Molecular simulations of fluid phase equilibria.

Berend Smit

Shell Research B.V., Koninklijke/Shell-Laboratorium, Amsterdam,
P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

Some applications of molecular simulations of phase equilibria are reviewed. It is shown that the conventional simulations techniques require too much cpu-time to simulate the phase behaviour of most systems of industrial interest. It is therefore essential to simplify the models or to develop novel simulation techniques. Examples of both approaches are discussed. Simulations are used to investigate the role of dispersive interactions in the phase behaviour of model polar fluids. A novel Monte Carlo technique is described which can be used to simulate the phase behaviour chain molecules. This technique is many orders of magnitude more efficient than the conventional techniques and allow us to determine, for example, the phase behaviour of long-chain alkanes at conditions where experiments are not feasible.

INTRODUCTION

Computer simulations are not novel in the process industry. It is common practice to use process simulators to design or to optimize a chemical plant. In such a simulator a reactor or separation unit are described macroscopicly. The molecular properties of the components enter as basic data or as parameters in various equations describing the thermodynamic properties. Since it is simply too expensive or too time consuming to measure all relevant basic data of interest for a given process, there is an increasing need to make a link between the molecular structure of a fluid and its thermodynamic properties. If we would have a thorough understanding of this relation, we would be able to predict or to extrapolate the thermodynamic properties with a minium amount of experimental data. The proceedings of this conference shows that this goals is actively pursued by many groups. In this article, I would like to demonstrate the role of molecular simulations.

Most applications of molecular simulations, that utilize molecular dynamics or the Monte Carlo technique are to systems containing atoms or small molecules. The reason for this is not only that ample experimental data exists for these simple fluids, but also because the available simulation techniques are very efficient for such systems. For example, a molecular dynamics simulation of, say, a hundred methane molecules for several picoseconds is sufficient to determine the thermodynamic or transport properties reliably. This is in sharp contrast to simulations of chain molecules which may take more than several nanoseconds solely to equilibrate. In particular for phase equilibrium calculations this 'slow' equilibration of complex fluids limits the range of applications of molecular simulations. Using conventional simulations techniques it would require many years of CPU-time to determine, for example, the vapour-liquid curves of of long-chain alkanes An alternative is to investigate the thermodynamic properties of *model* fluids. Instead of trying to model a molecule

as realistically as possible, we simplify the system as much as possible such that simulations are possible within a reasonable amount of CPU-time. The aim of such a simulation is to gain insight and eventually to use this insight for practical applications.

If we would be able to develop techniques to simulate phase equilibrium of complex molecules more efficiently, simulations may become an "engineering tool" for estimating properties of systems of industrial importance. Also the simulations of model systems can be of importance, however, these type of simulations require a second step the translation the simulations results of model systems into concepts that can be applied to real fluids —this second step may turned out to be more difficult than the first.

Let us consider two example of these approaches: the phase behaviour of polar fluids and of fluids of long-chain alkanes.

POLAR FLUIDS

The phase behavior of polar fluids is more difficult to describe compared to non-polar fluids. An interesting question is whether modern statistical mechanical theories of polar fluids can be used to arrive at a better description. Since several theories on polar fluids have been published, it is not obvious which one is the best to use. Moreover, these theories are based on a well defined intermolecular potential and to keep these theories tractable the potentials have a simple form. For dipolar fluids, the simplest model is the dipolar hard sphere. If we would use one of these theories to predict the properties of real polar compounds, we would probably find that the agreement with the experimental data is poor. Of course, the theorists would argue; a real polar fluid differs from a dipolar hard-sphere fluid and therefore we should find a disagreement. Unfortunately, the fact that we find such a disagreement does not imply that the ideas underlying the theory are correct. It is, however, possible to use simulations to generate "exact" thermodynamic data for the dipolar hard-sphere fluid. These data can be compared directly with the predictions of the theories, since there is no discussion whether or not the fluid is suitable to test the theory. In this way we are able to find out which theory is the best candidate to be extended to realistic fluids. Simulations were used to validate a theory *before* it is extended for systems of practical interest. Considering the importance of vapour-liquid equilibria for practical applications, we addressed the question which theory can predict the vapour-liquid curve of the dipolar hard-sphere fluid sufficiently accurate? At least this was the aim at the time this project was started.

Historically, phase equilibria has been a topic of considerable interest. For example, one of the very first molecular dynamics simulations, the seminal work of Alder and Wainwright [1], concerned the at that time controversial issue whether or not hard-sphere interactions are sufficient to observe fluid-solid phase equilibria. At present, the fact that a hard-sphere fluid has a fluid-solid phase transition is well established. It is also well known that for a vapour-liquid phase transition attractive forces are required to provide the cohesive energy to stabilize the liquid phase [2]. Since all common molecular fluids have a liquid phase, it is tempting to assume that, if attractive forces are present, vapour-liquid equilibria will always be observed at sufficiently low temperature. Also for the dipolar hard-sphere fluid the existence of a liquid phase appears to be well established. Since the orientationally averaged interaction between two dipoles is a van der Waals-like $1/r^6$ attraction, de Gennes and Pincus conjectured a vapour-liquid coexistence similar to that of a conventional van der Waals fluid [3]. Kalikmanov [4] used this conjecture to estimate the critical point. Also more sophisticated liquid theories such as Mean Spherical Approximation [5] and perturbation theory [6] predict the occurrence of a vapour-liquid curve. Finally, simulations of Ng *et al.* [7] lent support to the theoretical predictions of the existence of liquid-vapor coexistence in a dipolar hard-sphere fluid and determined a coexistence

curve that was located in between the curves predicted by the Mean Spherical Approximation and the one predicted by perturbation theory. The simulations of Ng *et. al.*, however, were performed on relatively small systems. Recently, there has been a significant progress in the development of techniques to determine vapour-liquid equilibria. These novel techniques have been used to confirm the results of Ng *et al.*

In the Gibbs-ensemble technique [8,9], simulations of the vapour and liquid phase are carried out in parallel. Monte Carlo moves which allow for changes in the volume and number of particles, ensure that the two boxes are in thermodynamic equilibrium with each other. The coexistence densities can be determined directly from the two systems. The advantage of this technique is that the two phase are *not* in direct contact, each box is a representative sample of the bulk liquid or vapour and the coexistence properties can be determined from a single simulation using a surprisingly small number of particles.

To our surprise, we were not able to detect phase separation for the dipolar hard-sphere fluid. This may imply that phase separation occurs at conditions that different than expected from the theories. Since we did not want to search at random for the coexistence curve, we used to following approach to search for the coexistence curve. We considered the following model polar fluid:

$$U_\lambda(\mathbf{r}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_i) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \lambda \left(\frac{\sigma}{r}\right)^6 \right] + \frac{\mu^2}{r^3} \left[\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j - \frac{3(\boldsymbol{\mu}_i \cdot \mathbf{r})(\boldsymbol{\mu}_j \cdot \mathbf{r})}{r^2} \right] ,$$

where μ is the dipole moment and $\boldsymbol{\mu}_i$ is the orientation of the dipole of particle i, $\mathbf{r}$ is the distance between the particles. The parameter λ controls the strength of the dispersive Lennard-Jones interactions interactions. It is interesting to consider some limiting cases of this model. For $\lambda = 1$, the model is identical to the so-called Stockmayer fluid [2] for which the vapour-liquid curve has been calculated using computer simulations [10,11]. For $\lambda = 0$, the model reduces to a dipolar soft-sphere fluid which is similar to the dipolar hard-sphere fluid.

In figure 1 the phase diagrams for $\lambda = 1$–0.35 are presented. In figure 2 the critical temperature and density are shown as a function of λ. As expected, if we decrease λ the critical temperature lowers due to the decrease of the dispersive interactions. More surprising is the decrease of the critical density. In figure 2 the predictions of the various theories and the simulation results of Ng *et al.* for the dipolar hard-sphere fluid are shown as well. If we would extrapolate our results to $\lambda = 0$, we would arrive at a much lower critical temperature and density than predicted by the theories and simulations of Ng *et al.* These results are in line with the simulations of Caillol [13], also Caillol could not detect any vapour-liquid coexistence at the conditions predicted by the theories. The simulations suggest that if there is vapour-liquid coexistence, it should be expected at much lower temperatures and densities. For values of $\lambda < 0.3$, however, we could not detect phase coexistence. At conditions where the coexistence curve is expected, we observed the formation of chains of dipoles aligning nose to tail. The formation of chains inhibits the phase separation, which is the reason why we could not detect vapour-liquid coexistence in our original simulations of the dipolar hard-sphere fluid.

These simulation results show that a minimum amount of dispersive energy is required to observe liquid-vapor coexistence in a dipolar fluid. If the dispersive energy is below this threshold, as for example in the hard-sphere dipolar fluid, the system forms chains of dipoles aligning nose to tail. The simulations did not give any evidence that these 'polymer' like systems phase separate into a liquid and vapour phase [11].

In the introduction, I have mentioned that simulating phase coexistence of chain molecules is much more difficult compared to systems containing small molecules or atoms. In the case of the dipolar fluids, we could stop our simulations as soon as we observed the formation of chains. In most practical applications, our interest is in the phase behaviour of chain molecules.
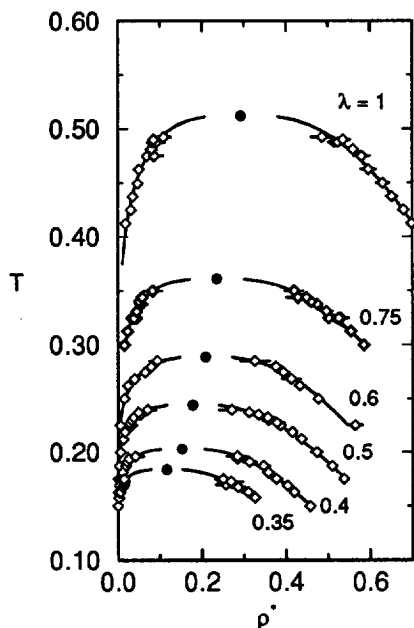
Figure 1: Vapour-liquid curves of the model dipolar fluids for various values of λ. The reduced temperature and density are defined using the dipolar hard-sphere fluid as a reference, i.e. $T^* = k_B T \sigma^3 / \mu^2$ and $\rho^* = \sigma^3 \rho$. The parameters are such that for $\lambda = 1$ the model reduces to a Stockmayer fluid with $\mu^{*2} = \mu^2 / \epsilon \sigma^3 = 4$. The points are the simulation data, the solid lines are fits to the simulations. Details on the simulations can be found in refs. [11,12].

LONG-CHAIN ALKANES

In the petrochemical industry long-chain alkanes are of particular interest. For this type of molecules the conventional techniques are not sufficiently efficient to determine the vapour-liquid coexistence curve routinely. It is instructive to consider the limitation of the conventional simulation techniques in some detail. Let us take as an example a phase equilibrium calculations of alkanes using the Gibbs-ensemble. To ensure that the two boxes containing the liquid and the gas are in equilibrium, we have to exchange particles between the two phases. Let us consider methane, since methane is a small molecule the probability of inserting a methane molecule successfully in the liquid phase, i.e. finding a place that does not overlap with the other methane molecules, is relatively large. We need of the order 1000 attempts to have one that is successful. For ethane, we need to find two those positions without overlap which requires of the order 10^6 attempts, and for propane we need of the order 10^9 attempts. Clearly, for the long-chain alkanes the number of attempts becomes rapidly astronomically large which makes such a simulation impossible.

To make Monte Carlo moves of long-chain molecules possible, Siepmann and Frenkel [14] have developed the configurational-bias Monte Carlo technique for lattice models. This technique is based on the early work of Rosenbluth and Rosenbluth [15] and Harris and Rice [16]. This technique has been extended to off-lattice systems [17,18]. The idea behind the configurational-bias Monte Carlo technique is to grow a molecule atom by atom instead of attempting to insert the entire molecule at random. Figure 3 shows one of the steps in this algorithm. Assume that $i-1$ atoms have been grown and that we now attempt to insert atom i. We generate a set of k trial positions, denoted by the arrows $b_1, \ldots, b_k$. Out of these we select the one with the lowest energy with the highest probability,
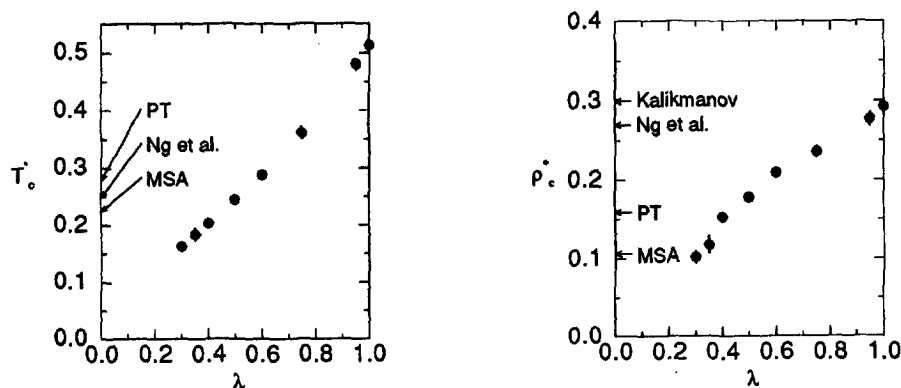
Figure 2: Critical temperature (left) and critical density (right) as a function of λ. The arrows indicate the various estimates of the critical temperatures for the dipolar hard-sphere fluid.

i.e. position $\mathbf{b}_i$ is selected with a probability

$$P(\mathbf{b}_i) = \frac{\exp[-\beta u(\mathbf{b}_i)]}{\sum_{j=1}^{k} \exp[-\beta u(\mathbf{b}_j)]} ,$$

where $u(\mathbf{b}_i)$ denotes the energy of an atom at position $\mathbf{b}_i$. This equation ensures that conformations with a low energy have a high probability of being selected. The above procedure is repeated until the entire molecule has been grown. This growing procedure introduces a bias, such that only the most favourable configurations will be generated. If we were to use the ordinary Metropolis acceptance rule, such a bias in the configurations of the molecules would lead to an incorrect distribution of configurations. Frenkel *et al.* [17] have proven that by adjusting the acceptance rules this bias can be removed exactly.

It is important to note that this is a Monte Carlo technique and therefore cannot be used directly to determine transport properties. One may consider using the configurational-bias Monte Carlo technique to enhance the equilibration of the system, but to determine the transport properties one has to do a molecular dynamics simulation. In many cases the interest is primarily in the thermodynamic properties, in which case the configurational-bias Monte Carlo technique can be extremely useful since it can be 100 orders of magnitude (!) more efficient than the conventional techniques. This technique to insert molecules can also be combined with the Gibbs-ensemble technique, an extensive discussion on the implementation of this algorithm as details can be found in refs. [19–21].

A problem of practical importance for the petrochemical industry is the phase behaviour of long-chain alkanes. Alkanes are thermally unstable above approximately 650K, which makes experimental determination of the critical point of alkanes which are longer than decane extremely difficult. This critical point is used in practical applications, for example, to correlate the parameters of the equation of state of long-chain alkanes [22]. Unfortunately, experimental data are scarce and contradictory, and one has to rely on semi-empirical methods to estimate the critical properties [22]. Siepmann *et al.* [21,23] have used the combination of the Gibbs-ensemble and configurational-bias Monte Carlo technique to simulate the phase behaviour of these alkanes. The alkanes are modelled with a realistic united atom model which includes bond bending and torsion [23]. Figure 4 shows the critical
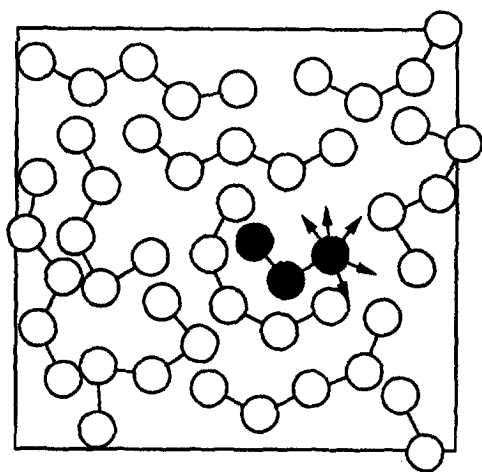
Figure 3: Schematic drawing of the growing of a molecule during a configurational-bias Monte Carlo move; the arrows indicate the k trial orientations to insert the fourth atom.
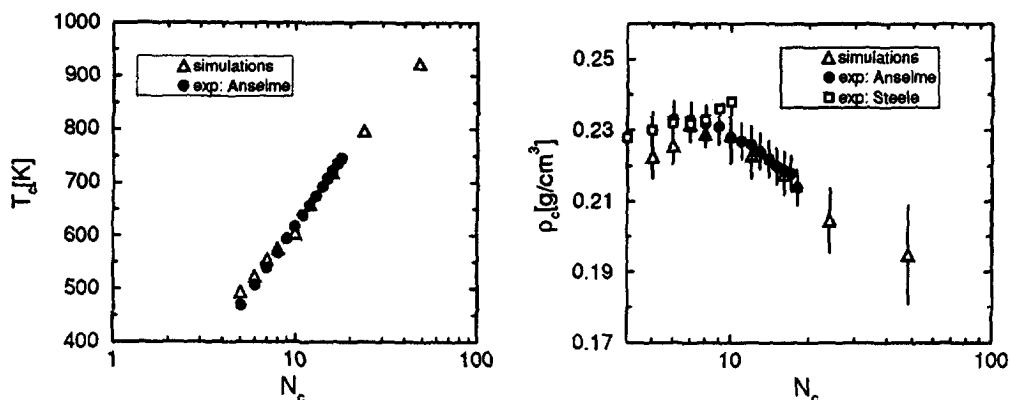

Figure 4: Critical temperature T_c (left) and density ρ_c (right) as a function of carbon number N_c. The simulation data are from refs. [21,23] and the experimental data from refs. [24,25].

temperatures and densities versus carbon number of various alkanes ranging from C_5 to C_{48}. The simulations reproduce the experimental critical temperatures very well. There is, however, considerable disagreement between the various experimental estimates of the critical densities. Much of our current knowledge of the critical properties of the higher alkanes is based on extrapolations of fits of the experimental data up to C_8. The most commonly used extrapolations assume that the critical density is a monotonically increasing function of the carbon number, approaching a limiting value for the very long alkanes [22,25]. In contrast to these predictions based on extrapolations, the experimental data of Anselme *et al.* [24] indicate that the critical density has a maximum for C_8 and then *decreases* monotonically. The data of Steele (as reported in ref. [25]), however, do not give any evidence for such a maximum. The simulations of Siepmann *et al.* indicate the same trend as that observed by Anselme *et al.* Since these calculations can also be performed for much longer alkanes, the results of Siepmann *et al.* strongly support those of Anselme *et al.* At this point it is interesting to note that Mooij *et al.* [19] and Sheng *et al.* [26] used Monte Carlo simulations to study the vapour-liquid curve of a polymeric bead-spring model for various chain lengths. These studies also show a decrease of the

critical density as a function of chain length. This indicates that the decrease of the critical density with chain length is a more general feature of chain molecules that does not depend on the details of a particular model.

CONCLUDING REMARKS

In this article, I have presented some applications of computer simulations in an industrial context. For polar fluids simulations are used to test theories *before* using these for practical problems. From a practical point of view the results of these simulations were disappointing. Instead of being able to demonstrate which theory gives the best predictions of the phase behaviour of the dipolar hard-sphere fluid, the simulations indicate that the dipolar hard-sphere fluid is not a good starting point to develop a theory for real polar fluids. In real polar fluids the dispersive interactions are essential to stabilize the liquid phase. This insight is of importance, but a second step is required; the translation of this insight in a concept that is of immediate practical use.

In the second example, we try to model the interactions of the molecules in a fluid as accurately as possible and to determine its thermodynamic properties. For most fluids of industrial interest the conventional simulation techniques are too slow to be used routinely. Recently, there has been considerable progress in the development of novel Monte Carlo techniques to simulate complex molecules. These techniques are for chain molecules many orders of magnitude more efficient than the conventional techniques to simulate phase equilibria. The use of these novel techniques is illustrated with a simulation of the phase behaviour of long-chain alkanes of which its phase behaviour can simulated at conditions where experiments are, at present, not feasible.

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