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# Analytical model for the effects of wetting on thermal boundary conductance across solid/classical liquid interfaces

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We develop an analytical model for the thermal boundary conductance between a solid and a liquid. By infusing recent developments in the phonon theory of liquid thermodynamics with diffuse mismatch theory, we derive a closed form model that can predict the effects of wetting on the thermal boundary conductance across an interface between a solid and a classical liquid. We account for the complete wetting (hydrophilicity), or lack thereof (hydrophobicity), of the liquid to the solid by considering varying contributions of transverse mode interactions between the solid and liquid interfacial layers; this transverse coupling relationship is determined with local density of states calculations from molecular dynamics simulations between Lennard-Jones solids and a liquids with different interfacial interaction energies. We present example calculations for the thermal boundary conductance between both hydrophobic and hydrophilic interfaces of Al/water and Au/water, which show excellent agreement with measured values reported by Ge *et al.* [Z. Ge, D. G. Cahill, and P. V. Braun, Phys. Rev. Lett. **96**, 186101 (2006)]. Our model does not require any fitting parameters and is appropriate to model heat flow across any planar interface between a solid and a classical liquid. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4870778]

## I. INTRODUCTION

The thermal boundary conductance across solid/solid interfaces has been an active area of research over the past few decades,[1,2] finding direct impact in advancing the understanding of heat transfer in solid nanosystems and devices.[3,4] Interestingly, even though the first extensive observation of thermal boundary conductance was reported between a solid and a liquid (superfluid liquid helium),[5] far less progress in the fundamental understanding of vibrational thermal conductance across solid/classical liquid interfaces has been made compared to their solid/solid counterparts. For example, a tremendous amount of experimental and computational work has gleaned insight into the fundamental physics driving electron and phonon thermal transport across planar solid-solid interfaces, and the role of interfacial properties such as roughness, impurities, and bonding at non-cryogenic temperatures (for a recent review of the experimental work, see Ref. 2). This has resulted in the advancement of analytical models that can accurately capture the scattering processes contributing to solid/solid thermal boundary conductance in this moderate temperature range.[6–17] However, experimental measurements of the thermal boundary conductance across planar solid and a liquid interfaces (i.e., not nanofluids) at non-cryogenic temperatures are limited.[18,19] Although a wealth of molecular dynamics (MD) simulations have elucidated physical processes at solid/liquid interfaces, a void still exists in terms of analytical modeling of thermal transport across solid/liquid interfaces to parallel that which exists across solid/solid

interfaces. This void severely limits the advancement of processes that rely on thermal coupling between a solid and a liquid, such as biological self-assembly,[20,21] heat pipe engineering and thermal ground plane development,[22,23] friction mitigation of liquid lubrication in magnetic hard disks,[24] and evaporative cooling of electronics.[25]

In response, we develop an analytical model to predict the thermal boundary conductance, $h_K$, across solid/liquid interfaces. Our theory is based off of the recent advances in the phonon theory of liquid thermodynamics.[26–28] By infusing concepts from this theory of phonon liquid thermodynamics and diffuse mismatch theory,[1] we derive a model that can predict the effect of wetting on the thermal boundary conductance across a solid/liquid interface. Our theory shows that the thermal transport dependence on wetting is due to the transverse mode coupling that varies based on the wetting of the liquid to the solid; this is consistent with Frenkel's[29] original theory of transverse modes in liquids being strongly affected by the shear state of the liquid. We confirm this wetting-dependency on the interfacial transverse modes at solid/liquid interfaces with MD simulations, which validates the assumptions of our model. The insight from our model elucidates the fundamental interactions of how wetting drives heat flow across solid/liquid interfaces. In addition, this model provides a formalism to predict thermal boundary conductance, and its dependency on interfacial chemistry, specifically for solid/liquid interfaces. Currently, this analytical modeling capability does not exist, and previous works have simply used models derived for solid/solid interfaces in discussions of solid/liquid interfacial thermal transport.[30] Therefore, the model presented in this work provides a relatively simple platform to analytically predict and study the

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thermal boundary conductance across solid/liquid interfaces, and the role of interfacial bonding on this thermal transport.

## II. BACKGROUND: SOLID/LIQUID THERMAL COUPLING

Several previous works have demonstrated the role that interfacial properties have on the heat transfer across solid/liquid interfaces. Ge et al.[18] experimentally measured the thermal boundary conductance across Au/water and Al/water interfaces with self-assembled monolayers to vary the degree of hydrophobicity; their measurements show that hydrophilic interfaces have higher thermal boundary conductances than hydrophobic interfaces. Similar measurements across Au/water interfaces were recently reported by Harikrishna et al.,[19] and they linked the thermal boundary conductance to the work of adhesion at the interface, directly relating the bonding at the interface to the thermal boundary conductance.

These experimental results are supported by nearly a decade of simulations. Barrat and Chiaruttini[31] used MD simulations to show that the solid/liquid thermal boundary conductance increases with an increase in the wetting of a surface; Murad and Puri[32] and Xue et al.[33] found this same dependence. Shenogina et al.[34] took this step further and demonstrated that $h_K$ across a solid/liquid interface varies linearly with work of adhesion, consistent with recent experimental work of Harikrishna et al.[19] Acharya et al.[35] showed that in addition to bonding considerations, $h_K$ at solid/liquid interfaces is also intimately coupled to chemical heterogeneity, roughness, and contact area.

Despite all of this computational work, an analytical phonon-based model has not been developed to predict $h_K$ across solid/liquid interfaces. Where the previously mentioned experiments and simulations demonstrate an unquestionable relationship between the solid/liquid bond and thermal boundary conductance, a deeper relationship of how the liquid molecules and subsequent thermal vibrations are influenced by the interfacial forces must be established to pursue a sound analytical theory that can capture changes in $h_K$ with varying wettability at an interface. Various studies on the structure, slip, and shear at solid/liquid interfaces give insight into the solid/liquid interaction that will form the basis of our model. For example, it is well established that the slip lengths of the liquid molecules at the interface are highly dependent on the wetting properties.[36,37] This slip length is strongly correlated to the surface/liquid interaction strength and surface roughness.[38]

From the discussion above, we can therefore establish that $h_K$ across a solid/liquid interface is dependent on slip length. This was confirmed by Torii et al.[39] and Ohara and Torii[24] via MD simulations conducted to demonstrate a direct relationship between $h_K$, slip, and the liquid motion parallel to the interface (i.e., shear of the liquid molecules at the solid wall). These works also established that the partition of energy to each degree of freedom for molecular motion at a solid/liquid interface differs in the vicinity of an interface compared to the "bulk" of the liquid; in other words, shear and longitudinal motion are decoupled at solid/liquid

interfaces. One of their major conclusions from this is that the surface potential and forces affect the molecular motion and heat transfer parallel to the solid/liquid interface (i.e., shear) yet not the motion perpendicular to the interface (i.e., longitudinal). Therefore, the slip length, which is the Kapitza length at solid/liquid interfaces,[37] is related to the shear motion in the liquid near the interface.

Based on these previous works, we therefore establish that the wetting at a solid/liquid interface directly affects the shear oscillations in the liquid at the solid/liquid interface. We calculate the thermal boundary conductance by considering a control volume in the liquid that is affected by the wetting at the solid/liquid interfaces. In this case, we treat the liquid not as a bulk liquid, but as a thin interfacial layer of liquid that is directly interacting with the solid and whose shear properties are driven by the solid/liquid interactions. This is consistent with the works of Murad and Puri[40] and Kim et al.[41] showing that boundary layers of liquid at a solid/liquid interface exhibit different thermal properties than the "bulk" liquid. This boundary layer has also been experimentally observed at solid/water interfaces, where the properties of this layer change with wetting.[42] Goicochea et al.[43] gleaned more in-depth insight into this liquid interfacial layer by demonstrating via MD simulations that the changes in the vibrational spectrum of surface atoms dictate the solid/liquid thermal boundary conductance.

Putting this together, we describe the wetting at the solid/liquid interface by imposing a varying shear state, which will affect the phonon modes in the liquid that are coupled to the solid and participating in thermal boundary conductance. In the limit of a completely de-wetted, hydrophobic interface, the shear modes of the liquid are described by the transverse phonon modes in the bulk liquid, which we can account for via the theory of liquid thermodynamics (reviewed in Sec. IV). At the other extreme of a hydrophilic surface, the zero slip condition is imposed on the liquid, which dictates that a liquid element adjacent to the surface assumes the velocity of the surface.[44] Therefore, when the interface is completely wetted, the velocities of the transverse modes of the liquid near the interface assume those of the transverse modes in the solid.

This shear-based modification to a liquid interfacial layer that we impose in our model is consistent with recent simulations by Ohara and Torii[24] who demonstrated that the thermal boundary conductance will increase when the shear rate of the liquid near the interface increases; for any given force, a higher shear rate would occur when the modulus of the monolayer at the interface is lower, consistent with the "near zero" shear modulus that defines a liquid. Furthermore, our assumption that the vibrational states in the monolayer of liquid adjacent to the solid boundary will be affected by the phonon states of the solid is consistent with the solid/liquid molecular dynamics simulations of Liang and Tsai;[45,46] we have also observed an additional effect of interfacial bonding of the vibrational states of solids atoms near interfaces.[47] It therefore follows that the solid/liquid interaction will affect the vibrations in the solid and liquid that drive thermal boundary conductance, which we discuss in more detail in Sec. III.

Using these assumptions, in Secs. III and IV we derive our analytical model for solid/liquid thermal boundary conductance. In Sec. III, we use MD simulations to study the role of solid/liquid interactions on the phonon modes near the interface. We specifically address how the bond strength between the solid and liquid interface affects the phonon modes that are transmitted across an interface from the solid, which we use to define the phonon flux participating in thermal boundary conductance in our analytical model. Using this knowledge from our MD simulations, we derive the diffuse mismatch model (DMM) for a solid/liquid interface based on the coupling of the transverse modes from the solid to the liquid. In other words, we account for wetting at the interface, and the effects of wetting on thermal boundary conductance through our definition of the liquid thermal flux of the liquid that are affected by the coupling to the solid. Our DMM accounts for liquid vibrational energy via the phonon theory of liquid thermodynamics[26] which gives explicit relationships for the phonons in a liquid and how the shear (transverse) phonon modes in a liquid behave below the Frenkel frequency.[29]

## III. MOLECULAR DYNAMICS SIMULATIONS: INSIGHT INTO DENSITY OF STATES AT SOLID/LIQUID INTERFACES

The previous works in the literature discussed in Sec. II have addressed how the longitudinal and shear velocities of liquid layer at a solid interface are affected by the bonding/wetting of the liquid to the solid. However, the following question regarding the coupling of vibrational energy between a solid and a liquid must be addressed to form an analytical theory of solid/liquid thermal boundary conductance: how are the transmission of phonon modes affected by the bond strength between the solid and the liquid? Specifically, how are the interfacial phonons on the solid surface affected by the liquid interaction energy? To answer these questions, and give insight into the nature of phonon transmission from a solid across a solid/liquid interface, we use MD simulations. Specifically, we use MD simulations to qualitatively understand how the phonons at the interface of a solid are affected by the interaction strength at the solid/liquid interface. We note that we take this approach to only gain qualitative insight into how the phonon modes in a solid are manipulated from the interactions with a liquid. From this, we infer how phonons from the solid are transmitted to the liquid, and how the relative strength of the solid/liquid bond affects this vibrational interaction. Note, we have successfully used this approach to study a similar phenomenon at solid/solid interfaces in our previous work.[47]

We perform molecular dynamics simulations using the LAMMPS package from Sandia National Laboratories.[48] The atoms in our computational cell were arranged in $10 \times 10 \times 40$ face centered cubic conventional unit cells with periodic boundary conditions in all directions. Our lattice was equally split midway on the $z$-axis into half solid-type and half liquid-type by prescribing different interaction strengths, $\varepsilon$, as described below. All interactions were calculated using the standard 6-12 Lennard Jones (LJ) potential,

$U(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]$, where $r$ is the interatomic separation and $\sigma$ and $\varepsilon$ are the LJ length and energy parameters, respectively. We chose Argon to parameterize the LJ potential with $\sigma = 3.045$ Å and the lattice constant $a_0 = 1.56\sigma$.[49] The cutoff distance or the radius beyond which the potential was truncated was set to $r = 2.5\sigma$. The energy parameter for the LJ solid atoms is prescribed to be $\varepsilon_{s-s} = 0.103$ eV. For the liquid atoms, we chose the energy parameter as $\varepsilon = 0.0103$ eV. This choice is reasonable since the melting point of the LJ solid is proportional to the energy parameter defining the solid-solid interaction and is approximately equal to $\varepsilon_{s-s}/2k_B$.[50] As we are interested in the effects of interfacial bonding between a solid and liquid on the phonon density of states, we set all atomic masses to 40 amu while varying the interaction strengths between the solid and liquid atoms. The value of the energy parameter for strong bonding is set to the value of $\varepsilon_{s-s}$ while the value for weak bonding is set to $\varepsilon_{l-l}$.

The system is equilibrated at a predefined temperature (at which the LJ system representing the liquid atoms melt) via a velocity scaling routine under the Nose-Hoover thermostat.[51] The time step used for equilibration was 0.5 fs and the energy of the system was equilibrated for 0.5 ns. We studied the vibrational densities of states of two representative monolayers in the solid in a microcanonical ensemble (NVE): the solid monolayer at the solid-liquid interface and a monolayer in the bulk solid. The velocities for the two solid monolayers were written to an output file after every 10 time steps for a total of 300 ps and were analyzed separately using a velocity autocorrelation function algorithm to obtain the phonon density of states in each monolayer.[47] The details of this procedure to determine the phonon density of states in MD simulations is detailed in our previous work.[47]

The results of these simulations for the "weak" (i.e., hydrophobic, $\varepsilon_{s-l} = 0.0103$ eV) and "strong" (i.e., hydrophilic, $\varepsilon_{s-l} = 0.103$ eV) interfacial bonds are shown in Fig. 1. In each plot, the density of states in the "bulk" of the solid is also shown; in other words, as a baseline, we show the density of states for some atomic layer in the solid away from the solid/liquid interface that is not affected by the liquid interactions. We expect the density of states of a free surface to differ from that of a confined plane,[52] which is evident from the density of states of the interfacial solid atoms shown in the "$\varepsilon_{s-l} = 0.0103$ eV" plot. As expected from a free, noninteracting surface, the density of the transverse modes at the interface is roughly the same as those in the bulk, yet slightly shifted in frequency. In addition, the longitudinal modes are diminished in the confined plane due to the low energy bond restricting longitudinal motion. However, when the bonds between the solid and liquid are strengthened, mimicking a hydrophilic interface, the peak in the density of states of the solid interfacial atoms associated with the transverse modes is diminished. Note, in the "hydrophilic" interface, the longitudinal peak is unaffected which is expected for a mass with identical nearest neighbor bonds and atoms.

We can now interpret these results in terms of what transverse phonon modes from the solid side of the interface will transmit energy into the liquid. The density of states of the solid interfacial layer are indicative of phonons that have not coupled vibrational energy into the liquid.[47] In other words,
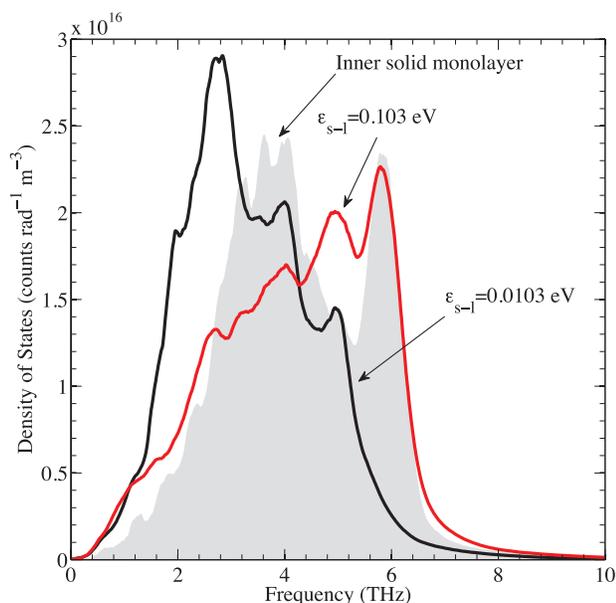
FIG. 1. Vibrational densities of states of the solid monolayer at the interface of a LJ solid and liquid in the case of a weak (left, $\varepsilon = 0.0103$ eV) and strong (right, $\varepsilon = 0.103$ eV) solid-liquid interaction. The density of states of a monolayer of atoms in the bulk of the solid, are also shown for comparison. In the weakly bonded case, the magnitude of the transverse modes in the density of states in the solid monolayers of atoms at the solid-liquid interface are unaffected. This indicates that no vibrational energy in the transverse modes is lost from the solid to the liquid, and this solid plane of atoms is effectively acting as a free surface. In the strongly bonded case, the transverse mode densities are strongly diminished as compared to the bulk due to coupling between solid and liquid transverse modes.

if the channel of energy transfer from some phonon energy in the solid to the same energy in the liquid is available, then the vibrations of that energy will be distributed among the two sides. This would result in a density of states reduction at that energy in the solid interfacial atoms. However, if there are weak interactions between the solid and the liquid, and phonon energies will not transmit from the solid into the liquid, the density of states in the solid at the solid/liquid interface will appear as a free surface. Comparing the solid interfacial densities of states for the weak case to the strong case, we observe a reduction in the transverse mode peak in the strong case compared to the weak case; this supports our previous discussion that transverse vibrational energies are coupled to the liquid at the strongly bonded interface, where the weakly bonded interface behaves like a free surface in which the transmission of the transverse vibrational energies to from the solid to the liquid is negligible. These MD results regarding transverse mode coupling provide an atomistically verified assumption that will be used in the development of our analytical model for solid/liquid thermal boundary conductance derived in Sec. IV.

## IV. DIFFUSE MISMATCH MODEL FOR SOLID/LIQUID INTERFACES

We now use the discussions in Secs. II and III to form the basis of our diffuse mismatch model for thermal boundary conductance across a solid/liquid interface. We have established in Sec. II that in the limit of a hydrophobic interface,

the interfacial layer of liquid at the interface will have similar velocities to that of the bulk liquid; conversely, in the limit of a hydrophilic interface, the zero slip condition applies and the interfacial layer of liquid at the interface will assume the transverse velocities of the solid. In each of these cases, the longitudinal modes remain unaffected. Turning now to the effects of bonding on phonon transmission, as we determined from our MD analysis in Sec. III, the degree of hydrophobicity at the solid/liquid interface affects the transmission of the transverse modes. In accordance with our MD results, at a completely hydrophobic interface, transverse modes in the solid will not contribute to thermal boundary conductance since they will not be transmitted across the solid/liquid interface. At the completely hydrophilic interface, however, transverse modes in the solid can couple with energetic vibrations in the liquid at the same energy. These assumptions, verified with our MD simulations in Sec. III, form the basis of the theory derived in this section.

The theory developed in this work is rooted in the basic assumptions of the diffuse mismatch model.[1] In this approach, the transmission of the power flux across an interface is determined from evoking the principle of detailed balance.[53,54] From this, the transmission of energy from the solid to the liquid is given by

$$\zeta = \frac{q_{\omega,\ell}}{q_{\omega,\mathrm{s}} + q_{\omega,\ell}}, \qquad (1)$$

where $q$ is the vibrational energy flux per unit time in the solid (S) or the liquid ($\ell$) at some frequency, $\omega$. In this work, we make the typical assumption of elastic scattering, or that a phonon in the solid with frequency $\hbar\omega$ will only couple with vibrations in the liquid with similar energies.[55] From this, we can define the fluxes of energies in the solid of Eq. (1) as

$$q_{\omega,\mathrm{s}} = \frac{1}{4} \sum_j \hbar\omega D_j f v_j, \qquad (2)$$

where $D$ is the density of states, $f$ is the Bose-Einstein distribution function, $v$ is the group velocity, and $j$ refers to the polarization (i.e., longitudinal or transverse). Defining the phonon flux in solids has been well documented for nearly a century,[56] and in the approach in this work, we approximate the phonon dispersion in the solids of interest with the lattice dynamical solution of a one-dimensional chain (the so-called "Born von-Karmen" dispersion approximation or "Sine-type" approximation)[57,58] while assuming an isotropic Brillouin zone. We note that this approximation for the phonon dispersion works well for calculating the thermal flux of solids with cubic symmetry and a single atom basis.[55] Our model calculations in this work are performed for Al/water and Au/water interfaces; we take the maximum frequency of the sine functions for our assumed phonon dispersions in Al and Au from lattice dynamics calculations of the phonon dispersions of Al and Au in the $\Gamma \to X$ direction presented in Refs. 59 and 60, respectively. Note, we slightly modify the sine function from the solution of a one-dimensional chain to account for the fact that the Brillouin zone edge in FCC Al and Au occurs at $2\pi/a$, where $a$ is the lattice constant.

Our approach to the treatment of the thermal flux in a classical liquid draws on recent advances in the phonon

theory of liquid thermodynamics.[26–28] This formalism of phonon liquid theory has shown exceptional agreement with the heat capacity of a wide variety of metallic and molecular liquids. As the heat capacity is the basis of thermal transport via our DMM calculations discussed in Sec. III, we use this formalism to describe the liquid flux in our thermal boundary conductance predictions ($q_{\omega,\text{liquid}}$ in Eq. (1)).

As outlined by Bolmatov *et al.*,[26] there are two types of atomic motion in a liquid: phonon vibrations and diffusional motion due to a liquid molecule jumping between two equilibrium positions. Therefore, the total energy of the liquid must account for both the kinetic and potential energies of phonon vibrations and molecular diffusion. The phonon motion in the liquid can be partially described by a longitudinal pressure wave, similar to that of solids. In addition, liquids can in fact support shear waves that oscillate with periods less than the liquid relaxation time, $\tau$, or the average time between two consecutive molecular diffusional scattering events.[61] At frequencies above the so-called Frenkel frequency, $\omega_F = 2\pi/\tau$ (Ref. 29), shear vibrations of the molecules are supported by the liquid and two transverse-like phonon modes exist. Therefore, by Frenkel's[29] original theory, phonon vibrations in classical liquids can be treated similar to solids, the only difference is the shear modes do not exist at frequencies below $\omega_F = 2\pi/\tau$. This hypothesis has since been verified.[61–64] In particular, liquid water, which is of interest in this work for model calculations, has a characteristic phonon spectra that is well described by a Debye approximation.[63]

We can therefore define the total energy of the liquid as

$$U = K_L + V_L + K_T(\omega > \omega_F) + V_T(\omega > \omega_F) + K_D + V_D, \tag{3}$$

where $K$ is the kinetic energy, $V$ is the potential energy, and the subscripts $L$, $T$, and $D$ stand for longitudinal phonon, transverse phonon, and diffusion. Note the energy of the transverse modes in the liquid are only defined at frequencies above the Frenkel frequency. In the following discussion, we simplify Eq. (3) based on fundamental concepts of the phonon theory of liquid thermodynamics[26–28] to derive the thermal flux in the liquid.

The diffusional potential energy can be omitted since $V_D \ll V_T$ due to the Frenkel mechanism.[27] The total kinetic energy in a liquid is $K = 3Nk_BT/2$ where $N$ is the atomic density of the liquid, $k_B$ is the Boltzmann constant, and $T$ is the temperature. This kinetic energy includes both vibrational and diffusional components. Using the Virial Theorem,[65] Eq. (3) can be rewritten in terms of the total energy of the longitudinal and transverse components as

$$U = U_L + U_T(\omega > \omega_F) + \frac{U_T(\omega < \omega_F)}{2}. \tag{4}$$

Each term in Eq. (3) can be calculated using the phonon free energy, given by

$$F = U_0 + T \sum_i \ln\left[1 - \exp\left[-\frac{\hbar\omega_i}{k_B T}\right]\right], \tag{5}$$

where $U_0$ is the ground state energy.[65] Using the relation that $U = F - T dF/dT$ and given that thermal expansion dictates

$d\omega_j/dT \neq 0$,

$$U_{\ell,j} = U_0 + \hbar \sum_i \frac{\omega_i - T\dfrac{d\omega_i}{dT}}{\exp\left[\dfrac{\hbar\omega_i}{k_B T}\right] - 1}. \tag{6}$$

Recasting in terms of the coefficient of thermal expansion, $\alpha$, via the quasi-harmonic Gruneisen approximation gives

$$U_\ell = \sum_j \left(U_0 + \left(1 + \frac{\alpha T}{2}\right) \sum_i \hbar\omega_i f\right). \tag{7}$$

The energy of each spectra of modes can be calculated by substituting the sum in Eq. (7) with the density of states. Recognizing that the thermal flux can be calculated by $q = Uv$, the thermal flux in the liquid via the phonon theory of liquid thermodynamics is given by

$$q_{\omega,\ell} = \frac{1}{4} \sum_j \hbar\omega D_j f v_j \left(1 + \frac{\alpha T}{2}\right), \tag{8}$$

where the ground state energy term disappears since there is no group velocity associated with these vibrations. In this work, we focus on only classical liquids, and therefore we assume $f = k_B T/(\hbar\omega)$ as the distribution of vibrational energy in the liquid. By using this classical statistical distribution of phonon energies in the liquid, we maintain the ability to model the coupling of specific phonon energies across the interface (i.e., our model includes frequency dependent, of spectral, phonon transmission).

In this work, we model the thermal boundary conductance across solid/water interfaces. We assume a Debye density of states for the liquid[63] given by the phonon theory of liquid thermodynamics, ($D_j = N\omega^2/(\omega_{j,\text{max}}^3)$) (Ref. 26). For the hydrophobic case, we take the longitudinal and transverse sounds speeds of water as 3200 and 1280 m s$^{-1}$, respectively.[63,66] For the hydrophilic case, we assume the transverse mode velocities are spectrally equal to those of the solid. From Ref. 26, we assume a maximum frequency of the longitudinal phonons as $\omega_{L,\text{max}} = 2\pi/\tau_D$, where $\tau_D = 150$ fs, and we make the harmonic approximation for water (i.e., $\alpha = 0$). For the maximum frequency of the transverse modes, we scale the longitudinal cutoff frequency by $v_T/v_L$. Finally, the Frenkel frequency of the liquid is $\omega_F = 2\pi/\tau_M = 2\pi G_\infty/\eta$, where $\tau_M$ is the Maxwell shear relaxation time, $G_\infty$ is the infinite-frequency shear modulus, and $\eta$ is the viscosity. For liquid water, $\eta = 853$ $\mu$Pa s and $G_\infty = 0.16$ Pa.

Given these stipulations, we can fully describe the phonon flux in the liquid, $q_{\omega,\text{liquid}}$ for calculations of the DMM transmission coefficient in Eq. (1). With this, and from the relationship that $h_K = \partial q/\partial T$, we can define the thermal boundary conductance from the solid to the liquid in the case of strong solid/liquid interactions (i.e., hydrophilic) as

$$q_{K,S\to\ell,\text{hydrophilic}} = \frac{1}{4} \sum_j \int_0^{\omega_{\text{max},j}} \hbar\omega D_j \frac{\partial f}{\partial T} v_j \zeta_{\text{hydrophilic}} \, d\omega, \tag{9}$$

where $\omega_{\text{max},j}$ is the maximum phonon frequency in the solid for polarization $j$, and $\zeta_{\text{hydrophilic}}$ is calculated with Eq. (1)

using Eq. (8) with the transverse velocities of the solid. Mathematically simplified, this is given by

$$\zeta_{\text{hydrophilic}} = \frac{k_B T (D_{L,\ell} v_{L,\ell} + D_{T,\ell} v_{T,S})}{\sum_j \frac{\hbar \omega D_{j,S} v_{j,S}}{1+\exp[\hbar\omega/(k_B T)]} + k_B T (D_{L,\ell} v_{L,\ell} + D_{T,\ell} v_{T,S})}.$$

(10)

In the limit of weak solid/liquid interactions at a hydrophobic interface, the transverse modes in the solid do not participate in interfacial energy transport. With this, we define the thermal boundary conductance from the solid to the liquid in the limit of weak solid/liquid interactions (i.e., hydrophobic) as

$$q_{K,S\rightarrow\ell,\text{hydrophobic}} = \frac{1}{4} \int_0^{\omega_{\max,L}} \hbar\omega D_L \frac{\partial f}{\partial T} v_L \zeta_{\text{hydrophobic}} \, d\omega.$$

(11)

Note in the definition of the hydrophobic flux, only the longitudinal phonon flux in the solid is assumed to participate in solid/liquid interfacial heat transport, consistent with our previous discussions in this paper. The transmission coefficient is given by

$$\zeta_{\text{hydrophobic}} = \frac{k_B T (D_{L,\ell} v_{L,\ell} + D_{T,\ell} v_{T,\ell})}{\frac{\hbar \omega D_{L,S} v_{L,S}}{1+\exp[\hbar\omega/(k_B T)]} + k_B T (D_{L,\ell} v_{L,\ell} + D_{T,\ell} v_{T,\ell})}.$$

(12)

We show calculations for hydrophilic and hydrophobic Au/water and Al/water interfaces in Fig. 2. Figure 2 plots the predicted thermal boundary conductances for these interfaces calculated via our DMMs given in Eqs. (9) and (11) as a function of the measured thermal boundary conductance at these same interfaces, reported in Ref. 18. Consistent with the experimental data, the stronger interactions between the solids and water in the hydrophilic case compared to the hydrophobic case lead to an increase in thermal boundary conductance. The dotted line in Fig. 2 represents perfect agreement between our solid/liquid DMM and experimentally measured
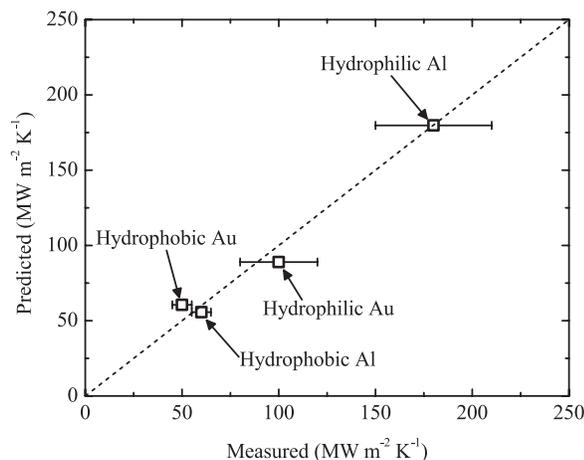


FIG. 2. Thermal boundary conductance predicted via the solid/liquid diffuse mismatch model derived in this work as a function of the thermal boundary conductance across four different interfaces measured by Ge *et al.*[18] We perform our DMM predictions for both hydrophilic and hydrophobic Al/water and Au/water interfaces. The dashed line represents perfect agreement between the prediction via our model and measured data. Our model shows remarkable agreement with the experimental data reported by Ge *et al.*[18]

data. Our model demonstrates exceptional agreement with the experimentally measured data at hydrophilic and hydrophobic interfaces reported by Ge *et al.*[18] We note that our model does not have any fitting or scaling parameters; all inputs are taken from literature values for Al, Au, and water. Our model gives insight into the thermal boundary conductance across hydrophobic and hydrophilic solid/liquid interfaces. That is, the weak bonding leads to a decrease in $h_K$ compared to the strong bonded case since transverse modes in the solid do not participate in interfacial heat transport. In the limit of the hydrophilic interface, the increase in $h_K$ compared to the hydrophobic case is not only due to the additional phonon flux from the transverse modes in the solid, but also the transverse modes in the liquid assume the transverse mode velocities in the solid due to the zero slip condition. We note that our model is applicable for any classical liquid.

## V. SUMMARY

In this work, we developed an analytical model to predict the thermal boundary conductance, $h_K$, across solid/classical liquid interfaces. Our theory is based off of the recent advances in the phonon theory of liquid thermodynamics[26–28] combined with diffuse mismatch theory of phonon transport across interfaces.[1] Our model is based on the following assumptions, which are strongly supported in the previous literature discussed in Sec. II and our MD simulations in Sec. III: (i) in the limit of a hydrophobic interface, the interfacial layer of liquid at the interface will have similar velocities to that of the bulk liquid; (ii) conversely, in the limit of a hydrophilic interface, the zero slip condition applies and the interfacial layer of liquid at the interface will assume the transverse velocities of the solid; (iii) in both hydrophobic and hydrophilic cases, the longitudinal modes remain unaffected; (iv) at a hydrophobic interface, transverse modes in the solid will not contribute to thermal boundary conductance since they will not be transmitted across the solid/liquid interface. Using these assumptions, we calculate the thermal boundary conductance with the solid/liquid DMM derived in this work for hydrophobic and hydrophilic Al/water and Au/water interfaces. We show remarkable agreement with previous thermal boundary conductance measurements by Ge *et al.*[18] Our model is applicable to any classical liquid.

The analysis in this work shows that the driving factor behind the change in thermal boundary conductance at solid/liquid interfaces with varying interaction strengths is due to the change in transmission, or interfacial coupling, of the transverse modes. This work was purposefully derived for a generic interface, and the MD simulations were performed using LJ solids to qualitatively understand the change in the density of states due to solid/liquid bonding. However, future MD simulations should focus on measuring the thermal boundary conductance across more specific solid/liquid interfaces with varying degrees of bonding, and relating these measured quantities to the local densities of states at the solid interface. Additional insight could be gained by utilizing wavelet transformations[67] to understand specific mode transmission across solid/liquid interfaces, and how the bonding state affects this conversion. Experimentally, measurements

of the thermal boundary conductance across planar interfaces between solids and various liquids with varying degrees of bonding are lacking in the literature.[18,19] Additional measurements at solid/liquid interfaces with both varying nanoscale geometries and surface chemistries would most certainly represent major path forwards to better understand the phenomena elucidated in this paper.

## ACKNOWLEDGMENTS

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