Molecular Dynamics for Hydrophobic Solutes in Water from Ambient to Supercritical Conditions

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Molecular dynamics simulations have been performed to investigate the translational diffusion process of hydrophobic solutes at various temperatures and densities of water. It is found that the diffusion coefficient of the hydrophobic solute is almost insensitive to the temperature near the critical density of water. According to the analysis by the generalized Langevin equation, the diffusion process of the solute molecule is dominated by the binary collision, which indicates that water structure around the solute mainly affects the diffusion process. Temperature insensitivity of the diffusion coefficient of the hydrophobic solute is interpreted as a balance between the surrounding water deficiency and the thermal activation. Molecular dynamics simulations have also been performed for the diffusion process of hydrophobic solutes under ambient condition. The relationship between solute diffusion and dynamics of the surrounding water molecules was discussed.

1. Introduction

Hydration of water molecules around hydrophobic solutes is one of the most fundamental and essential problems in physical chemistry of water, and recently its importance increases in various fields of chemical engineering, polymer science, and biochemistry [1, 2]. Since Frank and Evans suggested the "iceberg" water structure model [3] which explains a negative enthalpy change for the dissolution process ($\Delta H < 0$) [4], hydrophobic hydration has been discussed from various viewpoints such as the solute effect [5], isotopic effect [6, 7], temperature and density effect [5, 8, 9], and so on.

Computer simulations have played an important role in understanding hydrophobic hydration at a molecular level, and various kinds of study have been performed until now [1, 5-14]. However, the translational diffusion process of hydrophobic solutes under various conditions of water has not been well investigated. In this paper, we have performed molecular dynamics (MD) simulations for diffusion coefficients of oxygen and methane-like molecules in supercritical water at various densities. It has been reported that there is water deficiency structure around a hydrophobic solute near the critical density of water [5, 8, 12-14]. It is an interesting issue how this deficiency affects the diffusion of a solute in it, and we have found a unique temperature dependence of the diffusion coefficient. We also investigated diffusive motion of various hydrophobic solutes under the ambient condition. Under the ambient condition, the diffusion process is strongly affected by the long time correlation in contrast to the case in supercritical water. We discussed the solute diffusion in relation to hydrogen bonding lifetime and resident time of the surrounding water molecules.

2. Methods

2.1 Model and Calculation Details We adopted the SPCE model as a potential model of water [15]. We used the potential model between an oxygen molecule and a water molecule proposed by Fois *et al.*[16] Other solutes in this work (rare gases, methane, and so on) were treated as a single site 12-6 Lennard-Jones (LJ) model, of which parameters were taken from the conventional values [17]. The potential parameters between solute and solvent were estimated from the Lorentz-Berthelot mixing rule [18]. The system of our simulation was composed of 254 water molecules and 2 solute molecules for all runs of hydrophobic solutes in water. We have also performed simulations in a solvophobic system, i.e., neon in xenon. The

system was composed of 858 xenon molecules and 6 neon molecules.

MD simulation runs were performed in an NVT ensemble with the Nosé-Hoover thermostat [18]. With a time step of 1 fs, we made an MD run over 250-500 ps after the equilibrium procedure 125 ps at least. Other details of simulation runs are described elsewhere [19, 20].

2.2. The Generalized Langevin Equation: The Friction on the Diffusion Process In order to analyze diffusion process, the memory function for the friction $\Gamma(t)$ was evaluated based on the generalized Langevin equation as [21, 22]

$$m\frac{d\mathbf{v}(t)}{dt} = -\int_0^t dt'\Gamma(t-t')\mathbf{v}(t') + \mathbf{f}(t) \qquad (1)$$

where m, $\mathbf{v}(t)$, and $\mathbf{f}(t)$ denote the mass of the molecule, the velocity of the molecule, and the random force, respectively. By using velocity autocorrelation function $Z(t)$, Eq. (1) can be transformed into

$$\Gamma(t) = -Z(0)^{-1}\{m\ddot{Z}(t) + \int_0^t \Gamma(t-t')\dot{Z}(t')dt'\}. \qquad (2)$$

$\Gamma(t)$ can be iteratively calculated from $Z(t)$ by Eq. (2). $\Gamma(t)$ is related to the diffusion coefficient (D) through the Einstein relationship as

$$D = k_B T \Big/ \int_0^\infty \Gamma(t)dt \equiv k_B T/\Gamma \qquad (3)$$

where Γ is a integrated value of $\Gamma(t)$.

2.3. Criterion of Hydrogen Bonding and Evaluation of Hydrogen Bonding Lifetime The existence of hydrogen bonding (HB) was defined as fulfilling the following two conditions between two water molecules i and j [23]: (a) the distance $r(O_iH_j)$ is less than 2.4 Å, and (b) the angle $O_iO_jH_j$ is less than 30˚, where O_i, O_j, and H_j denote the oxygen atom of i, that of j, and the hydrogen atom of j, respectively (here j is donor of hydrogen atom).

We calculated HB lifetime by the method of Rapaport [24]. Briefly, the step function was defined which takes 1 when HB exists and 0 otherwise. Then an autocorrelation function of the above step function, $C_{HB}(t)$, was calculated by the simulation traces. The HB lifetime (τ_{HB}) was evaluated from the decay rate of $C_{HB}(t)$. Rapaport considered two types of correlation functions: "intermittent" and "continuous." In the following, we discuss only "continuous" correlation function.

With a similar idea, we have calculated the resident time of water molecules in the solvation shell [25]. The boundary between solvation shell and bulk was defined at the distance where the radial distribution function takes the first minimum. The step function was defined which takes 1 when a water molecule exists in the shell, and takes 0 otherwise. Then an autocorrelation function of this step function $C_{res}(t)$ was defined as the resident time correlation function. The resident time (τ_{res}) was calculated from the decay rate of $C_{res}(t)$.

In order to evaluate dynamic properties in the solvation shell quantitatively, we have calculated the correlation functions while molecules stay in the solvation shell continuously. When molecules go out of the shell, they are excluded from calculation of correlation function.

3. Results and Discussion

3.1. Oxygen and Methane Diffusion in Supercritical Water: Temperature Insensitivity of Diffusion Coefficient Table 1 summarizes the results of the self-diffusion coefficients of water (D_W) and oxygen molecule (D_{O2}) and methane-like molecule (D_{Me}) at various temperatures and densities [19,20]. The results of D_W are consistent with those of

Table 1. Summary of the simulation results in the oxygen/water system. Density (ρ), temperature (T), the self-diffusion coefficient of water (D_W), that of oxygen in water (D_{O2}), and that of methane in water (D_{Me}).

ρ / kg m^{-3}	T /K	D_W	D_{O2} / 10^{-9} m^2 s^{-1}	D_{Me}
115	647	228 ± 4	397 ± 9	355 ± 10
	773	291 ± 10	391 ± 12	384 ± 7
	873	320 ± 8	388 ± 12	405 ± 8
	973	387 ± 9	401 ± 7	---
217	647	114 ± 3	197 ± 3	187 ± 10
	673	148 ± 3	182 ± 8	---
	773	178 ± 7	183 ± 7	203 ± 6
	873	193 ± 5	189 ± 12	210 ± 7
	973	220 ± 6	218 ± 8	225 ± 8
426	647	72 ± 3	83 ± 3	78 ± 2
	773	95 ± 3	89 ± 2	81.5±1.0
	873	104 ± 3	87 ± 3	92 ± 3
	973	110 ± 4	93 ± 2	---

Table 2. Summary of the simulation results in the system of neon in xenon. Density (ρ), temperature (T), the self-diffusion coefficient of xenon (D_{Xe}) and that of neon in xenon (D_{Ne}).

ρ / kg m^{-3}	T /K	D_{Xe} / 10^{-9} m^2 s^{-1}	D_{Ne} / 10^{-9} m^2 s^{-1}
610	310	43.1±0.9	178 ± 4
	325	53 ± 3	176 ± 9
	340	57 ± 3	183 ± 5
1020	310	26 ± 3	93 ± 6
	370	34 ± 2	91 ± 3
	400	41 ± 2	101 ± 4

previous simulations [26-28]. This table shows temperature insensitivity of D_{O2} and D_{Me} clearly, in contrast to the dramatic increase of D_W with increasing temperature. As is shown in the table, at 115 and 217 kg m^{-3} the values of D_{O2} even decrease with increasing the temperature up to 773 and 873 K. In other words, the activation energies of D_{O2} and D_{Me} are negative or nearly zero.

In order to see that the observed temperature invariance is due to the uniqueness of hydrophobic hydration, we made simulations for a solvophobic system composed of LJ molecules;i.e., neon in xenon. Table 2 shows the results of the self-diffusion coefficients of xenon (D_{Xe}) and those of neon in xenon (D_{Ne}). As is shown in the table, D_{Ne} is relatively insensitive to the temperature as in the case of aqueous system.

In order to examine the origin of this temperature invariance, we will discuss the frictions acting on the solute molecules. Figure 1(a) shows the memory functions Γ(t) of oxygen molecule in water from 647 K to 973 K at 217 kg m^{-3}. The memory functions consist of a Gaussian-like fast decay part and a longer slight negative part. The longer part is small enough to be neglected in the following discussion. The memory functions have a similar shape at all temperatures and densities under the supercritical conditions. The memory functions for methane-like molecule show similar behavior.

Γ(t) of neon in xenon has a similar shape as that of oxygen as is shown in Fig. 1(b). However, the temperature dependence of memory function is different from that of hydrophobic solute in water. The contribution of binary collision part, i.e., the integrated value of the Gaussian-like part of Γ(t) (earlier than about 0.2 ps), is almost constant at 310, 325, and 340 K, while in the case of aqueous

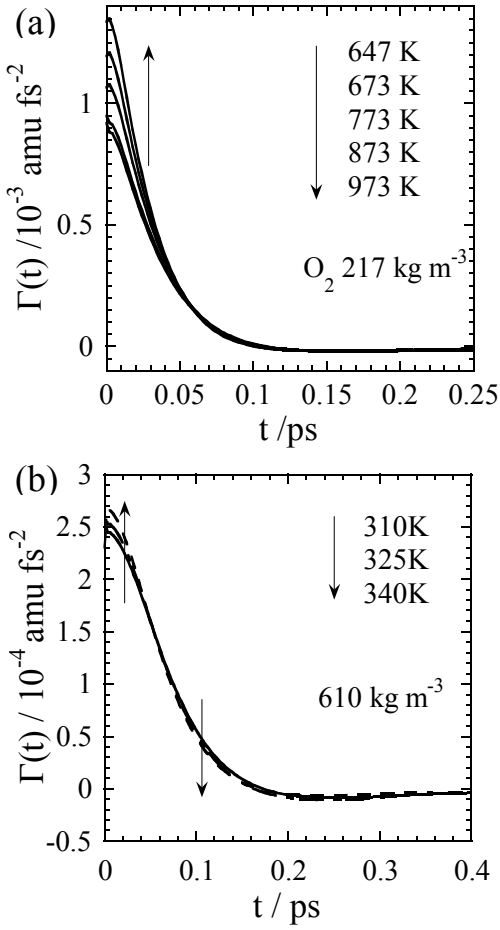

Fig. 1. The memory functions Γ(t) of oxygen molecule in water from 647 K to 973 K at 217 kg m^{-3} (a), and those of neon molecules in xenon from 310 K to 340 K at 610 kg m^{-3} (b). amu denotes atomic mass unit.

system, the Gaussian contribution increases with increasing the temperature. Further the amplitude of the long time negative part is relatively larger in the LJ case.

Generally the Gaussian part corresponds to a friction due to binary collisions, and the long time contribution of the friction is due to collective motions [21, 22]. Therefore, the diffusion process of oxygen in supercritical water is dominated by binary collision. Since binary collision reflects solvent structure around the solute, the unique temperature dependence of diffusion coefficients of solutes is related to its surrounding water structure. Figure 2 shows radial distribution functions (RDFs)

between O_W and O_{O2}, and between O_W and O_W, where O_W and O_{O2} denote an oxygen atom of a water molecule and that of an oxygen molecule, respectively. RDFs between O_W and O_{O2} show that water density around oxygen molecule is deficient compared with bulk. This characteristic deficiency appears clearly with decreasing temperature. On the other hand, RDFs between O_W and O_W grow rapidly with decreasing temperature at each density.

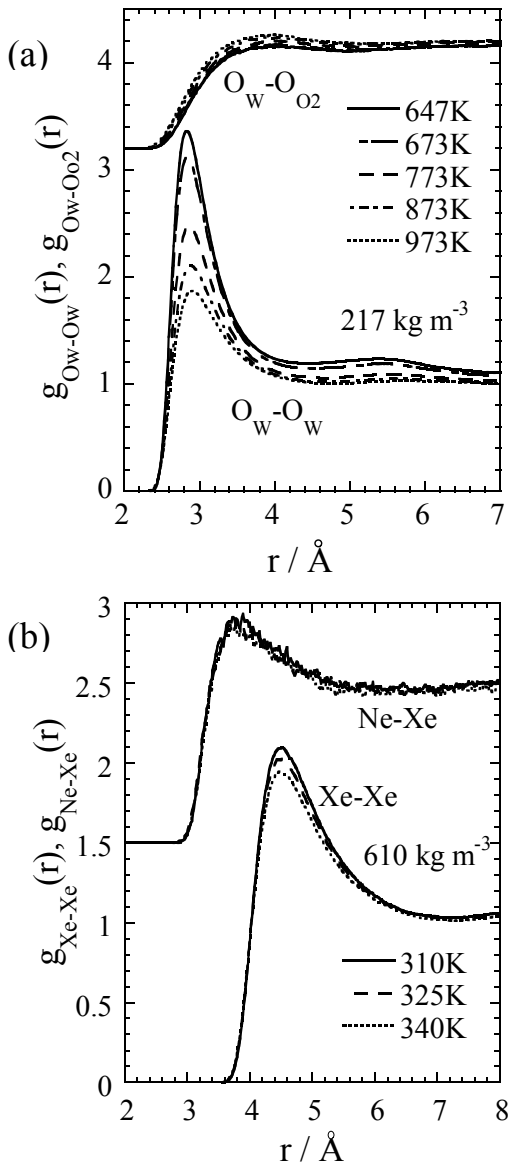

Fig. 2. The radial distribution functions for O_W-O_{O2} and for O_W-O_W at 217 kg m^{-3} and various temperatures (a), and those for Ne-Xe and for Xe-Xe at 610 kg m^{-3} and various temperatures (b).

That is, when temperature decreases, water molecules approach each other and simultaneously oxygen molecules are excluded. Intuitively, this deficient structure is advantageous for the diffusion. According to Eq. (3), the deficient structure affects the diffusion coefficient through a decrease of the term Γ. On the other hand, temperature contributes to the diffusion through the term k_BT of Eq. (3) as thermal activation. The competition between the terms k_BT and Γ is a main reason of the temperature insensitivity of diffusion coefficient of hydrophobic solute. In other words, the water deficiency due to the cooperative action of water and oxygen molecules competes with the thermal activation. In the case of methane-like molecule, similar temperature dependence of memory functions and RDFs is obtained, and a similar story can be applied to explain the temperature dependence of the diffusion process of methane-like molecule.

On the other hand, the RDF for Ne-Xe does not show solvent deficiency. Although the temperature range studied here is not so large, the RDF for Ne-Xe is small in contrast to the Xe-Xe RDF. This means that the initial part of the memory functions is insensitive to the temperature. However, the diffusion coefficient should be linearly dependent on temperature. Therefore another contribution from the long time contribution of $\Gamma(t)$ affects D_{Ne}. Therefore the mechanism of the temperature invariance is somewhat different from the hydrophobic solute.

3.2. Diffusion Process of Various Hydrophobic Solutes in Ambient Water We have evaluated diffusion coefficients of various hydrophobic solutes under the ambient condition (298 K and 1000 kg m^{-3}), which are shown in Table 3. Figure 3 shows the memory functions of the friction on the solute diffusion. The shape of the memory function is different from that in supercritical water (Fig. 1). Under the ambient condition, there is a long time positive contribution of the friction. The relaxation times τ_Γ are obtained from the fit of the longer time component to an exponential function are also listed in Table 3. As is mentioned previously, the long time contribution of the friction is due to collective motions around the solute environment. Therefore, we considered that water molecules in the solvation shell are closely related to this contribution. In the following, we call the first solvation shell around a hydrophobic solute simply a shell.

The structure and dynamics of the shell is mainly characterized by the coordination number and the resident time of water molecules. Many earlier studies have indicated HB enhancement of hydrated water molecules around a hydrophobic solute [10-14]. We have investigated the relationship of the solute dynamics and HB enhancement in the shell. Figure 4 shows comparison between $C_{HB}(t)$ in the shell and that of bulk. $C_{HB}(t)$ in the shell decays slightly slower than that of bulk. We have fitted $C_{HB}(t)$ by a double-exponential function and estimated τ_{HB} as the slower lifetime (see Table 3). The functional shape and the HB lifetimes are similar irrespective of hydrophobic solutes.

We have also evaluated the pair potential energy functions between water molecules in the shell of

Table 3. The self-diffusion coefficient of solutes (D_{solute}), the time constant of the longer part of memory functions (τ_Γ), hydrogen bonding lifetime of water molecules in the shell (τ_{HB}^{shell}), and the resident time of water molecules in the shell (τ_{res}). The self-diffusion coefficient and hydrogen bonding lifetime of bulk water are also listed.

Solute	D_{solute} / $10^{-9}m^2s^{-1}$	τ_Γ / ps	τ_{HB}^{shell} / ps	τ_{res} / ps
He	10.0±0.9	0.78	0.67	1.2
Ne	4.9 ± 0.2	1.1	0.71	2.8
Ar	2.4 ± 0.1	1.4	0.68	3.8
Kr	2.1 ± 0.1	1.6	0.72	4.0
Xe	1.6 ± 0.1	1.7	0.72	4.4
CH_4	1.99±0.06	1.3	0.71	3.9
CCl_4	0.95±0.07	1.7	0.72	5.9
O_2	2.8 ± 0.2	1.5	0.71	3.7
	D_W		τ_{HB}^{bulk}	
Water	2.38±0.02		0.66	

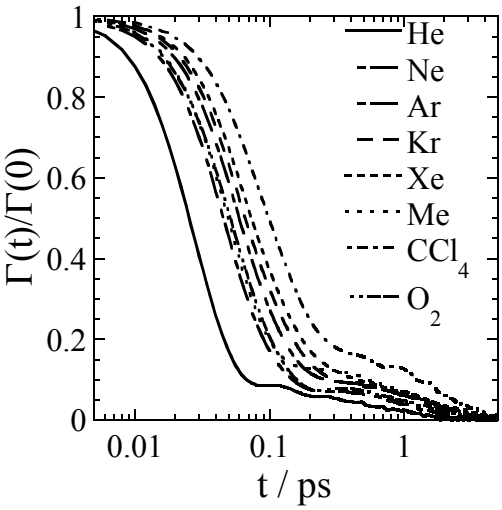

Fig. 3. The memory functions $\Gamma(t)$ of various hydrophobic solutes in water at 298 K and 1000 kg m^{-3}, where "Me" denotes methane-like molecule.

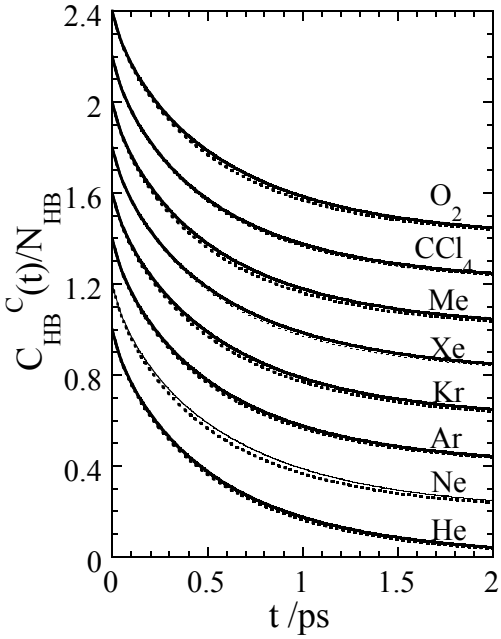

Fig. 4. $C_{HB}(t)$ of water molecules in the shell of various hydrophobic solutes at 298 K and 1000 kg m^{-3} (solid lines) and $C_{HB}(t)$ of bulk water molecules (dashed lines), where "Me" denotes methane molecule. These are shifted by every 0.2.

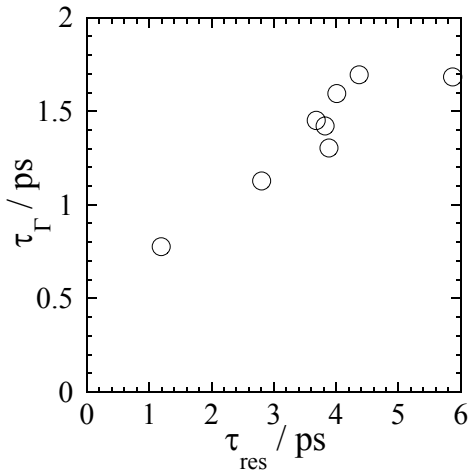

Fig. 5. The relationship between τ_Γ and τ_{res}

various solutes. In comparison with the energy at the maximum distribution of bulk water, the energy inside the shell shows a slight shift to the larger value in the absolute (~ 1%). Further the number of the HB inside the shell was nearly equal or smaller than that of bulk. Therefore, HB in the shell is slightly enhanced. However, the tendency was not dependent on the solute species.

We consider that the difference of the longer time dynamics of the friction is related to the number of water molecules participates the surrounding dynamics: i.e., the coordination number N_{cor} and the resident time of water molecules in the shell τ_{res}. Figure 5 shows the relationship between τ_Γ and τ_{res}, which shows a good correlation between them. It is quite reasonable that the dynamics which water molecules stay inside the shell prevents the diffusive motion of the solute.

4. Conclusions

We have performed MD simulations on the translational diffusion of hydrophobic solute in supercritical water and ambient water. The diffusion coefficient of hydrophobic solute near the critical density of water shows little temperature dependence, which can be explained by the competition between the water deficiency structure around the solute and the thermal activation. Under the ambient condition, the memory function of the friction for the translational motion has a longer time tail, of which the decay rate is dependent on the hydrophobic species. The decay time is found to be correlated with the coordination number of water molecules within the first solvation shell and the residence time of water molecules within the shell.

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References and Notes

[1] W. Blokzijl and J. B. F. N. Engberts, *Angew. Chem. Int. Ed. Engl.*, **32**, 1545 (1993).
[2] A. Ben-Naim, *Hydrophobic Interactions* (Prenum Press, New York, 1980).
[3] H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).
[4] J. A. V. Butler and W. S. Reid, *J. Chem. Soc.*, 1171 (1936).
[5] B. Guillot and Y. Guissani, *J. Chem. Phys.*, **99**, 8075 (1993).
[6] G. C. Kresheck, H. Schneider, and H. A. Scheraga, *J. Phys. Chem.* **69**, 3132 (1965).
[7] Y. Marcus and A. Ben-Naim, *J. Chem. Phys.*, **83**, 4744 (1985).
[8] N. Matubayasi and M. Nakahara, *J. Chem. Phys.*, **112**, 8089 (2000).
[9] J. Hernández-Cobos, A. D. Mackie, and L. F. Vega, *J. Chem. Phys.* **114**, 7527 (2001)
[10] J. C. Owicki and H. A. Scheraga, *J. Am. Chem. Soc.* **99**, 7413 (1977).
[11] P. J. Rossky and M. Kurplus, *J. Am. Chem. Soc.* **101**, 1913 (1979).
[12] P. G. Debenedetti and R. S. Mohamed, *J. Chem. Phys.*, **90**, 4528 (1988).
[13] P. T. Cummings, H. D. Cochran, J. M. Simonson, R. E. Mesmer, and A. Karaborni, *J. Chem. Phys.*, **94**, 5606 (1991).
[14] J. C. Rasaiah, J. P. Noworyta, and S. Koneshan, *J. Am. Chem. Soc.*, **122**, 11182 (2000).
[15] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.*, **91**, 6269 (1987).
[16] E. S. Fois, A. Gamba, G. Morosi, P. Demontis, and G. B. Suffritti, *J. Chim. Phys. Phys. –Chim. Biol.* **84**, 751 (1987), in which the potential V_{OO} were corrected by the authors in private communication: $V_{OO} = 42633.292\ r^{-10} - 364.42088\ r^{-6}$.
[17] R. C. Reid, J. M. Prausnitz, B. E. Poling, *The Properties of Gases and Liquids*, (McGraw- Hill, New York, 1987).
[18] See, M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University press, New York, 1987).
[19] T. Ohmori and Y. Kimura, *J. Chem. Phys.* **116**, 2680 (2002).
[20] T. Ohmori and Y. Kimura, *J. Chem. Phys.* **119**, 7328 (2003).
[21] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, London, 1986).
[22] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Oxford University press, New York, 1994).
[23] J. Martí, J. A. Padro, and E. Guàrdia, *J. Chem. Phys.* **105**, 639 (1996).
[24] D. C. Rapaport, *Mol. Phys.* **50**, 1151 (1983).
[25] D. Chandler, *J. Chem. Phys.* **68**, 2959 (1978).
[26] W. J. Lamb, G. A. Hoffman, and J. Jonas, *J. Chem. Phys.*, **74**, 6875 (1981).
[27] T. I. Mizan, P. E. Savage, and R. M. Ziff, *J. Phys. Chem.*, **98**, 13067 (1994).
[28] Y. Guissani and B. Guillot, *J. Chem. Phys.*, **98**, 8221 (1993).