Degree-of-freedom resolved thermal transport in the C_{60} molecular crystal

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The fullerene C_{60} and its derivatives (e.g., PCBM) are low thermal conductivity molecular crystals that have application in photovoltaic, thermoelectric, and phase change memory devices. Though fullerene thermal conductivities have been measured, the mechanisms of thermal transport are not well understood.

In addition to vibrational degrees of freedom (DOF) that are intramolecular (i.e., between atoms on the same molecule) and intermolecular (i.e., collective effects between molecules), C_{60} has rotational DOF that lead to orientational disorder at room temperature. That is, while the molecules all sit on the lattice sites of a face-centered cubic crystal, their relative orientations are not correlated.

We use molecular dynamics simulations to investigate how these three types of DOF contribute to thermal transport in C_{60}. Three systems are considered between temperatures of 100 and 400 K. In the first, all atomic DOF are activated. In the second, the molecules are treated as rigid bodies that can translate and rotate. In the third, the molecules are replaced by point masses interacting through an effective potential, so that only translational DOF are present. While the bulk moduli predicted for the three systems fall within a range of 20%, the thermal conductivities predicted using the Green-Kubo method, plotted in Fig. 1, show a large variation and different features.

For the full DOF system, the integral of the heat current autocorrelation function shows two distinct plateaus. The first leads to a temperature independent thermal conductivity that we associate with intramolecular interactions. The second contribution to thermal conductivity is temperature dependent and with similar magnitude and trend to that from the rigid body simulations. We associate this contribution with collective molecular motions. The thermal conductivity of the point mass systems is significantly higher than the full DOF and rigid body systems, pointing to the importance of the rotational DOF in limiting thermal transport.

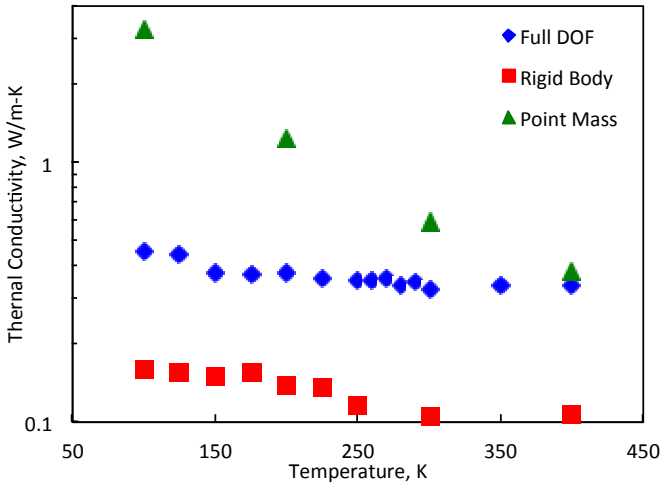

Fig. 1: Thermal conductivity of the C_{60} molecular crystal vs. temperature predicted from molecular dynamics simulations for full DOF, rigid body, and point mass systems.