Multi-Scale Analysis for Rarefied Gas Flows

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Abstract. A practical method for solving the nonequilibrium rarefied gas flows is introduced in this paper. This method based on the multi-scale analysis connects the thermofluid phenomena that occur in the different time scale and spatial scale by constructing the reasonable physical model among them. As an example of the analysis, the molecular collision of silane gas, which is widely used in the semiconductor manufacturing process, is considered here. First, the new intermolecular potential model is determined from the accurate \textit{ab initio} molecular orbital (MO) calculations. Next, the collision models such as the collision cross section and the scattering angle are constructed by the statistical analysis of classical trajectory (CT) calculations using the new potential model. Finally, these collision models are applied into the direct simulation Monte Carlo (DSMC) calculation. In this way, this multi-scale model does not require the empirical parameters such as the transport coefficients and is widely applicable to the various rarefied gas flows including the nonequilibrium flow.

INTRODUCTION

Recently much attention has been paid to the particle simulation such as the DSMC method [1] in order to analyze the very complex flow field like the semiconductor manufacturing processes. These processes are usually executed under the very low pressure condition and the highly nonequilibrium rarefied flow field is achieved. Besides, the slight difference of molecular collisions has the large influence on the eventual thin film properties because of the high Knudsen number. In these numerical simulations mentioned above, the several collision models are necessary for calculating the collision cross section, the scattering angle, the internal energy transition probability and so on. These models of micro scale phenomena usually have the empirical parameters that are decided from the macro scale properties such as viscosity, diffusivity and thermal conductivity. Thus, it is doubtful whether these models can be applied to all the conditions of flow filed. In addition to this, there are a lot of atoms and molecules about which no reliable data of macro scale properties are known. Obviously the accurate numerical simulation is impossible in such a condition.

In this study, the practical methodology based on the multi-scale analysis is introduced in order to establish the general procedure for rarefied gas flows. The schematic of the method is shown in Fig.1. In the high vacuum silicon process a large amount of molecular collisions form the distribution of temperature and number density in the reactor. The molecular collisions are determined by the interactions among electrons and nucleus. Therefore the intermolecular potential energy among them is determined if the Schrödinger wave equations of the electrons and the nucleus are solved. And the collision models are obtained when the motion of atoms and molecules are calculated by the intermolecular potential energy. Finally the thermofluid structure is obtained by applying the collision models to the particle simulation like the DSMC method. In this manner the macro-scale phenomena are related to the micro-scale structures without empirical parameters. In this paper, as an example of the multi-scale modeling, we focus the LPCVD process using SiH$_4$ molecules and deal with the interaction of SiH$_4$-SiH$_4$ pairs.
The first step for multi-scale modeling is the construction of the intermolecular potential model. There are a few intermolecular potential models for SiH₄ but all of them are isotropic models that cannot reproduce molecular rotation or anisotropy of chemical reaction. Therefore pair potential model is developed in this study. The accurate \textit{ab initio} MO calculations with the CPC correction [2] are used to calculate the potential energy as a function of relative orientation and Si-Si distance between SiH₄ dimer. The calculated intermolecular energies are used in order to develop an analytical potential model.

The MO calculations are done at MP2/Aug-cc-pVTZ set, which is chosen after confirming that we can obtain the almost same result as higher level theory and larger basis set. The various orientations and the distances of SiH₄ dimer must be considered to express the anisotropy as in ref. [3]. The total number of calculation points is 162 (18 different distances for each 9 orientation). The calculated energy is divided into the two physical parts, that is the repulsion term and the dispersion term in order to remove the mathematical difficulty when determining the parameters of the potential model by the least square fitting. In this study we assume that the HF calculations only include the repulsion term and that the difference between MP2 and HF calculations express the dispersion term.

First, we will develop the analytical model for the repulsion term. There are 16 H-H, 8 Si-H and 1 Si-Si interaction and the simultaneous least square fitting to decide H-H, Si-H and Si-Si potential parameters is executed for the various analytical potential models. After trying the several models like $r^n$, $\exp(ar)$, it turned out that the modified exponential function was the best to describe SiH₄-SiH₄ repulsion term. The actual form is expressed as below.

$$
E^{rep} = \begin{cases} 
  c_0 \exp\left(-c_1\left(r/r'\right)^n\right) & \text{for Si-Si} \\
  c_0 \exp\left(-c_1\left(r/r'\right)^3\right) & \text{for Si-H, H-H} 
\end{cases}
$$

Equation 1 means that the potential function is different between Si-Si and others. The comparison between this model and the MO calculations for the various orientations is shown in Fig.2. It shows the good agreement among them and the standard deviation was 9.2% even if the potential energy is considered up to 1eV. This value seems accurate enough to apply the practical problem. Next, the analytical model for the dispersion term is determined in the same way. There is the theoretical formula known as the London’s formula to describe the dispersion term.

\textbf{FIGURE 1.} Concept of multi-scale analysis for rarefied gas flows.
based on the dipole interaction. It is expressed as the expansion into power series of the distance. Though only the first term of $r^{-6}$ is usually considered, it turned out to be inadequate in this case. And the expansion up to the second term is needed in order to improve the accuracy as shown in Eq. 2.

$$E^{\text{disp}} = c_2 \left( \frac{r'}{r} \right)^6 + c_3 \left( \frac{r'}{r} \right)^8$$  \hspace{1cm} (2)

Figure 2 also shows the comparison of dispersion term between Eq. 2 and the MO calculations. The good agreement is achieved and the standard deviation was only 8.1% by including the second term of the London’s formula. The final form of the analytical intermolecular potential model of SiH₄ is obtained by the sum of the repulsion and the dispersion terms. Each coefficient is listed in Table 1 and the potential curves are indicated in Fig. 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Si–Si</th>
<th>Si–H</th>
<th>H–H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r'$ [Å]</td>
<td>4.560</td>
<td>3.232</td>
<td>2.638</td>
</tr>
<tr>
<td>$c_0$ [$\times 10^{19}$ J]</td>
<td>240.9</td>
<td>1.527</td>
<td>1.743</td>
</tr>
<tr>
<td>$c_1$ [-]</td>
<td>8.868</td>
<td>4.436</td>
<td>5.645</td>
</tr>
<tr>
<td>$c_2$ [$\times 10^{-21}$ J]</td>
<td>−4.557</td>
<td>−2.473</td>
<td>−0.7568</td>
</tr>
</tbody>
</table>
The problem that we must consider next is whether this model is appropriate to reproduce the real physical phenomena. Therefore we tried to evaluate the viscosity of SiH$_4$ numerically by the equilibrium MD simulations. 216 SiH$_4$ molecules are set into a calculation region with periodic boundary condition and the calculation volume is adjusted to reproduce the atmospheric pressure. The new potential model for SiH$_4$ molecules is applied and the vibrational motion is neglected. The leap-frog algorithm is used for the time integration of the Newton’s equation. The calculation time step is 2.0 fs and the number of integration step is $5.0 \times 10^7$. 5 runs are executed in total for the different temperature from 200K to 300K. The Green-Kubo formula is applied as shown in Eq.3 in order to calculate the viscosity from the result of the MD calculations [4].

$$\eta = \frac{1}{kT} \int_0^{\infty} \langle J_{zz}(t) \cdot J_{zz}(0) \rangle dt$$

where

$$J_{zz}(t) = \sum_{j=1}^{N} m v_{x_j}(t) v_{z_j}(t) + \sum_{i=1}^{N} \sum_{j=1}^{N} \left\{ z_i(t) - z_j(t) \right\} F_{x_j}(t)$$

This formula relates the transport coefficient to the time integral of the time dependent correlation function. Figure 4 shows the comparison of viscosity from the MD simulations and the empirical formula derived from experiments [5]. The error bars plotted in Fig.4 are mainly caused by the small amount of the averaging events for the correlation function. The longer time step must be required to improve the accuracy. However, the very good agreement can be obtained between the result of the MD simulation and the empirical formula.

**MOLECULAR COLLISION MODEL**

The second step of the multi-scale modeling is to develop the molecular collision model. It was observed in the preceding chapter that the new analytical potential model of SiH$_4$ was successfully developed. Therefore the motion of molecules can be simulated using the model. Since the actual silicon process is executed about 1000K, molecules can be assumed as rigid rotors and the vibration is neglected. In addition to it, almost all the collisions are binary one in the low pressure reactor. Hence it is reasonable to use the CT calculation in order to develop the collision model in this case because the CT calculation provides the exact solutions for the molecular collision problems within the assumption of classical mechanics [6]. In this chapter a large number of collisions of SiH$_4$ pair are...
calculated for various energy, impact parameter and initial phase and through the statistical analysis the total cross section model and scattering angle model are constructed as the similar way in ref. [7], [8].

Figure 5 shows the schematic diagram of the CT calculation of SiH₄. The collision pair is set at the appropriate position so that the initial potential energy is small enough. Again the leap-frog algorithm is used for the time integration of the Newton’s equation. One trajectory calculation is continued until the collision pair separates each other to the same distance as the initial condition. This calculation is repeated for 10,000 times per one translational energy while randomly changing the initial phase, the direction of the rotational vector, the impact parameter and the rotational energy from 0.0eV to 0.35eV. The initial relative translational energy \( E_{tr} \) is varied from 0.0075eV to 0.4eV.

Figure 6 shows the relation between the scattering angle \( \chi \) and the impact parameter \( b \) for \( E_{tr} = 0.025\text{eV}, 0.25\text{eV} \). From this figure it turns out that the scattering angle \( \chi \) is close to \( \pi \) because of the strong repulsion force when the impact parameter \( b \) is very small. As the impact parameter \( b \) becomes larger, the scattering angle \( \chi \) decreases gradually and becomes negative by the attractive force. But finally the molecules do not interact each other when the impact parameter \( b \) becomes large enough. Now, we must define the largest impact parameter \( b_{max} \) by the particular threshold of the scattering angle \( \chi \) for calculating the total cross section since the collisions are treated as the classical mechanics. In this study the threshold is determined as the scattering angle \( \chi = 1^\circ \). This means that the molecules colliding with the smaller impact parameter \( b \) than \( b_{max} \) are defined as "collision molecules" and others are considered as "no-collision molecules". Thus the total cross section \( \sigma_T \) is calculated as

\[
\sigma_T = \pi b_{max}^2
\]
Equation 4 is calculated for the various $E_{tr}$ and the result is shown in Fig. 7. From this figure it is clear that the total cross section $\sigma_T$ decreases as translational energy $E_{tr}$ increases. Since this is the similar result with the Chapman-Enskog theory [9], we consider the same relational expression with this theory as the total cross section model of SiH$_4$. That is to say the model is expressed as

$$\sigma_T = \sigma_{T,0} \left( \frac{E_{tr}}{E_{tr,0}} \right)^\omega \quad \omega = -0.33$$

where the parameter $\omega$ is decided from the least square fitting.

Next we consider the scattering angle model for SiH$_4$. There is the analytical exact solution of the scattering angle for the spherically symmetric molecules [10] as

$$\kappa^{ib} = \pi - 2 \int_0^{W_a} \left\{ 1 - W^2 - \frac{E_{pot}}{E_{tr}} \right\}^{-\frac{1}{2}} dW$$

$$W = b/r, \quad W_a = \left( 1 - \frac{E_{pot}}{E_{tr}} \right)^{1/2}$$

Figure 7. Total cross section model as function of relative translational energy.

Figure 8. Comparison of differential cross section between CT calculation and the new model. Left: $E_{tr}=0.025$ eV, right: $E_{tr}=0.25$ eV.
And this is shown in Fig.6 as the curved line. There is the close relationship between the theory and the scattering angle by the trajectory calculations when the impact parameter \( b \) is smaller than \( b_r \), which gives the rainbow scattering. And they agree very well for the larger impact parameter \( b \) than \( b_r \). If we suppose that the scattering angle is expressed as

\[
\chi = \chi^\text{th} + \Delta \chi
\]  

(7)

The next step is to evaluate the \( \Delta \chi \) that means the deviation between the theoretical solution and each trajectory. Considering that the initial phase is given randomly and that the spherically symmetric molecule is the geometrical mean of the anisotropic polyatomic molecules, \( \Delta \chi \) can be regarded as the deviation from the average. Therefore it may be assumed that \( \Delta \chi \) obeys a normal distribution. The probability distribution of \( \Delta \chi \) is examined for each small division of impact parameter \( b \) and this assumption is reasonable for almost all the impact parameter \( b \). Therefore the scattering angle model can be described as

\[
\Delta \chi = \begin{cases} \sqrt{2/\pi}S^2 \exp\left(-\Delta \chi^2 / 2S^2\right) & \cdots b < b_r, \\
0 & \cdots b \geq b_r, \end{cases}
\]  

(8)

Equation 7 and Eq.8 mean that the scattering angle \( \chi \) is the sum of the theoretical angle of the spherically symmetric molecules and the deviation from it. And the deviation is given by the statistical manner using the uniformly random numbers. Finally the validity of the total cross section model and the scattering angle model is confirmed by calculating the differential cross section. The result is shown in Fig.8 and the good agreement is obtained between the trajectory calculation and the simulation result of the collision model. Here, we have seen that the new collision models as to the total cross section and the scattering angle are constructed and that they can reproduce the result of CT calculations.

**DSMC CALCULATION**

Now we can calculate the simple collision problem of SiH\(_4\) by applying the newly constructed collision model into the DSMC method. Usually several models are needed in the DSMC method. For example, the NTC method, the Null-collision method and the maximum collision number method are used to determine the number of collisions. The VHS or the VSS model are used for calculating the total cross section and the scattering angle, and the Larsen-Borgnakke model for the internal energy transfer, and so on. In this chapter, the new models are applied instead of the VHS or the VSS model and the validity is confirmed.

As one example of calculation the translational relaxation is calculated. 100,000 particles of SiH\(_4\) molecules at 300K and the same number of particles at 1,000K are put into a single cell initially. The maximum collision number method and the Larsen-Borgnakke model with the constant relaxation collision number are used. The particles are allowed to undergo several million collisions, after which the thermal equilibrium is achieved. Figure 9 shows the translational relaxation process as a function of time. This figure indicates that the reasonable result of the equilibrium temperature at 650K is obtained successfully without any unnatural fluctuation. And there is no increase or decrease of momentum of the system. Then the distribution functions for the molecular speed are investigated as shown in Fig.9. It is clear that both the distribution for the particles of 300K and 1000K undergo the transition into the Maxwell-Boltzmann distribution of 650K from this result. It follows that the new collision models can reproduce the collision process and that they are very effective in the DSMC method.
It is concluded, from what has been discussed above, that the multi-scale analysis is an effective method for the rarefied gas flows. In this study the site-to-site intermolecular potential model for SiH₄ was constructed at first. Next, the total cross section model and the scattering angle model were developed using the CT method with the new analytical potential. Finally, these models were incorporated into the DSMC method and the equilibrium distribution of molecular speed was reproduced. The advantage of this methodology is that we need almost no arbitral parameter and that this can be used widely including the chemical reaction in gas phase and the surface reactions.

REFERENCES