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Adsorption deformation of microporous
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We study here the behavior of flexible adsorbent materials, or soft porous crystals, when used in practical applications as nanostructured composites such as core-shell particles or mixed matrix membranes. Based on simple models and the well-established laws of elasticity, we demonstrate how the presence of a binder results in an attenuation of the adsorption-induced stress and deformation. In the case where the adsorbent undergoes adsorption-induced structural transitions, such as the gate opening phenomenon occurring in some metal-organic frameworks, we show that the presence of the binder will result in shifts of the adsorption-induced transition pressures.

The discovery of soft porous crystals^{1,2} and their potential use for adsorption separations,^{3,4} catalysis,⁵ drug delivery,⁶ sensing,⁷ and more generally as functional molecular materials⁸ has triggered within last decade an explosion in experimental, theoretical, and modeling studies of the phenomenon of stimuli-responsive framework materials⁹ in general, and of the phenomenon of adsorption-induced deformation in particular.^{7,10–12} Guest molecules adsorbed in nanoscale pores exert significant stress, of the order of gigapascals,^{13,14} which causes deformation^{15–17} and in some case morphological transformations in the host solid structure.¹⁸ Most prominent are gate opening and breathing transitions, which have been explored in great detail by using *in situ* XRD scattering drawing on a variety of metal-organic framework (MOF) materials.^{10,19,20} Microscopic mechanisms of MOF flexibility have been examined by detailed first principles and atomistic molecular dynamic and Monte Carlo simulations performed on the crystal cell level.^{21–25} A rigorous thermodynamic approach¹¹ has been proposed to predict the

adsorption stress from adsorption isotherms.²⁶ However, these studies are limited to single adsorbent particles, while the vast majority of practical applications require the use of composite materials,²⁷ such as micrometer size adsorbent particles embedded into a permeable matrix^{28–30} or thin films anchored on a support.^{31,32} Although composite MOF materials have been studied from the point of view of adsorption and gas separation, such as *e.g.* MOFs coated with mesoporous silica,³³ there has been so far no specific study focused on flexibility, which is still a completely open question.

In this letter, we explore the flexibility of composite materials formed by a soft porous crystal and a non-adsorbing matrix. In particular, we study the extent to which the elastic properties of the non-adsorbing matrix affect the adsorption-induced deformation of the adsorbent particles and the composite as a whole. Using a simple yet instructive spherical core-shell model, we find that adsorption deformation in composite is reduced compared to unconfined particles and the magnitude of this effect is determined by the both elastic moduli of the matrix and the morphology of the nanostructured composite. The reduction of adsorption deformation leads to the shift of the positions of morphological transformations, which can be even suppressed due to matrix rigidity. These conclusions have important implications on the feasibility assessment of the potential applications, which are based on the effects of adsorbent flexibility. For example, widening the hysteresis loops in adsorption-desorption behavior can improve the amount of mechanical energy stored in a high-pressure liquid intrusion.²³ Tuning the flexibility of the framework will also impact the heat released during the transition, a key property for adsorption-based separation processes.³⁴

As a model system, let us consider a composite spherical particle made of an adsorbing core of radius R_1 (in our case, a particle of soft porous crystal) and non-adsorbing elastic

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shell of external radius R_2 . Both adsorbent and matrix materials are assumed isotropic. The elastic properties of the composite are characterized by the volumetric modulus K_a of the adsorbent, whose deformation is considered uniform, and by the Young modulus E and Poisson's ratio ν of the matrix. Under the action of adsorption-induced stress σ_a , the adsorbent core is deformed uniformly with linearly progressing radial displacement u_r and constant radial strain u_{rr} given by

$$u_r = \frac{\sigma_a - P_1}{3K_a} r; u_{rr} = \frac{\sigma_a - P_1}{3K_a} \text{ at } r < R_1 \quad (1)$$

where r is radial coordinate.³⁵ The external pressure P_1 acting on the core-shell boundary $r = R_1$ is unknown and is determined from the solution of the classical Lamé problem of the deformation of the outer spherical shell under action of internal P_1 and external P_2 pressures.³⁵ The general solution of the Lamé problem implies that in the shell, the radial displacement u_r , strain u_{rr} , and stress σ_{rr} are given by the following equations:

$$u_r = ar + b/r^2, u_{rr} = a - 2b/r^3, \sigma_{rr} = \frac{E}{1-2\nu} a - \frac{2E}{r^3} b, \text{ at } R_1 < r < R_2 \quad (2)$$

The constants a and b are determined from the boundary conditions,

$$\sigma_{rr}(R_1) = -P_1 \quad (3)$$

$$\sigma_{rr}(R_2) = -P_2, \quad (4)$$

as

$$a = \frac{P_1 R_1^3 - P_2 R_2^3}{R_2^3 - R_1^3} \frac{1-2\nu}{E} = g(P_1 - (1-g^{-1})P_2)/3K \quad (5)$$

$$b = \frac{R_1^3 R_2^3 (P_1 - P_2)}{R_2^3 - R_1^3} \frac{1+\nu}{2E} = \frac{1}{4\mu} g R_2^3 (P_1 - P_2) \quad (6)$$

The volumetric K and shear μ moduli are used in the right-hand side of eqn (5) and (6) instead of Young's modulus E and Poisson's ratio ν , to which they are related in an isotropic elastic medium by:

$$K = \frac{E}{3(1-2\nu)}, \mu = \frac{E}{2(1+\nu)} \quad (7)$$

Note that the composite morphology is characterized by the ratio g of the adsorbent and matrix volumes,

$$g = \frac{R_1^3}{R_2^3 - R_1^3} \quad (8)$$

The unknown pressure P_1 is determined from the third boundary condition of equality of the displacements in the core and in the shell at $r = R_1$, namely:

$$u_r(R_1) = (\sigma_a - P_1)R_1/3K_a = aR_1 + b/R_1^2 \quad (9)$$

Combining condition (9) with (5) and (6) one arrives at a linear equation for the boundary pressure P_1 , which solution gives:

$$P_1 = \frac{\sigma_a + \left(\frac{3(1+g)}{4}\mu - \frac{1-g}{K}\right)K_a P_2}{1 + K_a \left(\frac{g}{K} + \frac{3(1+g)}{4}\mu\right)} \quad (10)$$

As such, the sought radial strain in the adsorbent core is given as

$$u_{rr} = (\sigma_a - P_1)/3K_a = \frac{\sigma_a}{3K_a} - \frac{\sigma_a/3K_a + (1-g)(1/4\mu - 1/3K)P_2}{1 + K_a(g/K + 3(1-g)/4\mu)} \quad (11)$$

Eqn (11) shows that the adsorption-induced strain σ_a is reduced by the elastic confinement, since the second term on the right-hand side is guaranteed to be negative. The extent of the lowering or "damping" of the deformation upon adsorption depends on both the geometrical characteristics of the composite material (through the ratio g) and the mechanical properties of the elastic shell (moduli K and μ). It should be noted that the volumetric strain ε , which is the quantity involved in thermodynamic descriptions and models of adsorption deformation, is equal to three times the radial strain u_{rr} , $\varepsilon = 3u_{rr}$. As such, eqn (11) can be rewritten in terms of the volumetric strain ε as a function of the adsorption stress σ_a and external pressure, $P_2 = P_{\text{ext}}$:

$$\varepsilon = \frac{\sigma_a}{K_a} - \frac{\sigma_a/K_a + (1-g)(1/4\mu - 1/3K)P_{\text{ext}}}{1 + K_a(g/3K + (1-g)/4\mu)} \quad (12)$$

We will now consider specific cases, schematized in Fig. 1, that are relevant for practical applications of composite materials containing soft porous crystals.

Let us first consider an unconfined adsorbent under external pressure P_{ext} . This case corresponds to $P_2 = P_{\text{ext}}$ and $g \rightarrow \infty$ that reduces to the standard equation

$$\varepsilon = (\sigma_a - P_{\text{ext}})/K_a \quad (13)$$

This is the equation used in thermo-mechanical models of adsorption-induced deformation of soft porous crystals when the pure MOF is considered.²⁶ In the absence of external mechanical pressure ($P_{\text{ext}} = 0$), it further reduces to the simple Hooke's law $\varepsilon = \sigma_a/K_a$, which will in the following serve as our baseline reflecting the behavior of flexible MOFs in the absence of confining phase.

In the case of an adsorbent particle in infinite elastic matrix, the volume of the exterior matrix is much larger than that of the crystal. It is a very simplified version of real composite materials used in practical applications, *e.g.* such as a mixed matrix membrane with particles of soft porous crystal embedded in a surrounding polymer phase.

This case corresponds to $P_{\text{ext}} = 0$ and $g \rightarrow 0$. The volumetric strain from eqn (12) is now equal to

$$\varepsilon = \frac{\sigma_a}{K_a} \left(1 - \frac{1}{1 + K_a/4\mu}\right) = \frac{\sigma_a}{K_a} \times \frac{1}{1 + 4\mu/K_a} < \frac{\sigma_a}{K_a} \quad (14)$$

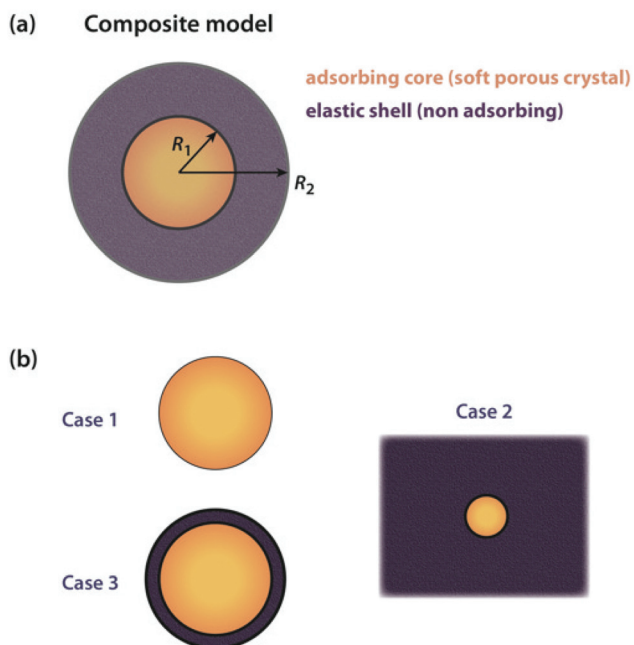


Fig. 1 (a) Model system representing a composite material. (b) Three special cases of the model system: case 1, unconfined spherical adsorbent particle; case 2, adsorbent in infinite elastic matrix; case 3, spherical core-shell particle.

From this equation, we see that the deformation of the material is reduced, by a constant factor that depends on the relative elasticity of the adsorbent and matrix: the stiffer it is, the more it prevents the core particle from changing its volume. The adsorption-induced stress is dampened, or diminished, by a factor of $\frac{1}{1 + 4\mu/K_a}$.

Another case of interest is that of core-shell nanoparticles, *i.e.* the general case in which g depends on the shell size but $P_{\text{ext}} = 0$. This geometry of a nanoparticle of MOF crystal coated (or surrounded) by a non-adsorbing matrix is particularly relevant for applications, where the shell could be used to reinforce the chemical and mechanical stability of the MOF core. For that case, the adsorption-induced strain is:

$$\varepsilon = \frac{\sigma_a}{K_a} \left(1 - \frac{1}{1 + K_a \left(\frac{g}{3K} + (1-g)/4\mu \right)} \right) < \frac{\sigma_a}{K_a} \quad (15)$$

Like in the previous case, the strain is reduced compared to the unconfined particle, but this time the factor depends on both the bulk (volumetric) K and shear μ moduli of the shell matrix, as well as the geometry (through g). For the specific case of a thin shell of thickness h (a coating of the MOF), this factor equals $g = R_1/3h$.

Finally, now turn to a composite material (soft porous crystal core and elastic shell) jacketed by a non-deformable outer container. In practice, this represents a composite that is surrounded by a much stiffer material. This case thus corre-

sponds to different boundary conditions, because the outer stress P_2 is undetermined, but the volume is conserved leading to a condition of zero displacement at $r = R_2$, $u_r(R_2) = 0$. Solution of the Lamé equations with this boundary condition gives the following equation for the volumetric strain (see mathematical derivation in Appendix):

$$\varepsilon = \frac{\sigma_a - P_1}{K_a} = \frac{\sigma_a}{K_a} \times \frac{1}{1 + \frac{gK}{K_a} + \frac{4\mu(1+g)}{3K_a}} < \frac{\sigma_a}{K_a} \quad (16)$$

Hence, despite the different nature of the boundary conditions, the end result is similar: additional constraints on the soft porous crystals cause further reduction in volumetric strain.

Finally, let us highlight the effect of the confinement-induced dampening of the adsorption deformation drawing on the example of a stimuli-responsive MOF. We consider here a MOF crystal undergoing a *gate opening* phenomenon, *i.e.* the adsorption-driven opening from a nonporous *closed* structure (or structure of lower pore volume) into a microporous *open* phase (or structure of large pore volume). Following the thermo-mechanical view (or “stress model”) of adsorption-induced structural transitions in soft porous crystals,²⁶ gate opening occurs upon adsorption when the outwards stress exerted by the guest molecules reaches a certain critical threshold, the limit of stability of this *closed* phase. Symmetrically, upon desorption the transition occurs when the adsorption-induced stress falls below another threshold, which is the limit of stability of the *open* phase. This mechanism results in step-wise adsorption-desorption isotherms forming a hysteresis loop exemplified in Fig. 2 (solid lines), taking for the adsorption stress profile a Langmuirian equation, as derived in ref. 26.

To illustrate the impact of the external confinement on the gate-opening phenomenon, we consider a crystal in infinite elastic matrix. The adsorption stress isotherm (stress *vs.* gas pressure) and the respective adsorption isotherm are plotted by dashed lines in Fig. 2. One can see that the changes in the adsorption stress lead to a shift in the position of the structural transition. In the example given in Fig. 2, this phenomenon leads to a widening of the hysteresis loop, with gate opening occurring at a higher pressure and gate closing at a lower pressure. It could also be possible, depending on the nature and shape of the adsorption stress profiles, to observe a reverse effect—*e.g.*, with gate closing at a higher pressure than in the unconfined soft porous crystal, or gate opening at lower pressure. Similar conclusions can be made for the case of core-shell particles.

In conclusion, we have shown that the elastic confinement present in composite materials affects adsorption-induced deformation of soft porous crystals. This effect is of particular interest, since flexible adsorbents in practical applications are used as composites such as core-shell particles or mixed matrix membranes. By deriving the mechanical equations for the deformation of model composite materials, we show that this effect depends on the geometric nature of the composite as well as on the respective elastic properties of the adsorbent (through its bulk modulus) and the elastic matrix (through its

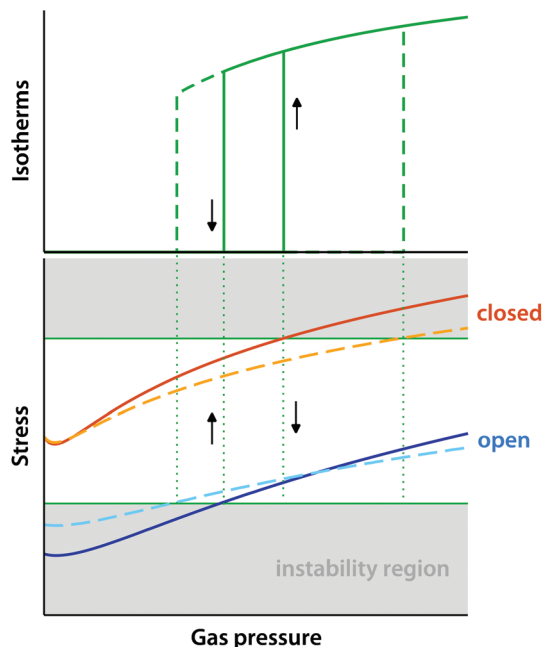


Fig. 2 Gate-opening phenomenon in an isolated crystal (solid lines) and in a crystal surrounded by an elastic matrix (dashed lines). Upper panel: adsorption–desorption isotherms; lower panel: adsorption-induced stress in both phases.

bulk and shear moduli). In all cases, however, the presence of the binder results in an attenuation of the adsorption-induced deformation. In the case where the adsorbent undergoes adsorption-induced structural transitions, such as the *gate opening* phenomenon occurring in metal–organic frameworks, the presence of a binder around the adsorbent can result in shifts of the transition pressures. In future works, it will be of interest to expand the study from the radial stress to the tangential stress at the crystal–binder interface. This tangential stress cannot exceed the limit of material integrity of the elastic medium that determines the conditions, at which the nanostructured composite “breaks down”, *i.e.* contact between the soft porous crystal and the surrounding elastic medium is lost. Noteworthy the analysis performed in this work is limited to isotropic crystals; its extension to anisotropic structures is highly desired yet involves a much more elaborated treatment of adsorption deformation. We hope that this first theoretical treatment of the open question of flexibility of MOF-based nanocomposite materials will spur experimental research in that direction.

Appendix. Derivation of adsorption-induced deformation in a jacketed composite

Let us consider a composite material jacketed by a non-deformable outer container. The boundary condition in this case is

$$u_r(R_2) = 0 \quad (17)$$

We start from the general solution to the Lamé problem in the shell region as given by eqn (2), which we re-write as

$$u_r = ar + b/r^2, u_{rr} = a - 2b/r^3, \sigma_{rr} = 3K_a - 4\mu b/r^3, \text{ at } R_1 < r < R_2 \quad (18)$$

The boundary conditions are

$$\begin{aligned} 3K_a - 4\mu b/R_1^3 &= -P_1 \\ aR_2 + \frac{b}{R_2^2} &= 0, \text{ or } b = -R_2^3 a \\ a + b/R_1^3 &= (\sigma_a - P_1)/3K_a \end{aligned} \quad (19)$$

Thus $a = -P_1/(3K + 4\mu R_2^3/R_1^3) = -P_1/[3K + 4\mu(1 + 1/g)]$ and $a = -(\sigma_a - P_1)g/3K_a$, so

$$(\sigma_a - P_1)[gK/K_a + 4\mu(1 + g)/3K_a] = P_1 \quad (20)$$

and thus we have:

$$P_1 = \sigma_a \frac{gK/K_a + 4\mu(1 + g)/3K_a}{1 + gK/K_a + 4\mu(1 + g)/3K_a} \quad (21)$$

We then derive the stress profile as

$$\sigma_{rr} = a \left[3K + \frac{4\mu R_2^3}{r^3} \right] = -P_1 \frac{3K + 4\mu R_2^3/r^3}{3K + 4\mu R_2^3/R_1^3} \quad (22)$$

$$P_2 = -\sigma_{rr}(R_2) = P_1 \frac{3K + 4\mu}{3K + 4\mu R_2^3/R_1^3} = P_1/[1 - 1/g(1 + 3K/4\mu)] \quad (23)$$

and for the strain in the adsorbent core

$$u_{rr} = (\sigma_a - P_1)/3K_a = \sigma_a/3K_a(1 + gK/K_a + 4\mu(1 + g)/3K_a) \quad (24)$$

$$\varepsilon = (\sigma_a - P_1)/K_a = \sigma_a/K_a(1 + gK/K_a + 4\mu(1 + g)/3K_a) \quad (25)$$

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References

- 1 K. Uemura, R. Matsuda and S. Kitagawa, *J. Solid State Chem.*, 2005, **178**, 2420–2429.
- 2 S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704.
- 3 P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgamo, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842–16843.
- 4 T. Remy, G. V. Baron and J. F. M. Denayer, *Langmuir*, 2011, **27**, 13064–13071.
- 5 R. K. Das, A. Ajjaz, M. K. Sharma, P. Lama and P. K. Bharadwaj, *Chem. – Eur. J.*, 2012, **18**, 6866.

- 6 P. Horcajada, C. Serre, G. Maurin, N. A. Ramsahye, F. Balas, M. Vallet-Regi, M. Sebban, F. Taulelle and G. Férey, *J. Am. Chem. Soc.*, 2008, **130**, 6774.
- 7 G. Férey and C. Serre, *Chem. Soc. Rev.*, 2009, **38**, 1380–1399.
- 8 C. Wang, D. Liu and W. Lin, *J. Am. Chem. Soc.*, 2013, **135**, 13222–13234.
- 9 F.-X. Coudert, *Chem. Mater.*, 2015, **27**, 1905–1916.
- 10 A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, *Chem. Soc. Rev.*, 2014, **43**, 6062–6096.
- 11 F.-X. Coudert, M. Jeffroy, A. H. Fuchs, A. Boutin and C. Mellot-Draznieks, *J. Am. Chem. Soc.*, 2008, **130**, 14294–14302.
- 12 F.-X. Coudert, A. Boutin, A. H. Fuchs and A. V. Neimark, *J. Phys. Chem. Lett.*, 2013, **4**, 3198–3205.
- 13 D. D. Do, D. Nicholson and H. D. Do, *J. Phys. Chem. C*, 2008, **112**, 14075–14089.
- 14 Y. Long, J. C. Palmer, B. Coasne, M. Sliwinska-Bartkowiak and K. E. Gubbins, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17163–17170.
- 15 A. V. Tvardovskiy, *Sorbent Deformation*, Elsevier, Amsterdam, The Netherlands, 2006.
- 16 P. I. Ravikovitch and A. V. Neimark, *Langmuir*, 2006, **22**, 10864–10868.
- 17 J. Weber, M. Antonietti and A. Thomas, *Macromolecules*, 2008, **41**, 2880–2885.
- 18 F.-X. Coudert, A. Boutin, M. Jeffroy, C. Mellot-Draznieks and A. H. Fuchs, *ChemPhysChem*, 2011, **12**, 247–258.
- 19 Y. Cheng, H. Kajiro, H. Noguchi, A. Kondo, T. Ohba, Y. Hattori, K. Kaneko and H. Kanoh, *Langmuir*, 2011, **27**, 6905–6909.
- 20 C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes and G. Férey, *Adv. Mater.*, 2007, **19**, 2246.
- 21 L. Chen, J. P. S. Mowat, D. Fairen-Jimenez, C. A. Morrison, S. P. Thompson, P. A. Wright and T. Düren, *J. Am. Chem. Soc.*, 2013, **135**, 15763–15773.
- 22 V. Haigis, Y. Belkhdja, F.-X. Coudert, R. Vuilleumier and A. Boutin, *J. Chem. Phys.*, 2014, **141**, 064703.
- 23 P. G. Yot, Q. Ma, J. Haines, Q. Yang, A. Ghoufi, T. Devic, C. Serre, V. Férey, G. Dmitriev, C. Zhong and G. Maurin, *Chem. Sci.*, 2012, **3**, 1100–1104.
- 24 J. E. Santander, M. Tsapatsis and S. M. Auerbach, *Langmuir*, 2013, **29**, 4866–4876.
- 25 F.-X. Coudert and A. H. Fuchs, *Coord. Chem. Rev.*, 2015, DOI: 10.1016/j.ccr.2015.08.001, in press.
- 26 A. V. Neimark, F.-X. Coudert, A. Boutin and A. H. Fuchs, *J. Phys. Chem. Lett.*, 2010, **1**, 445–449.
- 27 Q.-L. Zhu and Q. Xu, *Chem. Soc. Rev.*, 2014, **43**, 5468–5512.
- 28 T.-H. Bae, J. S. Lee, W. Qiu, W. J. Koros, C. W. Jones and S. Nair, *Angew. Chem., Int. Ed.*, 2010, **49**, 9863–9866.
- 29 J. Caro, *Curr. Opin. Chem. Eng.*, 2011, **1**, 77–83.
- 30 B. Zornoza, C. Tellez, J. Coronasa, J. Gascon and F. Kapteijn, *Microporous Mesoporous Mater.*, 2013, **166**, 67–78.
- 31 A. Bétard and R. A. Fischer, *Chem. Rev.*, 2012, **112**, 1055–1083.
- 32 D. Bradshaw, A. Garai and J. Huo, *Chem. Soc. Rev.*, 2012, **41**, 2344–2381.
- 33 Z. Li and H. C. Zeng, *J. Am. Chem. Soc.*, 2014, **136**, 5631–5639.
- 34 J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi and J. R. Long, *Nature*, 2015, **527**, 357–361.
- 35 L. D. Landau and E. M. Lifshitz, *Mechanics*, Butterworth-Heinemann, 3rd edn, 1976, vol. 1.