Scattering and Trapping of Ar-Pt(111) System Using Phantom Particle Model

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Abstract. Energy exchange and trapping probabilities for interaction of gas molecules with a metal surface are calculated by the Molecular Dynamics method using the Phantom Particles model as a solid surface. The validity of the Phantom Particle model is confirmed through the power spectra of three directions, the velocity distribution in each layer and the response to an abrupt change of a preset temperature. Then the Phantom Particle model is applied to gas-surface interaction for Ar-Pt(111) system. The flux distributions, the TOF spectrum of gas atoms scattered at the specular angle and the trapping probabilities are calculated and compared with those of molecular beam experiments, leading to good quantitative agreement as well.

INTRODUCTION

In these years, space simulation chambers in large scale have been constructed in many facilities in America and Europe to analyze the impingement of thruster jet with the satellite body and the solar arrays during the firing of an attitude control thruster. In the interaction between solar panels and a thruster jet, it is pointed out that the heat load may damage the surfaces and that the contamination on a solar panel reduces a lifetime and a transmission of the panel. To develop the MEMS (micro electro-mechanical system), where the characteristic dimension is smaller than the mean free path, it is necessary to understand the flow field structure at the molecular level, including the accommodation or adsorption of gas molecules to the solid surface. We cannot obtain the high quality thin films for ULSI devices without knowledge of the interaction between plasma gas and a solid surface, such as chemical reactions and trapping of gas molecules on a solid surface. Therefore, acquisition of accurate data related to gas-surface interaction is an urgent necessity for space science and high technologies including micro fluid flows.

For experimental studies of gas-surface interaction, a molecular beam method mainly has been used. And we can obtain the information of the energy exchange of gas molecules to the solid surface from the flux intensity distribution of scattered molecules and the data such as mean velocity, temperature, Mach number from the TOF spectra. Since these experimental data are obtained in a plane including both the surface normal and incident beam, we cannot obtain the trapping probabilities and accommodation coefficients which need to detect all scattered molecules. If a computational method can be developed to realize the flux intensity distribution and velocity of the scattered molecules consistent with the experimental results, more precise data for gas-surface interaction can be obtained by combining the calculated data with experimental ones.

In the present study, the Phantom Particle model is applied to predict fundamental properties of gas-surface interaction, whose validity has been investigated in a preliminary simulation through the power spectra of three directions compared with the Debye frequency, the response to an abrupt change of a preset temperature, and the velocity distribution in each layer. The basis of this model had been introduced by Adelman and Doll, extended to a three-dimensional model by Tully, and developed by Blömer and Beylich. However Blömer and Beylich have neither applied this method to simulation of gas-surface interaction in the same condition as the molecular beam experiments nor demonstrated the flux distribution or TOF spectra of the scattered molecules. We independently have decided a parameter of an interaction between a single real atom and a single Phantom Particle. Also the number of the real atom simulated is extended to 36 in each layer, and the periodic boundary condition is
added to produce an infinite surface plane. This model is applied to interactions of Ar with Pt(111), leading to quantitative agreement with experimental data performed by a molecular beam method.

**PHANTOM PARTICLE MODEL**

The molecular dynamics method gives the fundamental properties on an interaction between a gas atom and a solid surface. A small part of a surface area is simulated in detail, where each real atom connects with one Phantom Particle. The Phantom Particles represent the other lattice atoms except some real atoms and act as a heat bath for real atoms without control of the surface temperature using the velocity scaling method. Figure 1 shows a schematic illustration of the Phantom Particle model in the present study. While each real atom interacts with a Phantom Particle and only 12 adjacent real atoms, Phantom Particles have no interactions with each other. In the present model, the trajectories of real surface atoms are calculated according to Newton's equation of motion while Phantom Particles follow the generalized Langevin equation including the harmonic, damping, and fluctuating force terms. The small part simulated in detail consists of three layers each of which 6x6 real atoms are placed in. The periodic boundary condition, however, extends the simulation area to the infinite surface.

![Figure 1. Schematic illustration of Phantom Particle Model](image)

Adelman and Doll(2) had led to the generalized Langevin equation including a harmonic oscillation for the gas-surface interaction, and then Tully(3) had extended the method to full three-dimensional motion for an fcc and bcc lattices. They indicated that the Phantom Particles act as the heat bath and that the properties of the bulk lattice can be reproduced. Tully(3) also illustrated characteristics of the surface from the Fourier spectra of autocorrelation of velocities of real atoms and examined an accommodation coefficient and trapping probabilities of xenon or argon molecules on the Pt(111) surface through the Phantom Particle model. Blömer and Beylich(4) combined this model with the molecular dynamics method to show the response to a change in the preset temperature and the change of the rotational temperature during gas-surface interaction. However Tully(3), and Blömer and Beylich(4) have neither applied this method to the simulation of gas-surface interaction in the same condition as the molecular beam experiments nor demonstrated the flux distribution or TOF spectra of the scattered molecules.

Before any calculations of gas-surface interaction, the validity of the Phantom Particle model as a solid surface was confirmed through the power spectra of the three directions, the response to change of a preset temperature and the velocity distribution in each layer, as already shown by Blömer and Beylich(4). In addition, the specific heat is examined originally by comparing with the Debye model in the present study. Figure 2 shows a dependence of the specific heat on the preset temperature, where the circle shows the specific heat calculated by the Phantom Particle model and the solid line that expected by the Debye model. In Fig. 2 it is found the calculation results agree with that expected by the Debye model in the range of temperature higher than the Debye temperature $\Theta_D$. This means that the Phantom Particle model gives the specific heat of $3Nk_B$, showing effectiveness in the range of temperature larger than $\Theta_D$. 

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The Phantom Particle model is applied to simulations of interaction of an Ar molecular beam with a Pt(111) surface. To verify its propriety from comparison of the simulation results with the experimental ones, in the simulation we use the same conditions as the experiment by Hurst et al. For example, the incident angle of Ar molecular beam is set at $\theta_i = 45$ degrees from the surface normal and temperature beam at 1.4 K, assuming the Maxwellian velocity distribution. Each trajectory of the argon molecule is continued to 50,000 time steps or until the argon molecule escapes from the Pt surface by $4r_0$, where $r_0$ is the distance to the potential well of the Lennard-Jones potential between the argon molecule and Pt atom. This cutoff distance $4r_0$ is determined from the calculation result of the total, kinetic and potential energies as shown in Figs. 4. The kinetic energy coincides with the total energy within 0.4% at the $4r_0$ from the surface. If the total energy of the argon molecule near the surface becomes less than $-2k_BT_s$, it is regarded as a trapping molecule and removed from the calculation. After calculation of each trajectory, the Pt surface is reset to the initial condition. For each combination of the incident energy and surface temperature, 50,000 trajectories are simulated.

**FIGURE 2.** Specific heat $C$ of the surface
**FIGURE 3.** Simulation space

**FIGURE 4.** Histories of the distance of Ar from the surface and three kinds of energy
SIMULATION RESULTS AND DISCUSSION

Flux Distribution

Figures 5 are the flux distributions of argon molecules scattered from the Pt(111) surface at the surface temperature $T_s = 250$ and 705 K, respectively. In Figs. 5 the abscissas are the reflection angle measured from the surface normal, the circles show the calculated distribution and the squares the experimental data by Hurst et al. (5) We can see from Figs. 5 that the peak of the distribution shifts toward the surface normal (toward the smaller reflection angle) and the width of the distribution becomes wider with an increase in the surface temperature. Also it is evident that the calculated flux distributions agree well quantitatively with the experimental data.

TOF Spectra

Figures 6 show the TOF spectra of argon molecules scattered at the specular angle from Pt(111) surface whose temperatures are set at $T_s = 250$ and 705 K, respectively. The abscissa of each figure means the arrival time normalized by the flight path divided by the mean velocity of the incident molecular beam. The solid curve shows the calculated spectrum and the broken curve the experimental one determined by Hurst et al. (5) In Figs. 6 we can see the peak of the spectra shifts toward shorter flight time with an increase in the surface temperature. The calculated spectrum agrees with the experimental one except slight difference between the peak positions. We calculate the experimental TOF spectrum of the scattered molecules assuming the Maxwellian distribution using the data of the macroscopic velocity and temperature given by Hurst et al. This means that the experimental velocity distribution shows only the direct scattering process of the molecules. In general, it is pointed out that the velocity distribution of the scattered molecules consists of the direct scattering process with the macroscopic velocity and the adsorption and desorption process without that. Therefore, the slight difference of the peak positions might be due to no consideration of the adsorption and desorption process for data by Hurst et al. We believe that the Phantom Particle model is very effective to predict the TOF spectra of the molecules scattered from the surface, especially the width of the spectra and change of the peak position depending on surface temperature.
Average Energy Distribution

Using the TOF spectra, one can calculate the average energies $\langle E_r \rangle$ of the scattered molecules normalized by the energy $E_i$ of the incident beam, as shown in Figs. 7. The abscissas in Figs. 7 are the reflection angle measured from the surface normal. In Figs. 7 the average energies show the tendency of the inelastic scattering explained by the hard-cube model at angles larger than 30 degrees where the calculated distribution is close to the experimental one by Hurst et al. At the small angles, however, the former deviates from the latter. This might be attributed to the statistical error, that is, the insufficient number of the scattered argon molecules as shown in Figs. 5.
Energy Exchange Rate

The energy exchange rates are examined separately for the normal and a tangential energy. The energy exchange rate of the normal energy is calculated from \( \frac{\langle E_r \rangle - \langle E_i \rangle}{\langle E_i \rangle} = \frac{\langle E_r \cos^2 \theta_r \rangle - \langle E_i \cos^2 \theta_i \rangle}{\langle E_i \cos^2 \theta_i \rangle} \) and that of the tangential energy \( \frac{\langle E_r \rangle - \langle E_i \rangle}{\langle E_i \rangle} = \frac{\langle E_r \sin^2 \theta_r \rangle - \langle E_i \sin^2 \theta_i \rangle}{\langle E_i \sin^2 \theta_i \rangle} \), where \( E_r \) and \( E_i \) are the kinetic energies of the incident and scattered molecule, respectively, and \( \langle \cdot \rangle \) means the average. Figures 8 show the energy exchange rate of the normal and tangential energy, calculated for several incident energies. In Figs. 8, the abscissa is the incident energy and the solid circles are the simulation results at \( \theta_i = 45 \) degrees and \( T_s = 250 \) K. The solid curve means the energy exchange rate for full accommodation of the Ar molecules to the Pt surface and the broken line means \( E = 2k_B T_s \) which equals to the average energy of the scattered molecules fully accommodated to the solid surface at \( T_s \). In the case of \( E = 2k_B T_s \), of course, the energy exchange rate equals zero theoretically.

It is clear from Figs. 8 that the energy exchange rates for the normal and tangential energy are very different. The normal energy indicates the similar tendency to full accommodation, whereas the tangential energy remains constant over the wide range of the incident energy. This means that the energy exchange of the gas molecules with the solid surface is dominated by the exchange of the normal energy, showing the same tendency as the previous studies for relatively low incident energy, i.e., the thermal scattering regime.

![Figure 8](image_url)

**FIGURE 8.** Exchange rates of (a) normal energy and (b) tangential one of Ar molecules.

Trapping probability

Figures 9 show the rates of the Ar molecules trapped on the Pt surface for several incident energies at \( \theta_i = 30, 45, 60 \) degrees, which are simulated by the use of the present model. With increasing the incident energy and decreasing the incident angle, as shown in Fig. 9(a), the trapping probability decreases as reported in many papers. Especially, these results also agree well with the experimental data obtained by Mullins et al.(6) If the trapping probability is dominated only by the normal energy, it scales with \( E \cos^2 \theta \), and the power of cosine decreases with an increase in contribution of the tangential energy to the trapping probability. The simulated data can scale with \( E \cos^2 \theta \), rather than with \( E \cos^{0.5} \theta \) given by Mullins et al. We think that this scaling of our data agrees with the experimental one reasonably, because the detection of all molecules scattered from the solid surface or all molecules adsorbed to that is very difficult and the experimental data may include some error.
The Phantom Particle model was applied to simulations for interaction of an Ar molecular beam with a Pt(111) surface. The validity of the Phantom Particle model as a solid surface was clarified by comparing the simulation results with the experimental ones, in which the same conditions as the experiments were used. As a result, we obtained the good results as follows.

1. The calculated flux distributions agreed well quantitatively with the experimental data in the wide range of the reflection angle.
2. The TOF spectra at the specular angle, especially the width of the spectra and change of the peak position depending on surface temperature, could be predicted by the use of the present model.
3. The calculated average energy was close to the experimental one at the reflection angle larger than 30 degrees whereas at the small angles the former deviates from the latter.
4. The calculated trapping probabilities agreed with the experimental ones except the calculated results could scale with $E_i \cos^{0.7} \theta$ rather than with $E_i \cos^{0.5} \theta$ given by Mullins et al.

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