Overview of Multiparadigm, Multiscale Research at MSC (2007-2008)

Andrés Jaramillo-Botero

http://www.wag.caltech.edu/multiscale/

Computer simulations have become the enabling tool for studying and understanding complex systems and natural phenomena that would otherwise be too expensive or dangerous, or even impossible, to study by direct experimentation.

In principle, all properties of all materials and phenomena are describable by quantum mechanics (QM) unfortunately direct use of computational QM is impractical for solving applications that involve a large number of particles (> ~1K), typically within a few nanometers in length. On the other hand, phenomenological-based continuum-level methods lack the required resolution to describe atomistically resolved phenomena with full chemistry and hence are incapable of capturing fundamental nanoscale intrinsic and extensive properties that define the behavior of matter.

Our research involves developing first principles-based theory, methods and efficient multiparadigm computational algorithms and tools to seamlessly bridge the length and time scales between a purely atomistic description and the continuum, to enable de novo design, characterization and prediction of material properties and processes and their application into solving currently "impossible" problems.

This brief talk will present some of the current research advances during the past year encompassing the development of new theory, methods and tools, including:

- **Bridging the mesoscale from atomistic molecular dynamics with systematic constrained and coarse-grain molecular dynamics (Comodin)** – [Jaramillo-Botero, A. and Goddard III, A.]. In the study of molecular systems using Molecular Dynamics (MD) simulations it is often desired to impose relative or absolute motion constraints on atoms or groups of atoms. This offers several different advantages, in particular for internal coordinate representations, including: a reduction in the total number of degrees of freedom (DOF), an increased integration time-step of the equations of motion. Constraints over high frequency vibrational modes lead to a reduction in the sampling frequency, faster energy exchange between low- and high-frequency modes. Implicit expression for relative constraints, decoupled contributions to SO(3), and an effective flattening (averaging) of the potential energy surface (PES) by reducing energy fluctuations and the number of potential local minima traps in the energy landscape allowing for a smoother exploration of the conformational space. Nevertheless, the efficiency of these methods lies in not only solving the EOM in time lower-bound computational efficiency but in finding a systematic coarse-grain representation and a new set of optimized coarse-grain forcefields for the coarse-grain model and avoiding the time-penalty of recovering from bad-contacts at large integration time-steps. We have addressed these issues. We have demonstrated a preliminary successful use of hybrid stochastic Genetic Algorithms-gradient based algorithms to systematically fit coarse-grain torsion-only force fields directly from atomistic MD energy gradients using a 1:1 mapping between Cartesian space force interactions with internal differential space torques which leads to improved integration time-steps and overall simulation time (30-40fs and 10’s of ns) for large biomolecules. Furthermore, we have designed a structure relaxation technique based on a torque-force Jacobian to avoid recalculating forces during a bad-contact time-step. Current applications include fast conformation search and structure prediction. See http://www.wag.caltech.edu/multiscale/constrained_md.htm

- **Development and coupling of computational tools for multiparadigm, multiscale simulations from QM to FEM and continuum, in The Computational Materials Design Facility (CMDF)** – [Jaramillo-Botero, A., Liu, Y. and Goddard III, A.] CMDF is a single-image materials and process modeling and simulation framework, integrated from different tools and engines, intended to allow hierarchical traversal between different length and time scales (first-principles quantum-mechanical <-> continuum mechanics), and between disparate paradigms (i.e. alternate methods) per scale. Its goal is to enable de novo design of new or optimized materials with improved performance and to enable first-principles predictive science in chemistry, physics and biology. An update on the current status of development will be given, including: new methods and components (e.g. empirical correction of DFT London dispersions), new prototype interfaces, among others.
A specific example of coupling Kinetic Monte Carlo schemes to first-principles atomistic reactive dynamics simulations (using reaxFF) will be mentioned related to the effect of Hydrogen surface coverage on diffusion over Silicon substrates (see poster by A. Barbato et al)

See: http://www.wag.caltech.edu/multiscale/multiscale_computations.htm

As well as multiscale, multiparadigm simulation solutions to fundamental and applied problems, including:

- **Predictive optimization of Nano and Bio-mechanical properties of hydrogel polymer networks for cartilage scaffold-supported therapies** – [Jaramillo-Botero, A., Blanco, M., Li, Y. and Goddard III, A. under NSF grant No. 0727870] Unlike bone, liver, skin, and other tissues with high cell-turnover rates, cartilage has a limited capacity for self-repair and traditional repair methods have proved to be ineffective in the long-term. Polymer gel based scaffold-supported cell therapies to promote the natural regeneration of cartilage promise to overcome the limitations of traditional methods. Unfortunately, the fundamental in-vivo nano and biomechanical properties of cartilage remain largely unknown and significant improvements are needed in their performance. Progress in this arena has been impeded by the inability of in-vivo experiments to measure the complex atomic level structures and their properties, and electrokinetics responsible for the overall macroscopic performance of the gel polymer matrix at various pressures and temperatures. We have developed realistic molecular models of multi-component, interdependent hydrogel networks and a strategy for using first principles theory and computation to predict and optimize their nanoscale mechanical properties, in particular those that regulate their dynamic response and the macroscopic viscoelastic properties under anisotropic loading (including non-linear strain-stress response, permeability, diffusion and electrokinetics as a function of temperature and pressure and the chemical polar/non-polar functionality). The generalization and application of these models and methods would enable the essential framework to simulate the critical nano bio-mechanical properties of hydrogel networks, including the complex structural and electrokinetic phenomena responsible for their mechanoregulation, and develop an increased understanding of the fundamental mechanisms that regulate in-vivo performance enabling us to postulate new enhanced materials. See http://www.wag.caltech.edu/multiscale/nanomechanics.htm

- **Predictive optimization of fire-fighting Aqueous Film Forming Foam (AFFF) surfactants from atomistic to coarse-grain models** – [Jaramillo-Botero, A., Liu, Y. and Goddard III, A. under subcontract from Air Force and Advanced Research Associates] This research is meant to understand and elucidate fundamental structures and properties of fire-fighting AFFFs, derived from the interfacial systems in Newton-Black Films, and to explore novel surfactant molecular structures suitable for hydrocarbon and alcohol based fuels. The resulting methods and tools will provide a means to obtain accurate, atomistically resolved, information about AFFFs composition and behavior thereby enabling Air Force Research Laboratory scientists to predict and optimize macroscopic quantities (e.g. optimum volumes) and compositions (e.g. reduce toxicity via reduction/replacement of fluorinated surfactants) of AFFF precursors for performance enhancement. The importance of this work lays on the Air Forces’ requirement for a) advanced technologies that facilitate contingency base operations and combat support functions, including the development of environmentally compatible, operational and cost effective fire extinguishing AFFFs, and b) a reduction in weight, volume, and costs of base emergency response, infrastructure support, and combat support systems.