The Role of Multi-Carrier Interaction in Thermal Transport and Energy Conversion in Crystal Materials

Abstract

by

Xufei Wu

Thermal properties play important roles in applications such as high efficiency thermoelectric materials and the thermal management of electronic devices. While electrons dominate thermal transport in metal, phonons (i.e., the quanta of lattice vibrations) are the primary energy carriers in crystalline insulators and semiconductors such as Silicon and Germanium. A fundamental understanding of the transport properties of multiple carriers including phonons and electrons can enable us to better design nanoscale materials. However, many of the current techniques to calculate the lattice thermal conductivity and interfacial thermal conductance involve major approximations.

The first part of this work involves studying the role of scattering strength, such as anharmonicity (i.e., high order phonon-phonon scattering) and electron-phonon coupling, on thermal conductance at interfaces, based on Molecular Dynamics (MD) simulations. We find that anharmonicity of crystals
enables the energy communication between different phonon modes and facilitates the energy to flow into those modes that can easily carry energy across the interface. Furthermore, electron-phonon coupling does not only apply an extra thermal resistance as thought by most researchers previously, it also helps the energy communication between phonon modes, and similar to anharmonicity of crystals, it has positive effects on the thermal conductance across the interface. These studies can guide people to improve the prediction power of interfacial thermal conductance and provide a better understanding on the physics behind phonon-phonon scattering and electron-phonon scattering for interfacial thermal transport.

The second part of this work involves building accurate tools to predict the thermal conductivity of crystal materials. Two methods are used to predict the phonon and electron properties. One method uses MD simulations. However, instead of using empirical interatomic interaction potentials, which may cause inaccuracy in thermal conductivity prediction, here we expand the interatomic potential using Taylor’s series around their equilibrium positions and the coefficients of second order (i.e., harmonic) and third order (i.e., anharmonic) expansion (i.e., force constants) can be directly fitted using linear regression model, from higher level first-principles density functional theory (DFT) calculations.

The other approach is lattice dynamics calculation from Boltzmann Transport Equations (BTE) combined with Fermi’s golden rule, based on the force constants fitted from first-principles calculations. Hamiltonian of the atomic system is first
quantized and expressed by creation and annihilation operators of phonons. Fermi’s golden rule helps us estimate the possible scattering rates due to different multi-carrier interactions. After that, the thermal conductivity prediction is based on the iterative solution of linearized BTE. It is so far the most accurate approach and is essential for the prediction of thermal conductivity in crystal materials.

With the completion of the tool for thermal conductivity prediction, several important semiconductor materials are studied using these first-principles methods. One is single layer molybdenum disulfide (MoS₂), a two dimensional material with an intrinsic bandgap of 1.8 eV and a high electron mobility around 200 cm²V⁻¹S⁻¹, which can potentially enable applications in transistors, photovoltaics, valleytronics and thermoelectrics. It is found that isotopes in MoS₂ can greatly reduce the thermal conductivity which can improve the thermoelectric conversion efficiency.

Another material studied is Wurtzite Zinc-Oxide (w-ZnO), a wide bandgap semiconductor that holds promise in power electronics and transparent electronics applications. By comparing to Wurtzite Gallium-Nitride (w-GaN), a currently popular wide bandgap semiconductor with the same crystal structure, the reason of the low thermal conductivity of w-ZnO is found, which is due to smaller phonon group velocities, larger three-phonon scattering phase space and larger anharmonicity.

Finally, with the proven predictive power of our methods, we discover a strategy to tune thermal conductivity via bond engineering by modifying the bond saturation of materials. Our predictions show that, the thermal conductivity of penta-graphene, which has unsaturated carbon-carbon bonds, can be significantly
increased after bond saturation. We find that penta-graphene and hydrogenated penta-graphene are promising candidates for future nanoelectronics applications due to their high lattice thermal conductivity. Furthermore, this helps providing a general guideline for the design of high thermal conductivity materials.

All these studies provide us a better understanding of thermal transport in solid state crystal materials and can potentially enable us to design materials with desirable thermal transport properties.