Challenges and Opportunities of Molecular Simulations for Negative Gas Adsorption

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CONSPECTUS: Negative gas adsorption (NGA) is a particularly eye-catching phenomenon, involving the spontaneous desorption of gas upon pressure increase during adsorption in a flexible nanoporous material. The material undergoes a structural transition from an "open-pore" phase to a contracted "closed-pore" phase upon gas adsorption, leading to macroscopic gas desorption visible to the naked eye. It was initially evidenced experimentally in 2016 for the adsorption of methane and *n*-butane in the DUT-49 metal–organic framework (DUT = Dresden University of Technology) and later demonstrated to be a general phenomenon, occurring for different gases and in a variety of materials with the same topology. NGA materials belong to the

category of metamaterials, displaying behavior that is not found (or rarely observed) in "natural" or simple materials. The negative adsorption transition takes place outside of thermodynamic equilibrium, and its characterization requires the use of many complementary experimental techniques (adsorption measurements, in situ X-ray diffraction, EXAFS, NMR, etc.), as well as molecular simulation techniques. In order to obtain a full and consistent picture of the NGA phenomenon, it is indeed necessary to combine computational modeling with a variety of methods, at different scales, in order to understand the microscopic behavior of the host framework and guest molecules to the macroscopic experimental results. At the smallest scale, density functional theory calculations have been used to understand the energetics and structure of the NGA materials, as well as the micromechanical properties of their organic linkers: the buckling of these linkers explains the large metastability of the open-pore phase and gives rise to the NGA transition. At a larger scale, classical grand canonical Monte Carlo simulations in the "rigid host" structures can predict the adsorption capacity of different phases, elucidating the driving force behind the structural transition. To explicitly couple the flexibility of the framework and the adsorption of guest molecules, molecular dynamics simulations (relying on a classical force field for the flexible metal–organic framework) can be coupled with free energy methods to investigate the thermodynamics of NGA, obtaining free energy profiles that determine the relative stability of different phases with varying amounts of adsorbed gas. Finally, mesoscopic-scale modeling methods are required in order to understand the phenomenon at a scale larger than one unit cell and explain experimental findings about the influence of crystal size effects on the NGA transition. This Account summarizes the computational approaches that have been used so far to better understand negative gas adsorption and highlights open questions and perspectives in this field of research.
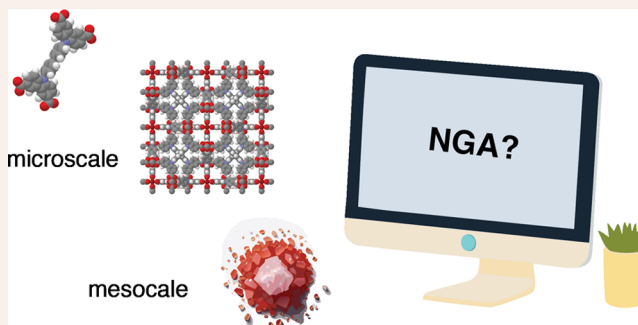
1. INTRODUCTION

The interaction of fluid molecules with nanoporous materials through adsorption, beyond applications in industrial processes such as gas storage, fluid separation, and heterogeneous catalysis, gives rise to a wide diversity of phenomena. While the fundamental interactions that give rise to physisorption are well-known and simple to understand, its represents a fascinating intersection of the fields of physical chemistry and materials science. The playing field has expanded over the past decade due to the rapid increase in the number of reported nanoporous materials with high structural flexibility,[1] including materials of families such as metal–organic frameworks (MOFs), covalent–organic frameworks (COFs), supramolecular organic frameworks (SOFs), etc. In particular, researchers are

reporting more and more occurrences of "soft porous crystals" (to follow the terminology of Horike et al.[2]): such materials can exhibit large-scale transformation of their structure upon stimulation by physical or chemical means, including adsorption of guest molecules.
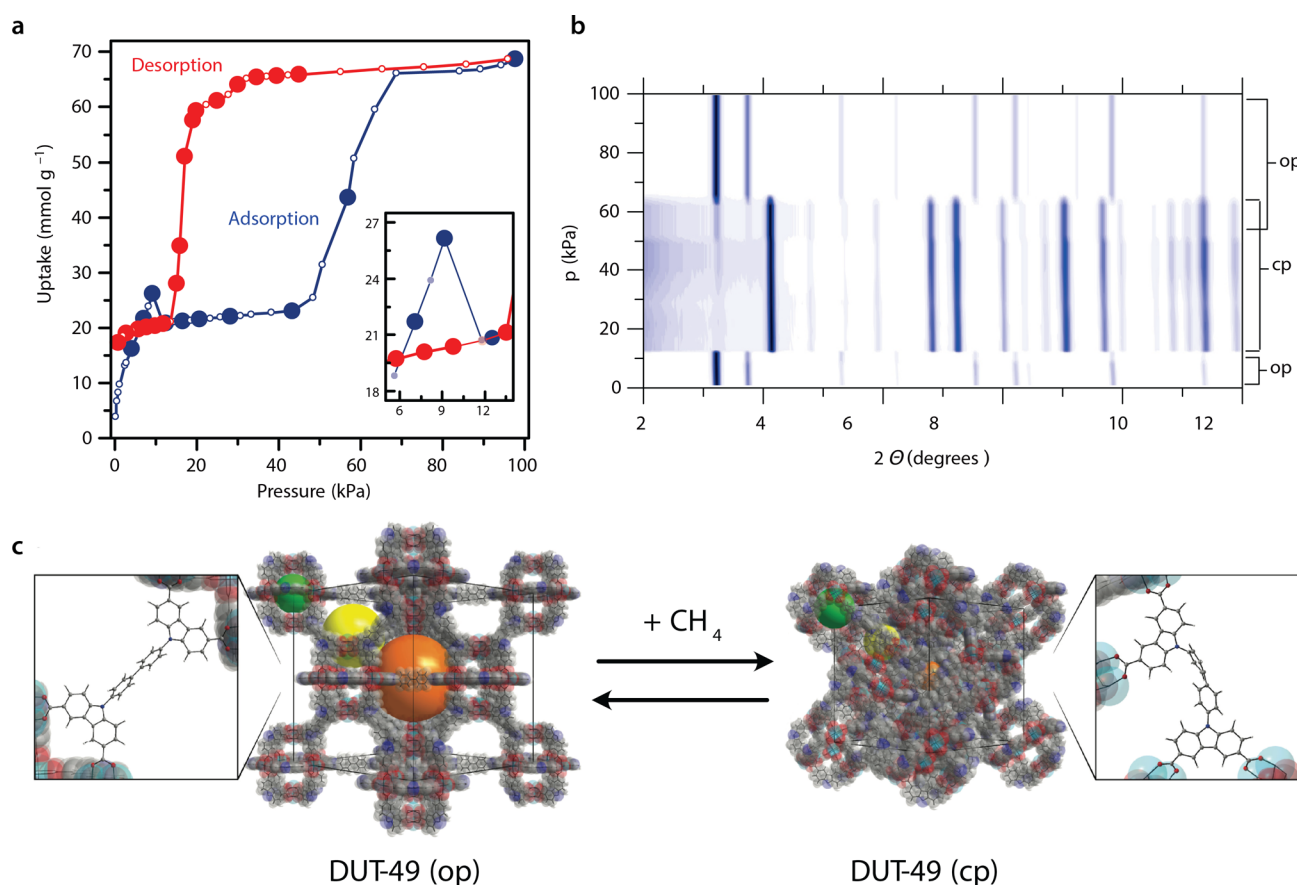
Figure 1. Schematic description of negative gas adsorption (NGA) in DUT-49. Adsorption and desorption isotherms for methane at 111 K (a). In situ powder X-ray diffraction patterns upon adsorption, with peaks characteristic of the op and cp phases labeled (b). View of the crystal structure of the DUT-49 op and cp phases and the conformation of the organic linker for each structure (c). Adapted from ref 7.

Among the wide range of flexible behaviors that can be triggered by adsorption are well-established phenomena, such as swelling,[3] gate opening,[4] breathing,[5] and chiral induction.[6] However, one particularly surprising phenomenon that was discovered, upon adsorption in several nanoporous materials, is negative gas adsorption (NGA). Initially evidenced experimentally for adsorption of methane and *n*-butane in the MOF DUT-49 (DUT = Dresden University of Technology),[7] NGA consists of a spontaneous desorption of gas upon pressure increase: this shows up as a downward step in the adsorption isotherm, $(\partial n/\partial P)_T < 0$, as seen in Figure 1a. Macroscopically, NGA is associated with a sudden release of adsorbed gas from the material, visible to the naked eye in the adsorption apparatus. Microscopically, it is linked to a structural transition from the original, "open-pore" (op) phase of DUT-49, into a contracted phase with higher density and decreased pore volume, the "closed-pore" (cp) phase (Figure 1b)—as evidenced by X-ray diffraction.

In addition to potential applications as mechanical actuators or threshold-sensitive micropneumatic devices,[8] the discovery of NGA posed a number of fundamental questions. In particular, negative adsorption $(\partial n/\partial P)_T < 0$ is thermodynamically impossible at equilibrium, adding NGA materials as a new category of metamaterials,[9] i.e., materials designed to have physical properties not available (or not easily attainable) in nature. As a result, the discovery of NGA produced many open questions to understand the microscopic features that give rise to this macroscopic phenomenon, to rationalize the criteria for

its occurrence, and to identify entirely new materials that could exhibit this unusual behavior.

Occurring out of equilibrium, NGA is a complex phenomenon involving two phases and a structural transition; thus, investigations have required the use of many complementary experimental techniques. The characterization methods provide both macroscopic information (through adsorption isotherms at various temperatures and with various guests, calorimetry, mechanical tests, etc.) and microscopic insight through in situ techniques (such as powder X-ray diffraction, EXAFS, EPR, DRIFT, NMR of the guest molecules, and solid-state ^{13}C NMR). Similarly, in order to obtain a full and consistent picture of the NGA phenomenon from computational chemistry, it is necessary to use a combination of different methods, at different scales. In this Account, we provide a short review of the computational approaches that have been used to describe negative gas adsorption, describe the fundamental questions that remain open, and highlight some challenges for molecular simulations in this field of study.

2. RESULTS AND DISCUSSION

Multiscale computational strategies are becoming increasingly common for investigating the chemistry of materials, but this approach is absolutely crucial to the description of NGA materials and the negative adsorption phenomenon. We highlight here how theoretical chemistry methods at different scales have been combined in order to form a complete and coherent picture of NGA, going from the initial understanding

of the phenomenon, to more predictive methods trying to identify novel materials in the same family, and finally to future perspectives in the field.

## 2.1. First Rationalization of the NGA Phenomenon

In the initial report of NGA upon methane and *n*-butane adsorption in the DUT-49 material, several computational and theoretical tools were combined with the experimental evidence available.[7] First, the structure and energetics of the bistable material were quantified using density functional theory (DFT) calculations, without taking into account the guest molecules. These calculations confirmed that both structures, DUT-49(op) and DUT-49(cp), corresponded to local minima in the potential energy surface of the material, even in the absence of guest, confirming the intrinsic bistability of the framework. They also showed that the "native" open-pore form is energetically more stable, by 2184 kJ mol^{-1} per unit cell, or 91 kJ mol^{-1} per linker— putting a number on the energetic price for contracting the material, mostly due to the deformation of the organic linker (Figure 1c).

Second, the adsorption capacity of the two phases was predicted through classical grand canonical Monte Carlo (GCMC) simulations. Such simulations employ a static representation of the framework for each phase ("rigid host" approximation) and a classical force field to approximate the host−guest and guest−guest interactions. These classical simulations highlight why the closed-pore phase is stabilized by adsorption: with its narrower pores, it has greater affinity for small-molecule adsorbates. In line with the experimental data available from calorimetry, GCMC simulations give a value of the difference in adsorption enthalpy in both phases. It was estimated to 145 kJ mol^{-1} per linker for methane at 111 K, matching in order of magnitude the energy cost for the op → cp transition. This explains how adsorption can act as a driving force by stabilizing the contracted phase.

However, while several "breathing" bistable materials have been reported in the past,[5] their structural transitions do not imply negative adsorption. We therefore proposed a thermodynamic model for negative gas adsorption, in order to rationalize the experimental observations, based on the thermodynamic potential of each phase in the osmotic ensemble, which accounts for both flexibility and adsorption.[11] This osmotic model for NGA (Figure 2) confirmed that it is impossible to have $(\partial n/\partial P)_T < 0$ at equilibrium and that the NGA phenomenon is linked to the existence of the guest-loaded open phase as a long-lived metastable state, with wide hysteresis upon adsorption due to the existence of a high free energy barrier between the op and cp states.

2.2. How Do Linkers Buckle? A Microscopic View

The computational studies in the original report for NGA in DUT-49 laid the basis for a multiscale simulation strategy but also had some important limitations, as later work showed. At the quantum chemical scale, very accurate modeling of the evacuated host material through DFT calculations is computationally expensive, and therefore the amount of information that can be calculated (even in the absence of guest molecules) is limited. All materials exhibiting NGA thus far are isoreticular and extremely structurally complex: the "parent" DUT-49 compound, with 1728 atoms per cubic unit cell of length 46.6 Å, is large enough to make systematic calculations, beyond relaxed structure and energetic, unfeasible. For example, harmonic vibration modes, second-order elastic tensor, and other linear response properties frequently used in the characterization of
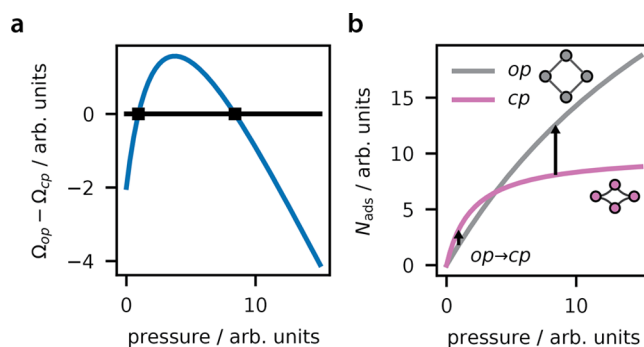
Figure 2. Example of osmotic potential as applied to transitions between two phases (op and cp) of an arbitrary porous material. The osmotic potential difference between the two phases indicates the thermodynamic transitions, corresponding to $\Delta\Omega = 0$, in panel (a). At thermodynamic equilibrium, the corresponding loading values necessarily correspond to positive adsorption steps (called "breathing"), as seen in panel (b). Reproduced from ref 10 under the CC-BY-NC-ND 4.0 license.

soft porous crystals are not readily accessible.[12] This is a strong limitation for the application of DFT-based methodology that is generally considered the most comprehensive available for the computational characterization of crystalline materials.

DFT calculations can be applied, however, to smaller subunits or the building blocks of the NGA materials, such as the organic linkers, to characterize their bending modulus. In Evans et al.,[13] we proposed to study the deformation of the DUT-49 organic linker, BBCDC = 9,9′-([1,1′-biphenyl]-4,4′-diyl)bis(9*H*-carbazole-3,6-dicarboxylate), which is involved in the NGA transition through a deformation localized on the biphenyl unit (Figure 3A). This was performed through constrained molecular DFT calculations on an isolated linker, with a series of fixed decreasing N−N distances. The stress−strain profile obtained from these calculations (Figure 3B) shows a surprising result: the mechanics of buckling in this nanometer-sized linker is similar to that of macroscopic materials, like steel bars or concrete pillars. In a first regime, for small deformations, the linker is rather stiff and compresses linearly, with the stress increasing steadily. Beyond a critical value of stress, however, the linker shows a sudden deviation from linearity (Figure 3C) and a nonlinear mechanical response, known as "buckling"—presenting a significantly lower stiffness past this transition.

These results provided better insight into the microscopic mechanism of the transition and explained at the level of the linker the origin of the large metastability for the open-pore phase before the transition is triggered—a key feature of DUT-49, giving rise to negative gas adsorption, instead of the more common "breathing" phenomenon. Beyond this fundamental understanding, it also opened the door to a qualitative characterization of the potential for buckling in any molecule, by measuring the value of critical stress. In later work, this approach was applied to several linkers in materials of the same family, explaining why DUT-48 does not exhibit NGA, with its shorter linker requiring three times more stress to produce the buckling.[14]

Beyond rationalization at the microscopic level of the macroscopic behavior observed in experimentally known materials, DFT calculations of isolated linkers have further been used in a screening approach to identify design criteria for the discovery of novel NGA materials and to engineer materials with targeted micromechanical properties—in a screening-type

a

b

c
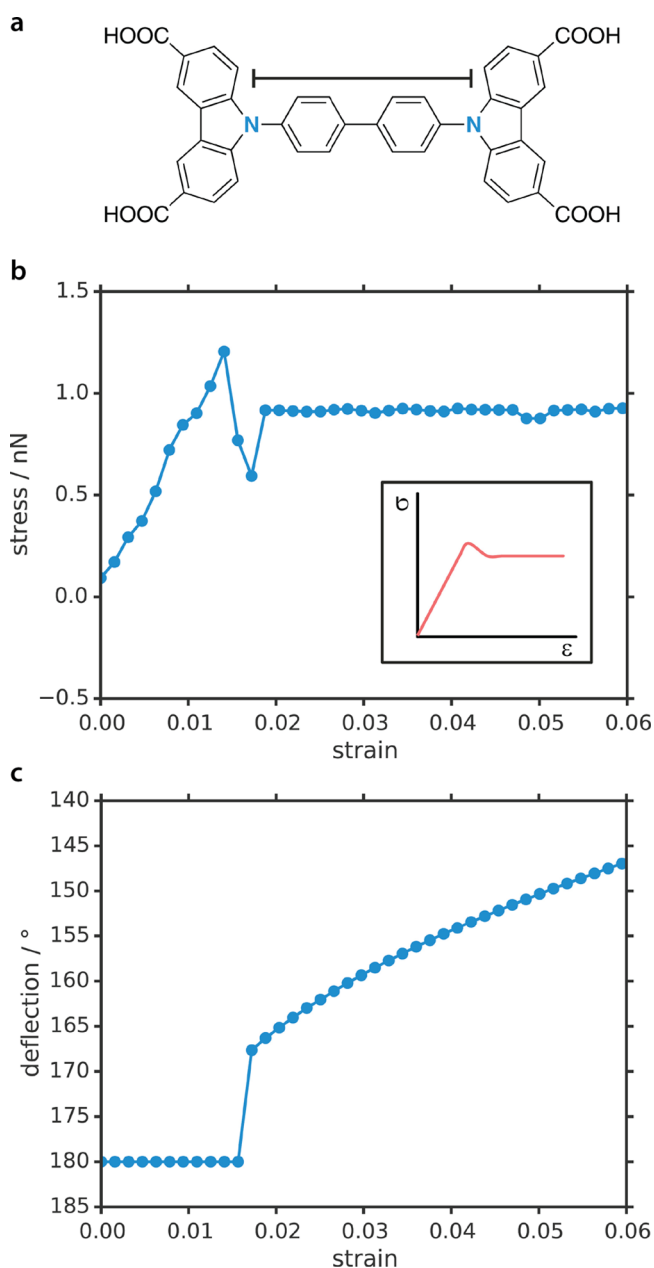
Figure 3. Organic ligand of DUT-49, with the constrained N−N distance highlighted (a). Stress−strain curve for the ligand, measured through constrained DFT calculations; inset: a typical stress−strain curve for a macroscopic material exhibiting buckling (b). Out-of-plane deflection of the ligand as a function of strain, demonstrating the symmetry-breaking buckling transition (c). Reproduced with permission from ref 13. Copyright 2016 Elsevier Inc.

workflow.[15,16] In 2019, a computational mechanical study of different expanded (longer) linkers showed that the occurrence of buckling was generic.[15] This lead to the discovery of DUT-50 as a new material with NGA transitions, which was confirmed by experimental investigations, including in situ X-ray and neutron diffraction, NMR spectroscopy, and calorimetry.

Following from that study, we expanded the computational screening of possible linkers,[16] reaching a total of 11 possible frameworks (Figure 4) in order to establish structure/property relationships. We could show, in particular, that widening of the linker backbone increases stiffness, while longer building blocks have a decreased critical yield stress for buckling. We also

demonstrated that functionalization of the backbone by incorporation of sp^3-hybridized carbon atoms leads to softening of the molecular building blocks, while they could be made stiffer through the addition of sp^2 and sp carbons. Relationships between the characteristics of the linkers and their mechanical properties are displayed in Figure 4 and show how it is possible to engineer the micromechanical behavior of soft porous crystals.

Finally, we note that another possible use of DFT calculations of linkers in flexible materials is their use for the training and validation of classical force fields with high accuracy.[17] This approach has been validated for several other flexible MOF materials,[18−20] showing that it can lead to a new generation of force fields that capture the fine balance of interactions involved in supramolecular flexibility and thus can enable more realistic and quantitative classical molecular simulations. Because of its high computational cost and relatively tedious optimization procedure, it has been applied to a limited number of systems. It has, however, proven very useful to expand the accuracy of molecular simulations for some NGA materials so far[21] and remains an important avenue to explore in future work.

2.3. Thermodynamics of NGA Using Free Energy Methods

As mentioned above, known materials exhibiting negative adsorption so far all have very large unit cells (both in cell size and number of atoms), meaning that simulations of the full material at the quantum level are computationally impractical. However, molecular simulation of flexible materials at the classical scale has seen large methodological progress in the past decade. While the first studies on flexible materials focused on obtaining separate adsorption isotherms in various (hypothetical) "rigid phases" of the host material, novel methods have been developed that can account for both the adsorption and flexibility, bypassing the exact but abstract direct osmotic ensemble simulations.[22] In particular, multiple groups have demonstrated the power of free energy methods for the study of adsorption-induced structural transitions in soft porous crystals.[23,24]

Following the initial report of NGA, the phase stability of DUT-49 in response to methane adsorption was investigated using classical molecular simulations, in order to allow access to the complex dynamics of this material—given that this was not possible at the DFT level. To obtain a good compromise between quantum chemical accuracy and classical force field computational cost, that work leveraged the highly accurate MOF-FF force field,[17] well validated on the copper paddle-wheel unit and its connection to the organic linkers, described with the MM3 model. Constant-pressure molecular dynamics simulations of the DUT-49 framework in the absence of guest molecules confirmed its bistability and demonstrated that the reversible op → cp transition can be triggered through a modest mechanical pressure of 60 MPa.[13]

Beyond direct MD simulations, we then employed free energy methods, based on thermodynamic integration of the internal pressure of the system as a function of volume $P(V)$, to obtain a free energy profile as a function of unit cell volume, $F(V)$, by a series of constant-volume MD simulations. This approach provides key insight into the coupling between adsorption thermodynamics and materials flexibility and has been used in other studies of soft porous crystals.[25] By calculating $F(V)$ profiles for different values of loading (i.e., different number of adsorbed molecules present), we could demonstrate that the relative free energy of the DUT-49 phases drastically changes
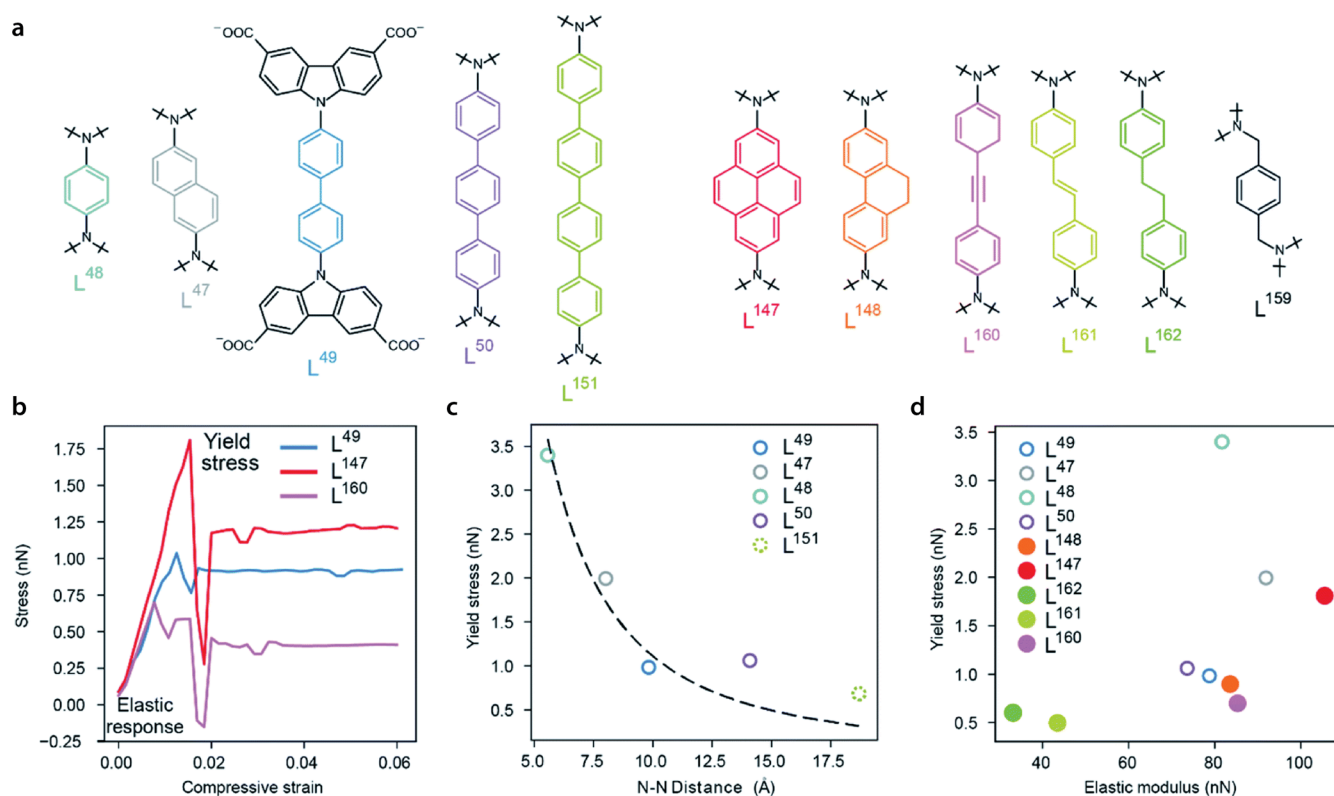
Figure 4. Eleven organic linkers studied through constrained DFT calculations. (a) Stress−strain curves for three specific linkers (b) and correlation between the micromechanical properties of the linkers and their geometrical characteristics (c and d). Reproduced from ref 16 under the Creative Commons Attribution-NonCommercial 3.0 Unported License. Copyright 2020 The Royal Society of Chemistry.

upon guest loading.[13] This provided this first atomistic insight into the thermodynamics responsible for the phase changes that produce NGA, and simulations of free energy allow quantitative determination of the thermodynamic driving force for the transition. While DUT-49 is intrisically bistable, with two local free energy minima for the op and cp phases, we see in Figure 5b that the cp phase is stabilized by adsorption, although a high free energy barrier remains—indicative of the metastability of the op state. Finally, as uptake continues to increase, the cp state is no longer compatible with the number of guest molecules and becomes heavily destabilized, leading to a second structural transition back to the op phase. While this work was performed at fixed temperature, the influence of temperature on the thermodynamics of NGA was studied in later work.[26]

To correctly capture the important interplay between material phase space and gas adsorption, simulations within the osmotic ensemble are necessary. In order to address this, Goeminne et al. combined GCMC moves with molecular dynamics trajectories to construct detailed osmotic potential energy surfaces describing the complete thermodynamic landscape of adsorption on DUT-49.[10] From the full knowledge of the osmotic thermodynamic potential $\Omega(V, N_{ads})$ as a function of the unit cell volume V and number of adsorbed molecules N_{ads}, we can derive the entire behavior of the material upon adsorption (Figure 5c). The metastability of DUT-49 phases can be quantified, along both adsorption and desorption isotherms, using this approach to predict and understand the phase changes observed, in this case NGA. We note that beyond this work, hybrid approaches combining GCMC and molecular dynamics are a key tool to reveal osmotic energy barriers present under gas

adsorption that dictate the features of NGA, as further discussed in the work of Zhao et al.[27]

2.4. A View toward Modeling at the Mesoscopic Scale

If we want to continue increasing the time and length scales addressed in simulations of NGA, we would have to consider modeling at the mesoscopic scale: so far, there is relatively little known about NGA materials at this level. We do expect interesting findings, and we know that it is a relevant scale to consider, from experimental characterization studies both with DUT-49 and with other soft porous crystals. It was demonstrated for several other flexible families of MOFs that there is nontrivial behavior beyond the single unit cell crystal: in particular, the crystal size, nature of the external surface, and textural properties interact with flexibility in various ways.[28,29] This can have a drastic impact on macroscopic properties, e.g., liquid-phase separation of xylene isomers.[30] More specifically, experimental results have shown that crystal size and defects have a drastic influence on the extent and characteristics of NGA properties in DUT-49.[31] Krause et al. investigated the solid−fluid interactions in DUT-49 crystals of different size, through in situ ^{129}Xe NMR spectroscopy at 200 K. They showed that the structural transition is hindered for smaller crystal sizes (lower than 2 μm), due to weaker solid−fluid interactions and therefore lower thermodynamic driving force. They also investigated the impact of the presence of defects in the material but ruled this out as a major contributing factor. Such factors could also explain the occurrence of op/cp phase coexistence near the transition (as can be seen in the in situ powder X-ray diffraction in Figure 1b).

In this area, theoretical modeling was limited, until recently, to analytical models, or simple numerical simulations relying on
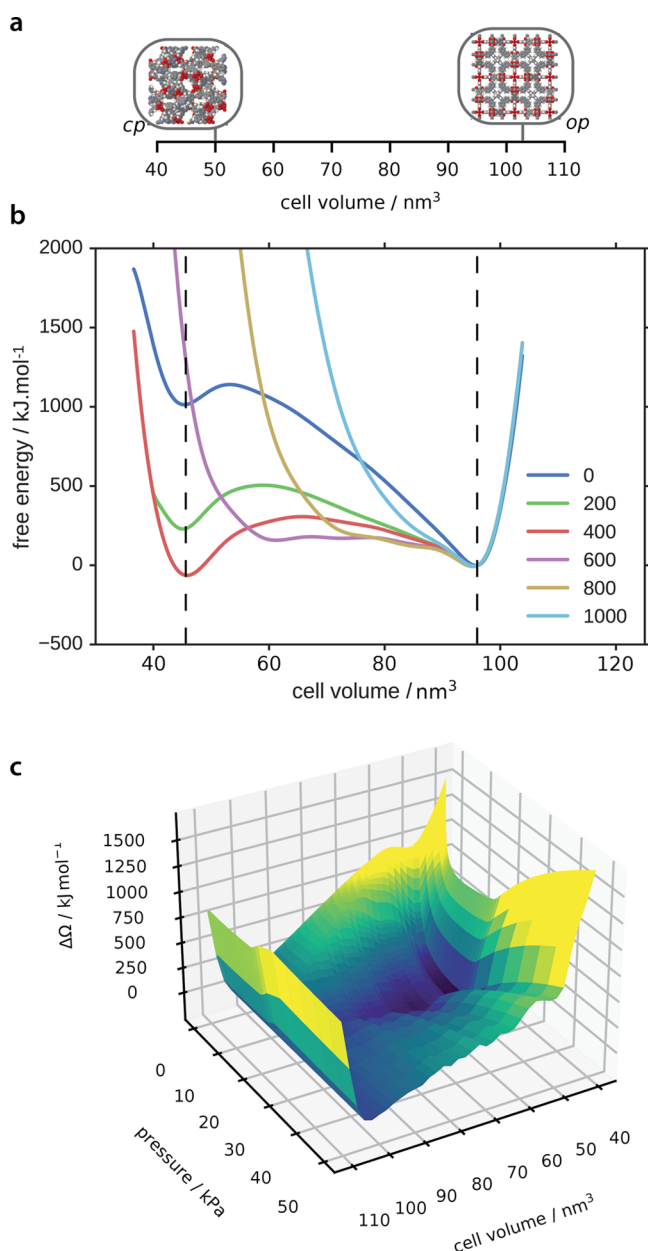
Figure 5. Thermodynamic characterization of adsorption of methane in DUT-49, as a function of pore volume. (a) Volume scale and representation of the cp and op phases. (b) Free energy profiles $F(V)$ for increasing values of methane loading (indicated at number of CH_4 per unit cell). (c) 2D surface of the osmotic thermodynamic potential $\Omega(V, P)$ as a function of volume and methane pressure. Reproduced with permission from refs 13 and 10 under the CC-BY-NC-ND 4.0 license. Copyright 2016 Elsevier Inc. and copyright 2021 American Chemical Society.

lattice-based[32] or finite elements approaches.[33] However, recent modeling work using advanced computing architectures has shown that crystal size effects of soft porous crystals can be modeled and understood, in particular when it comes to the phase separation or phase coexistence in bistable materials.[34] For example, computational efficiency of machine-learned potentials can allow for simulations to consider size effects.[35]

Importantly, Schmid and co-workers were able to demonstrate that direct molecular simulation of nanoscale discrete crystallites of flexible MOFs is achievable for handful of materials.[36,37] They were able to achieve these simulations by

removing periodic boundary conditions and free energy sampling employing distance restraints.[37] Moreover, to recreate realistic conditions, without using distance constraints, Schmid et al. have also demonstrated an approach to capture the pressure medium.[38] These current simulations do appear to provide a path forward for the simulation of finite-size effects, although the chemical accuracy of the description of the external crystal surface remains an important open question.

3. PERSPECTIVES

While the thermodynamics of negative gas adsorption have been thoroughly established, as described in this Account, the extensive studies and literature on soft porous crystals in the last two decades have shown that they demonstrate eye-catching behavior when adsorption is coupled to other physical or chemical stimuli.[2,39] In particular, it is captivating to consider coupling NGA with mechanical pressure,[40] anisotropic stress, gas mixture coadsorption or even coupling NGA with photoresponsive organic linkers, to create a light-switchable NGA material.[41] Screening potential materials for these conditions and establishing the feasibility of specific couplings between stimuli is an ambitious task (and a difficult test) for the development of future multiscale modeling strategies.

We have demonstrated here the importance in bridging methods from different scales for understanding the origin of NGA in DUT-49. Only by combining methods and taking information at one level to a higher scale could this phenomenon be understood. However, the transfer of quantitative information between modeling scales is, at the present time, still relatively limited. Methods at the different scales (DFT, classical MD, Monte Carlo, mesoscopic modeling) combine to form a coherent and complete picture of flexible materials in general and NGA in particular, but they do not systematically provide direct quantitative input from one scale to another. This is an open perspective, which would lead to tighter integration of the methods. It could be achieved, for example, by training classical force fields based on DFT data[18] or by using physical parameters from classical simulations (elastic constants, adsorption equilibrium constants, etc.) to mesoscale models as Hamiltonian parameters.

The development of classical potentials, attempting to capture quantum accuracy by approximate functions, is both time-consuming and often lacking in accuracy. The accelerating development of machine-learned potentials (MLPs) has revolutionized the transfer of DFT accuracy to the scale of classical MD.[35,42] While we are only at the beginning of their widespread use, there are now several widely available implementations of neural-network-based MLPs,[43] and such functionality is interfaced with standard molecular simulations codes[44] and parallelized across multiple GPUs.[45] Very recently this approach has shown the ability to be applied to adsorption[46] which paves the way for a workflow to rapidly assess the thermodynamics of NGA in a variety of materials at DFT accuracy.

Another barrier to a wider screening of NGA for materials and fluids is the development of novel simulation methodologies. One such example is the need for hybrid GCMC:MD simulations: these combined Monte Carlo and molecular dynamics protocols, which properly account for the combination of adsorption and structural flexibility, require a wide and extensive sampling approach.[24] While several models have been employed to provide near-quantitative insight into NGA, their general application remains limited. New efficient and robust

methodologies are needed to describe the features of NGA (massive changes in pore volume and number of guests) and apply this to large databases of potential candidates. In addition, the widespread application of hybrid GCMC:MD simulations requires accurate classical potentials that may be realized by MLPs. Going beyond the specific case of NGA, further development on the methodological side is also needed to describe the adsorption of liquids and charged species into flexible nanoporous materials. The intrusion of complex liquids (water, hydrocarbons, etc.) or electrolytes at high pressure into soft porous crystals remains a widely open question from a computational perspective, one that cannot be investigated by GCMC alone and where novel methodologies are being developed, such as alchemical transformations[47]—an area where the biological chemistry community has developed powerful and efficient simulation workflows, such as osmostats[48] and alchemical free energy calculations,[49] to realistically describe electrolytes and salt conditions.

Overall, we have summarized the current state of computational modeling strategies at various scales for the description of negative gas adsorption, as well as the investigation of materials that exhibit NGA. We have seen that combining molecular simulations at the DFT level, the classical level, and the mesoscopic scale allows to obtain a complete picture of the NGA behavior, but there remains a number of open questions that will require future work using novel methodologies or tighter integration of existing methodologies at different scales.

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Notes

The authors declare no competing financial interest.

Biographies

Jack D. Evans completed his Ph.D. at the University of Adelaide, Australia, in 2016 and relocated to Europe to join research groups at Chimie ParisTech, France, and then TU Dresden, Germany. There he developed atomistic simulations to investigate exciting materials with counterintuitive physical or chemical properties. The Ramsay Fellowship returned Jack to the University of Adelaide to establish an independent research group that uses these innovative simulation methods to design advanced heterogeneous catalysts. Recently, Jack received the prestigious Australian Research Council Discovery Early Career Award.

François-Xavier Coudert is a senior researcher at the French National Centre for Scientific Research (CNRS) and a professor at PSL University/École normale supérieure. His group applies computational chemistry methods at various scales to investigate the physical and chemical properties of nanoporous materials, their responses to external stimuli, and the behavior of fluids at fluid/solid interfaces. He obtained his Ph.D. from the Université Paris-Sud (France) in 2007 for work on the properties of water and solvated electrons confined in zeolite nanopores and worked as a postdoctoral researcher at University College London (U.K.) on the growth of metal–organic frameworks on surfaces.

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