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Effect of Flexibility on Thermal Transport in Breathing Porous Crystals

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Cite This: J. Phys. Chem. C 2020, 124, 18604-18608



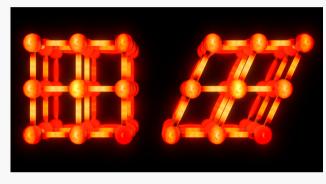
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ABSTRACT: With the aim of understanding heat transfer during structural changes in breathing porous crystals upon gas loading, we study the effect of pore expansion on the thermal conductivity of a series of idealized materials containing adsorbed gas using molecular dynamics simulations. We calculated the thermal conductivity in three main axes of the crystal lattice starting from a tilt angle of 40° to represent the closed form of the crystal up to a tilt angle of 90° to represent the open form. With no gas present, the thermal conductivity increases in the tilt direction with pore expansion whereas thermal conductivity in other directions remains unchanged. In the presence of adsorbed gas, porous crystals at all states of expansion experience reduced thermal conductivity due to



phonon scattering introduced by gas—crystal interactions. Similarly, the thermal conductivity in the tilt direction increases as the pore expands; however, the increase is less pronounced compared to the case with no gas present in the pores. We also show that the diffusivity of gas increases during pore expansion, facilitating mass transport.

■ INTRODUCTION

There is considerable recent interest in the use of so-called "breathing" porous crystals for a wide range of gas adsorption and separation applications, such as for improved natural gas fuel tanks in cars. 1-7 These crystals, exemplified by metalorganic frameworks (MOFs), have pores that are flexible and can undergo reversible phase transformations in response to external stimuli such as host-guest interactions, temperature, and pressure.⁸⁻¹⁰ In particular, the pores can expand considerably when loaded with gas molecules. Unlike rigid porous crystals, flexible porous crystals show a step-shaped gas uptake behavior that makes them inherently more practical for pressure/temperature-swing adsorption/separations, working with smaller pressure/temperature differences and much higher working capacities.² Without considering transient thermal effects, the mechanisms of phase transitions in breathing crystals have been extensively investigated. $^{11-14,1,15,16}$ However, an often overlooked challenge in using porous materials for gas storage is that the process of gas adsorption (or desorption) generates (or consumes) significant amounts of heat. For rapid loading, this leads to sharp temperature spikes, 17 which inhibits further adsorption of gas and largely mitigates the benefits of using a porous adsorbent in the first place. Similarly, for rapid unloading, the sharp temperature drop exacerbates the stranded gas problem as the gas molecules are more likely to condense onto the pore walls. Efficient thermal transport can reduce this effect by facilitating heat dissipation. In this regard, previous studies have investigated thermal transport in rigid MOFs using atomistic

modeling^{18–24} and experiments.^{25–28} Whereas the thermal effects of adsorption in rigid porous crystals are now somewhat understood, the more complicated thermal behavior of flexible porous crystals, which show even greater promise for many applications, has not been studied at all.

In this paper, we study the thermal conductivity of idealized breathing porous crystals. We perform molecular dynamics (MD) simulations on a series of idealized model structures representing porous crystals at different stages of pore expansion and apply the Green–Kubo method to predict their thermal conductivities with and without adsorbed gas. We find that upon pore expansion, thermal conductivity parallel to the direction of change increases while thermal conductivity in the other directions remains unchanged. This result is counterintuitive as typically a lower density crystal has a correspondingly lower thermal conductivity. We also observe that, similar to our previous studies, 21,22 the presence of adsorbed gases reduce the thermal conductivity. However, the reduction is less pronounced when the pores are in the fully contracted state.

Received: May 14, 2020 **Revised:** July 27, 2020 **Published:** July 30, 2020





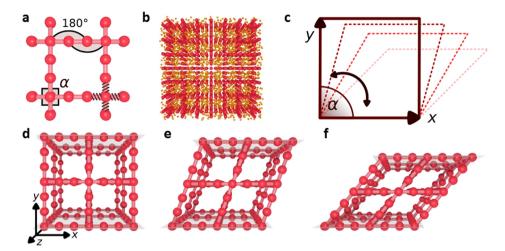


Figure 1. (a) Cross-sectional view of the idealized simple cubic structure and the harmonic bonds and angles used in the potential. (b) Simulation snapshot of the porous crystal structure (red) filled with adsorbate molecules (orange). (c) Tilt angle, α , is adjusted in 10° increments to switch from the closed form to the open form. (d–f) Snapshots of the idealized structure tilted at different angles to generate different stages of transition from contracted to expanded pores.

METHODS

To obtain these results we use idealized structures with pores tilted at various angles, as shown in Figure 1. We start with a 40° tilt angle to represent the closed form and go up in 10° increments to a cubic pore with a 90° tilt angle to represent the open form. This breathing model was adapted from our idealized cubic structures described in prior work.²¹ The simple cubic lattice structure is built using 7 atoms per unit cell. We should note that the pore expansion studied in this work is different from the effect of pore size studied in our earlier work²² as here the linker does not change in length. As depicted in Figure 1a, we define two-body bonded and threebody angular interactions between atoms, which are modeled using harmonic potentials. To determine meaningful spring constants for the potentials, we screened spring constants between 1 and 10 kcal/mol for the 90° structure. We picked the parameters that resulted in a thermal conductivity of ~1 W/m K and a simulation box volume that is within 5% of the ideal volume (see Supporting Information for the force field parameters used). For all angle bending potentials, we used an equilibrium angle of 180° except for the angles containing corner atoms, for which we use different equilibrium angles $(90^{\circ}, 80^{\circ}, 70^{\circ}, 60^{\circ}, 50^{\circ}, \text{ and } 40^{\circ}).$

To investigate the effect of adsorbed gas on thermal transport, for all structures, a gas density of 5 molecules/nm³ was used. As the volume of the simulation box is changed with angle, the initial number of molecules was adjusted accordingly. For each angle different gas molecule configurations were generated; however, for the same angle the same initial configuration was used for different simulations using a different initial velocity distribution. The gas is methane, which is modeled as a point particle with force field parameters provided in the Supporting Information.

All thermal conductivity predictions were done using the Green–Kubo approach²⁹ and equilibrium molecular dynamics (MD) simulations. All simulations were carried out at a temperature of 300 K and atmospheric pressure using a time step of 1 fs. The partial enthalpy terms required to analyze multicomponent systems were implemented as discussed in ref 30. The MD simulations were performed using a version of the Large-Scale Atomic/Molecular Massively Parallel Simulator

(LAMMPS)³¹ software which has the correct implementation of heat flux for many-body potentials.³² Periodic boundary conditions were applied in all directions. To gain further insight into the thermal conductivity predictions, we also calculated the corrected diffusivity of gas molecules within the porous crystals, which is associated with the gas mobility.³³ The corrected diffusivity is based on a Green–Kubo relation and is defined as the time integral of the center of mass velocity autocorrelation function for the gas component. Details of the Green–Kubo calculations for both thermal conductivity and diffusivity are provided in the Supporting Information.

■ RESULTS AND DISCUSSION

The thermal conductivities of the structures at different stages of expansion were first predicted without any adsorbed gas. As shown in Figure 2a, thermal conductivity in the *y* direction, which is the only direction where the box length changes (see

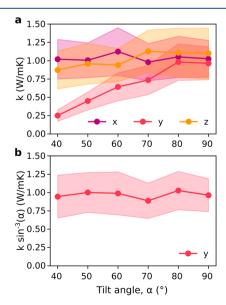


Figure 2. (a) Thermal conductivity vs tilt angle. (b) Thermal conductivity in the *y* direction scaled with $\sin(\alpha)^{-3}$ vs tilt angle. Shaded areas represent error bars.

Figure 1b), increases as the pore is expanded (tilt angle increases to 90°). However, thermal conductivities in the x and z directions remain unchanged. This trend is likely due to the fact that bonds become less effective in transferring heat in the y direction when tilted. In the absence of gas, these bonds are the means of transporting heat through the atomic vibrations (i.e., phonons) in a dielectric solid. Supporting this argument, as shown in Figure 2b, thermal conductivity scaled by $\sin(\alpha)^{-3}$ becomes nearly constant (α is the tilt angle).

To further shed light on the effect of pore contraction on thermal transport, thermal conductivity was decomposed into the contributions from different interatomic potentials (bond and angle). The decomposition was made possible by the Green–Kubo method, where forces and energies from any potential can be separately treated in the equation. Figure 3

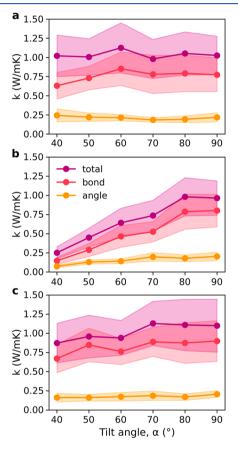


Figure 3. Thermal conductivity contribution from bond and angle potentials in the (a) x, (b) y, and (c) z directions.

shows the contributions from bond and angle potentials on the overall thermal conductivity. It is observed that overall, the angle contribution is much smaller than the bond contribution. Interestingly, the decrease of the overall thermal conductivity for smaller angles is due to the decrease of the bond contribution. This further confirms the reason mentioned earlier, that is, the thermal conductivity in any direction depends on how bonds are aligned in that direction. For the structure with 90° , the thermal conductivity is the highest because the bonded atoms are parallel to the y axis, while for smaller angles bonds are tilted from the y axis.

We then predicted the thermal conductivity of the porous materials loaded with gas at a density of 5 molecules/nm³. The results are plotted in Figure 4. Like the case without gas,

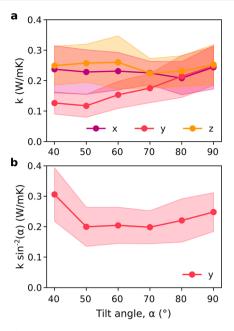


Figure 4. (a) Thermal conductivity of gas-loaded structures vs the angle which resembles the stage of expansion. (b) *y*-Direction thermal conductivity of the gas-loaded structure scaled by $\sin(\alpha)^{-2}$ vs angle.

thermal conductivity in the y direction decreases as the pores contract. However, the decrease in thermal conductivity is not as significant. With gas present in the pores, the thermal conductivity for the structure with a 40° tilt angle is approximately one-half of its value at a 90° tilt angle. However, for the structures without gas, the thermal conductivity of the structure with a 40° tilt angle is almost 20% of its value for the structure with a 90° tilt angle.

Next, we address the relative effect of adsorbed gas on the thermal conductivity of porous crystals at various stages of contraction. As shown in Figure 5a, the overall thermal

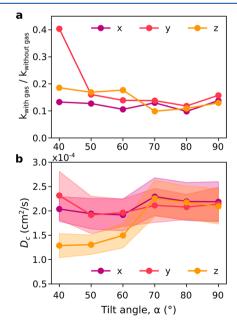


Figure 5. (a) Ratio of thermal conductivity for gas-loaded and empty crystals at different stages of pore expansion. (b) Corrected gas diffusivity for gas-loaded crystals at different stages of pore expansion.

conductivity is significantly decreased upon loading structures with gas, a phenomenon previously observed in our studies. Lacept for the fully contracted pores (i.e., 40° tilt angle), the thermal conductivity of the gas-loaded structures is 25% of that of the structures without gas. At the fully contracted state (40°), the thermal conductivity of the gas-loaded structure is 50% of that without gas. The observed weaker effects from gas—crystal collisions on the thermal transport in the contracted system compared to other systems is likely due to the already shorter intrinsic lifetimes of phonons.

The other important parameter that could affect the rate of gas adsorption in the pores during expansion is the gas diffusion through pores. To better understand the gas molecule dynamics inside the pores, we calculated corrected gas diffusivities, which are plotted in Figure 5b. The diffusivities in the x and y directions are nearly constant. However, in the z direction, the only direction where the pore cross-sectional area changes with changing angle, the diffusivity increases with pore expansion. This is due to the pore expansion which allows higher gas mobility in the z direction. It shows that during gas adsorption, upon pore expansion, the diffusion of gas molecules into pores would be facilitated.

CONCLUSIONS

With the purpose of understanding heat transfer in breathing porous crystals, we studied a series of idealized model systems using molecular dynamics simulations. We investigated the effect of pore expansion on the thermal conductivity with and without adsorbed gases. We showed that, in the direction that the pore changes, the thermal conductivity of empty porous crystals increases with expansion. In contrast, the thermal conductivity in other directions does not change with pore expansion. Our study also reveals that the presence of gases decreases the thermal conductivity in all states of the pores, with the lowest effect on the fully contracted pores. Lastly, we show that the gas diffusion increases during pore expansion, leading to easier transport of gas.

The use of breathing porous crystals for adsorption applications, particularly when gases are adsorbed and desorbed rapidly, must carefully take into account thermal transport. The simulation results from this study may help in the future design of these novel adsorbents. Finally, it is worth noting that, at the time of writing, no measurements of single-crystal thermal conductivities of breathing porous crystals exist in the literature.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c04353.

Procedure for determining suitable force field parameters, convergence of thermal conductivity calculations, procedure for adding adsorbate molecules to idealized structures, and details for Green-Kubo thermal conductivity calculations (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from the National Science Foundation (NSF), awards CBET-1804011 and OAC-1931436. This research was supported in part by the University of Pittsburgh Center for Research Computing through the resources provided.

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