Molecular Simulation of the Vapor–Liquid Coexistence Curve of Methanol

Monica E. van Leeuwen* and Berend Smit

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

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Several parameter sets have been presented in the literature for a three-site united-atom model for methanol. We compare the Gibbs ensemble Monte Carlo simulation results for the prediction of vapor–liquid equilibrium for the various sets. Furthermore, we present a new parameter set, which predicts phase coexistence properties of methanol with higher accuracy over a wide range of temperatures and densities.

Introduction

Polar fluids differ from nonpolar fluids in having orientation-dependent interactions, which lead to nonideal thermodynamic behavior. Molecular simulations provide us with a tool to investigate the effect of microscopic (molecular) interactions on macroscopic properties. Methanol is a relatively simple molecule of which the macroscopic behavior is relatively complex as it is a polar fluid (with a dipole moment of 1.71 D) that can form hydrogen bonds. Because of the importance of methanol in practical applications, several methanol models have been developed, with which various aspects of its thermodynamic behavior have been studied.^{1–6} However, these studies were mainly at ambient temperature and density. To investigate whether these models also describe properties of methanol beyond the conditions for which the models were optimized, we compare the performance of various methanol models regarding the phase coexistence prediction. In addition, we present the results of a new model.

Using the Gibbs ensemble Monte Carlo (GEMC) computer simulation technique,⁷ one can simulate data on the coexisting vapor and liquid phases for a given temperature with one single simulation. The GEMC technique has been applied to a variety of systems (for a review see ref 8). More recently, the method has been extended to allow for simulation of chain molecules.^{9,10}

Jorgensen¹ proposed an intermolecular potential for methanol, a three-site united-atom approach combining Lennard-Jones and Coulombic interactions:

$$U_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right] + \frac{q_{\alpha}q_{\beta}e^2}{r} \quad (1)$$

where U is the internal energy, r is the site–site separation, $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the Lennard-Jones energy parameter and size parameter, respectively, and $q_{\alpha}e$ is a point charge located at site α (e denotes the electronic charge). Multisite united-atom intermolecular potentials are considered an important class of potentials, as they contain sufficient detail to distinguish one substance from another whereas molecular simulation calculations remain accessible. The set of parameters for this model has been refined by both Jorgensen and Haughney *et al.*; we will refer to the parameter sets as J1,² J2,⁴ H1, and H2.³ The J1 parameter set was adjusted to reproduce gas-phase dimer properties. J2 was developed within the framework of optimized potentials for the homologous series of alkanols and was optimized to reproduce the liquid density at ambient temperature and pressure. H1 and H2 focus on different characteristics of

TABLE 1: Parameter Values for a Three-Site Intermolecular Potential for Methanol (Eq 1), As Used by Jorgensen (J1,² J2⁴), Haughney *et al.* (H1 and H2³), and This Work^a

	ϵ_O/k_B [K] ϵ_C/k_B [K]	σ_O [Å] σ_C [Å]	q_O [e] q_C [e] q_H [e]
J1	87.94 91.15	3.083 3.861	−0.685 0.285 0.400
J2	85.55 104.17	3.071 3.775	−0.700 0.265 0.435
H1	87.94 91.15	3.083 3.861	−0.728 0.297 0.431
H2	113.0 15.0	3.069 3.931	−0.660 0.228 0.432
this work	86.5 105.2	3.030 3.740	−0.700 0.265 0.435

^a For all sets, ϵ_H/k_B and σ_H are taken to be zero. For all sets except H2, the geometry of the methanol molecule is based on gas-phase values of the intramolecular bond lengths and angles, which are kept fixed at $r_{CO} = 1.4246$ Å, $r_{OH} = 0.9451$ Å, and $\alpha_{COH} = 108.53^\circ$. The H2 model uses results obtained from neutron diffraction data on the liquid: $r_{CO} = 1.4175$ Å, $r_{OH} = 1.0285$ Å, and $\alpha_{COH} = 108.63^\circ$.

the hydrogen-bond strength. In Table 1 the parameter sets applied in this work are summarized.

As the models were tested at ambient temperature, it is an important question which model describes the phase behavior of methanol most accurately over a wide range of temperatures and densities. Mezei¹¹ and Veldhuizen *et al.*¹² calculated the phase diagram, a stringent test of a model, for the J2 model. We compared GEMC simulation results of vapor–liquid equilibrium calculations for the various models.

We used the same GEMC procedure as described earlier,¹³ the simulations being performed with 216 molecules. The Lennard-Jones potential was truncated at half the box size, and the standard long-tail corrections were added.¹⁴ The long-range dipolar interactions were handled with the Ewald summation technique using “tin foil” boundaries.¹⁵ (Note that Jorgensen^{2,4} only applied a spherical cutoff for the dipolar interactions.) The data were analyzed with the techniques described in refs 16 and 17, and the critical point was estimated using the method described in ref 13.

Results

The GEMC results for the various models are summarized and compared against experimental values in Figure 1. In

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Figure 1. Coexistence curves for methanol, as calculated via GEMC simulation for various parameter sets (circles, J1; triangles, J2; squares, H1). For most results, the error bars are smaller than the symbol. The solid lines are fitted to describe the coexistence data and used to estimate the critical point (indicated by filled symbols). The experimental data (dotted line with diamond for the critical point) are taken from Smith and Srivastava.²²

Figure 2. Simulated coexistence curve for methanol as calculated with the new set (circles with error bars). The experimental data (dotted line) are taken from Smith and Srivastava.²²

Figure 3. Simulated vapor pressures (circles with error bars) for methanol as calculated with the new set. The experimental data (dotted line) are taken from Smith and Srivastava.²²

accordance with results from other simulations,⁵ the J2 model performed best, but clearly not yet satisfactorily. Our J2 results compare favorably with the lower-temperature results of Mezei.¹¹ At higher temperatures, our results for the averaged densities (used to estimate the critical point) show a better consistency than those of Mezei. Therefore, we believe that our critical point estimate is more accurate. Strauch and Cummings¹⁸

Figure 4. (a, bottom) Snapshot of a metastable phase of methanol, as described by the H2 parameter set. Long winding hydrogen-bonded chains, formed by the hydroxyl group, are clearly visible as alternating oxygen (red) and hydrogen (white) atoms. The gray atoms represent the methyl group. (b, top) Snapshot of a stable liquid phase, as generated by the J2 parameter set. Note the much higher density and the absence of long hydrogen-bonded chains.

observed excellent results for methanol–water mixtures based on SPC–water and H1–methanol. They suggest that, as SPC–

water yields too low a critical temperature,^{19,20} compensating errors must be involved in the mixture results.²¹ Our H1 results fully supports this suggestion.

All parameter sets were optimized to predict liquid properties at ambient temperature and pressure. In Figure 1, results for these conditions are given as well. Indeed, J2 and H1 approximate the coexistence behavior at room temperature but fail to describe the coexistence curve over a large temperature range. This discrepancy motivated us to investigate whether it is possible to develop a new parametrization for the three-site model that describes the vapor–liquid coexistence curve more accurately over a wide range of temperatures. We chose to optimize the parameters so as to describe the experimental liquid coexistence density at $T = 400$ and 450 K.

In Figure 2 the GEMC results for this model are given and compared with experimental values; in Figure 3 we show the corresponding vapor pressure results. The critical properties were determined as $T_c = 512 \pm 6$ K, $\rho_c = 277 \pm 8$ kg/m³, and $p_c = 99 \pm 134$ bar, which compare favorably with the experimental values of $T_c = 512.64$ K, $\rho_c = 272$ kg/m³, and $p_c = 80.92$ bar.²² For all thermodynamic properties calculated in the GEMC simulations (coexistence densities, vapor pressures, enthalpies of vaporization, critical properties) the model developed in this work performs better than the other models. At ambient temperature, the predictions of the new model for liquid density, vapor pressure, and heat of vaporization are comparable with those of the other models. An intermolecular potential consisting of Lennard-Jones and Coulombic interactions, developed to represent complex interactions such as hydrogen bonding, has its limitations.²³ Nevertheless, we have shown that with this potential it is possible to represent the phase-coexistence properties of methanol with good accuracy.

An interesting observation was that it was impossible to simulate a vapor–liquid phase split for H2. At $T = 350$ K, the fluid appeared to be supercritical. At $T = 300$ K the beginning of a phase split was observed, which never reached equilibrium. The simulation was ended when two metastable glass phases were formed, consisting of long winding chains of hydrogen-bonded methanol that stabilize the configuration. One of these configurations is shown in Figure 4a. The chains, formed by the hydroxyl group of methanol, are clearly visible as alternating oxygen (red) and hydrogen (white) atoms. This can be compared with a snapshot of a saturated-liquid density at the same temperature, generated on the basis of the J2 model, in Figure 4b.

The main reason why the H2 model yields such qualitatively different results is undoubtedly to be found in the exceptionally low energy parameter of the methyl group (see Table 1). In developing the H2 model, Haughney *et al.*³ focused on the strength of the hydrogen-bond interaction by optimizing on the peak height of the pair distribution function measured by X-ray scattering experiments. They found that, within the confines of a three-site model, the only means of getting a better fit was to increase the O–O Lennard-Jones interaction term at the expense of the C–C and C–O terms. However, the strength of the hydrogen bond is overestimated to such an extent that the resulting chain formation is too dominant to allow for a regular vapor–liquid phase split. This behavior strongly resembles the behavior of the dipolar hard sphere, which has recently received renewed attention.^{24–27} For this model fluid, the dispersive attractive interactions are too weak to stabilize a liquid phase such that a vapor and a liquid phase can coexist. From the results of a dipolar transition potential,²⁶ we know that, in order to induce a vapor–liquid phase split, the intermolecular potential must contain sufficient dispersive (attractive) interactions. The H2 model clearly overestimates

the strength of a hydrogen bond or, reversely, underestimates the dispersive interactions in methanol. The GEMC calculations are therefore a quite stringent test for the quality of the model parameter sets.

Conclusions

GEMC calculations proved quite sensitive to intermolecular potential parameter sets. We showed a qualitative difference between the J1, J2, and H1 sets and the H2 set: for the latter the dipolar interactions are so strong that they prohibit the occurrence of a liquid–vapor phase split. We proposed a new parameter set for the methanol model, which showed a quantitative difference to the J1, J2, and H1 sets. This set was optimized to describe liquid coexistence densities at two temperatures and predicts the vapor–liquid curve and related thermodynamic properties with much higher accuracy.

Qualitative results from studies based on the J1, J2, and H1 sets (such as refs 28–30) will probably not change when the refinements of our set are applied. However, for quantitative studies (such as refs 18, 31, and 32) it is important to have a set of parameters that predicts the phase behavior of the pure fluid accurately.

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