

## **Narrative Progress Report**

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“Fundamental Study of Heat Transfer Mechanisms in Metal-Organic Frameworks During Gas Adsorption, with Applications to Adsorbed Natural Gas Storage Systems”

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### **Summary**

In this proposal, we were initially drawn to the challenge of improving adsorbed natural gas (ANG) storage. ANG storage is attractive for applications where space, weight, and/or cost constraints prevent the use of compressed or liquefied natural gas (CNG or LNG, respectively). A challenge with ANG storage systems is that the heat generated during adsorption must be dissipated quickly, which requires the adsorbent to have a high thermal conductivity (i.e., greater than 5 W/mK). Metal-organic frameworks (MOFs) have shown promise as adsorbents for ANG storage based on their high adsorption capacity, but they typically have low thermal conductivities (i.e., less than 0.5 W/mK). Furthermore, the mechanisms of heat transfer in porous crystals like MOFs during gas adsorption were not well understood.

To design better MOFs for ANG applications and to better understand these heat transfer mechanisms, we originally proposed to use equilibrium and non-equilibrium molecular dynamics (EMD and NEMD, respectively) to study heat transfer phenomena in MOF/gas systems: first in a idealized crystal/gas systems and then in well-studied real MOFs. Our objectives were to answer fundamental questions about heat transfer in MOFs in the presence of adsorbed gas, such as what the temperature dependence of thermal conductivity was, and what were the primary sources of phonon scattering? Another important objective was to determine how thermal conductivity relates to MOF properties such as surface area, void fraction, pore diameter and topology. These structure-property relationships would help us design better MOFs for ANG applications.

During the research effort, we discovered that very little was known about heat transfer in porous materials, in general, and by trying to design better MOFs for ANG storage, we had inadvertently contributed in a much more fundamental way to our basic understanding of these systems. The text that follows summarizes four key findings from our research activities, each of which resulted in its own paper.

### **1. Mechanisms of heat transfer in porous crystals containing adsorbed gases: Applications to metal-organic frameworks**

Our first study revealed that the thermal conductance of a crystal and gas system is dominated by lattice thermal conductivity in the crystal, and that conductance is reduced as the concentration of gas in the pores increases.<sup>1</sup> This mechanism was observed from classical molecular simulations of a monatomic gas in an idealized porous crystal structure. We showed that the decreased conductivity associated with increased gas concentration is due to phonon scattering in the crystal due to interactions with gas molecules. Calculations of scattering rates for two phonon modes revealed that scattering of the lowest frequency mode scales linearly with gas density. This result suggested that the probability of a phonon-gas collision is simply proportional to the number of gas molecules in the pore.

## 2. Effect of pore size and shape on the thermal conductivity of metal-organic frameworks

Next, we investigated the effect of pore size and shape on the thermal conductivity of a series of idealized MOFs containing adsorbed gas.<sup>2</sup> With no gas present, the thermal conductivity decreases with increasing pore size. In the presence of adsorbed gas, MOFs with smaller pores experience reduced thermal conductivity due to phonon scattering introduced by gas-crystal interactions. In contrast, for larger pores (>1.7 nm), the adsorbed gas does not significantly affect thermal conductivity. This difference is due to the decreased probability of gas-crystal collisions in larger pore structures. In contrast to MOFs with simple cubic pores, the thermal conductivity in structures with triangular and hexagonal pore channels exhibits significant anisotropy. For different pore geometries at the same atomic density, hexagonal channel MOFs have both the highest and lowest thermal conductivities, along and across the channel direction, respectively.

## 3. Transient mass and thermal transport during methane adsorption into the metal-organic framework HKUST-1

Finally, we considered methane adsorption into the real MOF, HKUST-1, and investigated the resulting heat generation and dissipation using molecular dynamics simulations. Transient simulations revealed that thermal transport in the MOF occurs two orders of magnitude faster than gas diffusion.<sup>3</sup> A large thermal resistance at the MOF/gas interface (equivalent to 127 nm of bulk HKUST-1), however, prevents fast release of the generated heat. The mass transport resistance of the MOF/gas interface is equivalent to 1 nm of bulk HKUST-1 and does not present a bottleneck in the adsorption process. These results provided important insight into the application of MOFs for practical gas storage applications, where steady-state conditions cannot be assumed.

## 4. Thermal transport in interpenetrated metal-organic frameworks

One of the common ways in which MOFs can be tuned is via interpenetration. In this work, which was featured on the front cover of *Chemistry of Materials*,<sup>4</sup> we showed how thermal conductivity was affected by interpenetration using molecular dynamics simulations. Further, we showed that a relatively simple analytical formula could be used by experimentalists to make an educated guess about the composite thermal conductivity of an interpenetrated system from knowledge of the individual MOF conductivities.

## Conclusion

Many open questions about thermal transport in porous materials remain. How do phonons behave in *flexible* porous materials (as some MOFs are famous for their ability to expand by several hundred percent volumetrically during gas adsorption)? Can engineering a low thermal conductivity in a MOF be accomplished in a way that is decoupled from its electrical conductivity? If so, that would allow for a breakthrough in thermoelectric materials.

## Works published as a result of this funded research:

1. Babaei, H. & Wilmer, C. E. Mechanisms of heat transfer in porous crystals containing adsorbed gases: Applications to metal-organic frameworks. *Phys. Rev. Lett.* **116**, 025902 (2016).
2. Babaei, H., McGaughey, A. J. H. & Wilmer, C. E. Effect of pore size and shape on the thermal conductivity of metal-organic frameworks. *Chem. Sci.* **8**, 583–589 (2017).
3. Babaei, H., McGaughey, A. J. H. & Wilmer, C. E. Transient mass and thermal transport during methane adsorption into the metal-organic framework HKUST-1. *ACS Appl. Mater. Interfaces* **10**, 2400–2406 (2018).
4. Sezginel, K. B., Asinger, P. A., Babaei, H. & Wilmer, C. E. Thermal transport in interpenetrated metal-organic frameworks. *Chem. Mater.* **30**, 2281–2286 (2018).