1 Interface Resistance and Thermal Transport in Nano-Confined Liquids

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1.1 INTRODUCTION

Miniaturization of microelectronic device components and the development of nano-electromechanical systems require advanced understanding of thermal transport in nano-materials and devices, where the atomic nature of matter becomes important and the validity of well-known continuum approximations becomes questionable [1]. In the case of semiconductors and insulators, heat is carried primarily by vibrations in the crystal lattice known as phonons. Phonon transport is classically studied by lattice dynamics based on harmonic wave theory in the frequency space. However, the anharmonic behaviors forming in a crystal structure cannot be described with this theory. Alternatively, the coupled motions of the atoms in real space can be modeled by molecular dynamics (MD), which provides the natural formation and transport of phonons via vibrations in the crystal lattice. Hence, MD has been widely employed to model phonon transfer in nanostructures and channels [2,3].

The performance and reliability of aforementioned devices strongly depend on the removal of heat either to the ambient or to a coolant. In such cases, phonon transport observed at the interfaces of nanoscale device components and surrounding/conf red f uid, or at the interfaces of suspended nanoparticles and f uid medium in nano- f uidic coolants plays a critical role. At such interfaces, heat transfer is interrupted with a temperature jump due to the deficiency in overlap between phonon dispersions of dissimilar materials. Classical theories considering specular or diffuse phonon scattering predict the upper or lower limits of interface thermal resistance (ITR), while a detailed investigation of intermolecular interactions is needed to resolve interface phonon scattering mechanisms.

In this chapter, we present interface phonon transfer at the molecular level, and investigate the validity of continuum hypothesis and Fourier’s law in nano-channels. First, we focus on the conventional ways of using MD for heat transport problems. Most of the previous MD research sandwiched a liquid domain between two solid walls and induced heat flux by fixing the wall
temperatures using a thermostat. However, imposing a constant temperature region in the solid domain results in an artificial thermal resistance previously overlooked in the literature. For such cases, we investigate the effects of applied thermostat [4]. Second, we question the intermolecular parameters employed at the interface. Previous works employed interaction parameters based on various mixing rules and did not validate the resulting surface wetting behavior. Hence, the previously reported interface resistance values are vague. By conducting a detailed water nano-droplet study, we relate the molecular interaction parameters to the macroscopic wetting behavior [5]. Next, we characterize the temperature dependence of the interface resistance for different wetting surfaces. By doing this, the temperature dependence of phonon transport and the near-surface density structure are distinguished [6]. Finally, using the proper silicon-water interaction parameters that capture the correct wetting behavior, we determine the silicon/water ITRs as a function of the surface temperature. Reported resistance values show perfect agreement with the experimental measurements in the literature.

Objectives of this chapter are

1. Demonstrations of length scales and conditions for onset of continuum hypothesis in nanoscale-confined liquids
2. Characterization of the artificial thermal resistance induced by the applied thermostat at the liquid/solid interface [4]
3. Revealing the relation between the surface wetting and interface phonon transport [5]

1.2 ONSET OF CONTINUUM BEHAVIOR

Heat transfer is a physical process of energy flow developed as a result of a temperature difference. From the continuum viewpoint, Fourier's law states that the heat flux is proportional to the developed temperature gradient while this proportionality is constant and independent of system size. Such consideration is questionable for nanoscales. Specifically, in a fluid domain, ordering of liquid molecules formed due to surface forces creates complications in the definition of a local temperature. As a start, we explored the validity ranges of the continuum hypothesis for nano-confined fluids by performing MD simulations of argon liquid inside nanoscale graphite and silver channels of different heights.

We studied the validity of Fourier's law for one-dimensional liquid heat conduction inside 3.57, 7.6, and 14.9 nm height channels. Different temperatures are imposed on opposite channel surfaces to create a thermal gradient in the system. Fluid domain is divided into small bins where the local temperatures are measured and averaged through the simulation time. Resulted liquid number density profiles showed density layering near surfaces while the oscillation of density converges to the desired value in the center region of the channels, except the 3.57 nm case. Hence, fluid in a 3.57 nm confinement is expected to show a non-continuum behavior as a result of the size effects.

In statistical mechanics sense, local temperature can be defined only if the local thermal equilibrium is established inside the local region of interest. First, we tested the local thermal equilibrium in our MD system by calculating the higher moments of velocity. At equilibrium, the velocity distribution at the point of measurement should have normal (Gaussian) distribution with zero skewness and kurtosis. We calculated higher moments of velocities in each local bin of the simulated domain. The results showed normal distribution of the thermal velocity, which validates that the local thermal equilibrium is maintained in our system. Time-averaged temperature profile exhibits a linear variation, typical of continuum predictions. Even for the smallest case of 3.57 nm height channel, temperature distribution agrees with the Fourier's law's expectations regardless of the observed density oscillations.

Next, we calculated the thermal conductivity of liquid argon. Generally, two methods can be applied for thermal conductivity calculations in MD simulations. One approach is the Green-Kubo method that is based on the fluctuation-dissipation theorem, and applicable for the equilibrium MD technique. The Green-Kubo method is derived from the linear response theory to extract
thermal conductivity from the energy current correlation function. The second approach is the utilization of Fourier’s law, which is based on a linear constitutive law, and may not be applicable in nano-confined geometries. First, we calculated the thermal conductivity of liquid argon using the Green-Kubo method. When there are no electronic contributions and net flow in the system, thermal motion becomes the sole contributor in the calculation of thermal conductivity. Our code successfully calculated the thermal conductivity of liquid argon using the Green-Kubo method, which matched with published values in the literature.

The thermal conductivity of liquid argon was also obtained using the Fourier’s law with heat flux and a time-averaged temperature gradient predicted from MD. The thermal conductivity calculated from the Fourier’s law matches well with the previously published thermal conductivity of liquid argon [7–13]. Independent of the developed heat flux and size of the computational domain, MD simulations successfully reproduce the thermal conductivity of liquid argon using the Fourier’s law. Comparison of thermal conductivity obtained from the Green-Kubo method with that extracted from the Fourier’s law of heat conduction enables the assessment of reliability of Fourier’s law in nano-confined dimensions. Hence, in this study, we presented the emergence of continuum behavior and the validity of Fourier’s law for liquid argon in channels with dimensions as small as 10 molecular diameters (≈3.5 nm).

1.3 BOUNDARY TREATMENT EFFECTS ON INTERFACE THERMAL RESISTANCE

Through the MD literature, the most widely used approach to create a heat flux in the domain is to employ thermostats to regulate the temperature in hot and cold regions, while utilizing a thermostat free zone in the middle. The thermostat applied regions often utilize the velocity rescaling, Nose-Hoover or Langevin thermostats [14]. Each of these algorithms constrains the temperature based on the kinetic energy of atoms. Many MD-based heat conduction studies for homogenous solid domains report emergence of an artificial thermal resistance (i.e., temperature jump) at the interface of the thermostat applied and thermostat free regions [15–24]. Phonon transport in solids arises from long-term correlated motion between neighboring atoms. Thermostat applies a random force to the atoms to keep them at the prescribed temperature. This de-correlates the motion between atoms at the interface of the thermostat applied and thermostat free regions, and leads to lower thermal conductivity with an artificial interface resistance. Although this phenomenon has been widely observed in solid systems, its significance at the liquid/solid interface is largely unknown.

In this study, we investigate heat conduction through the liquid argon–solid silver interface using non-equilibrium MD simulations by employing three different thermal boundary treatments. Hence, we investigate the effect of this artificial thermal resistance and distinguish it from the actual Kapitza resistance at the liquid/solid interface. In order to achieve these goals, we present heat conduction results in the solid–liquid–solid domains obtained by applying Langevin thermostat to all wall layers (Case 1); only to a small number of wall layers that are sufficiently away from the liquid/solid interface (Case 2); and by injecting and removing energy from the wall layers (Case 3). All results are organized to characterize the artificial thermal resistance, Kapitza resistance, and length using simple heat conduction analysis. Results of systematic studies obtained by varying the wall temperatures are also presented.

1.3.1 THREE-DIMENSIONAL MD SIMULATION OF ARGON/SILVER SYSTEM

We studied liquid argon confined between two parallel solid silver walls by using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator), an MD code from Sandia National Laboratories [25]. Figure 1.1 illustrates a snapshot of the simulation domain. Total dimensions in longitudinal (x), vertical (y), and lateral (z) directions are 16.4, 3.7, and 3.7 nm, respectively. The domain was constructed using 1830 argon and 7776 silver molecules. The first silver domain lies between 0 and 48 Å, and the second silver domain is from 118 to 166 Å, while the liquid
argon is confined to 70 Å spacing between the two walls. The corresponding number density of argon is \( \rho = 0.8 \, (\# / \text{nm}^3) \). The walls on each side of the domain contain 24 silver layers that are 0.2043 nm apart from each other. Each silver layer contains 162 molecules resulting in number density of 5.7 (\# / \text{nm}^3). Periodic boundary conditions are applied in the vertical (y) and lateral (z) directions. Silver walls are modeled as face-centered cubic (FCC) structures with (0, 0, 1) crystal plane facing the fluid. Atoms in the outmost layer of both silver walls are fixed to their original locations to maintain a fixed volume system, while the remaining atoms throughout the domain are free to move.

Mass for an argon molecule is \( m = 6.63 \times 10^{-26} \, \text{kg} \), its molecular diameter is \( \sigma = 0.3405 \, \text{nm} \) and the depth of the potential well for argon is \( \varepsilon = 119.8 \times k_b \). Lennard-Jones (L-J) 6-12 potential was utilized to model the van der Waal’s interactions between argon–argon and argon–silver molecules with a cutoff distance of 1 nm. The truncated (6–12) L-J potential is given as

\[
\Phi_{\text{truncated}}(r_{ij}) = 4\varepsilon \left( \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right) - \left( \left( \frac{\sigma}{r_c} \right)^{12} - \left( \frac{\sigma}{r_c} \right)^6 \right),
\]

where

- \( r_{ij} \) is the intermolecular distance
- \( \varepsilon \) is the depth of the potential well
- \( \sigma \) is the molecular diameter
- \( r_c \) is the cutoff radius [14]

Lorentz–Berthelot mixing rule is employed to calculate the L-J parameters for argon–silver interactions [26]. Silver–silver interactions are calculated using the embedded atom method (EAM), which is a many-body potential for slightly more computational cost than the pair potential, and works especially well for FCC structures [27,28].

Simulations are started from the Maxwell–Boltzmann velocity distribution for all molecules at 115 K. Initial particle distribution is evolved \( 10^6 \) time steps (4 ns) to reach an isothermal steady state using 4 fs time steps. During this process, the Nose–Hoover thermostat is applied to the molecules to maintain the system’s temperature at 115 K. Afterward, temperatures of the silver walls are modified to serve as heat baths to induce heat flux through the liquid/solid interfaces. At the same time, NVE ensemble (constant number of molecules, constant energy, and constant volume) is applied to liquid argon domain. Simulations are performed for an additional \( 10^6 \) time steps (4 ns) to ensure that the system attains equilibrium in presence of the heat flux. After which,
time averaging of desired properties is performed for $2 \times 10^6$ additional time steps (8 ns). Longer time averaging has also been performed to confirm the convergence of density and temperature profiles to steady state.

Two different heat bath techniques are employed to investigate their effects. First, a constant surface temperature is maintained using Langevin thermostat. Langevin damping factor is taken to be 0.1 ps, which is prescribed by the phonon frequency of solid silver ($f_D = 0.223$ ps) at Debye temperature of $T_D = 215$ K [29,30]. Different wall temperatures are assigned to create heat flux through the liquid/solid interfaces. Langevin technique is employed as a global thermostat on the specified number of solid layers for each case. Second, a constant heat flux is obtained by injecting and removing energy through the heat baths to support a temperature gradient across the system. The simulated cases are summarized in Table 1.1. The computational domain is divided into 200 slab bins with the size of 0.083 nm. In order to interpret the temperature profiles obtained using fine bins, we also obtained temperature distribution using 20 slab bins. Temperature profiles from the fine and coarse bin cases were consistent and showed that local thermal equilibrium is reached in the simulations using fine bins. Coarse bin results are omitted for brevity of this work. A achievement of local thermal equilibrium in such nanoscale-confined domains was addressed earlier.

Irving–Kirkwood (I–K) expression is utilized to compute the heat flux vector for an $N$ particle system using unity differential operator approximation as follows [31,32]:

$$J_k = \frac{1}{\text{Vol}} \left\{ \sum_{i=1}^{N} V^i_k \left(E^i + \Phi^i\right) + \sum_{i<j}^{N} \left(r^i_k - r^j_k\right) W^{i,j}\right\},$$  

$$E^i = \frac{1}{2} m^i \left(\left(V^i_x\right)^2 + \left(V^i_y\right)^2 + \left(V^i_z\right)^2\right),$$  

$$W^{i,j} = \frac{1}{2} \left( V^i_x f^{x,i,j} + V^j_x f^{x,i,j} + V^i_z f^{z,i,j} \right),$$

where the first term on the right-hand side of Equation 1.2 is the kinetic and potential energies carried by particle $i$

the second term is the energy transfer to particle $i$ by force interactions with the surrounding particles

In the first term, $V^i_k$ is the peculiar velocity component of particle $i$ in $k$-direction, while $k$ is the axes of the Cartesian coordinate system; $E^i$ is the kinetic and $\Phi^i$ is the potential energy of particle $i$ calculated using Equations 1.1 and 1.3, respectively. In the second component of Equation 1.2, $(r^i_k - r^j_k)$ is the $k$th component of the relative distance vector between particles $i$ and $j$. The $W^{i,j}$ term is given in Equation 1.4, where $f^{l,i,j}$ is the intermolecular force exerted on particle $i$ by particle $j$ in the Cartesian coordinate direction $l$.

### 1.3.2 CONSTANT SURFACE TEMPERATURE

Case 1 utilizes constant temperature surfaces, where all 23 silver layers of the left and right surfaces are maintained at 140 and 90 K, respectively, using a Langevin thermostat. The number density profiles shown in Figure 1.2 illustrates the system consisting of three distinct domains. Argon density exhibits strong near-wall layering due to the wall force field effects and local argon–argon interactions [33]. The density layering extends approximately 2 nm from each surface, after which the liquid argon density reaches nearly a constant value of 0.8 ($\#a^3$/nm$^3$). Slight density variation in
this bulk liquid region is due to the temperature gradient, where the argon density increases with decreased temperature. Local argon density near the high temperature (left) wall is less than that near the low temperature (right) wall. Argon density fluctuates severely near the surface, resulting in nearly zero molecules within certain bins. Depletion of argon molecules near the surfaces has profound effects on the definition of local liquid temperature. Very few liquid molecules are present at these density minima, where local temperature cannot be defined accurately. In order to address this problem, we omitted presentation of temperature in these “empty” bins as can be observed from the near-wall temperature profiles.

Figure 1.2 also shows the temperature profiles obtained using 200 slab bins. While the silver surfaces are kept at constant temperatures, liquid argon temperature varies linearly in bulk of the nano-channel. Temperature jumps at the liquid/solid interfaces are apparent in the results. These temperature jumps can be associated with an interfacial thermal resistance ($R_K$), known as the Kapitza resistance [34], for given a heat flux $\dot{j}$ as

$$\Delta T = -R_K \cdot \vec{n} \cdot \vec{j},$$  

where $\vec{n}$ is the outward unit normal from the wall. Alternatively, it is possible to define a thermal resistance (Kapitza) length ($L_K$), by extrapolating the temperature profile from liquid into the solid, where the wall temperature is reached. The Kapitza length can be predicted using

$$\Delta T = L_K \left. \frac{\partial T}{\partial n} \right|_{\text{liquid}},$$

where $\partial T/\partial n$ is the thermal gradient on the liquid side,

$$\Delta T = T_{\text{liquid}} - T_{\text{wall}}$$
In order to characterize the temperature distribution in the bulk of liquid argon, we performed linear least square fits to the MD data and measured sum of the squares of the residual, which is a measurement of how well the least square fit represents the data. The values are all below 1%, indicating that the temperature profile is linear in the bulk of the channel. Slight curvature in the temperature profile can be attributed to the temperature dependence of argon’s thermal conductivity. Surprisingly, linear temperature profiles are observed up to the second argon-density peak, approximately 0.5 nm from the silver wall. Hence, strong density fluctuations do not significantly affect the temperature profile beyond 0.3 nm from each wall. In addition, the fine bin temperature distribution in liquid argon near the silver surface, especially within the first density peak near the walls, shows steep temperature variations compared to the bulk region. This behavior can be attributed to strong interactions of the silver–argon molecules.

Next, we calculate the Kapitza length, $L_K$, by using Equation 1.6. First, we obtained the local temperature gradient from the MD results and matched this with the slope of the linear curve fits to the temperature profiles in the bulk of the channel. Then, we extrapolated the liquid temperature onto the solid surface, which was assumed to be the center of the last silver layer facing the liquid, and calculated the local temperature jump ($\Delta T = T_{\text{liquid}} - T_{\text{wall}}$). As suggested by Equation 1.6, this temperature jump and the linear slope of argon temperature profile yield the value of $L_K$. In the current case, when thermostat is applied to all 23 silver layers, $L_K$ of argon/silver interface is 11.1 and 9.4 Å at the hot (140 K) and cold (90 K) surfaces, respectively. These results clearly indicate the temperature dependence of $L_K$. In the mean time, we also calculated the heat flux, and utilized the temperature gradient obtained from MD result to calculate the thermal conductivity using the Fourier’s law. Thermal conductivity for liquid argon at average temperature of 115 K is 103.9 mW/mK, which matches the published bulk values well [9,35].

In order to investigate the thermostat effects, we created Case 2 by applying the Langevin thermostat to the outer most second, third, and fourth layers of the left and right silver slabs (note that the outer first layer of each wall is fixed to define a constant simulation volume). As a result, the remaining 20 silver layers are left to interact freely to develop their own temperature profile based on phonon scattering of silver surfaces. By considering that the wall layers are 0.2043 nm apart from each other, 20 silver layers separate the thermostated molecules from the liquid/solid interface by approximately 15 atomic spacing. Such large distances minimize the thermostat effects at the liquid/solid interface. Figure 1.3 shows the temperature profile for Case 2. Sudden temperature drops at the interface of the thermostat applied and thermostat-free regions are observed inside the silver domains. This is due to the dynamic rescaling of thermostat, which results in phonon mismatch at this interface. A ny thermostat altering particle motions corrupts this autocorrelation by reducing the thermal conductivity at the interface of the thermostat applied region. This implies that the Langevin thermostat leads to reduced conductivity between the thermostat applied and thermostat-free silver layers and creates an artificial thermal resistance. Similar behavior has also been consistently observed for Berendsen and Nose–Hoover thermostat techniques with different amounts of temperature jumps.

Figure 1.3b shows zoomed view of the temperature distribution in silver. After the temperature jump due to the artificial thermal resistance, silver temperature is reduced linearly to 136.8 K at the argon/silver interface. This reduction in silver temperature is due to heat flux through the solid wall. Similar to the hot wall, the cold wall also experiences a temperature jump, owing to linear increase in silver temperature to 92.7 K. Linear least square fits to silver and argon temperatures result in good fits with measured sum of the squares of the residual lower than 1%. We must note that MD simulations here consider only the intramolecular vibrational energy transfer, while thermal transport in metals is dominated by electron interactions. As a result, calculated thermal conductivity of silver is less than the reported bulk material values. Despite this limitation, silver blocks serve as heat baths to induce heat flux on the argon/silver interfaces. Because of the definitions of the Kapitza resistance and Kapitza length given in Equations 1.5 and 1.6, heat transfer in silver domains has negligible effects on our investigation. Similar to the earlier calculations, $L_K$
found by using Equation 1.6. Extrapolation of argon temperature onto the center of the last silver layer facing liquid argon enabled us to calculate the local temperature jump ($\Delta T = T_{\text{fluid}} - T_{\text{wall}}$), thus the value for $L_K$. When thermostat is applied only to the outer three layers of silver walls, $L_K$ at the argon/silver interface is found to be 5.8 and 3.1 Å on the hot (136.8 K) and cold (92.7 K) surfaces, respectively. Values of the Kapitza length are approximately half of the values calculated in Case 1. This proves the thermostat effect on the silver/argon interface. Interestingly, the calculated heat flux values for both cases are almost identical revealing that the total thermal resistance of the simulation system is approximately kept constant regardless of the location where the thermostat is applied. Slight reduction in the heat flux in Case 2 is due to heat conduction in silver slabs.

### 1.3.3 Constant Heat Flux

In an NVT ensemble (constant number of molecules, constant volume, and constant temperature), the main aim of the thermostat mechanism is keeping the temperature constant. Thermostat adding energy to the molecules at an incident when their instantaneous temperature is lower than the desired value, may remove energy from the same group of molecules if their temperature is higher at any following time step. This behavior corrupts the vibrational nature of the material and affects phonon transfer, resulting in a temperature jump between the thermostat applied and free regions. Instead of assigning a constant surface temperature using a thermostat, one can maintain heat flux in the system by simply injecting and removing energy from the left and right heat baths, respectively. Different than using a thermostat, non-translational kinetic energy is added to the molecules of hot reservoir (and removed from the molecules of the cold reservoir) at every time step continuously, regardless of their instantaneous temperatures. In such case, NVE ensemble is obtained where the heat flow is constant and the surface

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**FIGURE 1.3** Temperature profile when Langevin thermostat is applied on three layers of silver walls to keep them at 140 and 90 K, respectively (Case 2). Result for Case 1 is also shown for comparison (a). Zoomed view of the hot surface shows presence of an artificial thermal resistance at the interface of the thermostat applied and thermostat-free regions of the solid domain (b).
temperature fluctuates. This approach is identical to the solution of heat conduction problem by assigning heat flux (Neumann boundary condition) on both boundaries, which makes the continuum solution of heat conduction equation ill-posed, due to the undetermined integration constant that fixes the temperature value. MD simulation of such a case has similar difficulties. Since the energy is added and removed at a constant rate, the surface temperature is continuously adjusted, and hence, actual temperature of the surface cannot be assigned a priori. For such cases, the initial temperature of the system plays a key role to obtain the desired temperature. For example, in order to create a case with 140–90 K surface temperatures, simulation should initially be brought to thermal equilibrium at 115 K, which is the average temperature. Then, energy is added and removed from the left and right walls, respectively, while the heat flux value is adjusted to obtain the desired temperature difference of $\Delta T \approx 50$ K between the two reservoirs. The temperature profile in the system, obtained by adding and removing energy from outermost three layers of the left and right silver slabs (Case 3), is shown in Figure 1.4. Unlike the cases that utilized thermostat, adding energy does not create unphysical temperature jumps inside the solid domains. Similar to the previous cases, we calculated the $L_K$ values at the liquid/solid interface, which are 5.9 and 3.0 Å on the 139.8 and 90.9 K surfaces, respectively. Consistent with our earlier observations, the Kapitza lengths obtained by adding heat are similar with Case 2, which utilized thermostat on outermost three layers of the walls. Since adding and removing energy from the solid domains eliminate the artificial thermal resistance observed in thermostat applied systems, this method seems to be the most proper way to investigate the ITR using non-equilibrium MD simulations.

Results clearly show that the Kapitza resistance and Kapitza length should be predicted either by using a large solid domain by applying thermostat to several wall layers away from the liquid/solid interface, or by adding and extracting energy from the surfaces. The latter approach can utilize smaller number of wall layers and minimizes the computational burden of simulating large number of wall molecules. It is also shown that the artificial thermal resistance varies between...
3.8 \times 10^{-9} \text{ and } 4.2 \times 10^{-9} \text{ km}^2/\text{W using a Langevin thermostat in 140–90 K range. The Kapitza resistance at liquid argon silver interface varies from } 5.4 \times 10^{-9} \text{ to } 2.2 \times 10^{-9} \text{ in the same temperature range.}

1.4 TEMPERATURE DEPENDENCE OF THERMAL RESISTANCE AT THE WATER/SILICON INTERFACE

Silicon and silicon-based materials as semiconductors have been widely used in integrated circuits. Parallel to the technological developments, the transistor density on a single circuit has been increasing exponentially each year according to the prediction of Moore’s law [36]. The main driving mechanism, enabling current developments, is the micro- and nano-fabrication technologies providing higher packing densities. It was also Richard Feynman’s vision 50 years ago, when he was pointing out the necessity to understand the unique physics governing the matter in small scale [37]. Since then, micro- and nanoscale physics of silicon-based materials attracted greatest attention of scientists and engineers.

MD has been utilized to investigate phonon transport through the interfaces [38–55]. There are quite a number of studies revealing the dependence of ITR to various molecular parameters; but the effect of surface temperature on ITR is still a question. For a solid/solid interface, it was validated that the temperature dependence of ITR is similar to the theoretical predictions where increase of temperature enhances the phonon density of states and decreases the ITR [53]. However, in the case of a solid/liquid interface, liquid molecular structure formed near the surface plays a dominant role on the interface phonon transport. Opposite to the theoretical expectations, our earlier studies showed increase of ITR with increased temperature [4–8,40]. Such behavior develops as a result of the temperature dependence of liquid density layering. For the studied monatomic liquid argon in contact with silver [4,7] and solid argon surfaces [8,40], liquid density was found to be higher and better packed near the cold surface; as a result, the ITR was lower than the hot side. Hence, correct characterization of temperature dependence of ITR needs a detailed investigation of near-surface liquid structure whose dependence on temperature shows variation for surfaces having different wetting behavior.

A liquid near a solid surface exhibits layering on the molecular scale due to the ordering of the liquid molecules under the influence of surface forces [33]. This density layering is a specific property of a liquid/solid couple and develops mainly as a function of the surface wettability driven by the intermolecular interactions. However, the parameters determining the interactions of the specific liquid/solid couples are still under investigation. Frequently, the interaction parameters of non-identical molecules are calculated from parameters of the pair of identical molecules by using the Lorentz–Berthelot mixing rule. However, the interaction parameters between identical molecules are optimized for a bulk material system and may need to be re-parameterized for the interaction of non-identical pairs instead of using the simple Lorentz–Berthelot mixing rule. Therefore, the intermolecular interaction parameters should be properly specified in order to capture the correct behavior of ITR for a given solid/liquid couple.

Many authors indicate their concerns about the Lorentz–Berthelot mixing rule and proposed ways to calculate the interaction parameters of nonidentical molecules accurately [56,57]. One methodology is the measurement of water contact angle to define the interactions of water with carbon [58] and silica [59] surfaces for rigid solid surfaces.

The angle at which a liquid/vapor interface meets the solid surface is known as the contact angle. Even though the hydrophobic or hydrophilic nature of a surface should be defined by also considering other additional surface properties [60,61], contact angle can be utilized as a measure of the wetting phenomena, qualitatively. When a drop of liquid is on a solid surface, it may remain as a spherical drop or spread to cover the solid surface. Specifically, wetting occurs when the contact angle is less than 90°, while the liquid does not wet the surface for contact angle values greater than 90°. The wetting characteristic of silicon has been of great interest for a vast number of applications.
From the earliest experimental studies, it was reported that the measured contact angle value is strongly dependent on the surface conditions of silicon. A thin layer (less than 1 nm) of silicon dioxide forms naturally on the surface when silicon is exposed to the ambient air. Hermanson et al. measured contact angles between 35° and 96° by varying the surface treatment that removed the native oxide layers on the surface at different amounts [62]. Silicon and thermally grown silicon dioxide are studied by Martinez by removing the native oxide formed on silicon with etching [63]. Water contact angle on silicon and silicon dioxide are reported to be 89° and 48°, respectively. Similarly, Arkles reported the contact angle between water and etched silicon between 86° and 88° [64]. In a recent study, Cho et al. measured the water contact angle as 70.1° on bare silicon surface [65]. Our personal communications with the authors point out the difficulties of obtaining and maintaining a silicon surface without any chemical termination. The amount and time scale of oxide layer growth was mentioned in [66], where freshly etched silicon exposed to air at room temperature is rapidly covered by a thin oxide layer of thickness 0.5 nm in a minute, followed with a logarithmic growth rate. Hence, measured contact angle values in the literature differ with the thickness of the SiO₂ layer and experimental conditions. Bare silicon surface without any chemical termination is hydrophobic, while the oxidized layer adds hydrophilicity, based on the oxide layer’s thickness. In this study, we use a contact angle value of 88° to compare with the MD calculated water contact angles on pure silicon surface.

The objective of this study is to predict the ITR between silicon and water for the case where the interaction parameters are properly tuned to capture the hydrophobic behavior of bare silicon surface. Starting with the classical mixing rule estimations, we varied the interaction parameters between silicon and water in order to match the microscopic contact angle calculated by MD with the experimentally measured macroscopic contact angle of 88°. In the meantime, an enhanced understanding of the near-wall density structure influences on ITR and its dependence on the surface temperature will be provided.

### 1.4.1 Three-Dimensional MD Simulation of Water/Silicon System

Liquid water is confined between two parallel solid silicon walls as illustrated in Figure 1.5. Total dimensions in longitudinal (x), vertical (y), and lateral (z) directions are 13.4, 2.7, and 2.7 nm, respectively. The domain was constructed using 2500 silicon and 5088 water molecules while the corresponding density of water is \( \rho = 1.006 \text{ g/cm}^3 \). Walls on each side of the domain contain 25 silicon layers, which are 0.136 nm apart from each other, and the spacing between two silicon walls is 6.4 nm in x-direction. Periodic boundary conditions are applied in the vertical (y) and lateral (z) directions. Silicon surface is modeled as diamond cubic structure with (0, 0, 1) crystal plane facing the fluid. Atoms in the outmost layer of both silicon walls are fixed to their original locations to maintain a fixed volume system, while the remaining atoms throughout the domain are free to move.

![Figure 1.5: Snapshot of the simulated water-silicon system.](image-url)
Many different models for liquid water have been developed by fitting some physical properties of water; as a result, different models show agreement with the different properties of water. A model requiring more fitting parameters gives better results, but becomes computationally inefficient due to its complexity. On the other hand, many studies showed that the thermodynamic properties of water models were most sensitive to the van der Waal’s repulsive, short range Coulomb, and the polarization components of the potential [67]. Thus, the model explaining the van der Waal’s and Coulombic interactions with a proper polarization of water structure provide a fair understanding of complex water behavior.

Water models can be classified by the number of points used to define the model, and whether the structure is treated as rigid or flexible. In our study, for the purpose of simplicity and computational efficiency, we chose SPC/E (Extended Simple Point Charge) model, which can be described as effective rigid pair potentials composed of Lennard-Jones and Coulombic terms [68]. This water model has three interaction sites, corresponding to the three atoms of the water molecules. Each atom gets assigned a point charge to model the long-range Coulombic interactions, and the oxygen atom also exhibits L-J potential to model van der Waal’s forces. The truncated (6–12) L-J potential given in Equation 1.1 is utilized.

SPC/E is a tetrahedral model with an OH bond length of 0.1 nm and H–O–H angle of 109.47°. SHAKE algorithm [69] is used to constrain the bond lengths and angle, thus making the model rigid. A short-range L-J term with a cutoff distance of 1 nm acts on the oxygen, while a charge $q_{o}(0.4238e)$ is on each hydrogen, compensated by a charge $-2q(-0.8476e)$ on the oxygen. The long-range Coulombic part has been treated with a particle-particle particle-mesh (PPPM) solver, which can handle long-range interactions for periodic systems with slab geometry more efficiently than the Ewald sum algorithm [70]. PPPM invokes a particle-particle particle-mesh solver, which maps atom charge to a 3D mesh. It uses 3D fast Fourier transforms to solve Poisson’s equation on the mesh, and then interpolates electric fields on the mesh points back to the atoms. Si-Si interactions were calculated by Stillinger-Weber potential, which considers two-body interactions with an additional many-body dependence [71]. SPC/E water molecules interact with silicon surface only by van der Waal’s interactions of silicon and oxygen using a cutoff distance of 1 nm. The molecular interaction parameters are given in Table 1.1. For the silicon-oxygen interactions, parameters can be calculated by the Lorentz–Berthelot (L–B) mixing rule given as,

$$\sigma_{Si-O} = \frac{\sigma_{Si-Si} + \sigma_{O-O}}{2}, \quad \varepsilon_{Si-O} = \sqrt{\varepsilon_{Si-Si} \times \varepsilon_{O-O}}$$

(1.7)

Using the corresponding parameters given in Table 1.1, the L–B mixing rule predicts the interaction parameters $\sigma^{*}_{Si-O} = 2.6305$ Å and $\varepsilon^{*}_{Si-O} = 0.12088$ eV.

Newton’s equations of motion were integrated using the Verlet algorithm with a time step of 0.001 ps. We use LAMMPS [25] as our MD solver. Simulations were started from the Maxwell–Boltzmann velocity distribution for all molecules at 323 K. NVT ensemble was applied with Nose–Hoover thermostat keeping the system at 323 K. Initial particle distribution was evolved $2 \times 10^6$ time steps (2 ns) to reach an isothermal steady state. Afterward, the Nose–Hoover thermostat is applied only on the outmost

<table>
<thead>
<tr>
<th>Molecular Interaction Parameters Utilized</th>
<th>Table 1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule Pair</td>
<td>$\sigma$ (Å)</td>
</tr>
<tr>
<td>O–O</td>
<td>3.166</td>
</tr>
<tr>
<td>H–H</td>
<td>0</td>
</tr>
<tr>
<td>Si–Si</td>
<td>2.095</td>
</tr>
</tbody>
</table>
Interface Resistance and Thermal Transport in Nano-Confined Liquids

second, third, and fourth layers of the both silicon slabs to induce heat flux through the liquid/solid interfaces by maintaining different wall temperatures. At the same time, NVE ensemble is applied to the remaining silicon and water molecules. Simulations are performed for an additional $4 \times 10^6$ time steps (4 ns) to ensure that the system attains equilibrium in presence of the heat flux. After which, time averaging of desired properties are performed through $24 \times 10^6$ additional time steps (24 ns).

Classically, energy fluctuation in an NVT system of a limited number of molecules is non-zero. In such case, increase of the averaging time decreases the fluctuations to a minimum value. This minimum value is a function of multiple molecular parameters, but mostly depends on the time scales of the molecular mechanisms that are modeled. We performed 20 ns averaging which is considered excessively long for a classical MD system. However, the phonon transport in our system occurs at different frequencies. Depicting time-averaged behavior of low frequency phonons requires excessively long simulation times that are computationally unfeasible. Further complexity develops due to the phonon scattering at the interface, which makes theoretical estimation of the time scale for the complete phonon spectra impossible. Overall, the fluctuations are mainly dependent on $\varepsilon_{\text{Si-O}}$ and the specified temperature difference, where high $\varepsilon_{\text{Si-O}}$ values and large temperature differences in the system result in lower fluctuations. Although the highest fluctuations in the temperature and density profiles are less than 2% and 1%, respectively, these variations result in higher fluctuations ($\approx 9\%$) in the ITR calculations. Due to these fluctuations, we performed statistical analysis of our results and report the ITR behavior with corresponding standard deviations (see Section 1.3 for details).

The computational domain is divided into 100 slab bins with the size of 0.1343 nm for temperature and 200 slab bins with the size of 0.0672 nm for density profiles. Smaller bin size, 800 slab bins with the size of 0.0168 nm, is also employed in order to resolve the fine details of the near-wall water density distributions. Irving–Kirkwood (I–K) expression given in Equations 1.4 through 1.6 is utilized to compute the heat flux vector for an $N$ particle system.

1.4.2 Influence of the Near-Wall Water Density Structure on ITR

In an earlier study [3], we investigated the effect of interaction parameters, specifically interaction strength, to the wetting angle of water on silicon surface. We decreased the interaction strength value starting from the classical mixing rules estimation, and observed transition from hydrophilic to hydrophobic behavior in the studied range. Decrease in the interfacial energy leads to lower wetting, and hence the water density distribution near the surface changes drastically. In this study, we further investigate the effect of interaction parameter on the ITR. For such purpose, we used the $\varepsilon_{\text{Si-O}}$ values of 0.4, 0.2, 0.125, 0.1, and $0.05 \times \varepsilon_{\text{Si-O}}^*$, where the $\varepsilon_{\text{Si-O}}^*$ is the value calculated by the L–B rule ($\varepsilon_{\text{Si-O}}^* = 0.12088$ eV). Our main purpose here is not only to understand the influence of the resulting near-surface fluid structure on the ITR, but also to reveal the importance of the interaction parameter values, since some of the interaction strength values used in this work are similar to the values utilized in previous investigations of ITR using silicon-SPC/E water model [49–51].

Temperature distributions obtained in a silicon–water–silicon system subjected to 353 and 293 K on its ends are shown in Figure 1.6. The temperature profiles vary with the change of interaction strength value. For silicon domain, we observed a temperature drop at the interface of the thermostat applied and thermostat free regions. This artificial ITR created by the thermostat is due to the dynamic rescaling of thermostat, which results in phonon mismatch at this interface. This artificial effect of the thermostat was investigated earlier [2]. Nose-Hoover thermostat creates temperature gradient inside the thermostat applied region different than the temperature gradient of the thermostat-free domain depending on the temperature and heat flux of the system, which was previously investigated in detail [2]. The remaining 21 silicon layers interacting freely develop their own temperature profile based on the phonon characteristic of silicon. Silicon temperature varies linearly sufficiently away from the interface. We observed nonlinear behavior near the interface extending $\approx 0.54$ nm into the silicon.
slab for the highest heat flux case. Such behavior is a strong evidence of phonon scattering mechanism from the interface, which needs further attention and will be investigated in detail in a separate study.

There are sudden temperature jumps at the liquid/solid interfaces. These temperature jumps are due to the mismatch in phonon spectrum of the water–silicon pair and results in the ITR. One can define a thermal resistance length ($L_K$), known as the Kapitza length, by extrapolating the temperature profile from liquid into the solid, where the wall temperature is reached. The Kapitza length can be predicted using Equation 1.6 where $\frac{\partial T}{\partial n}$ is the thermal gradient on the liquid side and $\Delta T = T_{\text{liquid}} - T_{\text{wall}}$. It is crucial to realize that Equation 1.6 requires onset of continuum behavior where a local temperature profile can be defined. In order to characterize the temperature distribution in the bulk of liquid water, we performed linear least square fits to the MD data, and measured sum of the squares of the residual, which is a measurement of how well the least square fit represents the data. The values are all below 1%, indicating that the temperature profile is linear in the bulk of the channel. Slight curvature in the temperature profile can be attributed to the temperature dependence of water’s thermal conductivity. Water temperature varies linearly except the near-wall region where temperature fluctuates as a result of density layering formed due to the surface forces. Such behavior depends on the chosen bin size. While we presented the data with a bin size of 0.1343 nm (100 bins), a slight increase in the bin size to 0.2686 nm (50 bins) resulted in linear behavior up to very near-surface region ($\approx 0.15$ nm away from surface). We discussed in an earlier study that in order to recover continuum behavior in such small environments, employed bin size should be equal to or bigger than one molecular diameter.

Next, we calculate the Kapitza length, $L_K$, by using Equation 1.6. First we obtained the local temperature gradient from the MD results, and matched this with the slope of the linear curve fits to the temperature profiles in the bulk of the channel. Then, we extrapolated the liquid temperature onto the solid surface, which was assumed to be the center of the last silicon layer facing the liquid; and calculated the local temperature jump ($\Delta T = T_{\text{liquid}} - T_{\text{wall}}$). As suggested by Equation 1.6, this temperature jump and the linear slope of water temperature profile yield the value of $L_K$. In the mean time, we also calculated the heat flux using Equation 1.3, and utilized the temperature gradient obtained from the MD result to calculate the thermal conductivity of confined water using the
Fourier’s law. Calculated thermal conductivity for liquid water at average temperature of 323 K is \( \approx 0.68 \, \text{W/km} \), which matches the published bulk values well. The calculated Kapitza lengths at hot (\( L_{K-H} \)) and cold (\( L_{K-C} \)) surfaces, heat flux, temperature gradients, and thermal conductivity of liquid water are given in Table 1.2 for five different interaction strength values.

In the studied system, phonon transport that propagates inside the silicon domain at different wavelengths creates thermal fluctuations. As a result, \( L_K \) cannot converge to a precise value. In order to have a fair judgment on \( L_K \) behavior, we performed a statistical investigation of \( L_K \) variation. Using a total simulation time of 24 ns, we obtained time averages at every 2, 4, 8, and 24 ns, resulting in 12, 6, 3, and 1 data sets, respectively. Using these total 22 differently averaged temperature profiles, 22 different \( L_K \) values are calculated. Later, the standard deviation of \( L_K \) and surface temperatures are calculated while the reported \( L_K \) value is the mean of the 22 \( L_K \) values. Standard deviations of the \( L_K \) values are given in Figure 1.7 as error bars. Overall, fluctuation of \( L_{K-H} \) is higher than \( L_{K-C} \). Also standard deviation increases with decreased \( \varepsilon_{\text{Si–O}} \) while the highest value of SD is around 7%.

The increase of interaction strength creates better coupling between the water and silicon molecules, and hence, decreases the ITR and \( L_K \) values. Variation of \( L_K \) values for different \( \varepsilon_{\text{Si–O}}/\varepsilon^{*}_{\text{Si–O}} \) at hot and cold surfaces are given in Figure 1.7a. Surface temperatures are also indicated on the plot. Since the temperature difference through the system is specified by the thermostat and fixed in the studied system, decrease of ITR results in increase of developed heat flux value. Regardless of this, resulted hot surface temperatures and cold surface temperatures for different \( \varepsilon_{\text{Si–O}} \) cases are very close to each other (\( T_H \approx 347 \, \text{K} \) and \( T_C \approx 295 \, \text{K} \)). Measured \( L_K \) values at cold and hot surfaces are found to be different. Since the \( L_K \) values of different \( \varepsilon_{\text{Si–O}} \) cases are different, we decided to normalize the \( L_{K-H} \) with \( L_{K-C} \) of the corresponding \( \varepsilon_{\text{Si–O}} \) case in order to understand the difference of \( L_{K-H} \) and \( L_{K-C} \) for each case (Figure 1.7b). While the \( L_K \) measured on the hot surface is lower than the cold surface values for \( \varepsilon_{\text{Si–O}} < 0.2 \times \varepsilon^{*}_{\text{Si–O}} \), we observed higher \( L_{K-H} \) than \( L_{K-C} \) for larger \( \varepsilon_{\text{Si–O}} \) cases. The interesting behavior of \( L_{K-H} \) and \( L_{K-C} \) for different \( \varepsilon_{\text{Si–O}} \) cases clearly indicates that \( L_K \) at a liquid/solid interface is not dominated by the surface temperature.

Next, we investigate the water and silicon density profiles in Figure 1.8, which illustrates the system consisting of three distinct domains. A constant silicon density of 2.35 g/cm\(^3\) is observed. Water density is constant and equal to 1.006 g/cm\(^3\) in the bulk of the channel. Near-surface water density exhibits well-known density layering due to the surface forces and local water–water interactions [3].

### Table 1.2

Kapitza Lengths at Hot (\( L_{K-H} \)) and Cold (\( L_{K-C} \)) Surfaces, Heat Flux, Temperature Gradients, and Thermal Conductivity of Liquid Water for Five Different Interaction Strength Values

<table>
<thead>
<tr>
<th>Case</th>
<th>( \varepsilon_{\text{Si–O}} ) (eV)</th>
<th>( \varepsilon_{\text{Si–O}}/\varepsilon^{*}_{\text{Si–O}} )</th>
<th>Contact Angle (°)</th>
<th>( q_x ) (W/m(^2))</th>
<th>( \Delta T/\Delta x ) (K/Å)</th>
<th>( k_{\text{water}} ) (W/km)</th>
<th>( T_H ) (K)</th>
<th>( L_{K-H} ) (nm)</th>
<th>( T_C ) (K)</th>
<th>( L_{K-C} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.048352</td>
<td>0.4</td>
<td>46.3</td>
<td>7.712</td>
<td>0.369</td>
<td>0.690</td>
<td>344.4</td>
<td>2.977</td>
<td>297.3</td>
<td>2.687</td>
</tr>
<tr>
<td>2</td>
<td>0.024176</td>
<td>0.2</td>
<td>57.8</td>
<td>5.691</td>
<td>0.281</td>
<td>0.67</td>
<td>345.8</td>
<td>5.263</td>
<td>296.1</td>
<td>5.119</td>
</tr>
<tr>
<td>3</td>
<td>0.01511</td>
<td>0.125</td>
<td>108.9</td>
<td>4.286</td>
<td>0.215</td>
<td>0.659</td>
<td>347</td>
<td>8.186</td>
<td>295.1</td>
<td>8.878</td>
</tr>
<tr>
<td>4</td>
<td>0.012088</td>
<td>0.1</td>
<td>129.7</td>
<td>3.588</td>
<td>0.173</td>
<td>0.684</td>
<td>347.1</td>
<td>10.597</td>
<td>295.1</td>
<td>11.57</td>
</tr>
<tr>
<td>5</td>
<td>0.006044</td>
<td>0.05</td>
<td>169.3</td>
<td>2.883</td>
<td>0.137</td>
<td>0.694</td>
<td>348.3</td>
<td>14.785</td>
<td>294.1</td>
<td>16.261</td>
</tr>
</tbody>
</table>

**Notes:** Hot and cold reservoirs are kept at 353 and 293 K, respectively. Contact angles for the corresponding interaction strengths are adopted from a water nano-droplet study.

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Increase in the interaction strength develops stronger water layering for $\varepsilon_{\text{Si-O}} \geq 0.2 \times \varepsilon_{\text{Si-O}}^*$, while the increase in the near-wall water density results in slight decrease of density in the bulk. By simple examination of Figure 1.8, one can conclude that the water density peaks near the hot surface are higher than the cold side for $\varepsilon_{\text{Si-O}} \geq 0.2 \times \varepsilon_{\text{Si-O}}^*$. However, a more detailed investigation should be conducted to understand the behavior of water density near the surface and the effects of near-wall density distribution on the ITR.

FIGURE 1.7 (a) $L_K$ values for different $\varepsilon_{\text{Si-O}}/\varepsilon_{\text{Si-O}}^*$ ($\varepsilon_{\text{Si-O}}^* = 0.12088$ eV) cases obtained at hot and cold surfaces. Surface temperatures are also given on the plot. (b) Variation of the hot wall $L_K$ value normalized with the corresponding cold surface $L_K$ value for different $\varepsilon_{\text{Si-O}}/\varepsilon_{\text{Si-O}}^*$ cases.
Water density variations near the hot and cold reservoirs are shown in Figure 1.9 using finer bin size of 0.0168 nm for various $\varepsilon_{\text{Si-O}}$ values. Similar to our earlier study, water penetration into the gap between the first and second silicon layers is observed, and the water density in this region increases with increased $\varepsilon_{\text{Si-O}}$. There also forms an additional density layer between the first density peak of water and silicon surface while these two density behaviors become profound for $\varepsilon_{\text{Si-O}} \geq 0.2 \times \varepsilon^*_{\text{Si-O}}$. These two new density layers are indicated with arrows in Figure 1.9c. Simply, decrease of ITR with an increased $\varepsilon_{\text{Si-O}}$ is the result of the stronger coupling between water and silicon molecules due to closer interactions. Comparisons of hot and cold side water densities of each case are also shown in Figure 1.9a through d. Water distributions near the hot and cold surfaces are identical for low $\varepsilon_{\text{Si-O}}$ values ($\varepsilon_{\text{Si-O}} < 0.2 \times \varepsilon^*_{\text{Si-O}}$). Starting with the $0.2 \times \varepsilon^*_{\text{Si-O}}$ case, the additional density layer near the surface is more prominent at the cold side, which creates a better phonon coupling resulting in the $L_{K-H}$ value being lower than $L_{K-C}$. While the densities for the $\varepsilon_{\text{Si-O}} < 0.2 \times \varepsilon^*_{\text{Si-O}}$ cases show no dependency on the surface temperature, density becomes more packed with decreased surface temperature for $\varepsilon_{\text{Si-O}} \geq 0.2 \times \varepsilon^*_{\text{Si-O}}$, which decreases the ITR. Thus, in Figure 1.7b, we observed not only the variation of ITR with temperature but also the temperature dependency of the water density, which affects the ITR value.

1.4.3 Temperature Dependence of ITR

Until now, we clarified that ITR strongly depends on the near-surface water density structure, which is a function of $\varepsilon_{\text{Si-O}}$ value. Therefore, we need to identify the proper parameters for water-silicon interactions. For this purpose, we conducted a nano water droplet study where we characterized the interaction parameters by matching the microscopic wetting behavior of water on silicon with the macroscopic experimental measurements [3]. Figure 1.10a through e shows the snapshots of the nanoscale droplets formed on bare (1, 0, 0) silicon surface and the microscopic contact angle values for the 0.4, 0.2, 0.125, 0.1, and 0.05 $\times \varepsilon^*_{\text{Si-O}}$ values. Increase of interaction strength decreases the contact angle so that the wettability changes from low to high in the studied range. By considering the line tension effects creating deviations between the nanoscale contact angle and the macro-scale value, an appropriate estimate for the interaction strength value.
FIGURE 1.9  (a–d) Comparison of the density distribution near the hot and cold surfaces for various $\varepsilon_{\text{Si–O}}/\varepsilon^*_{\text{Si–O}}$ cases.

FIGURE 1.10  (a–e) Snapshot of the nanoscale water droplets formed on bare (1, 0, 0) silicon surface and microscopic contact angle values at the corresponding interaction strength values.
was found as $\varepsilon_{\text{Si-O}} = 0.125 \times \varepsilon_{\text{Si-O}^*}$, which recovers the experimental macroscopic contact angle of water on pure silicon surface as 88° [3]. Details of this result and the methodology for calculation of the line tension effects to relate the wetting angles of nanoscale and macroscopic droplets can be found in [3].

Using the proper interaction strength value of $\varepsilon_{\text{Si-O}} = 0.125 \times \varepsilon_{\text{Si-O}^*}$, we investigated the temperature dependency of $L_K$ at the water–silicon interface. For this purpose, we assigned different temperature values on the hot reservoir as 363, 353, and 343 K while the cold reservoir was kept at 283, 293, and 303 K, respectively. Temperature profile for each case is shown in Figure 1.11. As the temperature difference assigned through the heat baths decreases, resulting heat flux values are decreased. The calculated $L_{K-H}$, $L_{K-C}$, heat flux, temperature gradients, and thermal conductivity of liquid water are tabulated in Table 1.3.

Before focusing on the $L_K$ variation at different surface temperatures, we should study the density structures near surface at each different temperature case. Density profiles of silicon–water–silicon system for different temperature differences are given in Figure 1.12. While Figure 1.12a shows slightly higher density peaks on the cold side for coarse bin (0.0672 nm) results, real behavior can only be characterized with a finer bin size (0.0168 nm) as shown in Figure 1.12b. Comparison of water densities near different temperature surfaces through Figure 1.12b validates that the near-wall water structure shows no dependency on the surface temperature, similar to our earlier results for low wetting surfaces.

### TABLE 1.3
Kapitza Lengths at Hot ($L_{K-H}$) and Cold ($L_{K-C}$) Surfaces, Heat Flux, Temperature Gradients, and Thermal Conductivity of Liquid Water of $0.125 \times \varepsilon_{\text{Si-O}^*}$ Case

<table>
<thead>
<tr>
<th>Case</th>
<th>$T_H$ and $T_C$ (K)</th>
<th>$\varepsilon_{\text{Si-O}} / \varepsilon_{\text{Si-O}^*}$</th>
<th>$q_x$ (W/m²)</th>
<th>$dT/dx$ (K/Å)</th>
<th>$k_{\text{water}}$ (W/km)</th>
<th>$T_H$ (K)</th>
<th>$L_{K-H}$ (nm)</th>
<th>$L_{K-C}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>363–283</td>
<td>0.125</td>
<td>5.411</td>
<td>0.271</td>
<td>0.661</td>
<td>355.5</td>
<td>8.213</td>
<td>286.5</td>
</tr>
<tr>
<td>2</td>
<td>353–293</td>
<td>0.125</td>
<td>4.286</td>
<td>0.215</td>
<td>0.659</td>
<td>347</td>
<td>8.186</td>
<td>295.1</td>
</tr>
<tr>
<td>3</td>
<td>343–303</td>
<td>0.125</td>
<td>2.843</td>
<td>0.14</td>
<td>0.672</td>
<td>338.4</td>
<td>8.321</td>
<td>303.8</td>
</tr>
</tbody>
</table>
Since the near-surface water density is independent of the wall temperature, we can now properly characterize the temperature dependency of $L_K$. Figure 1.13 gives the $L_K$ values at different temperature surfaces with the corresponding standard deviations, where lower temperature difference cases exhibit higher fluctuations. Similar to the theoretical predictions, ITR decreases with increased temperature since the phonon density of state is higher at high temperatures, which creates better coupling. Calculated $L_K$ values ($\approx 9$ nm) are consistent with the experimental measurements, where 6–12 nm $L_K$ values are found for hydrophilic and hydrophobic surfaces [72].

FIGURE 1.12  (a) Density profiles for different temperature cases. (b) Comparison of water distributions near the surfaces at different temperatures.
1.5 SUMMARY

In this chapter, we investigated molecular level interface phonon transfer between solids and liquids. The continuum hypothesis and Fourier’s law in nano-channels were studied while they found valid in channels with dimensions as small as 10 molecular diameters ($\approx 3.5$ nm). Afterward, we focused on the MD techniques for heat transport problems. We started with questioning the current thermostat use for creating a heat flux with the non-equilibrium dynamics. Using three distinct boundary treatment methods, we investigated heat conduction in liquid argon-filled silver nano-channels with the objective of characterization of the Kapitza resistance. The first and most common approach utilizes constant temperature surfaces imposed via a thermostat (Case 1). However, the Kapitza resistance calculated with this method results in artificially large values, compared with Case 2, which thermostats the outermost three wall layers. In fact, Case 2 exhibits artificial resistance at the edge of the thermostat applied region as an unphysical temperature jump in the homogenous silver domain. Detailed thermal resistance analysis of both cases clearly show that the isothermal wall approach suffers from the artificial thermal resistance due to the thermostat effects. The alternative approach of adding and extracting energy at three outermost layers of silver walls (Case 3) eliminates the artificial thermal resistance, and results in Kapitza resistance values consistent with Case 2. However, this approach has its own limitations, such as the inability to assign wall temperature, which is similar to the undetermined temperature based on integration of heat conduction equation using Neumann boundary conditions. Unlike the continuum-based approach, MD converges to a temperature distribution determined by the initial temperature of the system. Results clearly show that the Kapitza resistance and Kapitza length should be predicted either by using a large solid domain by applying thermostat to several wall layers away from the liquid/solid interface, or by adding and extracting energy from the surfaces.

Next, we studied temperature dependence of the water/silicon ITR with proper emphasize on the surface wetting properties and liquid layering near the surface. Results show that the ITR between
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A liquid and solid is dominated by the liquid structure formed on the surface under high wetting conditions. In such case, change of temperature not only alters the phonon transport, but also creates different coupling between liquid and solid molecules due to the variation of liquid ordering near the surface. As a result, interface resistance increases with increased temperature for high-wetting surfaces. The opposite behavior is true for low-wetting surfaces, where the density structure near the surface is independent of the surface temperature. As a result, change of surface temperature only affects phonon transport. Similar to the theoretical expectations, ITR decreases with increased temperature of a surface with wettability. In the light of these results, the wetting behavior of a liquid/solid couple should be properly considered in order to characterize the behavior of ITR. For such cases, we also clarified that the classical mixing rules frequently employed in the literature are not suitable to capture the correct interface behavior. The interaction strength value predicted by the Lorentz–Berthelot mixing rule creates highly hydrophilic silicon surface opposite to the experimental measurements. Hence, by conducting a nanoscale water droplet study, we properly tuned the interaction parameters in order to recover the real hydrophobic nature of bare silicon surface. Using the proper parameters, we characterized the temperature dependence of Kapitza length at the water/silicon interface, where MD-predicted Kapitza length values ($\approx9$ nm) agree with the experimental results for slightly hydrophobic surfaces.

REFERENCES


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