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Local pressure components and interfacial tension at a liquid-solid interface obtained by the perturbative method in the Lennard-Jones system

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A classical molecular dynamics simulation was conducted for a system composed of fluid molecules between two planar solid surfaces, and whose interactions are described by the 12-6 Lennard-Jones form. This paper presents a general description of the pressure components and interfacial tension at a fluid-solid interface obtained by the perturbative method on the basis of statistical thermodynamics, proposes a method to consider the pressure components tangential to an interface which are affected by interactions with solid atoms, and applies this method to the calculation system. The description of the perturbative method is extended to subsystems, and the local pressure components and interfacial tension at a liquid-solid interface are obtained and examined in one- and two-dimensions. The results are compared with those obtained by two alternative methods: (a) an evaluation of the intermolecular force acting on a plane, and (b) the conventional method based on the virial expression. The accuracy of the numerical results is examined through the comparison of the results obtained by each method. The calculated local pressure components and interfacial tension of the fluid at a liquid-solid interface agreed well with the results of the two alternative methods at each local position in one dimension. In two dimensions, the results showed a characteristic profile of the tangential pressure component which depended on the direction tangential to the liquid-solid interface, which agreed with that obtained by the evaluation of the intermolecular force acting on a plane in the present study. Such good agreement suggests that the perturbative method on the basis of statistical thermodynamics used in this study is valid to obtain the local pressure components and interfacial tension at a liquid-solid interface. [http://dx.doi.org/10.1063/1.4890036]

I. INTRODUCTION

The physics and chemistry at a liquid-solid interface are related to phenomena that occur over a wide size range. Such phenomena have been intensely studied for many years from macro- and nano-scopic points of view, and attract much attention even today.[1,2] One of the most fundamental thermodynamic quantities which has a dominant influence on the phenomena at the liquid-solid interface is the interfacial tension, and its importance for applications is widely recognized also in the engineering fields which deal with interfacial phenomena such as wetting, drying, and adhesion. However, compared to the liquid-vapor interfacial tension on which many studies have been conducted using molecular simulations, the properties of the liquid-solid interface have not been sufficiently elucidated, especially at the molecular scale. To address this need, new approaches to calculate the liquid-solid interfacial tension have been proposed.[3,4]

The general description of liquid-solid interfacial tension at the molecular scale is provided by statistical theory,[5] in which contributions of normal and tangential pressure components affected by the liquid-solid interactions are considered. However, the calculation of the liquid-solid interfacial tension at a planar solid surface has usually considered only the pressure component normal to the solid surface; the tangential components affected by the liquid-solid interactions have generally been ignored because of the periodicity of the arrangement of the solid atoms.[3,4,6–8] However, from a more accurate two-dimensional molecular perspective, there actually should exist tangential pressure components affected by the solid atoms in the vicinity of the solid surfaces. Furthermore, for a surface rough at the nanometer-scale, the tangential components affected by the liquid-solid interactions play a significant role and need to be considered.[9]

Perturbative methods to calculate pressure components and interfacial tension, based on statistical thermodynamics, include the volume-perturbation (VP) method[10,11] and the recently developed test-area (TA) method.[12] These methods may be applied to vapor-liquid interfaces, and the results provide details not only for the overall liquid-vapor interface tension but also the local interface tension.[13,14] However, application of these methods to the liquid-solid interface has been limited to a few studies. In Ref. 15, the TA method was applied to obtain the liquid-solid interfacial tension for a system composed of fluid molecules sandwiched between two flat solid surfaces consisting of solid atoms, although the paper gives no details about the method and the results are not fully

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examined. In a 2012 paper, Míguez *et al.* extended the TA methodology to the grand canonical ensemble and applied it to a system of fluid molecules confined in a pore.[16] The results showed the consistency of the Irving-Kirkwood (IK) method including only the normal pressure component affected by the liquid-solid interaction because of the integrated form of the fluid-solid interaction function. In those studies no results of the local pressure components and interfacial tension at the liquid-solid interface were presented, and the effects of the tangential pressure components affected by the liquid-solid interactions were not considered. The local normal pressure component was addressed in recent results reported on the contact angle of a droplet on a flat solid surface using the virial expression, although the tangential components affected by the fluid-solid interactions were ignored.[8]

Throughout the studies mentioned above, a perturbative method to obtain the local pressure components and interfacial tension at a liquid-solid interface has not been established, and a general description of the method that includes the effects of the tangential pressure components affected by the solid atoms was not presented. It should be also noted that the previous studies were focused on obtaining results in one dimension (namely, perpendicular to the interfaces), and the pressure components and interfacial tension at a liquid-solid interface were not obtained in two dimensions.

In the present study, a classical molecular dynamics simulation is conducted for a system composed of fluid molecules between two planar solid surfaces, and whose interactions are described by the 12-6 Lennard-Jones form. The purpose is to develop the perturbative method and establish a general description of the method to obtain the local pressure components and interfacial tension of the fluid at a fluid-solid interface which includes contributions of tangential pressure components affected by interactions with solid atoms. This paper proposes such a method and applies it to the liquid-solid interfacial system. The local pressure components and interfacial tension at a liquid-solid interface are obtained and examined in one- and two-dimensions. To increase the certainty of these numerical results, they are compared with those obtained by two alternative methods: the first method evaluates the intermolecular force acting on a plane, and the second is the conventional method based on the virial expression. The accuracy of the numerical results is discussed comprehensively through the comparison of the results obtained by each method.

This article is structured as follows. In Sec. II, a general description is given of the pressure components and interfacial tension obtained by the perturbative method for a system which interacts with an external field, and a method to consider the tangential pressure components affected by the solid atoms is proposed. The description is extended in Sec. III to subsystems, and the local pressure components and interfacial tension at a liquid-solid interface are obtained by the perturbative method. Two alternative methods to calculate these quantities are also presented to compare and confirm the accuracy of the local liquid-solid interfacial tension results. In Sec. V, the results of the local pressure components and interfacial tension in one- and two-dimensions are presented, and the validations are discussed. The conclusions of this study are summarized in Sec. VI.

II. GENERAL DESCRIPTION OF THE PRESSURE COMPONENTS AND INTERFACIAL TENSION AT A FLUID-SOLID INTERFACE OBTAINED BY THE PERTURBATIVE METHOD

As discussed above, while the perturbative method based on the statistical thermodynamics to obtain local pressure components of a liquid-vapor interface are well-established,[11–14] this is not the case for a fluid-solid interface at which fluid molecules interact with solid atoms. The derivation for the grand canonical ensemble is presented to obtain the fluid-solid interfacial tension by the TA method.[16] This is applied to the system composed of fluid molecules in a pore, whose fluid-solid interactions were found in a prior work[16] to depend only on the normal direction of the solid surface because of the integrated form of the fluid-solid interaction function, and tangential components affected by the fluid-solid interactions were not considered. In this section, a general description of the perturbative method on the basis of statistical thermodynamics to obtain the pressure components and interfacial tension at a fluid-solid interface is presented for a system in the canonical and grand canonical ensembles which interacts with an external field.

A. Canonical ensemble

Consider a classical inhomogeneous system which consists of N identical and spherical particles in a volume V interacting with an external field. The state of the system is specified by the $3N$ coordinates and $3N$ momenta, and then the Hamiltonian of the system H is written as[17]

$$H(\mathbf{r}^N, \mathbf{p}^N) = K(\mathbf{p}^N) + U(\mathbf{r}^N) + \Phi(\mathbf{r}^N), \tag{1}$$

where K is the kinetic energy of the particles, U is the potential energy between particles in the system, and Φ is the potential energy contributed from the external field. For the canonical ensemble in which the system is described by Eq. (1), the Helmholtz free energy F is expressed as

$$F = -\frac{1}{\beta} \ln Q_{NVT}, \tag{2}$$

where

$$Q_{NVT} = \frac{1}{\Lambda^{3N} N!} \int \mathrm{d}\mathbf{r}^N \exp(-\beta(U(\mathbf{r}^N) + \Phi(\mathbf{r}^N))) \tag{3}$$

is the canonical partition function, and $\beta = 1/(k_B T)$ with the Boltzmann constant k_B and absolute temperature T. The de Broglie thermal wavelength Λ is defined as $\Lambda = \sqrt{h^2/(2\pi m k_B T)}$ with the Planck constant h and mass of the particle m. The ξ component of pressure acting on a plane A_η which is perpendicular to the η coordinate, $P_{\xi\eta}$ ($\xi,\eta = x,y,z$) and the interfacial tension γ are defined as the partial derivatives of the Helmholtz free energy with respect to the volume and interfacial area, respectively,

$$P_{\xi\eta} = -\left(\frac{\partial F}{\partial V}\right)_{L_{\neq\xi} NT}, \quad \gamma = \left(\frac{\partial F}{\partial A_s}\right)_{NVT}, \tag{4}$$

where V is defined as $V = L_x L_y L_z (L_x = L_y = L_z)$, and A_s indicates the interfacial area in the system. Describing the partition function of the initial and perturbed state as $Q_{NVT,0}$ and $Q_{NVT,1}$ respectively, it follows from Eq. (3) that[11,12]

$$\frac{Q_{NVT,1}}{Q_{NVT,0}} = \frac{\int \mathrm{d}\mathbf{r}_1^N \exp\left(-\beta\left(U\left(\mathbf{r}_1^N\right)+\Phi\left(\mathbf{r}_1^N\right)\right)\right)/(\Lambda^{3N}N!)}{\int \mathrm{d}\mathbf{r}_0^N \exp\left(-\beta\left(U\left(\mathbf{r}_0^N\right)+\Phi\left(\mathbf{r}_0^N\right)\right)\right)/(\Lambda^{3N}N!)},$$

$$= \frac{\int \mathrm{d}\mathbf{r}^{*N} V_1^N \exp(-\beta(U_0+\Phi_0))\exp(-\beta\Delta(U+\Phi))/(\Lambda^{3N}N!)}{\int \mathrm{d}\mathbf{r}^{*N} V_0^N \exp(-\beta(U_0+\Phi_0))/(\Lambda^{3N}N!)},$$

$$= \left\langle \left(1+\frac{\Delta V}{V_0}\right)^N \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 . \tag{5}$$

In the above equation, $\Delta V = V_1 - V_0$, $\Delta U = U_1 - U_0$, $\Delta\Phi = \Phi_1 - \Phi_0$, the subscripts 0 and 1 indicate values of the initial and perturbed states, respectively, $\mathbf{r^*}$ is a coordinate scaled with the size of the system, and $\langle\,\rangle$ represents the time average. Then the free energy difference from F_0 at the initial state to F_1 at the perturbed state, $\Delta F(=F_1-F_0)$ is expressed from Eqs. (2) and (5) as

$$\Delta F = -\frac{1}{\beta}\ln\left(\frac{Q_{NVT,1}}{Q_{NVT,0}}\right),$$

$$= -\frac{1}{\beta}\ln\left\langle\left(1+\frac{\Delta V}{V_0}\right)^N \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 . \tag{6}$$

Assuming the free energy difference from the initial state to the perturbed state by infinitesimal variation of the volume ($\Delta V = V_1 - V_0$) and of the area ($\Delta A_s = A_{s,1} - A_{s,0}$), the substitution of Eqs. (6) into (4) gives

$$P_{\xi\eta} = -\left(\frac{\partial F}{\partial V}\right)_{L_{\neq\xi}NT} = \frac{1}{\beta\Delta L_\xi A_{\eta,0}}\ln\left\langle\left(1+\frac{\Delta V}{V_0}\right)^N \times \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 \tag{7}$$

and

$$\gamma = \left(\frac{\partial F}{\partial A_s}\right)_{NVT} = -\frac{1}{\beta\Delta A_s}\ln\left\langle\exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 , \tag{8}$$

where $\Delta L_\xi = L_{\xi,1} - L_{\xi,0}$. It is to be remarked that in Eq. (7) ΔF is evaluated at $A_{\eta,0}$, and the system needs to be a cube in the case of $\xi \neq \eta$.

B. Grand canonical ensemble

For a system of constant chemical potential μ, V, and T, the grand canonical potential is defined as

$$\Omega_{\mu VT} = -\frac{1}{\beta}\ln\Xi_{\mu VT}, \tag{9}$$

where, the grand canonical partition function $\Xi_{\mu VT}$ is

$$\Xi_{\mu VT} = \sum_{N=0}^{+\infty}\frac{\exp(N\beta\mu)}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^N \exp\left(-\beta\left(U(\mathbf{r}^N)+\Phi(\mathbf{r}^N)\right)\right). \tag{10}$$

The pressure components and the interfacial tension are defined as the partial derivatives of the grand potential with respect to the volume and interfacial area, respectively,

$$P_{\xi\eta} = -\left(\frac{\partial\Omega}{\partial V}\right)_{\mu L_{\neq\xi}T}, \quad \gamma = \left(\frac{\partial\Omega}{\partial A_s}\right)_{\mu VT}. \tag{11}$$

Then, the ratio of the grand canonical partition function of the perturbed state $\Xi_{\mu VT,1}$ to $\Xi_{\mu VT,0}$ at the initial state is given by

$$\frac{\Xi_{\mu VT,1}}{\Xi_{\mu VT,0}} = \frac{\sum_{N=0}^{+\infty}\frac{\exp(N\beta\mu)}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}_1^N \exp\left(-\beta\left(U\left(\mathbf{r}_1^N\right)+\Phi\left(\mathbf{r}_1^N\right)\right)\right)}{\sum_{N=0}^{+\infty}\frac{\exp(N\beta\mu)}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}_0^N \exp\left(-\beta\left(U\left(\mathbf{r}_0^N\right)+\Phi\left(\mathbf{r}_0^N\right)\right)\right)},$$

$$= \frac{\sum_{N=0}^{+\infty}\frac{\exp(N\beta\mu)}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^{*N} V_1^N \exp(-\beta(U_0+\Phi_0))\exp(-\beta\Delta(U+\Phi))}{\sum_{N=0}^{+\infty}\frac{\exp(N\beta\mu)}{\Lambda^{3N}N!}\int \mathrm{d}\mathbf{r}^{*N} V_0^N \exp(-\beta(U_0+\Phi_0))},$$

$$= \left\langle\left(1+\frac{\Delta V}{V_0}\right)^N \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 . \tag{12}$$

This expression enables $\Delta\Omega_{\mu VT}$ ($=\Omega_{\mu VT,1} - \Omega_{\mu VT,0}$) to be expressed as the same form of ΔF of the canonical ensemble

$$\Delta\Omega_{\mu VT} = -\frac{1}{\beta}\ln\left(\frac{\Xi_{\mu VT,1}}{\Xi_{\mu VT,0}}\right), \\ = -\frac{1}{\beta}\ln\left\langle\left(1+\frac{\Delta V}{V_0}\right)^N \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0. \quad (13)$$

Thus, the final equations become

$$P_{\xi\eta} = -\left(\frac{\partial\Omega}{\partial V}\right)_{\mu L_{\neq\xi}T} = \frac{1}{\beta\Delta L_\xi A_{\eta,0}}\ln\left\langle\left(1+\frac{\Delta V}{V_0}\right)^N \times \exp\left(-\beta\Delta(U+\Phi)\right)\right\rangle_0 \quad (14)$$

and

$$\gamma = \left(\frac{\partial\Omega}{\partial A_s}\right)_{\mu VT} = -\frac{1}{\beta\Delta A_s}\ln\langle\exp\left(-\beta\Delta(U+\Phi)\right)\rangle_0. \quad (15)$$

Equations (7), (8), (14) and (15) suggest that in an equilibrium state, the pressure components and the interfacial tension can be evaluated by the same expressions whether the system is defined as the canonical ensemble or grand canonical ensemble. This fact plays a significant role in extending this method to obtain the quantities in subsystems as shown for the vapor-liquid system in Ref. 13.

The procedures to evaluate ΔU in Eqs. (7), (8), (14) and (15), are presented in detail for a vapor-liquid system in Refs. 11 and 12. For instance, P_{zz} is given by the perturbation of the system from the initial state of $V_0 = L_{x,0}L_{y,0}L_{z,0}$ to the final state of $V_1 = L_{x,1}L_{y,1}L_{z,1}$, where $L_{z,1} = L_{z,0}(1+\lambda)$, keeping the $L_{x,1}$ and $L_{y,1}$ constant: $L_{x,1} = L_{x,0}$ and $L_{y,1} = L_{y,0}$. Here, perturbation parameter λ is the infinitesimal quantity, but it actually expresses a small finite quantity in simulations. In order to obtain the interfacial tension γ, it is not necessary to change the volume: the alternative method uses a constant volume through the perturbation such that $L_{z,1} = L_{z,0}/(1+\lambda)$, $L_{x,1} = L_{x,0}\sqrt{(1+\lambda)}$, and $L_{y,1} = L_{y,0}\sqrt{(1+\lambda)}$, where z is the direction normal to the interface, while x and y are the tangential directions. It should be noted that the pressure components and interfacial tension are defined as the partial derivatives expressed in Eqs. (4) and (11), which can be evaluated in simulations by the forward, backward, and central difference methods.[12]

Special attention is required to deal with $\Delta\Phi$ in Eqs. (7), (8), (14) and (15), due to the fact that the volume of the system is defined as the region of fluid particles. This means the distance between fluid particles and solid atoms should be extended or shortened, depending on the relative positions of the fluid particles to the solid atoms in the x and y directions (i.e., the tangential directions to the solid surface). The transformation of positions of the fluid particles in the system through the volume perturbation in the x and y directions imposes the conditions

$$x_{fs,1} = x_{fs,0}(1+\lambda) \quad \text{for} \quad x_{f,0} > x_{s,0}, \\ x_{fs,1} = x_{fs,0}(1-\lambda) \quad \text{for} \quad x_{f,0} < x_{s,0}, \quad (16)$$

and

$$y_{fs,1} = y_{fs,0}(1+\lambda) \quad \text{for} \quad y_{f,0} > y_{s,0}, \\ y_{fs,1} = y_{fs,0}(1-\lambda) \quad \text{for} \quad y_{f,0} < y_{s,0}, \quad (17)$$

where x_{fs} and y_{fs}, respectively, represent the x and y components of the distance between the fluid particles and solid atoms. The subscripts f and s indicate the values for the fluid particles and the solid atoms, respectively. In the case of the constant volume, it follows that

$$x_{fs,1} = x_{fs,0}\sqrt{1+\lambda} \quad \text{for} \quad x_{f,0} > x_{s,0}, \\ x_{fs,1} = x_{fs,0}\sqrt{1-\lambda} \quad \text{for} \quad x_{f,0} < x_{s,0}, \quad (18)$$

and

$$y_{fs,1} = y_{fs,0}\sqrt{1+\lambda} \quad \text{for} \quad y_{f,0} > y_{s,0}, \\ y_{fs,1} = y_{fs,0}\sqrt{1-\lambda} \quad \text{for} \quad y_{f,0} < y_{s,0}. \quad (19)$$

The z component normal to the solid surface can be treated in the same manner as the usual transformation,[12] since the relative positions of the fluid particles to the solid atoms are the same in the direction normal to an interface.

III. METHODOLOGY TO OBTAIN THE LOCAL PRESSURE COMPONENTS AND INTERFACIAL TENSION

In this section, we describe the perturbative method used to obtain pressure components and interfacial tension in subsystems for a system which interacts with an external field. Two alternative methods are also presented to compare the results of the local interfacial tension calculation: the first method evaluates the intermolecular force acting on a plane, and the second is the conventional virial expression based on the Irving and Kirkwood definition.

A. Perturbative method

In order to obtain the pressure components and interfacial tension in subsystems, it is reasonable to use Eqs. (14) and (15) which are derived in the μVT ensemble. This requires the assumption that the system is in equilibrium, keeping μ, V, and T constant in each subsystem. Under this assumption, the thermodynamic properties in each subsystem can be evaluated appropriately. For a system in a volume V which consists

of subsystems with volumes V_k($V_k = dx_k \times dy_k \times dz_k$, $dx_k = dy_k = dz_k$, and $V = \Sigma_k V_k$), the local pressure components $P_{\xi\eta,V_k}(\xi,\eta = x,y,z)$ and interfacial tension γ_{V_k} are described on the basis of Eqs. (14) and (15) as

$$P_{\substack{\xi\eta \\ (x,y,z)\in V_k}}(x,y,z) \equiv P_{\xi\eta,V_k} = \frac{1}{\beta\Delta(d\xi_k)A_{\eta,V_k}} \ln\left\langle \left(1+\frac{\Delta V_k}{V_k}\right)^{N_{V_k}} \times \exp\left(-\beta\Delta\left(U_{V_k}+\Phi_{V_k}\right)\right)\right\rangle \quad (20)$$

and

$$\gamma_{\substack{(x,y,z)\in V_k}}(x,y,z) \equiv \gamma_{V_k} = -\frac{1}{\beta\Delta A_{s,V_k}} \ln\left\langle \exp\left(-\beta\Delta\left(U_{V_k}+\Phi_{V_k}\right)\right)\right\rangle, \quad (21)$$

where $\Delta(d\xi_k) = \lambda \times d\xi_k$, $\Delta A_{s,V_k} = \lambda A_{s,V_k}$, and the subscript V_k indicates that the quantity is defined in V_k. It should be noted that in Eq. (20) the pressure components at the volume V_k are obtained by considering only the interactions through the area A_{η,V_k} which is perpendicular to the η coordinate. These equations are the same forms as those derived by using Eqs. (7) and (8) in the canonical ensemble, which suggests that the pressure components and interfacial tension are formally obtained in subsystems based on Eqs. (20) and (21), respectively, in the canonical ensemble simulation if the system is in equilibrium.

B. Evaluation of the force acting on a plane

Todd and co-workers[18] have presented a method to consider contributions of the interactions between the particles to the pressure components by evaluating the intermolecular forces acting on a plane, and this method is used as one of the methods to calculate the pressure components.[19] This approach can be extended to formalism applicable to subsystems. Consider a plane in the volume V_k:A_{η,V_k}, which is perpendicular to the axis η, and through which the ith particle and jth particle may interact. For a region in the vicinity of the fluid-solid interface, in which a substrate is located below fluid molecules, it follows that the contributions of the interactions to the pressure components of the fluid exerted on the plane are straightforwardly calculated by the evaluation of the intermolecular forces, and the pressure components are given by

$$P_{\substack{\xi\eta \\ (x,y,z)\in V_k}}(x,y,z) \equiv P_{\xi\eta,V_k} = \frac{1}{V_k}\left\langle \sum_{i\in V_k} \frac{p_{i\xi}p_{i\eta}}{m_i}\right\rangle + \frac{1}{2A_{\eta,V_k}}\left\langle \sum_{(i\neq j),\mathbf{r}_{ij}\cap A_{\eta,V_k}} f_{ij\xi}\left[\Theta(\eta_i-\eta)\Theta(\eta-\eta_j)-\Theta(\eta_j-\eta)\Theta(\eta-\eta_i)\right]\right\rangle + \frac{1}{A_{\eta,V_k}}\left\langle \sum_{(i,j),\mathbf{r}_{ij}\cap A_{\eta,V_k}} f'_{ij\xi}\left[\Theta(\eta_i-\eta)\Theta(\eta-\eta_j)+\Theta(\eta_j-\eta)\Theta(\eta-\eta_i)\right]\right\rangle, \quad (22)$$

where $V_k = (d\eta_k)A_{\eta,V_k}$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, m_i is the mass of ith particle, $p_{i\xi}$ and $p_{i\eta}$ are the ξ and η components of the momentum of the ith particle in the volume V_k, respectively, $f_{ij\xi}$ represents the ξ component of the intermolecular force acting on the ith fluid particle due to the jth fluid particle, $f'_{ij\xi}$ is the ξ component of the intermolecular force acting on the ith fluid particle due to the jth solid atoms, and Θ is the Heaviside step function. In Eq. (22), the third term is obtained considering only the forces acting on the ith fluid particles,[19] and the second part in the third term, $f'_{ij\xi}\Theta(\eta_j-\eta)\Theta(\eta-\eta_i)$ is needed to include effects of the components of the fluid-solid interaction force which are tangential to the fluid-solid interface. Then, the local interfacial tension at the volume V_k is defined in the present study as

$$\gamma_{V_k} = dz_k\left(P_{zz,V_k} - \frac{P_{xx,V_k}+P_{yy,V_k}}{2}\right), \quad (23)$$

for the system in which z is the component normal to the interface, and x and y are the tangential components.

C. Irving and Kirkwood definition

The normal and tangential pressure components, $P_N(z) = P_{zz}(z)$ and $P_T(z) = (P_{xx}(z)+P_{yy}(z))/2$, which depend only on the direction normal to the interface in a planar system, are expressed by the conventional virial equations which are based on the Irving and Kirkwood definition.[19] For a region in the vicinity of the fluid-solid interface, in which a substrate is located below fluid molecules,

$$P_N(z) = \rho(z)k_BT - \frac{1}{2A}\left\langle \sum_{i\neq j}\frac{|z_{ij}|}{r_{ij}}\frac{\partial u(r_{ij})}{\partial r_{ij}} \times \Theta\left(\frac{z-z_i}{z_{ij}}\right)\Theta\left(\frac{z_j-z}{z_{ij}}\right)\right\rangle + \frac{1}{A}\left\langle \sum_{i,j} f'_{ijz}\Theta(z_i-z)\Theta(z-z_j)\right\rangle, \quad (24)$$

$$P_T(z) = \rho(z)k_BT - \frac{1}{4A}\left\langle \sum_{i\neq j}\frac{x_{ij}^2+y_{ij}^2}{r_{ij}}\frac{\partial u(r_{ij})}{\partial r_{ij}}\frac{1}{|z_{ij}|} \Theta\left(\frac{z-z_i}{z_{ij}}\right)\Theta\left(\frac{z_j-z}{z_{ij}}\right)\right\rangle, \quad (25)$$

where ρ is the density, A is the interfacial area, and u and $r_{ij} = \sqrt{x_{ij}^2 + y_{ij}^2 + z_{ij}^2}$ are the potential energy and distance between the particles, respectively. In Eqs. (24) and (25), the first and second terms on the right hand side are the respective contributions of the fluid molecules' kinetic part and the intermolecular forces between fluid molecules. In Eq. (24), the third term on the right hand side is the contribution of the intermolecular forces acting on fluid molecules due to the solid atoms. A number of published studies obtain the pressure components by using these equations.[3,16,19] The local interfacial tension for the planar system is defined in the present study as

$$\gamma_{V_k} = \gamma_{dz_k} = \mathrm{d}z_k \left(P_N(z) - P_T(z) \right). \tag{26}$$

IV. SYSTEM AND NUMERICAL DETAILS

In the present study, a classical molecular dynamics simulation is conducted for the system in which 4050 fluid molecules are confined between two planar solid surfaces. The system is in vapor-liquid equilibrium which includes three interfaces (vapor-solid, vapor-liquid, and liquid-solid) which are parallel to the solid surfaces (xy plane) perpendicularly located along the z axis. The Hamiltonian of the system is described as

$$H(\mathbf{r}, \mathbf{p}) = \sum_{i}^{N_f} \frac{|\mathbf{p}_i|^2}{2m_i} + \frac{1}{2} \sum_{i \neq j}^{N_f} u_{ff}(r_{ij}) + u_{ext}, \tag{27}$$

where N_f is the number of the fluid molecules, $u_{ff}(r_{ij})$ is the potential energy between the fluid molecules which depends on the distance between the molecules, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and $u_{ext} = \Sigma_{i=1}^{N_f} \Sigma_{j=1}^{N_s} u_{fs}(r_{ij})$ with the number of the solid atoms N_s and the potential energy between the fluid molecules and the solid atoms u_{fs}. All the interactions between molecules or atoms are assumed to obey the 12-6 Lennard-Jones (LJ) potential, of the form,

$$u(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{6} \right]. \tag{28}$$

The fluid molecules are assumed to be argon (Ar), and reduced units are used as given in Table I by using the Boltzmann constant, k_B, and the LJ parameters of the fluid molecules, m_f, σ_{ff}, and ε_{ff} in the present study. The cutoff distance of the LJ potential is 5.0. The solid substrates are assumed to be platinum (Pt), with Lennard-Jones interaction parameters of $\sigma_{ss} = 0.746$ and $\varepsilon_{ss} = 65.39$.[20] The fluid-solid interaction is also described by the LJ potential with $\sigma_{fs} = (\sigma_{ff} + \sigma_{ss})/2 = 0.873$ and ε_{fs}, in which ε_{fs} is varied as a ratio to the ε_{ff} in the present study. The volume of the system is defined as $V = L_x \times L_y \times L_z$, where $L_x = 15.4$, $L_y = 15.4$, and $L_z = 44.1$. Periodic boundary conditions are applied in the x and y directions which are tangential to the interfaces. The velocity Verlet algorithm is applied to integrate the equations of motion. Each solid part consists of 3 layers of the solid atoms where the outermost layer is fixed and the temperature of the middle layer is controlled by the Langevin method,[21,22] at a constant value $T^* = 0.8$. Artificial forces are not added to the third layer, and the atoms in the third layer can move freely around the center of oscillation by the interactions with other atoms. The simulation consists of 2028 solid atoms arrayed in a fcc lattice structure with the (111) surface in contact with the fluid molecules.

The temperature of the fluid molecules is kept constant by the velocity scaling control for 500 000 steps with a time interval of $\Delta t = 9.3 \times 10^{-4}$, followed by 2 000 000 steps of the relaxation calculation conducted to equilibrate the system without the velocity scaling control. The density, pressure, and interfacial tension are obtained as the time averaged values for at least 2 000 000 steps.

TABLE I. Reduced units and their values.

Quantity	Unit	Value
Mass	m_f	6.634×10^{-26} kg
Distance	σ_{ff}	3.405×10^{-10} m
Energy	ε_{ff}	1.670×10^{-21} J
Temperature	ε_{ff}/k_B	120.9 K
Time	$\sigma_{ff}\sqrt{m_f/\varepsilon_{ff}}$	2.146×10^{-12} s
Interfacial tension	$\varepsilon_{ff}/\sigma_{ff}^2$	1.440×10^{-2} Nm^{-1}
Pressure	$\varepsilon_{ff}/\sigma_{ff}^3$	4.230×10^{7} Nm^{-2}
Density	$m_f \sigma_{ff}^{-3}$	1.680×10^{3} kgm^{-3}

V. RESULTS AND DISCUSSIONS

A. One dimension

Figures 1(a) and 1(b) present typical results obtained by the perturbative method on the basis of Eq. (20). The figures show the normal and tangential components of the reduced pressure and the reduced density of fluid molecules in the z direction near the lower substrate for $\lambda = 5.0 \times 10^{-10}$, and for $\varepsilon_{fs} = 0.25$ (Fig. 1(a)) and $\varepsilon_{fs} = 0.50$ (Fig. 1(b)). The partial derivatives as expressed in Eqs. (4) and (11) were evaluated by the central difference method. The results were obtained by averaging the pressure and density values after 5 000 000 time steps. For the pressure results, the figures show error bars calculated using five averaged results of 1 000 000 time steps. The system is divided into subsystems with the height of 0.088 in the z direction, in which the pressure components and density of fluid molecules are calculated. As shown in Fig. 1, the normal pressure component $P_N^*(= P_{zz}^*)$ is constant in the z direction, ensuring that the system is in equilibrium, while the tangential pressure component $P_T^*(= (P_{xx}^* + P_{yy}^*)/2)$ fluctuates in the vicinity of the liquid-solid interface and is almost constant in the bulk of the liquid. The error bars obtained by the 5 simulation runs indicate that the results are obtained with considerable accuracy in the present study. Comparing Figs. 1(a) and 1(b), it is evident that the fluctuation of P_T in the vicinity of the liquid-solid interface becomes pronounced with the increase of ε_{fs}.

Figure 2 shows effects of the perturbation parameter λ on the reduced local liquid-solid interfacial tension $\gamma_{V_k}^*$ obtained on the basis of Eq. (21) by the forward difference for $\varepsilon_{fs} = 0.25$. The figure shows $\gamma_{V_k}^*$ as a function of z^*, and is normalized to the corresponding values for the case of $\lambda = 5.0$

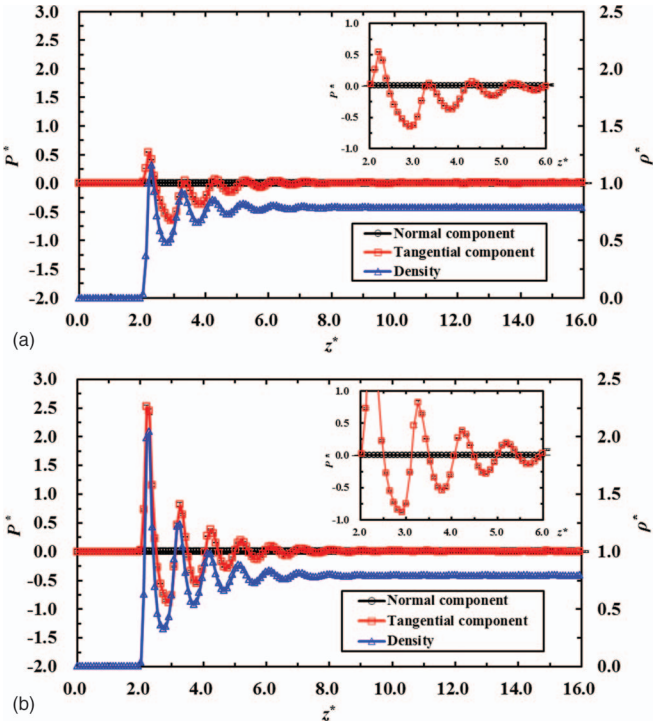

FIG. 1. Normal and tangential components of the reduced pressure P^* and the reduced density of fluid molecules ρ^* in the z direction, obtained on the basis of Eq. (20) in the vicinity of the liquid-solid interface for $\lambda = 5.0 \times 10^{-10}$, and for (a) $\varepsilon_{fs} = 0.25$ and (b) $\varepsilon_{fs} = 0.50$. The circles and squares correspond to the results of the normal and tangential components of the pressure, respectively. The triangles are the results of the density of the fluid molecules. The results of the pressure components and density are calculated as the averaged values of 5 000 000 time steps.

$\times 10^{-10}$. As shown in Fig. 2, with increasing λ, the value of the local interfacial tension differs markedly from that in the case of $\lambda = 5.0 \times 10^{-10}$, especially in the bulk of the liquid; this is due to the quite small values of the local interfacial tension in the bulk. This result suggests that the use of the forward difference alone is not sufficient to obtain accurate local interfacial tension when the value of λ is relatively large ($>5.0 \times 10^{-6}$), as in the present study. Therefore, us-

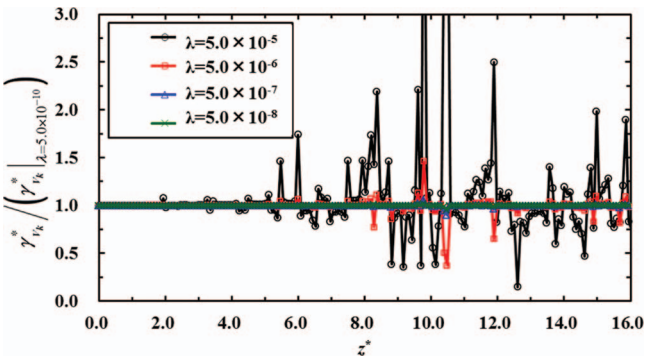

FIG. 2. Effects of the perturbation parameter λ on the reduced local liquid-solid interfacial tension $\gamma^*_{V_k}$ obtained on the basis of Eq. (21) by the forward difference for $\varepsilon_{fs} = 0.25$. Values of $\gamma^*_{V_k}$ are normalized to the value in the case of $\lambda = 5.0 \times 10^{-10}$, $\gamma^*_{V_k}|_{\lambda=5\times10^{-10}}$. The circles, squares, triangles, and crosses are the results for $\lambda = 5.0 \times 10^{-5}$, 5.0×10^{-6}, 5.0×10^{-7}, and 5.0×10^{-8}, respectively. Each result is calculated as the averaged value of 2 000 000 time steps.

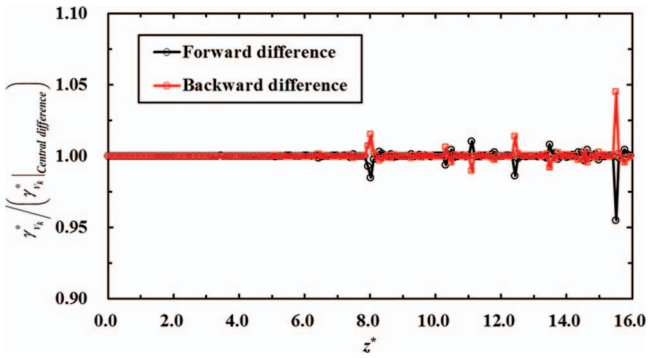

FIG. 3. Effects of the forward and backward difference methods on calculating the reduced local liquid-solid interfacial tension $\gamma^*_{V_k}$ obtained on the basis of Eq. (21) for $\lambda = 5.0 \times 10^{-10}$ and $\varepsilon_{fs} = 0.25$. Each value is normalized to that obtained by the central difference, $\gamma^*_{V_k}|_{Central\ difference}$. The circles and squares indicate the results of using the forward and backward difference methods, respectively. Each result is calculated as the averaged value of 2 000 000 time steps.

ing smaller values of λ or switching to the central difference method is strongly recommended. The value of $\lambda = 5.0 \times 10^{-10}$ is adopted as the standard in the following calculations.

Figure 3 shows effects of using forward and backward differences on the calculated local liquid-solid interfacial tension for $\lambda = 5.0 \times 10^{-10}$ and $\varepsilon_{fs} = 0.25$, in which each value is normalized to the value obtained by the central difference. Relatively high peaks are observed in the bulk of the liquid, but the profile is symmetric about the value of the central difference ($\gamma^*_{V_k} = 1.0$), which means that the result obtained by the central difference is the most reliable compared with the other approaches. However, from the fact that the maximum error was found to be at most 5% in this study, it can also be said that the forward and backward differences are suitable when such a small value of λ is chosen ($\lambda = 5.0 \times 10^{-10}$), if high accuracy is not required for the calculation of the local liquid-solid interfacial tension.

Figure 4 gives the results of the reduced local liquid-solid interfacial tensions in one dimension calculated by the

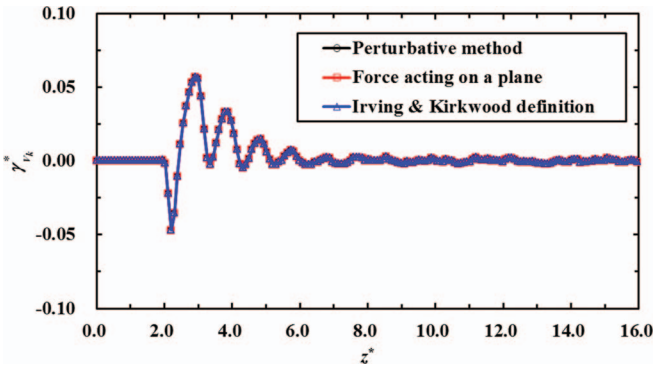

FIG. 4. Reduced local liquid-solid interfacial tension $\gamma^*_{V_k}$ calculated by the perturbative method (Eq. (21)), the evaluation of the intermolecular force acting on a plane (Eq. (23)), and the virial expression based on the Irving and Kirkwood definition (Eq. (26)) for $\varepsilon_{fs} = 0.25$. The values of the perturbative method are calculated by the central difference method. The circles, squares, and triangles indicate the results obtained by the perturbative method, the evaluation of the intermolecular force acting on a plane, and Irving and Kirkwood definition, respectively. Each result is calculated as the averaged value of 5 000 000 time steps.

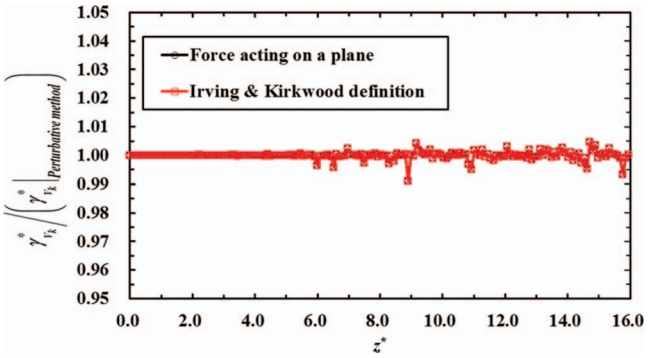

FIG. 5. Reduced local liquid-solid interfacial tensions $\gamma^*_{V_k}$ calculated on the basis of Eqs. (23) and (26) for $\varepsilon_{fs} = 0.25$. The results are normalized to that obtained by the perturbative method (Eq. (21)), $\gamma^*_{V_k}|_{Perturbative\ method}$. The circles and squares indicate the results obtained by the evaluation of the intermolecular force acting on a plane (Eq. (23)) and Irving and Kirkwood definition (Eq. (26)), respectively. Each result is obtained as the averaged value of 2 000 000 time steps.

perturbative method (Eq. (21)), the evaluation of the intermolecular force acting on a plane (Eq. (23)), and the virial expression based on the Irving and Kirkwood definition (Eq. (26)) for $\varepsilon_{fs} = 0.25$. These results are shown normalized to the values obtained by the perturbative method in Fig. 5. According to Fig. 4, all the results have good agreement at each local position, and confirm that the local liquid-solid interfacial tension obtained by the perturbative method in this study is valid in one dimension. A detailed comparison of the results as shown in Fig. 5 reveals that the values of the local interfacial tension at each position agree well, but differences are observed in the bulk of the liquid where the values of the local interfacial tension are quite small as shown in Fig. 4. In Fig. 5, effects of the tangential pressure components affected by the solid atoms can be evaluated by the result of Irving and Kirkwood definition obtained based on Eq. (26) in which no contributions of the tangential pressure components affected by the fluid-solid interactions are considered. The results of the local liquid-solid interfacial tensions obtained by the perturbative method and the force acting on a plane confirm that the tangential pressure component affected by the solid atoms almost vanishes in one dimension, as indicated in the previous works.[3,19]

B. Two dimensions

The perturbative method based on Eqs. (20) and (21) was applied to the calculation system to obtain the pressure components and interfacial tension at a liquid-solid interface in two dimensions. The system is divided into subsystems with the area $A_k (= \mathrm{d}x_k \times \mathrm{d}z_k = 0.088 \times 0.088)$ in the xz plane, and results are obtained as the averaged values of 5 000 000 time steps. Figure 6 shows reduced density distributions of the fluid molecules in the vicinity of the liquid-solid interface; Fig. 6(a) shows the result for $\varepsilon_{fs} = 0.25$ and Fig. 6(b) for $\varepsilon_{fs} = 0.50$. In Fig. 6, the x^* positions of the first layer of the solid atoms facing the fluid molecules are 0.0, 0.592, and 1.184. The results indicate that the density distribution of the fluid molecules fluctuates in the vicinity of the liquid-solid interface and is affected by the positions of the solid atoms in two dimensions.

Figure 7 presents two-dimensional contour plots of the local tangential component of the reduced pressure of the fluid, obtained based on Eq. (20) using the central difference method for $\lambda = 5.0 \times 10^{-10}$, and for $\varepsilon_{fs} = 0.25$ (Fig. 7(a)) and $\varepsilon_{fs} = 0.50$ (Fig. 7(b)). The tangential pressure component in the xz plane fluctuates at the liquid-solid interface and becomes pronounced with the increase of ε_{fs}, displaying the same tendency as that obtained in one dimension. Three-dimensional contour plots of the local tangential pressure component are shown in Fig. 8 for $\lambda = 5.0 \times 10^{-10}$, and for $\varepsilon_{fs} = 0.25$ (Fig. 8(a)) and $\varepsilon_{fs} = 0.50$ (Fig. 8(b)). The latter shows that the peaks of the tangential pressure component fluctuate in the x direction due to the effects of the solid atoms, while the effect is weak in the case of $\varepsilon_{fs} = 0.25$ as shown in Fig. 8(a). Figure 9 gives the results of the reduced local interfacial tension in the vicinity of the liquid-solid interface in the xz plane; results were obtained on the basis of Eq. (21) for $\lambda = 5.0 \times 10^{-10}$, and for $\varepsilon_{fs} = 0.25$ (Fig. 9(a)) and $\varepsilon_{fs} = 0.50$ (Fig. 9(b)). The profiles of the local interfacial tension are the

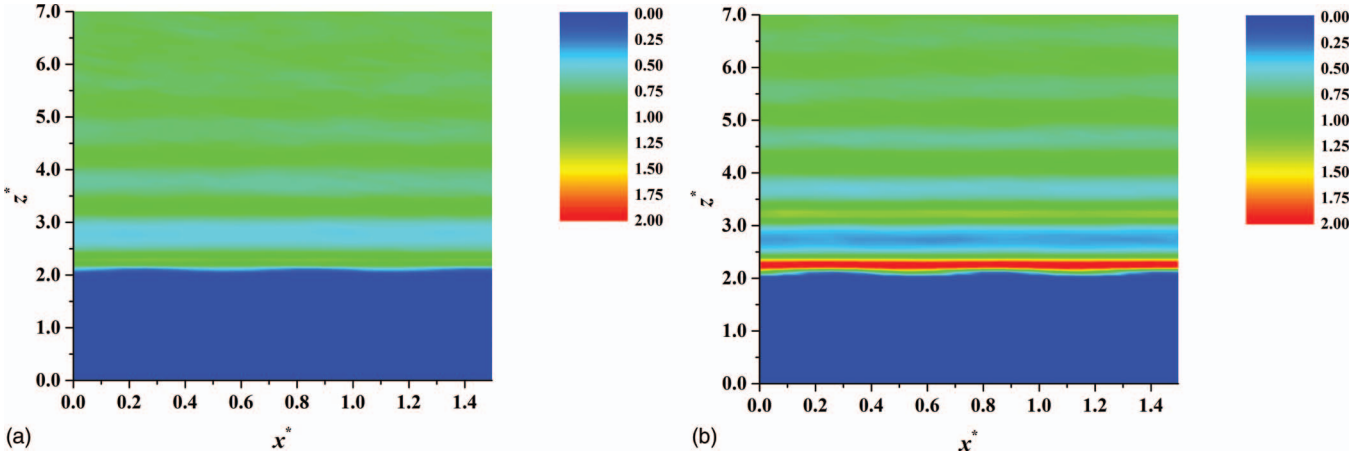

FIG. 6. Reduced density distributions of fluid molecules in the vicinity of the liquid-solid interface, for (a) $\varepsilon_{fs} = 0.25$ and (b) $\varepsilon_{fs} = 0.50$. Each result was obtained as the averaged value of 5 000 000 time steps and shown on each area $A_k (= \mathrm{d}x_k \times \mathrm{d}z_k = 0.088 \times 0.088)$.

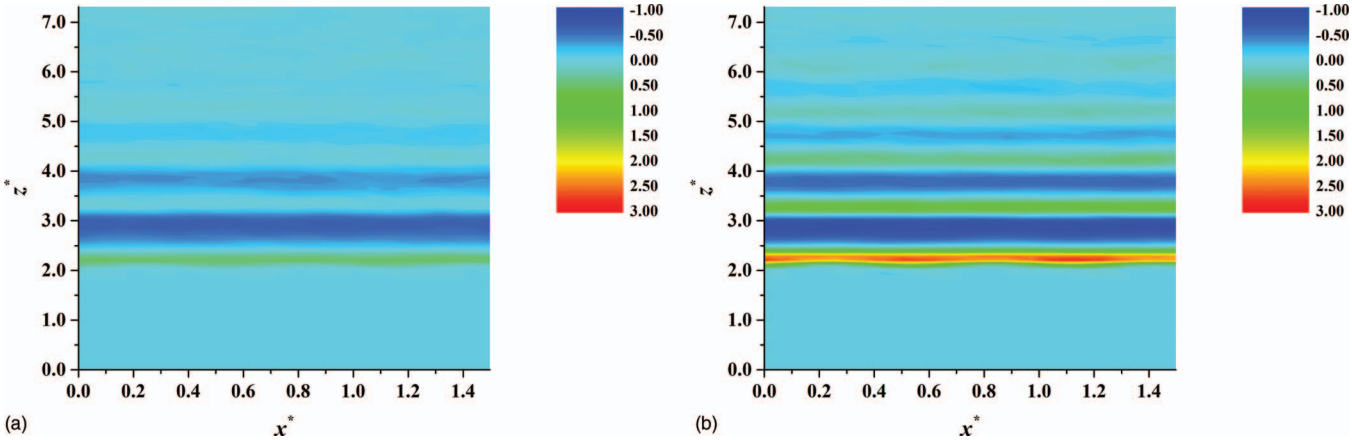

FIG. 7. Two-dimensional contour plots of the reduced local tangential pressure component P_T^* in the vicinity of the liquid-solid interface in the xz plane, obtained on the basis of Eq. (20) for $\lambda = 5.0 \times 10^{-10}$, and for (a) $\varepsilon_{fs} = 0.25$ and (b) $\varepsilon_{fs} = 0.50$. Each result is obtained as the averaged value of 5 000 000 time steps.

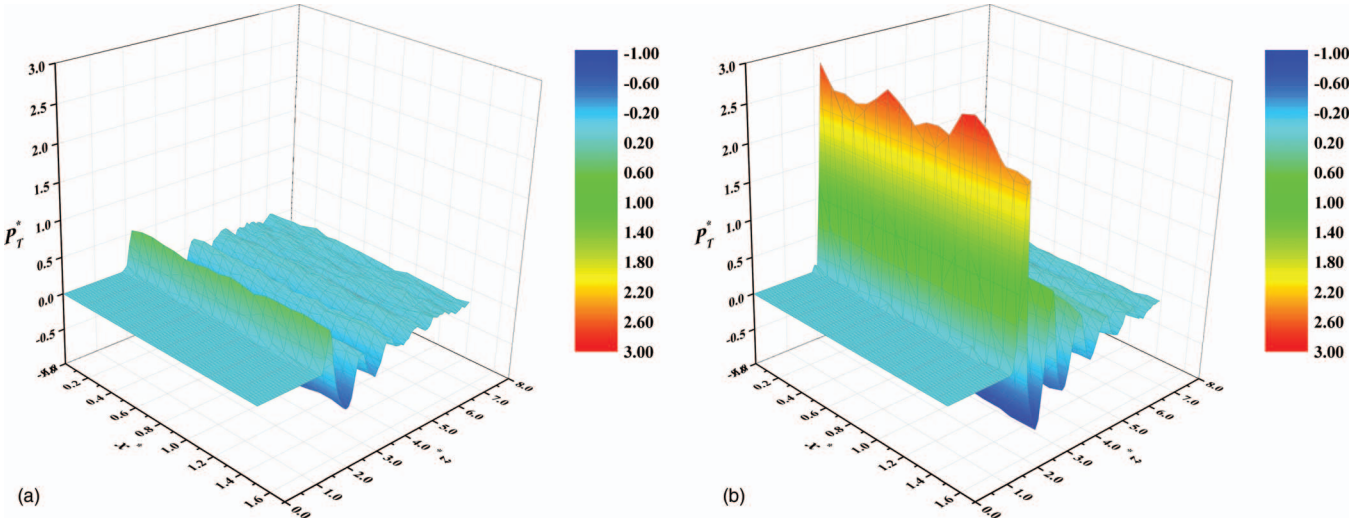

FIG. 8. Three-dimensional contour plots of the reduced local tangential pressure component P_T^* in the vicinity of the liquid-solid interface in the xz plane, obtained on the basis of Eq. (20) for $\lambda = 5.0 \times 10^{-10}$, and for (a) $\varepsilon_{fs} = 0.25$ and (b) $\varepsilon_{fs} = 0.50$. Each result is the averaged value of 5 000 000 time steps.

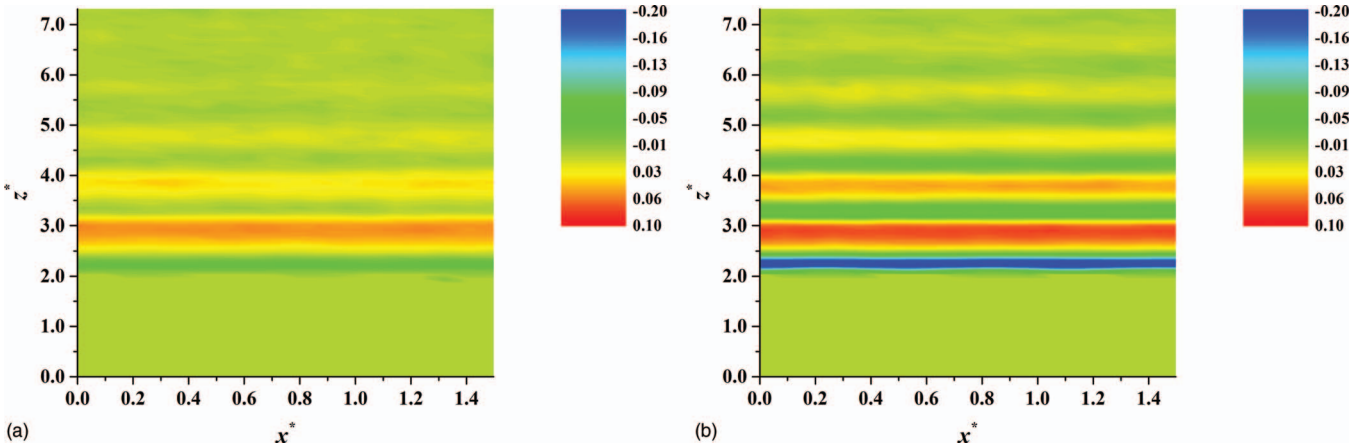

FIG. 9. Two-dimensional contour plots of the reduced local interfacial tension $\gamma_{V_k}^*$ in the vicinity of the liquid-solid interface in the xz plane, obtained on the basis of Eq. (21) for $\lambda = 5.0 \times 10^{-10}$, and for (a) $\varepsilon_{fs} = 0.25$ and (b) $\varepsilon_{fs} = 0.50$. Each result is the averaged value of 5 000 000 time steps.

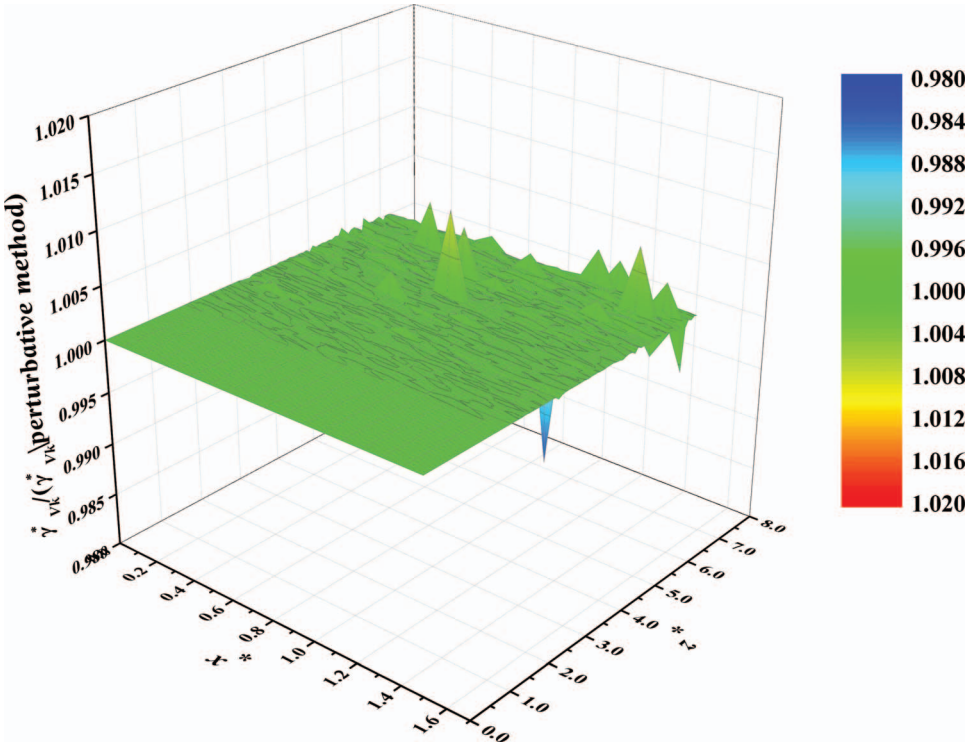

FIG. 10. Three-dimensional contour plot of the reduced local interfacial tension $\gamma^*_{V_k}$ in the vicinity of the liquid-solid interface in the xz plane, obtained on the basis of Eq. (23) for $\lambda = 5.0 \times 10^{-10}$ and $\varepsilon_{fs} = 0.25$. The result is normalized to the value obtained by the perturbative method, $\gamma^*_{V_k}|_{Perturbative\ method}$. The result is the averaged value of 5 000 000 time steps.

same as those obtained in one dimension, which ensures the validation of the method in two dimensions.

Figure 10 gives the three-dimensional contour plot of the reduced local liquid-solid interfacial tension in the xz plane obtained by the evaluation of the intermolecular force acting on a plane, using Eq. (23) with $\lambda = 5.0 \times 10^{-10}$ and $\varepsilon_{fs} = 0.25$. The result is normalized to the value obtained by the perturbative method. According to the result, the difference between the two methods becomes relatively pronounced toward the bulk part of the fluid, but the error is under 2% in the calculation region. The results suggest that the perturbative method is valid for the calculation of the local liquid-solid interfacial tension in this study, even if the values are evaluated in two dimensions.

VI. CONCLUSION

A classical molecular dynamics simulation was conducted for a system composed of fluid molecules between two planar solid surfaces, and whose interactions are described by the 12-6 Lennard-Jones form. This paper presents a general description of the pressure components and interfacial tension at a fluid-solid interface obtained by the perturbative method on the basis of statistical thermodynamics, proposes a method to consider the pressure components tangential to an interface which are affected by interactions with solid atoms, and applies this method to the calculation system. The description of the perturbative method is extended to subsystems, and the local pressure components and interfacial tension of the fluid at a liquid-solid interface are obtained and examined in one- and two-dimensions, and the results are compared with those obtained by two alternative methods: (a) an evaluation of the intermolecular force acting on a plane, and (b) the conventional method based on the virial expression. A general description of the method to evaluate the intermolecular force acting on a plane which is applicable to subsystems is also presented.

In one dimension, the local interfacial tension was obtained with various perturbation parameters, and the results revealed that quite a small value (on the order of 1.0×10^{-10}) is required to obtain relatively accurate values of the local interfacial tension using the forward difference method in the present study. The calculated local interfacial tension agreed well with the results of the two alternative methods at each local position. In two dimensions, the results showed a characteristic profile of the tangential pressure component which depended on the direction tangential to the liquid-solid interface, which agreed with that obtained by the evaluation of the force acting on a plane in the present study. Such good agreement suggests that the perturbative method used in this study is valid to obtain the local pressure components and interfacial tension at a liquid-solid interface.

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