Available online at www.sciencedirect.com
ScienceDirect
Current Opinion in Chemical Engineering

Adsorption–strain coupling at solid surfaces

Jörg Weissmüller[1,2]

This brief review inspects how chemistry or electrochemistry at a solid–vapor or solid–electrolyte interface couple to the mechanics of the solid. Emphasis is on the complementarity of two at first sight unrelated phenomena: on the one hand, adsorption or electric charging change the local tangential stresses in the solid surface; on the other hand, a tangential strain of the surface changes the adsorption enthalpy and the chemical or electric potential. One and the same materials parameter underlies these phenomena. The phenomenology and the Maxwell relations behind that observation are discussed and the underlying microscopic mechanisms addressed, with particular attention to symmetry and sign of the coupling coefficients.

Addresses
[1] Institute of Materials Physics and Technology, Hamburg University of Technology, Hamburg, Germany
[2] Institute of Materials Research, Materials Mechanics, Helmholtz-Zentrum Geesthacht, Geesthacht, Germany

Corresponding author: Weissmüller, Jörg (weissmueller@tuhh.de)

Current Opinion in Chemical Engineering 2019, **24**:45–53

This review comes from a themed issue on **Separations engineering: advances in adsorption**

Edited by **Gennady Gor** and **Benoit Coasne**

https://doi.org/10.1016/j.coche.2018.12.012

Introduction

The interaction between chemistry and mechanics is crucial for many materials phenomena. Its impact on processes *in the bulk of solids* is thoroughly studied and of eminent technological importance in metallurgy. As just one example, the martensite transformation — which relies on the elastic distortion of a crystal lattice to enhance its solubility for interstitials, such as carbon in iron — has been exploited for millennia for hardening steel. The present article is focused on the coupling between chemistry and mechanics *at solid surfaces*, which is a more recent topic. Since many adsorption phenomena involve ions, and since electrochemistry provides a particularly convenient and quantifiable way of manipulating the chemistry at surfaces, the coupling phenomena here also include the aspect of local electric charging. Thus, any discussion of *chemo-mechanical* coupling at surfaces requires that the more general issue of *electro-chemo-mechanical* coupling is included. It is even more important to realize that there are two complementary views on the science underlying the various coupling phenomena, which will now be addressed.

The first view focuses on the fact that solid surfaces are afflicted with local stresses — quantified by the phenomenological parameter 'surface stress' — and that these stresses change during adsorption or electric charging. This phenomenon can be observed in experiments which monitor the change in macroscopic dimensions of solid bodies as they are exposed to varying environments — porous bodies swell or shrink, cantilevers bend. The surface-stress-induced deformation is of relevance for such diverse topics as actuation with carbon nanostructures [1] and metal nanostructures [2] or sensing with microscale [3] and nanoscale structures [4•] and the extraction of shale gas [5]. Its impact on the strength and even crystal lattice stability of nanoscale metals is under discussion [6,7].

The second view focuses on changes in the adsorption energy on solid surfaces when strain in the tangent plane is imposed on the surface. In the consequence, experiments observe the decoration of local stress concentrations at surfaces by adatoms [8] and the variation of adsorption enthalpies [9,10••] or electrode potentials [11•,12•] when surfaces are uniformly strained. Experiment also confirms this phenomenon as a means for modulating the reactivity of surfaces in electrocatalysis [13••].

Both views are open to inspection by electron-theoretic density functional theory (DFT) computation. Much of the current interest in heterogeneous catalysis with strained surfaces can be traced back to early predictions from that latter technique [14••]. Furthermore, DFT confirms that the surface stress of metals varies during adsorption [15] and the work function of metals in vacuum [16] — closely related to their electrode potential in electrolyte — as well as adsorption energies on metal surfaces [17,18••] vary during straining.

Here, we briefly summarize the current view on electro-chemo-mechanical coupling, with an emphasis on the complementarity of the above two points of view. In the interest of simplicity, much of the current literature is focused on surfaces of high symmetry, where attention can be restricted to isotropic stress and strain and to scalar materials parameters. Yet, interesting phenomena arise when lower symmetry is admitted. Our discussion therefore starts out with considering coupling at general, anisotropic surfaces and introduces isotropy in the plane of the surface as a special case. The phenomenological description of the surface behavior will form the center of the discussion; it will be supplemented by remarks on atomic-scale processes and by selected examples for numerical values of materials parameters derived from experiment or from *ab initio* computation.

This article touches on several points that have either been the subject of controversial discussion or that deserve more detailed discourse. Brevity requires that the reader is referred to the relevant literature. Specifically, this relates to the notion that stress at solid surfaces is quantified by the surface stress and explicitly *not* by the surface tension [19•], to the distinction between the Shuttleworth equation for surface stress in laboratory coordinates and the simpler defining equation in Legendre coordinates that is embraced here [20], and to the description of the mechanical interaction of a fluid with a solid surface in terms of, alternatively, the 'pressure tensor' in the fluid or, as here, the surface stress [21•].

Fundamentals

Our analysis rests on the discussion of surface mechanics in the seminal work by Gurtin [22•] and its extension to electrode surfaces by Weissmüller and Kramer [23•]. Briefly, we consider a solid body which may be nonuniformly stressed in its bulk and which is immersed in a uniform fluid. An interfacial free energy density, ψ, represents the local excess (over the homogeneous phases) in free energy per area at the solid–fluid interface. Focusing first on electrolyte (superscript E) as the fluid, we take ψ^{E} a function of the state variables superficial charge density (per area), q, and tangential strain, $\mathbb{E}$. The fundamental equation, which identifies the energy-conjugate variables electrode potential, E, and surface stress, $\mathbb{S}$, is

$$\mathrm{d}\psi^{\mathsf{E}} = E\,\mathrm{d}q + \mathbb{S} : \mathrm{d}\mathbb{E}. \tag{1}$$

Electrode surfaces can behave in an ideal capacitive manner, so that q varies with E and there is no adsorption. Here, as during an ideal electrosorption process, q and the specific excess, Γ, (molecules per area) of adsorbate are linked since electric charge is here exclusively transported by the adsorption of ions. This also implies a link between E and the chemical potential, μ of the adsorbate in the fluid:

$$\mathrm{d}q = -zF\,\mathrm{d}\Gamma \tag{2}$$

$$-zF\delta E = \delta\mu \tag{3}$$

with F Faraday's constant and z the signed valency of the adsorbed molecule in solution.

For surfaces in contact with gas (superscript G), adsorption is controlled by μ, and the fundamental equation is

$$\mathrm{d}\psi^{\mathsf{G}} = \mu\,\mathrm{d}\Gamma + \mathbb{S} : \mathrm{d}\mathbb{E}. \tag{4}$$

Maxwell relations for electrocapillary coupling and sorption–strain coupling

Gokhshtein [11] first pointed out that the same materials parameter of an electrode surface describes on the one hand the coupling between surface stress and charge density and on the other hand the coupling between electrode potential and strain. Haiss [24••] demonstrated that the magnitude of the coupling provides insights into electrode processes at a molecular level. The team of the present author has designed modern experimental approaches to verify the two sides of the underlying Maxwell relation and found excellent agreement [12•,25]. Two variants of the Maxwell relation emerge naturally from Eqn 1 and 4, namely

$$\mathbb{K}^{\mathsf{E}} = \left.\frac{\mathrm{d}\mathbb{S}}{\mathrm{d}q}\right|_{\mathbb{E}} = \left.\frac{\mathrm{d}E}{\mathrm{d}\mathbb{E}}\right|_{q} \tag{5}$$

for electrolyte and

$$\mathbb{K}^{\mathsf{G}} = \left.\frac{\mathrm{d}\mathbb{S}}{\mathrm{d}\Gamma}\right|_{\mathbb{E}} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}\mathbb{E}}\right|_{\Gamma} \tag{6}$$

for gas.

The tangential superficial tensors $\mathbb{S}$ and $\mathbb{E}$ describe a stress and strain, respectively, that act tangentially in the plane of the surface and that can be anisotropic in the plane. The electrocapillary coupling parameters $\mathbb{K}$ have analogous characteristics. As second derivatives of the state function ψ, the $\mathbb{K}$ are materials parameters of the surface.

Surfaces in contact with gas or vacuum have no defined capacitance and so cannot, as a rule, be charged. There is here no analogon to the capacitive charging of electrode surfaces. However, the work function W provides a measure for the chemical potential of the electrons in the solid. The coupling of the work function to strain is in fact open to straightforward evaluation by DFT [16]. The relevant coupling parameter is

$$\mathbb{K}^{\mathrm{W}} = \frac{1}{F}\,\frac{\mathrm{d}W}{\mathrm{d}\mathbb{E}} \tag{7}$$

for electron exchange.

Strain-dependent adsorption enthalpy

The quantity $\mathbb{K}^{\mathsf{G}} = \mathrm{d}\mu/\mathrm{d}\mathbb{E}|_{\Gamma}$ in Eqn 6 can be linked to a strain derivative of the adsorption enthalpy, Δh_{ads}.[3] This is readily illustrated for the example of the Langmuir isotherm for adsorption of non-interacting molecules at a surface with a discrete number density, $\Gamma_{\max}$, of adsorption sites per area,

$$\mu = \mu_0 + \Delta h_{\mathrm{ads}} + RT \quad \ln[\theta/(1-\theta)], \tag{8}$$

with $\theta = \Gamma/\Gamma_{\max}$ the fractional coverage and μ_0 the chemical potential in a reference state. Taking the strain derivative of μ in Eqn 8 at constant Γ and, hence, at constant θ, gives

$$\mathbb{K}^{\mathrm{ads}} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}\mathbb{E}}\right|_{\Gamma} = \left.\frac{\mathrm{d}\Delta h_{\mathrm{ads}}}{\mathrm{d}\mathbb{E}}\right|_{\theta} \tag{9}$$

This result continues to hold when, in a generalization of the Langmuir isotherm, interactions between adsorbate molecules are permitted and Δh_{ads} is allowed to depend explicitly on θ.

Isotropic surfaces

The surface stress must be isotropic in the plane of surfaces with threefold or higher symmetry, such as the (111) and (100) surfaces of face-centered cubic crystals. Then $\mathbb{S} = f\mathbb{P}$ with f a scalar surface stress parameter and $\mathbb{P}$ a tangential unit tensor in the plane. It follows that the electrocapillary or adsorption–strain coupling are also isotropic, and *scalar* coupling parameters ς (for electrode processes and electron emission) and ζ (for adsorption from gas) can be defined as

$$\varsigma = \operatorname{trace} \mathbb{K}^{\mathsf{E}} = \mathrm{d}f/\mathrm{d}q|_{e} = \mathrm{d}E/\mathrm{d}e|_{q} \tag{10}$$

$$\zeta = \operatorname{trace} \mathbb{K}^{\mathsf{G}} = \mathrm{d}f/\mathrm{d}\Gamma|_{e} = \mathrm{d}\mu/\mathrm{d}e|_{\Gamma} \tag{11}$$

$$\zeta^{\mathrm{ads}} = \operatorname{trace} \mathbb{K}^{\mathrm{ads}} = \mathrm{d}\Delta h_{\mathrm{ads}}/\mathrm{d}e \tag{12}$$

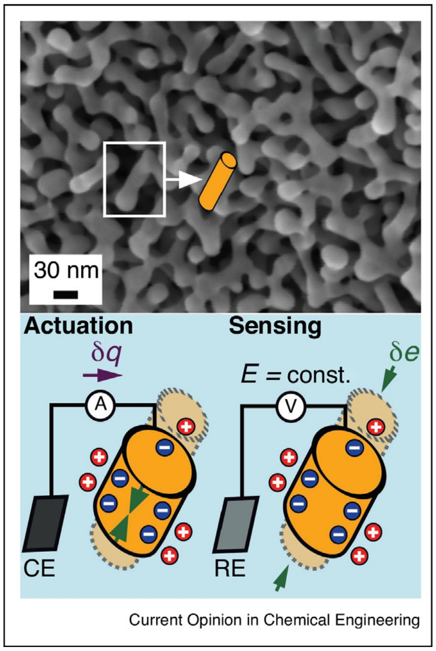
$$\varsigma^{\mathrm{W}} = \operatorname{trace} \mathbb{K}^{\mathrm{W}} = F^{-1}\mathrm{d}W/\mathrm{d}e \tag{13}$$

with $e = \operatorname{trace} \mathbb{E}$ the relative change in surface area (measured in laboratory coordinates) by elastic strain.

In electrolyte, the two sides of the Maxwell relation, Eqn 10, have been explored by cantilever bending or porous metal expansion experiments that probe surface stress variations and by dynamic electro-chemo-mechanical analysis (DECMA), probing potential variation in response to strain. Density functional theory provides data for the coupling at solid surfaces in contact with gas. For Au (111) in vacuum, the DFT value [16] of the work-function strain coupling, $\varsigma = -1.89$ V, is quite precisely (to within 5%) equal to surface stress-charge and electrode potential–strain coupling parameters, which are -2.0 V [26,27•] and -1.9 V [12•], respectively. The agreement provides strong support for the Maxwell relation, and it also suggests that the electrocapillary coupling parameters for charge-exchange at the solid–vacuum interface, ς^{W}, and at the solid electrolyte interface, ς, connect to the same physics and agree in magnitude.

Figure 1 illustrates the complementarity of surface-stress charge and electrode potential–strain coupling that is

Figure 1



Current Opinion in Chemical Engineering

Complementarity of surface-stress charge and electrode potential strain coupling explored by actuation and sensing experiments with a porous metal sample, Ref. [4•]. Top frame: scanning electron micrograph showing microstructure of nanoporous gold, indicating idealized concept of a 'ligament' of the metal network structure as a cylindrical strut. Lower left frame illustrates actuation, indicating contraction of ligament when negative charge, δq, is deposited on the strut and compensated by positive counterions in electrolyte in the pore space. Lower right frame illustrates sensing where an externally imposed local strain δe at constant electrode potential, E, induces polarization of the initially charge neutral electrode surface. CE and RE: counter-electrode and reference-electrode, respectively.

---

[3] Energy or enthalpy of adsorption? With attention to fluids, phenomenological thermodynamics distinguishes energy and enthalpy by their state variable for mechanics, namely volume or pressure, respectively. Adsorption at a solid–fluid interface typically involves mixed boundary conditions: The constant pressure in the fluid fixes the normal component of the *stress* in the solid whereas the stiffness of the underlying crystal fixes the tangential component of the *strain*. Thus, there is no obvious basis for referring to the work which is done during adsorption as either, an energy or an enthalpy of adsorption. Here we adopt — somewhat arbitrarily — the term 'adsorption enthalpy'.

embodied in the Maxwell relation, Eqn 10, for the example of an actuation and sensing experiment with a porous metal body (nanoporous gold, Ref. [4•]). Wetting the pore surfaces with electrolyte and transferring charge by applying an external voltage leads to surface stress and, hence, macroscopic strain of the porous body. Conversely, applying a macroscopic load leads to local strain of the metal backbone; this polarizes the metal-electrolyte interface and leads to charge transfer [4•].

The agreement between DFT for the work function strain response in vacuum and experimental results for the electrocapillary coupling in electrolyte exemplifies that processes involving exchange of the same particle (electron, atom or molecule) have sensitively the same strength of coupling, irrespective of whether the process acts in gas or in electrolyte. The electrocapillary and sorption–strain coupling coefficients are then simply related by

$$\varsigma = \frac{1}{-zF}\zeta \tag{14}$$

Specifically, for monovalent anions ($z = -1$) the electrocapillary coupling parameter in units of V has the same numerical magnitude as the sorption–strain coupling parameter in units of eV.

Anisotropic coupling

The surface stress will generally be anisotropic in the plane of surfaces of lower than threefold symmetry. The (110) surfaces of face centered cubic crystals provide a simple example [28], while more complex structures of low symmetry are found in reconstructions of many other crystal surfaces. The reconstruction can in fact be driven by the strife of the surface to reduce its energy by relieving the surface stress. For instance, terraces of clean Au(111) can undergo a 'herringbone reconstruction' by compression along the $\langle\bar{1}10\rangle$ direction [29,30], relieving the tensile surface stress of the bulk terminated surface. As a consequence of the surface stress anisotropy, the orientation distribution of domains with different crystallographic orientation along the surface couples to uniaxial strains that are externally imposed on the surface [31]. Low symmetry reconstructions of initially high symmetry surfaces are often the consequence of adsorption, as exemplified by the 'striped phase' of twofold symmetry on oxygen covered Au(111) [32,33].

Vicinal surfaces, which are slightly misaligned relative to a nearby low index orientation, provide another obvious example of low symmetry. Crystallographically, the misalignment is realized by step edges. These linear defects interact by short-range, dipole-like stress and strain fields [34,35,36•]. On top of that, steps are associated with long-range tangential stresses that add to the surface stress of the terraces [37]. In a coarser picture of the surface as an elastic continuum, corrugation or roughness may be anisotropic. Here, the amplitude and orientation of the corrugation affect the magnitude and anisotropy of the effective surface stress that acts on the underlying crystal [38,39]. Some adsorbates attach preferentially to step edges, reducing their energy and thereby promoting morphology changes of the surface, between faceted (few step edges) and rough (many step edges). Cyclic transitions between rough and faceted states of transition-metal or noble-metal surfaces during catalytic reactions provide striking examples [40••,41].

Even high symmetry surfaces can offer adsorption sites of low symmetry. For instance, the bridge site on (111) or (100) surfaces of fcc crystals connects two neighboring surface atoms. This is a local configuration with twofold symmetry. It has recently pointed out that the coupling between adsorption enthalpy and strain of such configurations depend on the strain direction [18••]. In other words, even though the surface has three- or fourfold symmetry, coupling is not adequately described by the scalar electrocapillary coupling parameter. Instead, the more general coupling of Eqn 9 applies. This observation is reconciled with the earlier considerations on symmetry when one considers that a uniaxial strain in the plane breaks the symmetry of the surface. It is tempting to dismiss this as a second-order effect, so that anisotropic coupling becomes relevant only at sufficiently large strain magnitude. Yet, surface science provides obvious examples for discontinuities of surface properties near high symmetry points. The pronounced cusps in the surface energy-versus-misorientation graphs of vicinal surfaces at their low index orientations [42•] provide a prominent example. Furthermore, the electrocapillary coupling parameters of clean and capacitively charged silicon surfaces exhibit discontinuities around $e = 0$ [43], which can be related to the symmetry-breaking effect of the strain on the electronic band structure. This confirms that the symmetry of an imposed strain, isotropic or uniaxial, may be relevant for the changes in adsorption phenomena.

Sign of the electrocapillary and sorption–strain coupling parameters

Electrocapillary coupling parameters for capacitive processes at transition metal surfaces are invariably negative valued and in the range −0.5 to −2 V [44]. Yet, the sign is not forceful, as exemplified by positive-valued ς in the sp-bonded metals Al and Mg [45•]. Furthermore, ς for Si surfaces can exhibit either sign, depending on the nature (compression or tension) of the strain and on the origin (conduction band or valence band) of the transferred electron [43]. Relevant microscopic phenomena, as summarized in Ref. [45•], are a decrease of the Fermi wavenumber ($\varsigma\uparrow$) and of the surface dipole strength ($\varsigma\downarrow$) by tensile strain, a relaxation of the outermost layer of atoms (which can be inward [$\varsigma\downarrow$] or outward [$\varsigma\uparrow$]), along with — typically — electron enrichment in the bonding regions in-between the surface atoms ($\varsigma\downarrow$) and a depopulation of screening orbitals around the ion cores (of transition metals; $\varsigma\downarrow$) upon electron accumulation in the surface. DFT studies of sp-bonded and transition metals reveal the relative contributions of these partly opposing phenomena. Yet, a simple predictive theory for the net value or of simply the sign of ς is not in view [45•].

In spite of the complexity revealed by detailed studies of the electrocapillary coupling, it is popular to discuss the coupling between strain and adsorption enthalpy in terms of a simpler approach termed the d-band model [14••]. With an eye on late transition metal surfaces, that model rests on the notion that tensile strain narrows the d-band and, in the consequence, increases the energy of its states, thereby making the surface more binding for adsorbate. Hence, $\zeta < 0$ — a trend which is indeed qualitatively born out by most of the known sorption–strain coupling parameter values. For instance, transition metal surfaces typically become more binding for hydrogen [10], oxygen species [46], and CO [9,14••] when strained in tension. However, there are also important exceptions. Experiments on oxygen species electrosorption on Au(111) provide a prominent example: in the early stages of the electrosorption process the adsorption becomes stronger upon tensile straining ($\zeta < 0$), yet in the later stages the trend is inverted and tensile straining weakens the adsorption, hence $\zeta > 0$ [47]. In this instance, the trends can be related to surface reconstruction: Oxygen adsorbs initially on pre-existing sites of the bulk-terminated gold surface, and this process is associated with the expected, negative-valued ζ. Subsequently, as one possible manifestation of the 'replacement turnover' process, gold atoms may move from terrace-site or step-site into adatoms sites and coordinate with oxygen. This reconstructed surface has a positive-valued ζ [47].

The observations on OH^- on Au emphasize the relevance of structural changes in the surface for the electrocapillary coupling. As already mentioned above, relaxation of the atomic positions of the substrate surface atoms in response to either, tangential strain or electric charging, is also an important contribution to the electrocapillary coupling during capacitive processes [45•,48•,49].

The discussion of chemo-mechanical coupling in this article is focused on strong bonds. Yet, based on DFT data in Ref. [50], Gor *et al.* [21•] have inferred substantial ζ-values also for van-der-Waals bonded adsorbates: For CH_4 and CO_2 on graphene, they quote $\zeta = -64$ and -69 mV, respectively.

Sorption–strain coupling during underpotential deposition

For certain combinations of two metals, the ions of one metal in solution can be electrochemically reduced — at electrode potentials positive of the bulk Nernst potential — to form up to one or sometimes two monolayer thick adsorbate layers on substrates from the other metal. This process is referred to as underpotential deposition (UPD). In view of the widespread notion that the sorption–strain coupling is regularly negative it is remarkable that Pd UPD on Au makes the surface stress more tensile (more positive f) [51]. Eqn 11 here implies $\zeta > 0$. The sign is immediately rationalized as an expression of the coherency stress in a pseudomorphic layer with a lesser lattice parameter than the substrate [51]. If the atoms in the layer are smaller than those of the substrate — as is the case for Pd on Au — then the layer is strained in tension. This implies a trend for more positive f when the layer is formed and, hence, a trend for $\zeta > 0$. Conversely, depositing larger atoms results in compression in the layer, hence a trend for more negative f and for $\zeta < 0$.

As a word of caution, it is noted that the link between size and adsorption-induced stress is by no means forceful. Several additional effects may be superimposed:

- Many UPD layers are reconstructed [52], as opposed to pseudomorphic. Reconstruction affects the stresses in the surface, see above.
- Even for pseudomorphic UPD layers, the effects of relaxation in the substrate and of charge-exchange between substrate and layer contribute to the variation in surface stress, on top of the misfit strain effect. The surface stress evolution during the UPD of Bi on Au exemplifies these effects [53,54]. Indeed, the numerical magnitude of the electrocapillary coupling parameter for Pd UPD on Au, $\varsigma = -0.14$ V, is substantially smaller than estimated based on misfit strain alone [51].
- UPD processes can involve the replacement of adsorbed anions by the metal [54], and the net change in surface stress will therefore depend on the difference between surface stresses in the respective two adsorbate layers, metal versus anion.
- In the limit of high coverage, some UPD layers undergo a transition from pseudomorphic (i.e. commensurate) to incommensurate. Again, Bi UPD on Au from electrolyte [53,55] provides an example. Gor *et al.* [21•] emphasize that the surface stress variation in the limit of a purely incommensurate adsorbate layer depends only on the adsorption isotherm for $\Gamma(\mu)$ and is otherwise independent of the adsorbate–substrate interactions. Under these conditions, one finds simply $df = -\Gamma d\mu$.[4] In other words, the transition from commensurate to incommensurate makes the size misfit irrelevant.

---

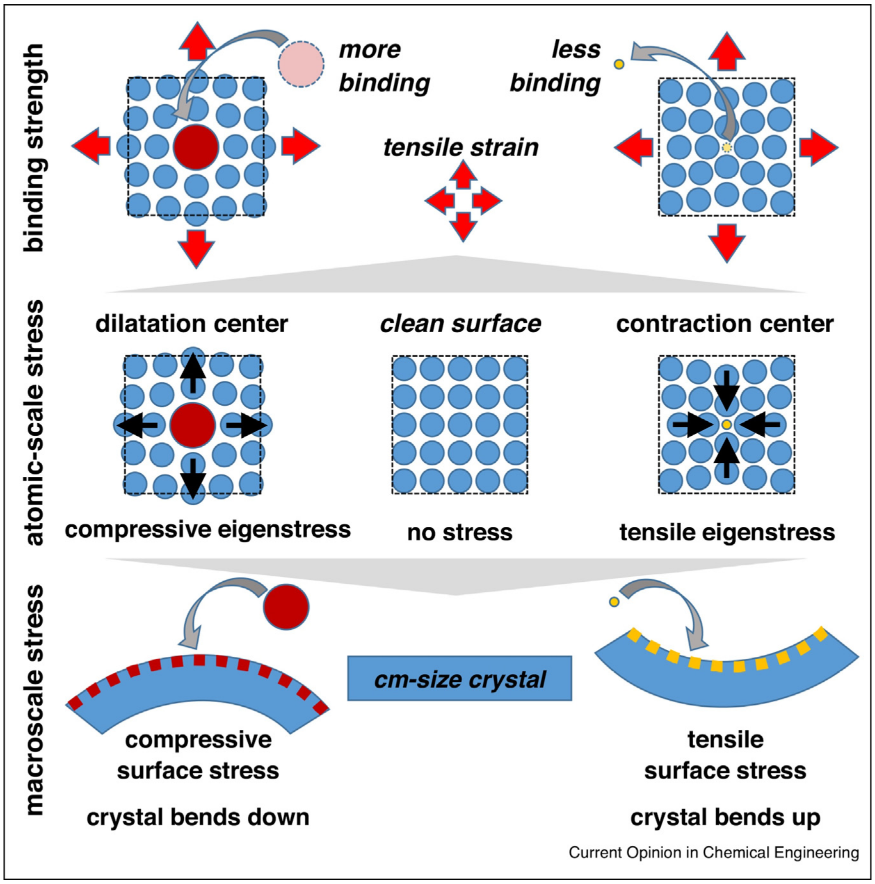
[4] This relation between df and $d\mu$ is the differential form of Eqn 25 in Ref. [21•] when there is no commensurate adsorption. The variation in the surface stress, f, is here identical to the variation in the surface tension, γ, yet this identity holds only under the restrictive condition of a saturated and incommensurate layer.

In spite of the importance of additional effects, empirical studies confirm that the size of the adsorbed atom or molecule can be decisive for the sorption–strain coupling. The role of size, which is illustrated schematically in Figure 2, is strikingly confirmed by studies of the surface-stress charge coupling as well as sorption–strain coupling for the UPD of H on Pd. Here again, several sets of experimental data can be compared: porous metal dilatometry suggests $\varsigma = +1.17$ V [56] for the surface stress-charge coupling, while DECMA and electrosorption on strained pseudomorphic Pd monolayers suggests the potential–strain coupling $\varsigma = +1.1$ V [57] and $\varsigma = +1.4 \pm 0.2$ V [58], respectively. These values are in reasonable agreement. Significantly, the sign and numerical magnitude of the coupling is correctly predicted by a continuum mechanics model that analyzes misfit strain in a H-rich superficial layer, relying on the partial molar volume of hydrogen in bulk Pd and on Pd's elastic parameters as only materials parameters: this model yields $\varsigma = +1.15$ V [56]. In other words, the size misfit is here a key parameter governing sign and magnitude of the sorption strain coupling.

A link between continuum approaches and atomistic theory

The success of continuum approaches in linking the enthalpy of adsorption to mechanics is not surprising in view of the well-known success of similar approaches for the enthalpy of absorption (or enthalpy of solution) in the bulk. Building on theory by Mott and Nabarro [60•] and by Eshelby [61], Miedema [62] confirmed that the elastic part of the enthaply of solution in bulk phases can be well estimated from the energy of the misfit strain field in the

Figure 2



Mechano-chemical coupling-relating atomic-scale interactions to the sign of the phenomenological coupling parameters and to experimental signatures in the macroscopic world. Adsorbed molecules can represent centers of dilatation or of contraction, leading to compressive or tensile local stresses ('eigenstress') in the surface, as depicted in the central row. Externally imposed tensile strain interacts constructively with the compressive eigenstress of dilatation centers (exemplified in the top row, left frame), enhancing the binding strength. The opposite applies to contraction centers (right frame). Dilatation centers give rise to compressive surface stress ($f < 0$, bottom row left), leading to measurable deformation of macroscale crystals — for instance the bending of cantilevers as illustrated schematically in the bottom row. Contraction centers induce $f > 0$ and opposite deformation (bottom row right). This connects measurements of surface stress by cantilever bending or by dilatometry to the coupling between adsorption energy and strain.
Reproduced from Ref. [59].

matrix crystal when the solute atom is treated as a misfitting sphere. The step from strain field to energy simply involves integrating the strain energy density that comes from the local distortion of the crystal lattice around the solute atom. The hydrostatic component of that strain can be compressive or tensile, depending on whether the solute locally expands (interstitials or large substitutionals) or contracts (small substitutionals) the matrix (Figure 2, central row). At the surface, adsorbing adatoms which act as centres of expansion (e.g. H on Pd) or of contraction (e.g. Pd on Au) makes the surface stress, respectively, more compressive or more tensile [51,56]. This is illustrated in Figure 2, bottom row.

The Maxwell relation, Eqn 11, immediately links the above-mentioned trends for solute with different misfit strain to sign and magnitude of the coupling, ζ, of the adsorption enthalpy to an externally imposed strain. Continuum mechanics clarifies the origin of this link: whereas the contribution of misfit strain to the energy of adsorption in the absence of external forces may be represented by a volume integral over the local misfit strain energy density, externally imposed deformations generate an extra energy term that is the integral over the product of the local misfit strain and the externally imposed stress [63]. This reasoning is confirmed by a recent atomistic evaluation of the interaction of the local stress fields around adsorbates ('eigenstress'): Atom-by-atom summation of the interaction energy integral reproduces the link between the sign of the misfit stress around adsorbates and the sorption strain coupling strength [18••]. Since the Maxwell relation includes the surface stress, and since surface stress leads to measurable deformation of mm-size or cm-size cantilevers or porous bodies, experiments exploring surface-induced deformation are immediately linked to the atomic scale interactions. Figure 2 illustrates that link.

Conclusion

The results compiled in this article emphasize that chemo-mechanical or electro-chemo-mechanical coupling at the interface of a solid with vacuum, gas or electrolyte can be described by a small set of parameters. Essentially, for each individual process — namely adsorption of a specific atom or ion or exchange of an electron on a specific surface — there exists a sorption–strain or electrocapillary coupling parameter that quantifies both, the impact of the surface process on the stress within the surface and the impact of a surface strain on adsorption enthalpy and electric or chemical potential. These parameters can often be represented as scalars, but low symmetry processes that require the representation by superficial tensors are not uncommon. At the state of the art, various experimental techniques are available for quantifying the coupling. Electron-theoretic density functional theory can also readily quantify these phenomena. The desorption–strain or electrocapillary coupling parameters allow experimentalists and theoreticians to quantitatively compare their results. Major advances in the field may be expected if this opportunity is systematically exploited in future work.

Acknowledgement

This work was supported by the German Research Foundation (DFG), grant We1424/16-1.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Baughman RH, Cui CX, Zakhidov AA, Iqbal Z, Barisci JN, Spinks GM, Wallace GG, Mazzoldi A, De Rossi D, Rinzler AG, Jaschinski O, Roth S, Kertesz M: **Carbon nanotube actuators**. *Science* 1999, **284**:1340-1344.

2. Weissmüller J, Viswanath RN, Kramer D, Zimmer P, Würschum R, Gleiter H: **Charge-induced reversible strain in a metal**. *Science* 2003, **300**:312-315.

3. Boisen A, Thundat T: **Design & fabrication of cantilever array biosensors**. *Mater Today* 2009, **12**:32-38.

4. • Stenner C, Shao L-H, Mameka N, Weissmüller J: **Piezoelectric gold: strong charge-load response in a metal-based hybrid nanomaterial**. *Adv Funct Mater* 2016, **26**:5174-5181.
Illustrates the quantitative equivalence between surface-stress charge and potential–strain coupling by comparing actuation and active strain sensing behavior of macroscopic bodies of nanoporous gold.

5. Karacan CO: **Swelling-induced volumetric strains internal to a stressed coal associated with CO_2 sorption**. *Int J Coal Geol* 2007, **72**:209-220.

6. Diao JK, Gall K, Dunn ML: **Surface-stress-induced phase transformation in metal nanowires**. *Nat Mater* 2003, **2**:656-660.

7. Mameka N, Markmann J, Weissmüller J: **On the impact of capillarity for strength at the nanoscale**. *Nat Commun* 2017, **8**:1976.

8. Gsell M, Jakob P, Menzel D: **Effect of substrate strain on adsorption**. *Science* 1998, **280**:717-720.

9. Schlapka A, Lischka M, Gross A, Kasberger U, Jakob P: **Surface strain versus substrate interaction in heteroepitaxial metal layers: Pt on Ru(0001)**. *Phys Rev Lett* 2003, **91**.

10. •• Kibler LA, El-Aziz AM, Hoyer R, Kolb DM: **Tuning reaction rates by lateral strain in a palladium monolayer**. *Angew Chem Int Ed* 2005, **44**:2080-2084.
A striking demonstration of how strain of a solid surface can substantially change adsorption enthalpy.

11. • Gokhshtein A: **Charge acquirement by an elastically strained electrode**. *Dokl Akad Nauk Sssr* 1969, **187**:601.
This paper was the first to highlight the complementarity between surface-stress charge and potential strain response.

12. • Smetanin M, Kramer D, Mohanan S, Herr U, Weissmüller J: **Response of the potential of a gold electrode to elastic strain**. *Phys Chem Chem Phys* 2009, **11**:9008-9012.
Presents a modern experimental approach for quantifying how the potential of an electrode varies in response to straining.

13. •• Deng Q, Smetanin M, Weissmüller J: **Mechanical modulation of reaction rates in electrocatalysis**. *J Catal* 2014, **309**:351-361.
The first direct and quantitative experimental demonstration that the activity of the surface in heterogeneous catalysis can be modulated by strain in the tangent plane of the catalyst surface.

14. •• Mavrikakis M, Hammer B, Norskov JK: **Effect of strain on the reactivity of metal surfaces**. *Phys Rev Lett* 1998, **81**:2819-2822.
This paper is influential in the field of heterogeneous catalysis with strained surfaces. It outlines the d-band model, rationalizing how strain of a transition metal surfaces shifts the adsorption strength.

15. Feibelman PJ: **First-principles calculations of stress induced by gas adsorption on Pt(111)**. *Phys Rev B* 1997, **56**:2175-2182.

16. Umeno Y, Elsasser C, Meyer B, Gumbsch P, Nothacker M, Weissmüller J, Evers F: **Ab initio study of surface stress response to charging**. *Europhys Lett* 2007, **78**:13001.

17. Sethuraman VA, Vairavapandian D, Lafouresse MC, Adit Maark T, Karan N, Sun S, Bertocci U, Peterson AA, Stafford GR, Guduru PR: **Role of elastic strain on electrocatalysis of oxygen reduction reaction on pt**. *J Phys Chem C* 2015, **119**:19042-19052.

18. Khorshidi A, Violet J, Hashemi J, Peterson AA: **How strain can break the scaling relations of catalysis**. *Nat Catal* 2018, **1**:263.
••
Discusses the coupling between adsorption enthalpy and strain in atomistic theory. Points out that surface sites of low symmetry can have an anisotropic enthalpy–strain coupling; confirms that they sign of the enthalpy strain coupling depends on the sign of the eigenstress.

19. Kramer D, Weissmüller J: **A note on surface stress and surface tension and their interrelation via Shuttleworth's equation and the Lippmann equation**. *Surf Sci* 2007, **601**:3042-3051.
•
A detailed synopsis of the various observations that require a distinction between surface stress and surface tension, along with a critical examination of objections to the concept of surface stress that have been raised in the literature.

20. Cahn JW: **Thermodynamics of solid and fluid surfaces**. In *Interfacial Segregation.* Edited by Johnson WC, Blakely JM. Metals Park, OH: ASM; 1978:3-23.

21. Gor GY, Huber P, Weissmüller J: **Elastocapillarity in nanopores: sorption strain from the actions of surface tension and surface stress**. *Phys Rev Mater* 2018, **2**:086002.
•
Shows that adsorption-induced deformation phenomena which have been discussed in terms of 'solvation pressure' may equivalently be understood as the consequence of surface stress.

22. Gurtin M, Murdoch AI: **A continuum theory of elastic material surfaces**. *Arch Ration Mech Anal* 1975, **57**:291-323.
•
The classic paper on stress and strain at the general, nonuniform and curved surfaces, analyzed from the point of view of solid mechanics.

23. Weissmüller J, Kramer D: **Balance of force at curved solid metal–liquid electrolyte interfaces**. *Langmuir* 2005, **21**:4592-4603.
•
Applies a simplified and less mathematical variant of Gurtin's approach to electrode surfaces which can be electrically charged or which experience adsorption processes. Provides a comprehensive account of the foundations of the theory in the present article.

24. Haiss W: **Surface stress of clean and adsorbate-covered solids**. *Rep Prog Phys* 2001, **64**:591-648.
••
Reviews the mechanics of surfaces with emphasis on electrodes and on atomic scale interactions behind electrocapillary coupling.

25. Weissmüller J: **Electrocapillarity of solids and its impact on heterogeneous catalysis**. In *Electrocatalysis: Theoretical Foundations and Model Experiments. Advances in Electrochemical Science and Engineering.* Edited by Alkire RC, Kibler L, Kolb DM, Lipkowski J. Weinheim, Germany: Wiley-VCH; 2013:163-220.

26. Smetanin M, Viswanath RN, Kramer D, Beckmann D, Koch T, Kibler LA, Kolb DM, Weissmüller J: **Surface stress-charge response of a (111)-textured gold electrode under conditions of weak ion adsorption**. *Langmuir* 2008, **24**:8561-8567.

27. Lafouresse MC, Bertocci U, Beauchamp CR, Stafford GR: **Simultaneous electrochemical and mechanical impedance spectroscopy using cantilever curvature**. *J Electrochem Soc* 2012, **159**:H816-H822.
•
Provides an in-depth description of surface stress measurement by cantilever bending approaches, including original aspects of dynamics.

28. Olivier S, Tréglia G, Saúl A, Willaime F: **Influence of surface stress in the missing row reconstruction of FCC transition metals**. *Surf Sci* 2006, **600**:5131-5135.

29. Barth J, Brune H, Ertl G, Behm R: **Scanning tunneling microscopy observations on the reconstructed Au(111) surface: atomic structure, long-range superstructure, rotational domains, and surface defects**. *Phys Rev B* 1990, **42**:9307.

30. Narasimhan S, Vanderbilt D: **Elastic stress domains and the herringbone reconstruction on Au(111)**. *Phys Rev Lett* 1992, **69**:1564-1567.

31. Men FK, Packard WE, Webb MB: **Si(100) surface under an externally applied stress**. *Phys Rev Lett* 1988, **61**:2469-2471.

32. Min B, Deng X, Pinnaduwage D, Schalek R, Friend C: **Oxygen-induced restructuring with release of gold atoms from Au(111)**. *Phys Rev B* 2005, **72**:121410.

33. Min BK, Alemozafar AR, Biener MM, Biener J, Friend CM: **Reaction of Au(111) with sulfur and oxygen: scanning tunneling microscopic study**. *Top Catal* 2005, **36**:77-90.

34. Marchenko V, Parshin AY: **Elastic properties of crystal surfaces**. *Sov Phys JETP* 1980, **52**:129-131.

35. Alerhand OL, Vanderbilt D, Meade RD, Joannopoulos JD: **Spontaneous formation of stress domains on crystal surfaces**. *Phys Rev Lett* 1988, **61**:1973-1976.

36. Müller P, Saul A: **Elastic effects on surface physics**. *Surf Sci Rep* 2004, **54**:157-258.
•
Reviews the mechanics of surfaces, including adsorption and the stress fields around defects.

37. Li WN, Duan HL, Albe K, Weissmüller J: **Line stress of step edges at crystal surfaces**. *Surf Sci* 2011, **605**:947-957.

38. Wang Y, Weissmüller J, Duan HL: **Mechanics of corrugated surfaces**. *J Mech Phys Solids* 2010, **58**:1552-1566.

39. Deng Q, Gosslar D-H, Smetanin M, Weissmüller J: **Electrocapillary coupling at rough surfaces**. *Phys Chem Chem Phys* 2015, **17**:11725-11731.

40. Vendelbo SB, Elkjær CF, Falsig H, Puspitasari I, Dona P, Mele L, Morana B, Nelissen BJ, van Rijn R, Creemer JF, Kooyman PJ, Helveg S: **Visualization of oscillatory behaviour of pt nanoparticles catalysing co oxidation**. *Nat Mater* 2014, **13**:884.
••
The *in situ* transmission electron microscopy in this work provide a striking illustration of cyclic changes in the surface atomic structure in response to adsorption.

41. Kamiuchi N, Sun K, Aso R, Tane M, Tamaoka T, Yoshida H, Takeda S: **Self-activated surface dynamics in gold catalysts under reaction environments**. *Nat Commun* 2018, **9**:2060.

42. Herring C: **Some theorems on the free energies of crystal surfaces**. *Phys Rev* 1951, **82**:87.
•
A classic paper on how the surface tension of a crystal varies as the function of the crystallographic orientation of the surface normal.

43. Hoppe S, Michl A, Weissmüller J, Müller S: **Ab-initio modeling of electromechanical coupling at Si surfaces**. *J Appl Phys* 2014, **116**:073507.

44. Albina JM, Elsaesser C, Weissmueller J, Gumbsch P, Umeno Y: **Ab initio investigation of surface stress response to charging of transition and noble metals**. *Phys Rev B* 2012, **85**:125118.

45. Michl A, Weissmüller J, Müller S: **Electrocapillary coupling at metal surfaces from first principles: on the impact of excess charge on surface stress and relaxation**. *Langmuir* 2018, **34**:4920-4928.
•
Summarizes the present understanding of how strain affects the electronic and atomic structure of metal surfaces, and how these effects propagate into electrocapillary coupling.

46. Mavrikakis M, Stoltze P, Norskov JK: **Making gold less noble**. *Catal Lett* 2000, **64**:101-106.

47. Deng Q, Gopal V, Weissmüller J: **Less noble or more noble: how strain affects the binding of oxygen on gold**. *Angew Chem Int Ed* 2015, **127**:13173-13177.

48. Weigend F, Weissmüller J, Evers F: **Structural relaxation in charged metal surfaces and cluster ions**. *Small* 2006, **2**:1497-1503.
•
Illustrates how electric charging leads to relaxation at a crystal surface and discusses how this relaxation feeds into the electrocapillary coupling.

49. Umeno Y, Elsaesser C, Meyer B, Gumbsch P, Weimueller J: **Reversible relaxation at charged metal surfaces: an ab initio study**. *EPL (Europhys Lett)* 2008, **84**:13002.

50. Dutta D, Wood BC, Bhide SY, Ayappa KG, Narasimhan S: **Enhanced gas adsorption on graphitic substrates via defects and local curvature: a density functional theory study**. *J Phys Chem C* 2014, **118**:7741-7750.

51. Stafford GR, Bertocci U: **In situ stress and nanogravimetric measurements during underpotential deposition of pd on (111)-textured Au**. *J Phys Chem C* 2009, **113**:261-268.

52. Kolb DM: **Structure studies of metal electrodes by in-situ scanning tunneling microscopy**. *Electrochim Acta* 2000, **45**:2387-2402.

53. Stafford GR, Bertocci U: **In situ stress and nanogravimetric measurements during underpotential deposition of bismuth on (111)-textured Au**. *J Phys Chem B* 2006, **110**:15493-15498.

54. Seo M, Yamazaki M: **Changes in surface stress of gold electrode during underpotential deposition of copper**. *J Solid State Electrochem* 2007, **11**:1365-1373.

55. Tamura K, Wang JX, Adzic RR, Ocko BM: **Kinetics of monolayer bi electrodeposition on Au(111): surface X-ray scattering and current transients**. *J Phys Chem B* 2004, **108**:1992-1998.

56. Viswanath RN, Weissmüller J: **Electrocapillary coupling coefficients for hydrogen electrosorption on palladium**. *Acta Mater* 2013, **61**:6301-6309.

57. Deng Q, Smetanin M, Weissmüller J: **Dynamic electro-chemo-mechanical analysis**. *Meet Abstr* 2012, **MA2012-01**:959.

58. Weissmüller J, Viswanath RN, Kibler LA, Kolb DM: **Impact of surface mechanics on the reactivity of electrodes**. *Phys Chem Chem Phys* 2011, **13**:2114-2117.

59. Weissmüller J: **Mechanochemistry breaks with expectations**. *Nat Catal* 2018, **1**:238-239.

60. • Mott NF, Nabarro FRN: **An attempt to estimate the degree of precipitation hardening, with a simple model**. *Proc Phys Soc* 1940, **52**:86.

A simple demonstration on how the local stresses around centers of compression or dilatation in a solid are analyzed in continuum mechanics.

61. Eshelby JD: **The determination of the elastic field of an ellipsoidal inclusion, and related problems**. *Proc R Soc Lond Ser A Math Phys Sci* 1957, **241**:376.

62. Miedema AR, de Châtel PF, de Boer FR: **Cohesion in alloys — fundamentals of a semi-empirical model**. *Physica B+C* 1980, **100**:1-28.

63. Fratzl P, Penrose O, Lebowitz JL: **Modeling of phase separation in alloys with coherent elastic misfit**. *J Stat Phys* 1999, **95**:1429-1503.