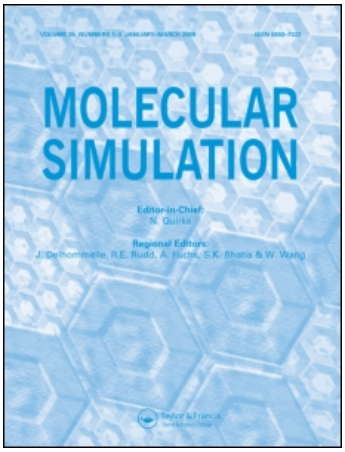

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular dynamics simulation of thermal conductivity of an argon liquid layer confined in nanospace

Qi-Xin Liu[a]; Pei-Xue Jiang[b]; Heng Xiang[b]
[a] School of Civil Engineering and Architecture, Chongqing University of Science and Technology, Chongqing, P. R. China [b] Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing, P. R. China

Online publication date: 24 November 2010

To cite this Article Liu, Qi-Xin , Jiang, Pei-Xue and Xiang, Heng(2010) 'Molecular dynamics simulation of thermal conductivity of an argon liquid layer confined in nanospace', Molecular Simulation, 36: 13, 1080 — 1085
To link to this Article: DOI: 10.1080/08927022.2010.504773
URL: http://dx.doi.org/10.1080/08927022.2010.504773

Molecular Simulation
Vol. 36, No. 13, November 2010, 1080–1085

Taylor & Francis
Taylor & Francis Group

Molecular dynamics simulation of thermal conductivity of an argon liquid layer confined in nanospace

Qi-Xin Liu[a], Pei-Xue Jiang[b]* and Heng Xiang[b]

[a]*School of Civil Engineering and Architecture, Chongqing University of Science and Technology, Chongqing 401331, P. R. China;* [b]*Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Thermal Engineering, Tsinghua University, Beijing 100084, P. R. China*

(*Received 10 November 2009; final version received 25 June 2010*)

Molecular dynamics simulations were used to study the thermal conductivity of liquid argon ultra thin films confined between two plates spaced several nanometres apart. The research focused on the dependence of the liquid argon thermal conductivity on the liquid layer thickness and the interaction between liquid and solid. The results show that the thermal conductivity of liquid argon ultra thin films confined between two plates depends on the distance between the two plates and the existence of solid-like liquid layering at the liquid–solid interface and the average migration frequency of all liquid molecules. Stronger interactions between the liquid and the solid resulted in a larger number of atoms in the solid-like liquid layer along the surface and hence smaller thermal resistance between the liquid and the solid. However, as the strength of the interaction with the solid increased, the thermal conductivity was reduced due to fewer atoms near the hot solid boundary and less molecular migration.

Keywords: molecular dynamics simulation; thermal conductivity; argon liquid; nanospace

1. Introduction

Micro- and nanofluidics studies have recently attracted considerable attention due to the growing interest in micro/nano systems in many fields. The properties of liquids confined in nanoscale spaces are important in many fields such as in biological systems. A liquid layer confined between two walls spaced several nanometres apart has different properties than the bulk liquid, such as the velocities and density which are dependent on the liquid's hydrophobicity. In addition, the energy transfer is related to the liquid molecular mobility, so the thermal conductivities of liquid layers confined in nanoscale spaces and the effect of molecular migration frequency on the thermal conductivity need further study.

Naguib et al. [1] observed the behaviour of water confined in nanometre channels of closed carbon nanotube (CNT) to find that the fluid motion of water in ultra thin channels, such as carbon nanotubes, is greatly retarded compared to that in macroscale channels which poses new challenges for modelling and device development. Direct observations or measurements of properties for liquids confined between ultra close plates are very difficult, so molecular dynamics simulations are widely used to study the nanoscale transport phenomena. Kumar et al. [2] performed molecular dynamics simulations of 512 water-like molecules interacting via the TIP5P potential and confined between two smooth hydrophobic plates separated by 1.10 nm. They found that the anomalous thermodynamic properties are shifted to lower temperatures relative to the bulk by about 40 K with different crystalline structures for 0.7 and 1.10 nm spacing between plates that have no counterparts in the bulk system. Giovambattista et al. [3] performed molecular dynamics simulations of water confined in nanoscale spaces to show how the water density varied near the surface. In the microscopic point of view, the energy transfer between the liquid and the surface is related to the liquid's structure near the surface which is needed to accurately predict the thermal conductivity of liquids confined between ultra close plates. Liu et al. [4] investigated the fluid structure and transport properties of water confined in single-walled carbon nanotubes and found that the axial thermal conductivity of water in CNTs is obviously larger than that of the bulk. In addition to water, Lennard-Jones (LJ) fluids have been widely studied by molecular dynamics simulations, with many studies [5–7] on their transport properties. Botelho et al. [8] studied the thermal conductivity of liquid argon using NEMD to show that the thermal conductivity in the fluid phase is independent of size. However, their studies only focused on thermal conduction in the liquid itself and did not consider the effects of the solid in contact with the liquid. Sofos et al. [9] studied the transport properties of liquid argon in krypton nanochannels using equilibrium molecular dynamics simulations, with their studies on the thermal

*Corresponding author. Email: jiangpx@tsinghua.edu.cn

ISSN 0892-7022 print/ISSN 1029-0435 online

DOI: 10.1080/08927022.2010.504773
http://www.informaworld.com

conductivity based on Green–Kubo's theory, which is based on equilibrium systems.

This paper presents molecular dynamics simulations of the thermal conductivity of an LJ liquid confined between two plates with emphasis on how the interaction between the solid and fluid and the liquid layer thickness affect the thermal conduction.

2. Physical–mathematical model and simulation method

In MD methods, the thermal conductivity is computed using either equilibrium MD which uses the Green–Kubo method or non-equilibrium MD which uses the so-called 'direct method'. However, the real thermal conduction is based on the temperature gradient which leads to the non-equilibrium state in the substance. The non-equilibrium MD method imposes a temperature gradient across the simulation cell which is analogous to experimental conditions. So, the non-equilibrium MD method is used in the present work.

The simulation model is illustrated in Figure 1. The model has periodic boundary conditions in the z- and y-directions. Along the cross-plane direction, the x-direction, each atom is assigned a type according to its spatial position as 'fixed', 'hot solid', 'liquid' or 'cold solid'. The fixed atoms are stationary during the whole simulation and serve as adiabatic boundary conditions. The 'hot solid' and 'cold solid' atoms are the temperature control boundary conditions where the velocities of each atom are controlled to maintain the desired temperature. These hot and cold regions apply a temperature gradient to the liquid to simulate the real thermal conduction progress.

In this paper, the argon liquid was studied, the molecular simulations used a simple model of the liquid and solid with both described by the LJ interatomic potential written as

$$\phi(r_{i,j}) = 4\varepsilon\left[\left(\frac{\delta}{r_{i,j}}\right)^{12} - \left(\frac{\delta}{r_{i,j}}\right)^{6}\right]. \tag{1}$$

The strength of the interactions between the solid atoms, ε_{ss}, was assumed to be eight times larger than between the liquid atoms, ε_{ll}. The binding energy for the solid–liquid interactions was given by $\varepsilon_{is} = c\sqrt{8}\varepsilon_{ll}$, where $\sqrt{8}$ corresponds to the traditional form for the interaction potentials of $\varepsilon_{is} = \sqrt{\varepsilon_{ss}\varepsilon_{ll}}$ and c corresponds to the interaction strength between the solid and the liquid. When c is 1.0, the simulation corresponds to a total wetting between the solid and the liquid. When c is zero, the simulation corresponds to a non-wetting surface. The value of δ was the same for the liquid and the solid.

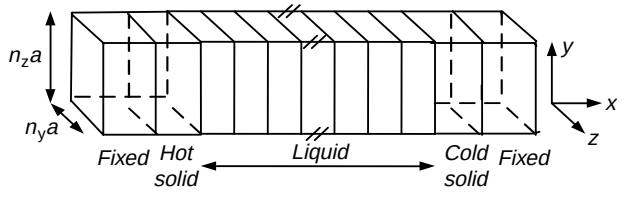

Figure 1. Simulation model.

The temperature distribution was obtained by dividing the entire film into layers along the x-direction, the number of layers depends on the thickness of the liquid argon layer. In this paper, the temperature of each layer was calculated using the formula

$$T = \frac{\sum_{i=1}^{N} m_i v_i^2}{3Nk_B}, \tag{2}$$

where N is the number of atoms in the layer. The heat flux was calculated from the change in the kinetic energy of the hot solid and cold solid atoms during each simulation time step,

$$\Delta E = \pm\frac{1}{2}m\sum(v_{old}^2 - v_{new}^2). \tag{3}$$

The minus sign is for the higher temperature boundary while the plus sign is for the lower temperature boundary.

Based on the Fourier law, the thermal conductivity of the film is

$$k = \frac{\Delta E_{hot} + \Delta E_{cold}}{2\tau A|\nabla T|}, \tag{4}$$

where τ is the simulation time, A is the cross-sectional area and $|\nabla T|$ is the absolute value of the temperature gradient in the cross-plane direction. The simulations used a simulation time of 2000 ps and the cross-section is 10×10 solid lattice layers. The temperature of hot solid atoms was set to 130 K, with the cold solid atoms at 110 K. The other critical input parameters for the simulations, which correspond to the values for argon, are listed in Table 1.

Table 1. Simulation parameters.

Parameter	Value
LJ well depth ε_{ll}	1.67×10^{-21} J
LJ equilibrium separation	3.4×10^{-10} m
Boltzmann's constant	1.38×10^{-23} J/K
Argon atomic mass	66.3×10^{-27} kg
Unit cells in each hot or cold region	4
Unit cells in each fixed region	3

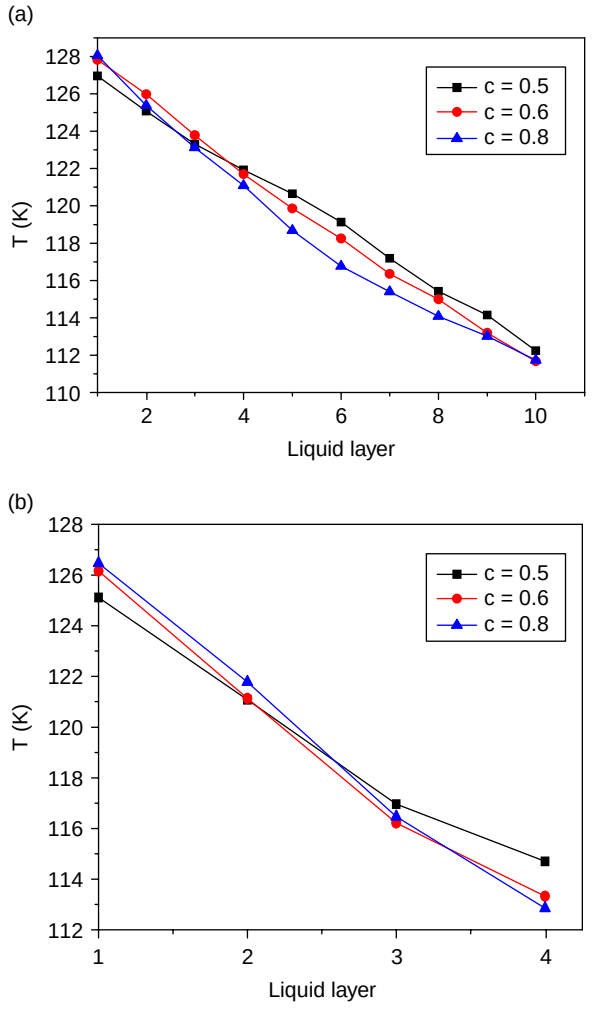

Figure 2. Temperature profiles for argon liquid film with different wetting conditions between the liquid and the solid: (a) 5.78 nm-thick argon liquid film and (b) 2.44 nm-thick argon liquid film.

3. Simulation results

3.1 *Temperature profile in the liquid argon*

The liquid temperature profiles obtained for 5.78 and 2.44 nm-thick argon liquid films with three wetting cases are shown in Figure 2. The temperature in the profiles is the averaged value of 200,000 simulation time steps.

From Figure 2, we can find two characteristics for temperature profiles of argon liquid film confined in two plates several nanometres apart. Firstly, unlike the solid argon thin films, all of these temperature profiles are not very linear and show some fluctuations. If the film is thicker, the fluctuation is more obvious. We consider the fluctuations as the result of liquid's higher mobility. Secondly, the temperature of the hot end is actually lower than the set temperature, and the temperature of the cold end is higher than its set temperature. This phenomenon is physically reasonable, since when the hot and cold boundaries are controlled at desired temperatures, energy is 'input' into the liquid through the hot solid and 'output' out of the liquid from the cold solid. The temperature difference is, therefore, a natural result of the heat transfer. However, one notable phenomenon is that the difference between the actual temperature and the set temperature is also dependent on the solid–liquid interaction. When the solid–liquid interaction is stronger, the temperature of liquid argon adjacent to the solid is closer to the set value due to the stronger energy exchange.

3.2 *Thermal conductivity of the liquid argon film*

The thermal conductivities of 5.78, 3.67 and 2.44 nm-thick argon liquid films were simulated for four different interactions between the solid and the liquid by changing the value of c in Equation (1) to 0.4, 0.5, 0.6 and 0.8. Larger c represents stronger interactions between the liquid and the solid. The thermal conductivities of these liquid argon films based on the Fourier law are listed in Table 2. It is clearly shown that the thermal conductivity depends on both the thickness of the film and the liquid's interaction with the solid. When the strength of the liquid's interaction with the solid is identical, the thermal conductivity of the liquid argon film increases with the increase in the film's thickness. On the other hand, for the argon liquid film at a certain thickness, stronger liquid's interaction with the solid causes higher thermal conductivity. Further, the film's thermal conductivities in our all simulation cases are smaller than the corresponding value of liquid argon at normal space, which means that the thermal conductivity of the argon liquid film confined in nanospace also shows a size effect.

3.3 *Molecular distribution*

Due to the close relationship between the liquid's properties including the thermal transport ability and the

Table 2. Thermal conductivity of liquid argon film for various film thicknesses and solid–liquid interactions.

c	0.4	0.5	0.6	0.8	Bulk
k (W/m K) for 5.78 nm thick	0.074	0.072	0.062	0.060	0.0845
k (W/m K) for 3.67 nm thick	0.061	0.055	0.052	0.050	
k (W/m K) for 2.44 nm thick	0.050	0.048	0.038	0.036	

liquid's molecular motion, the researches on the liquid's molecular distribution in nanospace are very significant. For liquid molecules immediate to the solid, their distribution is neither as scattered as it is in normal space nor as regular as solid atoms, these molecules are usually named as solid-like layer.

Yu et al. [10] observed molecular layering in a liquid at a solid–liquid interface using X-ray reflectivity. In our study, the liquid layering at the solid–liquid interface is shown by the x–z projection of the atomic configurations of the liquid and solid in Figure 3. The liquid layering is circled in Figure 3. It is clearly shown that the stronger interactions between the solid and the liquid order the liquid layer to look more like the solid.

Figure 4 shows the number of atoms profiles for 2.44 nm-thick and 5.78 nm-thick films with different values of c. For two cases shown in the figure, the number near the solid surface clearly increased. The stronger interactions between the solid and the liquid result in more liquid molecules near the solid. The liquid molecule number along the temperature gradient is very uneven with more liquid molecules at the cold end and few liquid molecules at the hot end, because the liquid layer mobility at lower temperature is less than at higher temperature.

Xue et al. [11] suggested that the solid-like liquid layer does not affect the thermal conductivity. However, our

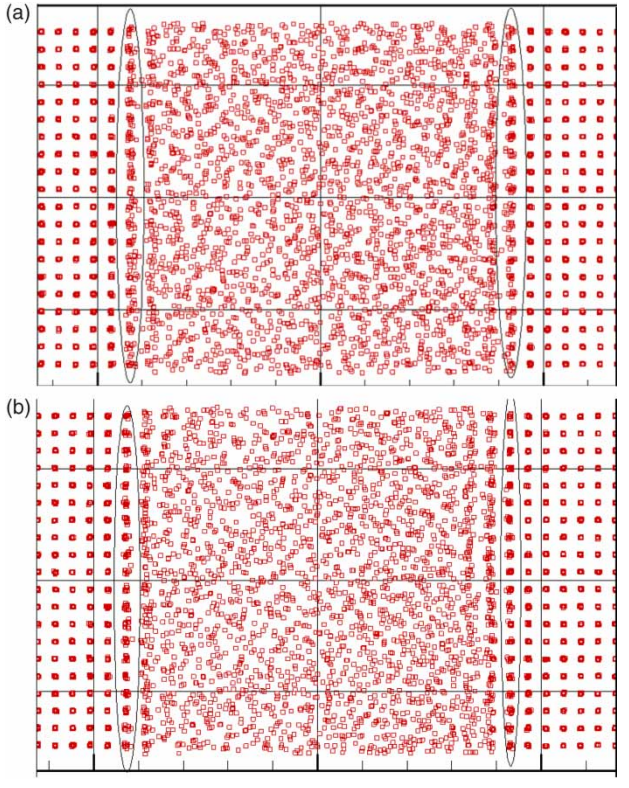

Figure 3. x–z projection of the atomic configuration for various liquid–solid interactions: (a) $c = 0.5$ and (b) $c = 0.8$.

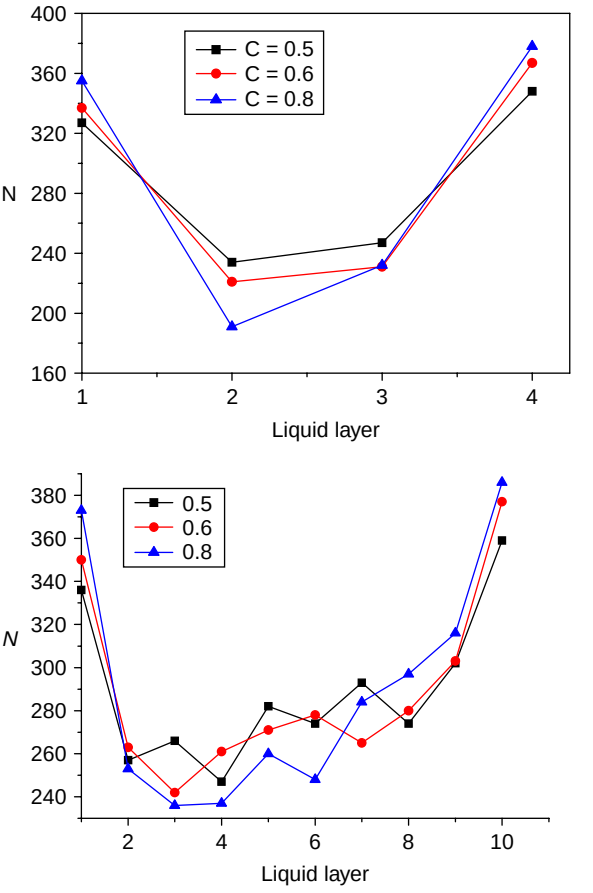

Figure 4. Atom distribution for 2.44 nm-thick (a) and 5.78 nm-thick (b) films with various values of c.

simulations show that the thermal conductivity of the liquid thin film is affected by the liquid's hydrophobicity. The simulation results shown in Figure 2 illustrate that near both solid surfaces when c is larger, the temperature of the liquid layer is closer to the set value. Thus, stronger interactions between the liquid and the solid reduce the thermal resistance between the liquid and the solid. However, Figure 4 shows that increases in the interaction force between the liquid and the solid decrease the number of atoms near the hot boundary. Few atoms result in less energy transport, so the thermal conductivity of the whole liquid argon film decreases as interactions between the solid and the liquid become stronger.

3.4 *Molecular migration frequency*

Unlike atom's vibration around the lattice equilibrium site in the solid, the liquid argon atoms can move freely in the space. The liquid molecular movements consist of vibration around one certain place and migration process in the whole space, so the molecular migration frequency plays an important role in the liquid's thermal conduction.

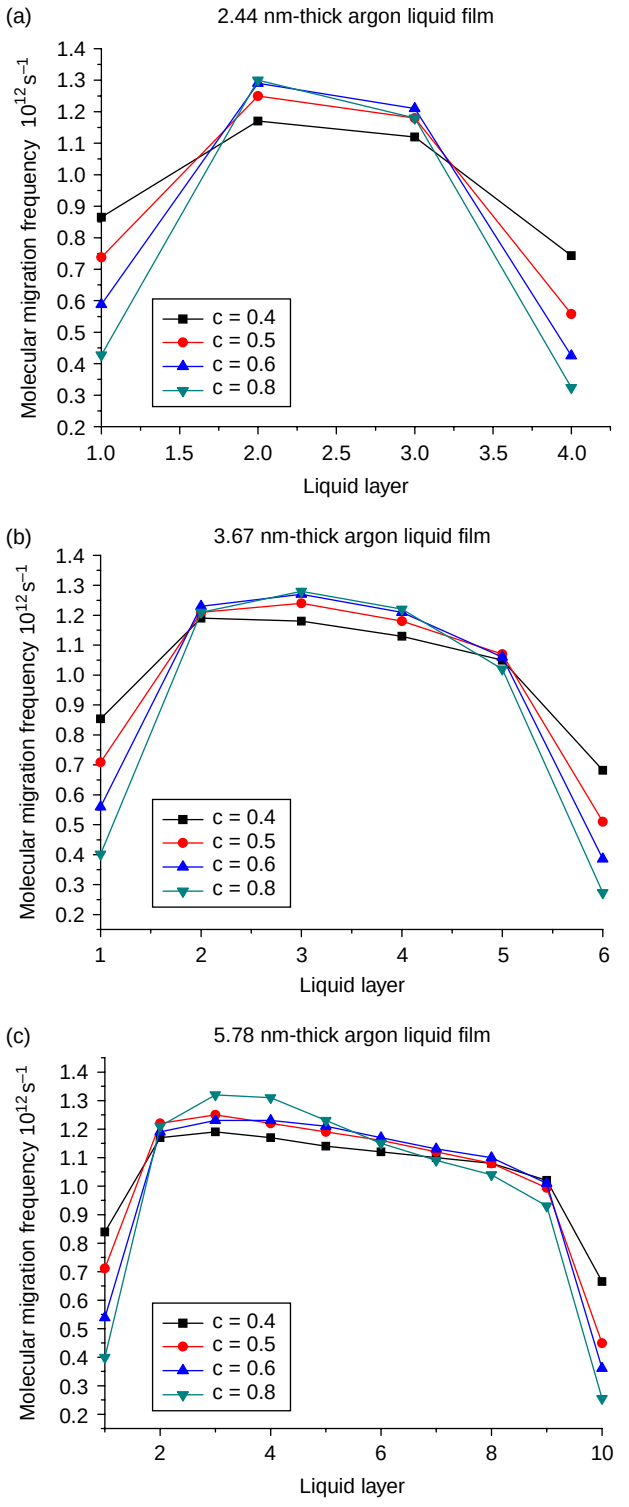

Figure 5. Molecule's migration in argon liquid films with different thicknesses and different solid–liquid interaction parameters.

In our simulations, the liquid argon molecular migration frequency was also recorded to study the effect of liquid argon molecular migration on the thermal conductivity.

Table 3. Thermal migration frequency ($10^{12}\,s^{-1}$) of the liquid argon molecule for various film thicknesses and solid–liquid interactions.

c	0.4	0.5	0.6	0.8
5.78 nm thick	1.05	1.04	1.02	0.994
3.67 nm thick	1.01	0.987	0.953	0.901
2.44 nm thick	0.975	0.932	0.878	0.808

In our simulations, if one liquid argon molecule's displacement is larger than 0.25 times the lattice constant, we consider that this molecule migrates from one place to another place and its migration frequency increases by 1. Figure 5 shows the molecule's migration in argon liquid films with different thicknesses and different solid–liquid interaction parameters. We divide the entire liquid argon film into several layers and the mean migration of molecule frequency in each layer is calculated. From Figure 5, it was seen that the molecule's migration frequency in each layer differs from each other. In addition to layers adjacent to the solid surface, the molecule's migration frequency in each layer shows the trend of decreasing with the decrease in temperature, which corresponds to the law that higher temperature causes faster molecular movements. For molecules in layers adjacent to the solid surface, a stronger interaction between the liquid and the solid surface leads to lower molecular migration frequency, which illustrate that a stronger interaction between the liquid and surface causes less mobility of liquid molecules adjacent to the solid surface. The average liquid molecular migration frequencies of the whole film are listed in Table 3. With the combination of Table 2, we can find that the liquid film with larger average molecule migration frequency has higher thermal conductivity which means that the thermal conductivity increases with the increase in molecular migration frequency. It can then be deduced that when the interactions between the liquid and the solid surface become stronger, the migration frequencies of molecules in liquid layers adjacent to the solid surface decline and further weaken the thermal conduction of the whole film.

4. Conclusions

Molecular dynamics simulations were used to study the thermal conductivities of liquid argon ultra thin films confined between two plates. The results show that the thermal conductivity of the thin argon liquid films depends on both the film thickness and the interactions between the liquid and the solid and increases with the strength of liquid molecular migration. In our studies, the thermal conductivity of the thin argon liquid film increases with the thickness. The results show that the liquid layering at the liquid–solid interface affects the thermal conductivity.

The number of atoms in the liquid layers near the solid surface is dependent on the temperature and the interactions between the liquid and the solid. Stronger interactions result in smaller thermal resistances between the liquid and the solid but also in few atoms near the hot solid and lower molecular migration frequency, which reduces the thermal conductivity of the liquid film.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (No. 50676047) and the Tsinghua Basic Research Foundation (No. JCpy2005049).

References

[1] N. Naguib, H. Ye, Y. Gogotsi, and A.G. Yazicioglu, *Observation of water confined in nanometer channels of closed carbon nanotubes*, Nano Lett. 4(11) (2004), pp. 2237–2243.

[2] P. Kumar, S.V. Buldyrev, F.W. Starr, N. Giovambattista, and H.E. Stanley, *Thermodynamics, structure, and dynamics of water confined between hydrophobic plates*, Phys. Rev. E 72 (2005), 051503.

[3] N. Giovambattista, P.G. Debendetti, and P.J. Rossky, *Hydration behavior under confinement by nanoscale surfaces with patterned hydrophobicity and hydrophilicity*, J. Phys. Chem. C 111 (2007), pp. 1323–1332.

[4] Y. Liu, Q. Wang, T. Wu, and L. Zhang, *Fluid structure and transport properties of water inside carbon nanotubes*, J. Chem. Phys. 123 (2005), 234701.

[5] M.F. Pas and B. Zwolinski, *Computation of the transport coefficients of binary mixtures of argon–krypton, krypton–xenon, and argon–xenon by molecular dynamics*, Mol. Phys. 73 (1991), pp. 483–494.

[6] R. Vogelsang and C. Hoheisel, *Thermal conductivity of a binary-liquid mixture studied by molecular dynamics with use of Lennard-Jones potentials*, Phys. Rev. A 35 (1987), pp. 3487–3491.

[7] G.A. Fernandez, J. Vrabec, and H. Hasse, *A molecular simulation study of shear and bulk viscosity and thermal conductivity of simple real fluids*, Fluid Phase Equilibr. 221 (2004), pp. 157–163.

[8] D.F. Botelho, P.S. Branicio, and J.P. Rino, *Thermal conductivity in nanoscale Lennard-Jones systems: Size effects in the fluid and solid phases*, Defects Diffusion Forum 258–260 (2006), pp. 310–315.

[9] F. Sofos, T. Karakasidis, and A. Liakopulos, *Transport properties of liquid argon in krypton nanochannels: Anisotropy and non-homogeneity introduced by the solid walls*, Int. J. Heat Mass Transfer 52 (2009), pp. 735–743.

[10] C.J. Yu, A.G. Richter, A. Datta, M.K. Durbin, and P. Dutta, *Molecular layering in a liquid on a solid substrate: An X-ray reflectivity study*, Phys. B 283 (2000), pp. 27–31.

[11] L. Xue, P. Keblinski, S.R. Phillpot, S.U.-S. Choi, and J.A. Eastman, *Effect of liquid layering at the liquid–solid interface on thermal transport*, Int. J. Heat Mass Transfer 47 (2004), pp. 4277–4284.