Molecular Dynamics Simulation Studies of Benzene, Toluene, and \( p \)-Xylene in NpT Ensemble: Thermodynamic, Structural, and Dynamic Properties

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Received October 31, 2001

In this paper we have presented the results of thermodynamic, structural, and dynamic properties of model systems for liquid benzene, toluene and \( p \)-xylene in an isobaric-isothermal (NpT) ensemble at 283.15, 303.15, 323.15, and 343.15 K using molecular dynamics (MD) simulation. This work is initiated to compensate for our previous canonical (NVT) ensemble MD simulations [Bull. Kor. Chem. Soc. 2001, 23, 441] for the same systems in which the calculated pressures were too low. The calculated pressures in the NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. The first and second peaks in the center of mass \( g(r) \) diminish gradually and the minima increase as usual for the three liquids as the temperature increases. The three peaks of the site-site \( g_{CC}(r) \) at 283.15 K support the perpendicular structure of nearest neighbors in liquid benzene. Two self-diffusion coefficients of liquid benzene via the Einstein equation and via the Green-Kubo relation are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene and \( p \)-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group. The friction constants calculated from the force auto-correlation (FAC) function with the assumption that the fast random force correlation ends at time which the FAC has the first negative value give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The friction constants calculated from the FAC’s are always less than those obtained from the friction-diffusion relation which reflects that the random FAC decays slower than the total FAC as described by Kubo [Rep. Prog. Phys. 1966, 29, 255].

Keywords: Molecular dynamics simulation, Benzene, Toluene, \( p \)-Xylene, NpT ensemble.

Introduction

In a previous paper\(^1\) we reported the results of thermodynamic, structural and dynamic properties of liquid benzene, toluene, and \( p \)-xylene in a canonical (NVT) ensemble at 298.15 K by molecular dynamics (MD) simulations. The molecular model adopted for these molecules was a combination of the rigid body treatment for the benzene ring and an atomistically detailed model for the methyl hydrogen atoms. The various thermodynamic properties reflected that the intermolecular interactions become stronger as the number of methyl group attached into the benzene ring increases. However, the calculated pressures were too low in the NVT ensemble MD simulations. The pronounced nearest neighbor peak in the center of mass \( g(r) \) of liquid benzene at 283.15 K provided the interpretation that nearest neighbors tend to be perpendicular. Two self-diffusion coefficients of liquid benzene at 283.15 K calculated from MSD and VAC function were in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene also agreed well with the experimental ones for toluene in benzene and for toluene in cyclohexane.

In NVT MD simulations, the density of system is automatically determined from the fixed number of molecules and the fixed volume. When one considers the change of the density of system, \( \rho = N/V \), the change of either the number of molecules \( N \) or the volume \( V \) is allowed. If the change of \( N \) is chosen, the simulation ensemble becomes a grand canonical ensemble (\( \mu \)VT), and the choice of the change of \( V \) means an isobaric-isothermal ensemble (NpT). Though the performance of MD simulations in NpT ensemble for molecular liquid is not easy, a \( \mu \)VT ensemble MD simulation involved with the creation and banishment of molecules is more difficult to carry out. Equations of motion for the NpT MD simulation of molecular liquids presented in the next section were derived by Evans.\(^2,3\)

In this study we have chosen an NpT ensemble in order to carry out MD simulations for liquid benzene, toluene, and \( p \)-xylene at 283.15, 303.15, 323.15, and 343.15 K. The primary purpose of this work is to compensate for our previous NVT MD simulations,\(^1\) and, secondly, to investigate the equilibrium thermodynamic properties, molecular structures, and diffusion coefficients and friction constants as a function of temperature.

This paper is organized as follows: In Section II, we present the molecular models and NpT MD simulation methods. We discuss our simulation results in Section III and present the concluding remarks in Section IV.

Molecular Models and NpT MD Simulation Methods

The molecular model used is the same as in the previous NVT MD simulation;\(^1\) the benzene ring is assumed as a rigid-body, but three C-H bonds in the methyl groups of toluene (\( \text{C}_6\text{H}_5\text{CH}_3 \)) and \( p \)-xylene (\( \text{CH}_3\text{C}_6\text{H}_4\text{CH}_3 \)) are not assumed to be rigid. Simple harmonic oscillation potentials for C-H bond stretching and C-C-H and H-C-H bond angle
bending in the methyl group are used, and the methyl groups are rotating according to a torsional potential. Potential parameters for the molecular model are given in Table 1.

The equation of translational motion for these systems are

\[ \mathbf{r}_i = \mathbf{p}_i + \dot{\mathbf{r}}_i \]  

(1)

\[ \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{F}_r - \mathbf{A}_i \]  

(2)

where \( \mathbf{F}_i \) is the force acting on molecule \( i \). The translational temperature constant parameter is given by Gaussian isokinetics:4

\[ \alpha_i = \frac{\sum_i \mathbf{p}_i \cdot \mathbf{F}_i}{\sum_i \mathbf{p}_i^2} - \dot{\varepsilon} \]  

(3)

and the dilation rate is given by

\[ \dot{\varepsilon} = \frac{\sum_i \mathbf{r}_i \cdot \mathbf{p}_i (\Phi''_{ij} + \Phi''_{ij}/r_{ij})}{m \sum_i \mathbf{r}_i^2 (\Phi''_{ij} + \Phi''_{ij}/r_{ij}) + 9pV} \]  

(4)

For polyatomic molecules with different site-site atomic potentials, the potential \( \Phi(r) \) is averaged from the site-site atomic potentials. For benzene, \( \Phi(r) \) becomes

\[ \Phi(r) = [36\phi_1(r) + 72\phi_2(r) + 36\phi_3(r)]/144, \]  

(5)

where \( \phi_1(r) \) is the C-C Lennard-Jones potential, \( \phi_2(r) \) the C-H, and \( \phi_3(r) \) the H-H.

The equations of rotational motion about the center of mass for molecular liquids using quaternions are as follows:8

\[ L_k = T_k - \alpha_k L_k, \]  

(6)

\[ L_k' = A_k \cdot L_k, \]  

(7)

\[ \omega_{ik} = L_{ik}' / I_k, \]  

(8)

\[
\begin{pmatrix}
\dot{q}_{11} \\
\dot{q}_{12} \\
\dot{q}_{13} \\
\dot{q}_{14}
\end{pmatrix} = \frac{1}{2}
\begin{pmatrix}
-q_{13} & -q_{14} & q_{12} & q_{11} \\
q_{14} & -q_{13} & -q_{11} & q_{12} \\
q_{12} & q_{11} & q_{14} & q_{13} \\
-q_{12} & q_{11} & -q_{13} & q_{14}
\end{pmatrix}
\begin{pmatrix}
\omega_{p1} \\
\omega_{p2} \\
\omega_{p3} \\
\omega_{p4}
\end{pmatrix}
\]  

(9)

where \( T_k \) is the torque on molecule \( i \) in the laboratory frame, and \( L_k' \) and \( \omega_{ik} \) the angular momenta and angular velocities of molecule \( i \) in its principle axis frame, respectively. \( A_k \) is the rotation matrix which transforms vectors form the laboratory to principal axis frame of molecule \( i \), and \( q_{ik} \) are the quaternions related to the Euler angles describing the orientation of molecule \( i \) and space. The rotational temperature constraint parameter \( \alpha_k \) is given by

\[ \alpha_k = \sum_i L_i \cdot T_i / \sum_i L_i^2. \]  

(10)

Since the volume of the system changes, the usual boundary conditions cannot be used. If molecule \( i \) moves outside the simulation box, its image enters through the opposing face in the usual way, but all the higher derivatives of \( \mathbf{r} \) and \( \dot{\varepsilon} \) are changed in this imaging procedure and they should be recalculated.5

The next consideration is the so called long-range correction due to the spherical cutoff of the potential which is a tail correction estimating the contribution from pairs of particles whose separation is greater than the cut-off distance \( r_c \). These corrections are calculated by assuming that the radial distribution function \( g(r) \) is unity for \( r > r_c \). If the distance between any two centers of mass is within this distance, all the interactions between the atomic sites of two molecules are considered. The correction is for the potential energy6

\[ E_{LRC} / N = \frac{1}{2} \int_{r_c}^\infty \Phi(r) g(r) 4\pi r^2 dr, \]  

(11)

for the pressure

\[ p_{LRC} = -\frac{1}{6} \int_{r_c}^\infty r \Phi(r) g(r) 4\pi r^2 dr, \]  

(12)

which is especially important in the NPT ensemble simulation, and for the denominator of Eq. (4)

\[ D_{LRC} = \frac{p}{2} \int_{r_c}^\infty [r^2 \Phi''(r) + r^2 \Phi''(r)] g(r) 4\pi r^2 dr, \]  

(13)

where \( \Phi(r) \) is given by Eq. (5).

The usual periodic boundary condition in the \( x \)-, \( y \)-, and \( z \)-directions and minimum image convention for pair potential were applied. A spherical cut-off of radius \( R_c = 1.25 \text{ nm} \) was employed for the pair interactions. For the integration over time, we adopted Gear’s fifth order predictor-corrector algorithm10 with a time step of 0.0002 ps. MD simulation runs of about several 150,000 time steps were needed for each liquid molecular system to reach equilibrium. The equilibrium properties were then averaged over 5 blocks of 150,000 time steps for a total of 750,000 time steps, and the configurations of molecules were stored every 10 time steps for analyses of structural and dynamic properties.

\[ \text{Table 1. Potential parameters for liquid benzene, toluene, and } p \text{-xylene} \]

<table>
<thead>
<tr>
<th>LJ parameters</th>
<th>( \sigma (\text{nm}) )</th>
<th>( \varepsilon (\text{kJ/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>0.3367</td>
<td>0.4656</td>
</tr>
<tr>
<td>C-H</td>
<td>0.2799</td>
<td>0.1722</td>
</tr>
<tr>
<td>H-H</td>
<td>0.2230</td>
<td>0.0731</td>
</tr>
<tr>
<td>bond stretching</td>
<td>( r_b (\text{nm}) )</td>
<td>( K_b (\text{kJ/mol nm}^2) )</td>
</tr>
<tr>
<td>C-H</td>
<td>0.110</td>
<td>147000</td>
</tr>
<tr>
<td>bond angle bending</td>
<td>( \theta_b (\text{deg}) )</td>
<td>( K_1 (\text{kJ/mol deg}^2) )</td>
</tr>
<tr>
<td>C-C-H</td>
<td>109.7</td>
<td>0.050209</td>
</tr>
<tr>
<td>H-C</td>
<td>107.9</td>
<td>0.050209</td>
</tr>
<tr>
<td>torsional</td>
<td>( \phi_b (\text{deg}) )</td>
<td>( K_b (\text{kJ/mol}) )</td>
</tr>
<tr>
<td>C-C-C-H</td>
<td>180</td>
<td>11.72</td>
</tr>
</tbody>
</table>

| \begin{pmatrix}
q_{11} \\
q_{12} \\
q_{13} \\
q_{14}
\end{pmatrix} = \frac{1}{2}
\begin{pmatrix}
-q_{13} & -q_{14} & q_{12} & q_{11} \\
q_{14} & -q_{13} & -q_{11} & q_{12} \\
q_{12} & q_{11} & q_{14} & q_{13} \\
-q_{12} & q_{11} & -q_{13} & q_{14}
\end{pmatrix}
\begin{pmatrix}
\omega_p^{p1} \\
\omega_p^{p2} \\
\omega_p^{p3} \\
\omega_p^{p4}
\end{pmatrix} \]  

\[ \text{Results and Discussion} \]

\[ \text{Thermodynamic properties} \]

Thermodynamic properties for liquid benzene, toluene, and \( p \)-xylene at 283.15, 303.15, 323.15, and 343.15 K obtained from our MD simulations are
listed in Tables 2, 3, and 4, respectively. The calculated pressures in our NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. In the previous NVT ensemble MD simulations,\(^1\) the volumes for benzene, toluene and \(p\)-xylene were fixed as 17.7, 21.2, and 24.6 nm\(^3\) respectively at 298.15 K.\(^1\) K which were apparently overestimated, and the calculated pressures in the NVT MD\(^3\) were too low.

The intermolecular energy increases negatively as the number of methyl group increases from liquid benzene to liquid toluene, and decreases negatively from liquid toluene to liquid \(p\)-xylene, which is the opposite trend to what we observed in the previous NVT ensemble MD simulations.\(^1\) This reflects that the calculated intermolecular energy depends on the volume of the system very much. When compared with the experimental solvation enthalpies of vapors condensing into liquids at 298.15 K\(^1\) which are \(-32.5, -36.6,\) and \(-41.1\) kJ/mol for benzene, toluene and \(p\)-xylene, respectively, the intermolecular energies for benzene and toluene are in good agreement but not for \(p\)-xylene.

The C-H bond stretching and the C-C-H and H-C-H bond angle bending energies of both liquid toluene and \(p\)-xylene increase roughly with the temperature. This reflects that the steric effect becomes larger and repels each other, which contributes to the larger repulsive interactions of the bond stretching and the bond angle bending potential energies, as the temperature increases. However, the values of the bond stretching length and bond angle bending angle are remained constant (not shown).

Toluene has two dihedral states which are doubly imposed torsional rotational potential on the same bond, and \(p\)-xylene has four dihedral states of which each two are doubly imposed torsional rotational potential on the same bonds. The average \% of C-C-C-H \(trans\) and the total barrier crossing T-G and G-T in toluene are related to the doubly imposed dihedral state in the way that if one dihedral state is \(gauche\), then the other should be in \(trans\), or \(vice versa\). That is why the average C-C-C-H torsional energy is the same as \(K_3\) since \(\phi_1 = 180^\circ - \phi_1\) for a given dihedral angle \(\phi_1\) and \(V_{average} = 1/2\) \(V(\phi_1) + V(\phi_2)\), where \(V(\phi_1)\) is the volume of the shell, and \(\leftrightarrow\) indicates the isothermal-isobaric ensemble (NpT) average. The center of mass T-G and G-T in toluene and \(p\)-xylene in our NpT ensemble MD simulations are higher than those in the previous NVT MD\(^\ast\) (about 25,510 for toluene and 60,140 for \(p\)-xylene, respectively, in 750,000 time steps at 298.15 K).\(^1\)

**Structural properties.** The radial distribution function, \(G(r)\), is defined as

\[
g(r) = \frac{1}{\rho_0} \langle \frac{N(r, \Delta r)}{V(r, \Delta r)} \rangle
\]

where \(\rho_0\) is the bulk density, \(N(r, \Delta r)\) is the number of molecules in a shell which is between \(r - \Delta r/2\) and \(r + \Delta r/2\) from the center of a molecule with \(\Delta r = 0.005\) nm, \(V(r, \Delta r)\) is the volume of the shell, and \(\langle \cdots \rangle\) indicates the isothermal-isobaric ensemble (NpT) average. The center of mass \(g(r)\) of liquid benzene, toluene, and \(p\)-xylene at 283.15, 303.15, 323.15, and 343.15 K are shown in Figures 1-3, respectively, and the site-site \(g_{C-C}(r)\) of liquid benzene, toluene, and \(p\)-xylene are in good agreement at 298.15 K.

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**Table 2.** Thermodynamic and structural properties for liquid benzene

<table>
<thead>
<tr>
<th>properties</th>
<th>T = 283.15</th>
<th>303.15</th>
<th>323.15</th>
<th>343.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure (atm)</td>
<td>4.18</td>
<td>4.54</td>
<td>5.17</td>
<td>9.31</td>
</tr>
<tr>
<td>volume (nm(^3))</td>
<td>16.2</td>
<td>16.0</td>
<td>16.4</td>
<td>16.7</td>
</tr>
<tr>
<td>inter LJ energy (kJ/mol)</td>
<td>-31.8</td>
<td>-30.8</td>
<td>-29.8</td>
<td>-28.9</td>
</tr>
<tr>
<td>inter elec. energy</td>
<td>-1.92</td>
<td>0.11</td>
<td>1.93</td>
<td>3.15</td>
</tr>
</tbody>
</table>

*Total of 750,000 time steps.*

**Table 3.** Thermodynamic and structural properties for liquid toluene

<table>
<thead>
<tr>
<th>properties</th>
<th>T = 283.15</th>
<th>303.15</th>
<th>323.15</th>
<th>343.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure (atm)</td>
<td>4.32</td>
<td>4.45</td>
<td>4.31</td>
<td>5.17</td>
</tr>
<tr>
<td>volume (nm(^3))</td>
<td>16.2</td>
<td>16.4</td>
<td>16.7</td>
<td>17.0</td>
</tr>
<tr>
<td>inter LJ energy (kJ/mol)</td>
<td>-42.0</td>
<td>-41.1</td>
<td>-40.0</td>
<td>-39.2</td>
</tr>
<tr>
<td>inter elec. energy</td>
<td>6.7</td>
<td>8.0</td>
<td>9.5</td>
<td>11.6</td>
</tr>
<tr>
<td>C-H stretching energy</td>
<td>0.129</td>
<td>0.152</td>
<td>0.178</td>
<td>0.168</td>
</tr>
<tr>
<td>C-C-H and H-C-H</td>
<td>1.04</td>
<td>1.13</td>
<td>1.24</td>
<td>1.23</td>
</tr>
<tr>
<td>angle bending energy</td>
<td>50.0</td>
<td>50.1</td>
<td>49.9</td>
<td>50.2</td>
</tr>
<tr>
<td>% of C-C-C-H (trans)</td>
<td>26184</td>
<td>28146</td>
<td>29472</td>
<td>30261</td>
</tr>
<tr>
<td>total barrier crossing T-G</td>
<td>26180</td>
<td>28137</td>
<td>29472</td>
<td>30263</td>
</tr>
</tbody>
</table>

*Total of 750,000 time steps.*

**Table 4.** Thermodynamic and structural properties for liquid \(p\)-xylene

<table>
<thead>
<tr>
<th>properties</th>
<th>T = 283.15</th>
<th>303.15</th>
<th>323.15</th>
<th>343.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressure (atm)</td>
<td>5.12</td>
<td>4.89</td>
<td>4.95</td>
<td>5.51</td>
</tr>
<tr>
<td>volume (nm(^3))</td>
<td>21.4</td>
<td>21.8</td>
<td>22.3</td>
<td>22.9</td>
</tr>
<tr>
<td>inter LJ energy (kJ/mol)</td>
<td>-41.8</td>
<td>-40.3</td>
<td>-39.1</td>
<td>-37.7</td>
</tr>
<tr>
<td>inter elec. energy</td>
<td>17.5</td>
<td>17.0</td>
<td>16.5</td>
<td>15.9</td>
</tr>
<tr>
<td>C-H stretching energy</td>
<td>0.063</td>
<td>0.072</td>
<td>0.082</td>
<td>0.079</td>
</tr>
<tr>
<td>C-C-H and H-C-H</td>
<td>1.14</td>
<td>1.25</td>
<td>1.36</td>
<td>1.37</td>
</tr>
<tr>
<td>angle bending energy</td>
<td>49.9</td>
<td>50.0</td>
<td>49.9</td>
<td>49.8</td>
</tr>
<tr>
<td>% of C-C-C-H (trans)</td>
<td>60363</td>
<td>62250</td>
<td>63945</td>
<td>65544</td>
</tr>
<tr>
<td>total barrier crossing T-G</td>
<td>60367</td>
<td>62237</td>
<td>63940</td>
<td>65555</td>
</tr>
</tbody>
</table>

*Total of 750,000 time steps.*

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*Table 2.* Thermodynamic and structural properties for liquid benzene.

*Table 3.* Thermodynamic and structural properties for liquid toluene.

*Table 4.* Thermodynamic and structural properties for liquid \(p\)-xylene.

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**Figure 1.** Center of mass radial distribution function for liquid benzene at 283.15, 303.15, 323.15, and 343.15 K.
As the temperature increases, the first and second peaks in the center of mass $g(r)$ diminish gradually and the minima increase as usual for the three liquids. When compared with the center of mass $g(r)$ in the previous NVT MD simulations at 298.15 K, the peaks diminish and the minima increase as if the temperature increases due to the large volumes of systems used in the NVT MD. It is also observed that the successive addition of methyl group into the benzene ring causes the width of the first solvation shell larger and the first peak lower, which indicates the variance of the distance between centers of mass as the molecular weight increases.

The center of mass radial distribution function for liquid benzene at 283.15 K is also shown in Figure 4.

As dynamic properties, we consider self-diffusion coefficients and friction constants of liquid benzene, toluene, and $p$-xylene. The mean square displacements (MSD’s) obtained from our MD simulations for liquid benzene are shown in Figure 5. But MSD’s for liquid toluene and $p$-xylene, and the first peak is completely disappeared in liquid $p$-xylene. Considering the first configuration above with the methyl group farthest from the center of mass of the other benzene molecule, it is easily understood that the three peaks are not changed and the fourth peak is related to the methyl group. In the site-site $g_{C-C}(r)$ of liquid benzene at 283.15 K in Figure 4, the first peak is disappeared and the fourth peak becomes clearer, which reflects a large possibility of the closeness of the methyl groups to the center of mass of the other benzene ring.

**Dynamic properties.** As dynamic properties, we consider self-diffusion coefficients and friction constants of liquid benzene, toluene, and $p$-xylene. The mean square displacements (MSD’s) obtained from our MD simulations for liquid benzene only are shown in Figure 5. But MSD’s for liquid...
toluene and \( p \)-xylene and velocity auto-correlation functions (VAC’s) for liquid benzene, toluene, and \( p \)-xylene are not shown. Self-diffusion coefficients can be calculated from MSD’s using Einstein relation:

\[
D_s = \frac{1}{6t} \lim_{t \to \infty} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle.
\]

Another route for self-diffusion coefficients calculated from the VAC’s is the Green-Kubo relations. The self-diffusion coefficient can be separated into two parts according to

\[
D_s = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt = \frac{1}{3} \langle v^2 \rangle A = \frac{3kT}{m} A,
\]

where \( \mathbf{v}(t) \) is the center of mass velocity of a single molecule. Since \( m \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle = m \mathbf{v}^2 = 3kT \), the integration value of the normalized VAC function, \( A \), is given by

\[
A = \frac{1}{3} \int_0^\infty \langle v(t) \cdot v(0) \rangle dt.
\]

Self-diffusion coefficients of the three liquids calculated from the slopes of the MSD’s between 5.0 and 20.0 ps and from the average of the integration of the VAC’s from \( t = 0 \) ps to 2.5 ps up to 20.0 ps are listed in Table 5. The MD simulation study of benzene and its fluorinated derivatives at 300 K by Caba 

\[14\] reported \( 1.2 \times 10^{-9} \text{m}^2/\text{s} \) as the self-diffusion coefficient of benzene, but the experimental measures \[15\]-\[18\] are comparable to our results. It is very fortuitous that both self-diffusion coefficients obtained from MSD and VAC of our MD simulations are in overall agreement with the experimental results.

Unfortunately there is no experimental result for the self-

\[D_s = \frac{1}{6t} \lim_{t \to \infty} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle.
\]

Table 5. Self-diffusion coefficients (\( D_s, 10^{-9} \text{m}^2/\text{s} \)) for liquid benzene, toluene, and \( p \)-xylene calculated from MSD’s and VAC’s. The numbers in parenthesis are \( D_s \) from VAC’s and the value of \( A (10^{-2} \text{ps}) \) in Eq. (17).

<table>
<thead>
<tr>
<th>Molecules</th>
<th>T = 283.15</th>
<th>303.15</th>
<th>323.15</th>
<th>343.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>0.76(0.72, 0.79)</td>
<td>1.25(1.19, 1.15)</td>
<td>1.52(1.53, 1.48)</td>
<td>2.09(2.16, 2.09)</td>
</tr>
<tr>
<td>toluene</td>
<td>0.67(0.61, 0.79)</td>
<td>0.92(0.90, 1.10)</td>
<td>1.24(1.21, 1.38)</td>
<td>1.67(1.62, 1.85)</td>
</tr>
<tr>
<td>( p )-xylene</td>
<td>0.51(0.52, 0.78)</td>
<td>0.75(0.76, 1.06)</td>
<td>1.01(1.00, 1.31)</td>
<td>1.32(1.33, 1.76)</td>
</tr>
</tbody>
</table>
As Kubo pointed out in his “fluctuation-dissipation theorem,” the correlation function of random force $R$ will decay in a time interval of $\tau$ (microscopic time or collision duration time), whereas that of the total force $F$ has two parts, the short time part or the fast similar to that of the random force and the slow part which should just cancel the fast part in the time integral (Kubo approximately described these two FAC’s in his original papers, see Figure 2 in Ref. 21). This means that the time integral of Eq. (18) up to $\tau = \infty$ is equal to zero. The time integral in Eq. (18) attains a plateau value for $\tau$ satisfying $\tau_c \ll \tau \ll \tau_r$, if the upper limit of the time integral, Eq. (18), is chosen that $\tau_c \ll \tau \ll \tau_r$ because the slow tail of the correlation function is cut off. However, we were unable to get the plateau value in the running time integral of the force auto-correlation function.

Kubo suggested above that the friction constants can be obtained from the random force auto-correlation (FAC) function not from the total FAC and that there exists a difficulty to separate the random force part from the total force. We could obtain the friction constants by the time integral of the total FAC with choosing the upper limit of as the time which the FAC has the first negative value by assuming that the fast random force correlation ends at that time. The friction constant is related to the diffusion coefficient $D$ using Einstein relation, Eq. (15):

$$
\zeta = kT/D.
$$

Table 6 contains the friction constants obtained from the time integral of the FAC using Eq. (18) and from Eq. (19) with $D$ obtained from MSD’s in Table 5. Both the friction constants give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The calculated friction constants from the FAC’s using Eq. (18) are always less than those obtained from Eq. (19) except liquid toluene at 343.15 K which reflects that the random FAC decays slower than the total FAC as described by Kubo.

### Table 6. Friction constants ($\zeta$, kg/mol ps) for liquid benzene, toluene, and $p$-xylene obtained from the FAC’s using Eq. (18) and from Eq. (19) (in parenthesis)

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$T$ (K)</th>
<th>$\zeta$ (kg/mol ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>283.15</td>
<td>1.85 (3.10)</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>1.76 (2.02)</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>1.67 (1.77)</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>1.62 (1.37)</td>
</tr>
<tr>
<td>toluene</td>
<td>283.15</td>
<td>1.96 (3.51)</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>1.89 (2.74)</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>1.81 (2.17)</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>1.75 (1.71)</td>
</tr>
<tr>
<td>$p$-xylene</td>
<td>283.15</td>
<td>2.13 (4.62)</td>
</tr>
<tr>
<td></td>
<td>303.15</td>
<td>2.03 (3.36)</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>1.96 (2.66)</td>
</tr>
<tr>
<td></td>
<td>343.15</td>
<td>1.87 (2.16)</td>
</tr>
</tbody>
</table>

### Conclusion

In this paper, we have presented the results of thermodynamic, structural, and dynamic properties of model systems for benzene, toluene and $p$-xylene in an isobaric-isothermal (NpT) ensemble at 283.15, 303.15, 323.15, and 343.15 K using equilibrium molecular dynamics (EMD) simulation. This work is initiated to compensate for our previous NVT MD simulations for the same systems at 298.15 K in which the calculated pressures were too low. The calculated pressures in the NpT ensemble MD simulations are close to 1 atm and the volume of each system increases with increasing temperature. The first and second peaks in the center of mass g(r) diminish gradually and the minima increase as usual for the three molecules as the temperature increases. It is also observed that the successive addition of methyl group into the benzene ring causes the width of the first solvation shell larger and the first peak lower, which indicates the variance of the distance between centers of mass as the molecular weight increases. The three peaks of the site-site g_{C-C}(r) at 283.15 K support the perpendicular structure of nearest neighbors in liquid benzene. Two self-diffusion coefficients of liquid benzene calculated from MSD via the Einstein equation and VAC function via the Green-Kubo relation are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene and $p$-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group. We have calculated the friction constants of liquid benzene, toluene, and $p$-xylene from the force auto-correlation (FAC) function with the assumption that the fast random force correlation ends at time which the FAC has the first negative value.

Both the friction constants give a correct qualitative trends: decrease with increase of temperature and increase with the number of methyl group. The calculated friction constants from the FAC’s are always less than those obtained from the friction-diffusion relation (Eq. (19)) except liquid toluene at 343.15 K which reflects that the random FAC decays slower than the total FAC as described by Kubo.

### Acknowledgment

This research was supported by Kyung- sung University Research Grants in 2000. This research is a partial fulfillment of the requirements for the degree of Master of Science for JHK at Department of Chemistry, Graduate School, Kyungsung University.

### References