Two regimes of thermal resistance at a liquid–solid interface

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Using nonequilibrium molecular dynamics simulations in which a temperature gradient is imposed, we determine the thermal resistance of a model liquid–solid interface. Our simulations reveal that the strength of the bonding between liquid and solid atoms plays a key role in determining interfacial thermal resistance. Moreover, we find that the functional dependence of the thermal resistance on the strength of the liquid–solid interactions exhibits two distinct regimes: (i) exponential dependence for weak bonding (nonwetting liquid) and (ii) power law dependence for strong bonding (wetting liquid). The identification of the two regimes of the Kapitza resistance has profound implications for understanding and designing the thermal properties of nanocomposite materials. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1525806]

Resistance to heat flow through a solid–liquid interface has been an area of ongoing interest ever since the pioneering work on the metal–liquid helium interface by Kapitza.[1,2] Due to the relatively good contact between liquid and solid, this interfacial resistance, also known as the Kapitza resistance, is rather low compared to the resistance of solid–solid interfaces. Scientific interest into the origin of the Kapitza resistance has, until now, been a primary motivation for the studies of thermal transport across the liquid–solid interface; understanding the Kapitza resistance is now, however, becoming a technological imperative also, driven by the recent interest in nanocomposite materials, including ceramics,[3] polymers,[4] and fluids.[5] Such nanocomposites contain a high density of interfaces.

The current theoretical understanding of the thermal resistance of solid–liquid interfaces is primarily based on the "acoustic mismatch model" (AMM) in which one considers the transmission and reflection of classical heat waves at the interface.[2] However, the AMM, derived from the requirements of continuity at the interfaces, includes only the bulk properties of the two materials, with no account being taken of the nature of the bonding between liquid and solid atoms at the interface.

In this paper we report the results of molecular dynamics simulations on a simple model solid–liquid interface that demonstrate the profound effect of the strength of the bonding between the solid and liquid atoms at the interface on the Kapitza resistance. In particular, when the bonding at the solid–liquid interface is weak, corresponding to nonwetting liquid, the Kapitza resistance increases exponentially as the strength of the bonding between liquid and solid atoms. With stronger bonding, corresponding to a wetting liquid, the Kapitza resistance is inversely proportional to the solid–liquid bond strength. Although qualitatively consistent with the results of recent MD simulations on a similar system,[6] here we go considerably further, in that we are able to identify and quantify two different regimes of behavior and reveal the associated simple functional forms relating the Kapitza resistance with the solid–liquid bonding strength.

For our molecular simulations we use a simple model of the liquid and solid, both described by the Lennard-Jones (LJ) interatomic potential, with the interaction energy associated with a pair of atoms equal to $4\varepsilon[(\sigma/r)^{12}-(\sigma/r)^{6}]$, where r is the interatomic spacing, and the parameters ε and σ are energy and length scales, respectively. Because the melting point for the LJ potential is proportional to ε, to allow the study of stable solid–liquid systems we choose the strength of the interactions between solid atoms, ε_{ss}, to be 10 times larger than that between the liquid atoms ε_{ll}. The binding energy parameter for solid–liquid interactions is $\varepsilon_{is}=\alpha\varepsilon_{ll}$. For our first simulations we chose $\alpha=\sqrt{10}$ which corresponds to the traditional form for the interaction potentials of $\varepsilon_{ls}=\sqrt{\varepsilon_{ss}\varepsilon_{ll}}$; in subsequent simulations α is varied systematically from 0.2 to 5. For simplicity σ is taken to have the same value for solid–solid and liquid–liquid and liquid–solid interactions (i.e., the atoms have the same size); the atomic mass of the liquid and solid atoms are also taken to be equal. For computational efficiency we use a cutoff for the interatomic potential of 2.3σ, and to avoid discontinuities in integration of numerical equations of motion we shift the forces and energies such that they are zero at the cutoff distance. We use MD time step of $0.007\tau^*$, where τ^*

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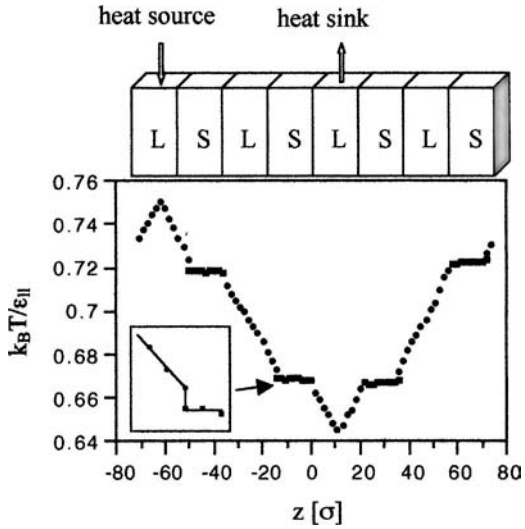

FIG. 1. Top panel: Schematic of the model system containing four solid slabs separated by four liquid slabs; the regions where heat is added and removed from the system are indicated by arrows. Bottom panel: A typical temperature profile showing a smooth temperature decrease through the liquid, an essentially constant temperature in the solid, and an abrupt drop at the solid–liquid interface (inset).

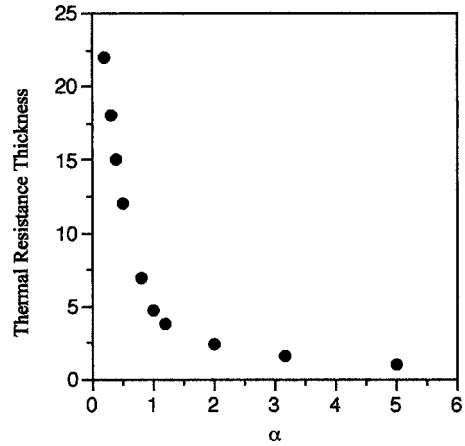

FIG. 2. Interfacial resistance in units of equivalent liquid thickness as function of solid–liquid interaction strength parameter, $\alpha=\varepsilon_{sl}/\varepsilon_{ll}$.

$=[48\varepsilon_{ll}/m\sigma^2]^{1/2}$, which conserves energy in microcanonical-ensemble simulations to four significant figures over one million MD steps.

The geometry of the simulation cell is depicted in Fig. 1. The initial atomic structure consists of a [100]-oriented perfect fcc crystal with size of $80a_0$ in the z direction and $7a_0$ in the x and y directions, where $a_0=1.56\sigma$ is the cubic lattice parameter; the simulation cell thus contains a total of 15 080 atoms. We designate atoms in alternating $10a_0$ wide slabs to be either liquid or solid, in turn, leading to 4 solid slabs separated by 4 liquid slabs. This structure is equilibrated at the reduced temperature $k_BT/\varepsilon_{ll}=0.72$, which lead to melting of liquid slabs, whereas the solid slabs remain crystalline. We also elongate the system in the z direction such that the reduced density, $\rho^*=\rho/\sigma^3$, of the liquid regions is equal to 0.84, such that the liquid phase is in the vicinity of the triple point.[7]

Following equilibration, we applied a heat source and a heat sink in the middle of two liquid regions, as shown in Fig. 1, using a variant of the energy-conserving algorithm from Ref. 8. With the above choice of simulation-cell geometry, the system contains 8 liquid–solid interfaces with 4 of them well separated from the heat source and sink. This allows us to minimize the size of possible spurious effects associated with the heat sources. Prior to taking averages we simulate for 500 000 MD steps such that the system reaches a steady state. Temperature profiles (separate for liquid and solid) were then obtained by slice-by-slice averaging over 2 000 000 MD simulation steps, using a slice thickness of 1.8σ.

The bottom panel in Fig. 1 shows temperature profiles obtained for the system and simulation procedure described above. Due to the periodic boundary conditions, the system is symmetric about both the heat source and heat sink. As clearly seen in Fig. 1, there are large temperature gradients in all liquid regions and almost flat temperature profiles in the solid regions; these correspond to low thermal conductivity and very high thermal conductivity, respectively. The fact that the solid has a very high thermal conductivity is not surprising considering that the mean free path of the phonons (lattice vibrations) that carry the heat in the crystal is much larger than the nanometer thickness of the solid slab. Figure 1 and its inset show that for the strongly wetting liquid ($\alpha \approx 3.3\varepsilon$) there are small, but distinct, temperature drops at the solid–liquid interfaces; these correspond to the Kapitza resistance.

To analyze the effects of bonding between liquid and solid atoms on the interfacial resistance we performed a series of simulations following the same procedure as described above but with various values of α ranging from 0.2 to 5.0. In Fig. 2 we present values of interfacial thermal resistance in units of the ''thermal-resistance thickness,'' defined as the width of the liquid over which there would be the same drop in temperature. All the results shown represent the averages over the eight interfaces present in the system. The data show strong dependence of the Kapitza resistance on α, with an almost an order of magnitude difference between the strongly-bonded/low-resistance regime and the weakly-bonded/high-resistance regime. These results demonstrate the critical importance of the bonding between liquid and solid for determining the interfacial thermal resistance.

To analyze the results further we performed a number of functional fits to the data in Fig. 2. Although we did not find a single functional form that well represents results over the entire range of α, by separating the data into two regions, $\alpha>1$ and $\alpha<1$, i.e., the regions of wetting and nonwetting liquid respectively, we were able to identify functional forms that do well represent our simulation data over these regimes. In the wetting region, as demonstrated by the log–log plot in Fig. 3 the interfacial resistance, R_K, is inversely proportional to the strength of the interactions between the solid and liquid, i.e., $R_K \sim \alpha^{-1}$. In the nonwetting region R_K is well represented by the exponential function of $R_K \sim \exp(\gamma\alpha)$, with $\gamma=-1.9$ (see inset in Fig. 3).

At the qualitative level, the origin of the power low behavior can be understood by consideration of two stiff solids

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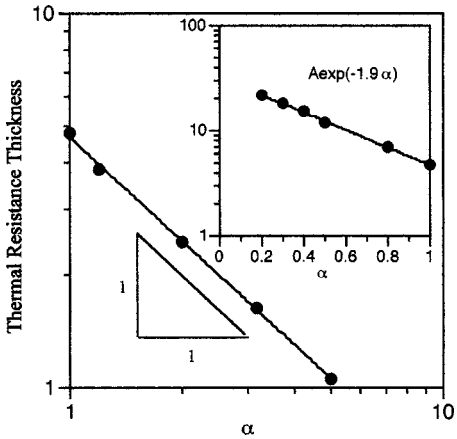

FIG. 3. The data in Fig. 2 replotted on a log–log scale and for the values $\alpha>1$ corresponding to the wetting regime, The insert shows data $\alpha<1$ (nonwetting regime) on log-linear axes.

separated by a thin layer of a softer solid. A simple analysis based on the acoustic mismatch model, results in the leading term that controls the interfacial resistance being proportional to $(Z_{\text{stiff}}/Z_{\text{soft}})^2$, where $Z=c/\rho$ is the acoustic impedance,[2] with c and ρ being the speed of sound and density, respectively. Assuming the same density and interatomic distance of both solid and recognizing that then c^2 is proportional to the effective stiffness of the springs connecting atoms, k, one gets $R_K \sim k_{\text{stiff}}/k_{\text{soft}}$, which for the LJ potential becomes $R_K \sim \varepsilon_{\text{stiff}}/\varepsilon_{\text{soft}}$.

Based on this argument, in the limit of a very high elastic mismatch between the soft layer and the adjacent stiff solids, the thermal resistance would diverge to infinity. This unphysical results originates from the assumption of the AMM that the forces between atoms are harmonic; it does not take into account the fact that, no matter how small is the attraction between solid and liquid atoms, there is always a repulsion preventing overlap of the atoms. Therefore even with absolutely no liquid–solid attraction, there is an energy transfer from the liquid to the solid due to elastic collisions, which implies that the interfacial thermal resistance will be always finite. Indeed, as shown in the inset to Fig. 3, in the nonwetting regime the Kapitza resistance remains finite and extrapolation to $\alpha=0$ results in $R_K \sim 32\sigma$.

In addition to the effects of liquid–solid interactions on thermal transport, we also analyzed the role of layering in the liquid adjacent to the solid.[9,10] As can be seen in Fig. 1 the slope of T versus distance does not significantly differ in the liquid region adjacent to the solid, which we verified is indeed layered, from the slope in the liquid farther away from the solid, which is structurally the same as bulk liquid. We also systematically varied the widths of the liquid slabs sandwiched between solids and even in the case of an extremely confined liquid just 5σ wide we observed essentially the same temperature gradient. The above observations indicate that structural layering in the liquid has little effect on its thermal-transport properties.

In summary, using molecular dynamics simulations and simple model of a solid–liquid interface we have demonstrated critical importance of the intermolecular interactions between solid and liquid on the interfacial thermal resistance, R_K, and identity two functional forms for R_K for wetting and nonwetting liquids, respectively. Our results indicate that nanocomposites or nanofluids characterized by weak atomic bonding at the particle-matrix interfaces will exhibit high thermal resistance. By contrast, for the wetting systems the interfacial resistance will be small and equivalent to a temperature drop in a liquid over several σ ($\sim$1 nm) and thus will play a minor role even in the limit of nanometer size particles. We envision that our findings will play an important role in the design of thermal properties of nanocomposites and in guidance of theoretical work towards a better understanding of the Kapitza resistance.

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