Review

Thermal conductivity modeling of hybrid organic-inorganic crystals and superlattices

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A B S T R A C T

Hybrid organic-inorganic materials have attracted intensive research interests due to the superb physical properties that take advantage of both organic and inorganic components and their promising applications in functional devices such as light emitting diodes, solar cells, and flexible thermoelectrics. Understanding thermal transport in hybrid materials is of importance for both the reliability and the performance of the hybrid material-based systems. The organic-inorganic hybrid materials can be classified as nanocomposites, superlattices and crystals depending on the strength of organic-inorganic bonding and the feature size of organic and inorganic components. Previous research on thermal transport mainly focus on hybrid nanocomposites where phonon-interface scattering dominates the thermal transport process. However, in hybrid superlattices and crystals, organic and inorganic components are blended at the atomic scale by chemical bonds without a clear interface, and the phonon transport physics is not well understood. This article reviews the recent progress in *ab-initio* modeling on phonon transport in hybrid crystals and superlattices. The predicted thermal conductivity of II–VI based organic-inorganic semiconductors, organometal perovskites and organic-intercalated TiS_2 superlattices are reviewed and compared with experimental data when available. This review provides guidance for modeling thermal conductivity of materials with complex atomic structures from the first principles, which could be a good tutorial for both graduate students and experienced researchers who are interested in thermal energy transport in emerging hybrid materials.

1. Introduction

Hybrid organic-inorganic materials (HOIMs) are synthesized by combining the organic and inorganic components over length scales from a few angstroms to ∼ 100 nm [1,2]. The most appealing feature of HOIMs is that they can be conveniently designed for properties that are difficult to achieve in either organic or inorganic materials alone. For example, superb electronic properties can be derived from the inorganic component while still maintaining structural flexibility due to the blending with organic components [2]. In the past decade, a variety of novel HOIMs have been synthesized with promising applications like light emitting diodes [3,4], flexible solar cells [5–11], and flexible thermoelectrics [12,13], to name a few. However, thermal transport in HOIMs is not well understood although thermal conductivity greatly affects the thermal stability and the performance of the hybrid material-based devices [14]. Due to the structural diversity and the wide range of organic-inorganic coupling strength in HOIMs, it would be helpful to categorize the HOIMs into different groups for a better understanding of

their mechanical and thermal properties. In Fig. 1, we illustrate that the organic-inorganic hybrid materials can be categorized into three groups (hybrid organic-inorganic nanocomposites, superlattices and crystals) according to the organic-inorganic coupling strength and the feature size of organic and inorganic components. The first group of HOIM is the hybrid organic-inorganic composites whose organic and inorganic components are coupled by weak van der Waals forces or hydrogen bonds. While organic-inorganic composite materials have been studied for many decades [15–18], significant efforts have been devoted to understanding the thermal and mechanical properties of nanocomposites when the feature size of the organic/inorganic structural units in these composites is on the order of a few nanometers. In these hybrid nanocomposites with distinguishable organic-inorganic interfaces, such as carbon nanotube-polymer composites [19,20], self-assembled materials [21–25] and nanocrystal arrays [26–28] and super-atomic crystals [29], thermal transport is determined by organic component, inorganic component, and most dominantly the phonon-interface scattering [27]. However, the organic-inorganic interfaces are not
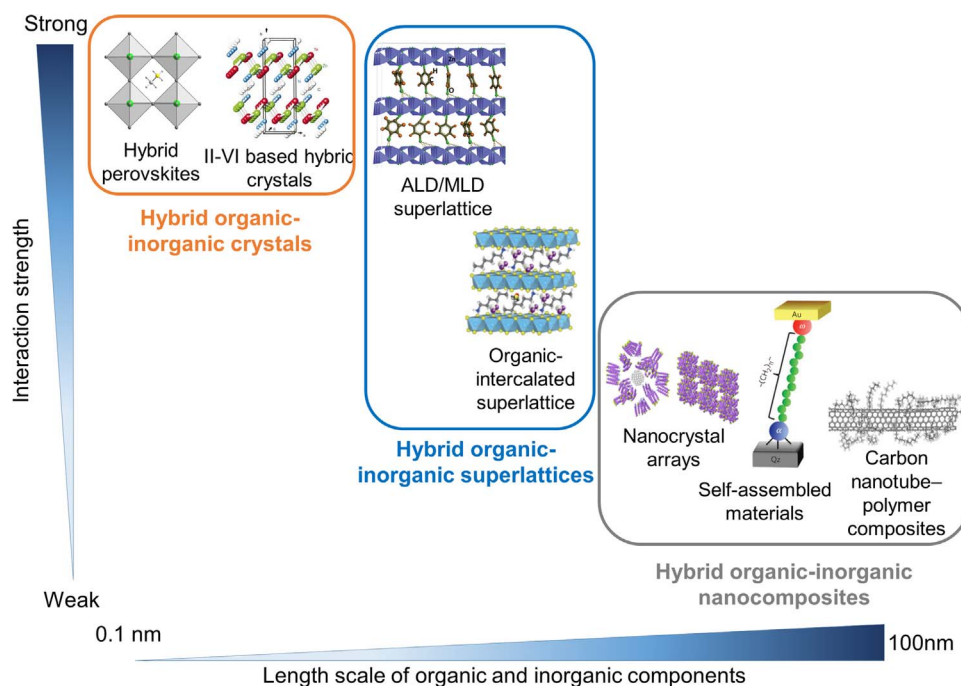
present in hybrid organic-inorganic crystals, when the blending of organic and inorganic constituents happens at the atomic scale [30]. In contrast to the hybrid nanocomposites with either amorphous organic or inorganic structures, the hybrid organic-inorganic crystals possess long range periodicity. A few examples of hybrid crystals are the family of group II–VI element based hybrid crystals [31] and the hybrid organometal halide perovskites [11, 32–35]. The dominant coupling mechanisms between the organic and inorganic constituents in these hybrid crystals are either covalent bonds (II–VI based hybrid crystals) or ionic bonds (hybrid perovskites). The third group of HOIMs is the hybrid organic-inorganic superlattices, which lies between the hybrid crystals and the hybrid nanocomposites, in terms of both the length scale of feature size and the bonding strength between the organic and inorganic components, as shown in Fig. 1. The most notable examples of hybrid organic-inorganic superlattices are the atomic/molecular layer deposited (ALD/MLD) organic-inorganic superlattice [36,37] and the organic intercalated superlattice [12,13]. In these superlattices, the organic-inorganic coupling strength can be in a wide range, from the strong covalent bonding in ALD/MLD superlattices to the electrostatic forces in the organic-intercalated superlattices. The feature size of the organic and inorganic component can also vary from sub-nanometer to a few nanometers. Although a few experimental research found that the hybrid crystals and superlattices usually have low thermal conductivity [30,36], it is still not well understood how phonons transfer their energy in these hybrid crystals and superlattices, and how the organic components affect the thermal transport.

In this Review, based on the authors' extensive experiences on modeling the thermal conductivity of organic-inorganic II–VI based hybrid crystals, the organometal halide perovskites, and the organic-intercalated TiS_2 superlattice, deriving from the contemporary study of nanoscale heat transfer [38–43], a general first-principle-driven computational methodology for calculating the lattice thermal conductivity of complex materials is discussed. It is noted that the hybrid crystals and superlattices described in this Review are semi-conductive, and the dominant heat carriers are lattice vibration (phonons). In Section 2, we outline the computational challenges in modeling the thermal conductivity of hybrid crystals and superlattices. In Section 3, a simulation strategy integrating first principles calculation and molecular dynamics simulations is reviewed. Section 4 reviews the implementation and the application of this general strategy to the materials we recently studied,

including organic-inorganic II–VI based hybrid crystals, the organometal halide perovskites, and the organic-intercalated TiS_2 superlattice. This review provides a good tutorial for those who are interested in thermal energy transport in emerging hybrid materials.

2. Computational challenges

Much progress has been made on modeling the thermal conductivity of nanostructured materials over the past two decades [44–49]. The most distinguished examples are first-principles-based simulation methods like Boltzmann transport equation (BTE) or *ab initio* molecular dynamics (AIMD), taking great advantage of the progress in computational power [50–53]. Without fitting parameters, such first-principles-based methods has been used to model the thermal conductivity of inorganic bulk crystals such as diamond [54,55], silicon [50,52,56], GaN [51] and two-dimensional materials such as graphene [38,57–59], silicene [38,60], black phosphorus [61–64] and many transition metal dichalcogenides [39,65,66]. Not only great agreements between theoretical calculations and measurement results on the thermal conductivity of materials have been found, but also these tools serve significantly speed up the materials discovery in both extremely high/low thermal conductivity and multifunctional thermal materials [50, 52–56, 66–67].

However, much less effort has been devoted to study phonon transport in hybrid organic-inorganic crystals and superlattices, not catching up the pace on the synthesis efforts for multifunctional thermal materials. This is understandable because there are significant computational challenges due to the structural complexity of hybrid organic-inorganic crystals and superlattices. For example, hybrid crystals usually have very large unit cells containing dozens of atoms, in comparison with only one to a few atoms in inorganic crystals. In addition the organic components usually have internal degrees of freedom of motion (for example, the organic ions in hybrid perovskite can rotate) instead of just vibrating around the local equilibrium [68–70]. To capture such dynamical disorder caused by the internal degrees of freedom of motion, a very large supercell is required to simulate phonon transport instead of just one unit cell with periodic boundary conditions. In superlattices, the organic components might even be amorphous. The lack of periodicity in the hybrid superlattices and the dynamical disorders in the hybrid crystals hinder the implementation of