

The scientific impact of this project is to develop the fundamental underpinnings to achieve the rational design and high-efficiency of heat exchanger using multi-phase systems. The proposed work focuses on verifying the hypothesis of an interfacial heat exchange dominant regime at the nanoscale. In order to determine the role of interfaces between different phases in the overall thermal performance, we have initially focused on understanding how vibrational spectra couple across the molecular interfaces. To do so, we have formed nanostructures with controlled thermal properties and measured their thermal boundary resistance using an ultrafast optical spectroscopy, in parallel to making ab initio predictions of the thermal conductance with molecular dynamics and density functional theory.

For decades, understanding liquid-involved interface transport has been far away from the level in contrast to that across solid-solid interfaces, despite the fact that the thermal boundary resistance was initially discovered at solid-liquid helium interface. In particular, thermal characterization techniques had been the main challenge impeding the exploration in this field. During the first year of this project, we have used the time-domain thermoreflectance technique [1] to directly measure heat transport across the designed nanoscale interfaces. Importantly, we have developed a new metrology, the asymmetric beam time-domain thermoreflectance (AB-TDTR) (Figure 1) [2] to measure three-dimensional anisotropic thermal transport. This new technique, using an elliptical laser beam with controlled elliptical ratio and spot size, is able to exploit the experimental signals to be dominantly sensitive to measure thermal transport along the cross-plane or any specific in-plane directions. We developed transport analytic solution for a multi-layer system to analyze the AB-TDTR signal in response to the periodical pulse, elliptical laser beam, and heating geometry. We have also performed a detailed sensitivity analysis to guide the optimal setting of different experimental configurations as proposed. Therefore, AB-TDTR enables reliable and anisotropic characterizations of the heat exchange between multi-phases in the complicated nanoscale interface systems.

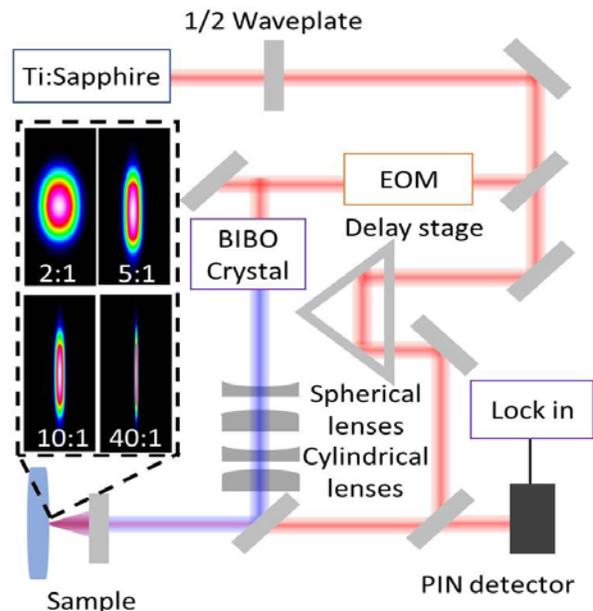


Figure 1. Our developed Asymmetric Beam Time-Domain Thermoreflectance (AB-TDTR) technique to enable the measurement of anisotropic thermal transport [2].

During the first year, we have also demonstrated a systematic measurement of solid-liquid interfaces for interfacial heat exchange measurement. To enable high sensitivity measurement over interface thermal resistance, we design the interfaces using new materials building blocks of varied thermal conductivities [3-5]. For samples prepared with high contrast of thermal conductivity values, we used pump laser pulse to heat up the solid surface and the thermal energy would dissipate to the liquid side. Simultaneously, the probe pulse is used to continuously probe the reflectivity of gold film by controlling the sub-picosecond delay time between the pump and probe pulses. Our ultrafast pump-probe measurements have observed that the liquid molecules have significant effects on thermal transport at the interfaces and revealed interesting coupling mechanisms. First, the surface molecules can bridge the thermal transport across the interfaces because of the better overlapping between vibrational density of states (DOS). We have tested different building blocks with varied DOS and verified this observation. Secondly, the improved interfacial bonding energy across the surfaces can also help thermal transport. To further quantify the vibrational mode dependent interface heat exchange, we performed the nonequilibrium molecular dynamics (MD) simulations. In the MD simulation domain illustrated in Figure 2, interface is sandwiched by two heating blocks. A periodic boundary condition is applied to all the directions and the real structure can be interpreted as a superlattice type of repetition of the interfaces, with heat source and heat sink layers lie in the center. Application of heat current

through the heat source to the heat sink forms a temperature gradient along the direction normal to the interface. By monitoring the temperature drop ( $\Delta T$ ) across the interface, the thermal boundary conductance can be calculated from  $G=Q/\Delta T$  (Figure 2). The steady-state temperature profiles across the interfaces are predicted by the MD simulation. Our MD simulation verified that the interface bonding energy has a strong effect on anisotropic interface transport. We found that increasing the interface bonding can lead to a larger interface heat transfer rate which is consistent with the experimental observation. With these experiment and modeling, our study provided important understanding of the relationship between interface heat transfer and molecular structures, opening up new opportunities in improve interface heat exchange between multi-phases and liquid molecules.

In the meanwhile, we also found that these factors couple with each other since the molecules are dynamic during the heat exchange. We are working on further identifying the atomistic mechanisms in the aim to provide design guidance for improving future multi-phase heat transfer. In the on-going work, our aim is to quantify the detailed contributions from each factor by carefully designing controlled interface systems at the nanoscale. In particular, we will manipulate atomic level defects, molecular chains, and bonding strengths. For example, we have recently developed a novel approach to integrate ultrafast optical spectroscopy and electrochemical control to control atomic defects [1]. This approach will be applied to enable the atomic-level manipulation of interface bonding and examine the impact from defect interactions over the interface heat exchange. We expect that such an independent control over individual factor will enable powerful manipulation and design paradigms to understand the interfacial heat exchange as our project goal. More specifically, we aim to (i) Clearly separate the effects of DOS match and other coupling factors; (ii) Demonstrate active manipulation of the interface heat transfer by tuning the liquid molecular bonding; (iii) Rational design surface molecules to maximize the interfacial thermal transport efficiency.

Professional career impact: For the PI, the support from ACS-PRF grant has allowed him to start this highly interdisciplinary project that integrates theory, transport characterizations, and molecular chemistry to investigate the coupling interactions of molecules and interfaces. This study has led to new fundamental understandings and several extended research directions in the PI's group, which has also resulted in a series of journal publications [2-5]. In addition, two graduate students have been partially supported by this fund to pursue their academic career. Based on the research from this project, one of the students has recently passed the qualify exam towards Ph.D. degree.

#### References:

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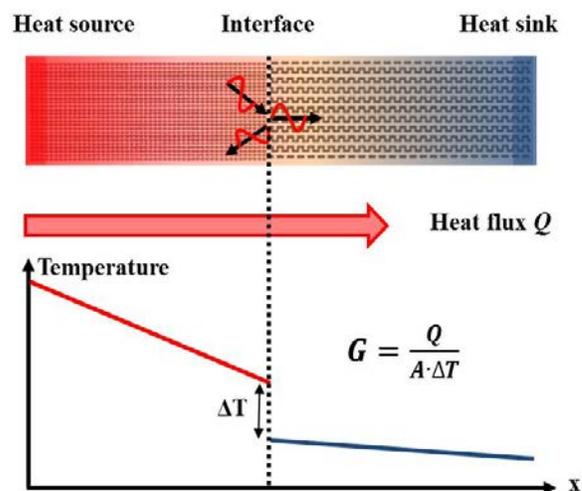


Figure 2. Schematic of interfacial heat exchange and molecular dynamic simulations of interface thermal boundary resistance.