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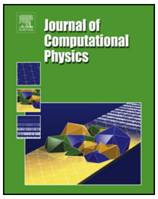

Development of EEM based silicon–water and silica–water wall potentials for non-reactive molecular dynamics simulations

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ABSTRACT

Molecular dynamics simulations of heat transfer in gases are computationally expensive when the wall molecules are explicitly modeled. To save computational time, an implicit boundary function is often used. Steele's potential has been used in studies of fluid–solid interface for a long time. In this work, the conceptual idea of Steele's potential was extended in order to simulate water–silicon and water–silica interfaces. A new wall potential model is developed by using the electronegativity-equalization method (EEM), a ReaxFF empirical force field and a non-reactive molecular dynamics package PumMa. Contact angle simulations were performed in order to validate the wall potential model. Contact angle simulations with the resulting tabulated wall potentials gave a silicon–water contact angle of 129°, a quartz–water contact angle of 0°, and a cristobalite–water contact angle of 40°, which are in reasonable agreement with experimental values.

1. Introduction

Since the invention of the integrated circuit in 1958, there has been a rapid development in the semiconductor industry. According to Moore's law, the number of transistors on integrated circuits doubles approximately every 18 months [1]. The industry's projection for the future is that the trend will continue because of the massively developing needs from the smartphone and tablet markets.

Understanding the transport phenomena in micro- and nanoscale systems is essential in the semiconductor industry as the devices are becoming increasingly smaller. However, in micro- and nanoscale systems, flow and transport properties of gases can no longer be described sufficiently by conventional continuum dynamics. These limits of continuum models can be overcome by using particle-based methods such as molecular dynamics (MD) [2,3], and the direct simulation Monte Carlo (DSMC) method [4–6].

Especially, MD can be used to investigate the influence of the gas–surface interaction in more detail, because this technique allows the walls to be modeled explicitly with an interaction potential. Explicit walls are expected to give the best results, but at the price of high computational costs. Since several layers in the wall need to be simulated, the number of particles in the wall may be larger than the number of particles in the fluid. Therefore, the majority of the computation effort is expended for the simulation of the wall particles.

Because of this, the solid wall is sometimes replaced by an implicit boundary condition. Different types of boundary conditions have been suggested over the years; examples include the reflective and thermal walls [7]. The reflective wall

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reverts the particle when it hits the wall, whereas the thermal wall introduces a stochastic force on a particle when it strikes the wall, giving the particle a new velocity sampled from a Maxwellian distribution. A more complex gas–surface interaction model, based on Cercignani–Lampis model [8], is also available.

A major drawback of these models is that they do not supply any information about the underlying configuration of the solid wall. They also neglect the gas–surface force interaction effects which can be significant in nano-channel flows. To be able to include such information, the boundary condition has to be derived from the solid's point of view. In their pioneering work, Lennard-Jones and Devonshire derived such relations for several types of crystals [9]. Subsequently, Hove and Krumhansl [10], and Steele [11] used these relations to derive potentials which describe the interaction between a gas molecule and a solid wall. Crucial in these derivations are the lattice sums using Fourier series to arrive at the proposed potential. Based on this work, Abraham [13] proposed four types of wall potentials: the Lennard-Jones wall as given by Steele, the Lennard-Jones (10-4) wall, a Boltzmann weighted wall and a reflective wall. Both Steele and 10-4 wall potentials have been used extensively over the years. For instance, Steele's potential has been used in studies on the solvent forces of dense fluids or on the dynamics of liquid filled pores and the 10-4 potential has been used in work on the solid–fluid interface, the flow in micropores, and in work on the velocity auto-correlation function of confined fluids [14–16].

Recently, further progresses have been reported in this field of wall potentials [17,18]. Spijker et al. [17] suggested a wall potential model which can be used for SC, FCC, and BCC type of solid wall crystal structure. Siderius et al. [18] suggested a model that can describe cylindrical, spherical, and other pore geometries. Unfortunately all Steele, Spijker and Siderius' studies are limited to van der Waals force interaction between an electrically neutral surface and argon molecules (Lennard-Jones potential). In semiconductor industry, one of the most common gas–surface interactions is the water–silicon interaction. And in many cases a silicon surface is filmed with silica: a thin layer of silicon dioxide forms naturally on the surface when silicon is exposed to the ambient air. To describe the water–silicon and water–silica interactions, it is necessary to develop a new wall model, which includes charge interaction, sophisticated crystal structure, and a more sophisticated potential than the Lennard-Jones potential.

The objective of this paper is to take the concept of the wall potential and to present a new method to develop a tabulated potential model [19] that can describe the interaction between water (a multi-atomic molecule) and silicon/silica (a multi-atomic solid wall) for non-reactive MD. By using the electronegativity-equalization method (EEM) [20] and the reactive empirical force field (ReaxFF) [21–23], we are able to develop a pairwise interaction potential between a water atom (oxygen, hydrogen) and a solid wall including charge interactions.

2. Tabulation process

Our study starts from the concept of Steele's potential. Steele showed that the total energy of an isolated gas atom interacting with the atoms in a crystalline solid of a given lattice symmetry can be decomposed as a Fourier series in the position variables in the plane parallel to the surface under the assumption of pairwise additivity and inverse power–law interaction [11].

In a similar concept, under the assumption of pairwise additivity, we numerically integrate the forces acting between an isolated gas atom and the atoms in a crystalline solid. We include a charge interaction in our model, which is omitted in most other conventional wall potential models.

It is important to have the right atomic charges to enhance physical realism of MD because atomic charges in molecules contribute most of the characteristic chemical properties [24]. In our model, the electronegativity-equalization method (EEM) is used to calculate the charge distribution of water atoms and silicon or silica atoms for different configurations. EEM will be used to derive a tabulated wall potential. Fig. 1 shows an overview of the tabulation process. A more detailed description for each process is shown in the next sections.

2.1. Crystal structure

In order to develop the wall potential for silicon and silica (silicon dioxide), we first need to find the crystal structure of each wall. Many solids have a specific crystal structure, for example a simple cubic (SC), face centered cubic (FCC) or body centered cubic (BCC). Silicon crystallizes in the same pattern as diamond, in a structure Ashcroft and Mermin called "two interpenetrating face-centered cubic" structure [25] (Fig. 2, left). The cube side for silicon unit cell is 0.543 nm. The angle between a and b is 90° and c is perpendicular to the other two.

Unlike silicon, silica does not have a specific crystal structure. We have chosen the most basic silica crystal structures for this study, which are the α-quartz model and the α-cristobalite model. The α-quartz wall is modeled using a silica slab that consists of $5 \times 5 \times 2$ unit cells of α-quartz. The lattice constant of one unit cell of α-quartz are chosen from the study of Will et al. [26] (Fig. 2, center), in which a and b are 0.491239 nm and c is 0.540385 nm. The angle between a and b is 120° and c is perpendicular to the other two.

The α-cristobalite was studied in order to investigate fused silica and the function of siloxane group. The α-cristobalite plate was modeled based on the work of Downs et al. [27] (Fig. 2, right). The a and b values are 0.49717 nm and c value is 0.69223 nm. The angle between a and b is 90° and c is perpendicular to the other two.

With these crystal structures, a wall is formed of several layers with the $(1, 0, 0)$-plane facing the fluid. The molecular structure of a silicon wall consists of 400 atoms as shown in Fig. 2. The molecular structure for α-quartz consists of 432