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Thermal conductivity of metal-organic framework 5 (MOF-5): Part I. Molecular dynamics simulations

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Abstract

The phonon thermal conductivity of MOF-5, a metal-organic framework crystal with a phenylene bridge, is predicted between temperatures of 200 K and 400 K using molecular dynamics simulations and the Green–Kubo method. The simulations are performed using interatomic potentials obtained using *ab initio* calculations and experimental results. The predicted thermal conductivity of MOF-5 is low for a crystal, 0.31 W/m K at a temperature of 300 K, and its temperature dependence is very weak. By decomposing the thermal conductivity into components associated with short- and long-range acoustic phonons, and optical phonons, the weak temperature dependence is found to be related to the mean free path of the majority of phonons, which is of the order of lattice parameter (and is essentially temperature independent). To interpret the results, an analytical thermal conductivity relation is derived, which reduces to the Cahill–Pohl and Slack models under appropriate assumptions. The relation contains a critical frequency, which determines the relative contributions of the short- and long-range acoustic phonons. The small long-range acoustic phonon contribution is found to be related to the long and flexible phenylene bridge, and to the mass mismatch between the cages and the bridges.
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1. Introduction

The metal-organic frameworks (MOFs), a sub-family of the nanoporous crystals, are characterized by metal-oxygen cages (vertices) connected by organic bridges [1–4]. MOFs currently attract intensive interest for their excellent potential for storing and separating gases (e.g., N_2, Ar, CO_2, CH_4, and H_2) [5–7]. By changing the organic bridge and/or its functionalization, new MOFs can be designed and synthesized without changing the underlying topology. Recent work has focused on their structural properties [2], adsorption characteristics [2,5–7], and the diffusion of light gases through them [8], but their thermal transport characteristics have yet to be considered. Since the gas absorption/desorption is sensitive to the unintended change in the ambient temperature and this response is related to the absorption/desorption bed thermal conductivity, the knowledge of the thermal conductivity of a MOF is crucial in predicting the behavior. Furthermore, the variety of MOFs available points towards the possibility of systematically designing materials with specified thermal properties. To prepare for such molecular design, an understanding of the relationship between a MOF structure and its thermal conductivity is required.

We report the investigation of the thermal transport in MOF-5 (shown in Fig. 1), which is the smallest of a series of MOFs that have a simple cubic crystal structure [2]. It is built from zinc–oxygen tetrahedra connected by 1,4-benzenedicarboxylate (BDC) bridges. It has a low density (610 kg/m^3), a large free cage volume (79%), and a pore diameter of 11.2 Å [2].

There are two standard approaches for predicting the thermal conductivity of a solid, both of which are based

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Nomenclature

a	mean atomic distance
b	constant
c	concentration
k	thermal conductivity
n	number density
P	pressure
q	charge
r	distance
t	time
$\mathbf{u}$	velocity
A	coefficient
B	coefficient
D	density of states
E	energy
I	spectral density
$\mathbf{M}$	dipole moments
M	atomic weight
N	number of particles
N_c	number of atoms in a primitive cell
R_c	cut-off radius
T	temperature
V	volume

Greek symbols

β	Wolf method parameter
γ_G	Grüneisen constant
κ_s	compressibility
λ	mean free path
v	Poisson ratio
ω	angular frequency
$\dot{\omega}$	heat current
ρ	density
τ	time constant
φ	potential energy

Subscripts

A	acoustic
CP	Cahill–Pohl
i	summation index, particle label
j	summation index, particle label
p	phonon
g	group
c	cell
O	optical
T	transversal
L	longitudinal
D	Debye
sh	short-range
lg	long-range
κ	wave vector
β	species

on the Fourier law. One approach is to use continuum transport theory and kinetic theory, such as the Boltzmann transport equation (BTE) approach of Callaway [9] and Holland [10]. The second is to use an atomistic technique, such as molecular dynamics (MD) simulations. The BTE can be used to study large systems rather quickly, but for a reliable calculation, a good understanding of the underlying phonon processes is required. Parameters such as the phonon relaxation times must be obtained from other approaches (e.g., by fitting to experimental data [9,10] or directly from MD [11]). Molecular dynamics is a more fundamental method, which tracks the positions and momenta of an ensemble of classically interacting atoms. For input, MD only requires a material structure and suitable interatomic potentials. In this investigation, MD will be used to predict the thermal conductivity of MOF-5. The data required for a BTE study is currently unavailable.

We first describe the development of the classical interatomic potentials (force fields) needed to perform MD simulations of MOFs. Using these potentials, the thermal conductivity of MOF-5 is predicted between temperatures of 200 K and 400 K. The thermal conductivity is decomposed into components associated with short- and long-range acoustic phonons and optical phonons. A model is formulated to explain the observed weak temperature dependence, and a critical frequency is introduced to separate the contributions of the two acoustic components. Finite size and quantum effects on the thermal conductivity prediction are also discussed. The relationship between the MOF-5 structure and its thermal behavior is explored, and a simplified structural model is proposed.

2. Classical interatomic potentials for MOF-5

To model the dynamics of MOF-5, the development of potentials for different interactions in MOF-5 is required. Previous MD studies have focused on the interaction of gases with the structure, and modeled the crystal as being rigid [8]. The main challenge in the construction of a potential set is related to the oxygen atom in the carboxylate moiety, which has a charge of −0.5. While potentials exist for Zn–O systems with formal charges [12], parameters are not available for this reduced charge state. To construct the potentials, we fit selected algebraic expressions to energy surfaces obtained from *ab initio* calculations.

The *ab initio* calculations are performed with Gaussian 98 [13], which is a software package for electronic structure calculation. First, to determine the appropriate method/basis set, the MOF-5 structure is relaxed using common combinations, e.g., RHF/6-311g (here RHF is the method and 6-311g is the basis). The resulting structures are then compared to the experimental data, as shown in Table 1.

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