Scale Effects in Nanoscale Heat Transfer for Fourier’s Law in a Dissimilar Molecular Interface

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ABSTRACT: The dependence of the heat transfer of a nanoscopic liquid channel residing at the solid–liquid interface is traditionally ascribed to the temperature jump, interfacial thermal resistance, wettability, and heat flux. Other contributions stemming from the channel width dependence such as the boundary position are typically ignored. Here, we conducted nonequilibrium molecular dynamics simulations to better understand the relation between channel width and boundary positions located at the solid–liquid interface. The system under investigation is a simple liquid confined between the solid from nanochannels of different sizes (3.27–7.35 nm). In this investigation, the existence of the correlation between the boundary position and the channel width is observed, which follows an exponential function. The thermal conductivity of the boundary positions is compared with the experimental value and Green–Kubo prediction to verify the actual boundary position. Atomistic simulation reveals that the solid–liquid boundary position, which matches the experimental value of thermal conductivity, varies with the channel width because of the intermolecular force and the phonon mismatch of the solid and the liquid.

1. INTRODUCTION

Recent advancements in micro-/nanofluidics have attracted a large number of applications in areas such as nano energy transport, energy storage, water purification, biochips, drug delivery, and integrated fuel cells. A clear understanding of interfacial thermal transport across the solid–liquid interface is crucial to increase both the performance and function of various micro-/nanoscale electronic devices. Because of the complexity of handling interfacial heat transfer in the nanoscale in an experimental environment, molecular dynamics (MD) simulations are ideal for addressing such issues as they are able to solve the equations of motion by determining the trajectory of the atoms. Most of the thermodynamic and transport properties of either solids or liquids can be reproduced by MD simulations. Thus, in this paper, MD simulations are performed to investigate the atomic-level details of the interfacial phenomena such as heat transfer in the nanoscale.

At the interface, because of the mismatch between the two dissimilar materials, a temperature discontinuity occurs when there is a heat transfer across the solid–liquid interface, resulting in a temperature jump \( \Delta T \). The temperature jump can be expressed in terms of thermal resistance \( R_K \) and heat flux \( J \) as follows

\[
\Delta T = -R_K J
\]

Heat flux \( J \) is calculated by using Fourier’s law, where thermal conductivity \( \lambda \) is constant. Thus, heat flux is expressed as follows

\[
J = -\lambda \frac{\partial T}{\partial z}_{\text{liquid}}
\]
Chaudhuri et al. investigated thermal conductance at the interface as a function of the solid–liquid interaction strength and showed that the strong interaction results in a layering of fluid molecules on the solid surface. When heat is transmitted, interfacial oscillation indicates the vibrational mismatch is decreasing and the heat transfer is increasing. The interfacial thermal resistance (ITR) between the solid and liquid is also known as the Kapitza resistance. The Kapitza resistance was first discovered by Kapitza in 1941 while studying superfluidity in cryogenic conditions. Alternatively, the Kapitza length (or thermal resistance length) can be defined by extrapolating the temperature profile from the liquid to the solid, similar to the velocity slip length. From the temperature jump, the Kapitza length can be predicted, which is as

\[
\Delta T = L_K \frac{\partial T}{\partial z_{\text{liquid}}} \tag{3}
\]

where \((\partial T/\partial z)\) is the temperature gradient on the liquid region (i.e., \(z\)-axis direction) and \(\Delta T = T_{\text{solid}} - T_{\text{liquid}}\). Using eqs 1 and 3, it can be written as \(L_K = R_K \Delta t\), where \(L_K\) is the Kapitza length. In a systematic study, at the solid–liquid interface, Kim et al. showed that the thermal resistance length depends on the thermal oscillation, wall temperature, temperature gradient, wettability, and channel width. Strong wettability enhances heat transmission from solid to liquid, which decreases \(L_K\) exponentially. It is also affected by the domain size and interfacial boundary position.

Several MD studies have been done to investigate the effect of the domain size on mechanical properties. Although in the classical law of mechanics, it is assumed that the mechanical properties are size effect-independent, in an MD simulation, the average density of a liquid decreases with decreasing channel width. When the size of the system is reduced down to the nanoscale, the surface-to-volume ratio starts to increase dramatically. Because of the large surface area to volume ratio, the liquid inside the nanoscale confinements reveals substantially different physics than what is observed in larger scales. Thus, it is necessary to investigate the domain size effect to understand the nanoscale transport phenomena.

Moreover, it is also important to investigate the scale effect on the boundary position because the boundary position significantly affects the mechanical properties in nanometer-scale systems. Prior studies have defined boundary positions at different points during the past decades. Some researchers defined the boundary position at the innermost solid layer, whereas Han et al. used the midpoint of the innermost solid layer as a boundary position. Furthermore, zero liquid density and the peak of the absorbed layer are also used as a boundary position. The lack of an exact boundary position may lead to some critical problems as the value of the velocity slip, the ITR, the local property adjacent to the solid–liquid, and the contact angle can increase or decrease depending on the boundary position. To address these challenges given above, a proper wall–liquid boundary definition, together with the thermal conductance, heat flux, and temperature jump, is essential for a better understanding of nanoscale physics, which can in turn lead to better design of nanodevices aimed at energy optimization. Recently developed semiconductors and fuel cell production processes are based on nanometer-scale fabrication. However, the exact atomic-level definition of the boundary position for a continuum description such as Fourier’s law is still not clear.

The definition of a boundary position is a complicated concept wherein the rate of heat loss reduces at an atomic scale because the scale of nanodevice modeling is equal to the size of the electron orbits of the atoms. Noh et al. revealed in their work that the boundary position changes when the temperature changes. Therefore, defining an atomic-level solid–liquid boundary position involves a temperature jump, temperature gradient, thermal resistance length, heat flux, and thermal conductivity.

In this paper, we use MD simulation to study the boundary position and heat conduction between parallel plates, which are separated by a thin layer of simple liquid, as shown in Figure 1. First, we show the effect of different channel widths, which contain different boundary positions, on temperature jump, temperature gradient, and thermal resistance length. Then, the difference of heat flux calculated using Fourier’s law in the case of MD simulation and the experimental assumption are shown under various channel widths and boundary positions. The thermal conductivity is calculated using Fourier’s law on the boundary positions where the boundary position is characterized as a function of channel width, thermal conductivity, and wettability to compare the calculated thermal conductivity at different positions with the experimental thermal conductivity. In other words, the main objective of this paper is to investigate the effects of different channel widths on the boundary positions, which is being probed for the first time in this paper.

2. RESULTS AND DISCUSSION

Figure 2 illustrates the typical definitions of temperature jump, gradient, density distribution, thermal resistance length, and boundary position at the solid–liquid interface. In this paper, we consider four boundary positions: the innermost solid wall position (A), the theoretical boundary position (A’), the first peak density position (A”), and the \(3\sigma_{\text{fl}}\) distance away from...
The innermost solid wall position (A‴). The innermost solid wall position is the center of the solid, which is adjacent to the liquid. In other words, the distance between the two innermost solid walls is the innermost solid width. Because of a higher solid–liquid interaction than a liquid–liquid interaction, liquid atoms create a solid-like liquid layer at the interface.20 Thus, the density at the interface fluctuates more than that at the bulk region. The first peak of the density in the solid-like liquid layer is defined as the first peak density position. The width between the center of an innermost solid wall, the wall–liquid boundary (i.e., the theoretical boundary position), the first peak density position, and the $3\sigma_{wl}$ distance away from the solid wall are represented by $L$, $L′$, $L″$, $L‴$ respectively, where $(L′)$ is calculated by

$$L′ = L - 2\left(\sqrt{2}\sigma_{wl} - \frac{\sigma_1}{2}\right)$$  \hspace{1cm} (4)$$

where $L$ represents the center-to-center of the solid wall width. The wall-liquid molecular diameter, $\sigma_{wl} = 2.978$ Å, was obtained using the Lorentz–Berthelot (L–B) mixing rule.

2.1. ITR in the Molecular Interface. Using the described atomistic model system, we first analyze the temperature distribution of the liquid, which is confined between solid plates along the $z$-direction, as depicted in Figure 3. The hot and cold reservoirs on the left and right surfaces are maintained at 140 and 90 K, respectively, using Langevin thermostats. The simulation domain is divided into a corresponding slab bin width of 0.3408 nm. Note that, as shown in Figure 3a–d, we keep the interaction strength of the solid–liquid constant at $\varepsilon_{wl} = 0.06$ eV while only changing the channel width. The interfacial region of the liquid defined near the wall–liquid interface is known to be approximately $3\sigma_{wl}$, and the bulk regions are observed beyond the $3\sigma_{wl}$ distance. Hence, the local temperature varies as a linear function when...
the presence of temperature difference in the system reaches a steady state with respect to the position in the liquid-bulk region. The existence of the temperature jump or thermal resistance at the interface between the solid and liquid domains indicates a mismatch between the vibrational densities of the two domains. To determine the interfacial temperature jumps, we apply the linear least squares method to extrapolate the linear temperature from the liquid region to the solid surfaces and vice-versa. In this analysis, the surface positions are determined where the innermost solid wall position is adjacent to the liquid. The results demonstrate that the temperature jump decreases as the channel width increases because the surface force effect lessens when the channel width increases. In addition, the liquid atoms at the interface are dominated by the solid atoms. We observed that in the solid region, the temperature is higher than in the liquid region because of the higher thermal conductivity of the solid atoms. At the interface of the thermostat-applied and thermostat-free regions, a sudden temperature drop is observed. The applied thermostat caused this artificial temperature jump, which maintains a set temperature by adjusting the atomic velocities.\(^\text{45}\)

To comprehensively understand the interface atom fluctuation, we investigate the vibrational density of states (VDOS) (i.e., the number of vibrational modes per unit volume and frequency) by performing the Fourier transform of the velocity autocorrelation function (VACF) to provide a better understanding of the interfacial thermal transport by using eq 9. The detailed computational information of VACF and VDOS are discussed in the theoretical background section. Principally, VDOS aids in quantifying the change of phonon spectrum across an interface due to the mismatch of the vibrational estate of the different crystal structures.\(^\text{46}\) Apart from this, at the dissimilar molecular interface, liquid atoms near the solid surface go in freezing mode and create a solid-like layer at the dissimilar interface because of the surface force and liquid–liquid strength in the nanoscale system. Xue et al. denoted this layer as the "solid-like liquid layer."\(^\text{20}\) Therefore, we consider the first liquid layered structure near the solid surface to calculate the VDOS of liquid particles. Note that the VDOS is calculated for only 3.27 nm of the liquid channel, as shown in Figure 4a. Here, the blue line represents the liquid interfacial layer, and the black and pink dotted lines represent the solid bulk layer and the interfacial solid layer, respectively. It can be seen from the figure that the decreasing VDOS indicates that the vibrational mismatch is decreasing and the heat transfer is increasing as the wettability increases. The reason is the following. Fluid atoms fluctuate more than solid atoms because of their amorphous condition. Hence, the vibration of liquid atoms at the interface is strongly affected by the solid–liquid interatomic forces. The vibration in the interfacial atoms is higher because of the dissimilar atoms and the existence of vibrational mismatch. The vibrational mismatch leads to the ITR, as shown in Figure 3. Furthermore, the thermal resistance decreases when the vibrational coupling increases. Essentially, the degree of overlap at the interface measures the degree of vibrational coupling. We determine the area under the interfacial liquid line, the interfacial solid line, and the solid bulk line, which are here denoted as \(A_{\text{IL}}\), \(A_{\text{IS}}\), and \(A_{\text{SB}}\), respectively. Figure 4b,c presents the effects of wettability on the ratio of area under the VDOS of interfacial solid and liquid regions and the interfacial temperature jump. Higher wettability reduces the temperature jump and increases the overlap at the interface. Consequently, the overlap area of the solid–liquid at the interface increases with the increase in wettability. Thus, thermal coupling at the solid–liquid interface is a key factor in controlling thermal resistance and
the performance of nanoscale devices. Typically, a good overlap between the spectra implies strong vibrational coupling and, consequently, a low-temperature jump. Liang and Tsai also worked on VDOS of a thin film between two different

Figure 5. (a) Effect of different liquid regions and boundary positions on the average temperature jump and (b) temperature gradient. (c) Effect of the temperature jump and gradient on the same boundary positions of the different liquid regions, where the slope represents the interface thermal resistance length. (d) Impact on interface thermal resistance length for the various liquid region and boundary positions.

Figure 6. Fourier’s law-based heat flux profile of different channel widths and boundary positions. The parameters of temperature difference are obtained from MD results using Fourier’s law (a), experimental assumption of the continuum world (b), and using I–K method (c).
solid materials. They found that efficient heat flow and harmonic vibrational coupling or resonant thermal transport can be obtained by a higher degree of overlap. That being so, higher wettability can reduce ITR and enhances heat transfer.

2.2. Limit of Fourier’s Law in the Molecular Interface.

To provide more insight into the effects of the channel width and boundary position, the temperature jump at the interface is shown in Figure 5a. We define temperature jump as the temperature difference between the solid and liquid atoms at the interface, as \( \Delta T = T_{\text{solid}} - T_{\text{liquid}} \). The interfacial interaction strength is obtained by using L–B rules, which is 0.06 eV. Temperature jumps exist at the interface because of thermal transport between dissimilar materials. For each channel width, temperature jump is observed at four different boundary positions at the interface. When the solid–liquid boundary position shifts from the innermost solid wall to the bulk region, the temperature jump at the interface begins to increase. We observed that this propensity is a look-alike in case of the smallest to the largest channel. In particular, because of the surface force and size effect, temperature jump increases when the boundary position shifts toward 3σwl from an innermost solid wall, and the channel width decreases, respectively. Under these circumstances, the boundary position-wise temperature jump of each channel follows the exponential decay function.

Figure 5b shows the temperature gradient in the liquid region for different channel widths and boundary positions. In Figure 5b, the temperature gradient changes when the channel width changes, whereas it remains constant at different boundary positions. Furthermore, it can be seen that the interfacial temperature jump is linearly proportional to the thermal gradient, which is shown in Figure 5c. The results reported in Figure 5d show the effect on the thermal resistance length calculated by using eq 3: the thermal resistance length changes because of the boundary position and channel width. However, it can also be seen from all three figures that the temperature jump and the temperature gradient decrease when the channel size increases, while variation in the channel width does not have a significant effect on the thermal resistance length at the interface. Hence, the ITR length is independent of the thermal gradient.

In Figure 6, the heat flux is calculated to obtain atomic-level insight into the heat transfer mechanism across the interface between the solid and the liquid. First, we calculated the heat flux by using Fourier’s law, as shown in Figure 6a; the value of the thermal conductivity is taken from the experimental results of Ziebland and Burton. In Figure 6a, the thermal gradient is taken directly from the MD temperature profile and used to calculate the heat flux using Fourier’s law. Figure 6a shows that when the channel width increases, the temperature gradient decreases in the liquid region, which lowers the heat flux. Furthermore, when the boundary position changes for a specific channel, the heat flux remains constant, which is close to the actual heat flux in the confined liquid, because the temperature difference \( (\partial T) \) changes linearly with the changing width \( (\partial z) \). On the other hand, in Figure 6b, heat flux is elucidated using the continuum characteristic, that is, the temperature difference is assumed to be constant (i.e., the difference between the hot and cold wall temperatures), and Fourier’s law. It can be seen that the heat flux calculated using experimental assumption changes with respect to the channel width, that is, channel width according to boundary position (Figure 6b). This is because of the constant value of the wall temperature. Specifically, the thermal gradients calculated using constant wall temperature for various channel widths according to boundary positions are different; so is the heat flux. This ambiguous definition of the boundary positions...
makes it difficult to apply Fourier’s law in a nanochannel exactly. Thus, from the above figures, if we maintain the temperature gradient and it is measured from the middle region of the channel width, then heat flux does not change, as shown in Figure 6a. However, if we assume the temperature gradient by the wall temperature (i.e., wall temperature is linear), then heat flux changes (Figure 6b). We then showed the heat flux directly obtained from the MD simulation as represented in Figure 6c, which follows a trend similar to that in Figure 6b. The reasons are as follows. The heat flux in MD simulation is calculated by using the I–K method (eq 8). Hence, heat flux changes with respect to different boundary positions because of the varying volume of the liquid region, that is, the heat flux decreases when the volume increases and vice versa. Specifically, this is because of the reduction of the temperature gradient in the liquid region. Moreover, it is found that the volume of the liquid region depends on the boundary position, which is in the axial direction. Thus, the width according to boundary position is important because it gives us the gradient. The imprecise temperature gradient will lead to the inaccurate heat flux. Therefore, comparing Figure 6a–c, it can be said that if the interface position is not carefully chosen, the properties produced, when Fourier’s law with the experimental assumption is used, does not really match with the exact heat energy in the system.

The thermal conductivity is shown in Figure 7, which is measured in the confined liquid region. To determine the thermal conductivity of the confined liquid, we use Fourier’s law \( J = -\lambda \nabla T \), which exploits the temperature gradient of the MD temperature profile. The thermal conductivity of the MD simulations is compared with the experimental results. Note that the thermal conductivity is a material property that is constant. In the figure, the experimental value of 100 K liquid thermal conductivity (i.e., \( \lambda = 0.10418 \text{ W/mK} \)) is represented by the solid black line, and the red dotted line is the thermal conductivity obtained by using the Green–Kubo (i.e., \( \lambda = 0.1032 \text{ W/mK} \)) equation. We calculate the thermal conductivity for weak and strong wettability at the same time. It is noticed that in the case of the smallest channel, when the wettability is weak (i.e., \( \sigma_{\text{wet}} = 0.03 \text{ eV} \)), the innermost boundary position is a good match with the experimental value of thermal conductivity and the thermal conductivity calculated by using the Green–Kubo. However, at strong wettability, the thermal conductivity is lower. The reasons are as follows. At the interface, the vibrational frequency of the dissimilar molecular atoms increases with the increase in the interface strength. When the vibrational frequency is higher, heat flux decreases, whereas heat flux is proportional to thermal conductivity according to Fourier’s law, which decreases at different boundary positions on the same channel. Thus, the effect of the interface vibration frequency reduces with the increase in the nano-confined channel width. The result from Figure 7 thus reveals that the boundary position, which matches the experimental value of thermal conductivity, changes toward the solid interface when the channel increases and the wettability decreases. The reason behind this is that the axial width of the volume is changing with the boundary position. In particular, when the channel width increases, the boundary position moves forward to the innermost solid wall. As regards wettability, the boundary position that matches the experimental value of thermal conductivity moves forward to the innermost solid wall as the wettability decreases and vice versa. Thus, the boundary position that matches the experimental value of thermal conductivity fluctuates more in the case of the small channel when the wettability increases because an increase in wettability increases the surface force effect in solid–liquid. Sääskilähti et al. studied the effect of the system size on thermal conductivity. Therefore, the volume with respect to the boundary position that matches the experimental value of thermal conductivity is the actual occupied volume of a specific liquid region.

**2.3. Scale Effect.** Figure 8 shows the scale effect on temperature jump at the interface at different boundary positions. From Figure 5a, it is observed that the boundary-wise temperature jump decreases exponentially. For this reason, the boundary-wise temperature jump is shown here for various channel widths (from 3.27 to 100 nm) with the help of MD results by using the exponential function. Here, we use the exponential decay equation, that is, \( y = a e^{-bx} \), where \( a \) and \( b \) are the exponential coefficients. Note that the exponential coefficients are different for each boundary position line; the values of the coefficients are shown in Table 1. It can be seen that after reaching the 40 nm channel,

![Figure 8](https://dx.doi.org/10.1021/acsomega.0c03241)  
**Figure 8.** Effect of the boundary position of different domain sizes on temperature jump.

| width | \( a \) | \( b \) |
|-------|--------|--------|
| \( L^* \) | 14.506 | 0.128 |
| \( L^* \) | 8.2205 | 0.104 |
| \( L' \) | 6.4024 | 0.086 |
| \( L \) | 4.0984 | 0.057 |

the temperature jumps on the different boundary positions of a channel become similar. It is also observed that the size effects can entirely be attributed to reveal the similar values of the temperature jumps as the channel width increase. This figure shows clearly how temperature jump decreases when the width of the liquid channel increases and the temperature jump gradually approaches zero.

### 3. CONCLUSIONS

In this work, we performed atomistic simulations of heat transfer on a nanoscale between the solid and liquid, focusing on the dissimilar molecular interface where the relation between channel width and boundary positions residing at the solid–liquid interface is investigated. In heat transfer studies, the temperature profile of the solid and liquid consistently exhibited temperature discontinuity at the interface. This is explained by the analysis of the phonon spectrum at the interface using the vibrational density of states. The temperature jump of the liquid near the solid surface differs.
with different boundary positions and channel widths. Particularly, when the channel width increases and the boundary position changes from $3\sigma_0$ toward the innermost solid wall, the temperature jump decreases. In addition, temperature jump is a function of the thermal gradient and is also affected by the thermal energy of the solid molecules. It is found that the temperature gradient changes when the channel width changes, whereas it remains constant regardless of the boundary positions. Furthermore, the temperature gradient decrease in the liquid region lessens the heat flux, while in terms of the boundary positions, the heat flux follows the same trend as the temperature gradient. The heat flux is calculated using Fourier’s law and the I–K method. The thermal conductivity of the boundary positions is compared with experimental value and Green–Kubo prediction. Our result reveals that the first peak density boundary position matches well with the experimental value and the Green–Kubo prediction of thermal conductivity. However, for the smallest channel, the boundary position that matches the experimental value of thermal conductivity fluctuates more than the larger channel and varies with different wettability values. The temperature jump for different boundary positions decreases with an increase in the channel width, which follows an exponential function; after reaching the 40 nm channel width, the temperature jump on different boundary positions of a channel becomes similar. It is also observed that the size effects can be entirely attributed to reveal the similar values of temperature jumps as the channel width increases. It shows clearly that the temperature jump decreases when the width of the liquid channel increases and the temperature jump gradually approaches zero.

4. THEORETICAL BACKGROUND

The simulation domain consists of argon as a simple liquid and two parallel solid silver walls. Both solid walls are modeled following the face-centered cubic (FCC) structures (with [001] oriented crystals plane facing in the liquid of length 9u across the x, y and 10u in the z-direction, where $a = 4.086$ Å is the lattice constant of silver). The distance that separates the two solid walls varies from 3.27 to 7.35 nm of confined liquid. The corresponding number-density of the liquid is always maintained at $\rho = 0.8 \rho = N\sigma^3/V$. The solid substrate in the simulation is performed using 20 layers of silver [001]. In total, 6480 silver molecules are contained in the solid domain.

To perform the nonequilibrium MD simulation of heat transfer through the z-direction of the systems, both sides of the simulation domains (the outermost layers) were fixed to their original position to maintain a constant volume. Periodic boundary conditions are applied along the x and y directions for both the solid and liquid domains. To describe the interatomic interactions, we apply truncated 12–6 Lennard-Jones (LJ) potential

$$V_{\text{truncated}}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right]$$

(5)

where $\epsilon$, $r_0$, $\sigma$, and $r_c$ are the depth of the potential well, the intermolecular distance, the finite molecular distance at which the interatomic potential is zero, and the cutoff distance, respectively. In this simulation, L–B mixing rules are used to calculate the interatomic potential parameters between the solid and liquid

$$\sigma_d = \frac{\sigma_s + \sigma_l}{2}, \quad \epsilon_d = \sqrt{\frac{\epsilon_s \times \epsilon_l}{2}}$$

(6)

The details of the interatomic potential parameters used in the simulations are given in Table 2. We set the same 12-6 LJ potential parameters for both the liquid–liquid and liquid–solid interactions, whereas the solid–solid interaction is calculated using the embedded atom model potential, which is a many-body potential with a slightly higher computational cost than the pair potential, specifically used for FCC structures.

Table 2. Intermolecular Interaction Parameters of the Solid and Liquid

| interaction       | $\sigma$ (nm) | $\epsilon$ (eV) |
|-------------------|---------------|-----------------|
| solid–solid       | 0.2551        | 0.408           |
| liquid–liquid     | 0.3405        | 0.01            |
| solid–liquid      | 0.2978        | 0.06            |

To verify the boundary position in a nanoscale regime and the scale effect, it is essential to calculate the heat flux, thermal conductivity, and temperature distribution. For the thermal conductivity calculation, two methods are generally utilized: (1) Green–Kubo and (2) Fourier’s law.12 Exploiting the Green–Kubo approach, which is based on the fluctuation–dissipation theorem, thermal conductivity can be calculated as

$$\lambda = \frac{V}{3K_B T^2} \int_0^\infty \langle f(0) \cdot f(t) \rangle dt$$

(7)

where $\lambda$, $V$, and $K_B$ are the thermal conductivity, the volume of the system, and the Boltzmann constant, respectively. The angular brackets reveal an autocorrelation function and the heat flux ($f$) in the liquid. The second approach, that is, Fourier’s law, is based on a linear constitutive law. Both methods require heat flux ($f$), which is calculated from the net energy of every molecule in the system by using the Irving–Kirkwood (1–K) expression

$$J = \frac{1}{V} \left[ \sum_i \epsilon v_i + \frac{1}{2} \sum_{i<j} (F_{ij}(v_i + v_j))r_{ij} \right]$$

(8)

where $\epsilon$, $v_i$, and $F_{ij}$ are the per-atom energy (including potential and kinetic energy), the velocity of atom $i$, and the force acting on atom $i$ from atom $j$, respectively. Note that the volume of liquid is fixed in each case. Thermal conductivity in the liquid region is measured by using Fourier’s law with the help of the heat flux.

To investigate the role of solid–liquid vibrational coupling, we examine the VDOS of atoms by performing a Fourier transform of the VACF

$$V(t) = \langle \vec{v}(t) \cdot \vec{v}(0) \rangle$$

(9)

where $\vec{v}$ is the atomic velocity, and the angular bracket indicates a statistical average over multiple time origins. The VDOS is explicitly described as follows

$$\text{VDOS} (\omega) = \int_0^{+\infty} Z(t) e^{-i\omega t} dt$$

(10)
The VDOS measures the number of vibrations per unit frequency and represents the spectral description of atomic motions.

We use the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), a molecular dynamics code from Sandia National Laboratories, for all of the MD simulations where the simulation time step was set to 1.0 fs. In the NVT ensemble (i.e., constant number of molecules, volume, and temperature), the system temperature is maintained at 100 K. In this stage, for the initial velocities of all the atoms, the Maxwell–Boltzmann velocity distribution is used, while the Nose–Hoover thermostat is applied and the system temperature is maintained at 100 K. Afterward, in order to induce a heat flux through the solid–liquid interfaces, the Langevin thermostat was applied to assign different temperatures on hot and cold reservoirs in the outermost second, third, and fourth layers for both hot and cold solid walls. Simultaneously, an NVE ensemble (i.e., constant number of molecules, volume, and energy) was applied to the remainder of the metallic walls and the fluid. The simulation is run for 12 ns, 2 ns for the NVT simulation to reach an equilibrium state, 10 ns for the NVE simulation to make steady-state (3 ns), and is time averaging for seven times (1 × 7) ns. To confirm convergence and calculate the heat flux and temperature profiles, the steady-state uses a longer time averaging.

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B.K. designed and supervised the research. M.M. performed the simulations and analyzed data. All authors wrote the manuscript.

**Notes**

The authors declare no competing financial interest.

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