What Drives Deformation of Smart Nanoporous Materials During Adsorption and Electrosorption?

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Abstract

Nanoporous solids have high surface area, so processes at the surface affect the sample as a whole. When guest species adsorb in nanopores, be they molecules adsorbing from the gas phase, or ions adsorbing from solution, they cause material deformation. While often undesired, adsorption- or electrosorption- induced deformation provides a potential for nanoporous materials to be used as actuators. Progress in this direction requires understanding the mechanisms of adsorption- or electrosorption- induced deformation. These two processes are rarely discussed together, and this Perspective aims to fill this gap to some extent, focusing on driving forces for both processes. Typically the main driving force for both is the solvation (disjoining) pressure, acting normally to the pore walls. However, in some cases, solvation pressure is not sufficient to describe the effects even qualitatively. We highlight examples in which the surface stress acting along the solid surface is an additional driving force for deformation.

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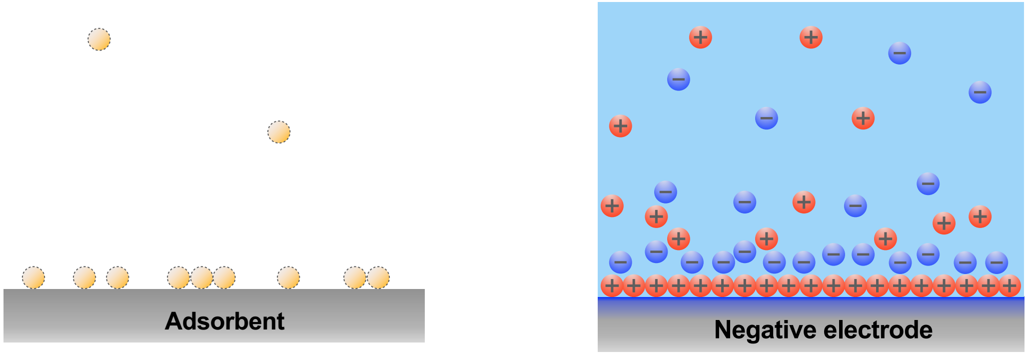
Introduction

All materials respond to external stimuli – electrical, magnetic, thermal, chemical, optical, etc. A response of a material to a certain external stimulus can be undesired, but the same response can be utilized for a practical application. A simple example is thermal expansion, which brings challenges when designing any device working in a broad range of temperatures. On the other hand, thermal expansion can be employed in a simple actuator – bimetallic plate, a thin plate composed of two metals with different thermal expansion coefficients which bends as a result of a temperature change. In recent years, there have been a lot of interest in developing "smart materials" – those that respond to stimuli in a controlled fashion, and can be used as actuators or sensors.[1]

Nanoporous materials are materials with characteristic pore size below 100 nm,[2] which provide high surface to volume ratio, so that the processes at the surface can control the volume of the material. Here we consider adsorption of atoms or molecules from the gas phase, or ions from the electrolyte solution in the pore space of nanoporous solids. However, it is important to keep in mind that the process is surface-driven (Fig. 1), according to the definition "*adsorption is the enrichment of molecules, atoms or ions in the vicinity of an interface*".[2]



(a) (b)

Figure 1: Adsorption on a planar solid surface: (a) atoms from the gas phase and (b) ions from an electrolyte solution.

Similarly to how the temperature variation is accompanied with deformation, i.e. thermal expansion, adsorption in nanoporous solids is also always accompanied with deformation.[3] In most cases, these deformations, similarly to thermal expansion are unwanted, however when they are well understood and controlled, they can be utilized for making sensors and actuators based on nanoporous materials.

The magnitude of the response of a material to adsorption depends on the material properties – the more compliant the material is, the more pronounced is the response. On the other hand, for the same material, the response can be made more pronounced if the driving force is enhanced. In this perspective we focus on discussing the driving forces for adsorption-induced deformation (AID) and electrosorption-induced deformation (EID) – the solvation pressure, acting normal to the pore surface, and the surface stress, acting along the pore surface. We are not aiming to overview the entire broad literature on either AID or EID , and refer the reader to several more detailed reviews.[3–6] Here we rather highlight the similarities between the mechanisms of both phenomena, and outline some open questions.

Experimental Measurements

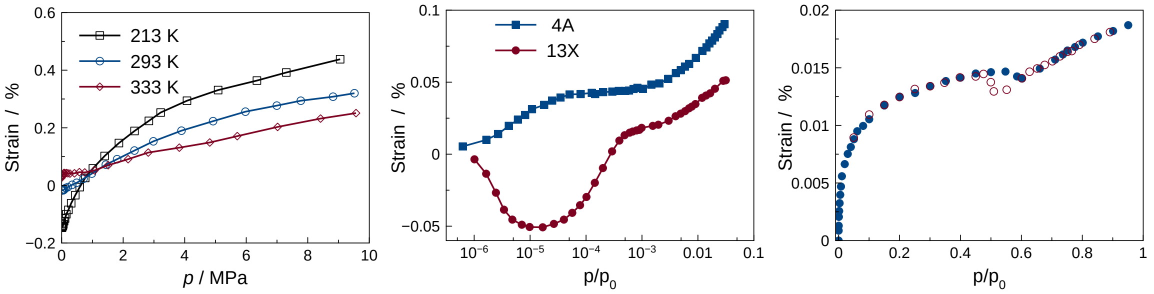
Gas Adsorption

First experiments on adsorption-induced deformation date back to 1920s, to the works by Meehan[7] and Bangham.[8] These studies utilized optical lever extensometry to measure the strain of monolithic charcoal samples during adsorption of CO_2 and other gases. The first measurements showed monotonic expansion of charcoal samples of the order of 0.1% with the increase of the gas pressure.[7] Bangham pointed out that the measured strain ϵ is proportional to the decrease of the surface energy γ due to adsorption,

$$\epsilon \propto -\Delta\gamma, \tag{1}$$

which is often referred to as Bangham's law.[9]

Adsorption-induced deformation of activated carbon, as one of the most common industrial adsorbent, has been repeatedly measured. For example, Figure 2a shows the strain isotherms of Sorbonorit-4 at various temperatures from a recent dilatometric experiments by Shkolin et al.[10] Activated carbon is hard to call a "smart material", however, it showed noticeable monotonic expansion upon adsorption of CH_4 at 333 K. Non-monotonic deformations at 213 K and 293 K demonstrates that Bangham's law does not hold. It is seen even better on dilatometric measurements of AID on zeolites (Figure 2b)[11,12] – while zeolite 4A expands with the increase of CO_2 pressure, zeolite 13X initially contracts and expands only at higher pressures. Figure 2c shows the strain isotherm for hierarchical mesoporous silica during N_2 adsorption,[13] showing two distinct expansion regimes, with a slight contraction around the capillary condensation. The three experiments highlighted in Figure 2 utilized *in situ* dilatometry to measure the strains on macroscopic scale. These examples are sufficient to demonstrate that AID is observed in various nanoporous solids, and is more complicated than just Bangham's expansion.



(a) (b) (c)

Figure 2: Adsorption-induced deformation. (a) Experimental measurements of strain of a charcoal sample resulting from adsorption of methane.[10] (b) Deformation of zeolites 13X and 4A during CO_2 adsorption[11,12] (c) Deformation of hierarchical mesoporous silica during N_2 adsorption,[13] filled and hollow markers represent adsorption and desorption paths respectively.

In addition to measuring macroscopic strains on monolithic samples by *in situ* dilatometry, AID of samples that have ordered structure on the scale of Angstroms or nanometers can be quantified by wide or small angle X-ray scattering (WAXS/SAXS) respectively. The former is applicable for studying AID in crystalline materials, e.g. porous silicon,[14] and the latter for materials having a lattice of pores, e.g. templated mesoporous silica.[15] Measurements of adsorption-induced deformation at the nanoscale allowed to quantify the strains in the materials which are not monolithic.

Progress in synthesis of hierarchical monolithic silica- and carbon- based porous materials allowed the experimentalists to combine *in situ* dilatometry with *in situ* scattering techniques, using not only X-rays but also neutrons[16,17] This combination provides adsorption-induced strains on nano- and macro- scales. Availability of monolithic nanoporous materials also makes AID more promising for practical applications for actuating and sensing.

Electrosorption

Similarly to AID , the history of experimental studies of electrosorption-induced deformation of porous materials goes back several decades. Soffer and co-workers reported electrosorption-induced strains in nanoporous carbon electrodes in the 1970s,[18,19] and pointed out the similarity with the experiments on gas adsorption by Bangham and others. Proliferation of carbon nanotubes in the 1990s helped making a transition from a concept to a working actuator[20] (Figure 3).

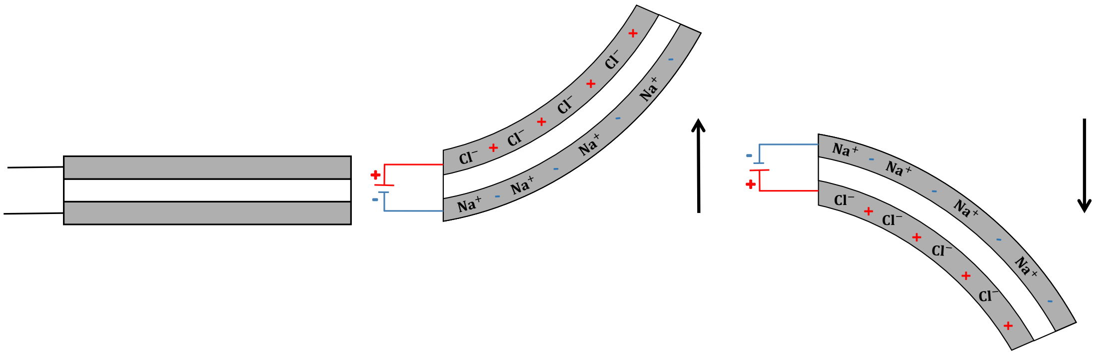
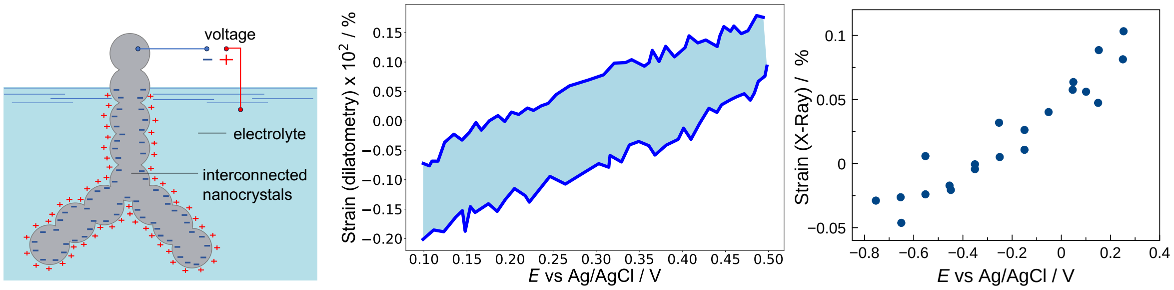


Figure 3: Schematic of a cantilever-based electrochemical actuator based on carbon nanotubes. The actuator is made of two strips of carbon nanotubes laminated together (grey) with a layer of double-sided Scotch tape (white) in between. The Na^+ and Cl^- ions represent the ions on the surface of nanotube bundles. The direction of bending of an actuator depends on the sign of the applied potential.

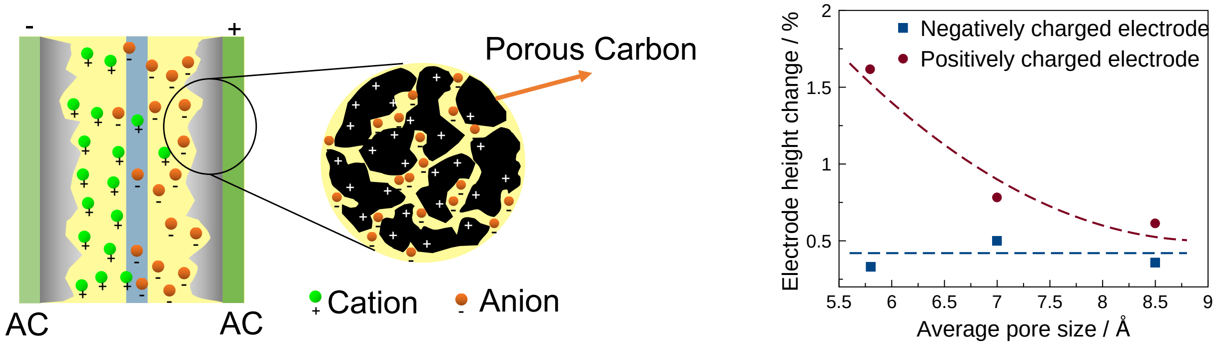
Soon after, Weissmüller and co-authors[21] designed electrosorption based actuator using metallic electrodes, aggregates of Pt nanoparticles, in aqueous electrolytes (Fig. 4). The strain of the electrode was measured by a dilatometer as a function of the difference in electric potential between the Pt electrode and the reference electrode immersed in the electrolyte. Three different electrolytes [H_2SO_4 (0.5 M), $HClO_4$ and KOH (1 M)] showed the same near-linear response, with the latter gave the strongest effects. In addition to the dilatometric measurements of the strain (Fig. 4b), the strain was measured by in situ X-ray diffraction, shown in Figure 4c. The strain on microscale was of the order of 0.1%, comparable to piezoelectric actuators.[21] Subsequent work focused mostly on nanoporous gold, which provided the increase of strain up to 1%, the details are discussed in the review by Jin and Weissmüller.[4]



(a) (b) (c)

Figure 4: (a) Schematic of electrosorption experiment on platinum nanoparticles accompanied with *in situ* dilatometry.[4,21] Electrosorption-induced strain measured using dilatometry (b) and X-ray diffraction (c).

Electrosorption in carbon nanopores attracted much attention in the last two decades with the appearance of electrical double-layer capacitors (a.k.a. supercapacitors), which utilize nanoporous electrodes and store the charge via electrosorption process,[22] schematically shown in Figure 5a. That interest revitalized dilatometric measurements on nanoporous carbon electrodes.[23,24] While measured electrosorption-induced strains were undesired for supercapacitors,[23] they presented an opportunity for actuators.[24] In situ dilatometry experiments on various carbon materials[23] showed that the magnitude of strain depends on the pore size (Fig. 5b), and attributed this dependence to the difference in ion diameters. The larger ions create a greater force during electrosorption in pores of comparable size. More recently a combination of in situ dilatometry with SAXS during the electrosorption process was performed on hierarchical carbon materials immersed in aqueous electrolytes.[25] The two measures of strains appeared consistent, as discussed in the next section.



(a) (b)

Figure 5: Electrosorption of ions in nanoporous carbons and resulting deformation. (a) Schematic of electrosorption based on the cartoon from.[5,26] Adapted, with permission from Ref.,[26] Copyright 2018 Elsevier Ltd. (b) Maximum strain of carbon electrodes with different pore sizes measured during electrosorption, based on the data from.[23]

Driving Force

Solvation Pressure from Gas Adsorption

Adsorption-induced deformation can be explained within a simple thermodynamic model, schematically shown in Fig. 6. As a results of adsorption the pores of the material, schematically shown as spherical cavities, are filled with fluid. The fluid in the pores is under solvation pressure P_s, which differs from the pressure p of the equilibrium vapor phase, and depends on the solid-fluid interactions, represented by the external potential u_ext,:

$$P_\mathrm{s} \sim \left\langle \sum -\nabla u_\mathrm{ext} \right\rangle. \tag{2}$$

Here, the summation takes place over all unique fluid-solid interaction pairs and $\langle \ldots \rangle$ is a time or ensemble average operator. In the infinite slit pore Eq. 2 represents the normal component of fluid force acting on the solid surface. The quantity P_s is often referred to as disjoining pressure.

Since the measured strains are small, the solvation pressure can be calculated using various thermodynamic theories of fluids in nanopores, assuming the pores are rigid.[27] Then, the deformation of the porous solid can be calculated based on the Hooke's law, taking solvation pressure equal to the stress, and knowing the elastic properties of the porous solid. For details, e.g. taking the pore shape and pore-size distribution into account when modeling the elastic response the reader is referred to reviews.[3,6] While the strains are fractions of a percent, the carbon materials have high elastic moduli, so the solvation pressure in this system is ≈ 37 MPa.[28]

This approach worked not only for microporous carbon materials,[28,29] but for microporous zeolites[12,30] (Fig. 2b), as well as in various mesoporous materials[13,31,32] (Fig. 2c). Unlike microporous materials, almost all mesoporous materials show monotonic expansion with the increase of gas pressure from zero, similar to the trend shown in Fig. 2c, which corresponds to $P_s > 0$, and also consistent with Bangham's law.[9]

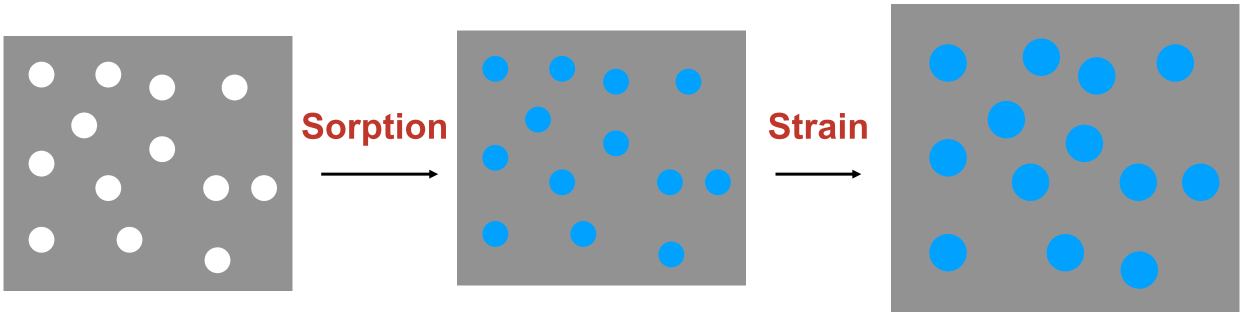


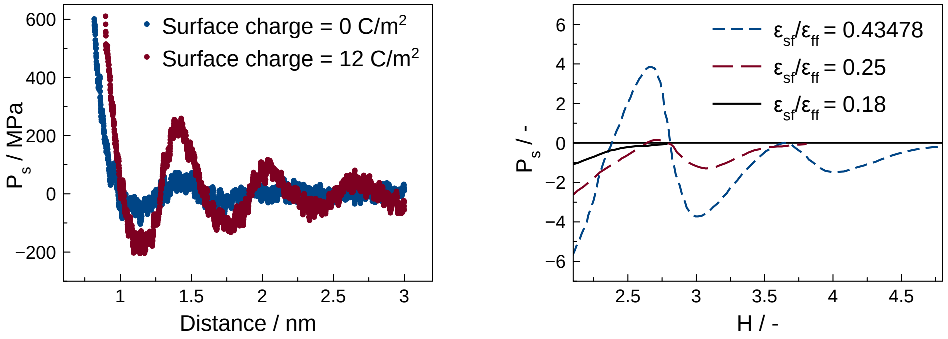
Figure 6: Adsorption-induced deformation. Schematic of the thermodynamic model of adsorption-induced deformation, which uncouples sorption and deformation. A porous solid material is initially undeformed. Then it adsorbs fluid in its pores, so that each fluid in the pore exerts solvation pressure on the pore walls. As a result the porous sample expands, or contracts if the pressure is negative.

The solvation pressure approach is consistent with other manifestations of high-pressure effects in the pores: for example departure of certain thermodynamic properties from the bulk values, and presence of different phases in the pores.[33–36] As we show below, the deformation induced by electrosorption is also interpreted by the action of solvation pressure in the pores.

Solvation Pressure in Electrochemical Systems

The studies of processes near a charged planar surface in electrolyte solution go back to late 1800s, early 1900s and is well-documented in the classical textbooks.[37] Ions form an electrical double layer (EDL), as shown in Fig. 1b, the structure of which, at low ionic concentrations and surface potentials, can be described using the Poisson-Boltzmann equation.[37] Things get complicated when instead of a planar surface, electrosorption takes place at a surface of a nanopore.

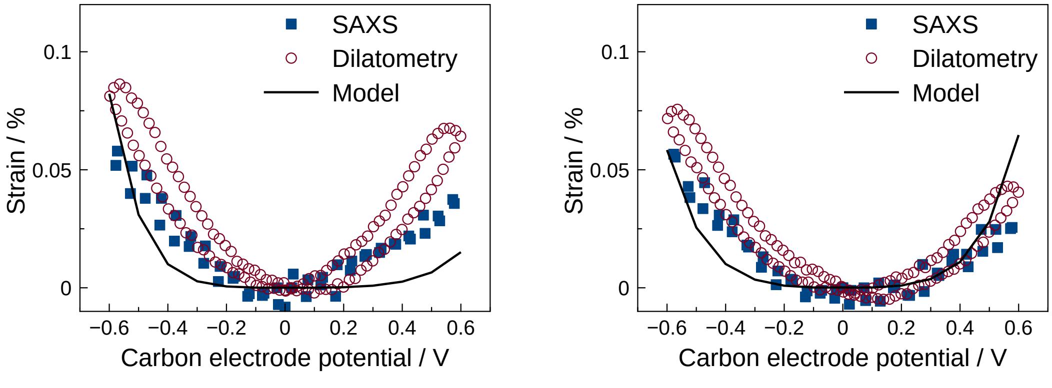
In the last two decades, ionic liquids emerged and found applications as electrolytes, therefore, many recent studies of electrosorption in nanopores are focused on them, see e.g. review.[38] A recent work, utilized molecular dynamics to study a range of pore sizes filled with ionic liquid from small micropores to mesopores and demonstrated that the solvation pressure in small pores oscillates as a function of the pore width (following the layering of ions), and quickly become consistent with the solvation pressure calculated from the macroscopic theories based on the Poisson-Boltzmann equation.[39] Oscillations of solvation pressure in the carbon pores filled with ionic liquid is a manifestation of short-range interactions rather than electrostatic ones[40] – Figure 7a. In addition, it was shown[40] that pore charging amplify the oscillation magnitude, which corresponds to an increase in solid-fluid interaction, and also agrees with results from Ref.[41] – behavior of solvation pressure in the system involving physisorption (see Fig. 7b). Overall, this comparison reveals a lot of similarities between the normal fluid-solid forces during adsorption and electrosorption in the pores. While the analysis of solvation pressure discussed here is limited to molecular simulation work, the experimental evidence of this behavior is well-known from the surface force apparatus. These experiments also showed elastic deformation of the surfaces as a result of solvation (hydration) forces.[42]



(a) (b)

Figure 7: The dependence of solvation pressure on the increase of external potential. Electric potential in case of electrosorption (a), and external VdW potential in case of vapor adsorption (b). In both cases, solvation pressure shows oscillations as a function of the pore size. Data from[41] and.[40]

The aforementioned modeling studies focused on slit pores. Progress in templated carbon materials stimulated more progress in experiments and modeling of EID ,[25,43] as well as AID .[17,32] Furthermore, these strains were reproduced almost quantitatively based on the solvation pressure calculations from the solution of the modified Poisson-Boltzmann in this geometry,[43] shown by the solid lines in Figure 8. Note that the maximum solvation pressure varies between ≈ 0.1 and 6 MPa depending on model parameters, which is noticeably lower that the solvation pressure due to nitrogen physisorption in the same materials.[32]



(a) (b)

Figure 8: Electrosorption-induced strains in nanoporous carbon materials measured by *in situ* dilatometry (hollow markers), by *in situ* small-angle X-ray scattering (filled markers), and predicted by a continuum model. (a) LiCl solution (b) CsCl solution. Experimental data from Ref.,[25] theory from Ref.[43]

Table 1 summarizes experimental sorption-induced strains and corresponding solvation pressures for selected nanoporous materials. By pore size here and elsewhere we mean pore width or diameter.

Table 1: Nanoporous materials studied experimentally with respect to adsorption- and electrosorption- induced deformation. For most studies, the values of solvation pressure are estimated based on the strain data and elastic constants.

Material	AID/EID	Pore size (nm)	ϵ (%)	P_s (MPa)	Ref.
Activated Carbon	AID	1	0.4	37	[10,28]
Mesoporous Silicon	AID	8	0.05	17	[44]
Mesoporous Silicon	EID	6.8	0.0017	0.6	[45]
Hierarchical Carbon	AID	9	2	20	[17,32]
Hierarchical Carbon	EID	7	0.08	6	[25,43]
Carbon Nanotubes	EID	1.7	0.2		[20]
Nanoporous Gold	AID	20	0.02	54	[46]
Nanoporous Au-Pt	EID	5	1.3	6	[47]
Hierarchical Gold	EID	30	6		[48]

From Solvation Pressure to Surface Stress

Several experimental studies on adsorption-induced deformation challenged the solvation pressure approach. One example is water adsorption on silica, which in some experiments revealed pore contraction at low pressures, which contradicts to Bangham's law.[49,50] Furthermore, AID has been observed in the systems without nanopores, when molecules or atoms adsorbing on a planar surface cause bending of a thin plate,[51,52] somewhat similar to a bimetalic plate, as depicted in Figure 9. Such deformation cannot be explained by a load normal to the surface (i.e. solvation pressure), and suggests that the stress along the surface is the driving force. This can be understood by introducing the concept of the surface stress, and its change during the adsorption.

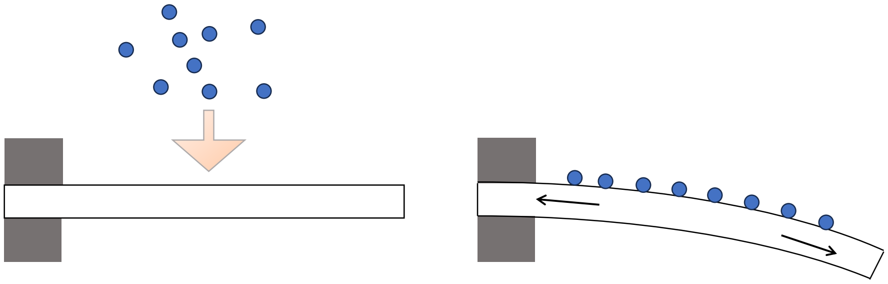


Figure 9: Schematics of cantilever bending experiment. After the deposition of adsorbate molecules on one side of the cantilever its surface bends as a result of the altered surface stress.

The surface stress f_{ij} is a tensor defined as

$$f_{ij} = \gamma\delta_{ij} + \frac{\partial\gamma}{\partial\epsilon_{ij}}, \tag{3}$$

where γ is the surface energy, δ_{ij} is the Kronecker delta, ϵ_{ij} is the strain tensor. The surface stress does not result from adsorption, a clean planar surface has a non-zero surface stress.[52] The surface stress of a clean surface appears due to the broken bonds of the surface atoms, which alter the electron density near these atoms and therefore the strength of interactions between them, compared to the same atoms in bulk (Figure 10).

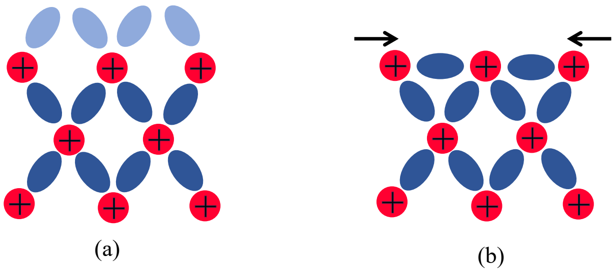


Figure 10: Schematic of a charge distribution in a metal (the bulk metal is at the bottom, the surface is on top). (a) The surface is created and bonds on top are broken. (b) The part of the bond charge near the surface moves into the space between the surface layer atoms, increasing the bond strength between them, and generating tensile surface stress $f > 0$ along the surface, shown by arrows. Based on the schematic and discussion in Refs.[51,52] Adapted, with permission from Ref.,[51] Copyright 1994 American Vacuum Society

Typically the clean solid surface is under tensile surface stress. Adsorption, can perturb the electron density near the surface, and the electron density tends to recover its "normal" distribution, corresponding to the bulk solid. Therefore, in most cases, a solid surface tends to release the tensile stress, and the surface is expanding, as shown schematically in Fig. 9. Such behavior is often observed during chemisorption of gases on the clean surfaces of metals[51,52] and confirmed by density functional theory calculations.[53] Moreover, this is consistent with the empirically observed Bangham's law – monotonic expansion upon adsorption. It is important to note that in the case of non-specific physisorption in mesopores, which follows Bangham's law, the deformation predicted based on the change of the surface stress is consistent with the deformation calculated based on the solvation pressure.[9] Other cases, such as water adsorption on silica surface, which involves chemisorption or hydrogen bond formation, show contracting behavior which cannot be explained by the solvation pressure approach.[49,50] However, can be interpreted as a result of the change of surface stress using either a phenomenological model,[9] or *ab initio* molecular dynamics simulations.[54]

Some of the experimental studies of EID have been also interpreted within the concept of surface stress and its change as a result of adsorption. Weissmüller et al.[21] also showed that the observed strains are consistent with the change of the surface stress due to electrosorption: localized charge of the order of $0.1e$ near each atom is strong enough to affect electron density and perturb the bonds between the atoms in plane. Even earlier experimental study, focused on EID of carbon nanotubes, pointed out that the dependence of the measured strain on charge, and in particular the mismatch between the minimum strain and the potential of zero charge, requires consideration on the quantum mechanical level.[20] Several studies utilized electronic structure density functional theory (DFT) to calculate the change of surface stress for metal surfaces (e.g. for gold[55] and other transition metals[56]) with charge. They provided the value of derivative of the surface stress on charge q, $(\partial f/\partial q)_\epsilon$ close to the experimental measurements. However, DFT calculations do not represent the experimental conditions, representing the system at 0 K temperature and ignoring the presence of liquid medium, leaving a lot of room for more rigorous models.

Moving Forward

Both gas adsorption and electrosorption of ions in nanoporous materials result in deformation. These two phenomena have a lot in common, but have been rarely discussed together. Recent progress in synthesis of monolithic nanoporous carbon materials, provides an opportunity to use the same materials for both gas adsorption and as electrodes.[57–59] During both processes they show a substantial mechanical response making them promising for applications as miniature actuators.

For stimuli-responsive applications, elastic properties of materials are the key. However, elastic properties of nanoporous materials are challenging to quantify even for relatively simple structures.[60] AID can serve as a method to measure the elastic constants of nanoporous samples.[44,61–63] If AID and EID are performed on the same samples, the elastic constants can be derived from AID to help eliminating the number of unknowns in the EID experiments. Furthermore, since modeling AID is a more mature area, development of models for EID , can benefit from simulation studies on the same materials. Complementary AID and EID on the same materials can help improving the verification of the models.

There are two mechanisms for sorption-induced deformation, which are also rarely discussed together. Both adsorbed ions and adsorbed gases exert solvation pressures in the pores, of the order of megapascals, which acts normal to the pore surfaces and cause deformation. In addition to the normal component, there is a component along the surface – surface stress, which can also contribute to the deformation. One of the reasons for the lack of models which consider both is in different nature of the two effects. Adsorption of gases or ions are typically modeled using classical molecular dynamics or Monte Carlo simulations, which, however, fail to capture the change in the surface stress. The standard interatomic potentials can not capture this, essentially, quantum effect. One path towards making progress in this direction, would be to utilize *ab initio* methods, which are rarely used to study adsorption. Several *ab initio* studies focused on gas (or vapor) adsorption on planar crystalline surfaces and calculation of the resulting changes in the surface stress.[53] However, to the authors knowledge, no studies of this kind for amorphous and/or porous materials, which are of interest for the current context, have been done. The problem of this direct approach is its computational cost – calculation of adsorption-induced surface stresses from *ab initio* molecular dynamics appeared extremely expensive even for a system of ten water molecules interacting with a planar quartz surface.[54] Another option is to focus on development of interatomic potentials (force fields) that treat surface atoms differently than bulk (see schematic in Figure 10), and can capture the change of the interaction strength upon interactions with adsorbate, while not taking into account the details of electronic structure.[64] Lastly, a hybrid, phenomenological model can be introduced, where the bonds are treated within the standard interatomic potentials, but are corrected during the simulation based on the interactions with adsorbate.

Recent studies of AID showed that models that don't take into account the coupling between adsorption and deformation, can result in incomplete picture of the process – modeling adsorption in rigid pores and calculating deformation based on the calculated stresses don't always result in correct behavior, and modeling adsorption and deformation in a fully coupled fashion is needed.[12,65–69] Recent study of electrosorption in mechanically strained system further supports the importance of such coupling.[70] Hence, we expect that modeling EID can benefit from adapting coupled models from AID .

Lastly, irrespective of the progress in understanding and controlling the driving force, the progress in smart nanoporous materials can be achieved by advancing the materials design. An example of such a solution was proposed by Detsi et al., using a hierarchical layered structure of nanoporous gold, which provided electrosorption-induced strains up to 6%.[48] Recent experiments on AID and EID utilize nanoporous carbons, which have lower elastic moduli compared to metals and can provide higher strains at the same loads.[25] Further progress can be achieved by utilizing even softer materials, e.g. conductive nanoporous polymers. The design using softer materials and higher strains will necessarily require developing fully coupled models.

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Biographies

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