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CHARACTERIZATION OF SCATTERING AND CONDENSATION PROCESS OF GASEOUS METHANE AT THE QUARTZ INTERFACE AND LIQUID METHANE INTERFACE

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KEY WORDS

Evaporation condensation coefficient, accommodation coefficient, molecular dynamics, boundary conditions, vapor liquid interphase

ABSTRACT

Flows and heat transfers in micro-nano conducts are subject to significant interphase phenomena linked to molecular interaction in the vicinity of the wall. In the literature, both experiments and simulations revealed evidence of an enhancement of flow-rate, originated from slip velocity at the solid boundary, due to collisions between gas atoms and the solid wall. Accommodation coefficient and condensation/evaporation coefficients are used to express these velocity boundary conditions. In this work, we have developed a kinetic boundary condition model by a statistical learning study from the incident and reflected velocities of the gas molecules (methane) on the solid wall (quartz), collected from molecular dynamics simulations, using a Lennard Jones potential for methane molecules and a Buckingham potential for quartz. We first obtained the density profiles of the methane gas/liquid at the quartz surface as well as the residence time and the penetration depth of CH₄ in the quartz substrate. The value of the saturated vapor density obtained is in excellent agreement with those of the literature. Finally, we have determined the accommodation and condensation/evaporation coefficients.

Introduction

The objective of the present work is to use Molecular Dynamics (MD) simulations to determine more accurately the scattering behavior of vapor at a solid or liquid interphase by including both mass and other accommodation coefficients for momentum and energy. This scattering model serves as a boundary for kinetic and continuum transport equations. To this end, the velocity, displacement and resident time of atoms are tracked and collected as data, which are then analyzed with standard learning methods. Specifically, the accommodation coefficients are determined via correlation analysis [1].

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Material and method

The models are composed of quartz (SiO₂) substrate and methane (CH₄) periodic in x, y directions. The geometric parameters of SiO₂ crystal are as follows: $a = b = 4.9137\text{\AA}$, $c = 5.4047\text{\AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ [2]. The solid rectangular substrate has dimensions $8a \times 9\sqrt{3}b/2 \times 4c$ and 864 Si atoms and 1728 O atoms. (see Fig. 1). The dimensions of the simulation box along x, y are equal to the corresponding dimensions of the silica substrate while the dimension along z is larger and varied so that we can fill with methane molecules. The Burckingham (BKS) force field [3] is used to describe the interaction between the Si and O quartz atoms

$$V_{ij}^{BKS} = C \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-b_{ij} r_{ij}) - \frac{c_{ij}}{r_{ij}^6} \quad (1)$$

and the Lennard-Jones (LJ) potential is used to describe the van der Waals interaction between CH₄ molecules, via TraPPE force field [4]

$$V_{ij}^{LJ} = \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2)$$

and between a CH₄ molecule and Si and O of solid quartz via Lorentz–Berthelot mixing rule from CLAYFF force field [5]. The good performance of the united atom model has been shown in literature. In Eq.(1, 2), r_{ij} is the distance between two atoms i and j of charges q_i and q_j . The constants A_{ij} , b_{ij} , c_{ij} are the parameters of BKS potential and ϵ_{ij} and σ_{ij} the parameters of LJ potential and C the energy conversion constant for the Coulombic term. The silica substrate is composed of one fixed lower layer and two upper layers maintained at temperature T_w by NVT thermostat. The other boundary of the simulation box is an elastic reflected wall. A suitable number of CH₄ molecules, N , is placed between the solid surface and the reflected wall so that after equilibration process at T_w , CH₄ is accumulated into a liquid film on the silica surface and diluted in the remaining space. The choice of temperature T_w is also important to guarantee the two phases coexist and the gas phase is sufficiently dilute. In all simulations, $T_w = 110\text{K}$, which is slightly above the triple point $T_{tp} = 90\text{K}$. In reduced LJ unit, we have $T^* = k_B T_w / \epsilon_{CH_4} = 0.7432$, where k_B is the Boltzmann's constant.

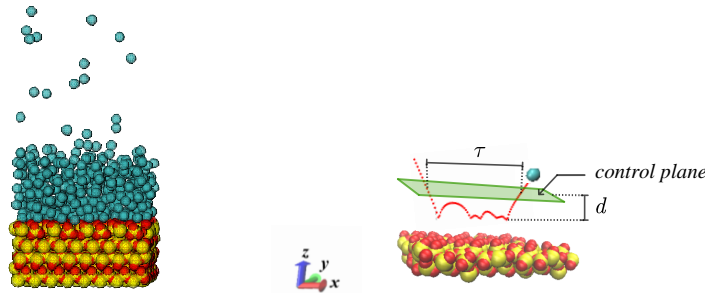


Figure 1: Left: Snapshot of MD system. Color code: blue for methane molecules (CH₄), red for oxygen atom (O) and yellow for silicon atom (Si). Right: illustration of penetration depth d and resident time τ .

The open source MD code LAMMPS [6] is used for all the simulations. Additional tools are developed to track the atom motions. The latter is placed at distance $\delta = 20\text{\AA}$ from the liquid-vapor interface.

Specifically, when atoms cross the control plane, we are interested in the following quantities: the incoming velocity c^{in} and the outgoing velocity c^{out} , the penetration depth d and the resident time τ between the incoming and outgoing events. Due to the small gas density, it requires 4×10^6 time steps of 0.0005 ps to reach equilibrium state and another 10^8 steps for outputting the data. Finally, we analyze the distribution of the data and construct the statistical based models for the liquid-vapor interface.

Simulation results

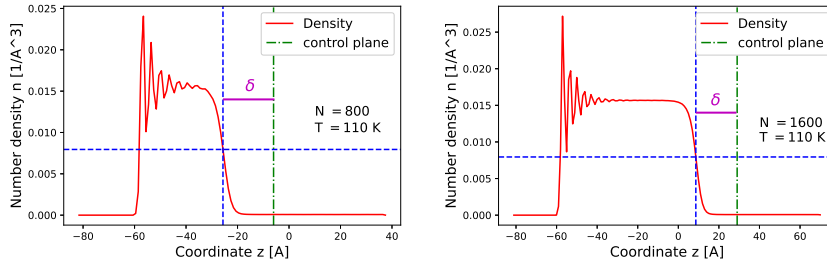


Figure 2: Density of the fluid across the system. The leftmost part of the profile corresponds to the silica wall and has zero density. The rightmost part corresponds to the small but non vanishing gas density.

The value of the saturated vapor density n_{sat}^v Fig. 2 can be obtained by fitting the density in the vapor phase with function

$$n(z) = a - b \tanh(2(z - c)/d) \Rightarrow n_{sat}^v = \lim_{z \rightarrow \infty} n(z) = a - b \quad (3)$$

In the case of a large volume of liquid and gas, $a = \frac{1}{2}(n_{sat}^{liq} + n_{sat}^v)$ and $b = \frac{1}{2}(n_{sat}^{liq} - n_{sat}^v)$, c the location of the interface and d the interface thickness [7]. In most simulations, the saturated vapor density is $n_{sat}^v \simeq 0.07 \times 10^{-3} \text{ \AA}^{-3}$ which corresponds to $n_{sat}^{v*} = n_{sat}^v \sigma_{CH_4}^3 = 0.0036$ at $T^* = 0.7432$. The value of n_{sat}^{v*} obtained is in excellent agreement with LJ fluid simulations also worth 0.0036 by [8]¹. The accommodation coefficient α and the condensation coefficient α_c (calculated as the fraction of condensing molecules N_c to all incident molecules N_{in}), from correlation analysis, associated to a quantity Q can be defined as follow:

$$\alpha_k = 1 - \rho(Q_k^{in}, Q_k^{out}), \quad \alpha_c = \frac{N_c}{N_{in}}, \quad (N_c = N_{in}), \quad k = x, y, z \quad (4)$$

where $\rho(Q_k^{in}, Q_k^{out})$ is the correlation coefficient between Q_k^{in} and Q_k^{out} . Assuming that the liquid surface is isotropic in the plane xOy , to improve the statistical signal, let us collect the two tangential velocity components c_x^{in} and c_y^{in} into one group c_{xy}^{in} and c_x^{out} and c_y^{out} into c_{xy}^{out} . Next we compute $\rho(c_{xy}^{in}, c_{xy}^{out})$ for a penetration depth $d < d_c$ where $d_c = \delta = 20 \text{ \AA}$, denoted shortly as

¹ Data available at <https://www.nist.gov/mml/csd/chemical-informatics-research-group/sat-tmmc-liquid-vapor-coexistence-properties-cut>

$$\rho_{xy}^d(d_c) = \rho_{c_{xy}^{in}, c_{xy}^{out}} |d > d_c \quad (5)$$

In Fig.3 are represented the distribution of the resident time and the penetration depth.

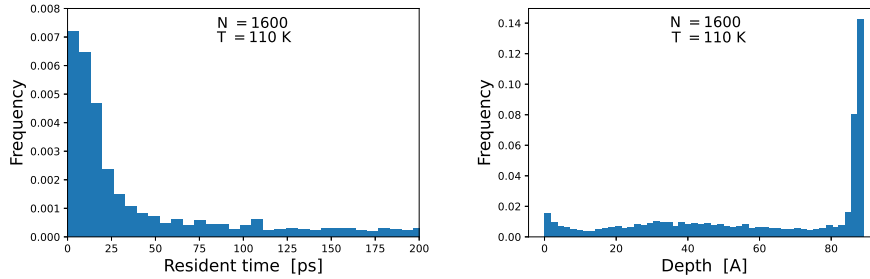


Figure 3: Left: Distribution of resident time. Right: distribution of penetration depth.

In Fig. 4, we find that the condensation and the tangential accommodation coefficients are not sensible to the choice of those parameters. The condensation coefficient lies in the range 0.87 – 0.89 and the accommodation coefficient 0.55 – 0.62. As $d_c = \delta = 20 \text{ \AA}$ has the physical meaning: atoms penetrating the liquid-vapor interface that we define previously, we shall adopt the criteria from now on.

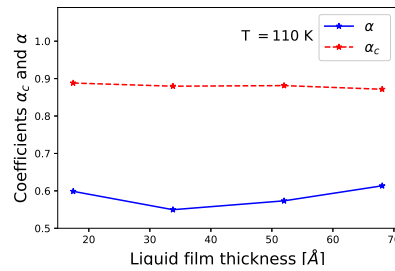


Figure 4: Variation of the tangential accommodation coefficient α and condensation coefficient α_c .

From Fig. 4, we find that the condensation coefficient decreases with increasing film thickness. Only when the film reach certain thickness, the coefficient start to stabilize and become constant. It is suggested the liquid layering has some impact on this coefficient as a large number of atoms are accumulated.

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