Molecular Dynamics Simulation for
Microscope Insight of Liquid Evaporation on a Heated Surface

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Abstract Molecular dynamics (MD) simulation is a very effective tool that gives a microscopic insight into the mechanisms of complex physical phenomena. This paper uses MD simulation to study the evaporation of a liquid from a heated surface. As for the argon/platinum model, a group of simulations starts from a fixed lower wall with the temperature of 110K. In this system, argon molecule numbers of 784, 1200, 1440 are simulated respectively. Additional simulations for argon models are based on superheat conditions, which indicate that the variation of ultra-thin liquid film thickness is very small with the different numbers of argon molecules. Also, it shows that if the argon molecule numbers increase, the extra molecules accumulate near the cooling wall. In terms of the MD simulation for the water/magnesium model, water evaporates from a magnesium heating wall at different temperatures and an initial study has been carried out. Moreover, further and more accurate simulations will be improved in the near future.

Keywords: Molecular dynamics, Water, Evaporation, Magnesium, Argon

1. Introduction

In recent years, microscopic calculation approaches are frequently used to investigate the physical phenomena of fluid–solid interactions at the very small scale [1–8], particular methods include molecular dynamics (MD) and Monte Carlo (MC) simulation. Using non-equilibrium molecular dynamics (NEMD) simulation with a temperature gradient imposed, Xue et al. have demonstrated that the layering of a simple mono-atomic liquid does not have any significant effect on liquid–solid interfacial thermal resistance [1]. Freund studied a two dimensional (in the mean) liquid drop centred on a cold spot on an atomically smooth solid wall with evaporating menisci extending from it onto hotter regions of the wall [2]. Ohara and Suzuki did the numerical simulation on liquid argon (without vapour phase) between two solid walls and studied the intermolecular energy transfer at the solid–liquid interface [3]. Yi et al. performed MD simulations of the vaporisation phenomena of an ultra-thin layer of argon on a platinum surface. They simulated the entire vaporisation process for two temperature cases and the condensation process after complete evaporation [4]. The effects of surface wettability on the behaviour of liquid atoms near a solid boundary were also studied by using MD simulation methods [5, 6]. Wemhoff et al. explored a hybrid approach to investigate a thin liquid argon film on a solid surface by combining a deterministic MD simulation of the liquid regions with a stochastic treatment of the far-field vapour region boundary [7]. Liu [8] has employed the MC method to study Lennard-Jones liquid film and its vapour with a consideration of attractive and short-ranged wall potential near the liquid–solid interface.

From the previous studies noted above, it can be seen that the MD method is often used to investigate the chemical reactions in bioscience and physical phenomena of fluid-solid interactions at the nano scale. [9] Moreover, based on the MD investigations of the typical argon model, in the past few years, many people have started to apply the MD method to simulate the heat transfer processes of other fluids, such as water, CO_2 etc. Mitsuhiro Matsumoto [10-11], used the MD

method to simulate the phase change of argon, water, CO_2, and SO_2, in order to find the thermal properties of these fluids. Hans W. Horn et al [12] simulated the liquid-vapour phase change of water by using the TIP4P (transferable intermolecular potential function) model. Swaroop Chatterjee [13] used a simple point charge Statistical Process Control (SPC) model to investigate the thermodynamics, structure, dynamics and behaviour of water. Yang Zhen [14] investigated the structure and dynamic properties of water near an Au nano-particle under room temperature, so that this investigation presumed the heat transfer process between water and metal.

Although many people have made significant efforts on the heat transfer process by using the MD method, so far, compared with the MD studies of argon, the MD simulations based on water and organic working fluids with metals or alloys in the thermal area are still infrequent and are at the basic stage of the heat transfer study area.

Therefore, this paper aims to investigate the boiling process of water in order to simulate the phase change of heat pipes in the future based on Ji and Yan's works [15-16] of Pt-Ar MD simulations. However, in terms of this initial MD simulation, there are a few difficulties existing in the whole process, for example the reactions between molecules. Thus, for my early work, consideration will only be given for processes without any chemical reactions, which means the Mg alloy wall is just a heating wall and thus simulates the movement trend of water molecules under temperature rises. Further and more accurate simulation will be carried out in the future.

2. Methodology

Molecular dynamic simulation starts from a set of molecules occupying a region of space, with each assigned a random velocity corresponding to the Boltzmann distribution at the temperature of interest. The interaction of the molecules is prescribed, commonly in the form of a two-body potential energy, and the time evolution of the molecular positions is obtained by integrating Newton's equations of motion.

$$F_i = m_i a_i \tag{1}$$

Based on the integration over time, the behaviours of the molecules such as the averages of density, velocity, stress, temperature, fields etc. can be calculated.

The Lennard-Jones (L-J) potential formula is a general and important method for MD simulation, which is regarded as a suitable reference fluid for modelling properties of real fluids [8]. Generally, it shows the transitions between vapour-liquid, solid-liquid and solid-vapour phases and the critical and triple points, which is expressed as follow:

$$\phi_{ij}(r_{ij}) = 4\varepsilon_{ij}[c_{ij}(\frac{\sigma_{ij}}{r_{ij}})^{12} - d(\frac{\sigma_{ij}}{r_{ij}})^{6}]. \tag{2}$$

The first term of the equation is an arbitrary but convenient short-range repulsion which prevents overlap of the atoms in space; while the second term represents the attractive polarised interaction of neutral spherical atoms. r_{ij} is the intermolecular separation distance between particles i and j. ε_{ij} and σ_{ij} are the minimum energy and the zero energy separation distance relative to the pair, respectively. c_{ij} and d_{ij} are adjustable parameters which can be chosen to control the molecular interactions, for example, the wetting characteristic of fluid-solid interactions. For the distances smaller than σ_{ij}, the resulting force is repulsive; whereas it is attractive for larger distances.

In terms of argon simulation, the L-J formula gives accurate simulation for these non-polar molecules. The L-J potential is known to give a reasonably quantitative description of liquid argon, with parameters:

$\varepsilon = 1.67 \times 10^{-21}$ J,
$\sigma = 0.3405$ *nm*,
and $c = d = 1$.

With regards to the water MD simulation, although it belongs to polar molecules, the L-J potential still can be used as the general method for the following study. However, the

force fields are quite different to argon. According to previous research, [9-14,17] taking water as an example, there are mainly three kinds of force fields frequently used: central force (CF), transferable intermolecular potential function (TIPS) and the simple point charge (SPC).

The central force (CF)

CF force field is given by the expression

H^+ -H^+ *interaction:*

$$V_{HH}(r) = \frac{36.1345}{r} + \frac{18}{1 + \exp[40(r-2.05)]} - 17\exp[-7.61277(r-1.45251)^2] \tag{2}$$

O^{2-} -H^+ *interaction:*

$$V_{OH}(r) = -\frac{72.269}{r} + \frac{6.23403}{r^{0.19912}} - \frac{10}{1 + \exp[40(r-1.05)]} - \frac{4}{1 + \exp[5.49305(r-2.2)]} \tag{3}$$

O^{2-} - O^{2-} *interaction:*

$$V_{OO}(r) = \frac{144.538}{r} + \frac{26758.2}{r^{8.8591}} - 0.25\exp[-4(r-3.4)^2] - 0.25\exp[-1.5(r-4.5)^2] \tag{4}$$

where r is distance between molecules.

Transferable intermolecular potential function (TIPS)

The TIPS force field evolved from the Monte Carlo method and it has been constructed with a rigid theoretical model.

$$V_{AB} = \sum_a^A \sum_b^B (\frac{q_a q_b e^2}{r_{ab}} + \frac{A_a A_b}{r_{ab}^{12}} - \frac{C_a C_b}{r_{ab}^6}) \tag{5}$$

where a and b represent atoms in different molecules. q_0 =-0.80, q_H =0.40 is charge of oxygen atom and charge of hydrogen atom respectively. Based on the force field above, a

series of similar force fields have been approached, such as TIP4P, TIP5P and others.

Simple point charge (SPC)

The water model is also assumed as a rigid theoretical model:

O^{2-} - O^{2-} *interaction:*

$$V_{OO}(r_{OO}) = \frac{q_O q_O e^2}{r_{OO}} + \frac{A}{r_{OO}^{12}} - \frac{C}{r_{OO}^6} \tag{6}$$

O^{2-} -H^+ *interaction:*

$$V_{OH}(r_{OH}) = \frac{q_O q_H e^2}{r_{OH}} \tag{7}$$

H^+ -H^+ *interaction:*

$$V_{HH}(r_{HH}) = \frac{q_H q_H e^2}{r_{HH}} \tag{8}$$

It can represent reasonable radial distribution function and thermodynamic properties by using SPC model. However, the SPC model leads to a large deviation with diffusion constant between theoretic data and experimental data (normally 200%-300%) [17]. Moreover, the following table shows a comparison of the parameters between SPC and TIPS models.

Table1: Parameters comparison of SPC and TIPS models.

Parameters	SPC	TIP3P	TIPS2	TIP4P
$r_{(OH)}$ / Å	1.0	0.9572	0.9572	0.9572
$\angle$HOH/(˚)	109.47	104.52	104.52	104.52
A×10⁻³ /(Å ^{12}·kcal/mol)	629.4	582.0	695.0	600.0
C/(Å ^{6}·kcal/mol)	625.5	582.0	695.0	600.0
q_O	-0.82	-0.834	0.0	0.0
q_H	0.41	0.417	0.535	0.52
q_m	0.0	0.0	-1.07	-1.04
$r_{(OM)}$ / Å	0.0	0.0	0.15	0.15

Based on the comparison above, TIP4P model will be used in this paper.

In addition, as for the integration time step, it can be selected as follows: the time step should be smaller than 10% of the system longest movement period. According to Infrared spectrometry method, the fastest frequency of the vibration is $v = 1.08 \times 10^{14} s^{-1}$ and period of the vibration can be calculated as $T = 1/v = 0.92 \times 10^{-14} s$ [17]. Therefore, the integration time step can be determined as $v \times 10\% = 0.92 \times 10^{-14} \times 10\% = 0.92 \times 10^{-15} s \approx 1 fs$.

3. Results and discussion

In the study of liquid–vapour–solid systems near the triple-phase contact line of flow boiling in a microchannel, Ji and Yan carried out MD simulation of Argon and found that systems with different numbers of argon molecules, the film thickness remains almost the same if the heater temperature is constant. Fig. 1 shows the ultra-thin liquid film of the system with different numbers of argon molecules under the same temperature conditions. For a fixed lower wall temperature at 110 K, the systems, respectively, with 784, 1200 and 1440 molecules are simulated. It can be seen that for a given superheat, the variation of ultra-thin liquid film thickness with different number of molecules is very small. With the increase of argon number, extra molecules are accumulated near the cooling wall (not shown in Fig. 1).
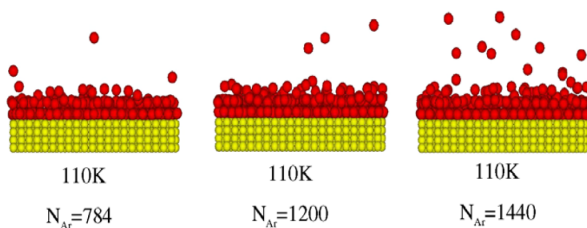

Fig. 1: Snapshots of different Ar molecule number system.

Additional simulations also mentioned that the liquid film thickness decreases with the increase of wall heating temperature. Fig. 2 shows the liquid film of a system of 1200 molecules under different temperature. When the heating temperature reaches 210 K, the liquid film still exists but its thickness is decreased to the order of only one layer of argon molecules.
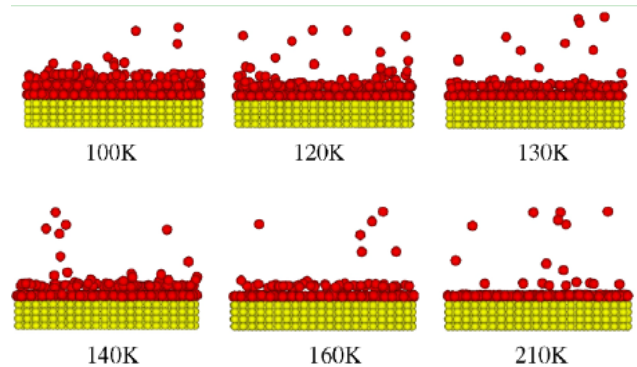

Fig. 2: Snapshots of 1200 Ar at different heat temperatures.

As for the water-magnesium model, regarding this initial simulation, the TIP4P model was chosen for the water model and an Mg wall was used in a hexagonal close-packed (hcp) lattice structure. The size of the computational domain is 5nm×5nm×8nm, which contains the magnesium atoms solid wall and water molecules. The Mg wall is placed at $z=0nm$ and the initial system temperature is the same as the experimental starting temperature (34ºC). The domain is presented in Fig. 3 and relevant time step set up as 1 fs.
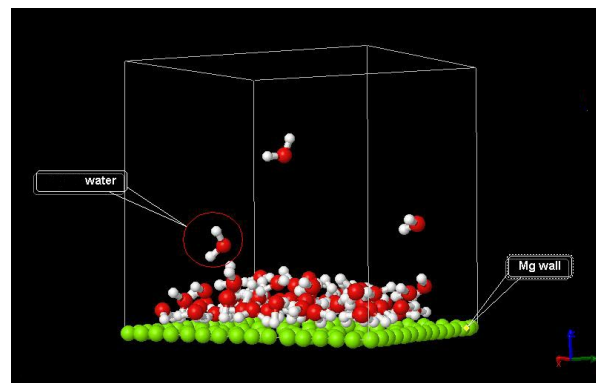

Fig. 3: Sketch of initial domain.

3D Snapshots of the computational domain are shown at different temperatures in Figure 4. The Mg wall atoms are denoted by the circle symbols in green, the H atoms and O atoms forming the liquid film are shown in silver and

red respectively. Fig. 4 (a) presents the equilibrium period at the start. As the operating temperature increases, the liquid water molecules become vapour molecules and keep rising, then they escape from liquid film (see Fig. 4 (b) & (c)). Fig. 4 (c) and (d) illustrates the evaporation process of the water liquid film. From this process, it can be seen that the stable system is distorted with the temperature growth and then becomes unstable; finally the system becomes saturated when the temperature of the heated wall passes the saturated point and boiling starts. Meanwhile, Fig. 4 (d) also indicates that under the Lennard-Jones [33] potential, there exists a gap between the H_2O liquid film and the Mg heated wall. Although this initial simulation does not provide accurate density value changes, the trend still clearly shows that with rising temperature, the more liquid vaporized the more vapour molecules presented in vapour phase.
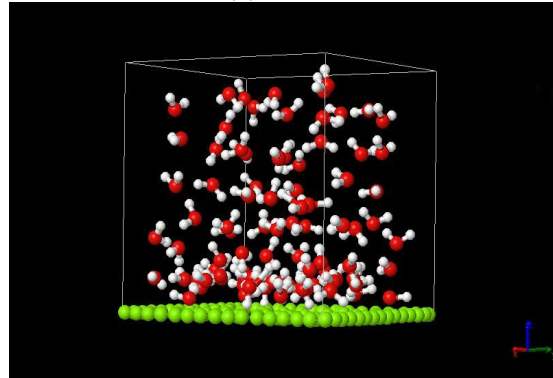

(c) 90 ℃
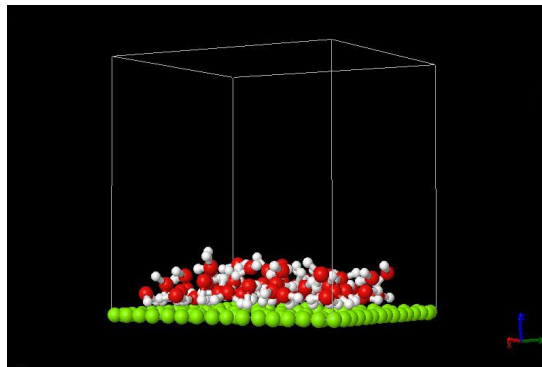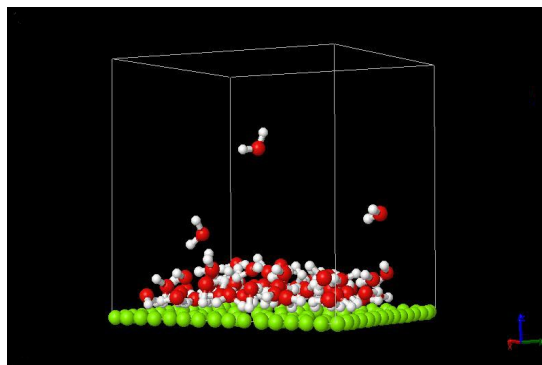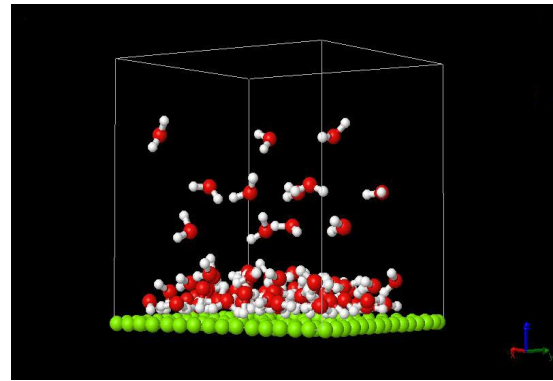
(d) 100 ℃

Fig. 4: Snapshots of water 3D simulation domain at different heating temperatures.

(a) 34 ℃

(b) 55 ℃

From the Ar-Pt studies (Ji's work), we know that the liquid film thickness is defined as the distance from the wall to the centre of liquid–vapour interfacial region and can be calculated from the density distributions. In Fig. 5 which is the density distribution of argon molecules, it can be seen that the densities in the z direction exhibit an oscillation structure and different regions of the liquid, interface and vapour. Fig. 5 shows that the region of liquid–vapour interface is specified by density distributions which will lead to some uncertainty; and also points out that the liquid film thickness is within 2 nm and has a tendency to decrease with an increase of heating temperature. This means that more liquid molecules may escape from the attractions of solid as the heater wall temperature continue to rise.

I, V: Liquid film
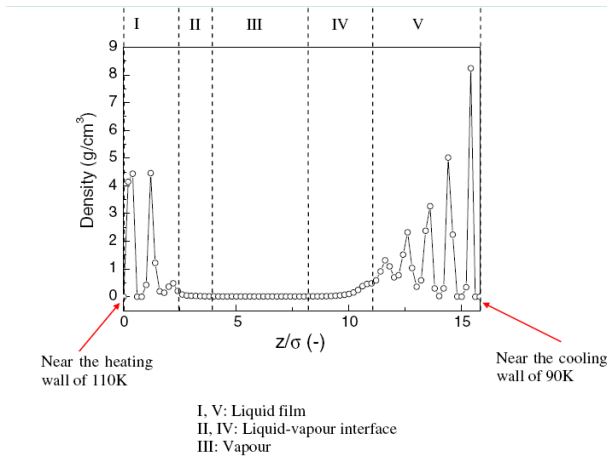II, IV: Liquid-vapour interface
III: Vapour

Fig. 5: Density distribution of 1200 Ar
molecules system (90–110 K).

Compared with Ar-Pt density chart, indicated in Fig. 6, is the variation in the number density of water along the height in Z direction. It can be seen that with the temperature increase, the number density of water molecules decrease gradually in the range of height from 0.1nm to 1.2nm, which shows that the liquid molecules reduces with more evaporation happen. Moreover, at a height of 1.2nm, the number density presents a huge difference, which can be recognized as the boundary between the liquid phase and the vapour phase. According to some literature when compared with this result, we might consider that the liquid film exists around this position. And then, after 1.2nm in height the liquid and vapour interface should be found, and then the vapour phase. Thus, the whole trend of density variation is similar with the change shown in previous sketches.
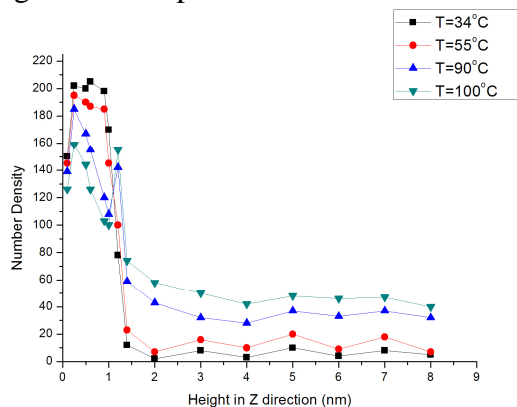

Fig. 6: Variation of water molecules number

density with different height in Z direction.

4. Conclusion

According to the MD simulations of argon and water, which are based on NEMD, some conclusions can be made as follow:

1. For the Ar-Pt system, under the system with different numbers of argon molecules, the film thickness remains almost the same if the heater temperature is constant. Moreover, the liquid film thickness decreases with the increase of wall heating temperature if molecule numbers are constant.
2. For the H_2O-Mg system, the liquid film position and vapour phase can be estimated based on NEMD.
3. Therefore, comparing these two systems, it can be seen that the trends of liquid film changes are similar. The liquid film thickness of H_2O-Mg system decreases when heating temperature increases as well.

However, compared with the Ar-Pt work, this initial study of H_2O-Mg MD simulation is not sufficient to reach firm conclusions about the use of magnesium alloys in heat pipes. Therefore, further work will be carried out using MD simulation, which will involve more detailed simulation and further accuracy correction.

Nomenclature

A   constant
a   acceleration
B   Constant
C   Constant
F   force, N
M   centre of mass
m   mass
q   charge
r   radius
V   force

Greek symbols

ϕ potential energy
ε energy parameter of L-J potential
σ length parameter of L-J potential
σ surface tension

Subscripts

a   atom on different H_2O molecules

b   atom on different H_2O molecules

c   atom on different H_2O molecules

OO   force between two oxygen atoms

OH   force between hydrogen and oxygen atoms

HH   force between two hydrogen atoms

OM   force between oxygen atom and centre of mass

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