A Monte Carlo Study of the Argon Fluid Around a Benzene Molecule

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A MONTE CARLO STUDY OF THE ARGON FLUID AROUND A BENZENE MOLECULE

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Monte Carlo simulations have been carried out for argon fluid containing one benzene molecule at the supercritical region. The purpose in this study is to examine the effect of plate-like molecule on the structure of neighboring fluid composed of simple spherical molecules of the system. In the first neighbor shell of argon from the center of benzene molecule, the average potential energy of argon atoms is confirmed to have a large density dependence. This potential energy is relatively large in the high density region. It is found that the spatial distribution of argon fluid is significantly affected by the molecular shape of benzene and it has little direct connection with the attractive interaction between benzene and argon.

KEY WORDS: Argon, benzene, Monte Carlo simulations, supercritical fluid

1 INTRODUCTION

The fluid systems consist of rare gas atoms and one aromatic molecule are characterized by the presence of interesting *van der Waals* complex. Recent studies on carbazole in argon [1, 2] and benzene in argon [3, 4] reveal that the existence of an aromatic molecule gives rise to specific structure and dynamics in rare gas clusters, which have been unknown for one-component clusters.

In the present study, the supercritical argon fluid containing one benzene molecule is studied by Monte Carlo (MC) simulations. It is wildly known that the "supercritical" fluid shows drastic changes in the solubility with a slight change in the pressure at just above the critical temperature; a large change can be expected in the solvent structure around the solute at this region. Our interest is to elucidate the role of aromatic molecule in determining the structure of argon fluid, especially at the supercritical region. On the basis of the simulation results, we discuss what is the most important factor in determining fluid structure around the solute and how the fluid property such as the potential energy depends on the density of fluid.

2 MODEL AND METHOD OF COMPUTATION

The present MC calculations have been carried out within an NVT ensemble using the conventional Metropolis scheme [5]. The fluid system consists of 500 argon

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Table 1 The parameters of LJ potentials

	$\varepsilon [kJ \cdot mol^{-1}]$	$\sigma [Å]$
Ar-Ar [6]	1.006	3.40
Ar-C [7]	0.4830	3.42
Ar-H [7]	0.5379	3.21

atoms and one benzene molecule with the usual periodic boundary condition. The benzene molecule is modelled by a rigid body of D_{6h} symmetry and the carbon-carbon and carbon-hydrogen bond lengths are 1.40 and 1.08 Å, respectively. The molecular diameter of benzene is 4.96 Å. This is small enough as compared with the smallest cell length, 30 Å, adopted in this study.

The internal energy of the system is represented by the superimpose of the following three effective pairwise site-site potentials,

$$V(r_{ic}, r_{ih}, r_{ij}) = \sum_{i,c} V_{RC}(r_{ic}) + \sum_{i,h} V_{RH}(r_{ih}) + \sum_{i<j} V_{RR}(r_{ij}), \tag{1}$$

where subscripts R, i, j are indices for argon, C and c for carbon, and H and h for hydrogen atoms, respectively. V is the potential energy and r_{ij} etc. are the distances between these interaction sites. All the three kinds of potential, V_{RC}, V_{RH}, and V_{RR}, are modelled by Lennard-Jones (LJ) type potential function as

$$V_{RC}(r_{ic}) = 4\varepsilon_{RC} \left\{ \left[\frac{\sigma_{RC}}{r_{ic}} \right]^{12} - \left[\frac{\sigma_{RC}}{r_{ic}} \right]^{6} \right\}. \tag{2}$$

Each set of LJ parameters, ε and σ, is taken from literatures [6, 7] as summarized in Table 1. Each potential function is truncated at the half of the cell length and the long-range correction is applied for the total energy and virial with the standard way [8].

The MC calculations in this work have been done at several different densities of the system. The experimental critical temperature of argon is 150.75 K. On the other hand, the estimated critical temperature with the parameters adopted for argon fluid in this paper is $1.35\varepsilon/k = 163.34$ K. Throughout this study, the temperature of the system is set to 180.00 K, which is slightly higher than these critical temperatures. Each new MC run starts from an equilibrated configuration of adjacent external condition as the new initial one, the first 10,000 steps are used for equilibration, and further 10,000 steps are for analyses. Here one MC step generates new 500 configurations in which every argon atoms are moved once, while benzene is kept without positional change.

3 RESULTS AND DISCUSSION

3.1 *Radial distribution function*

Fluid structures of argon around benzene molecule can be described by the radial distribution function (RDF) from the center of solute benzene molecule. In order to examine possible heterogeneity in the distribution of argon caused by the
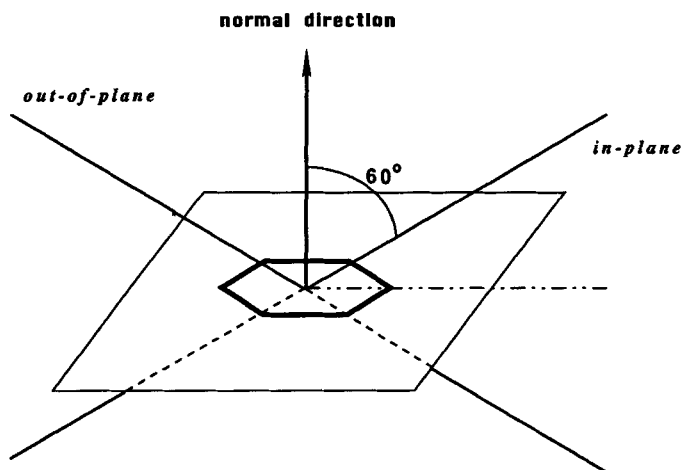
Figure 1 The defined regions for the in-plane part and the out-of-plane part.

introduction of plate-like benzene molecule, we divide argon fluid into two regions depending the argon atom in question is on the benzene plate or in the normal direction to the benzene plate. As seen in Figure 1, we define the two regions as in-plane part and out-of-plane part.

The RDFs for each part as defined accordingly are shown in Figures 2 (a) and (b) as a function of the density of the fluid. It is found that the RDF shows the feature of liquid state except for the lowest density. Moreover,

1. If one compare the two parts at a common density, first peak for the out-of-plane part is higher than that for the in-plane part.
2. The existence of the solute benzene causes a difference of 1 Å for the position of the first peak between the two parts.

These observations indicate that there is a large difference in the density dependence of fluid structure between the two parts. Hereafter, we focus attention to the first peak region, namely, the first solvation shell of each parts which are between 4.4 and 7.6 Å for the in-plane part and between 2.8 and 6.4 Å for the out-of-plane, respectively. Perpendicular dashed lines given in Figures 2 (a) and (b) show these divisions. The first peak regions are expected to be sensitive the change in the configuration of argon fluid around benzene.

3.2 Internal energy vs. density

Figure 3 shows the density dependence of the average value of internal energy in the volume region between 30 to $150 \, cm^3 \cdot mol^{-1}$. The density range of this study is $0.266 \sim 1.233 \, g \cdot cm^{-3}$ (the experimental critical density of argon is $0.533 \, g \cdot cm^{-3}$). In this density range, the pressure shows little difference (138.20 atm at $\rho = 0.777 \, g \cdot cm^{-3} \sim 64.79$ atm at $\rho = 0.266 \, g \cdot cm^{-3}$) except for the higher density region. The average internal energy for the whole system is compared
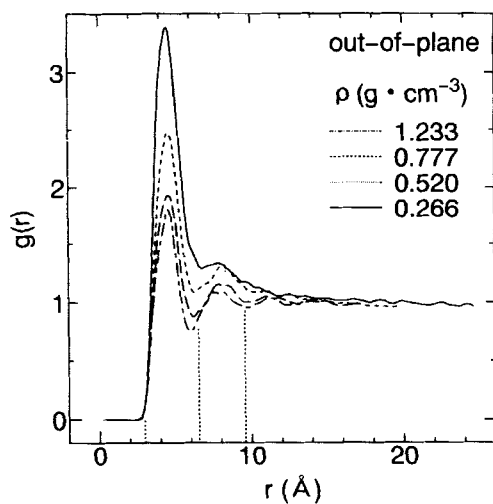
Figure 2(a) The radial distribution functions from the center of benzene molecule for the in-plane part.
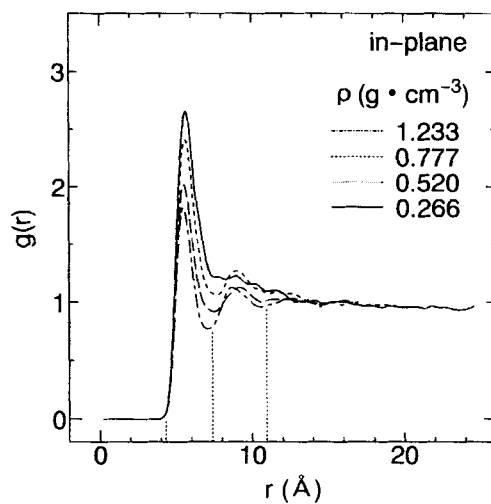

Figure 2(b) The radial distribution functions from the center of benzene molecule for the out-of-plane part.
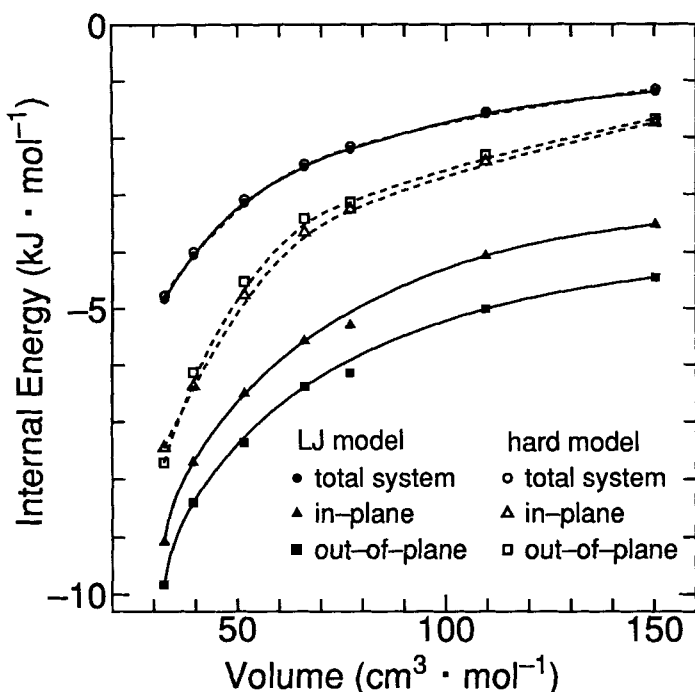
Figure 3 The density dependence of the particle-average energy. In this figure, the solid lines are based on the LJ model and the broken lines are based on the hard model.

with those for the first peak regions of the two parts. The results may be summarized as below:

1. The average internal energies for the first peak regions are 3 to 5 kJ·mol⁻¹ lower than that for the whole system.
2. The average internal energy of the first peak region of the out-of-plane part is about 1 kJ·mol⁻¹ stabilized as compared with that for the in-plane part.
3. The three curves (solid line) for the LJ model show a large density dependence; especially, the two curves for the first peak region are steep in the high density conditions.

3.3 Effect of benzene-argon interaction

In order to examine the effect of solute-solvent interactions on the energy vs. density relation in the present fluid system, further MC calculations have been carried out by the use of a modified potential which is written as

$$V(r_{ic}, r_{ih}, r_{ij}) = \eta \times \left\{ \sum_{i,c} V_{RC}(r_{ic}) + \sum_{i,h} V_{RH}(r_{ih}) \right\} + \sum_{i<j} V_{RR}(r_{ij}), \qquad (3)$$

where the correction factor for solute-solvent interaction η is set to be as 0.02 from experience. This assignment means that practically no attractive interaction
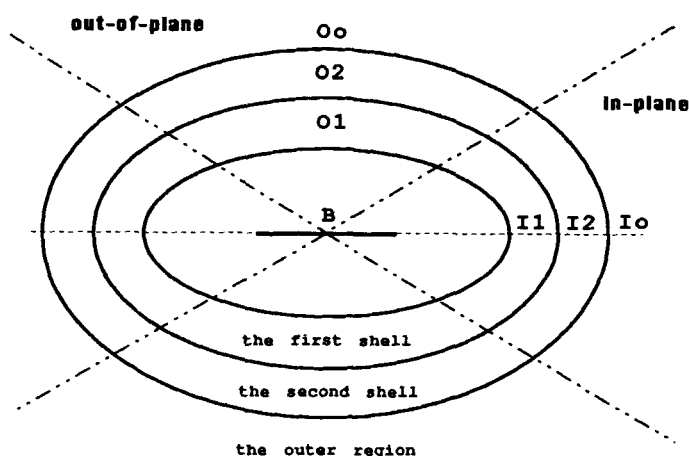
Figure 4 The each region of argon fluid around a benzene molecule.

exists between benzene and argon. Hereafter we call the two models as LJ model (equation 1) and hard model (equation 3). The results of calculations with this hard model (broken line) are also shown in Figure 3. Comparison between the two models in the figure leads us to the following conclusions.

1. The energy of whole system vs. density relation for the hard model is almost the same as that for the LJ model. This suggests that the contribution of benzene-argon interaction is almost negligible to the energy of the whole system.

2. Although the internal energy for the first peak region in the case of the hard model is only 2 or $3 \, kJ \cdot mol^{-1}$ lower than that for the whole system, its density dependence is almost the same as that for the LJ model. Then the steep slope of energy vs. density relation in the high density (small volume) range cannot be explained by the attractive interaction between benzene and argon.

3. The energy difference between the in-plane and out-of-plane parts almost disappears when we use the hard model. This difference is smaller than that in the case of the LJ model and is attributable to the presence or lack of the attractive interaction between benzene and argon.

4. In the low density range, the energy difference between the whole system and the first peak region is rather small. On the other hand, fairly large difference of over $3 \, kJ \cdot mol^{-1}$ exists in the high density range. This difference is obviously due to the existence of benzene, but cannot be attributed to the attractive interaction between benzene and argon.

3.4 *Further analysis of energy vs. density relation*

Further analysis has been made for the energy partitioning around benzene. For this purpose, we divide the whole fluid system into seven regions, B, I1, I2, Io, O1, O2, and Oo. These divisions are shown schematically in Figure 4. Here I and O are in-plane and out-of-plane parts, respectively and 1, 2 and o indicate the first peak

region, the second peak region and the region outside the second peak, respectively. As shown in Figures 2 (a) and (b), we define the second peak regions as that between 7.6 and 10.8 Å for the in-plane part and that between 6.4 and 9.6 Å for the out-of-plane part, respectively.

In accordance with this guideline, we divide the average potential energies of the two first peak regions into components described in Figures 5 (a)–(d).

First, Figures 5 (a) and (b) for the in-plane part are used to compare between the LJ and the hard models. Two interesting results are worth to mention. Among all the components, those due to I1-B interaction show noticeable difference between the two models. They have no density dependence and the energy shift is only about $1 \, \text{kJ} \cdot \text{mol}^{-1}$. The contributions due to I1-I2 interaction are important and largely responsible for the density dependence of the whole system.

Next, similar comparison is made for the out-of-plane part in Figures 5 (c) and (d). Although O1-B interaction has no density dependence, as same as the in-plane part, the energy shift is about $2 \, \text{kJ} \cdot \text{mol}^{-1}$ which is twice that for the in-plane part. The contribution of O1-O2 interaction is again predominant; for this part, O1-I1 interaction also has a significant contribution.

The above analysis indicates that, among various contributions of argon-argon interactions, those by I1-I2 interactions for the in-plane part and O1-O2 and O1-I1 interactions for the out-of-plane part are important because their average energy has a large density dependence and there is a large energetic stabilization in the high density range. These facts have no relation to the attractive interaction between benzene and argon.

We then ask what is the origin of such behavior. Two factors may be responsible: the change in the pair average energy and the average particle number in the region examined. The former is proved to be almost independent of the density of the fluid; on the other hand, the latter shows significant change. The results are shown for both the first and second peak regions in Figure 6. It is obvious that the change in average particle number of the second peak region is responsible for the density dependence. Finally, we call attention to the fact that the shape of the solute benzene molecule is considered to be responsible for the large energetic stabilization.

4 CONCLUDING REMARKS

Monte Carlo simulations have been carried out for the supercritical argon fluid around a benzene molecule. Discussion is focused on the first peak region of the radial distribution function from the center of benzene molecule. In order to examine the effect of non-spherical plate-like molecular shape of benzene, the first peak region is divided into the in-plane and out-of-plane parts and average potential energy is calculated for each part as a function of the density of the whole system.

It is found that the average potential energy shows a large density dependence and that a large energetic stabilization is observed especially in high density range.

It is concluded that the density dependence comes from the change in the average particle number in the second peak region and that the large energetic stabilization of argon in the first peak region is due to the shape (repulsive interaction) of benzene molecule but not due to the attractive interaction between benzene and argon.
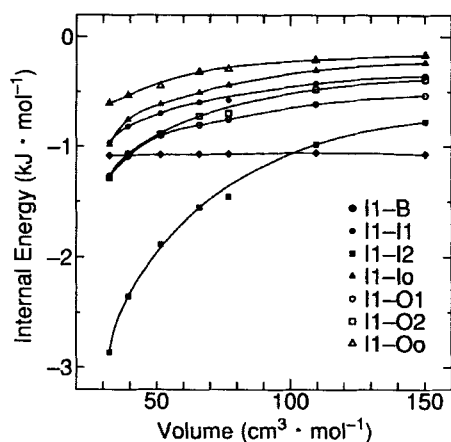
Figure 5(a) The density dependence of the site-site components divided from the particle-average energy in the first shell for the in-plane part in the case of the LJ model.
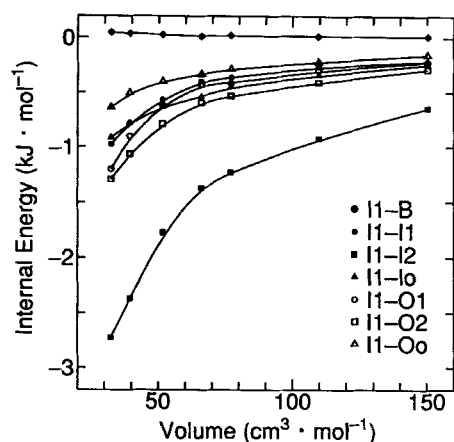
Figure 5(b) The density dependence of the site-site components divided from the particle-average energy in the first shell for the in-plane part in the case of the hard model.
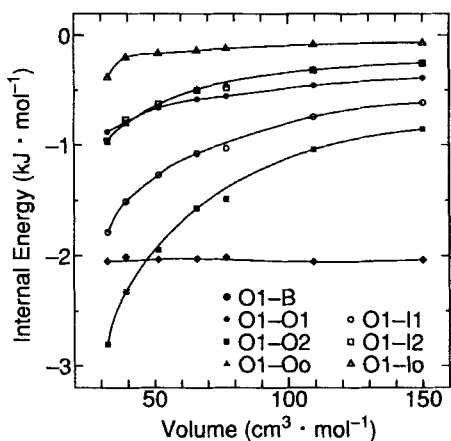
Figure 5(c) The density dependence of the site-site components divided from the particle-average energy in the first shell for the out-of-plane part in the case of the LJ model.
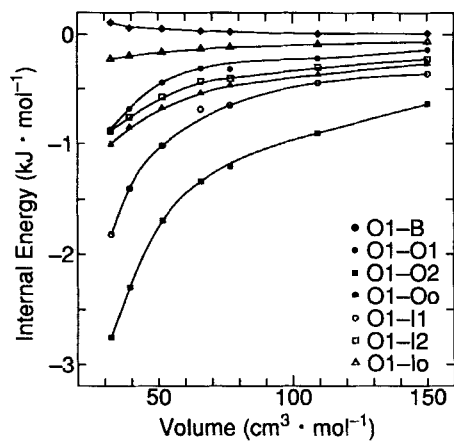
Figure 5(d) The density dependence of the site-site components divided from the particle-average energy in the first shell for the out-of-plane part in the case of the hard model.
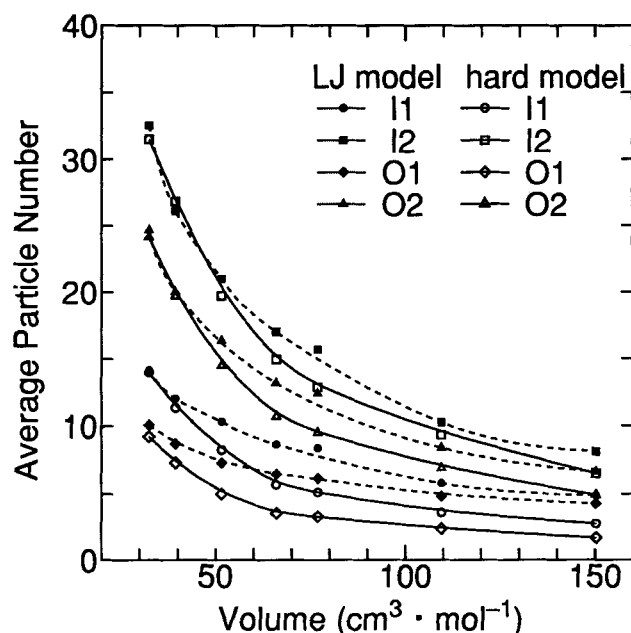
Figure 6 The average particle number in the first and second shells. In this figure, the solid lines are based on the hard model and the broken lines are based on the LJ model.

Acknowledgements

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