Chemical Potential of Benzene Fluid from Monte Carlo Simulation with Anisotropic United Atom Model

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Received 12 August 2013; Accepted 16 September 2013

ABSTRACT

The profile of chemical potential of benzene fluid has been investigated using Anisotropic United Atom (AUA) model. A Monte Carlo simulation in canonical ensemble was done to obtain the isotherm of benzene fluid, from which the excess part of chemical potential was calculated. A surge of potential energy is observed during the simulation at high temperature which is related to the gas-liquid phase transition. The isotherm profile indicates the tendency of benzene to condensate due to the strong attractive interaction. The results show that the chemical potential of benzene rapidly deviates from its ideal gas counterpart even at low density.

Keywords: Benzene, Anisotropic United Atom, chemical potential, Monte Carlo simulation

INTRODUCTION

Benzene is an attractive subject from both scientific and industrial perspectives. It represents the interaction of aromatic π-systems which immensely control the stability of protein and nucleic acid [1]. Benzene is widely used in laboratory, petrochemical, and other industry either as additive, solvent, or raw materials. The extent of benzene usage increases the risk of benzene exposure to the environment. US Environmental Protection Agency classified benzene as a carcinogen, and recommended activated carbon adsorption as a control to prevent benzene intrusion to the environment [2].

Grand Canonical Monte Carlo (GCMC) simulation is useful to study the adsorption of a compound at equilibrium condition, in which the chemical potential of component in the adsorbed phase is equivalent to the bulk phase [3]. Nguyen and co-workers had investigated the adsorption of benzene in graphitic slit pore in the presence of water molecules [4], and Klomkiang had reported the multilayer adsorption of benzene on a graphite surface [5]. Both used GCMC simulation with TraPP-EH model of benzene [6] which consists of 12 Lennard Jones and Coulomb interaction sites; thus the calculation of potential energy of a system with N molecules of benzene would involve 24^2×N(N−1) pair-interactions. The chemical potential of benzene was treated by assuming benzene fluid as an ideal gas in both works.

Contreras and co-workers had reported the usage of Anisotropic United Atoms (AUA) model of benzene in their Monte Carlo simulation [7]. In this model, an interaction site is located between carbon and hydrogen atom, making a total of six interaction sites in benzene. The number of pair interaction that occurs between two molecules of benzene is then 6^2×N(N−1), which is 1/16 times fewer than TraPP-EH model; thus reducing the
computational resources needed to carry out the simulation. The model has been reported to accurately reproduce the physical properties of benzene [7]. Similarly, the rigid body model of water, for example, is known to reproduce many important properties of water [8] with less computational cost as compared to some flexible models of water [9]. In case of cyclic organic compound model, the inclusion of pseudorotation in a twist-model of tetrahydrofuran has been reported to give a negligible difference on thermodynamic data obtained with a simpler planar model [10].

While the AUA is a promising model to be utilized in the study of benzene system, the chemical potential of benzene fluid (gas and liquid) using this model is not known. The chemical potential information is essential to carry out a GCMC simulation for the study of adsorption, for example. Even though some works [4, 5] had reported the treatment of chemical potential of benzene using ideal gas assumption, it is intriguing to question the density limit of which benzene fluid can be fairly treated as an ideal gas. In this work, we provide a realistic chemical potential of benzene fluid of AUA model using simple calculation from the isotherm data which were priorly obtained using Monte Carlo simulation in canonical ensemble. The characteristic of potential energy and chemical potential of this model is also discussed. We show that the chemical potential of benzene fluid rapidly deviates from ideal state even at low density due to the strong intermolecular interaction.

**SIMULATION METHOD**

**Interaction model**

The potential energy of system $\Phi$ is described as the sum of pair-interaction $\phi_{ij}$ between a pair of benzenes (noted here as $i$ and $j$) in the absence of any external field

$$\Phi = \sum_i \sum_{j>i} \phi_{ij}(r_i, r_j, \Omega_i, \Omega_j)$$

where $r$ is the position and $\Omega$ is the orientation of benzene molecule. The interaction between a pair of benzene molecules is described with Anisotropic United Atom (AUA) potential model. In this model, six interaction sites are located outside of constituent atoms (Figure 1), and each site is described as Lennard-Jones (LJ) 12-6 potential. The potential energy arises from a pair of benzene molecules is then

$$\phi_{ij}(r_i, r_j, \Omega_i, \Omega_j) = \sum_{a(i)} \sum_{b(j)} 6 \varepsilon \left\{ \left( \frac{\sigma}{r_{ab}} \right)^{12} - \left( \frac{\sigma}{r_{ab}} \right)^{6} \right\}$$

with $a$ and $b$ represent interaction site in each benzene. The LJ parameters ($\sigma$ and $\varepsilon$) and geometry parameters (the distance shift of potential site from carbon atom $\delta$, the distance of carbon atom from the center of mass $r_{CC}$, and the angle between carbon atoms $\Theta$) used in this research are summarized in Table 1. These parameters have been reported to accurately reproduce several thermodynamics data such as saturated vapor pressure, vaporization enthalpy, and liquid density [7]. The pair potential energy is truncated smoothly at $(r_c = 12 \text{Å})$ and the discontinuity is avoided by using a switching function $f_s$ [11],

$$f_s(r) = \frac{(r - r_c)^3 \{10(r - r_l)^2 - 5(r - r_l)(r - r_c) - (r - r_c)^2\}}{(r_l - r_c)^5}$$
where \( r \) is the distance between two center of mass, \( r_c \) is the distance where the pair-potential is truncated, and \( r_1 \) is the distance where the switching function begins to take effect with \( r_c - r_1 = 2 \) Å.

**Figure 1.** Anisotropic United Atom model for Benzene. The interaction sites, showed as red circles, are located between carbon and hydrogen atom.

**Table 1.** The optimized parameters for AUA model of benzene

| Parameter | Value          |
|-----------|----------------|
| \( \sigma \) | 3.2464 Å      |
| \( \varepsilon \) | \( 7.428 \times 10^{-2} \) kJ mol\(^{-1} \) |
| \( \delta \) | \( 4.071 \times 10^{-1} \) Å      |
| \( r_{CC} \) | 1.8071 Å      |
| \( \Theta \) | \( \pi / 3 \) |

**Simulation Procedure**

Monte Carlo simulations in canonical ensemble are carried out to obtain the isotherm data of benzene fluid. In this ensemble, the number of molecules \( N \), temperature \( T \), and volume \( V \) are kept constant during the simulation. The temperature state is chosen to be 298.15 and 373.15 K, and the investigated density is chosen from \( 10^{-5} \) to 1.0 g mL\(^{-1} \). Benzene molecules \( (N = 216) \) are implemented in a cubic simulation cell with a starting configuration of simple cubic crystal. Standard periodic boundary condition with minimum image convention is adopted in this simulation to overcome the surface effects due to the limited size of the simulation cell [12]. Each Monte Carlo step consists of a trial to translate and rotate a benzene molecule, which is chosen randomly based on uniform distribution, and the transition from old configuration \( m \) to the new configuration \( n \) has a probability \( P \) of

\[
P_{m \rightarrow n} = \frac{P_n}{P_m} = e^{-(E_n-E_m)/k_B T} \left( \frac{\sin \Theta_n}{\sin \Theta_m} \right)
\]

with \( E \) is the potential energy of system, \( k_B \) is Boltzmann constant, \( T \) is temperature, and \( \Theta \) is one of the Euler angle component of the benzene molecule. Each simulation consists of a minimum of \( 10^7 \) Monte Carlo steps.
RESULT AND DISCUSSION
Characteristic of the Pair Potential Energy

The potential energy arising from pair-interaction between two molecules of ben- zene with AUA model, which consists of six LJ interaction sites, are presented in Figure 2. The switching function is not applied in this case. The orientation of a benzene molecule greatly affects the potential energy arising from its interaction with the sur- rounding molecules. The variation of potential energy due to the change of orientation of benzene molecules is expressed in Figure 2a as the standard deviation bar. Neverthe- less, the average of potential energy is following the shape of LJ 12-6 potential. When the distance between molecules is close, the variation of potentials energy are expectedly large due to the possibility of an overlap between constituent atoms. As the separation distance grows large, the effect of orientation to the potential energy become less signifi- cant. The variation is less than 1 kJ mol\(^{-1}\) at a distance larger than 12 Å, which is the reference for choosing the pair-potential cut-off distance \(r_c\).

As a comparison, the potential energy of interaction between a pair of individual interaction sites is shown in Figure 2b. It shows that the combination of interaction sites in a benzene molecule gives an energy profile with deeper curve which vanishes slower, i.e. the interaction has a longer range, compared to the individual interaction site. These phenomena are not exclusive to atomic case since aggregate of molecules, such as in colloid system, is known to have long range interaction compared to individual molecule in solution system.

Figure 2. Pair potential energy \(\phi_{ij}\) of benzenes (a) averaged over all orientation with the variation is described as the standard deviation bar and (b) compared to the potential energy between a pair of individual interaction sites (red curve).

Potential energy of the system

Figure 3 shows that the tendency of potential energy of benzene fluid system is to decrease with the increase of density up to \(\rho = 0.85\) g mL\(^{-1}\). Roughly, the negative gradient indicates that the system is less stable at lower density under the studied tem- perature. Lower temperature also provides lower potential energy of the system. Further compression, however, caused the potential energy to increase rapidly as the system be- come dense and repulsion between molecules is dominating. At \(T = 373.15\) K, there is a surge of energy of 6.4 kJ mol\(^{-1}\) at \(\rho = 0.025\) g mL\(^{-1}\). This phenomenon indicates the gas-liquid phase transition which is possibly related to the imposed temperature that is higher than the boiling point of benzene, as the surge was not observed at \(T = 298.15\) K.
Figure 3. The potential energy of benzene fluid system as a function of density $\rho$

 Isotherm of benzene fluid

The pressure $p$ of system in the Monte Carlo simulation is obtained by calculating the internal Virial term $w$, that is the cross product of pair distance $r_{ij}$ and force $F_{ij}$ summed over all pairs:

$$ pV = Nk_B T + \frac{1}{3} \sum_i \sum_{j>i} r_{ij} \cdot F_{ij} $$

(5)

$$ F_{ij} = -\nabla \phi_{ij} $$

(6)

The relation of density and pressure of benzene fluids obtained from Monte Carlo simulation at constant temperature is shown in Figure 4. The negative pressure indicates the tendency of benzene to condensate under the studied condition. At higher temperature, the tendency of benzene to condensate is lower as indicated by the increase of pressure overall. It is important to note that the negative pressure is peaked near the density of 0.85 g mL$^{-1}$ at $T = 298.15$ K, which is close to the density of benzene fluid as observed in experiment at 298.15 K and 1 atm. Further compression lead to the rapid increase of pressure.

Figure 4. Isotherm of benzene fluid.
Chemical potential of benzene fluid

The chemical potential of a single-component system $\mu_g$ can be calculated by [13]

$$
\mu_g(T,p) = k_B T \left\{ \ln \{\rho \Lambda \}^3 - 1 + \ln \left\{ h^2 / 4\pi^2 I k_B T \right\} \right\} + \int_0^\rho (p - \rho k_B T) / \rho^2 \, d\rho + p / \rho
$$

(7)

where $\Lambda$ is thermal De Broglie wavelength, $h$ is Planck constant, and $I$ is the inertia moment. The first term in Eq. 7 is the ideal chemical potential and the latter term is the excess chemical potential which can be solved numerically using isotherm data.

The results are shown in Figure 5 together with the chemical potential of benzene as an ideal gas. The chemical potential of benzene fluids resembles its ideal gas counterpart at low density where interactions between benzene molecules are practically negligible due to long separation distance. However, as the density increases, the interaction between benzene molecules caused the chemical potential to deviates from those of ideal gas. In particular, strong interaction between benzene molecules, as shown in Figure 2, caused the deviation to occur rapidly at even low density. At $T = 298.15$ K, the deviation occurs when the density of benzenes fluid is higher than $1 \times 10^{-3}$ g mL$^{-1}$, which correspond to the system pressure of $3.27 \times 10^{-1}$ atm. On the other hand, at $T = 373.15$ K, the deviation start to occur when the density is higher than $2.5 \times 10^{-2}$ g mL$^{-1}$. Considering that benzene is more stable as a gas phase at higher temperature, it is reasonable that the deviation takes place at higher density for high temperature, compared to those at low temperature. At $T = 298.15$ K, the chemical potential also has its lowest value around density of 0.85 g mL$^{-1}$ which indicates the benzene preference to this density. At low density, the chemical potential of benzene at $T = 373.15$ K is lower than that of $T = 298.15$ K; but following the increase of density, this situation is reversed.

Figure 5. The chemical potential $\mu$ of benzene fluids and ideal gas as a function of density $\rho$. Note that the density axis is in logarithmic scale.
CONCLUSION
The isotherm of benzene fluid can be obtained by performing a Monte Carlo simulation in canonical ensemble with the Anisotropic United Atoms model. The excess part of chemical potential of benzene fluid of this model then can be calculated using the isotherm data to give a realistic chemical potential whose trend is conceivable at 298.15 and 373.15 K. The results shows that benzene fluid deviates from ideal gas behavior even at a density as low as $1 \times 10^{-3}$ g mL$^{-1}$ (gas phase), which correspond to the pressure of $3.27 \times 10^{-1}$ atm; thus highlight the importance of the excess part of chemical potential in the study of benzene.

ACKNOWLEDGMENT
The simulations were carried out using Intel Xeon hexacore workstation which was arranged from PHBI research grant through DIPA Universitas Brawijaya No. 0636/023-04.2.16/15/2012 from The Directorate General of Higher Education, Indonesian Ministry of Education.

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