

Unravelling the Thermodynamic Criteria for Size-Dependent Spontaneous Phase Separation in Soft Porous Crystals

S. M. J. Rogge¹, M. Waroquier¹, V. Van Speybroeck¹

¹Center for Molecular Modeling, Ghent University, Belgium, Sven.Rogge@UGent.be

Soft porous crystals (SPCs) or flexible metal-organic frameworks (MOFs) harbour an unparalleled potential as functional nanoporous materials owing to their tuneable morphing between different crystalline phases in response to external stimuli.^{1,2} These large-amplitude phase transitions are generally assumed to occur cooperatively throughout the whole crystal, thereby retaining the material's perfect crystalline order. However, this traditional picture of a 'perfect MOF crystal' for flexible MOFs sharply contrasts with the intrinsic spatial disorder recently discovered in rigid MOFs, varying from point-like defects to completely amorphous or glass-like phases lacking any long-range structural order. While one might assume that also flexible MOFs are much more disordered than originally thought, it is still generally accepted that a flexible MOF crystal can only exhibit a single phase at any given time. Here, we disprove this preconception through mesoscale first-principles based molecular dynamics simulations, demonstrating that phase transitions in SPCs induce spatial disorder in the material that propagates along preferential directions determined by the SPC's topology. Interestingly, this instantaneous coexistence of multiple metastable phases within a given sample can be stabilized by carefully tuning the experimental control variables such as pressure, temperature, and chemical potential. The observed phase coexistence forms a key ingredient to rationalize yet elusive phenomena in SPCs, such as the impact of crystal downsizing on their flexible behaviour, adding the crystal size as an easily controllable but crucial design parameter for future SPC-based stimuli-responsive devices.

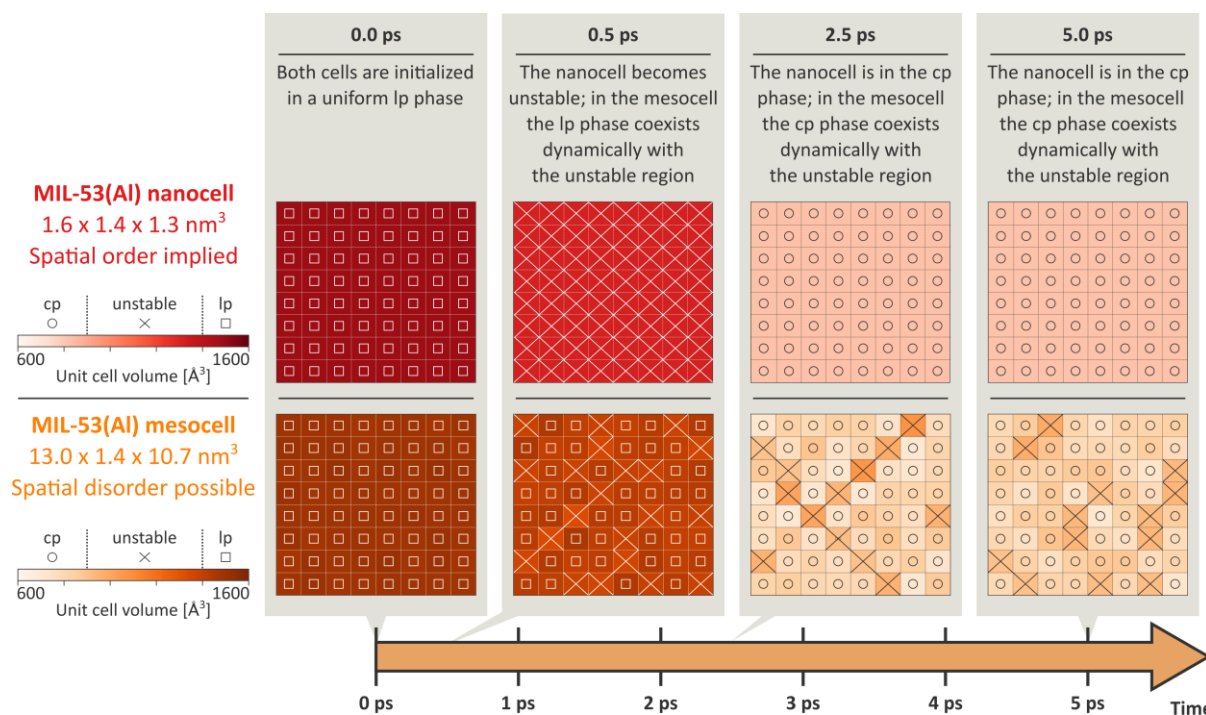


Figure. Spontaneous phase coexistence of large-pore (lp), unstable, and closed-pore (cp) states in MIL-53(Al) when accounting for spatial disorder in a mesocell simulation at 300 K and 40 MPa.

References

- [1] S.M.J. Rogge, M. Waroquier, V. Van Speybroeck, *Acc. Chem. Res.* **51**, 138, 2018
- [2] L. Vanduythuys, S.M.J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, V. Van Speybroeck, *Nat. Commun.* **9**, 204, 2018

Preferred presentation type: oral