Phonon Thermal Transport Along the Chain Direction of Crystalline Polyethylene

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ABSTRACT

It was once believed that the thermal conductivity (κ) in crystalline polyethylene (PE) is higher than 100 W/mK. Here, we applied the stochastic self-consistent harmonic approximation (SSCHA) [1] combined with phonon Boltzmann transport equation to predict the κ of PE. Our calculation scheme incorporates the quantum, thermal, and anharmonic effects in force constants. It is found that the room-temperature κ of PE is only $\sim$ 18 W/mK, which matches the previous thermoreflectance experiment well.

INTRODUCTION

Polymers have the properties of being lightweight, cost-effective to manufacture, and soft, thereby having great potential in LEDs, electronic packaging, flexible electronics, *etc*. The thermal conductivities in polymers are usually ≈ 0.2 W/mK, which is relatively low and becomes the bottleneck in many applications. To address this issue, it was proposed to achieve very high thermal conductivity (> 100 W/mK) by stretching and ordering polyethylene (PE) chains[2]. This inspires lots of theoretical studies to explore the upper limit of the thermal conductivity of PE, either by molecular dynamics simulation [3] or first-principles calculations [4], [5]. However, those theoretical predictions generally overestimate the κ for PE, which is incomparable to the time-domain thermoreflectance (TDTR) experiment[6].

THEORY AND METHOD

In this work, the SSCHA [1] is employed to obtain the temperature-dependent force constants (FCs). This method rigorously incorporates the quantum, thermal and anharmonic effects on FCs. The NequIP potential [7] is adopted to address the huge computing burden in SSCHA calculations. The thermal conductivity is obtained by solving the phonon Boltzmann transport equation using the exact diagonalization method [8].

RESULTS AND DISCUSSIONS

The lattice structure of PE is shown in Fig. 1(a). The phonon dispersions from harmonic approximation and the Hessian calculation including anharmonic effects are shown in Fig. 1(b). Overall, the phonon frequencies from theoretical prediction matches experimental results. There is a pronounced renormalization in the harmonic phonon frequency, which indicates there are large modifications in FCs. The κ along the chain direction of PE is shown in Fig. 2. The κ is mainly contributed by the high-frequency longitudinal acoustic phonons, which hold relatively large lifetime and group velocity. The κ predicted by our method matches the TDTR experiment well, while the classical DFT and the temperature-dependent effective potential method significantly overestimate the value.

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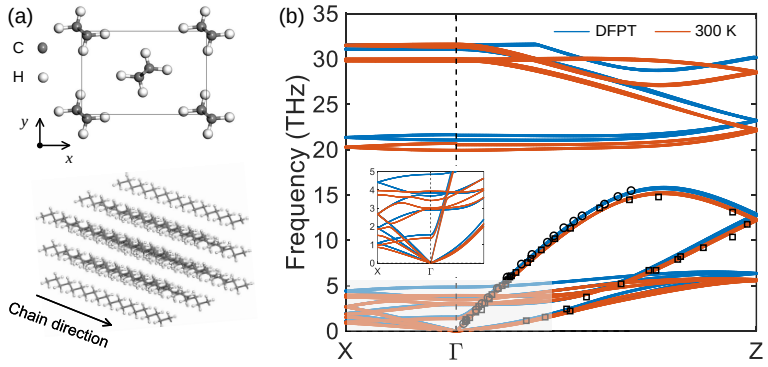

Fig. 1: (a) The lattice structure of crystalline PE. There are 4 carbon atoms and 8 hydrogen atoms in the unit cell. (b) The phonon dispersions from density functional perturbation theory (DFPT) and Hessian calculation at 300 K. The inset shows a zoomed-in region near the Γ-point. The black scatters are data from experiments respectively.[9], [10].

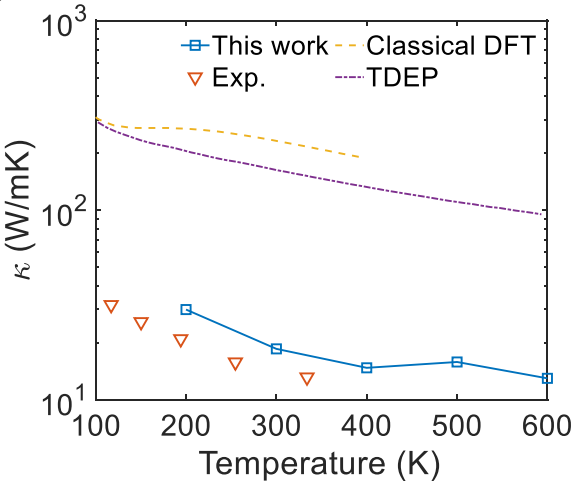

Fig. 2: The thermal conductivity along the chain direction of crystalline PE from this work, the TDTR experiment (Exp.)[6], the classical DFT [5], and the temperature-dependent effective potential method (TDEP)[4]. In classical DFT, force constants were extracted at 0 K using the finite difference method.

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