Monte Carlo simulation of phase equilibria of aqueous systems

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Abstract

Monte Carlo simulation of aqueous systems

1. Semi-empirical two-body potential models
2. Representation of vapor–liquid equilibria of the pure water, including the critical region
3. The calculation of low and high pressure phase equilibria of water–hydrocarbon
4. The simulation of highly dense system(s) and systems of long chain molecules
5. The comparison of simulation results and experimental data
Introduction

1. The thermodynamic properties and phase behavior of aqueous systems
2. Necessities of molecular simulation
3. Intramolecular and intermolecular interactions
4. Two-body interactions vs. Many-body effects (such as polarizability)
5. The Gibbs ensemble Monte Carlo (GEMC) method

► Semi-empirical two-body potential models have gained considerable popularity for phase equilibrium calculations.
The choice of appropriate potentials for **water and hydrocarbon**

A suitable simulation procedure

The **molecular simulations** performance

The comparison of simulation results and experimental data

1 Water

- a three-site model
  - an oxygen site (exhibiting non-polar and electrostatic interactions)
  + two hydrogen sites (exhibiting electrostatic interactions, only)
SPC, SPC/E and MSPC/E model

Schematic representation of the molecular model [SPC-and SPC/E-] for water
The interaction energy between two water molecules

- For the SPC, SPC/E and MSPC/E model,

\[ u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] + \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \frac{1}{4\pi \varepsilon_0} \frac{q_\gamma q_\delta}{r_{\gamma\delta}} \]

- For the exp-6 model,

\[ u(r) = \begin{cases} \frac{\varepsilon}{1 - (6/\alpha)} \left[ \frac{6}{\alpha} \exp \left( \alpha \left( 1 - \frac{r}{r_m} \right) \right) - \left( \frac{r_m}{r} \right)^6 \right] + \sum_{\gamma=1}^{3} \sum_{\delta=1}^{3} \frac{1}{4\pi \varepsilon_0} \frac{q_\gamma q_\delta}{r_{\gamma\delta}} & \text{for } r > r_{\text{max}} \\ \infty & \text{for } r < r_{\text{max}} \end{cases} \]
### Table 1. Critical parameters for pure water

<table>
<thead>
<tr>
<th>Model</th>
<th>$T_c$ (K)</th>
<th>$P_c$ (bar)</th>
<th>$\rho_c$ (g/cm$^3$)</th>
<th>$Z_c$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC</td>
<td>587</td>
<td>–</td>
<td>0.27</td>
<td>–</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>596</td>
<td>126</td>
<td>0.289</td>
<td>0.158</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>593.8</td>
<td>129</td>
<td>0.271</td>
<td>0.173</td>
<td>[14]</td>
</tr>
<tr>
<td>SPC/E</td>
<td>640</td>
<td>160</td>
<td>0.29</td>
<td>0.187</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>630.4</td>
<td>–</td>
<td>0.308</td>
<td>–</td>
<td>[38]</td>
</tr>
<tr>
<td></td>
<td>630</td>
<td>148</td>
<td>0.295</td>
<td>0.172</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>638.6</td>
<td>139</td>
<td>0.273</td>
<td>0.173</td>
<td>[14]</td>
</tr>
<tr>
<td>MSPC/E</td>
<td>602</td>
<td>148</td>
<td>0.310</td>
<td>0.172</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>609.8</td>
<td>139</td>
<td>0.287</td>
<td>0.172</td>
<td>[14]</td>
</tr>
<tr>
<td>Exp-6</td>
<td>645.9</td>
<td>183</td>
<td>0.297</td>
<td>0.207</td>
<td>[14]</td>
</tr>
<tr>
<td>Experimental</td>
<td>647.1</td>
<td>220.64</td>
<td>0.322</td>
<td>0.229</td>
<td>[39]</td>
</tr>
</tbody>
</table>
Fig. 1. Pure water vapor–liquid equilibria

Fig. 2. Pure water–vapor pressure.

- Experimental data (solid line), and molecular simulation results from SPC (triangles), SPC/E (diamonds), MSPC/E (squares) and exp-6 (open circles) models
Potential models (6)


Pure water vapor pressure simulation data
Potential models (7)

2 Hydrocarbon molecules

- Non-bonded intramolecular and intermolecular interactions
  
  Using a Lennard–Jones potential, the so-called TraPPE potential and an exp-6 potential

- Non-polar interactions between unlike groups
  
  Using the Lorentz–Berthelot combining rules
Simulation methodologies (1)

- **Pure water vapor–liquid equilibrium**
  
  .... Using the GEMC-NVT method

- **The average pressure simulation**
  
  .... Using an equation based on the molecular virial expression

- **The size of the system**; 200–250 molecules

- **Water–methane and water–ethane mixtures at high pressure**
  
  .... Using GEMC-NPT simulation
  .... In this case, a typical simulation consisted of approximately 200 water and 100 hydrocarbon molecules.
Simulation methodologies (2)

Small hydrocarbon solubilities in water

Using standard thermodynamic relations, the Henry's law constant can be expressed in terms of the hydrocarbon excess chemical potential in water

\[
H_{hc\rightarrow w} = \lim_{\rho_{hc}\to 0} \left( \frac{\rho_w}{\beta} \exp(\beta \mu_{hc}^{ex}) \right)
\]

where \( \rho_w \): the pure water number density

\( \beta = 1/k_B T \)

\( \mu_{hc}^{ex} \): By using the Widom test particle insertion method
Widom’s test particle insertion method

- The infinite-dilution excess chemical potential
- To remove a test particle from the system (going from an $N$-molecule system to an $(N-1)$-molecule system) and calculate the corresponding energy change

$$
\beta \mu^\text{ex} = -\ln \left( \frac{1}{V} \frac{Z(N, P, T)}{Z(N - 1, P, T)} \right) = -\ln \left( \frac{1}{V} \frac{\prod_{i=1}^{N-1} H(r_{i,N})}{\prod_{i=1}^{N-1} H(r_{i,N}) \exp(\beta U^{(N)}(\vec{r}_1, \ldots, \vec{r}_N)) / V} \right)_{N,P,T}
$$

- The test-particle insertion method has been used successfully at low to moderate fluid densities.
Fig. 3.

Henry's law constant of methane in water

- Experimental data (solid line)
- Widom insertion Monte Carlo simulations
  - For water
    * SPC/E model (diamonds)
    * MSPC/E model (squares)
  - For methane
    * TraPPE model
Results and discussion (1)

Fig. 4. Water–methane phase equilibria

Fig. 5. Water–ethane phase equilibria

Complete miscibility
Results and discussion (2)

Fig. 6. Henry's law constant of $n$-butane and of $n$-hexane in water

Fig. 7. Henry's law constant of cyclohexane and of benzene in water
Conclusion

1. Significant advances have been made recently in the development of novel methodologies for the efficient molecular simulation of highly non-ideal mixture phase equilibria.

2. It is possible to obtain quantitative results for systems at remote conditions, as for example at very high pressure.

3. Based on the results presented here and elsewhere, it is apparent that more complex potentials that account explicitly for polarizability and other many body effects are necessary.
References