

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

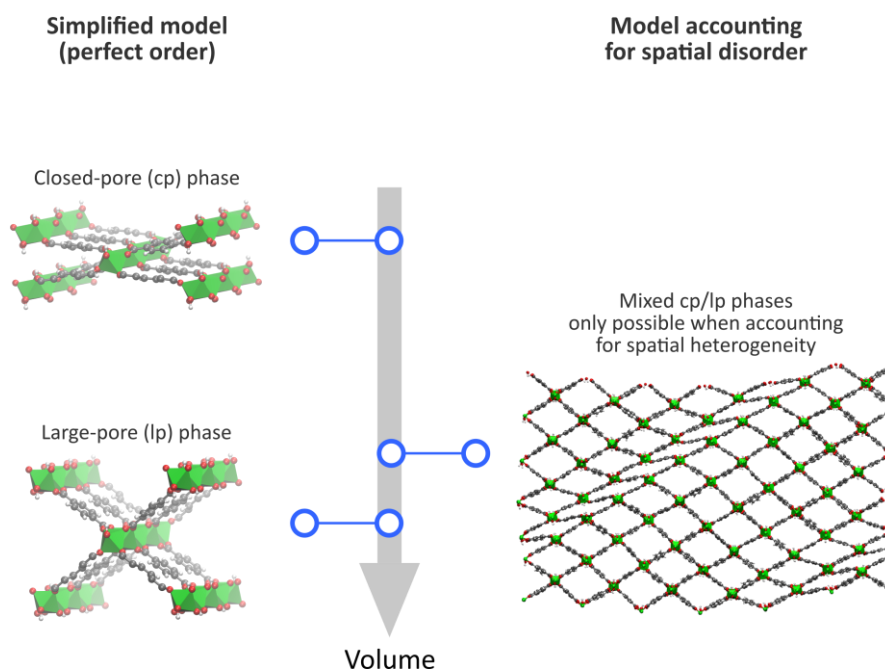
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Soft porous crystals (SPCs) harbor an unparalleled potential as functional nanoporous materials owing to their tuneable morphing between different crystalline phases in response to external stimuli including temperature, pressure, and gas adsorption [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. In this contribution, we disprove this preconception through mesoscale first-principles based molecular dynamics simulations, demonstrating that these phase transitions 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 behavior, adding the crystal size as an easily controllable but crucial design parameter for future SPC-based stimuli-responsive devices.



[1] S.M.J. Rogge, M. Waroquier, and V. Van Speybroeck, *Acc. Chem. Res.* **51**(1): 138-148, 2018.

[2] L. Vanduyfhuys, S.M.J. Rogge, J. Wieme, S. Vandenbrande, G. Maurin, M. Waroquier, and V. Van Speybroeck. *Nat. Commun.* **9**: 204, 2018.