Exploring the opportunities in strain engineering: from introducing flexibility in rigid MOFs to classifying elusive amorphous states

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We recently introduced strain engineering as a new *in silico* materials engineering design tool to fundamentally alter a nanostructured material's polymorphism and macroscopic functionality by introducing well-defined strain fields in the material [1,2]. Strain engineering is built on the observation that polymorphism-inducing external triggers – stress, adsorption, temperature – and internal disorder both deform a material, resulting in time-dependent strain fields that propagate through the material and may interact with one another. As a result, by introducing well-chosen disorder, the material can be designed to exhibit targeted flexibility under well-defined external triggers. In this contribution, we will highlight two recent case studies of strain engineering on metal-organic frameworks (MOFs) and the essential role that AI plays in developing this materials engineering methodology.

We first focus on the rigid UiO-66 MOF (Figure 1). By creating well-defined linker vacancies, we show that this rigid MOF becomes locally flexible [1]. Besides forming an intermediate between completely rigid and completely flexible MOFs, the so-created reversible crumple zones in this strain-engineered material also focus the strain, thereby preserving the integrity and adsorption capacity of the remainder of the material. This size-independent observation can be further amplified by combining orthogonal crumple zones [1], which may find applications in shock absorbers or sensors. Furthermore, these strain-engineered materials hint toward a mechanical analogy of Braess' paradox [1]. The counterintuitive flexibility observed for this rigid MOF is akin to the stimuli-induced phase coexistence induced earlier in the soft porous crystals CoBDP, DMOF-1(Zn), and MIL-53(Al)-F [1,3]. They are easier to synthesise than the strain-engineered UiO-66 materials above and illustrate our strain-engineering approach's general applicability. We demonstrate that increasing the temperature or adsorbing guests leads to a dynamic redistribution of the strain in the material disfavouring phase coexistence [1]. In addition, we reveal the existence of buffer layers at the interface of the two coexisting phases [1]. This can be exploited to design strain-engineered materials in which well-defined zones of the material are stabilised in one phase while others remain in a different phase.

In a second case study, we focus on the rich polymorphism of zeolitic imidazolate frameworks (ZIFs), especially ZIF-4 [4]. Compared to polymorphism in crystalline materials, phase transitions to amorphous states are ill-understood, mainly because of a lack of tools to properly characterise the structure of these states lacking long-range order. As a result, structure-function relationships, which are abundant in crystalline materials, remain scarce in amorphous materials. Therefore, in this second case study, we trained a machine-learning potential on the fly to explore how combining strain engineering with a nuclear magnetic resonance (NMR) protocol characterises the different states encountered in amorphous states. As a result, we can map the different local states in amorphised ZIF-4, which can, in turn, be correlated with the macroscopic function exhibited by these materials, opening up the opportunity to create structure-function relationships for amorphous materials.

References

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Figures

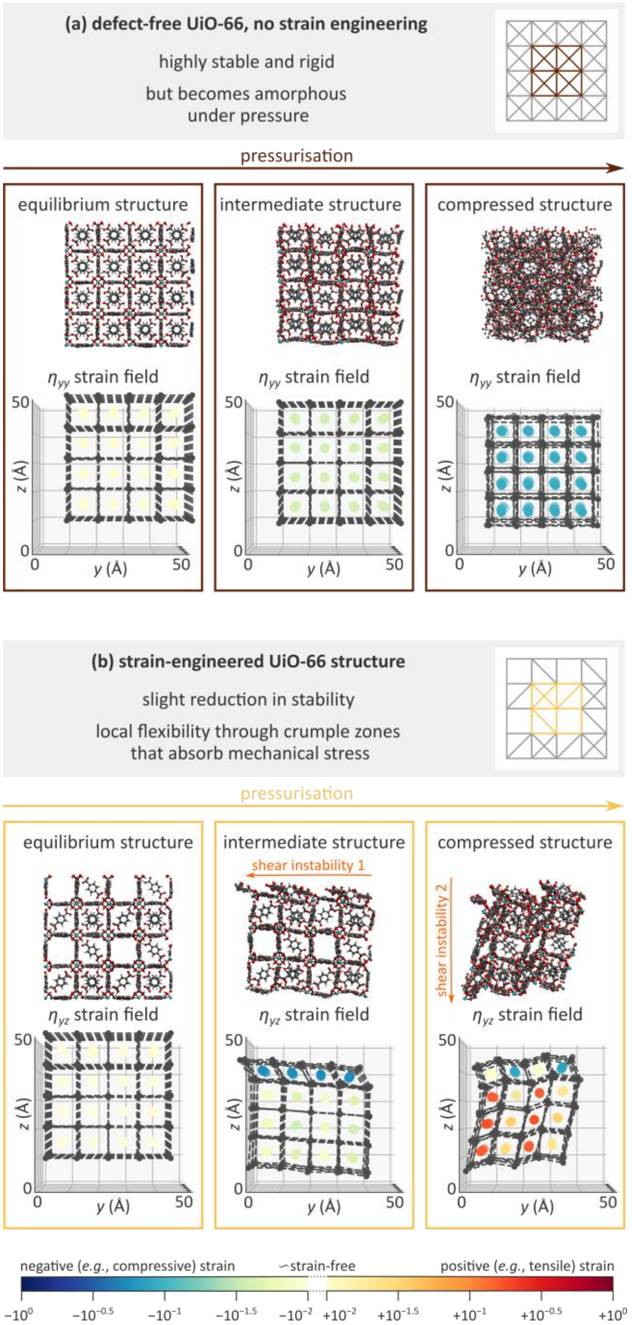

Figure 1. Illustration of how strain engineering UiO-66 from its defect-free (top) to strain-engineered form (bottom) alters its ability to absorb strain. **a**. Upon pressurisation, an external source of strain, the defect-free UiO-66 compresses and amorphises, losing its adsorptive function. **b**. By strain engineering linker defects as crumple zones, an internal source of strain, the external strain focuses in well-defined regions while preserving the integrity of the remainder of the material. Figure adapted from [1].