Scattering Properties of Gas Molecules on a Water Adsorbed Surface

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Abstract. The thermal problem of a rarefied argon (Ar) gas between two parallel walls is considered to investigate the characteristics of the reflected gas molecule at a platinum (Pt) wall surface which physically adsorbs water (H_2O) molecules. The analysis is based on the molecular dynamics (MD) method for the interaction of gas molecules with the water adsorbed wall surface together with the direct simulation Monte-Carlo (DSMC) method for the motion of gas molecule. The accommodation coefficients of energy and normal momentum are obtained. The temperature distribution between two walls and the velocity distribution function of the reflected molecule are also obtained. It is found that the accommodation coefficients for the water adsorbed surface decrease with increasing the adsorption rate.

INTRODUCTION

The gas-wall interaction is one of the important problems in a rarefied gas flow because the interaction of gas molecules with solid wall surface has a great influence on the whole flow field. The diffuse reflection is generally assumed as a practical boundary condition for engineering application, but there are many cases for which this condition cannot be applied. The scattering properties of gas molecules depend on the state of the wall surface as well as the gas-wall interaction. The surface may be contaminated with other molecules than the gas molecule concerned. The water vapor is generally contained in the air and is easy to stick to a solid surface. Therefore, it is interesting to study the behavior of the reflected gas molecules on the wall surface which physically adsorbs water molecules.

The present authors have studied a rarefied gas flow between two parallel plates by applying the DSMC method for gas motion together with the MD method for the gas-wall interaction [1]-[3]. Along this line, in the present study, we consider the thermal problem of a rarefied argon gas between two walls and investigate scattering properties of argon molecules reflected at a water adsorbed surface. The objective of this study is to provide data for better understanding of characteristics of reflected gas molecules on complex structures of wall surfaces.

METHOD OF ANALYSIS

The method of analysis is almost the same as in the previous study [3]: We take a model of a thin platinum layer. One sheet of the layer consists of 10 Pt atoms in the X direction and another 10 atoms in the Z direction on the surface. Four molecular sheets are taken normal to the surface in the negative Y direction. The periodic boundary condition is applied in the direction parallel to the surface in the analysis. This layer is a model of a smooth and clean platinum wall. On the surface of the layer, the water molecules may be physically adsorbed. In this study, we use the SPC/E model [4] for a water molecule. The Lennard-Jones potential is chosen for the interaction potential between platinum wall atoms (Pt-Pt). The potential function between adsorbed water molecules (H_2O-H_2O) is given by the Lennard-Jones potential for O-O combined with the Coulomb potential between point charges q in each atom [4]. We use the model developed by Spohr and Heinzinger [5] for H_2O-Pt interactions. In the present study, we
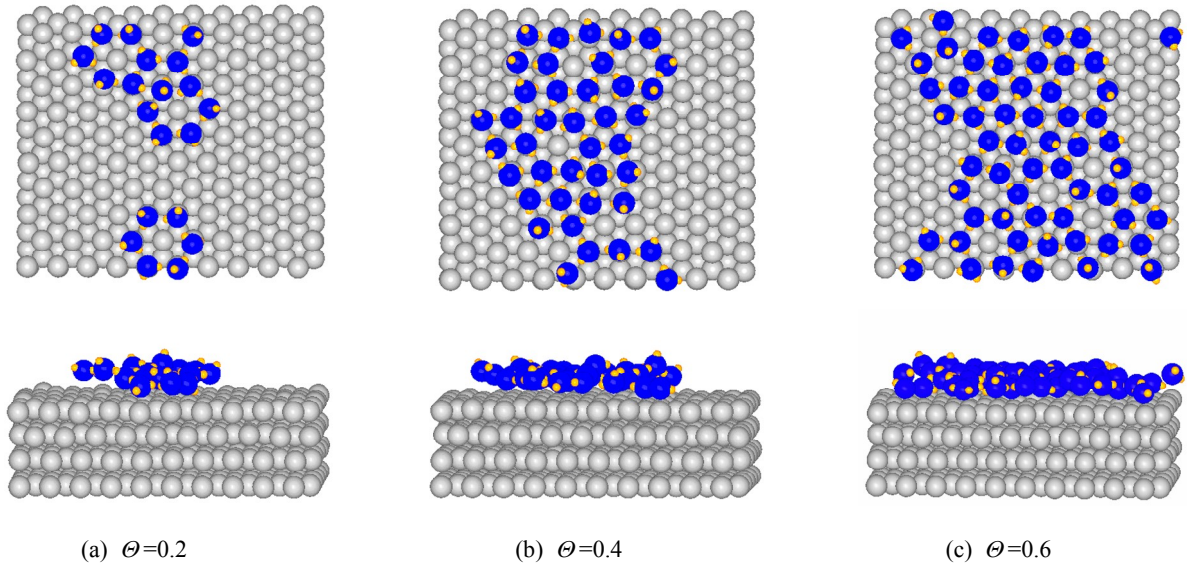
(a) Θ=0.2   (b) Θ=0.4   (c) Θ=0.6

FIGURE 1. A view of water adsorbed surfaces.

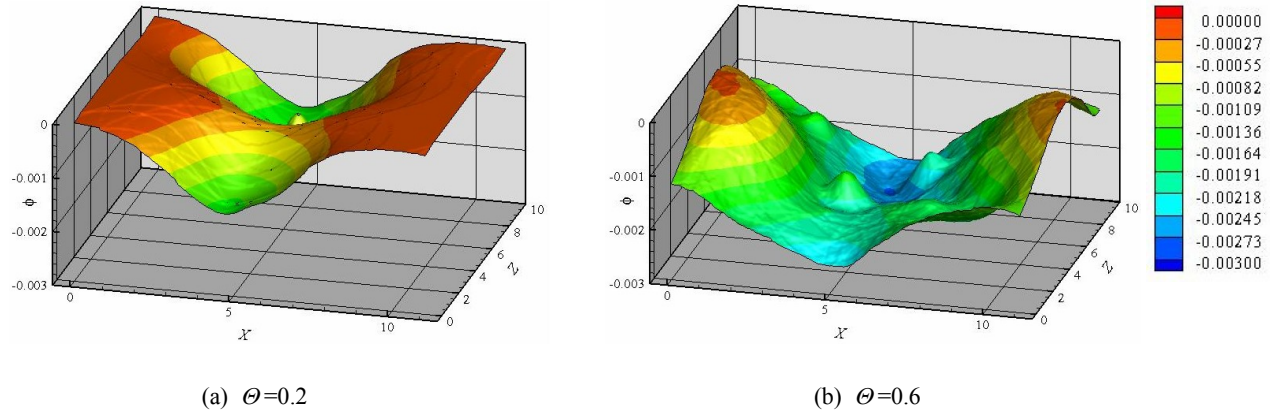(a) Θ=0.2   (b) Θ=0.6

FIGURE 2. Interaction potential distribution (3.25σ_{Pt} above the top Pt molecular layer).

consider argon molecule (Ar) for the gas molecule. The interaction potential for Pt-Ar is the same as in the previous study [1]. We shall use the potential based on the first principles calculation [6] for Ar-H_2O interactions. The numerical values of interaction potentials are listed in the previous paper [3].

In order to construct a water adsorbed surface, water molecules are injected to the clean platinum wall whose temperature is T_W =300K. We find that some water molecules are physically adsorbed on the smooth surface. Observation of behaviors of the water molecules reveals that the adsorbed water molecules move relatively slowly compared with the motion of a gas molecule (Ar molecules) on the surface, and they make a form like a hexagonal arrangement when Θ is large. Here, we define the adsorption rate Θ as a ratio of the number of adsorbed water molecules to that of platinum molecules constituting the top surface. The water adsorbed surface in cases of Θ=0.2, 0.4, 0.6 are shown in Figure 1(a) ~ (c), respectively. Figures 2(a) and (b) show the interaction potential distributions for an argon molecule at a height of 3.25σ_{Pt} from the top platinum molecule corresponding to the surfaces of Figs. 1(a) and (c), respectively. The interaction potential is normalized by ε_{Pt}, where σ_{Pt} is the core diameter and ε_{Pt} is the potential well depth for Pt-Pt interaction. We can see that the potentials are negative at this height and have deep negative wells near the positions where water molecules are adsorbed. The potential distribution of Θ=0.6 has a broad and deep negative area than that of Θ=0.2 because of many adsorbed molecules.
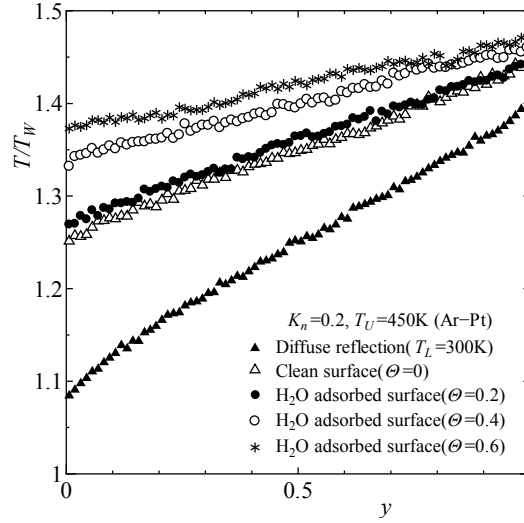
FIGURE 3. Temperature distributions T/T_W between two walls in case of T_U=450K when K_n=0.2.

We consider a slightly rarefied argon gas between two walls. Let the distance between two walls be L and the reference number density of the gas be n_0. The temperature of the lower wall ($T_L = T_W$) is taken to be 300K and the upper wall (T_U) has 360 or 450K. We assume that the gas molecular is diffusely reflected at the upper wall and we apply the MD method at the lower wall for the gas-wall interaction. The DSMC method is applied to the analysis of gas motion between two walls, and the gas molecule is assumed to be a hard sphere for this analysis. The Knudsen number defined by $K_n = l_{HS}/L$ is taken to be 0.2 in the present analysis. Here, l_{HS} is the mean free path of the molecules. When a gas molecule hits on the lower wall in the process of DSMC simulation, we switch to the analysis based on the MD method at this point to trace the motion of every gas molecule that is going to interact with the water adsorbed surface. In the numerical calculation, it is found that no argon molecule is adsorbed on the surface.

RESULTS

Temperature Distributions

Figure 3 shows the temperature distributions T/T_W in case of T_U=450K. Here, T_W is the lower wall temperature taken to be 300K. The abscissa y is normalized by the distance between two walls L, and y =0 is on the lower wall surface. In this figure, the filled and open circles, and asterisk represent the distributions of the water adsorbed surface in cases of Θ=0.2, 0.4 and 0.6, respectively. The open triangle means the distribution for the clean surface (Θ =0) where no molecule is adsorbed. The distribution of the diffuse reflection wall is also shown by filled triangles for comparison. It will be seen that the temperature jump at the lower wall (y=0) increases with increasing the adsorption rate Θ. This result indicates the global interaction of gas molecule with the wall surface becomes weak because of the adsorbed water molecules.

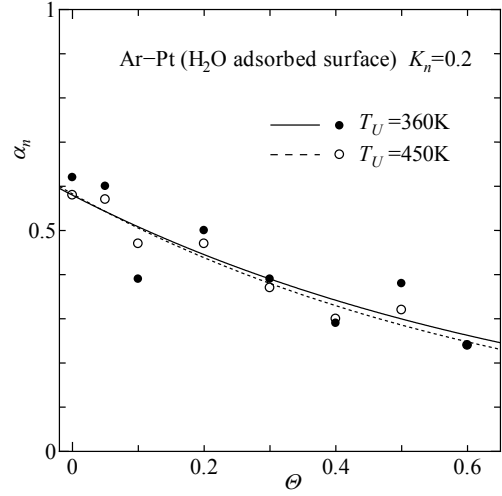## Accommodation Coefficients and Heat Flux

The translational energy accommodation coefficient α_E of gas molecule and the normal momentum accommodation coefficient α_n are defined by

$$\alpha_E = \frac{E_i - E_r}{E_i - E_w}, \qquad \alpha_n = \frac{p_i - p_r}{p_i - p_w}, \qquad (1)$$
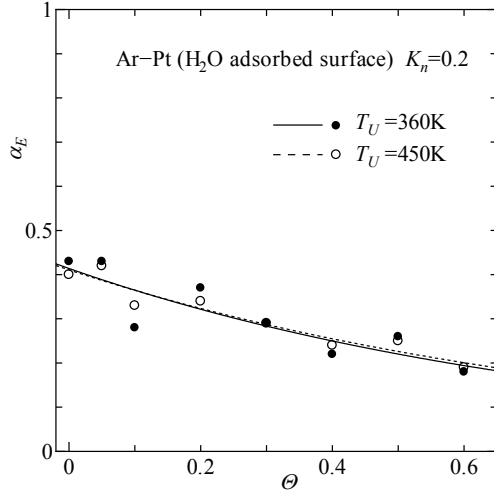
(a) Energy accommodation coefficient α_E (b) Normal momentum accommodation coefficient α_n

FIGURE 4. Accommodation coefficients versus adsorption rate Θ.

TABLE 1. Heat flux normalized by $mn_0C_m^3$.

	Clean surface	Water adsorbed surface						
T_U	$\Theta=0$	$\Theta=0.05$	$\Theta=0.1$	$\Theta=0.2$	$\Theta=0.3$	$\Theta=0.4$	$\Theta=0.5$	$\Theta=0.6$
360K	0.017	0.017	0.013	0.016	0.013	0.011	0.012	0.010
450K	0.045	0.046	0.040	0.040	0.036	0.032	0.032	0.026

where E is the kinetic energy of the molecules and p is the normal momentum, and the subscripts i, r, and w mean the values of incident, reflected and diffusely reflected molecules, respectively. Figure 4(a) shows the translation energy accommodation coefficient α_E versus the adsorption rate Θ. The value of α_n is also shown in Fig. 4(b). In Figs. 4(a) and (b), the filled and open circles represent the accommodation coefficients in cases of T_U=360K and 450K, respectively. The curves are obtained to fit the data by using the least squares method. No difference between the filled and open circles appears. The accommodation coefficients of energy and normal momentum decrease with increasing the adsorption rate. It is seen that the variation of α_n with Θ is larger than the variation of α_E.

Table 1 shows the heat flux toward the lower wall surface. The heat flux is normalized by $mn_0C_m^3$, where m is the mass of the gas molecule, $C_m=(2kT_W/m)^{0.5}$ is the most probable speed, and k is the Boltzmann constant. When the adsorption rate is high, the heat flux of the water adsorbed surface is much smaller than that of the clean surface.

It might be thought that the argon molecule is strongly accommodated with a contaminated wall surface with water molecules compared with a clean surface. However, we find that this is not so, but the argon molecule is not so well accommodated at the water adsorbed surface as the adsorption ratio becomes large. We here explain why the argon molecule has weak accommodation at the water adsorbed wall surface. For this purpose, we represent the potential distribution between the water adsorbed platinum surface and an argon molecule close to the surface. Figures 5(a) and (b) show the interaction potential distributions at the height of $2.86\sigma_{Pt}$ from the top platinum molecule for Θ=0.2 or 0.6. The potential is seen to have large positive values near the adsorbed water molecules. The number of positive peaks increases with increasing the adsorption rate. Therefore, the argon molecule will get a strong repulsive force near the peaks and may be reflected from the wall surface without having much interaction with the platinum atoms. That is, the argon molecule with small kinetic energy coming to the water molecules first moves towards the water molecules by the attractive force as shown in Fig. 2 and then it is repelled by the strong repulsive force caused by the water molecules. It does not have much time to interact with the platinum surface. This tendency becomes strong as the adsorption rate becomes large. If the number of adsorbed water molecules is small,
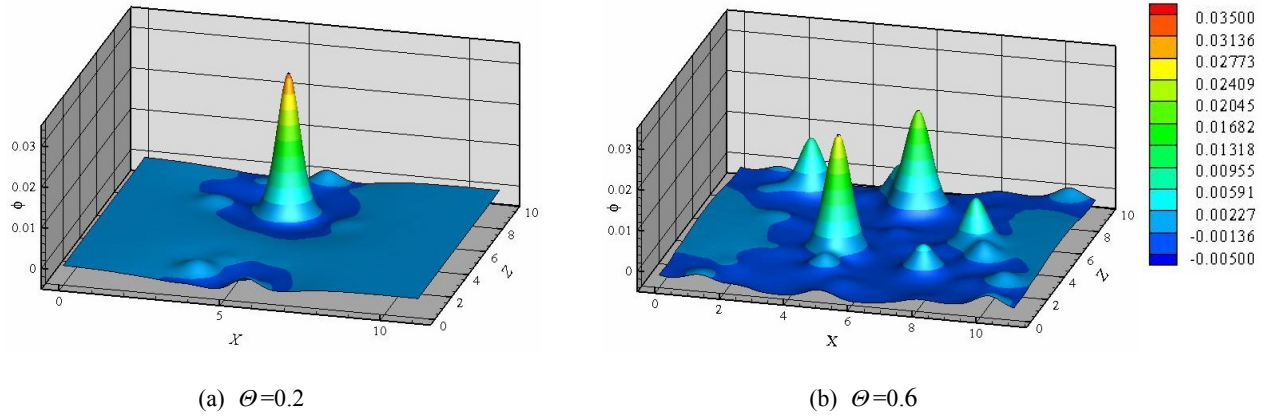
(a) Θ=0.2	(b) Θ=0.6

FIGURE 5. Interaction potential distribution ($2.86\sigma_{Pt}$ above the top Pt molecular layer).

the potential is still low. The argon molecule comes close to the wall surface and will have much time to interact with the surface molecules, and it is well accommodated with the wall.

Distribution Function of Molecular Velocity at Lower Wall Surface

Figures 6(a)~(c) show the distribution functions of the velocity of molecules at the wall surface before and after the reflection in case of Θ=0.6, and T_U=450K. Figure 6(a) shows the distributions in the X direction, while Fig. 6(b) illustrates the distributions normal to the wall. Figure 6(c) is the distributions of molecular velocity in the Z direction. In these figures, the molecular velocity V is normalized by the most probable speed C_m, the filled circle represents the distribution of the incident molecules, and the open circle shows the distribution of the reflected molecules obtained in the present study. The distribution of the diffuse reflection is shown as a solid curve for comparison. The dashed curve is the normalized distribution drawn from the Maxwell-type reflection condition [2] as follows:

$$f_x^+ = \alpha_E f_w + (1 - \alpha_E) f_x^- \qquad (V_y > 0) \,, \qquad f_w = \frac{1}{\sqrt{\pi}} \exp(-V_x^2), \qquad (2)$$

$$f_y^+ = \alpha_n f_w + (1 - \alpha_n) f_y^- \qquad (V_y > 0) \,, \qquad f_w = 2V_y \exp(-V_y^2), \qquad (3)$$

$$f_z^+ = \alpha_E f_w + (1 - \alpha_E) f_z^- \qquad (V_y > 0) \,, \qquad f_w = \frac{1}{\sqrt{\pi}} \exp(-V_z^2). \qquad (4)$$

Here, the energy accommodation coefficient α_E is taken in the X and Z direction, and the normal momentum accommodation coefficient α_n is used in the normal direction to the wall. The function f^- is the distribution function of the incident molecule, which is shown by the filled circle in Figs. 6(a)~(c), and f_w is the Maxwellian distribution of the wall surface. We take α_E=0.19 and α_n=0.24 in case of Θ=0.6 from Figs. 4(a) and (b). It is seen from Figs. 6(a)~(c) that the distribution of reflected molecule can be described by the distribution based on the Maxwell-type reflection condition very well. It is also found that the velocity distributions of reflected molecules obtained by the Maxwell-type reflection condition agree well with those of the MD calculation for all Θ, although we will not show them here.

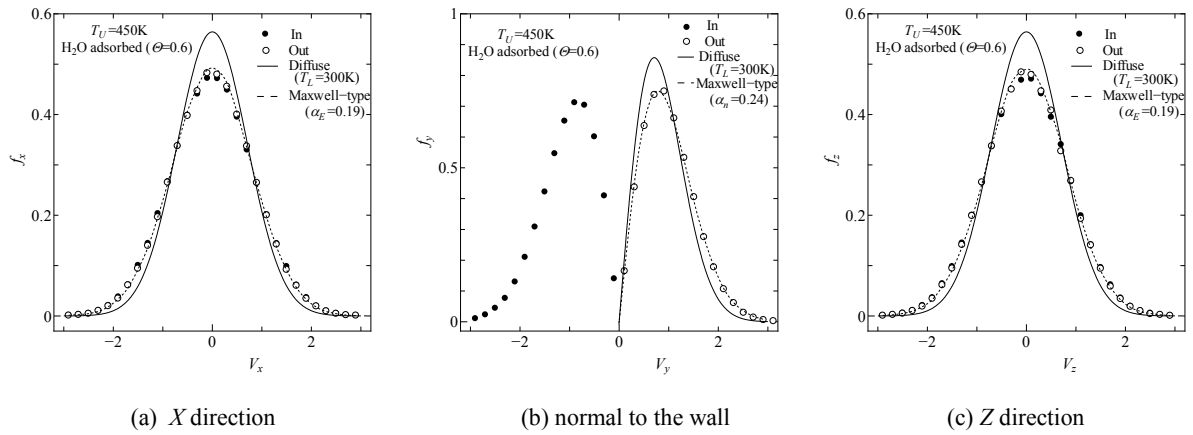| (a) *X* direction | (b) normal to the wall | (c) *Z* direction |

FIGURE 6. Velocity distributions of gas molecules at lower wall in case of Θ=0.6, and T_U=450K.

CONCLUSIONS

We have analyzed the thermal problem of a rarefied gas between two walls. The gas is taken to be argon and the wall is made of platinum surface which physically adsorbs water molecules. The analysis is based on the DSMC method for the motion of gas molecule and the MD method for the interaction between a gas molecule and the wall surface. The present investigation leads to the following conclusions:

(1) The temperature jump at the lower wall increases with increasing the adsorption rate Θ.
(2) The accommodation coefficients of energy and normal momentum for the water adsorbed surface decrease with increasing the adsorption rate Θ, and the variation of the normal momentum accommodation coefficients α_n with Θ is larger than the variation of the energy accommodation coefficients α_E.
(3) The velocity distribution of the reflected molecule at the water adsorbed surface is very close to that of the Maxwell-type boundary condition if we take proper accommodation coefficients.

ACKNOWLEDGMENTS

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