Molecular Dynamics Simulation Studies of Benzene, Toluene, and *p*-Xylene in a Canonical Ensemble

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We have presented the results of thermodynamic, structural and dynamic properties of liquid benzene, toluene, and *p*-xylene in canonical (NVT) ensemble at 293.15 K by molecular dynamics (MD) simulations. The molecular model adopted for these molecules is a combination of the rigid body treatment for the benzene ring and an atomistically detailed model for the methyl hydrogen atoms. The calculated pressures are too low in the NVT ensemble MD simulations. The various thermodynamic properties reflect that the intermolecular interactions become stronger as the number of methyl group attached into the benzene ring increases. The pronounced nearest neighbor peak in the center of mass g(r) of liquid benzene at 293.15 K, provides the interpretation that nearest neighbors tend to be perpendicular. Two self-diffusion coefficients of liquid benzene at 293.15 K calculated from MSD and VAC function are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene also agree well with the experimental ones for toluene in benzene and for toluene in cyclohexane.

Keywords : Molecular dynamics simulation, Benzene, Toluene, *p*-Xylene.

Introduction

Similar-shaped molecules show clearly different physicochemical properties according to their shapes. For example, pentane, an alkane compound which has five carbon atoms, has three isomers - normal pentane, isopentane, and neopentane. These three compounds have the same molecular weight, but have different physicochemical properties according to their C-C bond forms, that is, different melting and boiling points, thermodynamic properties, and transport coefficients - diffusion coefficient, viscosity and thermal conductivity. Conducting equilibrium molecular dynamics (EMD) simulations for the above pentane systems, Lee *et al*. reported the result for the structural properties, thermodynamic properties, and transport coefficients of the three liquid pentane isomers[1] and after that, they reported the results for the shear viscosity of the three liquid pentane isomers, through non-equilibrium molecular dynamics (NEMD) simulations.[2]

This study has chosen three similar-shaped molecules - benzene, toluene, and *p*-xylene - in order to study the structural, thermodynamic, and dynamic properties through EMD simulations. The molecules are not homogeneous isomers.

Benzene actually is more stable than might be expected for a system of six carbon-carbon single bonds and three carbon-carbon π bonds. The molecule is planar, the carbon atoms are at the corners of a regular hexagon and the delocalization of the π electrons is complete. Each C-C bond has a length of 0.140 nm, a value intermediate between a double bond (0.133 nm) and a single bond (0.154 nm). Benzene has a C_6 axis perpendicular to the plane of the molecule and passing through the geometric center, and six additional C_2 axes lying in the molecular plane. In this example, C_6 is the axis having the higher order, and becomes the principal axis. The center is at the intercept of the C_6 axis and of the six C_2 axes.

Toluene is the special name of the simplest of the alkylbenzenes, methylbenzene, In toluene, a rotation of 120° about C(1)-C(2) axis interchanges the three hydrogen atoms. But these atoms can be considered equivalent only if free rotation of the methyl group is assumed. Toluene is an interesting model in this aspect because it shows that the time factor is of importance to the concept of group equivalence. If, in toluene, methyl rotation is fast relative to the time scale of the means of observation, then "free rotation" is observed, and the three hydrogens appear equivalent. If methyl rotation is slow in the observer's time scale, equivalence is lost.

p-Xylene having two CH_3 groups was attributed to the coupling of the intermolecular rotational vibrations with the intramolecular CH_3 torsional vibration. The crystal structure of *p*-xylene belongs to the space group C_{2h} with two molecules in the unit cell and the six rotational intermolecular vibrations are distributed among the *Ag* and *Bg* symmetry species as $3Ag + 3Bg$. The *x* axis is taken perpendicular to the molecular plane and the *y* and *z* axes in the plane with the *z* axis passing through the methyl groups.

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

Molecular Models and Molecular Dynamics Simulation Methods

We assume that benzene ring is modeled as a rigid-body, but three C-H bonds in the methyl groups of toluene ($C_6H_5CH_3$) and *p*-xylene ($CH_3C_6H_4CH_3$) are not assumed to

be rigid and they are rotating according to a torsional potential. Simple harmonic oscillation potentials for C-H bond stretching and C-C-H and H-C-H bond angle bending in the methyl group of toluene and *p*-xylene are used.

Atoms on different molecules interact through a 12-6 Lennard-Jones (LJ) potential:

$$u^{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \quad (1)$$

and electrostatic charges are assigned to each atom to describe the intermolecular Coulomb interaction:

$$E_{elec} = \frac{q_i q_j}{r_{ij}}. \quad (2)$$

The partial charges q_i are obtained by *ab initio* calculation using Gaussian 98. The values of the electrostatic charges are shown in Figure 1. It is worth noting that we do not consider any internal LJ and Coulomb interactions between the methyl hydrogen atoms and the rigid benzene ring atoms on the same molecule since those interactions in MD simulation of toluene lead to an artificial dynamics, for example, a huge self-diffusion coefficient.

Bond stretching denotes the interaction between two neighbouring atoms which are chemically bonded. The potential energy associated with bond stretching between atoms i and j is assumed to be harmonic and is given by

$$V_b(r_{ij}) = K_0(r_{ij} - r_e)^2, \quad (3)$$

Here, r_{ij} is the bond length, r_e is the equilibrium bond length, and K_0 is the force constant.

Bond angle deformation denotes the interaction between three chemically bonded atoms i, j and k. The potential energy associated with bond angle bending is given by

$$V_b = K_1(\theta - \theta_0)^2 - K_2(\theta - \theta_0)^3, \quad (4)$$

where θ is the bond angle, θ_0 is the equilibrium bond angle, and K_1 and K_2 are the force constants. The force constants K_0, K_1 and K_2 are those used by Lee *et al.*[3] and Chynoweth *et al.*,[4-6] which are originally provided by the work of White and Boville,[7] and are given in Table 2 with the LJ potential parameters.

Table 1. Potential parameters for liquid benzene, toluene, and *p*-xylene

LJ parameters	σ (nm)	ε (kJ/mol)
C-C	0.3367	0.4056
C-H	0.2799	0.1722
H-H	0.2230	0.0731
bond stretching	r_e (nm)	K_0 (kJ/molnm^2)
C-H	0.110	147000
bond angle bending	θ_o (deg)	K_1 (kJ/mol · deg^2)	K_2 (kJ/mol · deg^3)
C-C-H	109.7	0.050209	0.000482
H-C-H	107.9	0.050209	0.000482
torsional	ϕ_o (deg)	K_3 (kJ/mol)
C-C-C-H	180°	11.72

Torsional rotation about a bond denotes the bonded interaction between four atoms i, j, k and l. The C-C-C-H torsional rotational potential is given by

$$V(\phi) = K_3[1 - \cos 3(\phi - \phi_0)], \quad (5)$$

where ϕ is the C-C-C-H dihedral angle, ϕ_0 is the equilibrium dihedral angle, and K_3 are the force constants.[8]

The MD simulation parameters such as number of molecules, mass, temperature, and length of simulation box are listed in Table 2. 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 $R_c = 1.25$ nm was employed for the pair interactions. Gaussian isokinetics[9] was used to keep the temperature of the system constant. For the integration over time, we adopted Gear's fifth order predictor-corrector algorithm[10] with a time step of 0.0002 ps. Evans's quaternion method[11,12] is employed for the internal orientation of the rigid geometry of the benzene ring. 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

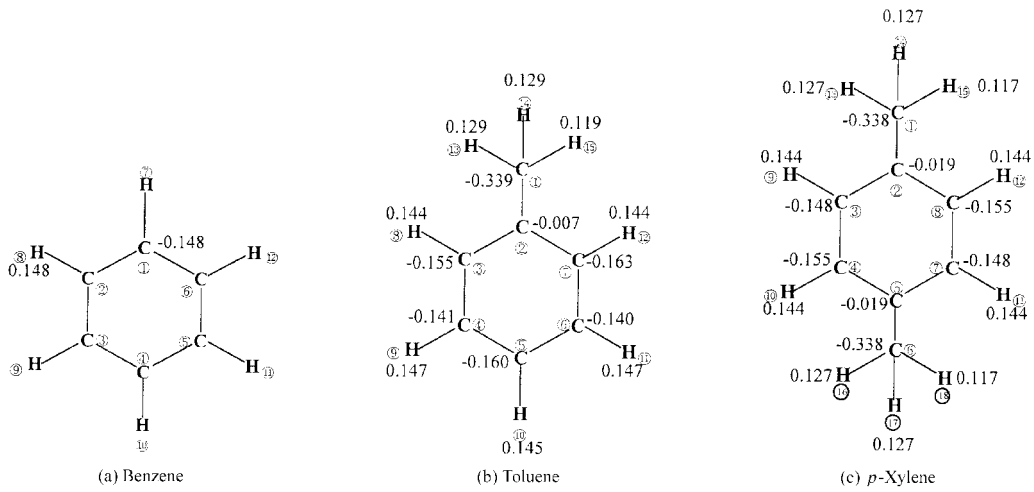

Figure 1. Geometries and atomic charges of liquid (a) benzene, (b) toluene, and (c) *p*-xylene.

Table 2. Molecular dynamics simulation parameters for model of liquid benzene, toluene, and *p*-xylene

Molecules	Number of molecules	Mass (g/mole)	Temperature (K)	Density (g/cc)	Length of box (nm)
benzene	120	78.11	293.15	0.8787	2.607
toluene	120	92.14	293.15	0.8669	2.767
p-xylene	120	106.17	293.15	0.8611	2.907

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.

Results and Discussion

Thermodynamic properties. Thermodynamic properties for liquid benzene, toluene and *p*-xylene at 293.15 K obtained from our MD simulations are listed in Table 3. In general, the calculated pressures are too low in our NVT ensemble MD simulations, in which the simulation box lengths and hence the densities are fixed as shown in Table 2. The usual route for the calculation of the pressure tensor in MD simulations is given by

$$\mathbf{P}_{\alpha\beta} = \frac{1}{V}\left(\sum_i \mathbf{p}_{i\alpha}\mathbf{p}_{i\beta}/m_i + \sum_i \mathbf{r}_{i\alpha}\mathbf{f}_{i\beta}\right) \quad (6a)$$

or

$$\mathbf{P}_{\alpha\beta} = \frac{1}{V}\left(\sum_i \mathbf{p}_{i\alpha}\mathbf{p}_{i\beta}/m_i + \sum_i \sum_i \mathbf{r}_{ij\alpha}\mathbf{f}_{ij\beta}\right) \quad (6b)$$

It is essential to use Eq. (6b) in a simulation that employs periodic boundary conditions. The off-diagonal ($a \neq b$) elements of the pressure tensor are essentially zero in the case of no external field. The ordinary pressure is given by $P = (P_{xx} + P_{yy} + P_{zz})/3 = (NkT + W)/V$, where W is defined by $W = \frac{1}{3}\sum_i \sum_{j>i} \mathbf{r}_{ij\alpha}\mathbf{f}_{ij\beta}$, and called "internal virial". Since the kinetic energy term, NkT, is always positive, the negative pressures are originated from the competition between the kinetic energy and the internal virial. Hence, for a given density of the system, the appropriate selection for the intermolecular potential functions is most important for the pressure of the system. The experimentally measured density of the system can be used for simulation studies of the system but is not expected to reproduce the exact pressure. NpT ensemble simulation is recommended for this kind of difficulty and is presently under study for the systems of liquid benzene, toluene, and *p*-xylene.

Table 3. Thermodynamic and structural properties for liquid benzene, toluene, and *p*-xylene

properties	benzene	toluene	*p*-xylene
pressure (atm)	–1160	–1670	–1840
intermolecular LJ energy (kJ/mol)	–27.6	–31.4	–35.3
intermolecular Coulomb energy	4.3	14.4	13.0
C-H stretching energy	–	0.050	0.063
C-C-H and H-C-H angle bending	–	0.655	1.112
C-C-C-H torsional energy	–	11.72	11.72
average % of C-C-C-H *trans*	–	50.2	50.1
total barrier crossing T-G	–	25,509/ 750,000	60,143/ 750,000
G-T	–	25,513/ 750,000	60,149/ 750,000

The intermolecular LJ energy increases negatively with increasing number of methyl groups, which implies the increasing interactions of methyl groups. The total potential energy of benzene is too low even though the long-range correction for the potential energy (–3.5 kJ/mol)[13,14] is added, when compared with the potential energy reported through an MD simulation study of benzene and its fluorinated derivatives at 300 K by Cabaço *et al.*,[15] –33.7 kJ/mol. They used an exp-6 potential function and different potential parameters, and the density of their system for benzene is 0.872 g/cm^3 and the calculated pressure was about 300 atm. The large difference of these calculated pressures is due to our consideration of the long-range correction for the pressure calculated from the site-site atomic potential.[14]

The C-H bond stretching and the C-C-H and H-C-H bond angle bending energies are both increased with increase in number of methyl groups. As the number of methyl group increases, the steric effect becomes larger and repels each other, which contributes the large repulsive interactions of the bond stretching and the bond angle bending potential energies. The values of the bond stretching length and bond bending angle, however, are remained constant (not shown).

Toluene has two dihedral states and *p*-xylene has four dihedral states as shown in Figure 1: 3-2-1-13 and 7-2-1-13 in toluene, and 3-2-1-13, 8-2-1-13, 4-5-6-16 and 7-5-6-16 in *p*-xylene. The dihedral states are almost fixed as shown in the total barrier crossing of T-G and G-T. There is one doubly imposed torsional rotational potential on the bond of 1-2 in toluene and two on the bonds of 1-2 and 5-6 in *p*-xylene. 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 the dihedral state of 3-2-1-13 is in *gauche*, then that of 7-2-1-13 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 the doubly imposed dihedral state gives $\phi_2 = 180^o - \phi_1$ for a given dihedral angle ϕ_1 and $V_{average}(\phi) = [V(\phi_1) + V(\phi_2)]/2 = K_3$.

Structural properties. The radial distribution function, g(r), is defined as

$$g(r) = \frac{1}{\rho_0}\left\langle \frac{N(r, \Delta r)}{V(r, \Delta r)} \right\rangle \quad (7)$$

where ρ_0 is the bulk density, N(r, Δr) is the number of molecules in a shell which is between r – Δr/2 and r + Δr/2 from the center of a molecule with $\Delta r = 0.005$ nm, V(r, Δr) is the volume of the shell, and $\langle\cdots\rangle$ indicates the canonical ensemble (NVT) average. The center of mass g(r) and the

site-site $g_{C\text{-}C}(r)$ of liquid benzene, toluene, and *p*-xylene at 293.15 K are shown in Figures 2 and 3, respectively.

In general, the center of mass g(r) of the three liquids at 293.15 K shows a typical liquid state structure. It is interesting to see 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.

When the center of mass g(r) of liquid benzene is compared with that of the previous study at 300 K,[15,16] the overall trend is in good agreement, but the heights of the first peak and the first minimum are lower since they used a different intermolecular potential of the form: $U(r) = Bexp(-Cr) - A/r^6$. In other words, their effective LJ parameter was larger than ours. The center of mass g(r) of another study by Evans and Watts[17] showed a totally different trend from ours - a configuration in which the pair potential contains a local minimum at the distance of 0.4 nm from the center of mass. This is the so-called 'stacked' configuration

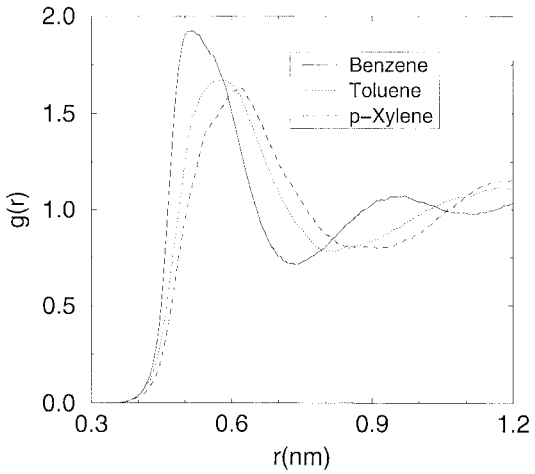

Figure 2. Center of mass radial distribution function for liquid benzene, toluene, and *p*-xylene.

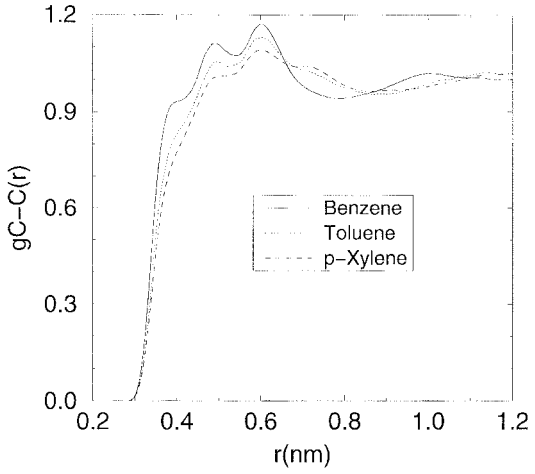

Figure 3. Site-site radial distribution function $g_{C\text{-}C}(r)$ for liquid benzene, toluene, and *p*-xylene.

in which one molecule lies on the top of the other. This structure is never found in our MD simulation results. The center of mass and the site-site radial distribution functions for liquid benzene based on the reference interaction site model (RISM) were reported,[18] and the result for the former is in good qualitative but crude quantitative agreement with that of our MD simulation. As discussed in Ref. 18 and supporting the validity of Narten's[19] ideas, the pronounced nearest neighbor peak can only be interpreted to mean that nearest neighbors tend to be perpendicular. The same interpretation is applicable to those of liquid toluene and *p*-xylene with variance due to the methyl groups.

The site-site $g_{C\text{-}C}(r)$ of liquid benzene at 293.15 K has an outshoot at 0.40 nm and two peaks at 0.48 and 0.60 nm which were observed in the study of the scattering of X-rays of liquid benzene at 298.15 K as three peaks.[19] The RISM results[18] also showed the same feature for $g_{C\text{-}C}(r)$ of liquid benzene. In the assumption that nearest neighbors in liquid benzene were parallel to one another, the relatively free rotation about its six-fold rotation axis would randomize the separation between C-C sites and as a result, the site-site $g_{C\text{-}C}(r)$ would give a peak. The outshoot and two peaks of the site-site $g_{C\text{-}C}(r)$ can support the perpendicular structure of nearest neighbors in liquid benzene at 293.15 K. As the number of methyl group increases, the outshoot at 0.40 nm disappeared, the two peaks are lowered, and a third peak at about 0.7 nm appeared. The clear appearance of the outshoot in the $g_{C\text{-}C}(r)$ of liquid benzene contrast to only two first peaks of the other two liquids indicates a large possibility of the closeness of C atoms in the benzene ring in the absence of the methyl group.

Dynamic properties. In this section, we consider only self-diffusion coefficients of liquid benzene, toluene, and *p*-xylene. In the next paper, we will discuss other transport coefficients, and rotational behaviour of these molecules in detail.[20] The mean square displacements (MSD) and velocity autocorrelation (VAC) functions obtained from our MD simulation for liquid benzene, toluene, and *p*-xylene at 293.15 K are shown in Figures 4 and 5, respectively. Self-diffusion coefficients can be calculated from MSD's using Einstein relation:

$$D_s = \frac{1}{6}\lim_{t\to\infty}\frac{d<|\mathbf{r}(t) - \mathbf{r}(0)|^2}{dt}. \quad (8)$$

Self-diffusion coefficients are also calculated from the VAC's using the Green-Kubo relations. The self-diffusion coefficient can be separated into two parts according to

$$D_s = \frac{1}{3}\int_0^\infty \langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(0)\rangle dt = \frac{1}{3}\langle v^2\rangle A = \frac{3kT}{m}A, \quad (9)$$

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

$$A = \frac{1}{3}\int_0^\infty \frac{\langle \mathbf{v}(0)\cdot\mathbf{v}(\tau)\rangle}{\langle \mathbf{v}(0)\cdot\mathbf{v}(0)\rangle}d\tau. \quad (10)$$

Self-diffusion coefficients of the three liquids calculated

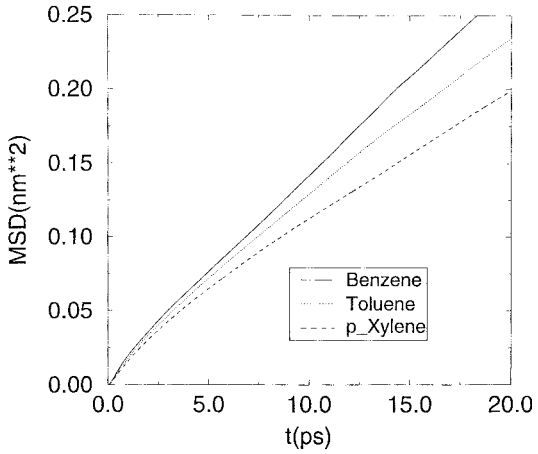

Figure 4. Mean square displacement as a function of time for liquid benzene, toluene, and *p*-xylene.

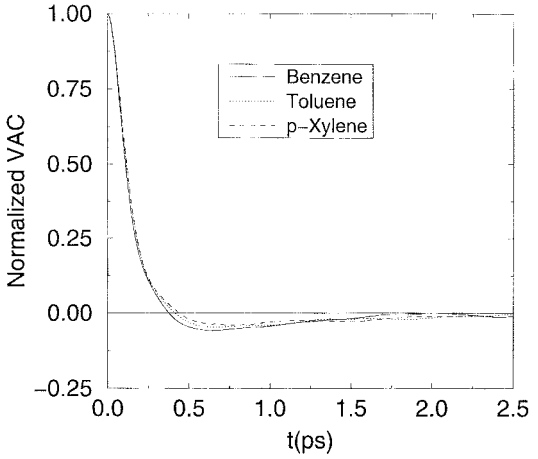

Figure 5. Normalized velocity auto-correlation function as a function of time for liquid benzene, toluene, and *p*-xylene.

from the slope of the MSD between 5.0 and 20.0 ps and from the average of the integration of the VAC from t = 0 ps to 2.5 ps up to 20.0 ps are listed in Table 4. In general, the self-diffusion coefficients calculated from VAC is slightly larger than those from MSD. The MD simulation study of benzene and its fluorinated derivatives at 300 K by Caba o *et al.*[15] reported 1.2×10^{-9} m^2/s as the self-diffusion coefficient of benzene, but the experimental measures showed 1.90,[21] 1.88,[22] 1.83,[23] and 1.70×10^{-9} m^2/s[24] at 288.15 K, and 2.27,[21] 2.15,[22] 2.13,[23] and 2.21×10^{-9} m^2/s[24] at 298.15 K. It is very fortuitous that both self-diffusion coefficients obtained from MSD and VAC of our MD simulations are in excellent agreement with the experimental results.

Unfortunately there is no experimental result for the self-diffusion coefficients of liquid toluene and *p*-xylene. The experimental diffusion coefficients, however, in different solvent are available for toluene. For example, 1.85 for toluene in benzene, 1.57 in cyclohexane, 3.72 in hepatne, 4.21 in hexane, and 0.85×10^{-9} m^2/s in water[25] at 298.15 K. When compared with these experimental results for toluene in benzene and for toluene in cyclohexane, our MD simulation results for the self-diffusion coefficients of liquid toluene also provide an excellent agreement. The self-diffusion coefficients of liquid *p*-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group.

Table 4. Self-diffusion coefficients (D_s, 10^{-9} m^2/s) for liquid benzene, toluene, and *p*-xylene calculated from MSD's and VAC's

Molecules	D_s (MSD)	D_s (VAC)	A (10^{-2} ps)
benzene	2.17	2.19	2.32
toluene	1.81	1.92	2.41
p-xylene	1.48	1.49	2.16

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 the NVT ensemble at 298.15 K using equilibrium molecular dynamics (EMD) simulation. The molecular model adopted here is a combination of the rigid body treatment for the benzene ring and an atomistically detailed model for the methyl hydrogen atoms.

The calculated pressures are too low in the NVT ensemble MD simulations. The various thermodynamic properties reflect that the intermolecular interactions become stronger as the number of methyl group attached into the benzene ring increases. The structural properties are well predicted from the center of mass, g(r), and the site-site radial distribution functions, $g_{C\text{-}C}(r)$. From the center of mass g(r) of liquid benzene at 293.15 K, the pronounced nearest neighbor peak provides the interpretation that nearest neighbors tend to be perpendicular. The clear appearance of the outshoot in the $g_{C\text{-}C}(r)$ of liquid benzene contrast to only two first peaks of the other two liquids indicates the large possibility of the closeness of C atoms in the benzene ring in the absence of the methyl group. Two self-diffusion coefficients of liquid benzene calculated from MSD *via* the Einstein equation and VAC function *via* the Green-Kubo relation are very close each other and are in excellent agreement with the experimental measures. The self-diffusion coefficients of liquid toluene obtained from our MD simulation also agree well with the experimental measures for toluene in benzene and for toluene in cyclohexane. The self-diffusion coefficients of liquid *p*-xylene are in accord with the trend that the self-diffusion coefficient decreases with increasing number of methyl group.

In conclusion, the overall agreement predicted by our molecular dynamics (MD) simulations of liquid benzene, toluene, and *p*-xylene is quite good, which means that our MD simulation methods are valid for the three liquids.

References

1. Lee, S. K.; Lee, S. H. *Bull. Korean Chem. Soc.* **1999**, *20*, 893.
2. Lee, S. H. *Mol. Sim.* **2000**, *23*, 243.
3. Lee, S. H.; Lee, H.; Park, H.; Rasaiah, J. C. *Bull. Korean Chem. Soc.* **1996**, *17*, 735.
4. Chynoweth, S.; Klomp, U. C.; Scales, L. E. *Comput. Phys.*

Commun. **1991**, *62*, 297.
5. Chynoweth, S.; Klomp, U. C.; Michopoulos, Y. *J. Chem. Phys.* **1991**, *95*, 3024.
6. Berker, A.; Chynoweth, S.; Klomp, U. C.; Michopoulos, Y. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1719.
7. White, D. N. J.; Boville, M. J. *J. Chem. Soc. Perkin Trans.* **1977**, *2*, 1610.
8. Chynoweth, S.; Klomp, U. C.; Scales, L. E. *Comput. Phys. Commun*. **1991**, *62*, 297.
9. Evans, D. J.; Hoover, W. G.; Failor, B. H.; Moran, B.; Ladd, A. J. C. *Phys. Rev.* **1983**, *A28*, 1016; Simmons, A. J. D.; Cummings, P. T. *Chem. Phys. Lett*. **1986**, *129*, 92.
10. Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equation*; Prentice-Hall: Englewood Cliffs, NJ; 1971.
11. Evans, D. J. *Mol. Phys*. **1977**, *34*, 317.
12. Evans, D. J.; Murad, S. *Mol. Phys*. **1977**, *34*, 327.
13. Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford Univ. Press.: Oxford, 1987; p 64.
14. Lee, S. H.; Kim, H. S.; Pak, H. *J. Chem. Phys*. **1992**, *97*, 6933.
15. Cabaço, M. I.; Danten, Y.; Besnard, M.; Guissani, Y.; Guillot, B. *J. Phys. Chem. B* **1997**, *101*, 6977.
16. Cabaço, M. I.; Danten, Y.; Besnard, M.; Guissani, Y.; Guillot, B. *J. Phys. Chem. B* **1998**, *102*, 10712.
17. Evans, D. J.; Watts, R. O. *Mol. Phys.* **1976**, *32*, 93.
18. Lowden, L. J.; Chandler, D. *J. Chem. Phys*. **1974**, *61*, 5228.
19. Narten, A. H. *J. Chem. Phys*. **1968**, *48*, 1630.
20. Kim, J. H.; Lee, S. H. in preparation.
21. Falcone, D. R.; Douglass, D. C.; McCall, D. W. *J. Phys. Chem*. **1967**, *71*, 2754.
22. Graupner, K.; Winter, E. R. S. *J. Chem. Soc*. **1952**, 1145.
23. Hiraoka, H.; Osugi, J.; Jono, W. *Rev. Phys. Chem. Japan* **1958**, *28*, 52.
24. Rathbun, R. E.; Babb, A. L. *J. Phys. Chem*. **1961**, *65*, 1072.
25. Landolt-Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, 6th Ed.; 1969; Vol. II/5a.