Medium-Range Order Structure Controls Thermal Stability of Pores in Zeolitic Imidazolate Frameworks

Christensen, Rasmus; Bokor, Yossi; Sørensen, Søren Strandskov; Biscio, Christophe; Fajstrup, Lisbeth; Smedskjær, Morten Mattrup

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[1]**Rasmus Christensen***, [2]Yossi B. Bleile, [1]Søren S. Sørensen, [2]Christophe A. N. Biscio, [2]Lisbeth Fajstrup, [1]Morten M. Smedskjaer

[1]Department of Chemistry and Bioscience, Aalborg University, Denmark, [2]Department of Mathmatical Sciences, Aalborg University, Denmark

AALBORG UNIVERSITY

1 Background and Objective

Zeolitic Imidazolate Frameworks (ZIFs), a familiy of Metal Organic Frameworks, have been proposed for application within many fields such as seperation, adsorption and drug delivery due to their highly porous structures

Certain ZIF compostions such as ZIF-4, ZIF-62 and ZIF-76 can form a glass upon melt quenching, improving moldability, transport, optical, and mechanical properties

Many ZIFs loose their porosity upon glass formation, limiting their potential applications

However, some compostions have shown the ability to retain porosity in the glass phase like ZIF-76-mbIm[1] and Co-ZIF-62[2]

To find out why some ZIFs collaps, while others remain porous, we investigate the mechansim controling pore collaps in ZIFs upon melting[3]

2 Simulation Method

We perform a computational study of three glass forming ZIFs

Studied crystals:

ZIF-4	$Zn(Im)_2$
ZIF-62	$Zn(Im)_{1.75}(bIm)_{0.25}$
ZIF-76	$Zn(Im)_{1.33}(mbIm)_{0.67}$

Ab Initio Molecular Dynamics simulations were performed in CP2K using the Quickstep package, employing Gaussian and Augmented plane waves.

Exchange-correlation energy assessed using Perdew-Burke-Ernzhof (PBE) approximation. Valence electrons were described by double-zeta valence polarized basis sets and Goedecker–Teter–Hutter pseudopotentials

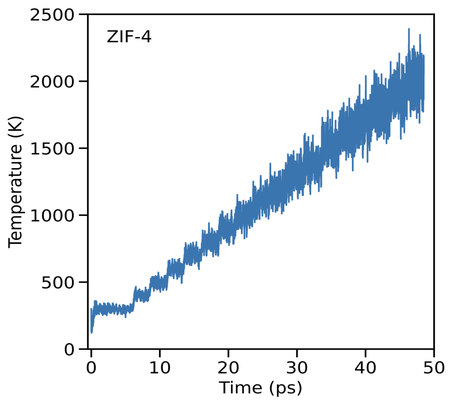
Heating Simulation:

Stepwise heating in 100 K steps from 300 K to 2000 K in NPT ensemble

Effective heating rate of 40 K/ps

0.5 fs timestep used

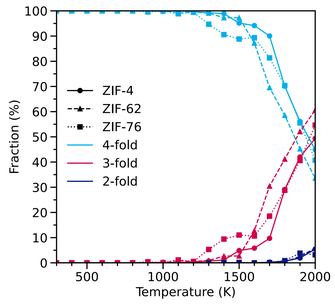
Three repetitions of the simulations were conducted for each crystal

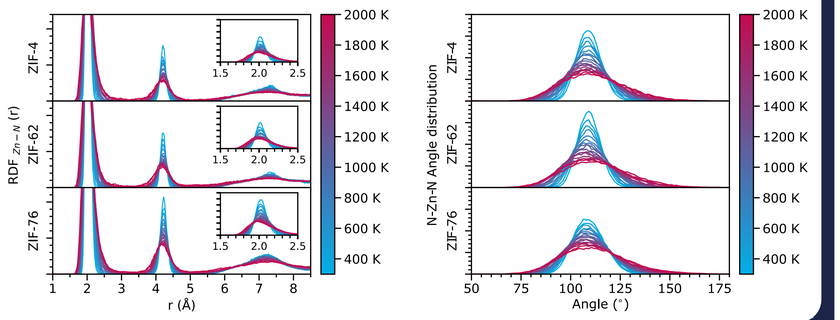


3 Short-range order disordering

As ZIF crystals heat up and melt, all crystals shows a change in their short-range order

- Widening of peaks in RDF
- Decrease in Zn coodination
- Widening of N-Zn-N bond angle





4 Persistent Homology for Medium-Range Order

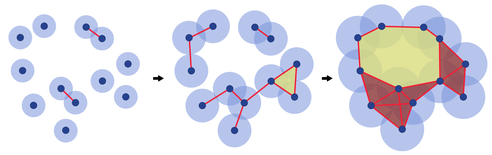
Persistent Homology:[4]

Atoms are represented as spheres with a radius

When radii of atoms overlap
- Edges are formed

When edges form a closed loop
- A loop is born

When a loop is filled in
- The loop dies

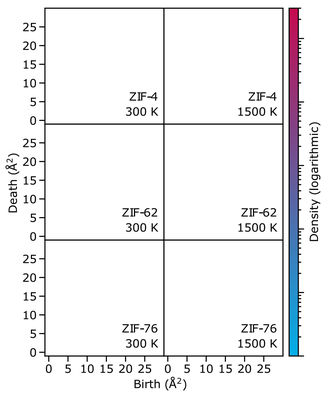


Identify Medium Range Order features
- 1D = Rings
- 2D = Voids

Persistence diagrams
- Plot birth vs death times of loops

Applied to simulations:
- Points spread out as temperature is increased
- Medium-range order changes during heating
- ZIF-76 appears most stable

Quantitative comparison is hard using persistence diagrams



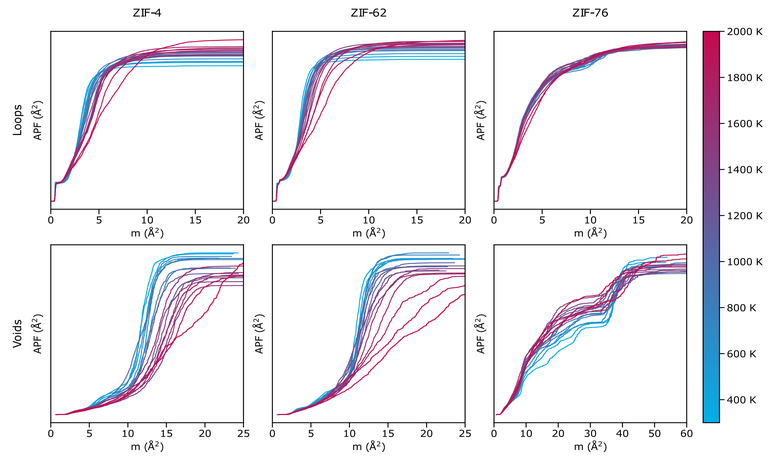
5 Medium-Range Order retention

Accumulative persistence function (APF)

Summation of persistence diagrams based on their lifetime and mean age

$$\mathrm{APF(t)} = \sum_{i:m_i \le t}(d_i - b_i) \quad , \quad m_i = \frac{b_i + d_i}{2}$$

Allows for quantitative comparison of persistence diagrams



A shift in the APF for ZIF-4 and ZIF-62 is seen upon heating, showing a break down of their medium-range order

Retention of medium-range order structures in ZIF-76 is observed upon heating from its more constant APF. This is despite the observed short range disorder, and shows that the MRO structures in ZIF-76 are more thermally stable.

6 Conclusion

Our findings point to a link between the ability of ZIFs to retain porosity after melt-quenching and the ability to retain medium-range order structures of the crystal phase during heating, even when the extent of short-range disorder increases

As such, our work provides the initial steps for understanding how to retain microporosity in MOF liquids and glasses through tailoring the medium-range order structures.

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7 References

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*Presenting author: rasmusc@bio.aau.dk