

Materials Modeling from Quantum Mechanics to The Mesoscale

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Abstract: Molecular modeling has established itself as an important component of applied research in areas such as drug discovery, catalysis, and polymers. Algorithmic improvements to these methods coupled with the increasing speed of computational hardware are making it possible to perform predictive modeling on ever larger systems. Methods are now available that are capable of modeling hundreds of thousands of atoms, and the results can have a significant impact on real-world engineering problems. The article reviews some of the modeling methods currently in use; provides illustrative examples of applications to challenges in sensors, fuel cells, and nanocomposites; and finally discusses prospects for future modeling approaches.

Keyword: molecular modeling, materials science, quantum mechanics, mesoscale modeling, multiscale simulation

1 Introduction

Molecular modeling is playing an increasingly important role in the design of new materials. Recent developments in catalysis [Cattlow, French, Sokol, and Thomas (2005)], polymer membranes [Wescott, Qi, Subramanian, and Capehart (2006)], alloys [Woodruff and Robinson (2003)], carbon nanotubes [Li and Zhang (2007)], and electronic materials [Vanhellemont and Simeon (2007)] have been aided by computational approaches. Engineering CAD/CAM methods will be familiar to many readers. Those approaches assume that the fundamental properties and behavior of the materials (compressibil-

ity, tensile strength, conductivity, etc.) are well-characterized and use macroscopic engineering principles to compute the behavior of structures. Typical examples are the design of aircraft to reduce drag, or the testing of large scale structures like oil rigs and bridges for stability.

By contrast, in this article we consider the methods of quantum mechanics, molecular mechanics, and mesoscale modeling that are used to predict fundamental properties and behavior of materials at much smaller length and time scales. The information obtained from such simulations may be used to generate parameters for engineering-scale calculations or it may directly provide answers that can be used in the search for new materials.

The idea of creating methods to span these scales is, of course, not new. The ICEM'2K conference in 2000, for example, recognized the limitations of finite element methods (FEM) and continuum mechanics for describing the behavior of materials at the micron level. It was recognized that a combination of approaches would be necessary to provide realistic simulations of nano- and micro-mechanics of materials [Ghoniem and Cho (2002)]. Progress is already being made in combining these scales, and we note just a few of many examples here. For example, a combination of continuum Green's function methods and molecular dynamics was introduced and used to model Au nanoclusters on Cu(001) [Tewary and Read (2004)]. More recently, a combination of molecular dynamics, mesoscale modeling and continuum methods was used to study nanoindentation on Cu(111) [Ma, Liu, Lu, and Komanduri (2006)] at both 0°K and finite temperatures. Finally, a combination of molecular mechanics and FEM was used to model bending and shearing in carbon nanotubes [Theodosiou and Saravanos

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(2007)].

This article focuses on how the methods of molecular modeling are being used to solve engineering problems, despite the fact that they typically operate on comparatively short length and time scales. These approaches offer the chance to perform simulations with high accuracy as well as the ability to include electronic and quantum effects, essential in nanoscale materials.

We begin by providing an overview as to how molecular modeling is employed in materials research and development. We then discuss the methods employed and the levels of approximation involved in addressing research problems across increasing time and length scales spanning electronic structure to the engineering level. We provide illustrative examples of how modeling can provide insight, help design new materials, and lead to improved products. Finally, the paper concludes with a discussion of new methods under development and their potential impact.

2 Molecular Modeling in Commercial R&D

The premise of modeling is that it provides information that supplements or complements that available from experiment. In some cases it might provide a very straightforward property, such as heat of formation, in much less time than experiment [Dewar, Zuebisch, Healy, and Stewart (1985); Curtiss, Raghavachari, Redfern, Rasslov, and Pople (1998); Delley (2006)]. In other cases, modeling provides fundamental information that would be very difficult to obtain experimentally, such as the degree of back-bonding that takes place when a reactant is adsorbed on the surface of a catalyst [Yamagishi, Jenkins, and King (2002)]. This detailed level of information can be used to provide a rational basis for the development of new materials and improved processes.

Because of the speed of contemporary modeling methods, we can expect to screen a large number of materials more rapidly with modeling than with experiment alone. In a typical approach, materials will be screened in the computer (*in silico*) for desirable properties (e.g., catalytic activity, corrosion resistance, electrical conductivity) and only

the most promising leads are actually synthesized and tested in the laboratory. This fundamental approach has led, for example, to the development of improved OLEDs [Thompson (2007)] at much lower cost than with experiment alone.

3 Multi-scale modeling: length and time scales

We break modeling down into four broad categories: quantum mechanical, molecular mechanical, mesoscale, and bulk scale. Figure 1 shows roughly the size of systems that are modeled in each domain and the length of time for which a dynamic process can be simulated. Generally speaking, as one moves to larger systems, more approximations are employed and the methods are less precise.

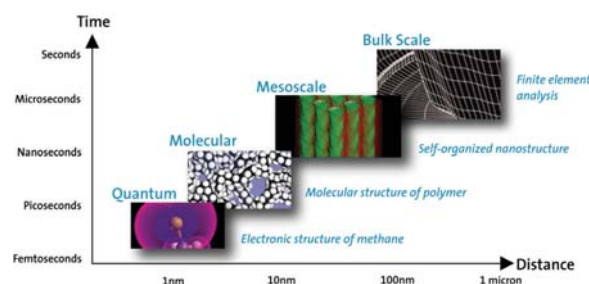


Figure 1: Length and time scales employed in modeling

As a rule, the cost of performing a simulation with quantum mechanical accuracy increases rapidly with the number of atoms in the system, anywhere between N^1 [Skylaris, Haynes, Mostofi, and Payne (2006)] and N^8 [Lee, Kucharski, and Bartlett (1984)], where N is the number of atoms. Most practical approaches scale in the neighborhood of N^2 - N^3 . To keep the calculations manageable, modelers introduce successive levels of approximations into the methods. While these reduce the computational cost, they also potentially compromise the accuracy of the results.

The modeling of systems at the nanoscale, say 10-100 nm, poses special challenges. Because of the size of these systems, modelers typically would use approximate methods in order to keep the computational requirements (CPU time, disk

space, memory) reasonable. Calculations on nanomaterials, however, require a high degree of accuracy. Furthermore, electronic and quantum mechanical effects play an important role even at the scale of $\sim 100\text{nm}$. Consequently, computationally expensive quantum mechanical-based calculations – or approximate methods that can reproduce quantum mechanical accuracy – are often necessary to study these materials

The development of methods capable of treating systems with 1,000's of atoms with the greatest possible accuracy represents an area of active research. The various approaches that are currently being employed are discussed in the next section.

3.1 Quantum scale

Methods based on quantum mechanics are the most accurate, and they are capable of predicting a large number of electronic, optical, and structural properties such as crystal structure [Milman and Winkler (1999); Le Page, Saxe, and Rodgers (2002)], optical spectra [Zerner, Loew, Kirchner, Mueller-Westerhoff (1980); Schmidt, Seino, Hahn, Bechstedt, Lub, Wang, and Bernholc (2004)], and catalytic activity [Catlow, French, Sokol, and Thomas (2005)]. These methods are also the most time-consuming. As already mentioned, some of the most accurate methods scale as N^8 . In the last decade or so, density functional theory (DFT) [Parr and Yang (1989)] has emerged as the method of choice in modeling materials, offering an excellent compromise between cost and accuracy and scaling on the order of N^2 - N^3 .

The so-called semiempirical quantum mechanical methods [Dewar, Zuebis, Healy, and Stewart (1985)] work by replacing the most computationally demanding portions of a quantum mechanical calculation with empirical parameters. Using this approach calculations on enzymes with 1,000s of atoms have been performed [Stewart (1997)]. The methods are limited in their accuracy, however, and more importantly do not work with all elements.

Another approximate quantum mechanical approach is DFT Tight-Binding (DFTTB) [Horsfield and Bratkovsky (2000); Elstner, Porezag, Jungnickel, Elsner, Haugk, Frauenheim, Suhai,

and Seifert (1998)]. Here, parameters are determined by fitting to DFT calculations rather than to a range of empirical data. The method has proved its strengths in a number of biomedical applications, but also works for a number of transition metals, and can be applied to solid materials [Elstner, Frauenheim, McKelvey, Seifert (2007)].

3.2 Molecular scale

Molecular scale modeling encompasses systems roughly one to two orders of magnitude larger than the quantum scale. Molecular mechanics approximates the interatomic interactions with empirically derived analytical expressions and parameters. Owing to the simplicity of these functional forms, calculations are very fast and can be performed on systems containing tens of thousands - or even hundreds of thousands - of atoms.

The atomic interactions may be divided into long-range and short-range terms. Behavior of covalently bonded systems will be dominated by short range interactions due to chemical bonds. Commonly, the energy is represented as a quadratic function of bond distances, bond angles, torsional rotations, and out of plane bends. In many cases, coupling terms among bonds, angles, and torsions are included in order to improve the results. Materials that are not dominated by covalent interactions frequently require more complicated short-range potentials, such as Morse, Buckingham, Lennard-Jones, or Axilrod-Teller potentials [Axilrod and Teller (1943)], to name just a few. A recent review covers these various potentials in more detail [Hill, Freeman, and Subramanian (2000)].

When considering ionic materials, the Coulomb interaction is by far the dominant term and can typically represent up to 90% of the total energy. The summation is most efficiently achieved through the Ewald method [P. Ewald, (1921)]. Dispersion energy constitutes the next largest long-range interaction, arising from dipole-dipole and higher-order terms. The long-range Coulomb and dispersion terms are not exclusive to ionic materials, but must also be accounted for in covalent systems, particularly when considering intermolecular interactions.

A given set of functions and parameters is called a force field. These force fields are empirical and are derived by fitting to experiment or to accurate quantum mechanical calculations [Dauber-Osguthorpe, Roberts, Osguthorpe, Wolff, Genest, and Hagler (1988); Sun (1998)]. A force field will be applicable only to systems similar to those used in the fitting. Hence, many different force fields can be found in the literature. Force fields have been developed for organic molecules (CVFF [Dauber-Osguthorpe, Roberts, Osguthorpe, Wolff, Genest, and Hagler (1988)]), zeolites [Schröder, Sauer, Leslie, Catlow, and Thomas (1992)], microporous materials (CVFF-AUG [Hill, Freeman, and Subramanian (2000)]), organic-inorganic interactions (COMPASS [Sun (1998)]) and metal oxides (GULP [Gale and Rohl (2003)]).

Molecular mechanics is commonly used for the design of new pharmacological compounds. Force fields such as CHARMM [Brooks, Brucoleri, Olafson, States, Swaminathan, and Karplus (1983); MacKerell, Brooks, Brooks, Nilsson, Roux, Won, and Karplus (1998)] and Amber [Case, Cheatham, Darden, Gohlke, Luo, Merz, Onufriev, Simmerling, Wang, and Woods (2005)] have been developed specifically for this purpose and are in wide use in the pharmaceutical industry.

One serious limitation of force fields is their inability to study chemical reactions. The functional forms being employed in classical force fields are not able to describe the formation or breaking of chemical bonds. Recently, however, force fields have emerged such as REBO [Brenner, Shenderova, Harrison, Stuart, Ni, and Sinnott (2002)] and ReaxFF [van Duin, Dasgupta, Lorant, and Goddard (2001)] that are capable of this. ReaxFF, for example, has been used to model transition-metal-catalyzed nanotube formation. At the current time, however, quantum mechanical methods remain the best option for studying reactions.

3.3 Mesoscale

The mesoscale approaches introduce an additional level of approximation on top of those

used in molecular mechanics. Dissipative Particle Dynamics (DPD) is essentially a coarse-grained molecular dynamics method in which the fundamental variables are the positions and momenta of fluid droplets rather than individual atoms (see Figure 2). Droplets interact via three forces: a conservative force, a dissipative force, and a random force. The latter two forces are generated to satisfy a state of detailed balance, which conserves the temperature of the system. All forces between beads are pairwise, implying linear and angular momentum conservation and therefore implicit inclusion of hydrodynamic forces. This approach [Hoogerbrugge and Koelman (1992); Groot and Warren (1997)] is derived from molecular dynamics simulations and lattice gas automata, and effectively opens up the mesoscopic length and time regimes in complex fluids to simulation. With this approach, systems with upwards of 1,000,000 atoms can be represented. Perhaps more importantly the coarse graining in DPD extends the effective time step so that several microseconds to even a millisecond of real time becomes feasible to simulate.

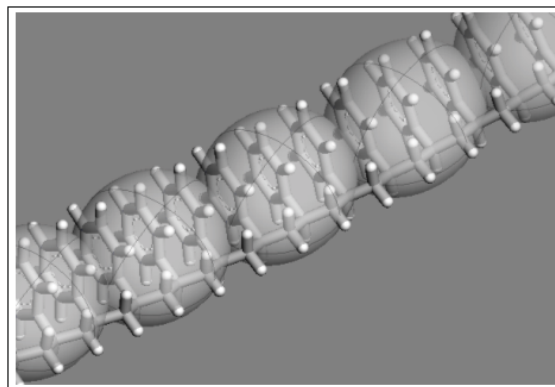


Figure 2: An atomistic representation of a polystyrene polymer showing regions that could potentially be abstracted into beads for a mesoscale level calculation

An alternative mesoscale approach is based on self-consistent field theory. In this field approach, a material is not seen as a collection of atoms or particles, but rather as density fields of the various components. Hence DPD is the explicit particle representation of the system, and the field

methods are the statistical mechanics representation expressed in terms of free energy equations.

Field methods such as MesoDyn® have been used successfully, in particular, in the area of block-copolymer phase behavior. Notably, the kinetics of phase transitions in nanostructured fluids have been simulated and found to agree very well with AFM observations, covering length scales from the nanometer to the micro scale, and timescales up to several hours [Knoll, Lyakhova, Horvat, Krausch, Sevink, Zvelindovsky and Magerle (2004)]

3.4 Bulk scale

Bulk scale methods like CAD/CAM are most familiar to engineers. These are entirely phenomenologically based and use well-understood engineering approaches to model problems such as fluid flow, structural stability, or the efficiency of chemical manufacturing plants. In some recent examples [Maiti, Wescott and Kung (2005); Maiti, Wescott, and Goldbeck-Wood (2005)] engineering parameters were computed from the results of mesoscale simulations, establishing a connection all the way from the quantum level to the bulk level. Other approaches, mentioned in the introduction, have also been used to link the atomic and engineering scales.

4 Illustrative applications

4.1 Design and selection of molecules for biosensors

Although conventional force fields and DFT methods are limited to relatively small length and time scales, they are nevertheless able to make significant contributions to problems at the engineering level. Take, for example, recent work done by Dr. Richard Gilbert at e2v technologies [Gilbert (2004)].

The electrochemical reaction chamber of a lab-on-a-chip device needs to provide several key properties and functions in order to be a successful product. These include:

- The formation of an organic monolayer on the gold electrode surface (to prevent dena-

turing of the proteins in the chamber);

- Efficient electron transfer from the electrode to a 'shuttle' molecule;
- Short diffusion times of this molecule to the proteins; and
- Docking and electron transfer to the protein.

E2V have used simulations at quantum and atomistic levels to great effect in the study of such chemical and physical processes. Indeed, it has been key to the so-called "lab-to-fab transition" and in this case, according to Dr. Gilbert, modeling found a solution in less than two weeks.

In the sensor, a molecular monolayer on a gold surface acts as a conductor. The presence of a particular antibody affects the conductivity of the surface, and measuring the change in conductivity signals the presence of the antibody.

The initial work used phenanthroline for the monolayer, since a stable monolayer on gold had been reported previously in the literature. Cyclic voltammetry measurements confirmed this, displaying peaks for charge and discharge processes at 21°C (Figure 3, dark blue curve). At the operating temperature of 37°C, however, the system failed (Figure 3, light blue curve). Simulations with the COMPASS force field demonstrated that at 37°C the monolayer was no longer stable, but would desorb from the surface, as illustrated in Figure 3.

Using simulations, it was possible to screen related molecules in order to identify potential replacements. Simulations allowed a wide range of modifications to the starting molecule as well as different concentrations of mixtures to be tested. Ultimately, it was found that attaching C₆₀ to a fraction of the phenanthroline stabilized the monolayer at 37°C (Figure 4). This was verified by subsequent experiments and led to successful operation of the cell.

4.2 Conductivity of carbon nanotube polymer composites

A class of nanomaterials receiving much recent attention is that in which single and multiwalled

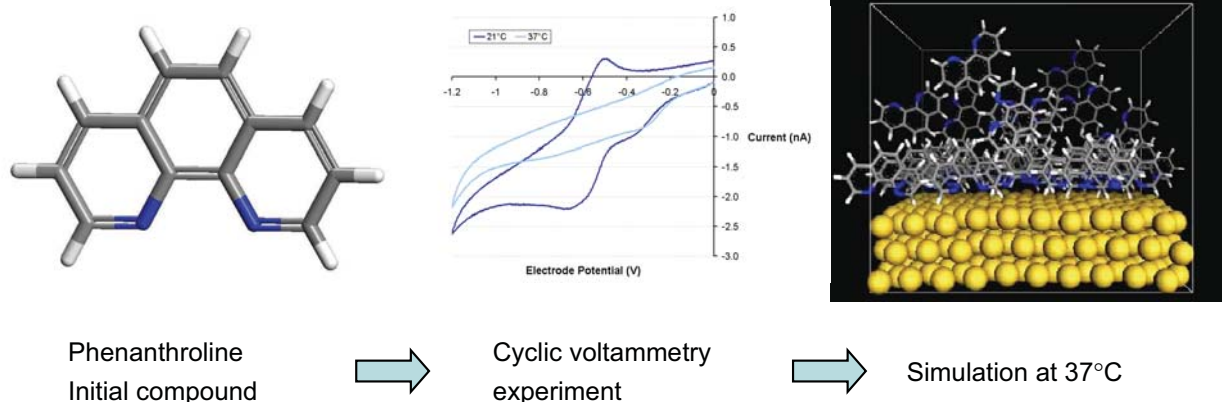


Figure 3: Initial monolayer on the gold surface. Phenanthroline is stable at 21°C but not at 37°C. Subsequent molecular modeling studies confirm that the monolayer desorbs at 37°C

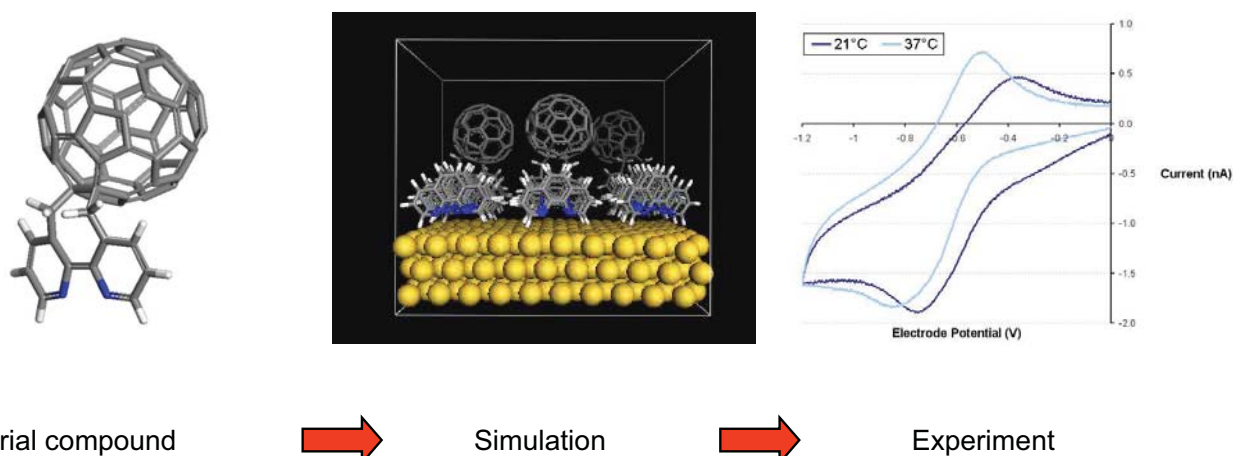


Figure 4: New monolayer designed by modeling. Modeling predicts that adding C₆₀ to the phenanthroline stabilizes the monolayer. Subsequent experimental work confirms this.

carbon nanotubes (CNTs) are dispersed within polymeric matrices [Ajayan, Scadler, and Braun (2003)]. The overall properties of a CNT-polymer composite material depend strongly on the uniformity of CNT dispersion within the polymer. This is especially true of electrical conductivity, which is several (to many) orders of magnitude higher for pure CNTs than for typical polymers. Thus, significant enhancement of such properties is expected when a conducting pathway, i.e., a percolation network, of CNTs forms between two opposite contacts.

Mesoscale simulations have been used [Wescott, Kung, and Maiti (2007)] to explore how topological patterns in block copolymer systems, such as lamellar, bicontinuous, and discrete micellar

phases [Bates (1991)], might be exploited to create controlled linkages of CNTs with potentially lower critical volume fractions (CVF) as compared to completely random CNT networks.

The coarse-grained representation used is schematized in Figure 5, which for a particular parameterization might typically correspond to a quasi-two-dimensional slab of 61 nanometers representing roughly one million atoms.

The miscibility of components with one another is governed by an interaction parameter Δa , which can be related to the Flory-Huggins χ parameter [Groot and Warren (1997)]. χ can be estimated from experimental sources if they are available or by using appropriate force-field based models to compute energies of interaction.

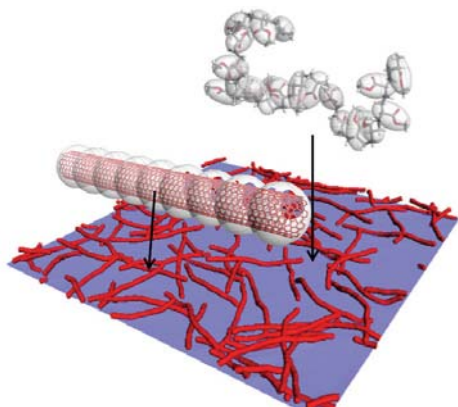


Figure 5: Schematic of the DPD model employed to represent thin slabs of polymer-CNT composite material. Polymers are represented by coarse-grained flexible chains of 20 beads. CNTs are rod-like particles constructed from 13 beads whose flexibility is restrained [Maiti, Wescott, and Goldbeck-Wood (2005)]

The evaluation of electrical conductivity, σ , from the composite morphologies used a continuum finite-element modeling (FEM) approach [Gusev (2001)] as implemented in the MESOPROP software. Averages of σ were taken to sample the many possible arrangements of CNTs explored in the long DPD simulations.

By assuming the case of perfectly insulating and miscible homopolymers and by simply varying the concentration of CNTs, a clear percolation threshold can be identified at about 0.5 vol% of CNT (Fig. 6). This is consistent with experimental and theoretical predictions of randomly oriented percolating rods [Wang, Chatterjee (2003); Foygel, Morris, Anez, French, and Sobolev (2005); Rahatekar, Hamm, Shaffer, and Elliott (2005)], although for actual CNTs with much larger aspect ratios percolation conduction at fractions down to less than 0.1 vol% have been reported.

The work then considered the case of a diblock copolymer matrix of the form $A_n B_{20-n}$ in which the CNT is preferentially miscible in the A component while A and B are strongly incompatible. The incompatibility of A and B drives the expected block copolymer phase separation, but the

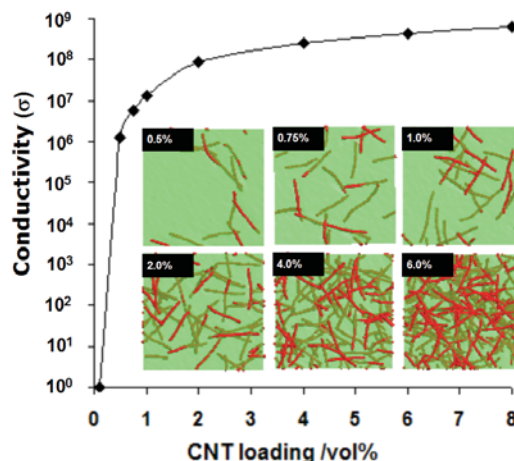


Figure 6: Plot of conductivity of polymer-CNT composite as a function of CNT loading. (Inset: typical arrangement of CNTs at 0.5, 0.75, 1.0, 2.0, 4.0 and 6.0 vol%.) The percolation threshold is somewhere between 0 and 0.5% for this model

way in which this impacts the electrical conductivity when CNTs are introduced turned out to be quite non-trivial, at least at the low CNT loading of most interest (Fig. 7).

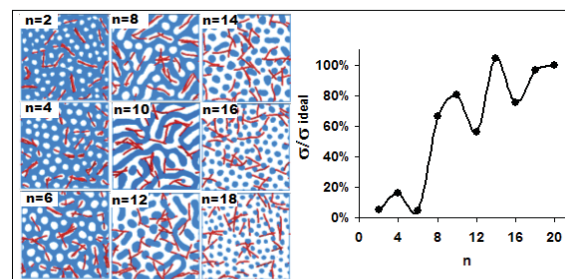


Figure 7: Left pane shows representative configurations from the simulations for 0.75 vol% CNTs in $A_n B_{(20-n)}$ block copolymers. Polymer density fields shown using white (A material) and blue (B material). Instantaneous positions of the CNTs beads are shown in red. Right pane shows conductivity of the composite vs. n . Conductivity is expressed as a fraction of the conductivity in pure A-polymer.

In fact, a non-monotonic behavior of conductivity persists for CNT loading up to 2% or 3%, but at higher loadings, where CNTs saturate the model,

the conductivity becomes again a simple function of the CNT concentration

4.3 Particle size/shape control of molecular solids

It is a reoccurring theme in nanotechnology that nanosized particles have a dramatically enhanced surface area relative to their bulk volume. On the one hand this often poses challenges as enhanced interface energies can hinder efficient dispersion of these particles in, e.g., a polymer matrix. On the other hand this enhanced surface area is at the very heart of many nanotechnology applications. The shape and size of finite (nanoscale) particles produced from molecular crystals – so called crystallites – add other dimensions to this technological challenge as the underlying crystal lattice fundamentally affects the particle shape and surface chemistry. The particle shape – also called crystal habit – dictates which functional groups are exposed to the environment and therefore tunes the interactions of the crystallites with the surrounding environment. Applications of this class of materials include pharmaceutical solid delivery forms and pigments in paints and coatings.

Modeling and simulation tools allow rationalization of these crystal habits in terms of energetic considerations. Computer algorithms can be used to cleave a virtual crystal, analogous to the procedure that would be followed for a real-world experiment. The resulting surface energies give rise to an idealized crystal habit, the so-called equilibrium morphology of a crystal. Alternatively, layers of material can be attached to surface orientations, and the energy released by this process can be used to construct a habit referred to as the growth morphology of the crystal.

Since the crystal lattice pins the molecular building blocks onto a rigid array, the surface orientations and their relative abundances dictate which functional groups of the molecule are predominantly exposed to the environment. This knowledge can be used as a guideline to design coating agents to improve the dispersion of the crystallites in the surrounding polymer matrix. For example, researchers at BASF investigated the habit

of perylene red pigments and designed a series of derivative perylene molecules with features that allowed strong bonding onto the predominant surfaces while at the same time maximizing favorable interactions with the surrounding polymer matrix [Erk, Hetzenegger, and Böhm (1997)].

Shape and size control are major challenges for the pharmaceutical industry, as the exposed surface will affect a number of properties, most prominently the dissolution rate, which in many cases directly relates to the bioavailability of a drug product. A common way to reduce the particle size is via wet milling. Lee, Variankaval, Lindemann, and Starbuck used modeling and simulation to evaluate the crystal morphology and the associated surface energetics in order to obtain a microscopic picture of the milling process, which subsequently allowed them to optimize milling conditions for problematic compounds [Lee, Variankaval, Lindemann, and Starbuck (2004)]. The authors point out that milling is not primarily affected by the bulk mechanical properties under external stress but by the propensity of a single crystal material to break along a certain orientation. This is relevant as the bulk material typically displays poorer mechanical properties than single crystals, and larger shear forces are therefore required to achieve effective particle size reduction than one would estimate from bulk properties. They established that the attachment energy – the energy released as a layer of material is attached to the growth front – provides an understanding of mass fracture of the crystallites.

Four different pharmaceutical compounds were investigated. For the first three compounds the lowest attachment energy did not vary significantly (from -31.1 to -42.2 kcal/mol). Milling of these compounds resulted in very similar particle size reductions as a function of shear frequency. The lowest attachment energy of the fourth compound was substantially higher (-88.5 kcal/mol). Milling this compound under identical conditions as before not only yielded significantly larger particle sizes, but micrographs revealed little mass fracture. Particle size reduction in this case, was primarily due to the breakage of agglomerated particles and attrition along edges. This suggested

that milling methods that exert higher energies are needed to effectively induce fracture of this compound. In fact, switching the experimental setup to a bead milling arrangement successfully fractured the crystallites into smaller units. The authors concluded that modeling of the crystal habit not only allowed them to understand the mass fracture process, but that the results can also be used as a quantitative guide to milling operations. In cases where adequate shape and size control cannot be achieved via post-processing (milling or other techniques), the crystal morphology can be directly influenced by tuning the crystal growth conditions, and in particular by changing the solvent environment. Tedesco, Giron, and Pfeffer computationally evaluated the crystal habit of a pharmaceutical compound and determined that the most predominant surface terminations are the (001), (100), and (010) orientations [Tedesco, Giron, and Pfeffer (2002)]. From evaluating the surface topologies they concluded that each of these surface orientations displayed a significantly different surface polarity and that by tuning the polarity of the solvent they could promote or inhibit selectively the growth of these individual facets. In particular, formation of needle-like shapes – which are especially unfavorable if the drug is intended to be delivered as an inhalant – should be inhibited by using polar solvents. These rationalizations were confirmed experimentally, and the powder characteristics could be improved.

4.4 Fuel cell membranes

Proton exchange membranes (PEMs) are key components of hydrogen fuel cells, and there is significant interest in enhancing the proton conductivity of these materials, as well as increasing their mechanical, thermal and chemical stability. This is required to satisfy pressing needs for increased power density, durability, and reliability of the cells, which will impact significantly the cost of deploying fuel cells widely in the next generation of motor vehicles and other power applications. Of key importance is knowledge of the nanoscale structure of the hydrated polymer membranes, since the pathways available for proton conduction and the mechanical performance

depend largely on the structure at this scale.

In the commonly used Nafion® material there has been much debate over the exact form of the morphology as a function of the water content. Experimental techniques characterizing the morphology are either indirect, such as atomic force microscopy which can only probe the surface structure, or have lead to ambiguous interpretations. For instance, small angle scattering data has been used to support a number of different morphological models. Application of a multiscale modeling approach, on the other hand, in this case atomistic and mesoscale simulations, are ideal for this type of problem since with suitable parameterization they provide a direct prediction of the phase morphology. Such a multiscale approach was used to investigate the development of morphology in Nafion 117 membranes at various levels of hydration [Wescott, Qi, Subramanian, Capehart (2006)].

Atomistic force field parameters play an important role in the scheme employed since they are used to derive the interactions between the coarse-grained (mesoscale) units or beads. This is the dominant driving force for the phase separation between components. Consequently, models of hydrated membranes at the Ångström level were constructed and molecular dynamics employed to ascertain the suitability of the force field. Expected features of polymer/water phase separation were indeed observed, as were clustering of water and hydronium molecules about the sulfonic acid moieties of the polymer. Having ascertained that the parameters were very likely to be an adequate characterization of the interaction energies, mesoscale parameters were developed for the system and Materials Studio® MesoDyn® was used to predict the morphology at hydration levels of $\lambda=2, 4, 8$ and 16 , where λ is the number of water molecules per protogenic group (in this case sulfonic acid).

The results showed that spherical water clusters form as the water content is increased to a level of $\lambda=4$ (Fig. 8) and that above $\lambda=4$, some of the water clusters also exhibit irregular shapes (elliptical or barbell shape) due to the coalescence of smaller clusters.

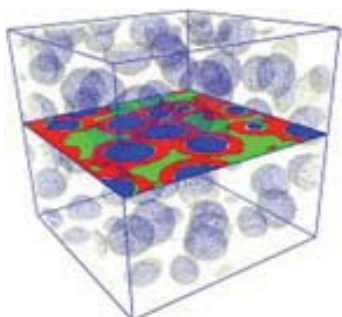


Figure 8: Inverse micelles of water density at a water level of $\lambda=4$ are shown as transparent blue isosurfaces. A density slice shows the water micelles (blue) contained within the PTFE matrix (red), within the water-PTFE interface, mediated by the ether-sulfonic side chain.

The small angle neutron scattering signal from the simulated density distributions was constructed in an attempt to produce data equivalent to that obtained experimentally. From these curves the dominant Bragg spacing was extracted, providing the characteristic size of the hydrophilic domains. A linear correspondence with hydration was observed (Fig. 9). Similar experimental small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) data has previously been used to assert that perfluorosulfonic acid (PFSA) has a lamellar structure [Litt (1997)], but these simulations, with an arrangement of nearly spherical domains that swell and coalesce, provide a counterexample to this.

In fact, the simulations appear to support the Yeager-Steck three-phase model [Yeager and Steck (1981)] of sulfonic side groups surrounding the polytetrafluoroethylene (PTFE) cavities, and are consistent with surface morphology determined by TEM and AFM [Xue, Trent, and Osseo-Asare (1989)].

Further simulations to model the drying of pre-hydrated membranes showed that path-dependent phases can also be explored with dynamic density functional theoretical calculations. In these situations segregated water domains remained after removal of water, and were in fact lower energy structures than those generated from a direct hydration of polymer at the same concentration.

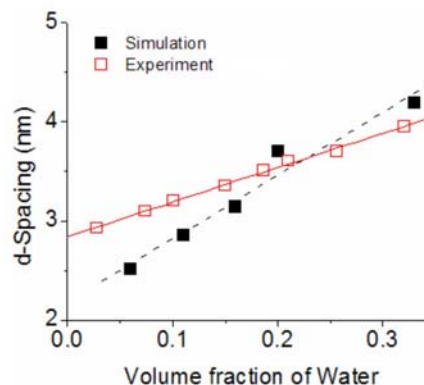


Figure 9: Comparison of the d-spacings of hydrophilic domains extracted from small angle scattering calculations with increasing water content. Experimental work from Young, Trevino and Tan (2002).

This suggests that a membrane cast and then dried may have significantly different performance than those produced by other methods.

In summary, the multiscale modeling approach was valuable in exploring morphology development in hydrated Nafion® membranes and captured the phase segregation at scales consistent with those experimentally observed at increasing levels of hydration. This has provoked additional discussion as to the impact that membrane processing may have on performance of the fuel cell stack.

5 Recent developments and future outlook

In the opening section of this article, we divided modeling into four domains. As our biosensor design example demonstrates, some devices function on the quantum and atomistic scales, and so existing software tools can already directly impact the design. However, other important phenomena occur across a continuum of scales and we have highlighted examples where protocols to couple domains are needed to address key materials design problems.

Whilst merely connecting scales is sufficient in some cases, others demand high-accuracy theoretical models even though such calculations with traditional methods are prohibitively expensive

from a computational point of view. Potential solutions to this issue are either to (a) extend the time and length scale capabilities of currently available methods, or (b) construct so-called hybrid simulations which integrate, for example, quantum and classical methods into one coherent approach.

Examples for the former are linear-scaling DFT methods, including the ONETEP method [(Skylaris, Haynes, Mostofi, and Payne (2005)), CONQUEST [Gillan, Bowler, Torralba, Miyazaki (2007)], SIESTA [Sánchez-Portal, Ordejón, Artacho, and Soler (1997)] and linear-scaling semi-empirical codes [Stewart (1997)]. Many technical issues had to be overcome since their first inception to make these codes work in a relatively robust way for a wide range of systems. Hence, only in the last couple of years has the number of studies been increasing. Today the ONETEP method, for example, enables high-precision (quantum mechanical-based) total energy calculations for systems of several thousand atoms, where previously calculations with this level of accuracy were limited to on the order of a few hundred. It brings new science and applications into the realm of quantum calculations, from chiral nanotube systems to binding calculations of protein-enzyme complexes.

Future developments will increase our understanding of how best to utilize linear-scaling methods, provide a wider range of property analysis, and potentially develop ways in which different levels of accuracy can be assigned to different parts of a system (in time and in space), thereby providing a kind of embedding scheme within a single method, rather than by means of hybrid simulations.

Hybrid QM/MM (Quantum Mechanical/Molecular Mechanical) approaches have traditionally been more widely applied in the life sciences, typically with codes that have been extensions of either QM or MM methods. In recent years more general interfacing codes have been developed that are able to connect a variety of QM and MM applications, and the methods have become more widely applied in the materials arena. These include QMMM

[Lin and Truhlar 2007)] as well as ChemShell [Sherwood, de Vries, Guest, Schreckenbach, Catlow, French, Sokol, Bromley, Thiel, Turner, Billeter, Terstegen, Thiel, Kendrick, Rogers, Casci, Watson, King, Karlsen, and Sjøvoll (2003)] which has been implemented in QMERA by Accelrys. While these methods provide the user with increasingly robust and flexible implementations, several key issues remain; these include the treatment of the boundary regions, handling of long-range interactions, as well as how to deal with cases where the QM “hot spot” moves dynamically. Promising new approaches such as the Learn-On-The-Fly technique [Csányi, Albaret, Moras, Payne, and de Vita (2005)] offer the chance to overcome issues of boundary regions and time dependent phenomena, but further validation for systems with long range interactions in particular is still required.

There are also recent advances in parameterized simulations that help to bridge important gaps. These include the aforementioned Density Functional Tight Binding methods (DFTB) [Horsfield and Bratkovsky (2000); Elstner, Porezag, Jungnickel, Elsner, Haugk, Frauenheim, Suhai, and Seifert (1998)] and Reactive Force field methods like REBO [Brenner, Shenderova, Harrison, Stuart, Ni, and Sinnott (2002)] and ReaxFF [van Duin, Dasgupta, Lorant, and Goddard (2001)]. From a user perspective these methods can reach system sizes and time scales which are close to those otherwise reached only with pure classical simulations, but with the major advantage that reactive processes, changes in valency, charge transfers, and so on can be handled. Crucial to the success of these approaches will be more streamlined and, ideally, automated parameterization methods.

A key driver for the development of such methods is not only size and time scales *per se*, but the need to study hybrid systems, such as organic-inorganic interfaces or even biological molecules interacting with electrodes for example in a bio-sensing device.

As the size scales that can be reached with quantum and atomistic methods increase and at the same time the feature scales of materials and de-

vices decrease, there is also clearly the opportunity and need to build bridges between the software tools of the chemistry, physics, and engineering worlds. The article has shown examples of existing tools and approaches that already begin to provide such links. Also, application examples such as the biosensor design demonstrate that in some cases the actual device functions on the quantum and atomistic scales, so these tools can already impact the design directly.

In other areas such as process engineering, methods are still evolving that allow a tighter communication between fundamental chemistry on one hand and chemical engineering on the other. In catalytic processes, for example, the conversion rates and so-called turn-over frequencies are modeled on the engineering level by computational fluid dynamics (CFD) and rate equation methods that provide a mean-field result [Kee, Miller, and Jefferson (1980)]. On the other hand, reactions can be handled from the bottom-up by calculating transition states and frequencies using ab initio approaches, followed by rate constants from transition state theory [Fernandez-Ramos, Ellington, Garret, and Truhlar (2007)], finally followed by kinetic Monte Carlo simulations of the process itself [Jansen (1995); Stampfl, Ganduglia-Pirovano, Reuter, and Scheffler (2002); Kieken, Neurock, and Donghai (2005)]. The future trend will be to combine these top-down and bottom-up approaches for a more complete understanding and more accurate predictions.

As the above examples show, the appropriate methods to employ in bridging towards the macroscale level depend very much on the application area, with mesoscale and kinetic Monte Carlo just two of many methodologies.

A key to successful multiscale modeling lies not only in establishing new methods but also in defining, implementing, and validating workflows that combine the relevant simulations, models, and data across all scales. In the engineering of a new polymer, for example, this could include the calculation of relevant polymer resin data such as glass transition temperature and cohesive energy densities from the molecular scale, subsequently feeding these results into mesoscale calculations

and engineering models, and finally focusing back on the electronic level to study interfaces with a method such as DFTB.

Software that improves the connections between disparate models and data structures – together with architectures that can handle large computational demands – is helping to drive modeling from quantum to molecular to mesoscale to macroscales. The long-term outlook is hence that of a largely data driven approach, where knowledge is gained from the combination of methods across the multiscale range.

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