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Coupling between adsorption and mechanics (and vice versa)

Matthieu VANDAMME

Université Paris-Est, Laboratoire Navier (UMR 8205), CNRS, École des Ponts ParisTech, IFSTTAR,
Marne-la-Vallée F-77455, France

Abstract

Adsorption can deform porous solids, and mechanical stresses or strains can impact the adsorption process: this mini-review is dedicated to this coupling. After introducing some frameworks used to predict adsorption-induced strains, the question of how important it is to take into account the impact of mechanics on the adsorption process is addressed. Finally, some specific complexities (e.g., of the microstructure, or of the mechanical behavior of the adsorbent) that the community aims at integrating into the prediction of adsorption-induced strains are addressed.

1. Introduction

The fact that adsorption can deform solids has been known for centuries, but has been the subject of renewed interest in the last decade or so, since the discovery that some metal-organic frameworks (MOFs) can exhibit large deformations upon adsorption. As I will try to address in this mini-review, not only does adsorption impact the mechanical response of the adsorbent, also does the mechanical response of the adsorbent impact the adsorption process: the coupling between adsorption and mechanics is a two-way coupling.

Depending on the size of their pores, porous bodies are referred to as microporous (i.e., with a pore size below 2nm), mesoporous (i.e., with a pore size between 2nm and 50nm), or macroporous (i.e., with a pore size greater than 50nm). The physics through which in-pore fluid can deform a porous body depends on this pore size: capillary effects (i.e., effects due to the presence of menisci between various phases of the in-pore fluid) and Gibbs-Bangham-like effects (i.e., deformations induced by adsorption on solid surfaces) in mesoporous materials, or pore filling (rather than surface covering) in microporous solids. Note that, even in macroporous solids (in which fluid is not adsorbed but behaves like a bulk phase), in-pore fluids can deform the body, through their pressure variations (see, e.g., [1]).

One can already find in the recent literature an extensive review of adsorption-induced deformations in porous solids [2], which I will partly complement with some most recent works. I also want to mention a recent review on the computational chemistry of soft porous crystals [3].

In this mini-review, I will first introduce some frameworks used to estimate adsorption-induced strains, before tackling the notion of the two-way coupling between adsorption and mechanics, and moving to specific complexities incorporated in the modeling of adsorption-induced deformations.

2. Some frameworks to predict adsorption-induced strains

The discussion in this section is quite generic and disregards specific complexities of the material, which will be addressed later in the manuscript.

A first pore-scale approach to predict adsorption-induced strains is a thermodynamic one, which consists in identifying the energy to minimize in the so-called osmotic ensemble, which is the right thermodynamic ensemble to address adsorption-induced deformations [4]. Through this approach, Ravikovitch and Neimark [5] first showed that adsorption induces a mechanical stress (sometimes

42 called ‘adsorption stress’) whose magnitude is equal to the solvation pressure and can be obtained
43 from the grand potential of the adsorbed fluid. For mesoporous materials, an alternative pore-scale
44 approach, more mechanistic, consists in considering the concept of surface stress, which is being
45 successfully used in electro-chemistry in particular (see, e.g., [6]).

46 To estimate the adsorption-induced deformations of an anisotropic mesoporous silica body
47 made of parallel cylindrical channels, both the thermodynamic approach [7] and the surface stress
48 approach [8] were used recently. The two approaches are compared in [8]: above capillary
49 condensation, they yield identical results, while, below capillary condensation (i.e., in the film regime),
50 they provide qualitatively similar but quantitatively different responses. To me, this difference might
51 at least partly be due to the fact that the input parameters for the two works are different: for instance,
52 the relation between thickness of adsorbed film and relative pressure is given by the BET model in [8],
53 while it is given by the DBdB theory in [7].

54 There exist other approaches, at a macroscopic scale, aiming at predicting adsorption-induced
55 strains through adaptation of the poromechanical framework. Here again, one can divide those
56 approaches into more thermodynamic ones (e.g., [9–11]) or more mechanistic ones (e.g., [12], in the
57 sense that it introduces an apparent porosity). For this type of approaches again, as explained in [8],
58 with different approaches, similar predictions can be obtained.

59

60 a. Notion of pore-load modulus

61 With most pore-scale approaches, the effect of adsorption is translated into a stress, which then
62 needs to be translated into a strain, for which purpose an elastic modulus is needed. To this effect,
63 there exists the notion of pore-load modulus M , which relates a strain ε to a pressure P of fluid in the
64 pore through: $M = dP/d\varepsilon$. A pore-load modulus is only valid for a specific direction and a specific
65 loading [8]. For transverse isotropic membranes of porous silicon exhibiting a random honeycomb
66 structure, by using n-heptane above capillary condensation, Rolley et al. [13] measured pore-load
67 moduli and showed that their magnitudes are consistent with elastic properties measured by direct
68 stretching of the membrane: pore-load moduli can be used to measure elastic properties of the porous
69 material.

70 With finite-element modeling (FEM), Rolley et al. [13] showed that, to retrieve the correct elastic
71 properties of those same membranes, the elastic modulus of the solid walls must be about 2 to 6 times
72 smaller than the bulk modulus of bulk silicon, depending on the direction considered: they attributed
73 this discrepancy to finite-size effects and defects of the solid walls. In contrast, based on adsorption
74 measurements with argon and n-hexane on Vycor (i.e., an amorphous mesoporous silica glass with
75 worm-like channels), Gor et Gurevich [14] succeeded in calculating the response of their porous
76 material by considering that the bulk modulus of the solid skeleton is close to the bulk modulus of a
77 solid Vycor matrix, as back-calculated from the dry moduli of Vycor using an elastic effective medium
78 theory. How to translate elastic properties of the solid skeleton into pore-load modulus or elastic
79 properties of the porous material in presence of fluid, although well established for macroporous
80 materials, appears, for nanoporous materials (i.e., for materials with a pore size below 100nm [15]),
81 to be system-dependent [13].

82 Recently, Puibasset [16] found out that, in presence of fluid, the apparent pore-load modulus
83 can differ from the one expected by considering the properties of the solid wall to be those of the bulk
84 non-porous solid, even though, on the dry material, a correct value is retrieved. The difference is
85 attenuated if the fluid-wall interaction is attenuated. He attributes the discrepancy to a surface effect,
86 namely a variation of the surface stress in presence of fluid, which he correlates to surface ordering.
87 Therefore, I would not rule out that relating pore-load modulus to properties of the solid skeleton in
88 the generic case could be improved through a better understanding of the solid-fluid interactions at
89 the solid surfaces.

3. Impact of mechanics on the adsorption process

If adsorption can deform a solid, deformations can also impact the sorption process, as already observed experimentally with porous membranes [17]. Consequently, in the generic case, the adsorbed amount n of adsorbate should be considered to depend not only on the chemical potential μ of the adsorbate and the temperature T , but also on mechanical stresses or strains. Whether considering this dependence is important is the topic of the next two sections (for what concerns estimations of adsorption-induced strains or of adsorbed amounts) before moving to other topics relevant to this coupling.

a. Importance of considering how adsorption depends on strains to estimate adsorption-induced strains

When adsorption occurs on surfaces, the surface stress σ^s , which deforms the solid surface, is related to the excess adsorbed amount Γ through Shuttleworth's equation [18]:

$$\left(\frac{\partial \sigma^s}{\partial \mu}\right)_T = \left(\frac{\partial \Gamma}{\partial \varepsilon^s}\right)_T$$

where ε^s is the surface strain of the solid surface. In a generic case (i.e., valid for micropores, mesopores, or macropores), the volumetric stress σ induced by the presence of the fluid is related to the amount n of fluid in the body through [9]:

$$\left(\frac{\partial \sigma}{\partial \mu}\right)_T = \left(\frac{\partial n}{\partial \varepsilon}\right)_T$$

where ε is the volume strain of the body. Those (Lagrangian) equations clearly show that, if the fluid induces a stress and deforms the porous body, this is because the adsorbed amount depends on the volume/surface strain. Consequently, how adsorption depends on strains is of prime interest to correctly estimate adsorption-induced strains.

For what concerns adsorption on solid surfaces, the celebrated Bangham model [19], which is valid for a wide variety of cases, states that:

$$\varepsilon \propto \Delta\gamma$$

such that strains should be proportional to variations $\Delta\gamma$ of surface energy. However, theoretically, strains should be proportional to variations of surface stress. Recently, this discrepancy was explained, and is in fact rooted in how adsorption depends on strains: in the framework of the BET model, Gor and Bernstein [20] showed that, if the energy of adsorption of first layer does not depend on the stretch of the surface, then variations of surface energy and of surface stress are equal, thus making it possible to retrieve Bangham's law. Their results suggest that Bangham's law should be verified for small strains and small molecules with non-specific interactions. In contrast, if this energy of adsorption of the first layer depends on the stretch of the surface, the authors show that you can predict contractions at low gas pressures, which are indeed observed experimentally.

To capture non-trivial dependency of the adsorbed amount on strain and its consequences on strains, Kolesnikov et al. [21], who calculate adsorption and deformation of a mesoporous film with cylindrical pores from a direct minimization of the appropriate thermodynamic potential in the osmotic ensemble, consider that the interaction between solid and fluid can depend on the pore radius. Like Gor and Bernstein [20], they conclude that taking into account this dependence is necessary to capture non-monotonic strain isotherms.

b. Importance of taking into account how adsorption depends on strains to estimate adsorption

Reversely, taking into account the dependence of adsorption on strains/stresses can be important to correctly estimate adsorbed amounts, with qualitatively significant impacts: deformations are shown to be the reason for observed negative adsorptions [22,23], and in presence of fluid mixtures the deformability of the adsorbent can impact the selectivity (e.g., [24]). Quantitatively, Kolesnikov et al. [21] showed that, in a mesoporous material, taking into account the flexibility of the adsorbent is necessary to explain why, above capillary condensation, increasing the relative pressure still makes it possible to increase the adsorbed amounts: adsorbed amounts increase not only by pore filling, but also by deformation of already-filled pores. Experimentally, on microporous carbons, micropores were shown to contribute to the adsorption isotherm on the full range of vapor pressures, even when micropores are already filled [25].

In a converse manner, stresses applied to the adsorbent can also impact adsorbed amounts: experiments show that, on compacted coal powders [26], applying effective stresses up to 35MPa can expel from 5% to 50% of the CO₂ initially present in the sample. Even if most of the fluid was expelled from in-between the coal grains, subsequent analysis confirmed that the stresses indeed expelled some fluid that was adsorbed in the coal matrix [27].

Whether taking into account this effect is required to properly estimate the adsorbed amounts depends on the magnitude of the applied stresses or of the adsorption-induced strains. Just to provide an order of magnitude, typically for a microporous solid such as coal, the relative variation of adsorbed amount is estimated to be equal to about 10 times the strain [28].

c. Impact of adsorption on mechanical properties

Adsorption can modify the apparent elastic properties of the adsorbent and lead to either an apparent stiffening or an apparent softening of the adsorbent [29,30]. The apparent stiffness of the adsorbent is a function of the stiffness of the dry adsorbent and of how the adsorption isotherm depends on both the strain of the adsorbent and the chemical potential of the adsorbate [9]. Confinement also modifies the mechanical properties of the fluid, as observed experimentally [31] or theoretically [32].

A way through which adsorption can modify the mechanical properties of the adsorbent is through its impact on the microstructure: Perrier et al. [33] showed that, in microporous materials, the apparent porosity can vary significantly upon the adsorption, and hence impact the poroelastic properties of the material. For a sandstone, whose dry mechanical behavior is nonlinear, variations of the elastic moduli with relative humidity could be explained by the impact of the variation of relative humidity on solvation pressure and hence effective stress [34]. Note however that, even in absence of nonlinearity or rearrangement of the microstructure, adsorption can impact the drained moduli of the porous material [29].

d. Modeling the coupling between adsorption and mechanics

Since adsorption induces strains, and since strains impact adsorption, one should take into account this two-way coupling into the modeling. Such coupling can be particularly significant in microporous solids, in which the adsorption stress depends strongly on the pore size [35]. One way to capture this coupling, when employing a thermodynamic approach, is to minimize the appropriate thermodynamic potential ensemble with respect to both parameters characterizing the adsorption process and parameters characterizing the deformation process. Such approach was adopted for a mesoporous material made of cylindrical pores [21], for MOFs [36] or for cellular solids [37]. This last work, formulated at a mesoscopic scale, shows that the solid-fluid interaction can lead to a hysteresis

178 of the adsorption strain isotherm. For nanoporous crystalline materials with rotatable ligands shared
179 between neighboring cages, a statistical mechanical model that captures the coupling was developed
180 [38], which includes energy penalization for the rotation of a ligand and an energy of an adsorbed
181 molecule that depends on the rotation of the ligands: the model captures inflections, steps, and
182 hysteresis.

183 4. Specific complexities for prediction of adsorption-induced strains

184 In this section I address recent complexities that the community aims at integrating into models
185 to predict adsorption-induced strains.

186

187 a. Complexity of the pore space: size, morphology

188 Porous materials are characterized by a pore size distribution (PSD). Since the solvation pressure (and
189 hence the adsorption-induced strains) depends on the pore size, using strain isotherms as an additional
190 input to adsorption isotherms to back-calculate PSDs was proposed [35,39]. Another question relevant
191 to the adsorption-induced deformation of generic materials is that of the shape of the pores, which
192 can be more complex than slit, spherical, cylindrical, or hexagonal pores. To this respect, adsorption-
193 induced deformations were recently studied in wedge-shaped graphitic pores [43].

194 The PSD can evolve in a complex manner upon adsorption, due to the inhomogeneity of the
195 microscopic deformations, as was shown numerically for a microporous carbon in presence of
196 methane [40]. The PSD being in fact stress-dependent, Siderius et al. [41] showed that how the PSD
197 evolves over the adsorption process theoretically contains information related to the flexibility and
198 deformation characteristics of the adsorbent. One question that arises when adsorption occurs in a
199 material in which pores are sufficient close to each other is whether the deformation of (or adsorption
200 in) one pore occurs independently of what happens in the neighboring pores: indeed, some adsorption
201 superlattice formation of the adsorbate in a metal-organic framework was observed [42].

202

203 b. Anisotropy

204 The stress induced by adsorption can be anisotropic (e.g., in a cylindrical pore, adsorption-
205 induced stresses are not identical in the axial and in the radial directions [7,8]). Also, pores can be
206 organized in an anisotropic manner, or the mechanical behavior of the material can also be anisotropic.
207 Consequently, there exist various potential sources of anisotropy because of which adsorption at the
208 microscopic scale can lead to a macroscopically anisotropic deformation. In coal for instance, the
209 anisotropy of the adsorption-induced strains was shown to be mostly due to the anisotropy of the
210 mechanical behavior, while the adsorption stress itself is mostly isotropic [44]. Anisotropic effects can
211 also add or counterbalance each other: in silica struts containing parallel cylindrical mesopores [7], the
212 cylindrical pore geometry makes the axial adsorption-induced stress about 3 times larger than the
213 radial one but, as consequence of the anisotropy of the mechanical properties of the porous struts,
214 deformations at the scale of a strut are roughly isotropic.

215

216 c. Beyond the linearity of the mechanical behavior of the solid

217 The simplest elastic behavior of a solid material is a linear one: stresses and strains are linearly
218 related, following Hooke's law. But many materials do not follow Hooke's law, as is the case for
219 instance for cracked media (upon compression, cracks close so that the stiffness of the material
220 increases), or for polymeric solids. For wood for instance, whose elastic behavior is also nonlinear,
221 adsorption-induced strains were modeled by taking explicitly into account the complexity of the free
222 energy of the dry porous solid [10]. Molecular simulations can help explore the complexity of the free
223 energy landscape: for another mechanism inducing flexibility in a MOF, namely the swing effect in ZIF-

224 8, Coudert [47] showed with the help of quantum chemistry calculations and first-principles molecular
225 dynamics that the flexibility is not a bistable system, but that the deformation evolves continuously
226 with the pore loading.

227 For some MOFs like MIL-53, depending on the environmental conditions (temperature, stress,
228 partial pressure of the adsorbate), two configurations of the adsorbent with very distinct strains can
229 be observed (sometimes called 'large pore' and 'narrow pore' configurations), around which the
230 material behaves in a linear elastic manner. The osmotic framework was adapted to such cases [45],
231 under the assumption that each configuration is rigid. For the same family of materials, by considering
232 a free energy of the dry porous material which exhibits two wells, the features of the energy landscape
233 (i.e., the depth of the two wells) were shown to impact the transitions between the two configurations
234 and the phase transitions of the pore fluid [46].

235

236 d. Upscaling

237 Upon adsorption, the porous adsorbent deforms at several scales: for instance, in a monolithic
238 silica sample with hierarchical porosity, strains at the scale of the pore lattice and at the macroscopic
239 scale of the sample can both be measured [48] and differ from each other. In a material containing
240 pores with a variety of sizes, deformations should vary from pore to pore. Since many models to predict
241 adsorption-induced strains are formulated at the pore scale, the question arises of how to translate
242 strains at this scale into strains at the macroscopic scale of the sample.

243 Even though the variations of the volume of the sample are sometimes assumed to be equal to
244 the variation of volume of the pores (e.g., in [21]), note that it is generally not the case, as the volume
245 of the solid skeleton can vary as well. When the geometry of the pores is well defined, one can find
246 out how stresses/strains at the pore scale translate into strains at a larger scale by using the finite
247 element method (FEM), as was done for an anisotropic mesoporous silica body made of parallel
248 cylindrical channels [7,8]. For the nanoporous crystalline MIL-53, to upscale information on the
249 breathing transition from the scale of the individual cage to the scale of a whole crystal, a Hamiltonian-
250 based model was proposed [49]. When some information is known about the microstructure, one can
251 try to inject this information in the prediction of the adsorption-induced strains: such was done for
252 instance for a synthetic activated carbon with a bi-modal distribution of pore sizes, for which models
253 of adsorption-induced deformations were derived, that take explicitly into account the fact that the
254 sample contains both nanopores that adsorb fluids and macropores that contain bulk fluid [50].

255 In practice, many materials are composite or heterogeneous. As a consequence of this
256 heterogeneity, an additional complexity in the upscaling process is that adsorption-induced
257 deformations can be heterogeneous, as was observed for coal in presence of methane, through 3D
258 digital image correlation of X-ray microtomography images [51]. On composite materials with a core-
259 shell microstructure, in which an adsorbing core is surrounded by an elastic binder, the presence of
260 the binder was shown to decrease the magnitude of the adsorption-induced stresses and strains [52].
261 Also, if the adsorbing core can be subjected to adsorption-induced structural transitions, the presence
262 of the binder impacts the pressures at which those transitions occur [52]. One way to decipher how
263 adsorption-induced strains at the scale of the microscopic phases translate macroscopically into a
264 strain of the macroscopic composite sample is to use FEM, as shown in [53] on composite microporous
265 materials.

266 5. Concluding comments

267 In this mini-review, I covered not only how adsorption impacts the mechanical behavior of the
268 adsorbent and deforms it, but also how mechanics (i.e., strains or stresses) impacts the adsorption
269 process and the importance of taking into account this coupling. There exist several well-established

270 frameworks to model adsorption-induced strains, and a trend in the modeling of adsorption-induced
271 deformations is to take into account as much as possible of the complexity of actual materials, in terms
272 for instance of microstructure (pore size distribution, pore morphology, heterogeneity,...) or of
273 mechanical behavior of the adsorbent (anisotropy, non-linearity,...).

274 Conflict of interest

275 The author declares no conflict of interest.

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