Abstract

Microscopic structures of a liquid-vapor interface are investigated by molecular dynamics simulations. In the previous studies, we proposed the local and instantaneous definition of the interface at the molecular level, which can capture the thermal fluctuation of the interface. By using this definition, the layering structure of water molecules at the interface was found, in other words, the structurization phenomena of water at the molecular level were clearly seen as usually found at the liquid-solid interface. In this study, we investigated the liquid-vapor interface of Lennard-Jones fluid. The effect of well depth of L-J potential parameter on the structure was also studied. Although the structurization was found at the L-J fluid as well as water, characteristic of this structure was clearly different from that of water. We consider that the difference is ascribed to the intrinsic structure of liquid and associative trend of molecules. We also discussed the anisotropic characteristics of the molecular diffusion at the interface. The anisotropy of the translational diffusion at the interface of water is stronger than that of the L-J fluid.

Key words: Molecular Dynamics, Liquid-Vapor Interface, Structurization, Lennard-Jones Fluid, Water

1. Introduction

Liquid-vapor interfaces are ubiquitously found in natural phenomena, engineering processes, or biological systems. Therefore, these kinds of interfacial phenomena have been widely studied not only from the viewpoints of physical chemistry, but from the biological interest. Moreover, understanding of microscopic properties of the interface becomes more critical factor in the recent microscopic-sized industrial processes or devices from the engineering viewpoint.

Recent experimental studies which intend to investigate the microscopic structure of the interfaces such as the vibrational sum frequency spectroscopy (VSFS) (1) or neutron and X-ray reflectivity techniques (2) have shown various microscopic information of the interface. Nevertheless, until now fewer studies are available mainly due to the inherent difficulties of experimental approach to the liquid-vapor interface. On the other hand, numerous theoretical and computational approaches have long been applied to predict the molecular-scale structure and interfacial physical quantities at the interface (see (3–8) and references therein), and these studies have yielded much wealthy knowledge to us.
In this study, we focus on the local structure of liquid-vapor interface at the molecular level. Previously, we presented the novel definition of the local and instantaneous interface which can capture the molecular scale fluctuations\(^{(9)}\). Applying this definition to the result of molecular dynamics simulations, the intrinsic structure of the water-vapor interface was clearly found, which has previously been discussed by using integro-differential equation\(^{(10)}\), density functional theory\(^{(11)}\), and molecular simulations\(^{(12)}\). We extended our work to simpler fluid, that is, Lennard-Jones fluid, and investigated the instantaneously intrinsic structure of the interface. Furthermore, we also evaluated the difference of the dynamic properties between water and L-J fluid adjacent to the interface.

As a result, we found that the layering structures in the liquid-vapor interface clearly appeared, but were apparently different between water and L-J fluid. In the water system, the first peak of the density near the interface is strong but the layering structure does not penetrate so deeply to the bulk region. On the other hand, L-J fluid has smaller peak and the deeper oscillatory profile. Translational diffusion coefficients with a directional component were also calculated and it was found that the anisotropy of diffusion in the interface region was not significant comparing with that of water.

2. Definition of instantaneous interface

Although we have already proposed the definition of the local and instantaneous interface in the previous study\(^{(9)}\), for the convenience of explanation we again summarize the outline of that definition in this section.

An instantaneous single particle density is written by the summation of Dirac delta function as follows,

\[
\rho_i^{(0)}(r) = \sum_{i=1}^{N} \delta(r - r_i),
\]

where \(r\) is the field position, \(r_i\) is the position of the particle \(i\), and here we assume the system containing \(N\) particles. To express this discrete quantity to a field quantity, the smoothed delta function is introduced instead of the above function as follows,

\[
D\left(r - r^{(par)}(\alpha)\right) = \begin{cases} 
(2k\Delta\alpha)^{-1} \prod_{\alpha} \left[1 + \cos\left(\frac{\pi}{k\Delta\alpha}(r_\alpha - r^{(par)}_\alpha)\right)\right], \\
0, \quad \text{otherwise},
\end{cases}
\]

where \(r^{(par)}\) is the position of the particle and \(\Delta\alpha\) is a grid spacing generated in the MD cell, and \(r_\alpha\) indicates Cartesian coordinate of each direction \((x, y, z)\). This function is distributed on each particles and the density value is summed up over all particles. An important variable \(k\) indicates the broadening of the delta function. Therefore, \(k\) determines the fluctuation scale of the interface which can be captured by this method. In this study, the value \(k\) is decided so that the broadening of the smoothed delta function approximately coincided with the mean intermolecular distance of particles. After the density field is obtained, the instantaneous interface is defined as the isosurface which has a certain density value. In this study, the density value at the interface is uniquely defined from the probability profiles of the density value\(^{(9)}\). The distance from the instantaneous interface (level set function) is defined so that positive value means liquid phase and negative value means vapor phase.

We showed that this instantaneous definition of the interface does not contradict the conventional Gibbs dividing surface\(^{(9)}\). In other words, the averaged position of the instantaneous interface shows good agreement with the position of Gibbs dividing surface determined from the averaged density profiles across the interface.
3. Molecular dynamics simulations

For the analyses of the liquid-vapor interface, we performed molecular dynamics simulations with the liquid-vapor equilibrated systems. The system has the liquid film in the rectangular periodic boundary cell. In this study, we used two kinds of fluid: one was the water molecule modeled by SPC/E potential \(^{(13)}\), and the other was the monatomic L-J fluid of which parameter was determined in a manner described later. The number of water molecules is 1024 and the number of L-J atoms is also 1024. The system size is \(30.0 \times 30.0 \times 120.0 \text{Å}^3\) in both computational set. Time integration was executed by the velocity-Verlet method \(^{(14)}\), with the timestep of 1.0 fs in both systems. All production runs for about 3 ns were carried out under the NVE ensemble, after the equilibration by the velocity scaling at target temperature of 300 K in both systems. In the water system, Coulomb interaction was evaluated by the SPME method \(^{(15)}\) with the grid spacing of 1.0 Å. Real space calculation of the Coulomb interaction and the L-J interactions were cutoff at the distance of 9.0 Å and 12.0 Å, respectively.

For the L-J potential, the two parameters have to be determined. In this work, for the purpose of comparison with the water system, the two parameters were determined such that the critical points coincide with each other. Namely, since the critical point of L-J fluid has been precisely investigated in the non-dimensional parametric space \(^{(16)}\), the critical point of SPC/E water \(^{(17)}\) can be reproduced by adjusting two parameters, \(\epsilon\) and \(\sigma\). Thus the two parameters are determined to be \(\epsilon = 6.616 \times 10^{-21} \text{J}\) and \(\sigma = 3.6016 \text{Å}\). By using this potential parameters, surface tension of the L-J fluid, which is an important physical quantity of the interface, was calculated from the virial route \(^{(18)}\). The obtained value was 80.2 mN/m, which is moderately larger than that of SPC/E water (62.8 mN/m). As described later, we also used the two varieties of \(\epsilon\) parameter; one is 20% larger and the other is 20% smaller, to investigate the effect of the interaction strength on the interface structure.

The snapshots of the computational system are shown in Fig. 1. In these pictures, we also show the instantaneous interface described in the previous section. It is observed that the instantaneous interfaces locally fluctuate at the molecular scale.

![Fig. 1 Snapshots of the computational system; (a) the SPC/E water system, (b) the L-J system. In the figure (a), red spheres and white spheres indicate the oxygen atoms and hydrogen atoms, respectively. In both figures, transparent surfaces represent the instantaneous interface. All figures are drawn by the VMD molecular graphics \(^{(19)}\).](image)
4. Intrinsic structure of Interface

First, the number density profiles across the interface, i.e., along with the z-axis (long side of the MD cell), are shown in the water system and L-J system in Fig. 2. In the figures, the density profiles are fitted by the tangent hyperbolic function\(^5\) and the profiles are found to be fitted well in both systems. It is also found that the profiles are smooth throughout the interface and layering characters do not appear in this frame.

Meanwhile, the density profiles according to the distance from the instantaneous interface are calculated. In contract with the profiles according to the z-axis, in this frame, the number density exhibits the oscillatory profiles clearly, namely, the layering structure at the free surface is found as shown in Fig. 3. Although the layering structures are appeared in both systems, intensity of the first peak is stronger in the water system. On the other hand, the oscillatory character goes though towards the bulk region more deeply in the L-J systems. It is considered that these differences come from the associative trends of molecule and the intrinsic structure of liquid. To show the latter point clearly, we show the radial distribution function of both liquids in Fig. 4. From the result, it is clearly found that the intrinsic structure of liquid remains further in the L-J systems. Therefore, affected by this property, the layering structure at the interface penetrates to the bulk phase deeply.

In order to investigate the effect of parameters of the L-J potential function on the intrinsic structure of the interface, we varied the intermolecular interaction, that is, the van der Waals well depth, \(\varepsilon\). The amount of the variation is +20% and −20% from the

![Fig. 2](image_url) Number density perpendicular to the interface; (a) the SPC/E water system, (b) the L-J system. In both figures, the center of the cell is \(z = 0.0\), and only half of the cell is shown because of the symmetry of the system.

![Fig. 3](image_url) Density profiles according to the distance from the instantaneous interface; (a) the SPC/E water system, (b) the L-J system. In both figures, \(\phi = 0.0\) means the position of the instantaneous interface, that is, the 0 level set. Broadening parameter, \(k\), is 5. Density values are normalized by that of bulk phase.
original value. Figure 5 shows the density profiles according to the distance from the instantaneous interface in each L-J system. In this figure, as is expected, it is found that the layering structure becomes more profound in the stronger interatomic interaction. However, the intensity of the first peak and the shape of the profiles do not seem to approach to that of the water system. Therefore, we speculate that the determination factor of the intrinsic structure of the interface is not only the strength of the intermolecular interaction, but also the aggregating ability such as creating the network structure in the water liquid.

5. Diffusion properties at the interface

Transport properties adjacent to the interface are significantly different from that of bulk properties. In this study, we evaluated the molecular diffusion properties across the interface paying attention to their anisotropic behavior.

Following the Green-Kubo fashion, the translational diffusion coefficient is calculated from the velocity autocorrelation function as (20),

$$C_{\alpha\beta}(t) = \langle v_\alpha(0) v_\beta(t) \rangle$$

(3)

$$D_{\alpha\beta} = \int_0^\infty C_{\alpha\beta}(t) dt$$

(4)

where we consider the anisotropic diffusion properties, that is, the directional index $\alpha$, $\beta$ is given. In this paper we only show the diagonal components of $xx$, $yy$, and $zz$. In eq. (3), $C_{\alpha\beta}(t)$ is the velocity autocorrelation function with a directional component at time $t$, and $v_\alpha$ is the particle velocity. In eq. (4), $D_{\alpha\beta}$ is the diffusion coefficient tensor.
In the case of water, we only calculated the translational diffusion of the center of mass (not including a rotational motion). The diffusion coefficient is calculated within the thin slabs configured across the interface with 1 Å thickness (slab geometry \(30 \times 30 \times 1\) Å).

First, the velocity autocorrelation functions in the water system in the \(x\) and \(z\) directions are shown in Fig. 6. The result for the \(y\) direction is omitted since it is almost identical to that for the \(x\) direction. In the vicinity of the interface, larger deviation is found in the case of \(zz\) direction than in the case of \(xx\) direction.

Translational diffusion coefficient tensors in the water system and the L-J system are shown in Fig. 7. At the liquid-vapor interface, the diffusion is generally more enhanced than that of the bulk phase, because the density of the molecules becomes low. This point has already been mentioned by using the molecular dynamics simulations\(^{(21,22)}\). From Fig. 7, it is observed that in the interface region translational diffusions are enhanced except for those of \(zz\) direction. In other words, molecular diffusion to the \(z\) direction is restricted, and therefore the anisotropy is clearly appeared both in the water and the L-J system. Especially, the anisotropic behavior of the diffusion of water molecules is more significant than that of L-J fluid. This means that at the interface water molecules can easily diffuse along the interface plane but not perpendicular to the interface. We will further investigate the relation between the surface enrichment or the structurization of molecules and the anisotropic diffusion characteristics precisely.

6. Conclusions

In this study, molecular dynamics simulations of the liquid-vapor interface were performed with two kinds of fluid; one was water and the other was monatomic L-J fluid.

![Fig. 6 Velocity autocorrelation function in the water system; (a) xx component, (b) zz component. Each line is drawn by the 1.0Å distance from the interface, and negative distance means the vapor phase and positive one means the liquid phase.](image)

![Fig. 7 Translational diffusion coefficient across the interface; (a) the water system, (b) the L-J system. \(\phi\) means the distance from the Gibbs surface.](image)
By using the previously proposed definition of the instantaneous interface, the intrinsic structure of the interface was investigated. As a result, we found that the layering structures in the liquid-vapor interface were apparently different between these fluids. In the water system, the first peak of the density near the interface is strong but the layering structure does not penetrate so deeply to the bulk region. On the other hand, L-J fluid has smaller peak and the deeper oscillatory profile. This tendency remains unchanged when the interatomic interaction is varied. We also calculated the translational diffusion coefficient tensors across the interface in both systems. It was found that the anisotropy of the diffusion clearly appears especially in the water system, that is, the diffusion perpendicular to the interface is restricted, while that parallel to the interface is enhanced. We will further analyze this properties associated with the intrinsic structure of the interface.

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References