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The X-Mechanics toolbox to solve Y-Mechanics problems

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Abstract

The philosophy of "X-Mechanics" is introduced, and a few examples of its application by the author and collaborators to study "Y-Mechanics" problems are presented.

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1. Introduction

Mechanics originally referred to Classical Mechanics, following from Newton's Philosophiæ Naturalis Principia Mathematica, which was developed to explain the motions of macroscopic bodies subject to external forces. The evolution of physical sciences led to the discovery of atoms as well as notions about heat, which drove the field of thermodynamics, whose fundamental underpinnings were captured by the theory of Statistical Mechanics. The failure of Classical Mechanics to describe the observed discrete states of electrons in atoms then gave rise to the creation of Quantum Mechanics. The classical mechanics of discrete bodies was also transformed into the mechanics of continuous media leading to the domain of Continuum Mechanics. The term "Mechanics" has thus persisted across the centuries as a basic term for understanding the physics of the natural world.

In recent years, the rapid development of computational power has enabled simulation methods such as Molecular Dynamics to investigate the collective behavior of many atoms interacting through non-local, non-linear many-body

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interatomic potentials. This domain is thus a mixture of Classical, Quantum, and Statistical Mechanics, but warrants its own name, Atomistic Mechanics (with an affiliated field of Nano-Mechanics). In the same era, it has become recognized that the collective behavior of complex non-linear systems can give rise to phenomena on length scales far above the atomic scale, but below macroscopic scales, and this domain has been generally termed "the mesoscale", with an associated theoretical framework of Mesoscale Mechanics (or dynamics). Finally, recognizing that many important physical problems involve phenomena occurring simultaneously over multiple scales, a new domain of Multiscale Mechanics has evolved to bridge length and time scales between different approaches.

As the field of Mechanics has diversified over the last fifty years, researchers have become increasingly specialized in specific domains of Mechanics. The physics student typically learns and applies Quantum Mechanics and Statistical Mechanics. The mechanical engineering student typically learns and applies Continuum Mechanics. Materials Scientists tend to sit in the middle, with an emphasis on Atomistic Mechanics. Domains from Physics to Mechanical Engineering engage in Mesoscale Mechanics for particular problems, such as pattern formation and dislocation dynamics, respectively. The historical connections among these Mechanics domains tend to have been lost as individual researchers have delved deeply into each important specific domain of interest.

The rise of "the nanoscale" – referring to phenomena above the scale of a few atoms but far below the usual scale of continua – has started to reverse the trend of specialization. Driven by interesting fundamental physical problems and by important potential applications, physicists, chemists, materials scientists, and engineers (mechanical, civil, electrical) have started to converge at the nanoscale. This convergence is bringing these fields of Mechanics back together, and generating greater interactions among domain-specific researchers. The combined power of Quantum + Statistical + Atomistic + Mesoscale + Continuum + Multiscale Mechanics is now being realized in the research community.

2. X-Mechanics: what and why

Following the above trends, it seems valuable for the community of researchers to become more unified in their applications of Mechanics across its full scope. To create a sense of this unification, I have suggested the term X-Mechanics, where X is the variable selected from among all the existing domains of Mechanics outlined above. So, X is meant to represent any/all of the domains (Quantum, Statistical, Atomistic, Mesoscale, Continuum, Multiscale) with the purposes of encouraging researchers (i) to view Mechanics holistically as a modern toolbox for research and (ii) to become fluent and proficient with this entire Mechanics toolbox, as a means for accelerating research progress.

The X-Mechanics philosophy is to treat all the domains of Mechanics like a real toolbox. To fix (solve) a problem, one usually needs a particular tool. To solve a multifaceted problem requires a set of tools, and the ability to use those tools properly. Without the right tools, the problem becomes extremely difficult or even impossible. The modern Mechanician must thus learn to use all the tools in the X-Mechanics toolbox. Since these tools are based on fundamental physics and mathematics, using the tools is not quite sufficient – the modern Mechanician should, at a minimum, understand the key principles underlying each tool so that the tool can be applied appropriately and accurately when needed.

An advantage of adopting the X-Mechanics philosophy is that technical problems can be chosen based on their importance rather than on what set of tools the researcher has available. With X-Mechanics, all the tools are available and ready for use. Of course, individual researchers will have particular strengths and interests in one or two domains, and will choose problems that are best tackled using these strengths. However, we cannot always guess in advance what is needed to solve a problem, and often it is valuable to be able to move easily from one tool to another as the need arises when tackling a challenging problem.

Another advantage of adopting the X-Mechanics philosophy is that the range of problems that can be tackled is rapidly increasing and broadening, and requires a multidisciplinary approach. For Mechanics, we are now in a world of Y-Mechanics problems, i.e. Nano-Mechanics, Bio-Mechanics, Chemo-Mechanics, or Electro-Mechanics with Y the second variable. The community is now finding many problems that are normally studied by biologists, chemists, materials scientists, or solid-state physics/electronics where the traditional "Mechanics" associated with Continuum Mechanics can play a central role. The integration of X-Mechanics into the solutions of Y-Mechanics problems is exciting, challenging, and potentially transformative in the Y fields. The X-Mechanician must team up with the bio-,

chemo-, electro- experts, but the combined expertise and points of view is already showing benefits in research progress.

The interplay between X = Continuum and X = Atomistic domains of Mechanics, which arises frequently in the Y = Nano domain, highlights some general advantages of an X-Mechanics approach. Both Continuum and Atomistic use the concept of "work". Discrete atomistics evaluates work as forces acting over displacements of particles while continuum mechanics evaluates work as stresses acting over strains of material elements. The two approaches are unified through the connections of (i) atomistic displacements and local strains and (ii) atomistic forces and continuum stresses. Strain and displacement are basic kinematic concepts, and the connection is easily made since Continuum Solid Mechanics is based on a Lagrangian description of the motion of material points. The connection between stresses and forces, or continuum-level and atomistic-level measures of stress, is more subtle and has been the topic of research in recent years[1]. For both stress and strain, the subtleties arise when the gradients of deformation in a material are substantial over atomistic scales. Then, the non-locality of interatomic bonding becomes important, and the continuum fields are not sufficient smooth to justify the continuum assumption of locality. High deformation gradients arise around defects in crystals, for instance, suggesting that X = Continuum has limited utility for defects (e.g. dislocations, solutes, crack tips, grain boundaries). However, continuum mechanics still provides a key concept for atomistic defects, namely the idea of a configurational force on a defect. The atomistic representation of a defect includes the self-field of the defect itself, which does not contribute to the configurational force. Standard molecular statics studies can only investigate equilibrium configurations of a defect. Thus, obtaining the force on a defect is challenging within atomistics. In contrast, the use of continuum elasticity, based on atomistically-derived eigenstrains or conservation integrals that can be evaluated at the atomic scale, permits a cleaner evaluation of the forces on the atomistic defect. Atomistic mechanics does resolve the singularities at the defect (dislocation core, crack tip) that arise in the continuum theory. Phenomena associated with the resolution of the singularity can play an important role in governing material properties by establishing the critical configurational force necessary to cause motion or reaction of the defect. Two examples are the resolution of (i) the dislocation core structure, which controls the Peierls stress required to move the dislocation and controls the energy barrier for screw dislocation cross-slip, and (ii) the crack tip structure, which controls the dislocation emission and cleavage phenomena that dictate intrinsic ductility of a material. In the above context, the combination of X = Continuum and X = Atomistic is seen to be highly beneficial to advance fundamental understanding of deformation mechanisms.

There are already many examples of the application of X-Mechanics to Y-Mechanics problems. Thus, it is only the terminology here that is, perhaps, new. But it is often valuable to have a means of succinctly describing a wide-ranging concept. It is also valuable to present specific examples to illustrate how the concept can implemented in practice. While examples could be culled from the recent literature, researchers have not framed the work within the scope of the X-Mechanics/Y-Mechanics paradigm because the paradigm is really just an early-stage terminology. Thus, to illustrate the concept, I have chosen several efforts from the work of my group, as described below, that show what can be achieved by adopting the holistic X-Mechanics perspective.

3. Y = Nano: Dynamic Strain Aging in Al-Mg

Macroscopically, dynamic strain aging (DSA) refers to the time-dependent change in strength of a material, usually a metal alloy. Under normal application conditions (moderate temperatures and slow strain rates 10^{-6}–10^{-2}/s), the plastic flow strength of a metal alloy is naturally dependent on temperature and the macroscopic applied strain rate, but not explicitly dependent on time. Rate dependence is normally due to thermally-activated processes, so that temperature and strain rate are inter-related, while applied driving stresses usually accelerate the rate of plastic flow. The strain-rate-sensitivity $m=d(\ln(\sigma))/d(\ln(\dot{\epsilon}))$ is then positive, $m>0$. In some materials, however, the flow strength changes with time. If the strength increases with time, then the material exhibits "negative strain rate sensitivity (N-SRS)", $m<0$, with the plastic flow stress increasing as the strain rate decreases, or as the temperature increases. Negative strain rate sensitivity thus gives rise to dynamic instabilities in materials, manifest as serrations in a stress-strain curve and localized Portevin-LeChatelier bands of intense deformation occurring throughout the material. Of even greater importance is that the ductility of a material with $m<0$ is reduced, leading to challenges in fabricating components from these materials. The origins of DSA and N-SRS have generally been understood as related to the time-dependent diffusion of solutes around dislocations. However, no quantitative or predictive models have been

developed in spite of the importance of the phenomenon in industrial alloys such as the Al-5xxx series alloys (Al strengthened by randomly distributed Mg solutes dissolved in the Al matrix).

We tackled this problem using what I can now identify as the X-Mechanics toolbox. The systematic flow of the study is shown in Figure 1[2]. X=Quantum calculations were used, within an X=Multiscale framework, to compute the interaction energies for Mg solutes at all locations around an edge dislocation in Al[3]. X=Atomistic and X=Statistical calculations were used by Picu to compute the migration barrier of Mg across the core of the dislocation[4]. The cross-core diffusion mechanism turns out to be the crucial new piece of physics in the problem. X=Atomistic and X=Continuum was used to determine how the cross-core diffusion would strengthen mobile dislocations[5]. X=Mesoscale was used by Picu to determine how changes in "line energy" (due to cross-core diffusion) would influence forest strengthening[6]. X=Continuum and X=Statistical were then used to develop the time/rate/temperature-dependent constitutive law when these mechanisms are operating[7,8]. This model was unsuitable for standard continuum numerical calculations, and so X=Continuum was used to create a constitutive model suitable for Finite-Element calculations[9]. X=Continuum studies on macroscopic tensile samples then showed the negative rate sensitivity and the loss of ductility due to the dynamic strain aging, in good agreement with experimental observations (especially the temperature range over which ductility is reduced)[2].

1. *X = Quantum + Multiscale:* Energies of Mg atoms around the Al edge core

2. *X = Atomistic + Statistical:* Migration barrier for Mg diffusion across core:

3. *X = Atomistic + Continuum:* Strengthening of mobile dislocations by cross-core diffusion

4. *X = Mesoscale:* Strengthening of forest junctions by cross-core diffusion

5. *X = Continuum + Statistical:* Rate/temperature/time dependent constitutive law

$$\dot{\varepsilon}(t) = \int_{-\infty}^{t} dt_p \, \dot{\varepsilon}(t_p) \nu(\tau(t), t - t_p) e^{-\int_{t_p}^{t} \nu(\tau(t'), t' - t_p) dt'}$$

6. *X = Continuum:* Reformulation of constitutive law usable for Finite Elements

$$\dot{\varepsilon}^p = \frac{b}{\sqrt{\rho_f}} \int_0^{\tau_c} \nu(\tau, \tau_a, \tau_{af}) \rho(\tau_a) d\tau_a$$

7. *X = Continuum:* Finite element computations of stress-strain curves showing loss of ductility due to DSA
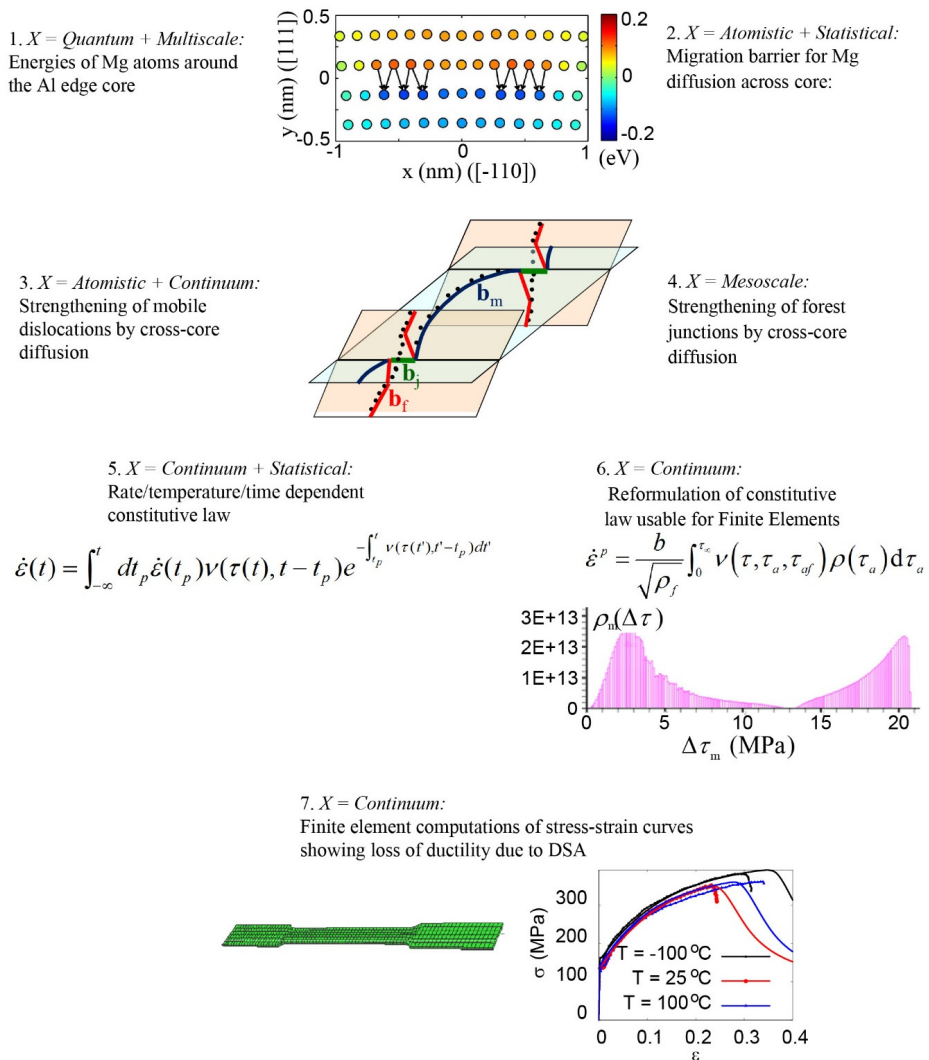
Fig. 1. Flow of application of X-Mechanics tools to predict dynamic strain aging and reduced ductility in Al-4%Mg at room temperature [see Ref. 2 for details].

It is valuable to point out, however, that the actual progression of the work did not follow the nice path outlined above. As noted, Picu had earlier evaluated a couple of aspects of the problem[4,6]. We then understood the key role of the cross-core diffusion and developed the model for aging of mobile dislocations[5]. We then developed the constitutive model, and found that m<0 could not be obtained from mobile aging alone[7], which would violate thermodynamics; this was also concluded (less obviously) by Hahner some time earlier[10]. We then returned to mechanisms, and introduced Picu's concept for the time-dependent forest strengthening[6], and introduced this into the constitutive model. Continuum level predictions of the stress-strain curves were then performed using the atomistic energies obtained with an EAM potential for Al-Mg, and the results were quantitatively inaccurate. We thus returned to the X=Quantum scale to develop more-accurate inputs for the solute/dislocation interaction energies[3], which then brought the entire model into good agreement with experiments[2].

Overall, it was essential to involve nearly all the X-Mechanics tools at some stage of the model development to achieve (nearly) parameter-free predictions of the dynamic strain aging behavior. The model, being based on underlying physical mechanisms and having a derived structure, also revealed other interesting features consistent with experiments. While one could envision ad-hoc constitutive models with increasing complexity being capable of achieving similar macroscopic predictions, the X-Mechanics model provides a real base for material design and material evolution, since the macroscopic observations/behavior are fully coupled to the atomistic phenomena that determine the energy, time, and temperature scales of the problem.

4. Y = Chemo: Stress-Controlled Catalysis

This work was initiated with the idea that application of stress to catalytically-active materials could shift various adsorption, desorption, and/or dissociation energies (see schematic of Figure 2) sufficiently to have a quantitative impact on catalytic reaction rates. Using X=Continuum thinking, we identified reactions at surface steps, where stress concentrations increase the local stress above the nominal "applied" value, as promising candidates for study.

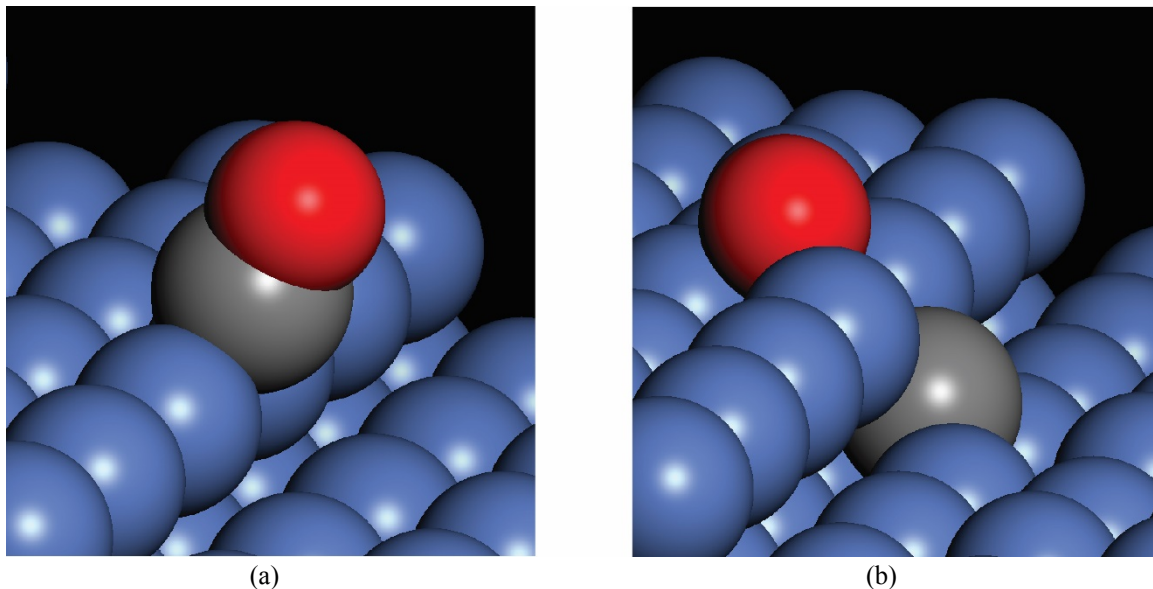(a)   (b)

Fig. 2. Dissociation reaction of CO dissociating into C and O at the (211) step of an fcc metal catalyst. (a) reactant state ; (b) product state.

The effect of strain on the binding of molecules to late transition metal surfaces has been well-understood as an electronic effect. Tensile strain narrows the electronic d-band, leading to an upward shift of the center of the d-band, and enabling stronger binding of adsorbates; thus, tensile strain increases the binding (Figure 3). This effect has been demonstrated using X=Quantum studies on flat surfaces of various metals, starting with work of Mavrikakis[11].

We used X=Continuum to develop the boundary conditions for X=Quantum studies of adsorbate binding at steps on metal surfaces[12]. The results showed that, in some cases, tensile strain would decrease the binding (weaker binding),

in distinct contrast to the results on flat surfaces (Figure 3). To understand the origin of the reverse trend in binding vs. strain, we used X=Continuum ideas to partition the binding energy into an "electronic" and "mechanical" contribution (Figure 4). The "electronic" contribution is computed without allowing the substrate ions to relax upon adsorbate binding and the "mechanical" contribution is computed as the remaining energy upon relaxation (deforming of the underlying substrate). Subtracting out the quantities at zero applied strains, the remaining effects due to the applied strain are, in many cases, dominated by the "mechanical" contribution (Figure 5). That is, the strain-dependent binding energy is not controlled by the standard electronic d-band effect found for flat surfaces.
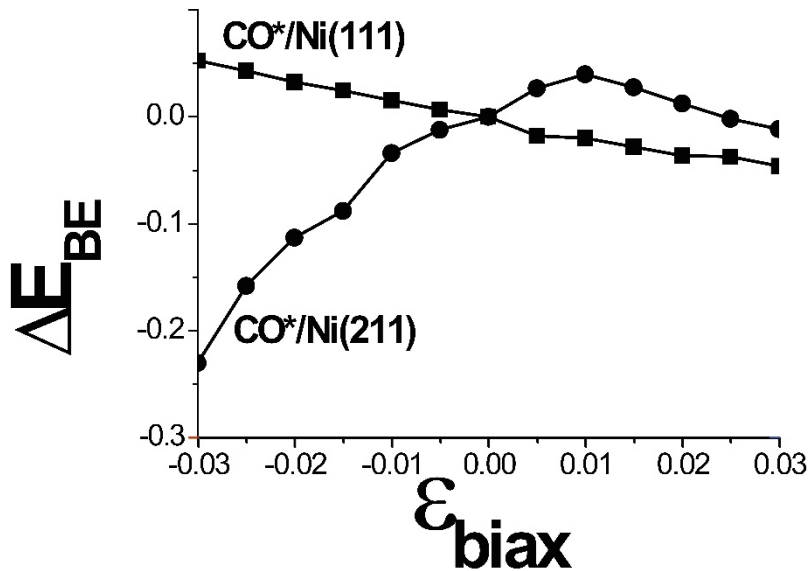
Fig. 3. Binding energy of CO on Ni, as a function of strain as computed using X = Quantum (density functional theory), on the flat (111) surface [binding becomes stronger (more negative energy) under tensile strain] and on the (211) stepped surface [binding becomes weaker (less negative energy) under tensile strain].
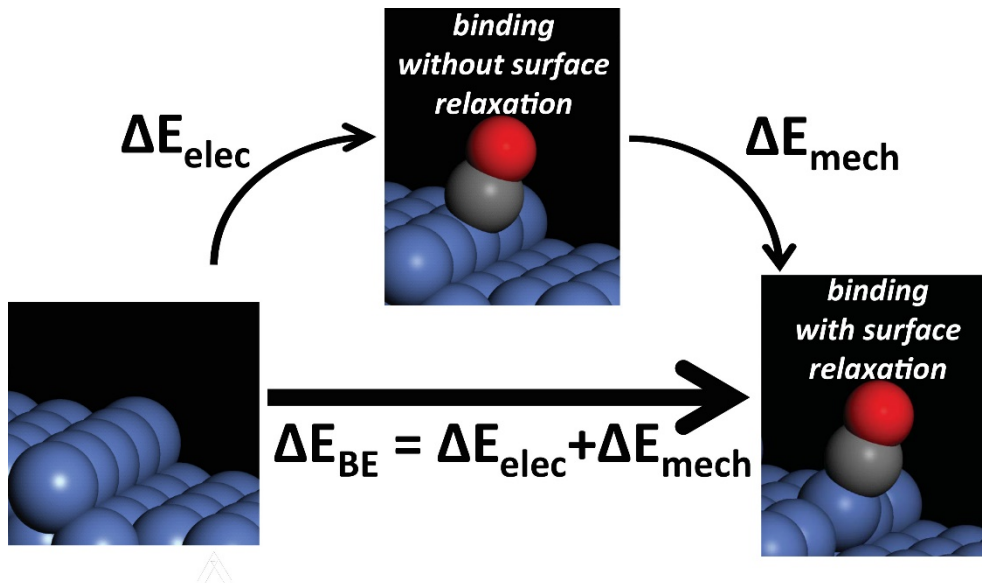

Fig. 4. Decomposition of the total binding energy into "electronic" and "mechanical" contributions.
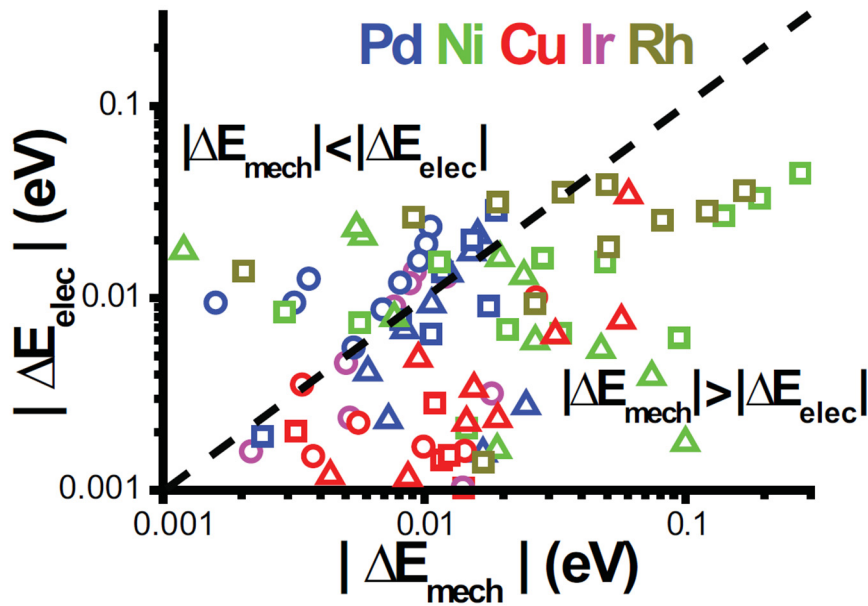
Fig. 5. "Electronic" vs. "Mechanical" contribution to binding energy of a CO molecule on various (211) stepped metal surfaces over a range of applied substrate stresses/strains. The dashed line delineates the regimes where mechanical or electronic contributions dominate; mechanical contributions are equal to or larger than electronic contributions for most cases (adapted from Ref. 12 with permission of the Nature Publishing Group).

The origin of the "mechanical" contribution emerges from application of standard X=Continuum concepts. When the substrate is strained without the adsorbate, there are stresses and strains in the substrate and associated stored mechanical energy in the substrate. When an adsorbate is introduced onto the surface of an unstrained substrate, the adsorbate itself causes structural deformations (stress and strains) in the substrate itself. Therefore, when the adsorbate is introduced onto a strained substrate, there is a mechanical interaction energy due to the work done by the adsorbate-induced strains $\epsilon_{ij}^{ads}(x)$ against the applied substrate stresses σ_{ij}^{app}. Within elasticity theory (X = Continuum), this interaction energy is simply

$$\Delta E_{mech} = \int_{V_{substrate}} \varepsilon_{ij}^{ads}(\vec{x})\sigma_{ij}^{app}(\vec{x})\,dV$$

This relationship rationalizes the X=Quantum computations, in particular predicting that when the adsorbate induces tensile strains of the substrate atoms the mechanical interaction energy will be negative (lowering the energy) under a compressive applied strain. The elasticity theory also shows that this energy change is distributed through the strained substrate around and underneath the adsorbate, and is not localized to the adsorbate. X=Quantum computations performed while constraining more and more ions in the system show that the "mechanical" contribution becomes smaller, and vanishes when all ions are constrained not to relax[12].

The ability of applied stress to significantly alter catalytic activity was demonstrated for the particular reaction of methanation on a Ni catalyst. The key step in this reaction is the dissociation of the CO molecule on the Ni surface, occurring at steps (see Figure 2). The absorption energy of CO on the step is dominated by the mechanical contribution while the absorption energy of the individual C and O elsewhere on the surface has a larger electronic contribution. The dissociation energy, which is the difference in these two absorption energies, thus shows a very strong effect of stress. The dissociation energy can be changed by ~0.3 eV by a tensile stress of 3% on the Ni surface. This is sufficient to move the activity of the Ni catalyst to the peak activity (the peak of the so-called Volcano plot)[12].

This example involves only two levels of X-Mechanics, but at the two different ends of the overall spectrum. In many problems, the combination of X=Quantum + X=Continuum or X=Atomistic + X=Continuum is very powerful as a means of understanding mechanics problems across various domains. Furthermore, many research efforts at the nanoscale have now established the usefulness of linear elasticity theory (X=Continuum) at very small scales. The theory may need to be augmented by additional terms, due to surface effects etc., but remains a very robust framework for understanding phenomena qualitatively and, very often, quantitatively.

As an example related to the present case of catalysis, Figure 6 shows the in-plane surface strains of a 5nm core-shell nanoparticle (inner shell = $Cu_{50}Pt_{50}$ alloy; outer shell = 1 nm Pt) as computed X=Atomistics (molecular statics with Cu-Pt EAM interatomic potentials) and using X=Continuum[13]. The X=Continuum model is simply linear elastic finite elements augmented by a surface constitutive model introduced by Gurtin and Murdoch[14], with all parameters calibrated to the EAM potential. The continuum model makes excellent predictions of the surface strains in middle of the facets (the theory does not include any edge or vertex effects), even though the theory is only linear elasticity and is being applied at the nanometer scale[13]. This example is not of practical use because it is easy to perform the X=Atomistic studies, but validation of the X=Continuum model shows that it can be executed using input from experiments or X=Quantum studies for any desired core and shell materials that maintain interface coherency. And the FE model can easily be used to then study effects of size and shape of the nanoparticles to tune the surface strains so as to optimize catalytic activity, as discussed in Ref. 13.
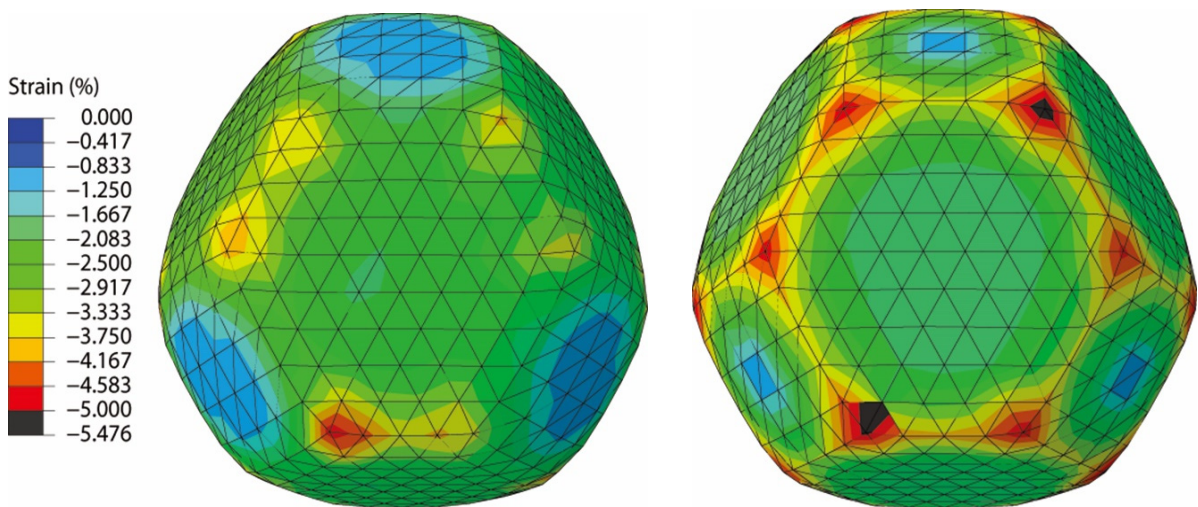

Fig. 6. In-plane biaxial surface strains for a truncated-octahedral CuPt core – Pt shell 5nm nanoparticle, as computed using (left) X=Continuum (linear elastic FEM) and (right) X=Atomistic (molecular statics). The strains on the particle faces are predicted well by the FEM even though the particle diameter is only 5nm. (adapted from Ref. 12 with permission from ACS Publishing).

5. Summary Remarks

The purpose of this article is to suggest that the general "Mechanics" community embrace the X-Mechanics philosophy. Training of PhD students in individual disciplines could, and increasingly does, include the teaching of non-traditional X-Mechanics topics. The natural examples are the teaching of X=Quantum and X=Statistic to Mechanical Engineering students and the teaching of X=Continuum to Physics students, beyond the basic continuum understanding typically gained by students in Physics. Concepts in the Continuum Mechanics of Defects are especially important for problems in the nanoscale domain.

Whether the actual term X-Mechanics is adopted is irrelevant. Any shorthand terminology that captures the philosophy of a Mechanics toolbox that spans from Quantum to Continuum could be used. The important goal is to push our communities toward a broader scope of "Mechanics" expertise. Then, research is selected not by one's small toolbox but rather by the value of the research problem itself, using the entire X-Mechanics toolbox as necessary to

solve the problem. This thinking may have a particularly "Engineering" flavor – the driving force being research aimed at solving technological problems, as opposed to uncovering new fundamental knowledge about the complex world around us. But, society is increasingly hoping and demanding that the Science and Engineering communities will bring forth solutions to the great challenges facing the world today.

Acknowledgements

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