bond length will also be undertaken. The ultimate goal of such a study is to develop a set of potential parameters and model which enables the prediction of the vapour-liquid equilibrium of any sort of hydrocarbon mixture.

Acknowledgements

A. Z. Panagiotopoulos, J. I. Siepmann, D. Frenkel, P. Ungerer, and L. Vega are gratefully acknowledged for fruitful discussions. We thank the Institut du Développement et des Ressources en Informatique Scientifique (IDRIS) of the CNRS in Orsay for a generous allocation of CRAY C98 computer time.

References

[1] Smit, B., Karaborni, S. and Siepmann, J. I. (1995). "Computer simulation of vapor-liquid phase equilibria of *n*-alkanes" *J. Chem. Phys.*, **102**, 2126.

[2] Siepmann, J. I., Karaborni, S. and Smit, B. (1993). "Simulating the critical behaviour of complex fluids", *Nature*, **365**, 330.

[3] Siepmann, J. I., Karaborni, S. and Smit, B. (1993). "Vapor-liquid equilibria of model alkanes", *J. Am. Chem. Soc.*, **115**, 6454.

[4] Toxvaerd, S. (1990). "Molecular dynamics calculation of the equation of state of alkanes", *J. Chem. Phys.*, **93**, 4290.

[5] Padilla, P. and Toxvaerd, S. (1991). "Self-diffusion in *n*-alkane fluid models', *J. Chem. Phys.*, **94**, 5650.

[6] de Pablo, J. J., Bonnin, M. and Prausnitz, J. M. (1992). "Vapor-liquid equilibria for polyatomic fluids from site-site computer simulations: pure hydrocarbons and binary mixtures containing methane", *Fluid Phase Equilibria*, **73**, 187.

[7] Panagiotopoulos, A. Z. (1987). "Direct determination of phase coexistence properties of fluids by Monte carlo simulation in a new ensemble", *Mol. Phys.*, **61**, 813.

[8] Panagiotopoulos, A. Z. (1992). "Direct determination of fluid phase equilibria by simulation in the Gibbs ensemble: a review", *Mol. Sim.*, **9**, 1.

[9] Panagiotopoulos, A. Z. (1995). "Gibbs ensemble techniques", in Observation, prediction and simulation of phase transitions in complex fluids, M. Baus, L.F. Rull and J.P. Ryckaert, eds, *NATO ASI Ser. C*, **460**, 463.

[10] Rosenbluth, M. N. and Rosenbluth, A. W. (1955). "Monte Carlo calculations of the average extension of molecular chains", *J. Chem. Phys.*, **23**, 356.

[11] Frenkel, D., Mooij, G. C. A. M. and Smit, B. (1992). "Novel scheme to study structural and thermal properties of continuously deformable molecules", *J. Phys.: Condens. Matter*, **4**, 3053.

[12] de Pablo, J. J., Laso, M. and Suter, U. W. (1992). "Simulation of polyethylene above and below the melting point", *J. Chem. Phys.*, **96**, 2395.

[13] Möller, D., Óprzynski, J., Müller, A. and Fischer, J. (1992). "Prediction of thermodynamic properties of fluid mixtures by molecular dynamics simulations: methane-ethane", *Mol. Phys.*, **75**, 363.

[14] Allen, M. P. and Tildesley, D. J. (1987). Computer Simulation of Liquids, Oxford University Press.

[15] Jorgensen, W. L., Madura, J. D. and Swenson, C. J. (1984). "Optimized intermolecular potential functions for liquid hydrocarbons", *J. Am. Chem. Soc.*, **106**, 6638.

[16] Panagiotopoulos, A. Z. (1989). "Exact calculations of fluid-phase equilibria by Monte Carlo simulation in a new statistical ensemble", *Int. J. Thermophys.*, **10**, 447.

[17] Prodany, N. W. and Williams, B. (1971)."Vapor-liquid equilibria in methane-hydrocarbon systems", *J. Chem. Eng. Data*, **16**, 1.

[18] Reiff, W. E., Peters-Gerth, P. and Lucas, K. (1987). "A static equilibrium apparatus for (vapour + liquid) equilibrium measurements at high temperatures and pressures. Results for (methane–*n*-pentane)", *J. Chem. Thermodyn.*, **19**, 467.

[19] Berry, V. M. and Sage, B. H. (1970).*NSRDS-NBS*, **32**.

[20] Arnaud, J. F. (1995). *Caractérisation des propriétés physiques et thermodynamiques des fluides pétroliers à haute pression.* Ph.D. thesis, Université de Pau.

[21] Bonjan, M. J., Vernov, A. V. and Steele, W. A. (1992). "Simulation studies of adsorption in rough-walled cylindrical pores", *Langmuir*, **8**, 901.