MOLECULAR SIMULATIONS AS A TOOL FOR PREDICTING PHASE EQUILIBRIA AND TRANSPORT PROPERTIES OF FLUIDS

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LES SIMULATIONS MOLÉCULAIRES COMME OUTILS POUR PRÉDIRE LES ÉQUILIBRES DE PHASES ET LES PROPRIÉTÉS DE TRANSPORT DES FLUIDES

Dans cet article, nous passons brièvement en revue les méthodes de simulation moléculaire applicables à la prédiction des propriétés thermophysiques des fluides et des mélanges. Nous montrons, d'une part, comment la méthode de Monte-Carlo dans l'ensemble de Gibbs permet de prédire le comportement de phase de fluides réels dans des conditions telles que l'acquisition de données expérimentales serait difficile, voire impossible. D'autre part, nous décrivons les méthodes de dynamique moléculaire utilisées pour prédire les propriétés de transport de fluides moléculaires. Enfin, nous discutons le potentiel de ces méthodes pour les applications futures.

MOLECULAR SIMULATIONS AS A TOOL FOR PREDICTING PHASE EQUILIBRIA AND TRANSPORT PROPERTIES OF FLUIDS

We briefly review the molecular simulation methods which can be used to predict thermophysical properties of fluids and fluid mixtures. It is shown in this paper, on the one hand, how the Gibbs Ensemble Monte Carlo Method allows phase behavior predictions for real fluids under conditions for which experimental data are difficult or impossible to obtain. On the other hand, the molecular dynamics methods used for predicting transport properties of molecular fluids are described. Finally we discuss possible future applications of these methods.

SIMULACIONES MOLECULARES UTILIZADAS COMO HERRAMIENTAS PARA LA PREDICCIÓN DES LOS EQUILIBRIOS DE FASES Y LAS PROPIEDADES DE TRANSPORTE DE LOS FLUIDOS

Se examinan breve y sucesivamente, los métodos de simulación molecular aplicables a la predicción del las propiedades termofísicas de los fluidos y de las mezclas. En este artículo se exponen, en primer lugar, cómo el método de Monte Carlo en el conjunto de Gibbs permite predecir el comportamiento de fase de fluidos reales en tales condiciones que la adquisición de datos experimentales sería difícil, por no decir imposible. En segundo lugar, se describen los métodos de dinámica molecular utilizados utilizados para predecir las propiedades de transporte de fluidos moleculares, Finalmente, se pone en discusión el potencial de estos métodos para las aplicaciones futuras.

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INTRODUCTION

Molecular simulation and molecular modeling techniques are profitably employed nowadays in several industrial sectors. The use of molecular simulation includes, for instance, the design of new molecules or phases through the prediction of their physical or chemical properties. Knowledge of phase equilibria and transport properties of multicomponent gases and oils is of great economic importance in reservoir modeling, as well as in the planning of transport and in the design of industrial plants. Although the physical properties have, in general, been well studied, certain areas remain extremely difficult to 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, there is a great deal of interest in studying these systems precisely because of the existence of oil-fields where extreme temperatures and pressures are found and because of the systematic occurrence of unavailable heavy hydrocarbons in crude oils. The reservoir models that are used to help produce these fields require knowledge of the phase behavior 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 predict accurately the behavior of systems such as alkane mixtures.

This paper is organized as follows. We first briefly describe the molecular models and the simulation methods employed. In the second part of the paper we show some of the recent results we have obtained for phase equilibria and transport properties of fluids and fluid mixtures.

1 MOLECULAR MODELS

Several different models for alkanes have been proposed for use in computer simulations. These models are an attempt to strike a balance between simplicity, in order to make the calculations possible, and enough complexity to predict quantitatively the behavior 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 linear alkanes, CH_3 and CH_2 groups are typically reduced to single sites.

In order to simulate alkane properties, we used the Padilla and Toxvaerd anisotropic united atom (AUA) model [1] where the united atom potential centers are displaced from the carbon atom positions. The bonds are modeled by constraining the distance between adjacent groups. This flexible chain model also includes bending and torsional motion. This *n*-alkane model is the least density and temperature dependent of the currently used flexible UA models. More details on the potential functions used in these simulations can be found elsewhere [2-4].

2 SIMULATION METHODS

2.1 Phase Equilibria

The simulations in this work have been carried out using the Gibbs ensemble technique. The Gibbs ensemble is a simulation technique developed specifically for the study of phase equilibria [5]. 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. Moves are also carried out within each cell.

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. We follow the procedure given by Smit *et al.* [6]. In addition we apply an additional bias for the insertion of the first bead of the chain [4]. 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. More details on this algorithm can be found in [4].

2.2 Transport Properties

We have employed two different Molecular Dynamics (MD) programs developed independently. The details of the program for workstations [7] and that used on a Cray T3E [8] can be found elsewhere. We have chosen to use the Green-Kubo (GK) formalism that yields all the transport properties simultaneously. We calculate the viscosity, η, the thermal conductivity, λ, the intra-diffusion coefficients, D_a, and the kinetic interdiffusion coefficients D^K_{12} by the usual correlation function integrals [3]. More details on the MD procedure can be found in [3].

3 RESULTS

Figure 1 shows the computed pressure-composition coexistence curve for the methane-*n*-pentane mixture [4]. The simulations were carried out for both the AUA model and the UA model of Smit *et al.* [6] at a temperature of 104.4°C. The results for the phase behavior are compared to experimental values [11].

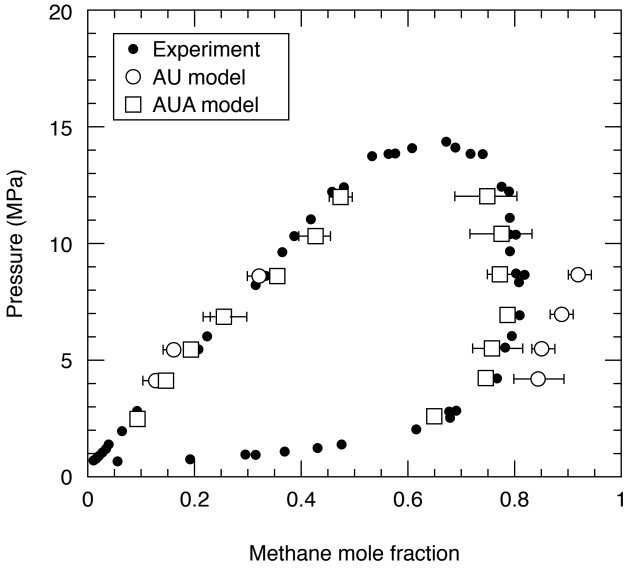

Figure 1

Pressure composition coexistence behavior for the methane-*n*-pentane mixture at 104.4°C. Full dots: experiments, open dots: UA model, open squares: AUA model. Reprinted from [4].

Both models give reasonable quantitative predictions for the densities of the liquid and vapor phases as compared to the experimental values, although 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 vapor phase, we find that the UA model significantly overestimates the fraction of methane while the AUA model continues to agree well with the experimental value.

The united atom approximation has been shown to be able to predict the phase behavior of pure *n*-alkanes from C_5 up to C_{48}, and the equation of state of alkanes at high or moderate densities is in good agreement with experiment [1] and [6]. This is remarkable for a model that includes a small number of adjustable parameters, namely the Lennard-Jones energy parameter and a size parameter for each united atom, and which relies on a simple (isotropic or anisotropic) united atom description of the molecules. It is of interest to observe whether the same model can be as successful when applied to mixtures of the same molecules. Our results [4] suggest that such an approach can provide a reasonable, but not a perfect, solution.

Figure 2 shows the computed methane-*n*-decane and ethane-*n*-decane viscosities at 333 K and 40 MPa. The methane-decane data are compared to experimental data from Knapstad *et al.* [9], the ethane-decane viscosities are compared to the empirical correlation of Assael *et al.* [10] The simulations underestimate the viscosities by up to 30% for mixtures rich in *n*-decanes. At $x > 0.5$ the deviations are not significant. The possible causes for these deviations have been discussed in detail in [3]. We conclude that the observed underestimation is mainly due to a poor *n*-decane potential.

MD simulations of three mixtures of dissimilar molecules have also been performed over the whole range of compositions, using simple one- and two-center Lennard-Jones (LJ) models for the light components methane and ethane, and the flexible AUA model for *n*-decane [3]. The viscosities are always underestimated with a maximum deviation of 30% at low gas content and a mean deviation of 16%. The diffusion coefficients are both under- and overestimated by up to 60%. The study has, to a certain degree, been able to separate three principal causes for the deviations:

- the imprecision of the pure *n*-decane potential (all transport coefficients are affected);
- the steric size and shape effects (the diffusion coefficients are more strongly affected than the viscosity and thermal conductivity) and
- the effects of the attractive cross interactions (the viscosity and thermal conductivity are not significantly affected, the intradiffusion coefficients are weakly and the interdiffusion is strongly affected). In sum, the potential models utilized seem to be both composition and property dependent, but the causes (and remedies) need to be further investigated.

4 FUTURE PROSPECTS

One of the main problems encountered in the molecular simulation prediction of phase equilibria and transport properties is the fact that the available semi-empirical potential functions are still not property and thermodynamic state independent. We are now carefully testing all the hypothesis made when designing these 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 is also being undertaken. Obviously some more basic physics and chemistry must now be included in the force fields in order to be able to reach a state where computer simulation can predict thermophysical data with an accuracy comparable to experiments. The ultimate goal of such a study is to develop a set of potential parameters and models which enables the prediction of the vapor-liquid equilibrium and transport coefficients of any sort of hydrocarbon mixture. The next step will then be to extend these methods for predicting equilibrium and non equilibrium properties of multi-component, multi-phase fluids.

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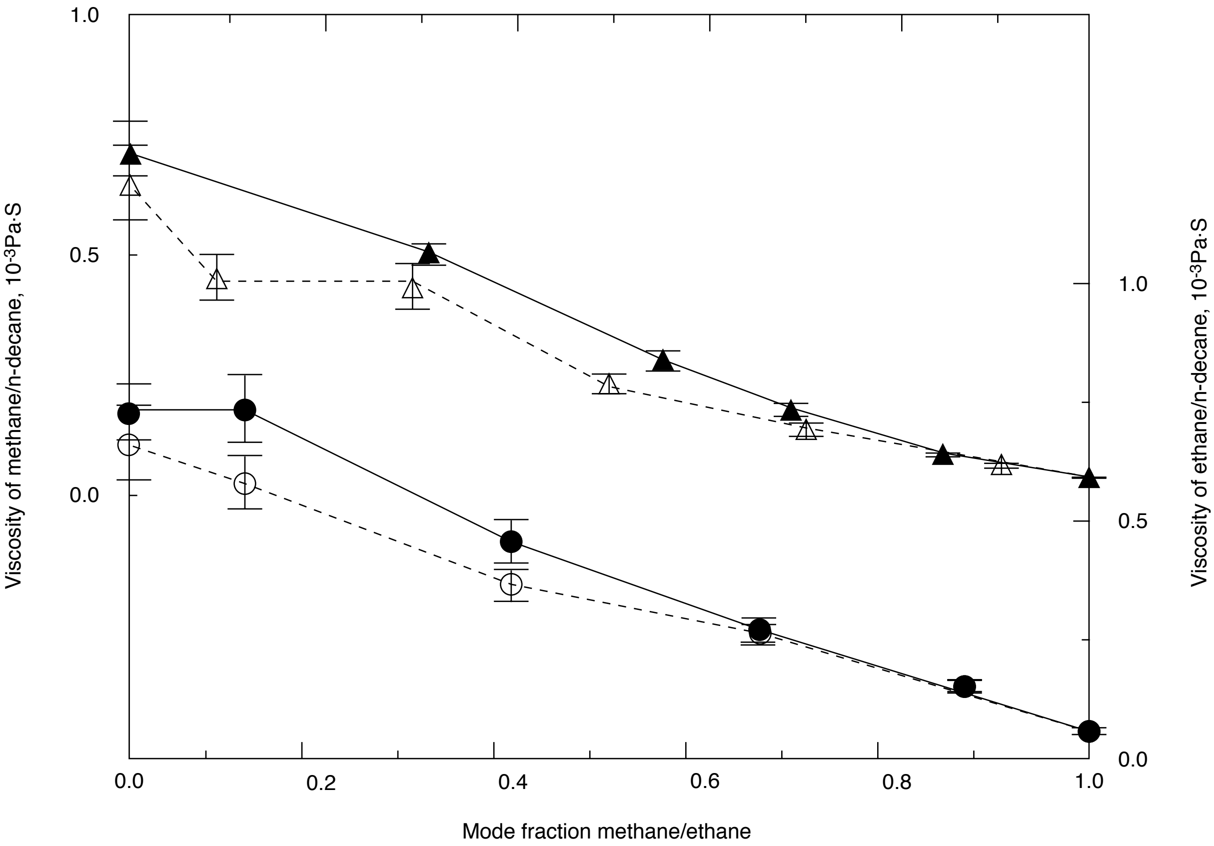

Figure 2

Viscosity in the methane/*n*-decane and the ethane/*n*-decane mixtures as a function of composition. Triangles: methane/decane, circles: ethanedecane. Open symbols: simulation, filled triangles: experimental, filled circle: experimental (pure fluid) and Assael correlation (mixture). Reprinted from [3].

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