A perspective on multi-scale simulation: Toward understanding water-silica

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Abstract. We discuss the conceptual and practical developments that evolved over the past seven-plus years as our multi-disciplinary team took on the challenge of understanding a single complex system – water and silica – through multi-scale modeling and simulation. The discussion provides the context for the ten contributions, from various groupings of the team, that make up this coordinated special issue. In the evolution of our project, we have come to appreciate the need for a framework that essentially defines the intellectual basis of computational science. We have found that the usual utilitarian notion of simulation is lacking a conceptual counterpart: by itself, it does not address the scientific challenge of analyzing complex phenomena, such as chemo-mechanical processes, across various length scales. The problem of water and silica is prototypical with regard to many complex systems of current interest. In them, the effects of chemical activity and dynamical stress are involved simultaneously and essentially. This essential dependence presents opportunities for a multi-scale strategy that combines quantum and classical methods of simulation. As often is the case with "obvious" approaches, one encounters many subtle aspects. We summarize the issues we have encountered, thus laying the ground work for the detailed topical papers that follow.

Keywords: multi-scale, simulation, silica

1. Introduction

We are concerned with chemo-mechanical processes, that is, processes in which system evolution depends critically upon concurrent chemical activity and mechanical strain. Why water and silica? A simple reason is their importance – over 70% of earth's surface is covered by water while the crust is dominated by silica (rocks containing SiO_n). A more technical reason is that the water–silica interaction is ubiquitous and fundamental in many physical and chemical phenomena that occur in areas as diverse as geoscience to glass technology and in many other areas of application [1–4] (Figure 1).

Within geoscience, the chemo-mechanical phenomenon of hydrolytic weakening of silica has been a classic issue ever since the 1960s [5]; to date hydrolysis of SiO_2

Figure 1. Water (Dihydrogen Oxide, H_2O) is a truly remarkable chemical compound, fundamental to life on Earth. Earth is the only planet in the Solar System where the present surface temperature and pressure allow the three forms of water, solid (ice), liquid (ocean), and gas (water vapor condensing in clouds) to exist simultaneously. Water in one of these forms accounts for everything visible in this view of Earth from space looking north at the Bering Sea and the coast of Alaska, USA, around Bristol Bay. Water World Credit: STS-45 Crew, NASA.

surfaces continues to be studied. For example, water molecules are known to be potentially invasive on silica surfaces and even inside bulk silica through dissociation and breaking of Si–O–Si bonds to form Si–OH hydroxyl groups. This bond breaking and re-formation process, which in essence reverses the sol-gel process [6], sometimes can penetrate to surface sub-layers and further damage the material especially when under external stress. Moreover, because silica is also a popular substrate choice for film growth or coatings, the degree of surface hydroxylation can influence a broad range of such processes.

Extensive efforts have been made to study absorption, diffusion, and penetration of water molecules on SiO_2 surfaces experimentally [7–20] and computationally [21–33]. These studies have yielded substantial data that enable understanding of the water-silica interaction at both macroscopic and microscopic levels. Besides extended systems, the study of such phenomena in nano-scale structures is yielding new insights. Modern techniques allow fabrication and investigations of silica nano-particles [34–46], nano-wires [47, 48], nano-tubes [49], nano-belts [50], and thin films of nanometer thickness [51, 52], as well as composite materials that consist of nano-silica objects [39, 40, 44, 53].

A notable trend which parallels the fundamental interest in silica–water systems is the rapid growth of computational research. In materials physics and chemistry research, atomistic and/or electronic level calculations have achieved significant success in the studies of silica systems, particularly since the 1990s. *Ab initio* quantum calculations have provided detailed information about interactions between water and crystalline surfaces such as quartz and cristobalites, as well as interactions in water–SiO_2 clusters [26, 27, 31, 54]. Classical molecular dynamics (MD) simulations on amorphous silica have provided statistical information [22, 23, 25, 55]. More recently, multi-scale simulation methods [30, 32, 56] that combine quantum and classical descriptions also have been developed and used to treat amorphous silica.

Because the amorphous SiO_2 network has a complicated, irregular character, it is not yet possible to perform a first-principles electronic structure calculations on

meaningfully sized samples ($\geq 10^3$ atoms) sufficient to represent a disordered silica surface properly. (The problem actually is more severe, since systematic comparison with ordered surfaces must be done even-handedly also.) Cleverness can help but has limits. β-cristobalite [27] or small clusters [26] sometimes are used to imitate the local environment of silica surfaces. However, these approaches lack a complete picture of the water-silica interaction. Experiments provide data averaged over the entire surface, which is sensitive to the type of sample used [7]. Calculations cannot be expected to reproduce these numbers from a few limited models. Therefore, a hybrid quantum and classical treatment is not only superior to conventional approaches but, in fact, inescapable.

2. An intellectual framework

The foregoing discussions deliberately emphasize a utilitarian or *instrumental* view of computational materials. Put simply, the instrumental view holds that there is no computational science, only the task of solving a set of equations prescribed by the researcher. The entire intellectual content of the description is conceived as being contained in the equations. In this view, computational approaches are viewed as a means to get otherwise inaccessible results. A particular approach is the consequence of compromises between expected levels of realism (as judged by the researcher) versus computational affordability.

We have come to realize that the instrumental viewpoint can introduce limitations of analysis and design of computational studies because it does not stress enough the intellectual aspects of computational modeling. It fails as a foundation for formulating better approaches and for critiquing existing ones. A counter-example to the instrumental view is any computational study in which plausible, thoughtful, utilitarian assumptions led to un-expected insights derived from the simulation results. Though not historians of science, we suspect that the utilitarian viewpoint arose from two sources, the necessity to validate computational science in the face of skepticism from experimenters and purist theorists, and a distaste by purist scientists for anything smacking of engineering. Today one usually encounters advocacy of the instrumental view as a camouflage adopted by opponents to computation in the competition for resources. Since many physical scientists and engineers are impatient with philosophical discussion, we ask the reader's forbearance. The outcome of the following discussion is a disciplined way to formulate useful computational science.

To articulate a useful intellectual basis for computational science, we believe a proper framework must be *intrinsically independent* of discipline (materials, subatomic particles, astronomy, manufacturing, etc.). This stipulation simply makes explicit the parallel with conventional theory and experiment. Reflection on the emergence of computational science suggest a focus upon clear distinctions among *Theory*, *Modeling*, and *Simulation* in the following sense.

A *Theory* is a set of axioms and interpretative procedures that constitute a mathematical description of the natural world. That description provides predictions about some domain of experimentally measurable (at least in principle) quantities. Familiar examples in the present context include non-relativistic Classical Mechanics, Continuum Mechanics, and non-relativistic Quantum Mechanics. A characteristic of a *Theory* is that it is general about physical systems, other than assuming their existence.

Both Classical Mechanics and Quantum Mechanics presume the existence of particles and assemblies (e.g. springs). Continuum Mechanics presumes the existence of matter distributions.

A *Model* is a prescribed physical description of a real-world system or class of systems formulated within the concepts of a *Theory*. For example, within Newtonian CM *Theory*, the task of predicting the behavior of a solid by tracking the motions of its constituents might be *model*ed as a collection of structure-less particles, called "atoms", that interact by a prescribed potential according to Newton's equations of motion. Clearly the "atoms" bear some definite relationship to the atoms of the periodic table but they are models: no electrons, no nuclear structure, no spin. The interatomic potential presumably bears some relationship to a classical limit of the QM energetics that describes the solid binding, but the potential *models* those energetics in order to escape the details of QM.

A *Simulation* is the computational realization of a particular *model*. Ordinary MD, for example, is a set of algorithms and rules (e.g. Gear predictor–corrector, periodic boundary conditions, number of particles, etc.) for reliable, refinable (in the sense of precision) calculation of the properties of Newtonian models. Though the term is not commonly applied to the electronic structure calculations of quantum chemistry and materials physics, in this framework such calculations are *Simulations*: they take a model (molecule or material with nuclei fixed in space, plus a prescribed QM approximation) and compute its consequences by a set of algorithms and rules (e.g. basis sets, pseudo-potentials, boundary conditions, etc.).

Improvements in the quality and reliability of computed results are *separable* in this framework: they can occur in two completely distinct ways. One is to adopt a more refined *Model*, either by choosing a more refined *Theory* or by adopting a more refined physical description of the real-world class of systems or both. An example within Newtonian CM models of materials would be the adoption of deformable ions instead of point particles or replacement of a pair potential by a three-body potential. *Independently*, the *Simulation* may be improved for a fixed model. An example, again within treatment of Newtonian CM models, might be the use of a better thermostat or finer time-step mesh.

Complementary to *separable* improvement is the feature of *fidelity*. The *Theory* → *Modeling* → *Simulation* framework explicitly disallows the exploitation of offsetting errors by different categories. What is done downstream must not offset limitations implicit in the choices upstream. The *Model* must not "fix" the *Theory* by reintroducing features not in the theory. The algorithms and rules in the *Simulation* must not offset the intrinsic limits of the *Model* being treated. In this regard, we disagree with the concept and vocabulary of the late John Pople, who originally used the term "a theory", and, later "a model" to describe what in our framework would be viewed as a combination of model and simulation that had a craftily selected set of offsetting errors [57].

Because separability of refinement is coupled with fidelity, the *Theory* → *Modeling* → *Simulation* framework explicitly supports systematic, quantitative exploration of the effects of empiricism. Convenient empirical assumptions can be replaced by more realistic ones and the consequences quantified. Moreover, the appraisal of computed data by visualization techniques is disciplined by explicit knowledge of the chain of relationships and assumptions contained in the *Model* and the *Simulation*.

3. Multi-scale modeling and simulation

To this point we have not mentioned the multi-scale aspects of theory, modeling and simulation explicitly. For materials science, this is an issue of the desired level of fundamental understanding. Consider the case of *dry* brittle fracture of silica which, in contrast to fracture in ductile materials, is abrupt and rapid. Early theoretical efforts based on the work of Griffith predicted the mechanical properties of materials with sharp cracks [58–63]. Such methods give the energetics of the macroscopic fracture event, but provide no description of atomic-level processes. Consequently, classical Newtonian atomistic models simulated by MD became the approach of choice [64–71]. Though useful in providing qualitative insight into the nature of crack propagation and the accompanying atomic rearrangement mechanisms, the limitations of computing power imposed by then-current computer platforms meant that typical MD simulations (consisting of 1,000–100,000 atoms) could not account fully for the long-range nature of stress fields around the tip of a crack. In other words, the spatial or temporal scales governing the stress fields are inaccessible to typical MD calculations. Notice that this can be viewed as a *Simulation* limitation, not a *Model* limitation. However, a more clever *Model* might be helpful in circumventing the *Simulation* limitations. On the other hand, the inability to handle chemistry – bond breaking (and formation) – in these calculations is a *Model* limitation.

Development of multi-scale models and the corresponding simulations is a direct consequence of these *Model* limitations. While the studies presented in this collection focus on materials failure, such multi-scale strategies are applicable in a wide variety of physical problems. In the *Theory* → *Modeling* → *Simulation* framework, a multi-scale model can be defined as one in which more than one theory is incorporated, each corresponding to one of several physically important scales involved in the model. For materials failure, the most critical is the length scale of chemical bond formation and rupture. Putting aside for a moment the question of how to determine and use the proper scale length, we ask, which theory? Of the available theories, only QM can provide an adequate description, but which QM? In principle, it is the time-dependent Schrödinger equation for *all* the nuclei and *all* the electrons. A brief survey of the literature is sufficient to conclude that adopting time-dependent QM would be overkill in most cases (except for such quantum solids as H_2, He, and Ne, QM dynamics is essentially irrelevant for aggregates) and prohibitively costly in any event. So we appeal to the model of electronic structure calculations, namely ground state QM and the Born–Oppenheimer approximation, to provide a *potential surface* (or *force field*) in which the nuclei move.

We now have a combination of two theories, QM to generate the forces, Newtonian CM for the dynamics, but *no* invocation of multi-scaling. In principle the entire system would be modeled with this combination of theoretical constructs as the *Theory*. Add the physical systems and the *Model* results. Add further MD, for example, and there is a *Simulation*. For real materials, such a *Model* and *Simulation* is intractable computationally and, again, overkill. Why do QM, which is computationally demanding, in a part of the system in which no significant chemical activity is occurring?

Multi-scale modeling introduces the exploitation of physically and chemically significant length scales. *IF* we can restrict the QM contribution to the *Model* to a

relatively small fractional volume and restrict the *Theory* in the rest to Newtonian CM—and there is *no* guarantee that this can be done—then we will have defined a *Multi-scale Model*.

Multi-scale Models can be categorized usefully as *serial* or *concurrent*. In *serial* methods, a set of calculations at the smaller length scale, along with the more refined *Theory*, is used to evaluate the parameters required by a more phenomenological *Theory* to be used at longer length scales. For example, atomistic simulations can be used to obtain the constitutive behavior of finite elements, which are then used to simulate larger scale problems [72]. Several research groups presently are working productively on such methods, and several applications can be found [73, 74]. Another example of serial multi-scaling relevant to material failure is the development of inter-atomic potentials from first principles calculations, with the objective of using those potentials in a Newtonian CM *Model* with MD or Monte Carlo *Simulation*.

Concurrent multi-scale Models rely on different *Theories* each of which is applied to a distinct region of the material. The regions are distinguished on the basis of length scales characteristic of the essential processes. For instance, a common concurrent model of a material undergoing dry brittle fracture partitions the system into two regions: the region in and around the crack-tip, and the far-field elastic region. A complete representation of the brittle fracture process has to consider both behaviors. Concurrent models attempt to distinguish them, yet join the two regions "seamlessly". Because of the elastic behavior far from the crack tip, that region can be treated using continuum elasticity theory (hence with simulation techniques such as the finite element method "FEM"). In contrast, the region around the crack tip has to be represented by an atomistic model such as Newtonian CM with an inter-atomic potential, with the simulation performed using MD techniques. For such a multi-scale model to be successful, there must be no loss of information at the interface of the two regions nor introduction of spurious behavior by that interface. Basic conservation laws (e.g. total energy conservation) must be preserved.

4. Coupling atomistic and continuum representations

In recent times, there have been a number of pioneering efforts in multi-scale modeling and simulations. We mention a few of the more pertinent studies. Broader discussion may be found in a recent compendium of articles describing the techniques and models of materials modeling [75].

To our knowledge, Mullins and Dokanish [72] were among the first to propose a concurrent scheme. In a finite element region they embedded pseudo-atoms which interact with the Newtonian CM atoms via an inter-atomic potential. Tadmor et al. [73] used a zero-temperature relaxation technique (with atomistics in each cell) and a finite element mesh to embed a crystalline defect within a continuum. Similar approaches were suggested for coupling discrete and continuum regions [76, 77].

Self-evidently, a concurrent model (e.g. a continuum-like region bridged to an atomistic region) is an approximation of a large, real system. In linear elasticity the fundamental properties such as stress, strain, and moduli are thermo-mechanical

quantities. These quantities are defined as thermodynamic averages over a sufficiently large number of microscopic constituents and arbitrarily long times. Calculating such quantities from classical atomistic models does not present significant difficulties so long as suitably large systems and long enough times are involved. This fact constitutes the basis for coarse graining models that enable the extension of atomistic systems into the realm of continuous models with seamless coupling between length scales.

Problems in bridging continuum and atomistic regions may arise when the continuum is pushed outside the thermodynamic and long-time limit. This is the case in many of the simulation methodologies just mentioned. Notice that the failure is in the *Simulation*, specifically because the finite elements coupled to an MD region are reduced to atomic-scale size. The spatial coupling between un-physically small finite elements and atoms implies also that the long-time limit may not be satisfied. In addition, an elastic continuum and a discrete atomic system do not obey the same physics over all possible wavelengths, hence the matching of sound velocities in the two regions is a necessary but not sufficient condition for physical realism.

Our discussion thus far addresses only the coupling of continuum and atomistic regions and the concomitant approximations. The implicit assumption is that regions of high strain would be represented satisfactorily by a classical Newtonian CM model and MD simulations. But brittle fracture is an intrinsically non-equilibrium process, hence one cannot justify the applicability of empirical equilibrium-based inter-atomic potentials to an atomistic region very near the crack tip. In that region, large bond deformations and electronic charge transfer processes must take place. Hence multi-scale models describing brittle fracture must include more than the atomistic and continuum scales.

Bond-breaking is chemistry, which brings us back to ground-state QM in the Born–Oppenheimer approximation. Now the *concurrent Model* involves a region in which the inter-atomic forces are determined by the Born–Oppenheimer ("BO") potential surface from a specified QM approximation. That region is embedded in a classical Newtonian CM region for which the potential is in fact an approximation to the BO potential surface. Note that the "handshaking" between the embedded and embedding regions introduces the issue of *fidelity* in our *Theory → Modeling → Simulation* framework. The *Simulation* consists of computing the forces in the QM region with algorithms suitable for the QM approximation and the Newtonian dynamics from MD. Computationally, the introduction of QM approximations as an ingredient of the *Model* adds a major cost. Roughly speaking, all QM methods are one or more orders of magnitude slower than ordinary MD with a potential. Moreover, the more accurate the QM approximation, the more costly it is computationally, hence there are difficult compromises regarding both methodological choice and the size of the QM region.

A fairly recent example of MD–QM multi-scale methodologies to model brittle fracture is the work of Bernstein and Hess (BH) [78]. They studied lattice trapping barriers to brittle fracture in silicon using Tight-binding QM and MD and showed that the relative amount of lattice trapping of the crack front plays an important role in the fracture process. A rather different approach was devised recently by Csanyi et al. [79] who chose to augment a selected simple form of the inter-atomic potential with information computed "on the fly" via QM calculations. In their scheme, the

system is initialized with a reasonable choice of parameters for the classical potential and propagated via MD for a certain number of time steps. Then, the local validity of the classical potential is evaluated on a site by site basis and a selected subset of atoms is identified to be the QM atoms. Using the chosen QM method, the parameters of the classical potential are parameterized once again for the QM atoms until the desired accuracy is obtained. The system is then reset to its initial state and propagated once again in phase space. In addition to recovering the results of BH, they also were able to capture the reconstruction of the crack surface, a process not treated by BH.

Many of the existing multi-scale approaches to crack propagation build on the assumption of localized stress concentration in the vicinity of the crack tip. However, additional issues arise in applying concurrent multi-scale simulations to failure in glasses. Numerous simulations [80–85] and experiments [86, 87] indicate that failure occurs by formation and coalescence of voids of nano-scale or less. For instance, in examining sodium silicate glasses consisting of 1,000–2,000 atoms with free surfaces under both tension and compression, Soules and Busby [36] noticed that under biaxial expansion the sample failed via void formation and cavitation. Keiffer and Angell [88] noticed a self-similar void structure in silica glass when the material was subjected to sudden isotropic expansion. Ochoa et al. [81–83] and Swiler et al. [84] examined the structure of a-SiO_2 as a function of uniaxial strain-rate. They noticed the formation and coalescence of sub-nano-scale voids with increasing strain, accompanied by non-trivial plastic deformation in the form of bond-rupture and atomic rearrangement. In their studies, strain was applied uniformly throughout the sample, which consisted of 1,000–2,000 atoms with periodic boundaries. They concluded that strain was relieved via alignment of individual silica tetrahedra with the direction of applied strain through thermal vibrations. Van Brutzel et al. [85] performed multi-million atom simulations on a-SiO_2 to study crack propagation. They applied uniaxial strains to the boundary atoms and observed formation of nano-scale voids and pores (40–50 nm in radius) in low density regions ahead of the propagating crack-tip. Recent investigations have indicated that the growth of "critical" voids could be correlated to the stress response of a-SiO_2 as it is uniaxially strained [89]. Specifically, when the material responds elastically to the applied strain there is elastic void deformation. Once the material begins to separate, critical voids grow rapidly, sometimes via the coalescence of surrounding "satellite" voids. These observations indicate that failure of amorphous solids that occurs via nucleation, growth, and coalescence of voids is not restricted to a small number of bond ruptures very near the tip of a crack, but may involve several additional length scales. A straightforward concurrent model with a local electronic-level model region at the tip of a crack embedded within a small atomistic region bridging the continuum scale may fail to capture the essential physics and chemistry associated with bond rearrangement and rupture associated both with the crack tip *and* with void formation beyond that immediate vicinity. Furthermore a simple multi-scale scheme with spatially limited electronic level and atomistic models may not be able to span the longer-scale phenomena associated with void coalescence. This problem may be exacerbated further in dealing with failure of an initially homogeneous brittle material for which one does not know *a priori* where catastrophic failure might develop.

5. Issues we have addressed

Early in our studies, our goal was to improve on the relatively primitive QM then being used in concurrent multi-scale models. As the work evolved, we found that multi-scale modeling and simulation is an enterprise that should be conceived from "inside out", rather than "outside in". By the latter we mean the original formulations of multi-scale simulations began with MD and inter-atomic potentials and attempted to make the description more realistic by identifying a QM zone and treating it using a simple QM method. "Inside out" starts with the realization that no amount of superb MD on massive samples can compensate for an inadequate treatment of the QM region. It follows that adequate treatment of the QM region leads to reformulating the whole enterprise in the *Theory → Modeling → Simulation* framework we have discussed above. Within this framework, concurrent multi-scale modeling has at least two requirements regarding the QM, (a) proper identification of the QM region, and (b) choice of suitable QM approximations. With respect to (a), most multi-scale simulations of fracture *impose* a QM region by introducing a crack and surrounding the crack tip by a region having enough particles to be physically meaningful and computationally tractable. One of the questions that has come up is how to avoid this *deus ex machina* approach. See Article 1 in the Set for a discussion of the *domain identification issue*

With respect to (b), there is the vexing problem that highly refined quantum chemistry methods known to give "chemical accuracy" also are well-known for their immense computational cost. Hence another theme to which we have given attention is to find approximate QM methods with substantially better accuracy/cost ratios than standard first-principles approaches. Articles 5 and 6 are devoted to this topic.

Reconsideration of the multi-scale modeling and simulation enterprise also leads to the recognition that there is a widely ignored incompatibility between the CM and QM regions in most concurrent multi-scale models. The issue is consistent embedding of the QM region in the CM region. To embed the QM region in a CM region, most multi-scale models use a published potential that has been successful in pure MD calculations. In general, such potentials will *not* yield forces that are consistent with the QM forces in the embedded domain, as most published potentials are not parameterized to ensure such consistency. We are then led to a third requirement, (c) provision of a consistent embedding potential. Only a little thought is required to realize that there is a closely related requirement, (d) realistic prescription for termination of bonds broken by the imposition of the QM–CM interface. Articles 2, 3, 4, and part of Article 8 all address these two problems.

We have considered two other major issues. One is perhaps obvious: how do modern methods actually work on real but simple examples of chemo-mechanical phenomena? Articles 7, 8, 9 address this question in the case of Silica–Water and Silica–Silicon systems. The other issue is the multi-code challenge. Concurrent multi-scale modeling simulations require multiple algorithm suites: MD, QM, FE, etc. Typically each suite is realized in the form of several different user application packages (codes). We have five different internally written MD codes (Cheng, Harris, Muralidharan, Sinnott, MIT) and one internationally distributed one, DL_POLY, for example. The challenge is to develop a systematic framework and protocols for interoperating such codes with minimal internal changes, without "by hand" operation

by a team of expert users, and without recompiling all the codes into one enormous, monolithic executable. Article 10 presents a systematic solution to this problem.

Acknowledgements

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