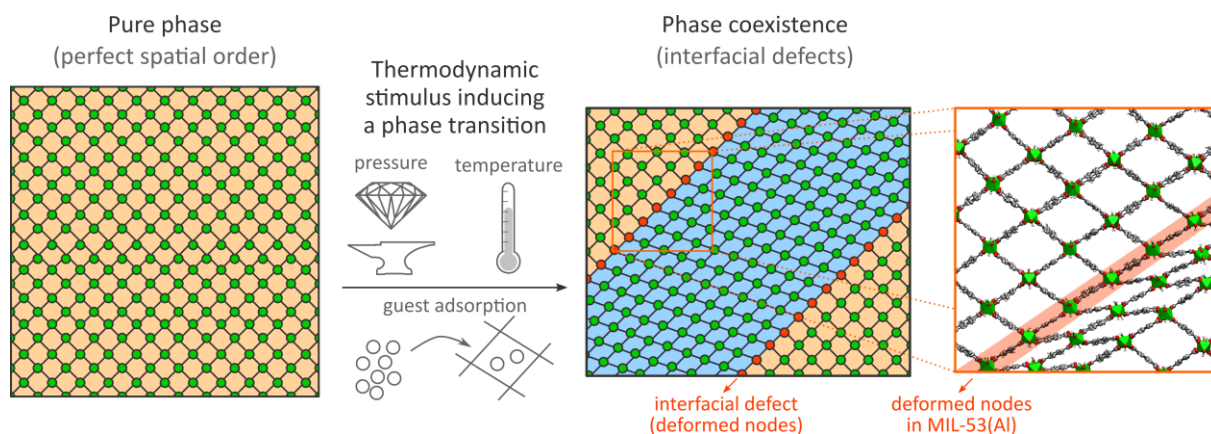


Unraveling the Thermodynamic Criteria for Size-Dependent Spontaneous Phase Separation in Soft Porous Crystals

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Soft porous crystals (SPCs) or flexible metal-organic frameworks (MOFs) are attractive materials owing to their tunable morphing between crystalline phases in response to external stimuli [1]. While rigid MOFs exhibit intrinsic spatial disorder, varying from point-like defects to completely amorphous phases lacking any long-range structural order, spatial disorder in flexible MOFs is much less understood. However, it is still generally accepted that SPCs can only exhibit a single phase at any given time, such that phase transitions would need to occur cooperatively throughout the crystal. Recently, we disproved this preconception through mesoscale first-principles based molecular dynamics simulations, demonstrating that phase transitions induce spatial disorder in the SPC material that propagates along preferential directions determined by the SPC's topology [2]. This instantaneous phase coexistence can be stabilized by carefully tuning the experimental control variables such as pressure and temperature. 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 behavior, adding the crystal size as a crucial design parameter for future SPC-based stimuli-responsive devices.



[1] L.Vanduyfhuys *et al.*, "Thermodynamic Insight into Stimuli-Responsive Behaviour of Soft Porous Crystals", *Nat. Commun.* **9** (2018) 204.

[2] S.M.J. Rogge *et al.*, "Unraveling the Thermodynamic Criteria for Size-Dependent Spontaneous Phase Separation in Soft Porous Crystals", *Nat. Commun.* **10** (2019) 4842.