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# Effect of film thickness and temperature on condensation and momentum accommodation at the liquid-vapor methane interphase in contact with a quartz substrate

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## Abstract

In this paper, we used the Molecular Dynamics method to simulate the equilibrium vapor-liquid methane in contact with a solid quartz substrate and study the condensation process and momentum exchange at the atomic level. A large potential cutoff radius is used to determine the vapor and liquid densities at good accuracy. By tracking the motions of fluid molecules exchanged between the vapor and liquid phases and carrying out statistical analysis of residence time, penetration depth and especially velocity correlation, the mass and especially, the velocity accommodation coefficients can be determined at the same time. The latter is based on the assumption that the reflected events take place over a short time, near the interface and thus atoms velocities are correlated while the condensation/evaporation events are not. The calculated coefficients are sensitive to the film thickness due to the presence of the quartz substrate and the layering effects. As temperature increases, atoms condense less and reflect more and the reflection is more dif-

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fusive due to increasing collision rate. Near the critical temperature, both the condensation and momentum accommodation coefficients vary significantly.

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

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## 1. Introduction

Liquid vapor phase change processes are ubiquitous phenomena in nature and have numerous industrial applications including power generation, water processing and environmental control, etc. Thus, understanding those  
5 phenomena is very important in both theoretical and technological aspects. While the characters of liquid and vapor in distinct bulk phase can be well described by transport equations at the continuum scale like Navier Stokes and Fourier equations etc., the correct description of heat and mass exchanges  
10 at the interface and their evolution require the implementation of molecular level approaches. In this case, Molecular Dynamics (MD) is a powerful method that can provide access to the atomic picture of the process and this information can be used to construct macro and mesoscopic models. This is the main motivation of the present work.

In literature, the condensation and evaporation coefficients [1, 2] were introduced to characterize the mass exchange between the two phases. Simple  
15 definition of these coefficients can be done as following. The condensation coefficient is the ratio between the condensing flux and the total incoming flux of vapor into the liquid phase. The evaporation coefficient is the ratio between the spontaneous evaporation flux and the total outgoing flux of liquid  
20 into the vapor phase. Under equilibrium conditions, when the evaporation and condensations fluxes are equal between them, these coefficients are equal while when evaporation or condensation flux occurs in non-equilibrium conditions, they could be different. However, in most applications, those two coefficients are usually assumed to be identical.

25 First notable theoretical estimates of the evaporation and condensation  
mass flux based on principles of the kinetic theory and involving the evapora-  
tion/condensation coefficients have been derived, such as the Hertz-Knudsen  
[1, 3] and the Schrage expressions [4, 5]. Later, the improved expressions  
for the evaporation and condensation fluxes were derived from the moment  
30 method by Anisimov [6] and then Ytrehus [7]. However, all these expressions  
involved unknown evaporation/condensation coefficients. Large amount of  
the experimental data on these coefficients can be found in the literature.  
Unfortunately all these data are very scattered: for example the measured  
values of the evaporation coefficients of water differ, according to various  
35 sources, in four orders of magnitude [8]. This fact can be explained by many  
reasons as difficulties of such kind of measurements, validity of models used  
for extraction of the data on the evaporation/condensation coefficient from  
the measured quantities etc.

An another way to identify these coefficients is to simulated the evaporation-  
40 condensation process by the Molecular Dynamics method. Different ap-  
proaches based on MD simulations have been proposed. Most of them are  
based on the travelling distance of molecules from one phase to the other  
[9, 10], and on the residence time of the molecules [11] or on the energy [12].  
Physically speaking, condensing vapor molecules have tendency to penetrate  
45 deeper and stay longer in the liquid phase. Various studies have been done to  
investigate cases of large molecules [13, 14], the dependency of curvature [15]  
and the verification of theoretical formula by MD simulations [16, 17, 18].  
However, the liquid and vapor phases are usually considered as the bulk  
phase, which is not true for the early stage of the condensation process  
50 where both the very thin liquid film and the substrate can interplay. While  
momentum and energy accommodation coefficients play significant role in  
determination of velocity slip and temperature jump at the interface [19],  
they are neglected in the studies of vapor-liquid interphases.  
The objective of the present work is to use MD simulations to determine more

55 accurately the scattering behavior of vapor at the interphase by determining  
the evaporation/condensation coefficients as well as the tangential momen-  
tum accommodation coefficient. The latter is largely used in a scattering  
model that serves as boundary conditions at a gas solid surface interface for  
kinetic and continuum transport equations at rarefied conditions, i.e. the  
60 ratio between the molecular mean free path and the characteristic dimension  
of a problem is large. To this end, the velocity, displacement and residence  
time of atoms are tracked and collected as data, which are then analyzed  
in the case of the methane vapor condensing on quartz substrate. Specifi-  
cally, the tangential momentum accommodation coefficients are determined  
65 via correlation analysis [20, 21]. Moreover, we also examine the case of thin  
liquid films of methane on the solid substrate, find that the film thickness and  
the substrate nature have impacts on those accommodation coefficients. The  
consideration of common geomaterials like methane and quartz also provides  
useful results for future applications. For examples, methane is a shale gas  
70 and shale is mainly a mixture of clay materials such as kaolinite and quartz  
or silica [22, 23, 24]. In addition, silica can also be a suitable material for  
methane storage [25]. Moreover, methane can efficiently be described by the  
united atom model [26] which simplifies the molecular dynamics simulation.  
The details of the present work will be presented in the following.

## 75 **2. Theoretical background**

### *2.1. Kinetic boundary conditions of Boltzmann equation*

As it was underlined in Introduction, during the condensation process a  
vapor is in its non-equilibrium state and the continuum approach fails to de-  
scribe accurately the condensation phenomenon. In this case, the Boltzmann  
80 equation is used to simulate the evolution of the distribution function  $f(\mathbf{c}, \mathbf{x})$   
of velocity  $\mathbf{c}$  in every location  $\mathbf{x}$  of the gas phase. It must be completed by  
boundary conditions at the interface with materials of different natures like

solid wall or liquid phase. Let us assume the interface, denoted in the following by  $w$ , is parallel to the  $z$  plane and define the input distribution  $f^{in}$  and the output one  $f^{out}$  as follows

$$f^{in}(\mathbf{c}) = \begin{cases} 0, & \forall c_z > 0 \\ f(\mathbf{c}), & \forall c_z < 0 \end{cases} \quad \text{and} \quad f^{out}(\mathbf{c}) = \begin{cases} f(\mathbf{c}), & \forall c_z > 0 \\ 0, & \forall c_z < 0 \end{cases} \quad (1)$$

so that

$$f(\mathbf{c}) = f^{out}(\mathbf{c}) + f^{in}(\mathbf{c}). \quad (2)$$

A general kinetic boundary condition (KBC) links the input distribution  $f^{in}$  and the output one  $f^{out}$

$$|c_z|f^{out}(\mathbf{c}) = \int_{c'_z < 0} B(\mathbf{c}|\mathbf{c}')|c'_z|f^{in}(\mathbf{c}')d\mathbf{c}', \quad c_z > 0, \quad (3)$$

where  $B(\mathbf{c}|\mathbf{c}')$  is the scattering kernel. In equilibrium, we must have

$$f^{in}(\mathbf{c}) = \frac{n_w}{2}\mathcal{M}(\mathbf{c}) \quad \forall c_z < 0, \quad f^{out}(\mathbf{c}) = \frac{n_w}{2}\mathcal{M}(\mathbf{c}) \quad \forall c_z > 0 \quad (4)$$

with  $\mathcal{M}(\mathbf{c})$  being the Maxwellian

$$\mathcal{M}(\mathbf{c}) = \left( \frac{m}{2\pi k_B T_w} \right)^{3/2} e^{-\frac{m|\mathbf{c}|^2}{2k_B T_w}}, \quad (5)$$

where  $m$  is the mass of the fluid molecule and  $n_w$  is the gas number density at the interface at temperature  $T_w$  and  $k_B$  is the Boltzmann constant. In the case of liquid-vapor phase change at the interface

$$n_w = n_{sat}^v(T_w), \quad (6)$$

where  $n_{sat}^v$  is the saturated vapor number density at the interface temperature  $T_w$ .

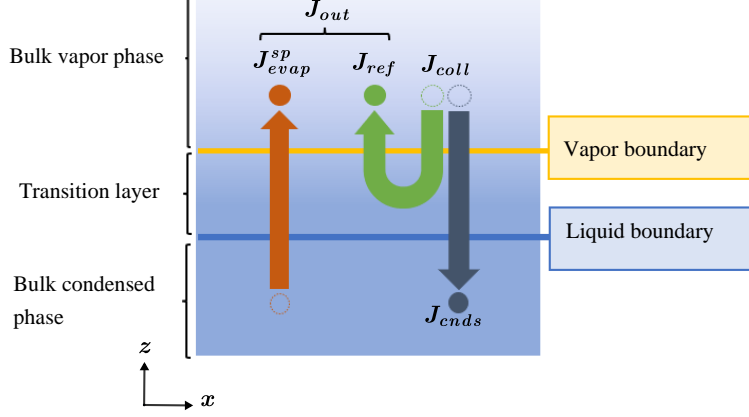


Figure 1: Sketch of the liquid-gas interphase and the fluxes. The positions of the liquid and vapor boundaries as well as the thickness of the transition layer are discussed in Section 3.1.

As shown in Fig. 1, a kinetic boundary model can be constructed by assuming that the flux of the molecules can be decomposed into evaporation (evap), condensation (cnds), and reflection (ref) processes. For example, we can write

$$f^{out} = f^{evap} + f^{ref/out}, \quad J^{out} = J^{evap} + J^{ref}, \quad c_z > 0 \quad (7)$$

100 and

$$f^{in} = f^{cnds} + f^{ref/in}, \quad J^{in} = J^{cnds} + J^{ref}, \quad c_z < 0 \quad (8)$$

with

$$J^a = \int |c_z| f^a(\mathbf{c}) d\mathbf{c}, \quad (9)$$

where superscript  $a$  stands for any of notations "in", "out", "evap", "cnds", or "ref/in" and, "ref/out". Due to the identity  $J^{ref/out} = J^{ref/in}$ , we use  $J^{ref}$  to denote both  $J^{ref/out}$  and  $J^{ref/in}$ . Well-known boundary conditions

105 [27] can be used

$$f^{out}(\mathbf{c}) = \alpha_e n_{sat}^v \mathcal{M}(\mathbf{c}) + (1 - \alpha_c)[\alpha n_w \mathcal{M}(\mathbf{c}) + (1 - \alpha)f^{in}(\mathbf{c}^s)], \quad c_z > 0, \quad (10)$$

with the number density of molecules,  $n_w$ , calculated from classical impermeability conditions

$$n_w = \sqrt{\frac{2\pi m}{k_B T_w}} \int_{c_z < 0} |c_z| f^{in} d\mathbf{c}, \quad (11)$$

and  $\mathbf{c}^s$  is the mirror velocity of  $\mathbf{c}$  with respect to the interface normal to  $\hat{\mathbf{i}}_z$

$$\mathbf{c}^s = \mathbf{c} - 2c_z \hat{\mathbf{i}}_z. \quad (12)$$

We can thus identify  $f^{evap} = \alpha_e n_{sat} \mathcal{M}(\mathbf{c})$  as the evaporation term and  
 110  $f^{ref/out} = (1 - \alpha_c)[\alpha n_w \mathcal{M}(\mathbf{c}) + (1 - \alpha)f^{in}(\mathbf{c}^s)]$  as the outgoing reflection term. The latter is composed of a diffusive part  $\alpha n_w \mathcal{M}(\mathbf{c})$  and a specular part  $(1 - \alpha)f^{in}(\mathbf{c}^s)$ . In addition, the relation  $f^{ref/in} = (1 - \alpha)f^{in}(\mathbf{c})$  is assumed for the incoming reflection term as in the Maxwell reflection model. The coefficients  $\alpha_c$  and  $\alpha_e$  are respectively the condensation and evaporation  
 115 coefficients and  $\alpha$  is the momentum/energy accommodation coefficient as in the classical Maxwell diffuse-specular kernel [28]. In equilibrium, the two coefficients evaporation and condensation are equal,  $\alpha_c = \alpha_e$ . For practical reason, this equality is also used for non equilibrium case, assuming that the condition is not far from equilibrium.

120 The boundary conditions can be more conveniently analyzed using the normalized probability distribution function associated with the flux crossing the interface, defined as

$$p^a(\mathbf{c}) = \frac{|c_z| f^a(\mathbf{c})}{\int |c_z| f^a(\mathbf{c}) d\mathbf{c}}. \quad (13)$$



Assuming  $\alpha_c = \alpha_e$ , we rewrite the evaporation and reflection terms using the normalized flux distribution as

$$p^{out}(\mathbf{c}) = \alpha_c p^{evap}(\mathbf{c}) + (1 - \alpha_c) p^{ref/out}(\mathbf{c}), \quad (14)$$

125 where the evaporation term reads

$$p^{evap}(\mathbf{c}) = \sqrt{\frac{2\pi m}{k_B T_w}} |c_z| \mathcal{M}(\mathbf{c}). \quad (15)$$

It is possible to relate  $p^{ref/out}(\mathbf{c})$  to  $p^{in}(\mathbf{c})$ , in a similar way as by Eq. (3) using a scattering kernel  $B(\mathbf{c}|\mathbf{c}')$  as

$$p^{ref/out}(\mathbf{c}) = \int_{c'_z < 0} B(\mathbf{c}|\mathbf{c}') p^{in}(\mathbf{c}') d\mathbf{c}'. \quad (16)$$

In this case expression for  $p^{ref/out}$  becomes

$$p^{ref/out}(\mathbf{c}) = \alpha p^{diff}(\mathbf{c}) + (1 - \alpha) p^{spec}(\mathbf{c}) \quad (17)$$

with

$$p^{diff}(\mathbf{c}) = \sqrt{\frac{2\pi m}{k_B T_w}} |c_z| \mathcal{M}(\mathbf{c}), \quad p^{spec}(\mathbf{c}) = p^{in}(\mathbf{c}^s). \quad (18)$$

130 It is known that the Maxwell model has different shortcomings, for example, the meaning of the coefficient  $\alpha$  is not clearly defined. It can be accommodation of tangential momentum or of energy. In addition, it exhibits discontinuity in velocity space and in reality, no molecule has an ideal specular reflection. An alternative way is the implementation of the Cercignani-  
 135 Lampis (CL) kernel which involves two accommodation parameters  $\alpha_t$  and  $\alpha_n$ , for accommodation of the tangential momentum and normal energy, respectively. Expressions for both Maxwell and Cercignani-Lampis kernels and the relation for the correlation between the velocities are given in Appendix

A.

140 In any case, for a fluid in equilibrium, we have the following remarks:

- The tangential velocity of a reflected molecule (associated to distribution  $p^{ref/out}$ ) is correlated with its incoming tangential velocity (associated to distribution  $p^{in}$ ) with correlation coefficient  $(1 - \alpha)$ .
- The velocity of an evaporated molecule (associated to distribution  $p^{evap}$ )  
145 is uncorrelated with its incoming velocity associated to distribution  $p^{ref/out}$ ),  
resulting in a zero correlation coefficient.
- The correlation coefficient between the incoming tangential velocity (associated to distribution  $p^{in}$ ) and the outgoing tangential velocity (associated to distribution  $p^{out}$ ) is  $(1 - \alpha)(1 - \alpha_c)$ .

150 These properties are valid for both Maxwell and Cercignani-Lampis kernels. In addition, to the statistical property, the condensed gas molecules tend to penetrate deep into the liquid phase and stay longer in it. Thus using the above observations, if we can distinguish the condensed molecules and reflected molecules, the condensation and the accommodation coefficients can  
155 be determined by correlation techniques.

We noted that in literature there are mainly two numerical methods of identifying the evaporation/condensation and tangential momentum accommodation coefficients characterizing interaction between a gas and a surface (solid  
160 or liquid). The first one is to beam atoms at fixed angles and velocities and measure the change of tangential velocities. However, due to the complex scattering behavior, the obtained coefficient is not constant and depends on the beaming angles [29]. It is also difficult to employ this method in the inter-phase problem as there are many atoms moving constantly across the liquid  
165 and vapor phases. The second method is to generate collision data with random angles and incoming velocities, e.g those issued from equilibrium state, then construct statistical scattering models and their parameters, including

correlation coefficients, to fit the data [30, 31, 20, 21]. The latter approach which is statistically robust and suitable for the interphase problem, will be  
 170 adopted in this work.

The presented above methods of identification of the coefficients characterizing gas surface (solid or liquid) interaction are consistent with the kinetic boundary conditions, Eq. (10) as in Refs. [9, 10]. Some literature works pro-  
 175 posed that those coefficients depend on the molecular kinetic energy [12, 14]. This corresponds to more sophisticate statistical modelling of the boundary conditions and will not be pursued further.

## 2.2. Molecular Dynamics simulations

The models are composed of quartz (SiO<sub>2</sub>) substrate and methane (CH<sub>4</sub>)  
 180 molecules with periodic boundary conditions in  $x, y$  directions. The geometric parameters of SiO<sub>2</sub> crystal unit cell are as follows:  $a = b = 4.9137\text{\AA}$ ,  $c = 5.4047\text{\AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . The solid rectangular substrate volume is  $8a \times 9\sqrt{3}b/2 \times 4c$  and in all our simulations, it is composed of 864 Si atoms and 1728 O atoms (see Fig. 2). The dimensions of the simulation box  
 185 along  $x, y$  are equal to the corresponding dimensions of the silica substrate, i.e.  $L_x = 8a = 39.3096\text{\AA}$ ,  $L_y = 9\sqrt{3}b/2 = 38.2985\text{\AA}$  while the dimension  $L_z$  is larger and varied so that we can fill the space with methane molecules.

The Burckingham (BKS) force field [32]

$$V_{ij}^{BKS} = C \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-b_{ij} r_{ij}) - \frac{c_{ij}}{r_{ij}^6} \quad (19)$$

is used to describe the interaction between the quartz atoms, Si and O. In  
 190 previous equation  $r_{ij}$  is the distance between 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,  $C$  is the energy conversion constant for the Coulombic term. The values of those constants are given in Table 1.

The Lennard-Jones (LJ) potential

$$V_{ij}^{LJ} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (20)$$

195 is used to describe the interaction between CH<sub>4</sub> molecules via TraPPE force field [26] within the unified atom model. The values of the parameters of LJ potential,  $\epsilon_{ij}$  and  $\sigma_{ij}$ , namely the depth of potential well (or dispersion energy) and the distance at which the particle-particle potential energy  $V_{ij}^{LJ}$  is zero (often referred to as size of the particle), are given in Table 2.

200 Results in Ref. [26] show that this model is very well suited to describe both liquid and gas phases of methane in the temperature range of the present work, i.e. 110-170 K. Moreover, the lowest energetic vibrational mode of CH<sub>4</sub> is the bending deformation mode associated with an equivalent temperature of 1879 K. The temperature of the simulations will not exceed 170 K, and Boltzmann’s statistics indicate that less than 0.002% of the molecules would be vibrationally excited at 170 K. The interactions between a CH<sub>4</sub> molecule and Si or O of the solid quartz are given via Lorentz–Berthelot mixing rule from CLAYFF force field [33]. The chemisorption process of CH<sub>4</sub> on quartz is supposed to be totally negligible.

210 The cutoff distance for force computation is  $r_{cut} = 5.09\sigma_{CH_4} = 19 \text{ \AA}$ , where  $\sigma_{CH_4}$  is the diameter of the methane molecule, and is less than half the shortest edge of the simulation box [34]. The reason to choose a value  $r_{cut}$  much larger than the usual value  $r_{cut} = 2.5\sigma_{CH_4}$  in most MD simulations is that cutting too short the attractive tail of the LJ potential can significantly affect the liquid vapor coexistence curve. In other words, choosing large  $r_{cut}$  allows producing saturated densities of the same order as experiments. The quartz substrate is composed of one fixed lower layer and two upper layers maintained at temperature  $T_w$  by NVT thermostat. The other  $z$  boundary of the simulation box is an elastic reflected wall. A suitable quantity of CH<sub>4</sub> molecules is placed in the middle of the simulation box so that after

220

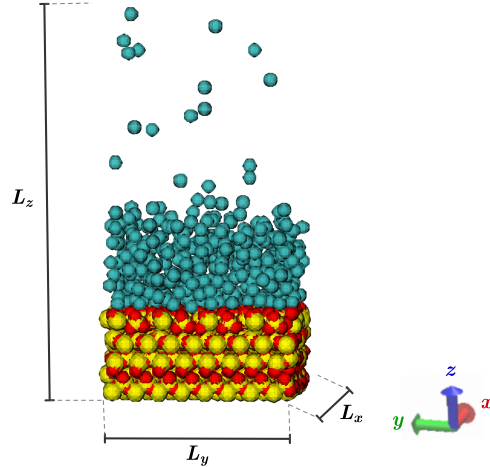


Figure 2: Snapshot of Molecular Dynamics system. Color code: blue for methane molecules ( $\text{CH}_4$ ), red for oxygen atoms (O) and yellow for silicon atoms (Si).

equilibration process at  $T_w$ ,  $\text{CH}_4$  is accumulated into a liquid film on the quartz surface and diluted in the remaining space. The choice of temperature  $T_w$  is also important to guarantee that the two phases coexist and the gas phase is sufficiently dilute. In simulations,  $T_w$  is varied from 110K to 170K, which is above the triple point  $T_{tp} = 90\text{K}$  and below the critical point  $T_c = 190\text{K}$ [35]. In reduced LJ units, we have  $T^* = k_B T_w / \epsilon_{\text{CH}_4} = 0.7432$  for 110K and  $T^* = 1.14$  for 170K.

The open source MD code LAMMPS [36] is used for all the simulations. Additional tools are developed to track atom motions and output atom values when they cross the control plane. The latter is placed at distance  $\delta$  from the liquid-vapor interface. Specifically, we are interested in the following quantities:

- the incoming velocity  $\mathbf{c}'$  and the outgoing velocity  $\mathbf{c}$
- the penetration depth  $d$  and the residence time  $\tau$  between the incoming and outgoing events.

Due to the small gas density,  $4 \times 10^6$  time steps of 0.0005 ps are required

Table 1: Parameters of BKS force field for quartz, Eq. (19).

	$A_{ij}$ [eV]	$b_{ij}$ [Å <sup>-1</sup> ]	$c_{ij}$ [eV Å <sup>6</sup> ]	$q_i$ [e]
O-O	1388.7730	2.7600	175.00	$q_O = -1.2$
Si-O	18003.7572	4.87318	133.5381	$q_{Si} = +2.4$

Table 2: Parameters of LJ potentials, Eq. (20).

	$\sigma_{ij}$ [Å]	$\epsilon_{ij}/k_B$ [K]
CH <sub>4</sub> -CH <sub>4</sub>	3.7300	148.10
CH <sub>4</sub> -Si	1.8650	0
CH <sub>4</sub> -O	3.4480	107.60

to reach the equilibrium state and other  $10^8$  steps for outputting the data. Finally, we analyze the data distributions and construct the statistical based models for the liquid-vapor interface.

### 240 3. Results and discussion

#### *3.1. Number density profile, saturated vapor number density and position of interface*

Figures 3 and 4 show how the fluid number density varies with the coordinate  $z$  for different film thicknesses, which depend on the number of methane molecules  $N$ . If the liquid film of methane is sufficiently thick, we can observe  
 245 a structuring effect near the quartz wall: the density is high and fluctuates strongly. Each peak corresponds to a layer of fluid molecules. Far from the solid wall, the fluid is more homogeneous and fluctuation is attenuated. Then, the number density decreases gradually in the transition zone and is  
 250 quasi constant in the gaseous phase. For the case of 4 methane molecules, we only find one peak as the molecules only form one fluid layer. As the temperature increases, the interphase zone thickness is dilated (around 10 Å at 110K vs 20 Å at 170K). This could affect the mass and momentum exchanges between the liquid and vapor phases.

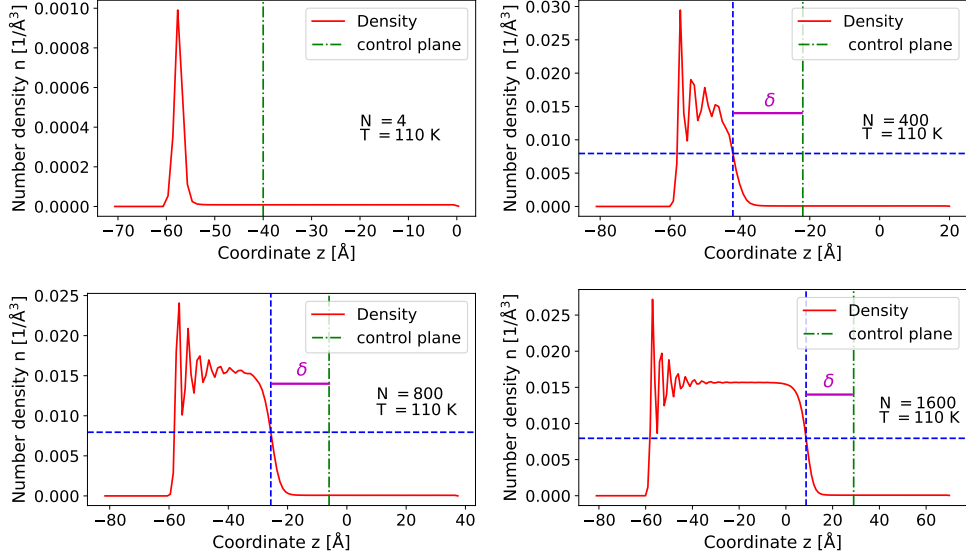


Figure 3: Number density of the fluid across the system at  $T = 110\text{K}$  and for different values of the methane molecules: (a)  $N = 4$ , (b)  $N = 400$ , (c)  $N = 800$ , (d)  $N = 1600$ . The leftmost part of each profile corresponds to the silica wall and has zero fluid number density. The rightmost part corresponds to the small but non vanishing gas number density. The vertical blue line corresponds to the liquid-gas interface, and the vertical green line to the control plane.

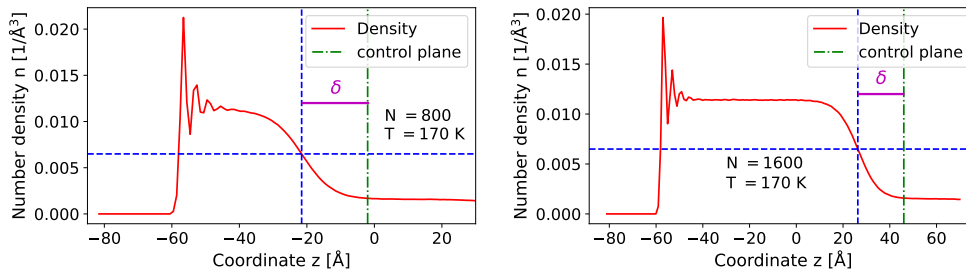


Figure 4: Number density of the fluid across the system at  $T = 170\text{K}$  and for different values of the methane molecules: (a)  $N = 800$ , (b)  $N = 1600$ . The leftmost part of the profile corresponds to the silica wall and has zero fluid number density. The rightmost part corresponds to the small but non vanishing gas number density. The vertical blue line corresponds to the liquid-gas interface, and the vertical green line to the control plane.

255 The value of saturated vapor number density  $n_{sat}^v$  can be obtained by fitting first the number density in the vapor phase with function

$$n(z) = a - b \tanh\left(2\frac{(z-c)}{d}\right), \quad (21)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are the fitting parameters. In addition,  $c$  is the location of interface and  $d$  is the interface thickness [37, 38]. Then, by looking for the limit value as

$$n_{sat}^v = \lim_{z \rightarrow \infty} n(z) = a - b. \quad (22)$$

260 In the case of large bulk liquid and gas phases,  $a = \frac{1}{2}(n_{sat}^v + n_{sat}^{liq})$  and  $b = \frac{1}{2}(n_{sat}^{liq} - n_{sat}^v)$ .

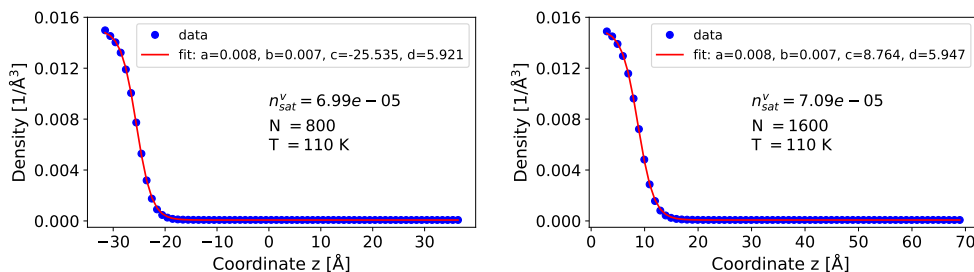


Figure 5: Saturated gas number density along direction  $z$  obtained from the numerical simulations (blue circles) and the fit according to Eq. (21) (red line).

At 110K, the saturated vapor number density is found to be  $n_{sat}^v \simeq 0.07 \times 10^{-3} \text{ \AA}^{-3}$  which corresponds to reduced vapor number density  $n_{sat}^{v*} = n_{sat}^v \sigma_{CH_4}^3 = 0.0036$  at reduced temperature  $T^* = 0.7432$  (see Figure 5). This value is lower than the MD results obtained by Liang *et al.* [11]  $n_{sat}^{v*} = 0.0063$  at  $T^* = 0.745$  using  $r_{cut} = 3.2\sigma_{Ar}$  for argon, but in excellent agreement with LJ fluid simulations,  $n_{sat}^{v*} = 0.0036$ , using much larger  $r_{cut}$ , by Errington[39]<sup>1</sup>

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



and 0.0033 by Stephan *et al.* [40]. It is also of the same order as  $n_{sat}^{v*} = 0.0031$  from experimental data and equation of state (EOS) for methane [35], see also Appendix B for more details. At 170K,  $T^* = 1.14864$ , the value of saturated vapor number density from simulations is even closer to the literature value  $n_{sat}^{v*} = 0.076$  which is identical to the value 0.076 obtained from EOS. In Ref. [39], the liquid–vapor phase equilibrium is directly determined using the transition matrix Monte Carlo (MC) simulation. In another recent work [40], the database composed of MC and MD simulations of the same equilibrium, found in literature, is examined and analytical formula that best fit the results are proposed.

The molecular mean free path  $\lambda$  of methane vapor is estimated from the vapor number density  $n$  and the LJ diameter of methane  $\sigma_{CH_4}$  as

$$\lambda = \frac{1}{\sqrt{2}n\pi\sigma_{CH_4}^2}. \quad (23)$$

The mean free path of methane vapor in saturated state is calculated from

$$\lambda = \frac{\sigma_{CH_4}}{\sqrt{2}\pi n_{sat}^{v*}} \quad (24)$$

and it is of order  $\lambda = 62\sigma_{CH_4} = 231 \text{ \AA}$  at 110K and  $\lambda = 2.95\sigma_{CH_4} = 11 \text{ \AA}$  at 170K. We note that at 170K, which is close to the critical temperature, the vapor phase is no longer dilute since the mean free path is of the same order as the cutoff distance of van der Waals forces.

Due to the transition zone, it is hard to determine the boundary between the liquid and vapor phases, i.e. the interface position. In the literature, there is no unique method to solve this problem. Moreover, the impact of the wall and the layering liquid structure, formed at the early stage of condensation, can pose additional difficulties. In this paper, we propose to locate the interface at the position where the fluid number density equals the average number

density of saturated vapor and saturated liquid

$$n_{int} = \frac{1}{2}(n_{sat}^v + n_{sat}^{liq}). \quad (25)$$

So defined interface position corresponds to the  $z$  coordinate value which equals to  $c$  in the fitting expression of the number density profile given by Eq. (21). This interface position (see vertical blue line on Figures 3 and 4) is thus also used to compute the nominal thickness of the liquid film condensed on silica.

When the liquid film is sufficiently thick, the wall is expected to have less impact on the exchange of molecules at the liquid-vapor interface and the transition zone is more dominant. As a results, it is important to define the limit of the liquid phase in the transition zone and the position of the control plane. The latter is used to determine the condensation and accommodation coefficients, or more generally the kinetic boundary conditions which represent probabilities of collision between a gas molecule and a liquid, and then the probability of condensation or reflection. The control plane is placed in the gaseous phase and at a certain distance  $\delta$  from the interface position. The value of  $\delta$  needs to be small when compare to the mean free path  $\lambda$  and the control plane must be sufficiently far from the liquid phase. This is due to the fact that we construct KBCs (Eq. (3)) associated with the evaporation/condensation and tangential momentum accommodation coefficients for the gaseous phase where the Boltzmann equation is valid. It is chosen so that gas molecule velocities are affected by the liquid only when crossing the control plane, in this case  $\delta = 20 \text{ \AA}$  (see Figures 3 and slightly larger than  $r_{cut} = 19 \text{ \AA}$ . In previous works, e.g Ref. [11, 15], this distance is also equal to  $\delta = r_{cut}$ . As the present work adopts a larger  $r_{cut}$  to obtain good saturated densities,  $\delta$  value is thus consequently larger. Other works, e.g Refs. [41, 42, 43], chose to use  $\delta$  as function of temperature and of the transition layer thickness which will result different evaporation/condensation coefficients. In our opinion, this consideration is also working as there is no

320 restriction, in terms of modelling, on where to apply the KBCs and those  
coefficients are expected to be associated with the KBCs position.

### 3.2. Residence time and penetration depth distributions

To study the condensation process, after each vapor molecule crosses  
the control plane towards the liquid phase, we track its motion to find how  
325 far and how long a molecule travels before reemerging at the control plane  
again. We assume that the incident flux can be decomposed into a reflected  
flux and a condensation flux, see Eq. (8). A reflected molecule is expected to  
be associated to a short residence time and a short penetration depth while  
a condensed molecule is expected to penetrate farther into the liquid phase  
330 and stay longer in it. We shall examine the Residence Time Distribution  
(RTD) and the Penetration Depth Distribution (PDD), and separate data  
associated to both types of fluxes (condensation and reflected) for further  
considerations. As above, we vary the number of methane molecules  $N$  in  
the model to study the influence of the liquid film thickness.

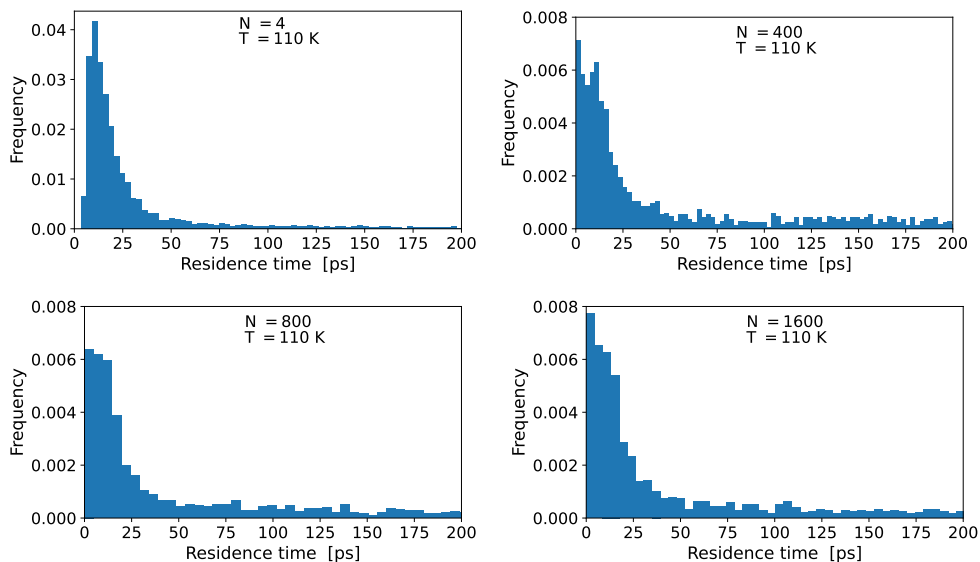


Figure 6: Residence time distributions at 110K.

335 From the histograms of the residence time  $\tau$  at 110K (see Figure 6), we  
 find that a large number of molecules has short residence time. The residence  
 time probability decreases sharply from 0 to 40-50 ps and then decays slowly  
 afterwards, ending by a long plateau. As a result, the residence time is clearly  
 divided into two types of populations associated to two distinct regimes, a  
 340 short residence time (shorter than 40 ps) and a long residence time (longer  
 than 40 ps). For the case  $N = 4$  molecules, the collisions occur mostly  
 between the gas and the solid wall. The gas molecules are expected to travel  
 the distance of order  $2\delta$  before reemerging at the control plane. As a result,  
 a peak at 10-12 ps is visible in the distribution, which can be attributed  
 345 to reflected molecules, given that the mean thermal speed equals  $3.8 \text{ \AA}/\text{ps}$   
 and  $2\delta = 40 \text{ \AA}$ . We also observe that a large portion of the gas molecules  
 is adsorbed and stays much longer than the peak value. For thicker liquid  
 films, in addition to collisions with the bulk liquid at distance  $\delta$ , the collisions  
 can also occur in the gaseous phase at different distances from the control  
 350 plane due to the presence of molecules in this area, showing a continuous  
 distribution starting from 0 ps.

In the logarithmic time scale in Fig. 7, we find that the tail of the resi-  
 dence time distribution can be represented by a straight line, corresponding  
 to an exponential distribution in long time regimes, i.e  $\tau \sim e^{-\tau/\tau_r}$  at large  
 355  $\tau$ , where  $\tau_r$  is the relaxation time. From Figures 6 and 7, it is clear that  
 the exponential regime tends to start for shorter residence times and to de-  
 crease with a faster rate (steeper slope in log scale) for higher temperatures,  
 meaning a shorter relaxation time  $\tau_r$ . For system composed of 800 molecules,  
 although penetration depth data cloud starts to scatter at  $20 \text{ \AA}$  and  $25 \text{ ps}$   
 360 (rather than 40 ps from RTD as discussed previously), we find that most  
 molecules with residence times longer than 1000 ps come from the adsorbed  
 liquid layers near the wall. This suggests that the main contribution of the  
 exponential regime comes from molecules adsorbed near the silica wall. As  
 the residence time can be considered as the sum of diffusion times in the gas

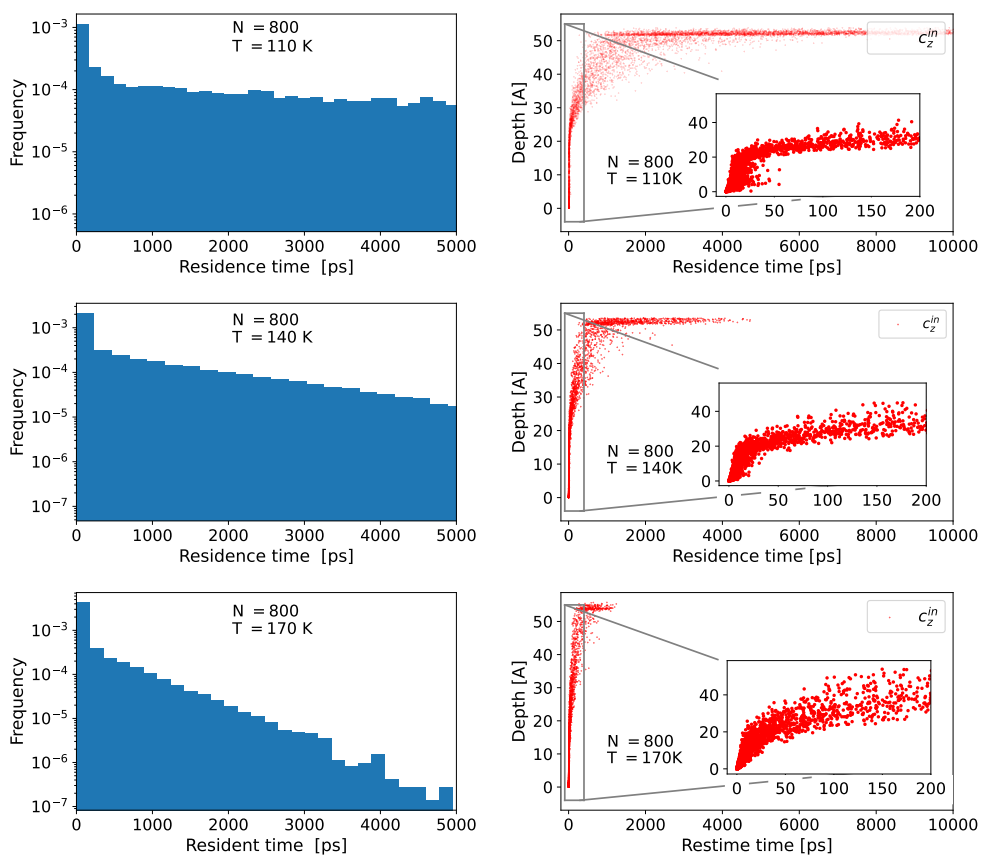


Figure 7: Left: Residence time distributions in **logarithmic scale** as a function of **residence time**. Right: Penetration depth as a function of residence time

365 phase, the bulk liquid (which has no layering structure) and the adsorbed  
 layers, we can conclude that the time that the molecules spent in the latter  
 is dominant. The data distributions also show three clear molecule motions  
 and residence time regimes, gaseous phase (data localized near the origin),  
 the bulk liquid (data scattered) and the adsorbed layers (data localized near  
 370 the wall).

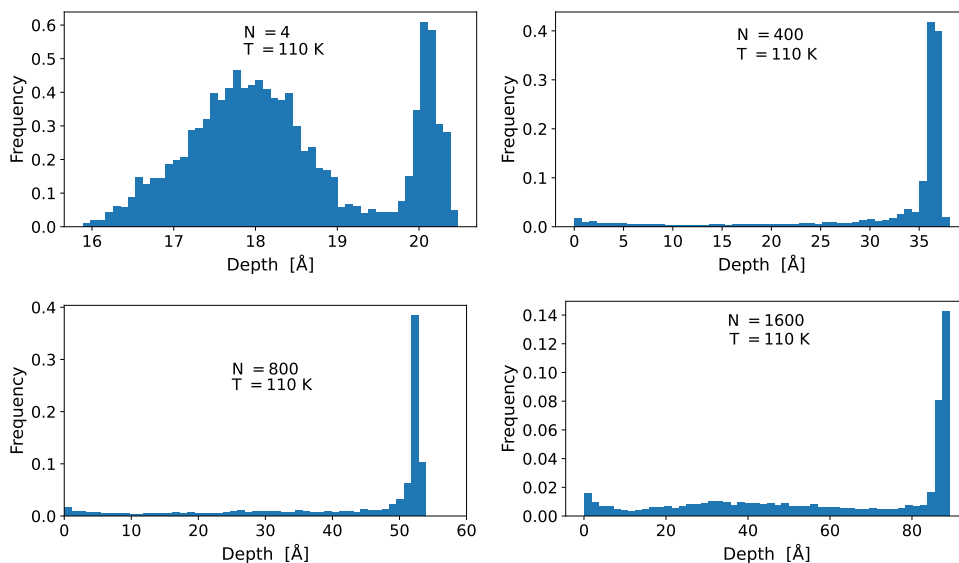


Figure 8: Penetration depth distributions at 110K.

Regarding the distributions of penetration depth in Figure 8, in all cases  
 where a liquid film is present ( $N \geq 400$ ), we find a peak corresponding to a  
 location near the solid surface. This shows that a large number of molecules  
 comes from that location and travels back to the gaseous phase. As the  
 375 liquid film thickness increases, this peak decreases as more molecules come  
 from inside the liquid bulk. Around the interface position at 20 Å, there is  
 no clear dominant behavior, thus making it hard to use penetration depth  
 to distinguish condensation molecules from penetration distribution. For the  
 special case  $N = 4$  where collisions are mostly between the gas molecules  
 380 on the solid wall, the distribution reveals the roughness structure of the

silica wall. We can find two peaks at distance of 2 Å which correspond to the different local minima in silica where CH<sub>4</sub> molecules are most likely absorbed.

Let us focus on molecules with residence time shorter than 40 ps and molecules with penetration depth longer than 20 Å. From the depth distribution of short residence time molecules (see Fig. 9), we find that a significant portion of molecules penetrates farther than 20 Å and without exceeding 27 Å. On the other hand, looking at the distribution of residence time for short penetration depths, we find that most molecules stay a time shorter than 40 ps between the control plane and the solid wall.

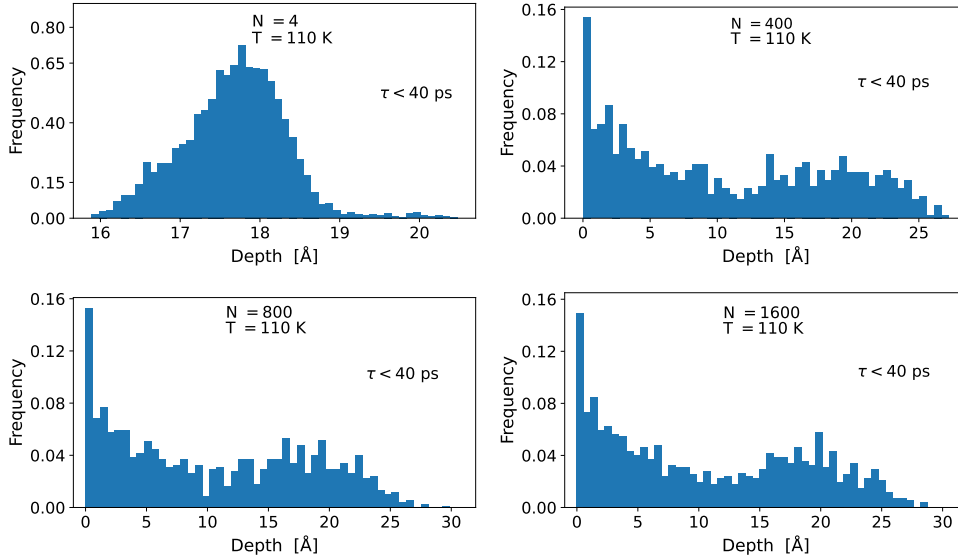


Figure 9: Penetration depth distributions for molecules with residence times shorter than 40 ps, and for different number of simulation molecules:  $N = 4, 400, 800$  and  $1600$ .

Similarly for the population with a penetration depth shorter than 20 Å, we can observe in Figure 10, the distribution of the residence time as a function of the number of methane molecules  $N$ . We can find that the number of molecules with residence time longer than 40 ps is very low. From the above observation, using penetration depths longer than 20 ps also guarantees the residence time to be longer than 40 ps but not vice versa.

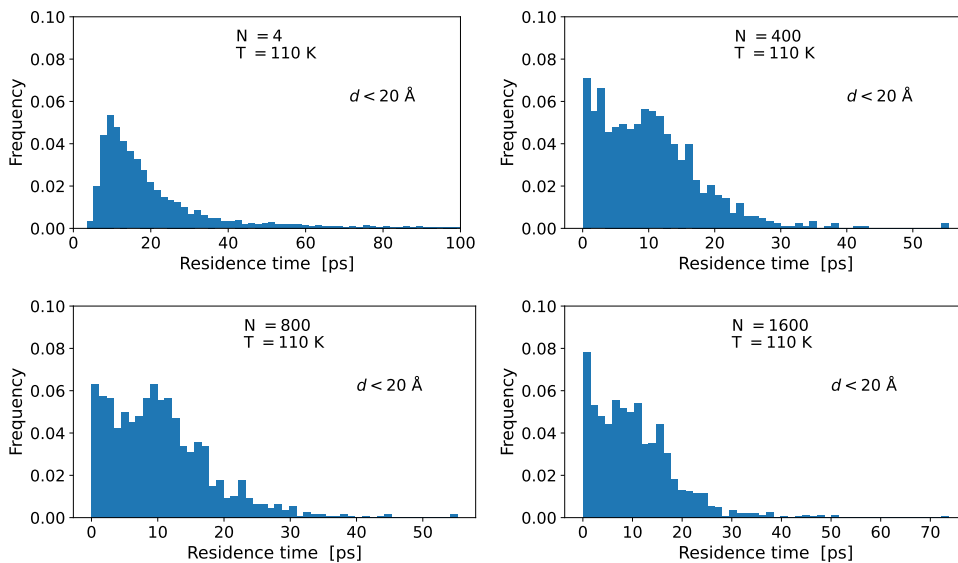


Figure 10: Residence time distribution for molecules with penetration depth shorter than  $20 \text{ \AA}$  and for different number of simulation molecules:  $N = 4, 400, 800$  and  $1600$ .

The above data distribution analysis shows us useful microscopic information of the atomic motion across the interface, especially how the long/short residence time is and how low/deep penetration depth is and also some explanation of their origins. We noted that the mass exchanges at the interface is complex and using the condensation coefficient is a simplification of the real condensation-reflection process as the differences between the condensation and reflected molecules are not very clear. The analysis suggests that using the penetration depth seems to provide a more coherent picture of the process. In the following, we introduce another tool based on correlation analysis which can allow calculating at the same time the condensation and the tangential momentum accommodation coefficients.

### 3.3. *Evaporation/condensation and accommodation coefficients from correlation analysis*

In this Section, we only focus on cases where the liquid film layer is formed and the use of condensation coefficient is meaningful. The early stage of the



condensation ( $N = 4$ ) is no longer considered as it should be treated with adsorption physics instead.

For data analysis, let us denote the full data set  $\mathcal{D}$  containing all the  $M$  events composed of the input velocity vector  $\mathbf{c}'$ , the output velocity vector  $\mathbf{c}$ , the residence time  $\tau$ , and the penetration depth  $d$  recorded by the simulation

$$\mathcal{D} = \{\mathbf{X}^{(i)} | i = 1, \dots, M\}, \quad \mathbf{X}^{(i)} = (\mathbf{c}'^{(i)}, \mathbf{c}^{(i)}, d^{(i)}, \tau^{(i)}). \quad (26)$$

We assume that the data set  $\mathcal{D}$  can be divided into two subsets:  $\mathcal{D}_{evap}$  for all evaporation events and  $\mathcal{D}_{ref}$  for all reflection events. To study this, we denote the subsets according to residence time threshold,  $\tau_c$

$$\mathcal{D}_{\tau < \tau_c} = \{\mathbf{X}^{(i)} \in \mathcal{D} | \tau^{(i)} < \tau_c\}, \quad \mathcal{D}_{\tau > \tau_c} = \{\mathbf{X}^{(i)} \in \mathcal{D} | \tau^{(i)} > \tau_c\} \quad (27)$$

and penetration depth threshold,  $d_c$

$$\mathcal{D}_{d < d_c} = \{\mathbf{X}^{(i)} \in \mathcal{D} | d^{(i)} < d_c\} \quad \mathcal{D}_{d > d_c} = \{\mathbf{X}^{(i)} \in \mathcal{D} | d^{(i)} > d_c\}. \quad (28)$$

Next  $\rho_{Q, Q' | \mathcal{A}}$  is the correlation coefficient between  $Q(\mathbf{c})$  and  $Q'(\mathbf{c}')$ , functions of velocity, for data belonging to data set  $\mathcal{A}$

$$\rho_{Q', Q | \mathcal{A}} = \frac{cov(Q', Q)}{\sigma_Q \sigma_{Q'}} = \frac{\sum(Q - \langle Q \rangle)(Q' - \langle Q' \rangle)}{\sqrt{\sum(Q - \langle Q \rangle)^2 \sum(Q' - \langle Q' \rangle)^2}}. \quad (29)$$

We note that the incoming velocity  $\mathbf{c}'^{(i)}$  is realization of  $p^{in}(\mathbf{c}')$  and the outgoing  $\mathbf{c}^{(i)}$  is realization of  $p^{out}(\mathbf{c})$ . We remark that for molecules staying longer and going deeper in the liquid phase, the outgoing velocity is less correlated with the incoming velocity. It is suggested that molecules which evaporate

can be identified by a zero correlation, in agreement with Eq. (14). First, we assume that the liquid surface is isotropic in the plane  $xOy$ . To improve the statistical signal, let us collect the two tangential velocity components  $c'_x$  and  $c'_y$  into one group  $c'_{xy}$  and  $c_x$  and  $c_y$  velocity components

430 into another group  $c_{xy}$  (see Fig. 11).

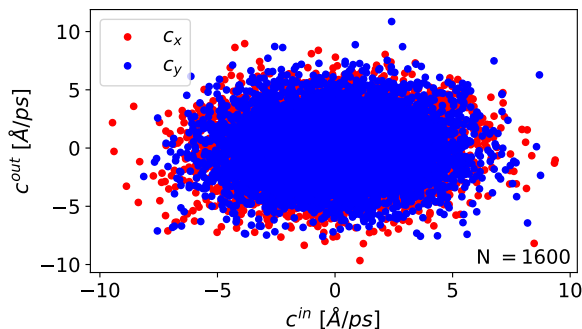


Figure 11: Data points of the input tangential velocities  $c'_x, c'_y$  and output tangential velocities  $c_x, c_y$  at 110K and  $N = 1600$ .

Next we compute the correlation coefficients between the quantities  $c'_{xy}$  and  $c_{xy}$  for a residence time  $\tau$  less than  $\tau_c$  or for a penetration depth  $d$  less than  $d_c$ , denoted shortly as

$$\rho_{xy}^d(d_c) = \rho_{c'_{xy}, c_{xy} | \mathcal{D}_{d > d_c}}, \quad \rho_{xy}^\tau(\tau_c) = \rho_{c'_{xy}, c_{xy} | \mathcal{D}_{\tau > \tau_c}}. \quad (30)$$

The evolution  $\rho_{xy}^d(d_c)$  of the correlation coefficients as a function of the penetration depth threshold is given in Figure 12 for different temperatures and molecules numbers of methane. As expected, the correlation coefficient decreases with the penetration depth. For the case of  $T = 110\text{K}$  the correlation coefficient has a value of  $0.05 - 0.06$  for small penetration depths and reaches a plateau at a value close to zero for penetration depths around  $18 - 20 \text{ \AA}$ . It is suggested using  $18 - 20 \text{ \AA}$  as threshold value for identifying an evaporated molecule, since a molecule outgoing through the control plane from this distance can be considered as independent of its initial state.

The same analysis can be made for the correlation coefficient  $\rho_{xy}^\tau(\tau_c)$  in terms of residence time threshold. The correlation coefficient decreases with time  $\tau_c$  and reaches a plateau after a certain residence time. This threshold value is about  $20 - 40 \text{ ps}$  and seems to decrease as the film thickness decreases,

i.e  $N$  decreases from 1600 to 400.

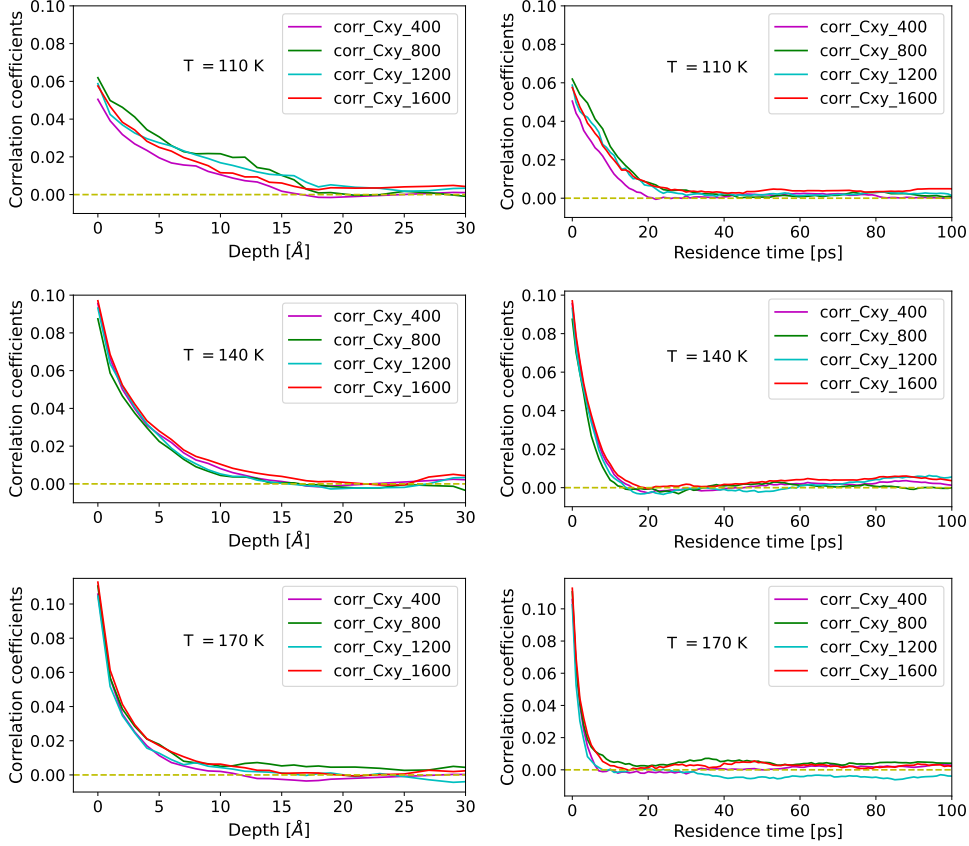


Figure 12: Evolution of the correlation coefficient of tangential velocity: left column,  $\rho_{xy}^d(d_c)$  in terms of the penetration depth threshold  $d_c$  and right column,  $\rho_{xy}^r(\tau_c)$  in terms of residence time threshold  $\tau_c$ , for different temperatures and molecules numbers of methane.

From the correlation map shown in Fig. 13, we find a strong correlation between the velocity components of the same direction  $(c_x, c'_x)$ ,  $(c_y, c'_y)$  and  $(c_z, c'_z)$  at short residence time and penetration depth thresholds while the velocity components of different directions are uncorrelated. It suggests that the components of different directions are independent.

The analysis of the correlation coefficients provided above leads that the tangential momentum accommodation coefficient  $\alpha$  and the condensation

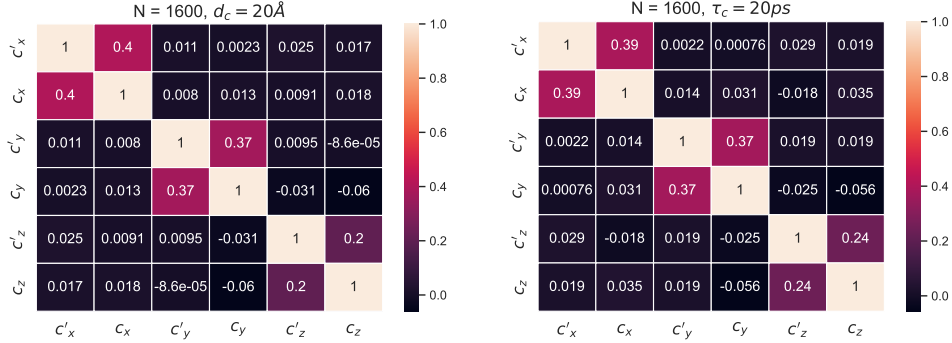


Figure 13: Correlation map between  $\mathbf{c}$  (outgoing velocity) and  $\mathbf{c}'$  (incoming velocity) for  $\mathcal{D}_{d_c < 20\text{\AA}}$  and  $\mathcal{D}_{\tau_c < 20\text{ps}}$ . The color in the cell  $(a, b)$  where  $a = c'_x, c'_y, c'_z$  and  $b = c_x, c_y, c_z$  represents the value of correlation  $\rho_{ab}$  between  $a$  and  $b$ . The black and white colors represent the values 0 and 1 and other colors represent intermediate values. Values close to 1 means strong correlation and values close to 0 mean weak correlation.

455 coefficient  $\alpha_c$  could be computed by the relations

$$\alpha_c = \frac{|\mathcal{D}_{evap}|}{|\mathcal{D}|}, \quad \alpha = 1 - \rho_{c'_{xy}, c_{xy} | \mathcal{D}_{ref}}, \quad \mathcal{D}_{ref} = \mathcal{D} \setminus \mathcal{D}_{evap} \quad (31)$$

with  $\mathcal{D}_{evap}$  being either  $\mathcal{D}_{\tau > \tau_c}$  or  $\mathcal{D}_{d > d_c}$ ,  $\tau_c$  varying from 20–40 ps and  $d_c$  varying from 18–20 Å. The notation  $||$  represents the data size or the number of elements of the data set. The last expression in (31) is due to  $\mathcal{D} = \mathcal{D}_{ref} \cup \mathcal{D}_{evap}$  and the backward-slash  $\setminus$  is the subtraction operation between the dataset.

460 The distribution of  $\mathbf{c}$  in  $\mathcal{D}_{evap}$  is expected to follow the distribution  $p^{evap}$  and  $\mathbf{c}, \mathbf{c}'$  in  $\mathcal{D}$  follow  $p^{out}, p^{in}$ ,  $\mathbf{c}, \mathbf{c}'$  in  $\mathcal{D}_{ref}$  follow  $p^{ref/out}, p^{ref/in}$ . As a result, the correlation is connected to the accommodation coefficient according to the remarks in Section 2.1 and Appendix A

In each model consisting of  $N$  methane molecules, we define the thickness of the liquid film as the distance between the top surface of the quartz crystal and the liquid-gas interface. By varying  $\tau_c$  (from 20 to 40 ps) and  $d_c$  (from 18 to 20 Å), see Fig. 14, we find that the condensation and the tangential momentum accommodation coefficients are almost insensible to the choice of

those parameters. The condensation coefficient lies in range  $0.85 - 0.9$  and  
 470 the tangential momentum accommodation coefficient between  $0.52 - 0.67$ .  
 To the best of our knowledge, there is no previous experimental and simula-  
 tion works on those coefficients for methane. We find that the condensation  
 coefficient is in the same range as the literature works [9, 11, 13, 15] in equi-  
 librium and non equilibrium cases on other fluids. But none of them have  
 475 considered and computed the tangential momentum accommodation coeffi-  
 cient as done in this work. In Ref. [9], non equilibrium MD simulations of  
 LJ fluid were done using reduced cutoff radius  $r_{cut} = 2.5\sigma$  and the conden-  
 sation and evaporation coefficients are found between 0.5-0.8. In Ref. [11],  
 the authors used equilibrium MD simulations with  $r_{cut} = 3.2\sigma$  and found the  
 480 condensation and evaporation coefficients between 0.75-0.98. In Ref. [13],  
 thin films are constituted of  $n$ -dodecanes, larger molecules with internal de-  
 gree of freedom, and  $\alpha_c$  ranges from 0.5-0.6. In Ref. [15], a liquid droplet is  
 considered and  $\alpha_c$  is found to be dependent on droplet curvature. The values  
 for infinite radius are around 0.8 for LJ fluid but can be as small as 0.1-0.2  
 485 for water.

It is interesting to note that using  $d_c = 20 \text{ \AA}$  or  $\tau_c = 20 \text{ ps}$  yields close  
 coefficient values, situated in the middle of the ranges. Using  $d_c = 18 \text{ \AA}$  and  
 $\tau_c = 40 \text{ ps}$  gives extreme values. As  $d_c = 20 \text{ \AA}$  has the physical meaning  
 previously explained and using  $\tau_c$  may omit atoms travelling near parallel to  
 490 the interface, we shall adopt this criteria for the following analysis.

From Fig. 14, we also find that the condensation coefficient decreases  
 slightly as the film thickness increases. It means that at the early stage of  
 condensation, molecules tend to condense more and to reflect less. Only when  
 the film reaches a certain thickness (around  $90 \text{ \AA}$ ), the coefficient starts to  
 495 stabilize and becomes constant. Due to the influence of the film thickness and  
 the presence of the solid substrate, the tangential momentum accommodation  
 coefficient slightly varies but with a rather complex trend. In particular, we  
 observe a local minimum at  $30 \text{ \AA}$  thickness.

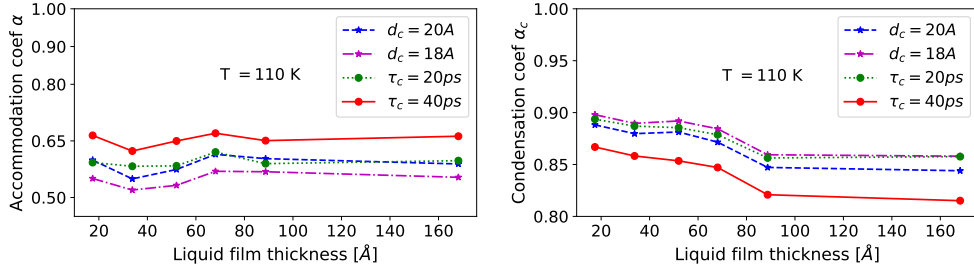


Figure 14: Variation of the tangential momentum accommodation coefficient  $\alpha$  and condensation coefficient  $\alpha_c$  with liquid film thickness.

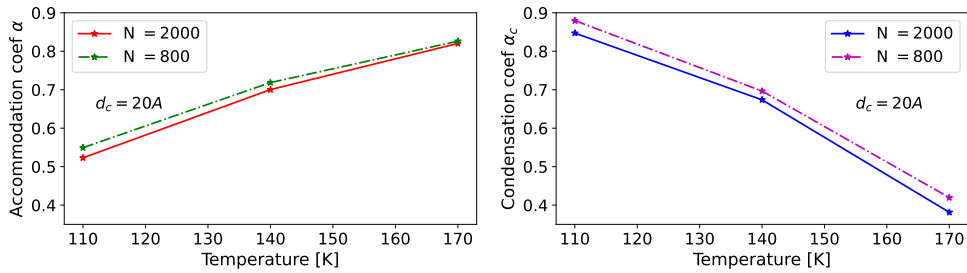


Figure 15: Variation of the tangential momentum accommodation coefficient  $\alpha$  and condensation coefficient  $\alpha_c$  with respect to temperature.

Finally, we examined the dependency of the two coefficients  $\alpha$  and  $\alpha_c$  with temperature. Fig. 15 shows that as the temperature increases from 110K to 170K, the condensation coefficient decreases and the tangential momentum accommodation coefficient increases with a variation of approximately 50% between the maximal and the minimal values. It is noted that at high temperature, the interface thickness is larger and the vapor phase is denser, making harder for molecules to cross and condense in the liquid phase. Molecules are more likely to collide with other molecules and to come back to the vapor, so  $\alpha_c$  decreases. Regarding reflected atoms, thick interphase with high density also reduces the mean free path and increases the number of collisions and thus the reflected atoms velocity is more diffusive, less correlated and consequently leads to a high tangential velocity accommodation coefficient  $\alpha$ .

$N$	$T = 110\text{K}$		$T = 140\text{K}$		$T = 170\text{K}$	
	$\alpha_c$	$\alpha$	$\alpha_c$	$\alpha$	$\alpha_c$	$\alpha$
400	0.89	0.60	0.70	0.69	0.45	0.80
800	0.88	0.55	0.70	0.72	0.42	0.83
1200	0.88	0.57	0.68	0.71	0.42	0.83
1600	0.87	0.61	0.70	0.69	0.39	0.83
2000	0.85	0.60	0.67	0.70	0.38	0.79
4000	0.84	0.59	0.64	0.72	0.41	0.79

Table 3: Condensation,  $\alpha_c$  and tangential momentum accommodation,  $\alpha$ , coefficients for different temperatures and different numbers of methane molecules  $N$ .

The summary of the condensation,  $\alpha_c$  and tangential momentum accommodation,  $\alpha$ , coefficients for different temperatures and different numbers of methane molecules  $N$  are provided in Table 3. The underlined above  
515 tendency of the condensation coefficient decreasing with increasing of temperature is clearly seen. Similar behaviour of decreasing of the condensation coefficient of mercury vapor with temperature rises was found by the authors of Ref. [18], where this coefficient was extracted from the experimental data. As it concerns the tangential momentum accommodation coefficient, we do  
520 not found any data on its sensitivity to the temperature, especially because this coefficient was extracted for gas-solid surface case and not for the case of reflected molecules from the liquid interface.

Quantitatively, we can reason that the velocity correlation coefficient of a particle after number  $N_{col}$  of independent collisions,  $\gamma_{N_{col}}$ , is equal to  $\gamma_1^{N_{col}}$ ,  
525 where  $\gamma_1$  is the velocity correlation coefficient after one collision. This coefficient is equal to  $3/7$  for hard sphere intermolecular potential [44]. As  $\gamma_1 < 1$ , the correlation decreases exponentially to 0 with the number of collisions  $N_{col}$  increasing. Since our transition layer has a finite size and is inhomogeneous, the number of collisions is not a constant for all molecules. To the first order  
530 of estimation, let us assume that the average number of collision  $N_{col}$  is of order  $l_c/\lambda$  with  $l_c$  being characteristic length of the transition layer and  $\lambda$  being the molecular mean free path. From Eq. (23),  $\lambda$  is inversely pro-

portional to the vapor number density and particularly to the characteristic interphase number density  $n_{int}$ , leading to the relation  $N_{col} \propto l_c n_{int}$ . As a result,  $(1 - \alpha) \propto \gamma_1^{l_c n_{int}}$  and  $\ln(1 - \alpha)$  is expected to be a linear function of the number density  $n_{int}$  with negative slope (due to  $\ln \gamma_1 < 0$ ). Taking  $n_{int} = 1/2(n_{sat}^v + n_{sat}^{liq})$  (Eq. (25)), and plotting its relation with the coefficient  $\ln(1 - \alpha)$  in Fig. 16, we find that a linear relation of type

$$\ln(1 - \alpha) = An_{int} + B, \quad or, \quad \alpha = 1 - e^{An_{int} + B} \quad (32)$$

with  $A = -404.38 \text{ \AA}^3$  and  $B = 2.5255$ , gives a good representation of the data in the temperature range 110 – 170K.

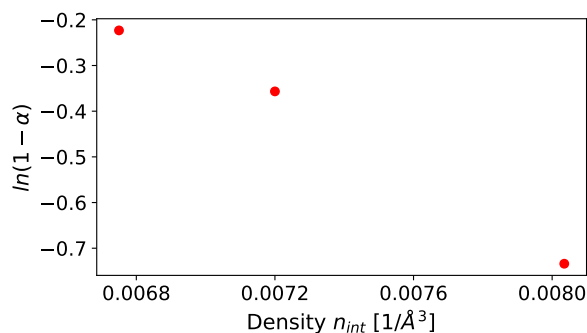


Figure 16: Relation between  $\ln(1 - \alpha)$  and  $n_{int}$

#### 4. Conclusions and perspectives

In this paper, we investigate the variation of number density, mass and momentum exchanges at the methane liquid vapor interface by Molecular Dynamics simulations. Information about residence time and penetration depth of each molecule crossing a control plane located 20  $\text{\AA}$  far from the interface, is collected and then analyzed. We show that by using correlation analysis, we can determine at the same time the condensation coefficient and tangential momentum accommodation coefficient. This approach is new and



has not been yet studied in literature works.

550

Regarding the saturated number density, the MD simulations based on a large cut off distance yield results closed to the experiments. We also find the dependency of those coefficients in terms of liquid film thickness and temperature. Especially, when temperature increases up to near the critical  
555 temperature of methane  $T_c = 190$  K, the condensation coefficient decreases and the momentum accommodation coefficient increases drastically, meaning molecules condense less and reflect more at the interface and the reflection is more diffusive. A physics based empirical formula for the accommodation coefficient depending on the interface number density is also proposed.

560

The present work provides tool to identify the condensation, evaporation and tangential momentum accommodation coefficients using equilibrium MD simulations by looking those processes at the microscopic (atomic) scale. In the next step, it is interesting to investigate non equilibrium systems and ex-  
565 amine how the microscopic processes deviate from equilibrium. Many open questions will be addressed, for example the difference between condensation and evaporation coefficients, the relaxation difference between the normal and the tangential directions [45], the presence of non-condensable gas [41]. The information from the simulations constitutes numerical evidences to con-  
570 struct more accurate KBCs in the future.

## Appendix A. Expressions for scattering kernels

Different scattering kernels can be used to determine the outgoing distribution function if the incident one is known as it is defined by Eq. (3). The expression of Maxwell scattering kernel is the following

$$B^M(\mathbf{c}|\mathbf{c}') = (1 - \alpha)\delta(\mathbf{c} - \mathbf{c}'^s) + \alpha\sqrt{\frac{2\pi}{\theta_w}}|c_z|\mathcal{M}(\mathbf{c}) \quad (\text{A.1})$$

575 where  $\delta$  is the delta dirac distribution and  $\mathbf{c}'^s$  is the mirror counterpart of the incoming velocity  $\mathbf{c}'$  like in Eq. (12).

For the Cercignani-Lampis scattering kernel this expression reads

$$B^{CL}(\mathbf{c}|\mathbf{c}') = \frac{e^{-\frac{(c_x-(1-\alpha)c'_x)^2+(c_y-(1-\alpha)c'_y)^2}{2\alpha(2-\alpha)\theta_w}}}{2\pi\theta_w\alpha(2-\alpha)} \frac{c_z e^{-\frac{c_z^2+(1-\alpha_n)c_z^2}{2\alpha_n\theta_w}}}{\alpha_n\theta_w} I_0\left(\frac{\sqrt{1-\alpha_n}c_z c'_z}{\alpha_n\theta_w}\right), \quad (\text{A.2})$$

580 where  $\theta_w = k_B T_w/m$  and  $I_0$  is the modified Bessel function of first kind and zeroth order. Here  $\alpha_n$  is the accommodation coefficient associated to the normal kinetic energy.

It is possible to show that the correlation parameters are connected to the accommodation coefficients  $\alpha$ . Let us take the Cercignani-Lampis kernel for example. The function  $B^{CL}(\mathbf{c}|\mathbf{c}')$  is the conditional probability function of reflected velocity  $\mathbf{c}$  for given incoming velocity  $\mathbf{c}'$ . The joint probability  $B^{CL}(\mathbf{c}, \mathbf{c}')$  can be computed by

$$B(\mathbf{c}, \mathbf{c}') = B(\mathbf{c}|\mathbf{c}')p^{in}(\mathbf{c}') \quad (\text{A.3})$$

and the correlation parameters between the tangential velocities  $c_x, c'_x$  is

$$\rho_{c'_x c_x} = \frac{\int B(\mathbf{c}, \mathbf{c}')c'_x c_x d\mathbf{c}d\mathbf{c}'}{\sqrt{\int (c_x)^2 p^{ref/out}(\mathbf{c})d\mathbf{c}} \sqrt{\int (c'_x)^2 p^{in}(\mathbf{c}')d\mathbf{c}'}} \quad (\text{A.4})$$

In equilibrium, the incoming and the outgoing distributions  $p^{ref/out}(\mathbf{c}')$  and  $p^{in}(\mathbf{c})$  are identical to

$$p^{ref/out}(\mathbf{c}) = \sqrt{\frac{2\pi}{\theta_w}} |c_z| \mathcal{M}(\mathbf{c}), \quad p^{in}(\mathbf{c}') = \sqrt{\frac{2\pi}{\theta_w}} |c'_z| \mathcal{M}(\mathbf{c}') \quad (\text{A.5})$$

and

$$B^{CL}(\mathbf{c}, \mathbf{c}') = \frac{e^{-\frac{(c_x^2 - 2(1-\alpha)c_x c'_x + c_x'^2)}{2\alpha(2-\alpha)\theta_w}} e^{-\frac{(c_y^2 - 2(1-\alpha)c_y c'_y + c_y'^2)}{2\alpha(2-\alpha)\theta_w}} |c_z c'_z| e^{-\frac{(c_z^2 + c_z'^2)}{2\alpha_n \theta_w}}}{2\pi\theta_w \sqrt{\alpha(2-\alpha)} \cdot 2\pi\theta_w \sqrt{\alpha(2-\alpha)} \cdot \alpha_n \theta_w^2} \times I_0\left(\frac{\sqrt{1-\alpha} c_z c'_z}{\alpha_n \theta_w}\right) \quad (\text{A.6})$$

This corresponds in fact to two independent bivariate Gaussian for  $c_x, c'_x$  and  $c_y, c'_y$  with the same correlation  $1 - \alpha$  multiplied with a special distribution of  $c_z, c'_z$  (Bessel and exponential). Using A.4, A.5, A.6, we can show that

595  $\rho_{c'_x c_x} = 1 - \alpha$ .

Regarding the Maxwell kernel, at equilibrium we have

$$B^M(\mathbf{c}, \mathbf{c}') = (1 - \alpha)\delta(\mathbf{c} - \mathbf{c}'^s) \sqrt{\frac{2\pi}{\theta_w}} |c_z| \mathcal{M}(\mathbf{c}') + \alpha \frac{2\pi}{\theta_w} |c_z c'_z| \mathcal{M}(\mathbf{c}) \mathcal{M}(\mathbf{c}') \quad (\text{A.7})$$

Due to the fact that the second term gives zero  $c_x, c'_x$  correlation, we have

$$\begin{aligned} \int B^M(\mathbf{c}, \mathbf{c}') c_x c'_x d\mathbf{c} d\mathbf{c}' &= (1 - \alpha) \int \delta(\mathbf{c} - \mathbf{c}'^s) c_x c'_x \sqrt{\frac{2\pi}{\theta_w}} |c_z| \mathcal{M}(\mathbf{c}') d\mathbf{c} d\mathbf{c}' \\ &= (1 - \alpha) \int c_x^2 \sqrt{\frac{2\pi}{\theta_w}} |c_z| \mathcal{M}(\mathbf{c}) d\mathbf{c} \end{aligned} \quad (\text{A.8})$$

Again substituting this result into A.4, A.5, A.7, we can show that

600  $\rho_{c'_x c_x} = 1 - \alpha$

## Appendix B. Expression for saturation number density of methane

From experimental data and equation of state (EOS) for methane [35]

$$\ln \frac{\rho_{sat}^v}{\rho_c} = \sum_{i=1}^6 a_i \left(1 - \frac{T}{T_c}\right)^{p_i}, \quad \rho_{sat}^v = n_{sat}^v m_{CH_4} \quad (\text{B.1})$$

with

$$\begin{aligned} a_1 &= -1.8802840, & a_2 &= -2.8526531, & a_3 &= -3.0006480, \\ a_4 &= -5.2511690, & a_5 &= -13.191859, & a_6 &= -37.553961 \\ p_1 &= 0.354, & p_2 &= 5/6, & p_3 &= 3/2, \\ p_4 &= 5/2, & p_5 &= 25/6, & p_6 &= 47/6, \end{aligned} \tag{B.2}$$

and  $T_c = 190.564\text{K}$  and  $\rho_c = 162.66 \text{ kg/m}^3$ .

## 605 Nomenclature

### Abbreviations and Sets

$\mathcal{D}$  full analysis data set, containing velocity, penetration depth, and residence time for all particles

$\mathcal{D}_{evap}$  subset of the dataset  $\mathcal{D}$  for all evaporation events

610  $\mathcal{D}_{ref}$  subset of the data set  $\mathcal{D}$  for all reflection events

$BKS$  force field for silica proposed by Besst, Kamer, and Santen

$KBC$  Kinetic Boundary Condition

$LJ$  Lennard-Jones

$MC$  Monte Carlo

615  $MD$  Molecular Dynamics

$PDD$  Penetration Depth Distribution

$RTD$  Residence Time Distribution

### Other symbols

	$\alpha$	momentum/energy accommodation coefficient
620	$\alpha_c$	condensation coefficient
	$\alpha_e$	evaporation coefficient
	$\alpha_n$	accommodation parameter of the normal energy component
	$\alpha_t$	accommodation parameter of the tangential momentum
	$\mathbf{c}'$	incoming velocity of the gas phase at the interface
625	$\mathbf{c}$	outgoing velocity of the gas phase at the interface
	$\mathbf{c}^s$	mirror velocity of $\mathbf{c}$ with respect to the interface normal to $\hat{\mathbf{i}}_z$
	$\mathcal{M}$	Maxwell-Boltzmann distribution (or the Maxwellian)
	$\delta$	distance between the control plane and the liquid-vapor interface
	$\epsilon_{ij}$	depth of potential well or dispersion energy
630	$\gamma_n$	velocity correlation coefficient after n independent collisions
	$\lambda$	molecular mean free path of methane vapor
	$\rho_x^d$	evolution of correlation coefficients for the velocity component $x$
	$\rho_x^T$	evolution of correlation coefficients for the velocity component $x$
635	$\rho_{Q,Q'/\mathcal{A}}$	correlation coefficient between $Q(\mathbf{c})$ and $Q'(\mathbf{c}')$ , functions of velocity, for data belonging to data set $\mathcal{A}$
	$\sigma_{ij}$	distance at which the particle-particle potential energy $V_{ij}^{LJ}$
	$\tau$	residence time of the gas particle as it crosses the control plane from the gas phase to the liquid phase and back to the gas phase
	$\tau_c$	residence time threshold

640	$B(\mathbf{c}/\mathbf{c}')$	scattering kernel relating the distribution of incoming and outgoing particles
	$C$	energy conversion constant for the Coulombic term
	$d$	penetration depth of the gas particle from the control plane into the liquid phase
645	$d_c$	penetration depth threshold
	$f^{in}$	distribution function of incoming gas particles at a interface
	$f^{out}$	distribution function of outgoing gas particles at a interface
	$l_c$	characteristic length of the transition layer between the vapor-liquid phase
650	$m$	mass of the fluid molecule
	$N$	number of methane molecules in the system
	$n$	vapor number density
	$N_{col}$	number of independent collisions of a particle
	$n_{int}$	number density at the boundary between the liquid and vapor phases
655	$n_{sat}^{liq}$	saturated liquid number density
	$n_{sat}^v$	saturated vapor number density
	$n_w$	gas number density at the interface at temperature $T_w$
	$p^a$	normalized probability distribution function associated with the flux crossing the interface
660	$q_i$	coulombic charges of the atoms $i$

	$r_{cut}$	cutoff distance for force computation
	$r_{ij}$	distance between atoms $i$ and $j$
	$T$	system temperature at equilibrium
	$T_c$	critical point temperature
665	$T_{tp}$	triple point temperature
	$T_w$	Temperature of the solid wall (quartz substrate)
	$V_{ij}^{BKS}$	pair potential between two atoms $j$ and $i$ according to the BKS model
	$V_{ij}^{LJ}$	pair potential between two atoms $j$ and $i$ according to the Lennard-Jones (LJ) model
670	$X^*$	Reduced state parameters $X$ in Lennard-Jones units

### Physics constants

$k_B$  Boltzmann constant

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