CHAPTER 1

INVESTIGATIVE TOOLS: THEORY, MODELING, AND SIMULATION

M. Lundstrom, P. Cummings, M. Alam[12]
***With contributions from*: M. Ratner, W. Goddard, S. Glotzer,**
M. Stopa, B. Baird, R. Davis

As subsequent chapters in this report will describe, theory, modeling, and simulation (TM&S) play a significant role in almost every branch of nanotechnology. TM&S consists of three distinct components. A *theory* can be defined as a set of scientific principles that explains phenomena—a succinct description of a class of problems. *Modeling* is the analytical/numerical applications of theory to solve specific problems. *Simulation* aims to faithfully render the physical problem in the greatest possible detail, so that the critical features emerge organically—not as a consequence of the ingenuity, insights, high level abstractions, and simplifications that characterize modeling. Each of the three TM&S components plays an important role, but the opportunities of the next decade will require a stronger emphasis on the modeling component. Multiscale modeling, in particular, will be essential in addressing the next decade's challenges in technology exploration and nanomanufacturing. Finally, it should be understood that each subdiscipline of nanotechnology has its own TM&S community; these communities share many commonalities in underlying theoretical foundations, numerical and computational methods, and modeling approaches. This chapter focuses on issues, challenges, and opportunities common to TM&S across the broad spectrum of nanotechnology.

1.1 VISION FOR THE NEXT DECADE

Changes in the Vision over the Last Ten Years

As noted when the U.S. national nanotechnology research agenda was first conceived, "Fundamental understanding and highly accurate predictive methods are critical to successful manufacturing of nanostructured materials, devices and systems" (Roco, Williams, and Alivisatos 1999, 25). Over the past ten years, the focus in TM&S research has been on elucidating fundamental concepts that relate the structure of matter at the nanoscale to the properties of materials and devices. As a result, theory, modeling, and simulation have played an important role in developing a fundamental understanding of nanoscale building blocks. Computational capability has increased by more than a factor of 1000, leading to more ambitious simulations and wider use of simulation. For example, the number of atoms simulated by classical molecular dynamics for 10 ns time durations has increased from fewer than 10 million in 2000 to nearly 1 billion in 2010. As discussed in Chapter 2, first-principles theory is increasingly coupled with characterization and metrology in the atomic-resolution

[12]For the institutional affiliations of authors, please see Appendix B, List of Participants and Contributors.

regime. Over the past decade, new theoretical approaches and computational methods have also been developed and are maturing, but our understanding of self-assembly, programmed materials, and complex nanosystems and their corresponding architectures is still primitive, as is our ability to support design and nanomanufacturing. New challenges must now be addressed.

Vision for the Next Ten Years

The promise of nanotechnology lies in the possibility of helping address the great challenges faced by human society by engineering matter on the nanoscale—i.e., in building human-scale systems with nanoscale building blocks. Nanotechnology is inherently a multiscale, multiphenomena challenge. Building on the substantial progress over the past decade, the focus for the next decade must be on making multiscale modeling and simulation pervasive. Multiscale modeling will be essential to support technology exploration, design, and nanomanufacturing. Faster computers and improved computational methods will be an important part of the solution, but a unified, conceptual framework for multiscale thinking and simulation must be developed as well. The right approach must be used for the scale of interest (Goldenfeld and Kadanov 1999), and approaches at one scale must be related to those at adjacent scales. To support design, appropriate, high level abstractions for designing complex nanosystems must be developed. As nanotechnology moves from science to applications, access to user-friendly software design tools will become more and more important.

Looking to the future, TM&S scientists must continue to clarify underlying concepts, develop nanoscale building blocks, improve computational methods and devise new ones, but the focus must shift to applications, which entails addressing multiscale/multi-phenomena problems. Addressing the multiscale challenge will require connecting "bottom-up" and "top-down" thinking (i.e., atomistic, first-principles simulations with phenomenological macroscopic simulations). The goal is to make multiscale/multiphenomena modeling and simulation of practical problems a reality across the broad spectrum of nanotechnology. By doing so, TM&S will support the development of nanotechnologies that address society's grand challenges.

1.2 ADVANCES IN THE LAST TEN YEARS AND CURRENT STATUS

Advances in Nanotechnology: The Role of TM&S

The last decade (2000–2010) witnessed many advances in nanoscience and nanotechnology. Theory, modeling, and simulation have played a supportive, sometimes even critical, role in these advances. A few examples follow.

- *Understanding of current flow at the molecular scale*. Theoretical and computational studies were critical in understanding measurements of electron current flow in molecules (Venkataraman et al. 2006a; Venkataraman et al. 2006a; Quek et al. 2007; Quek et al. 2009).
- *Evolution of microelectronics into nanoelectronics.* TM&S helped to identify limits, issues, and possibilities for transistor scaling (e.g., Lundstrom and Ren 2002).
- *Discovery of graphene and development of carbon-based electronics*. Closely coupled experimental/theoretical/computational studies shed light on the physics of carbon-based electronics (Javey et al. 2003; Heinze et al. 2002; Cao et al. 2008; Cao et al. 2009).
- *Emerging applications of spin torque*. Theoretical predictions (Slonczewski 1996; Berger 1996) were experimentally demonstrated (Tsoi et al. 1998; Katine et al. 2000).

- *Discovery of iron-based high-Tc superconductors (Kamihara et al. 2008)*. Very large-scale simulations showed how the electron pairing arises that is the key to high-Tc superconductivity (Maier, Poilblanc, and Scalapino 2008).
- *Ten-orders-of-magnitude improvement in the sensitivity of biosensors*. The performance of a wide range of biosensors (Li et al. 2004; Li et al. 2005; Star et al. 2006) was interpreted within a scaling theory of diffusion-limited transport of nanoparticles (Nair and Alam 2006; 2007).

Advances in Theory: Enabling Modeling and Simulation

Nanoscience requires new theoretical ideas and new modeling approaches as well as more powerful computational capabilities. New methods and advances in computation permit larger and more complex problems to be addressed, but analytical and coarse-grained models are central to multiscale modeling. These sorts of models (e.g., the Marcus model for electron transfer and transport, the Langmuir-Hinshelwood model for adsorption, the Shockley diode equation, etc.) are also the way scientists and engineers think about, envision, and imagine the world. TM&S is especially effective when results the results of complex simulations are expressed in the language used by experimentalists and designers.

The last decade has witnessed many advances in the underlying theory of nanoscience. Examples of accomplishments include:

- Advances in *ab initio* theory beyond density functional theory (DFT), including improved GW algorithms; DFT + dynamical mean field theory for strongly correlated systems; the DFT+Σ approach for cheap, approximate, parameter-free treatments of many-body effects (Quek et al. 2009); and increased use of hybrid functionals and post-Hartree-Fock methods (e.g., Pisani et al. 2008; Hafner et al. 2008).
- Advances in linear-scaling quantum mechanics. Building on foundations established in the 1990s, advances continued in areas such as purification theory (Niklasson, 2002) and new boundary conditions for divide and conquer (Wang et al. 2008).
- Reactive force fields for reactive dynamics simulation of materials processes (Goddard et al. 2006). Reactive force fields allow one to simulate structure with chemistry, enabling potential impact on drug discovery and catalysis, both of which require precise differentiation between the energy costs of various reaction pathways.
- Enhanced sampling techniques such as metadynamics (Liao et al. 2008) for free energy surfaces to find important configurations for specific systems and improved methods for determining rate constants (van Erp et al. 2003).
- Development of the non-equilibrium Green's function (NEGF) approach as a conceptual (Datta 2005) and computational (Quek et al. 2007) framework for describing quantum transport at the quantum and atomistic scales (Figure 1.1). Applications range from molecular electronics to practical applications in the semiconductor industry, where the approach has been used to connect the underlying material properties to improving the performance of the transistor.
- New statistical theories for conduction in nanostructured materials such as carbon nanotubes and semiconductor nanowire networks (Figure 1.2) and phase-segregated organic solar cells, leading to quantitative predictions for the performance of devices (Cao et al. 2008; Cao et al. 2009).

Advances in Computing: Powering TM&S

While theory provides the foundation for modeling and simulation, computing makes it possible. Over the past decade significant computing advances have been achieved. As

illustrated in the examples of Section 1.8, these advances have contributed to the increasing role of simulation in nanoscience and have set the stage for an even more ambitious agenda for TM&S in the next decade.

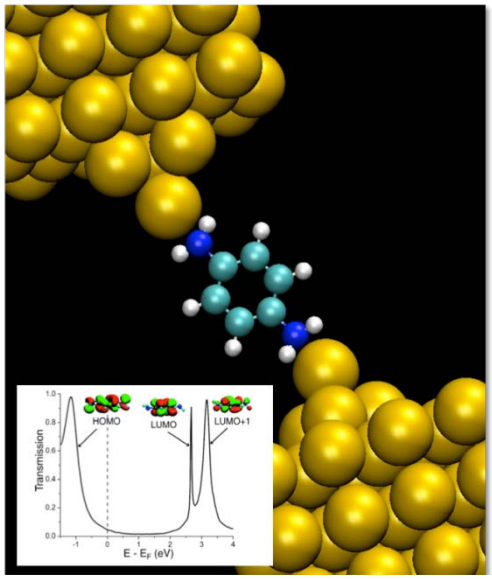

Figure 1.1. First-principles density functional theory (NEGF-DFT) simulations of the conductance of molecular junctions have led to improved understanding and quantitative agreement with experiments. The figure shows the calculated atomic geometry of benzene-diamine suspended between Au electrodes; the inset shows the computed electron transmission vs. energy (Quek et al. 2007).

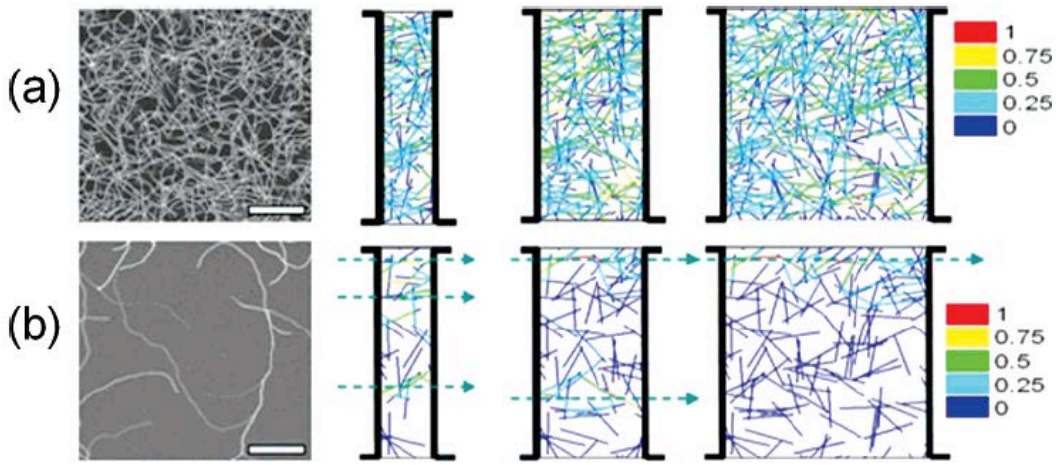

Figure 1.2. SEM images (*left*) and simulated normalized current distribution for carbon nanotube networks with high (*a*) and low (*b*) coverage. Measurements were reported on SWNTs grown by chemical vapor deposition with systematically varying degrees of alignment and coverage in transistors with a range of channel lengths and orientations perpendicular and parallel to the direction of alignment. A stick-percolation-based transport model provides a simple yet quantitative framework to interpret the sometimes-counterintuitive transport measured in the devices that cannot be reproduced by classical transport models (after Kocabas et al. 2007).

Examples of advances in computing that have been important for TM&S include the following:

- High-performance computing (HPC) power (as measured by the most powerful machine in the biannual top-500 supercomputers list, http://top500.org) has increased by three orders of magnitude since 2000, which enables larger simulations and brings ambitious simulations into the realm of the "every-day" computing world of theorists and experimentalists. Leadership-class computing is necessary to address grand challenges in computational nanoscience; it is also needed to perform the atomistic level simulations that provide the fundamental data for the coarse-grained methods used in multiscale simulation.
- The impact of the exponential growth in computing power has had great impact on classical molecular dynamics (CMD) over the past decade, and this will continue into the next decade. For systems with short-range forces, the compute time is linear in system size, N, as well as linear in the number of time steps, Tsim (usually ~1 fs). The computational complexity (CC) is approximately Tsim N. What can be done in one day of computing? Consider the recent simulation by Schulz et al. (2009) of a 5.4 M-atom system on 30720 cores of Jaguar, the current Number 1 machine on the top-500 list. The computational complexity possible on Jaguar is TstepN = 6 x 1014, from which we can project that on Jaguar, a billion-atom CMD simulation would execute at 0.6 ns/day.
- Parallel computing has had great impact. Figure 1.3 shows estimated CMD computational complexity for the highest- and lowest-performing machines on the top-500 list (based on assuming CMD performance scales with benchmark performance), as well as a single central processing unit (CPU) and a graphical processing (or "general-purpose") unit (GPU).[13] This graph is, at best, qualitative and indicative of trends; it does, however, try to capture the impact of multicores and the impact of GPUs. As shown in Figure 1.4, the introduction of multicore CPUs has considerably accelerated the rate of progress in CPU performance.

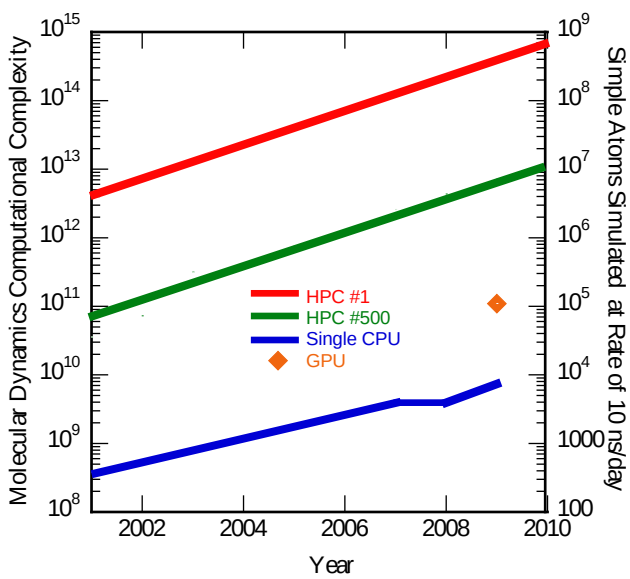

Figure 1.3. *Left axis*: Estimate of CMD computational complexity (equal to the product of the number of time steps and the number of atoms simulated in one day) on the #1 supercomputer in the top 500 (*top line*), #500 in the top 500 list (*middle line*), a single CPU (*bottom line*) and a GPU (*diamonds*). *Right axis*: For simple monatomic fluid, the number of atoms that can be simulated for 10 ns in one day (data from P.T. Cummings).

[13] CPUs process information serially; GPUs process information in parallel. In the past, CPUs generally have had one, two, or four cores, whereas GPUs have had a larger number of cores, up to 100 or more.

- The introduction of GPU chips, originally driven by the gaming industry, is a disruptive technology that is leading to dramatic increases in computing performance for algorithms like many-particle dynamics that are easily parallelized. For example, NVIDIA's Fermi chip announced in 2010 provides 120 times the performance of a single CPU. To achieve this performance, science codes must be rewritten for GPU chips, and new mathematical libraries must be developed. The recent development of high-level programming languages for GPUs (e.g., CUDA) is rapidly accelerating the application of GPUs to scientific computation, including computational nanoscience (Owens et al. 2008; Garland et al. 2008; Anderson 2010).

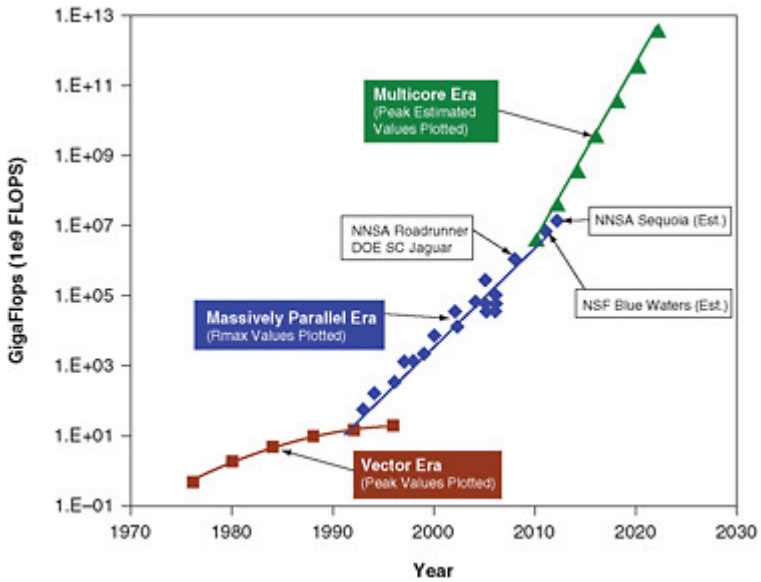

Figure 1.4. Gigaflops in CPU performance vs. time (from an NRC study on modeling, simulation and games, compiled from data from http://top500.org) (NRC 2010).

Advances in Simulation and Design of Nanomaterials

The increasingly close connection between simulation and metrology has been a significant development over the past decade. Figure 1.5 shows some of the experimental probes that cover spatio-temporal scales that overlap with the TM&S methods. The coincidence of experiment and TM&S methods at the nanoscale offers many opportunities for strongly integrated theoretical/experimental studies (e.g., Zhang et al. 2004).

Large investments have been made in nanotechnology research, and the resulting progress has been substantial. Most research and development in nanotechnology, however, is still done by expensive and time-consuming experiments. Industry demands faster and less expensive solutions. Modeling and simulation will be essential to addressing this challenge, and advances over the past decade have set the stage for the predictive design of materials by simulation.

Predictive materials design requires improvements in simulation methods for maximum accuracy. Over the past decade, significant progress has occurred in the individual components of a predictive materials simulation framework:

- Quantum mechanics (challenge: increased accuracy)
- Force fields (challenge: chemical reactions)
- Molecular dynamics (challenge: extract properties for materials design)

- Biological predictions (challenge: simulation in liquids and on biological timescales)
- Mesoscale dynamics (challenge: simulation on relevant time and size scales)
- Integration: (challenge: multiscale)

A key challenge for the next decade will be to develop methods that address the role of defects and disorder in nanomaterials.

Examples of the predictive simulation capabilities currently being developed include simulations of etching for damage-free semiconductor fabrication, ReaxFF reaction dynamics simulations of catalytic processes for high temperatures and pressures, reactive dynamics of hydrocarbon reactions, silicon nanowire growth, dendrimer-enhanced nanoparticle filtration for water purification, and self-assembly.

Self-assembly is increasingly a new frontier for materials research. "Assembly engineering" seeks to create building blocks that are (nearly) fully tailorable and reconfigurable, with changeable shape and/or interactions. The goal is to realistically simulate hierarchical assembly to achieve novel functions.

Advances in Multiscale Simulation and Modeling

Figure 1.5 shows the range of computational methods currently employed in nanoscale TM&S, from *ab initio* methods, to atomistic and united atom molecular dynamics, to particle-based coarse-grained simulations, and finally to continuum methods. For integrated nanosystems, additional layers of high-level abstractions are required in order to capture functional and systems aspects and to enable design. Nanoscale TM&S studies increasingly traverse more than one of the scales shown in Figure 1.5.

Different methods are used at different scales, but true multiscale simulation would use automatic upscaling (moving information from a more fundamental, lower scale up to a higher scale, such as force field data from *ab initio* to atomistic CMD) and downscaling (such as a finite element calculation invoking molecular simulation to obtain a diffusivity at a new state condition). Although true multiscale simulations are rare, it is common in TM&S today to use multiple methods to solve a single problem. For example, *ab initio* methods are commonly used to calibrate atomistic force fields for CMD simulations. Today, however, atomistic force fields are handcrafted in a type of "nano cottage industry," which makes it difficult to address a broad range of multiphenomena problems. Improvements in coupling different computational techniques resulted in the successful simulation of the oxidation of nanometer-sized clusters (Vashishta et al. 2006).

Significant progress has occurred in methods development for multiscale simulation. Upscaling methods now exist for bridging many of the scales (e.g., Izvekov et al. 2004; Reith, Pütz, and Müller-Plathe 2003). Downscaling methods are less well developed, and true multiscale methods even less so, but specific methods tailored for narrow problem domains have been developed (e.g., Csányi et al. 2005), and general methods are beginning to be proposed (e.g., Papavasiliou and Kevrekidis 2007).

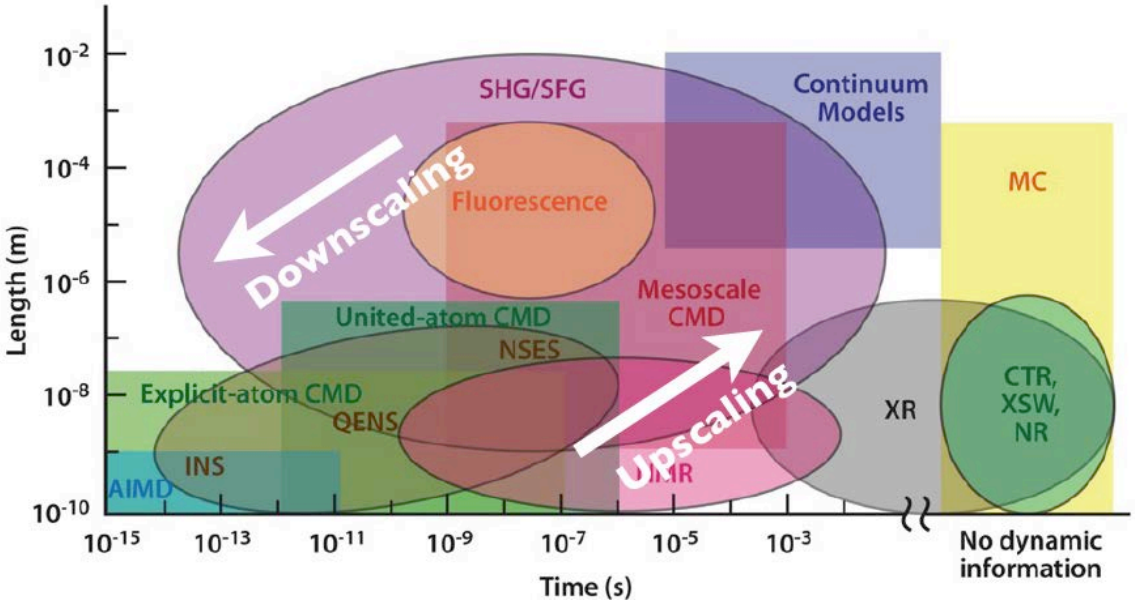

Figure 1.5. Hierarchy of TM&S methods relevant to nanoscale science and technology, along with some corresponding experimental methods, and the time and length scales over which each is applicable (from P. T. Cummings and D. J. Wesolowski, 2010, to be published).

Acronyms (and corresponding methods) indicated in the figure: TM&S methods (*in rectangles*) AIMD: *ab initio* molecular dynamics; CMD: classical molecular dynamics; MC: Monte Carlo Experimental techniques (*in ovals*) INS: inelastic neutron scattering; QENS: quasi-elastic neutron scattering; NSES: neutron spin echo spectroscopy; NMR: nuclear magnetic resonance; XR: X-ray reflectivity; SHG: second harmonic generation; SFG: sum frequency generation; CTR: crystal truncation rod (an X-ray method); XSW: X-ray standing wave; NR: neutron reflectivity.

1.3 GOALS, BARRIERS, AND SOLUTIONS FOR THE NEXT 5–10 YEARS

Theory, modeling, and simulation provide investigative tools that support nanotechnology. To support nanotechnology in the next decade, these tools must be enhanced to solve larger problems, and to do so more accurately and efficiently. With the increasing focus on applications of nanoscience, TM&S must address the larger challenge of multiscale modeling and simulation. Successfully doing to will transform research, technology development, design, and manufacturing.

Goals for Multiscale Theory, Modeling, and Simulation

Multiscale modeling is essential for exploring the numerous, new technology possibilities that research in nanoscience is creating. It is essential for identifying promising ideas, for developing them into real technologies, and it will be essential for nanomanufacturing. Faster computers and better computational methods will be important, but the real challenge is to develop new conceptual and modeling frameworks. New conceptual models must be developed to relate atomistic physics and chemistry to nanoscale structure and then nanoscale structure to the performance of complex materials and integrated nanosystems, finally ending up in the language that experimentalists and product designers use. These new theories will provide a computational framework for multiscale modeling, and they also will provide an intellectual framework to link those who work at the bottom with those who work

at the top. Examples of multiscale modeling exist, but the goal is to make "atoms to applications modeling" pervasive across the field of nanotechnology.

Multiscale modeling should support the development of:

- Programmed materials that make use of self-assembly
- Process and bottom-up assembly models
- System-level design models that allow for billions of components and that comprehend defects and disorder
- Design methods that combine TM&S, nanoinformatics, and expert systems
- Nanomanufacturing – including nanomaterials, nanodevices, and nanosystems as well as modeling process variations and repeatability.

A longer-term goal is to develop true multiscale simulation, which involves the use of different methods at different scales with automatic upscaling (moving information from a more fundamental, lower scale up to a higher scale) and downscaling. Different methods scale differently with the number, N, of atoms in the system. Thus, an atomistic simulation could faithfully represent, for example, catalytic reactions at surfaces by treating via first-principles methods only the region in the vicinity of the reaction, and only when a reaction is probable. Addressing these problems fundamentally will require development of general, numerical methods to automatically up-scale and downscale and traverse the relevant spatio-temporal scales.

Goals for the Predictive Design of Nanomaterials

Advances over the past decade have raised the possibility of truly predictive design by simulation. The goal is to achieve predictive design for real-world applications using an overlapping hierarchy of methods to connect the fine scale to the coarse scale. The goal of realizing predictive design of materials with the accuracy to replace experiments to a large degree is within reach over the next 10 years—if the problems are carefully selected, if a sustained commitment is made to developing the new methods that will be needed, and if strong industry input is obtained to direct the research to critical needs in nanomanufacturing. To address this challenge, TM&S will need: (1) increased computing capability, (2) improved computational infrastructure, (3) critical input from experiments, and (4) to learn how to address defects, disorder, and variability in materials.

Goals for Computing and Building Block Simulations

Computational capability must address larger problems more accurately. Consider the treatment of electronic structure with Hartree-Fock methods, which require 100 times more computing power than a DFT simulation. Assuming a linear-scaling approach is employed, the calculation of the electronic structure of a 10 nm quantum dot would need an increase in computing power by approximately a factor of 10,000. Some of this increase will come from advances in computing hardware, but some must come from improved numerical methods.

The past decade witnessed a factor of 1000 increase in computational power; the goal is to achieve another factor of 1000 in the next decade. GPUs will bring high-performance computing to the desktop and modest supercomputer-class computing to clusters where they will impact computational nanoscience and provide increased capabilities to theorists and to experimentalists. For applications that parallelize efficiently on multicore CPUs, the benefits will be significant. Also, given the relatively low cost of GPUs, leadership-class computers will feature multi-core compute nodes with attached GPUs for acceleration of on-node

computation, thus making them integral to the fabric of high-performance computing. To achieve the performance improvements beyond the factor of 1000 thought to be possible from new computing hardware, new theoretical approaches and numerical methods will be needed.

Computation can accelerate progress in both theoretical and experimental research, so it is important to also strive to make computing and simulation more ubiquitous and put these new capabilities in the hands of people whose focus is on problem-solving rather than on computation. For example, to support the increasingly tight connection between metrology and computation, high-performance computing must become ubiquitous and user-friendly.

As investigative tools that support nanotechnology and as components in multiscale simulation, simulations must improve. For example the accuracy and speed of *ab initio* electronic structure calculations and molecular dynamics simulations must advance. Many existing, well-developed, and extensively used codes will need to be rewritten to exploit the capabilities of new hardware.

Barriers

A significant challenge for nanotechnology in general and for the development of multiscale/multiphenomena modeling in particular is the need to develop a long-term dialogue between the different disciplines spanning nanoscience and engineering. Experts must acquire knowledge from experts in other fields, which can take considerable time. Funding models often emphasize short-term achievement, making it difficult to engage in such long-term objectives. The dispersion of expertise across the globe represents another barrier, both within the TM&S community and for connecting with experimentalists seeking solutions to multiscale problems.

Scientific and engineering research are often separated, and this represents another barrier to the development of nanotechnologies. Opportunities for new technologies can be missed, and impractical outcomes and poor return on investment can also occur. To realize the promise of nanotechnology, the science and applications must be brought together in application-driven research that addresses well-defined grand challenges.

The education system's traditional departmental boundaries can also be a barrier. New pedagogical materials are being developed to convey the principles of nanotechnology to students and practicing engineers and scientists, but often they are simply extensions of traditional educational approaches. To realize the transformative potential of nanotechnology, educators must rethink the intellectual foundations of disciplinary fields from a "nano" perspective to give students the broad conceptual scientific foundation to be creative contributors to the development of nanotechnology. Programs should be encouraged that truly integrate disciplines while still giving students the depth in a single discipline that makes them useful contributors to multidisciplinary teams. Computing is increasingly sophisticated, so there is a need to train a generation of computational nanoscientists with expertise in advanced, numerical algorithms, parallel computing, and in exploiting the unique characteristics new generations of computing technology, such as GPU chips.

Solutions

To achieve the ambitious goals outlined above, a ten-year focus on four key areas is needed.

A. Multiscale Modeling and Simulation of Complex Materials and Integrated Nanosystems

Why? Shaping the properties of matter at the nanoscale to realize devices and systems at the human scale is the vision of nanotechnology. To realize this vision, nanoscience theorists and analysts must develop new conceptual frameworks for multiscale problems, new numerical approaches that span spatio-temporal scales, and new multiscale simulations that are predictive. TM&S can help identify ideas with technology potential and set the stage for experimental work.

Why now? The first decade of the NNI has given us a much better understanding of nanoscale building blocks. There is a growing appreciation that understanding integrated nanosystems involves much more than understanding the atomistic and nanoscale components. TM&S is moving up in scale to larger systems. Nanoscience has produced so many ideas that it is not possible to thoroughly explore each one experimentally, and increasingly predictive simulations have the potential to actually replace experiments to a significant extent.

Strategy: Combine "up-scaling" and "down-scaling" (top-down vs. bottom-up) approaches and people. Both viewpoints are necessary to develop unified conceptual and computational frameworks for both multiscale modeling and simulation. Support teams are needed that couple application developers with computational experts and couple industry with academia.

Drivers: Application drivers include drug discovery, catalysis design, organic photovoltaics, batteries, programmed materials, patchy particles, searches for a new logic switch, transformative thermoelectric technologies, etc.

B. Nanotechnology Fundamentals and Numerical Methods

Why? While the focus of the next decade must shift to larger, more complex systems, our fundamental understanding of the underlying processes and components is still incomplete and must not be neglected. Research on new computational methods is also needed because increases in hardware performance alone will not be sufficient.

Why now? Much has been learned over the past decade, but there is still much that is not understood about conduction in molecules, the quantum to classical transitions, thermal transport across van der Waals bonded interfaces, etc. Much more effective numerical techniques are also needed (e.g., to enable automatic up- and down-scaling in multiscale simulation.)

Strategy: Target funding for individuals and small groups that simultaneously engages experimentalists, theorists, and computational experts to address critical areas where improved understanding is needed.

Drivers: Fundamental studies should be directed at acquiring knowledge that ultimately contributes to nanotechnology effectively addressing grand challenges in energy, the environment, and health. Examples of TM&S problems to be addressed include improved understanding of many-body effects, weak force interactions, thermal dissipation in molecular systems and at van der Waals bonded interfaces, and working principles of self-assembly as well as mathematical theories that increase the speed and accuracy of simulations and permit computer-driven up- and down-scaling.

C. Pervasive High-Performance Computing

Why? Reducing CPU execution time can make high-end computing ubiquitous, thus enhancing the capabilities of theorists, experimentalists, designers, and educators.

Why now? Advances in CPUs (e.g., multicore configurations and graphical processing units) increasingly make high-end computing part of mainstream research practices. Sophisticated instrumentation requires embedded simulation. Nanomanufacturing will require a new generation of design and manufacturing tools. Powerful scripting platforms have blurred the lines between theory and simulation.

Strategy. Increase the power of scripting platform computing, create and support open-source science codes, exploit cyberinfrastructure and cloud computing to broaden access to computing, create supercomputer/software facilities that provide "end-station" service to high-end users.

Drivers. The computational end-station concept described in Section 1.4 below should be driven by national lab–university partnerships to address scientific and computational grand challenges. Cyberinfrastructure and science gateways should be exploited to make the use of simulation tools ubiquitous and to cooperatively engage both experimentalists and computational experts.

D. Education for Nanoscience and Engineering and Computational Nanoscience

Why? The promise of nanotechnology will be realized as practicing engineers and scientists and the new engineers and scientists who are being educated now learn how to transform technology by understanding and applying the new capabilities that nanoscale science provides.

Why now? The first decade of the NNI has greatly improved our understanding of nanoscale phenomena. Educational materials are beginning to appear, but the textbooks being used are still traditional, with nanoscience "add-ons." What is needed is an ambitious initiative to rethink the intellectual foundations of the separate fields of science and to develop a new class of textbooks that unites scientific knowledge, breaks down disciplinary boundaries, inspires students, and prepares them to contribute to the development of nanotechnology.

Strategy: Support teams that include experts in TM&S with experimentalists to reinvent the curricula in fields such as materials science, electronics, photonics, biomedical engineering, chemical engineering, and chemistry, etc. The educational materials produced by these teams should be made available as "open courseware" resources to serve as resources for self-study and as models for instructors worldwide. Programs to train students in the art of scientific computation using leading edge algorithms and new computing architectures should be developed and presented on a continuing basis.

Drivers: The new knowledge emerging from research should drive the new intellectual constructs and innovative educational materials developed to support nanotechnology.

1.4 SCIENTIFIC AND TECHNOLOGICAL INFRASTRUCTURE NEEDS

Traditionally, infrastructure for TM&S has meant leadership-class supercomputing facilities, but the infrastructure needs for TM&S are much broader. The emergence of so-called cyberinfrastructure over the past ten years has created new technologies to address several important needs. Leadership-class supercomputers are increasingly important, but access models need to evolve. Often overlooked is the fact that numerical methods, mathematical libraries, community science codes, etc., are critical parts of the infrastructure for TM&S.

Finally, new types of institutes that can provide the focus and concentration of expertise needed to turn nanoscience into nanotechnologies should be considered.

Cyberinfrastructure

Cyberinfrastructure has demonstrated its effectiveness in facilitating nanotechnology R&D through initiatives such as the TeraGrid, Open Science Grid, and nanoHUB.org. In the next decade, cyberinfrastructure should play an increasingly important role in:

- Testing and validating databases (e.g., for interatomic potentials and pseudo-potentials)
- Broadly disseminating new research methods and software
- Providing broad access to online simulation services for experimentalists and educators
- Disseminating cross-disciplinary and novel educational resources
- Workforce development and in-service training (e.g., parallel programming for GPU chips)
- Connecting theorists and experimentalists in collaborative research
- Technology transfer of computational tools from academia to industry

The Network for Computational Nanotechnology's nanoHUB (http://www.nanoHUB.org) is an example of the power of cyberinfrastructure. The marriage of a software development platform with cloud computing technology (e.g., the Rappture toolkit: https://nanohub.org/infrastructure/rappture/) enables computational experts to share tools with collaborators or with the nanotechnology research and educational community broadly. Live simulation services, not just software codes, are provided through a web browser. By coupling simulation services with resources for training and education in nanotechnology, a major international resource has been developed that serves more than 150,000 users annually. Broader and more creative applications of cyberinfrastructure in the next decade can enhance the impact of TM&S on the development of nanoscience and nanotechnology. Sustained funding in support of computational science and engineering cyberinfrastructure will be necessary to realize this potential.

Supercomputing Infrastructure

The NSF TeraGrid and Open Science Grid provide researchers with access to high-performance computing services, and national laboratories make leadership-class supercomputing available through competitive processes. Computational nanoscientists have benefitted from these facilities. In the future, supercomputing facilities must evolve to address the needs of computational nanoscientists.

At the leadership-class end of computing—currently petascale, and before the end of the decade, exascale—costs are very high, making such computational facilities affordable by only a few large organizations. A number of user facilities for experimentalists exist. These user facilities operate in the mode that a sponsoring Federal agency builds and manages a core facility that supplies a unique high-end resource, and then user communities (including researchers from other Federal agencies, academia, and industry) build and maintain "end-stations" consisting of specialized instrumentation to make use of the resource. As an example, the Department of Energy (DOE) manages the Spallation Neutron Source, consisting of a proton accelerator, storage ring, target building, and several core instruments, which provide researchers with neutrons via end stations that are partially or completely funded by

NSF, NIH, and industry.[14] Given the cost and difficulty of operating leadership-class computing facilities, the user facility/end station model is one that is increasingly being applied. This concept is already being embraced at DOE's Oak Ridge National Laboratory in the National Center for Computational Sciences, where an end station for nanoscience is being developed by the Center for Nanophase Materials Sciences (CNMS) in collaboration with computer scientists in the Computer Science and Mathematics Division at Oak Ridge. Broad access to these kinds of facilities will be required to address computational grand challenges in nanotechnology.

Methods Development

Significant investments have been made in supercomputer facilities, but less attention has been directed at the systematic development of new computational methods. For example, to exploit the capabilities of GPU chips, much of the TM&S community's existing simulation code will need to be rewritten. Optimized math libraries are needed. In the U.S. funding model for physical, materials, and chemical sciences, researchers are funded to solve scientific problems, not to develop computational software and numerical methods. Predictive simulation of materials and multiscale modeling are areas where methods development is critical and must be funded long term. A great deal of funding already goes into theory and simulation, but no good mechanism exists for funding research on the new methods the community codes that can lead to real breakthroughs in computation. Numerical methods and algorithms and open-source science codes should be considered part of the critical infrastructure for TM&S. The education and training to make effective use of these resources should also be considered part of the TMS infrastructure.

Problem-Specific Institutes

To effectively address grand challenge problems in nanotechnology, problem-specific institutes that engage industry and academia, experimentalists and experts in TM&S, scientists, and technologists could play an important role. Participants would spend time in residency at these institutes. The synergy of different people with different expertise and experience focusing collectively on a common problem would accelerate progress in turning nanoscience into nanotechnologies.

Virtual Institutes for Simulation-Driven Research

Problem-driven institutes would focus on specific problems, and TM&S expects would play a supporting role in teams of experimentalists and application designers. A second kind of institute, one led by experts in TM&S, should also be considered. In these institutes, teams of theorists and modeling and simulation experts, guided by experimentalists and application designers would be charged to computationally assess and prototype potential new technologies. The goal would be to set the stage for subsequent experimental work, but this kind of work would also spur the development of multiscale modeling and simulation capabilities.

[14] See http://www.er.doe.gov/bes/brochures/files/BES_Facilities.pdf for an overview of DOE user facilities.

1.5 R&D INVESTMENT AND IMPLEMENTATION STRATEGIES

Over the course of the next decade, significant sustained (or renewable) investments are needed in:

- Principal investigator (PI)–driven research to address nanoscience fundamentals.
- Small interdisciplinary research groups. Support should be renewable to provide the long-term continuity necessary for successful multi-disciplinary teams.
- Large-scale and problem-focused research centers and institutes that specifically address the grand challenges of complex materials and integrated, functional nanosystems.
- Large-scale, problem-driven and simulation-driven institutes that also address grand challenge problems and that set the stage for subsequent experimental programs.
- Research on computational methods, including open-source science codes, algorithms for new computing architectures, etc. Special emphasis is needed on methods specifically directed at exploiting the capabilities of new multi-core and graphical processor architectures and on revising widely-used community codes to take advantage of these new capabilities.
- Pervasive simulation (fast, user-friendly, accurate, reliable, transitioning from laboratory codes to community codes for research and education used by computational experts as well as by others). The need for user-friendly software designed for non-experts will dramatically increase to support design and nano-manufacturing.
- Strategies to promote university-industry and international partnerships.
- Cyberinfrastructure to support pervasive computing, collaboration, and dissemination of simulation services, research methods, community-wide databases, educational resources, etc.

1.6 CONCLUSIONS AND PRIORITIES

The past ten years have witnessed numerous advances in nanoscience as well as in theory, modeling, and simulation for nanoscience. In particular, the understanding of and ability to simulate nanoscale building blocks has advanced substantially. The stage has been set, and the priority for theory, modeling, and simulation now is to address the challenge of turning advances in nanoscience into nanotechnologies. To address this challenge, the TMS community must focus on atoms to applications multiscale/multi-phenomena simulation. Such multiscale frameworks will make use of scale-specific simulations (e.g., quantum chemistry, molecular dynamics, electron transport, etc., codes, so support on the underlying fundamentals of nanoscience building blocks and on numerical and computational methods cannot be neglected.

Three broad priorities for TMS during the next decade can be identified:

- Application-driven, team-based TMS research directed at identifying solutions to specific, high priority challenges in energy, the environment, health, and security. A closely-related objective should to develop broadly applicable conceptual and computational frameworks for multiscale modeling and simulation rather than problem-specific, ad hoc solutions. Priority applications include predictive design of materials and programmed materials, and design and manufacturing of large, complex, engineered nanosystems.
- Nanoscience fundamentals research addressed at proposals for new experiments and at exploring and elucidating new fields of nanoscience.
- Computational and numerical methods research directed at achieving a 10^3-10^4 increase in the size of problems that can be simulated by exploiting the capabilities of new

computing architectures and at devising improved numerical algorithms. Such developments would allow simulation, computer testing, and design of complex nanosystems leading to fundamentally new products in the third and fourth generation of nanotechnology development (see preliminary chapter, The Long View of Nanotechnology Development, Figure 6).

1.7 BROADER IMPLICATIONS FOR SOCIETY

The promise of nanoscience lies in its potential to develop new technologies to address the great challenges that human society faces in energy, the environment, health, and security. As discussed in subsequent chapters, TM&S often plays a supporting role in the creation of nanoscience understanding and in the development of new technologies. The use of TM&S leads to shorter design cycles, which increases the impact of nanotechnology on society. In the next decade, TM&S also has an opportunity to play a leading role in the development of nanotechnology. Predictive simulation has the potential to greatly accelerate R&D in fields such as catalysis design and drug discovery. If this promise of predictive design can be realized, the impact on society would be substantial. Broader use of multiscale/multiphenomena simulation could also influence technology development directions. Nanoscience generates possibilities for new technologies, but it generates many more potential technology paths than can be experimentally explored. TM&S has the potential to rapidly explore and assess potential technologies and to then guide subsequent experimental work. In this way, TM&S can amplify the impact of nanotechnology on society.

It has been said that "The purpose of computing is insight, not numbers" (Hamming 1971). Simulation coupled with powerful human interfaces and visualization can promote public understanding of nanoscience and its potential benefits to society. Moreover, the insights and understanding that emerge in the course of developing computational tools can be extremely important pedagogically. New ways of understanding nanoscience and technology facilitated by TM&S research have the potential to reshape educational paradigms and impact students at all levels, including college, pre-college, and post-college.

1.8 EXAMPLES OF ACHIEVEMENTS AND PARADIGM SHIFTS

1.8.1 Quantitative Simulation and Prediction of Molecular Conductance

Contact persons: J. B. Neaton, Lawrence Berkeley National Laboratory
L. Venkataraman, Columbia University
S. Hybertsen, Brookhaven National Laboratory

Understanding and control of electron flow through matter at the molecular level presents fundamental challenges to both experiment and theory. For more than a decade, researchers have sought to trap and "wire up" individual molecules into circuits and to probe the electron transport properties of the smallest, single electrical components imaginable. The experimental challenge lies in assembling these devices in a reproducible manner, which requires exquisite control of electrical contacts, or "alligator clips," between molecules and leads at length scales currently beyond resolution limits of experimental characterization techniques. The theoretical challenges lie in modeling the possible distribution of junction structures at the atomic scale and computing the electron transport through such junctions, a fundamentally non-equilibrium problem. Ultimate goals for both experiment and theory are elucidation of different fundamental regimes of electron transport, and the discovery of molecular structures that support a significant nonlinear electrical response, such as switching.

Since the junction conductance fundamentally derives from electron tunneling processes at the single molecule length scale, predictive theory requires the average positions of all atoms within the junction—as well as a self-consistent description of their bonding and electronic energy level alignment—when the junction is under bias. A decade ago, atomistic first-principles methods for computing electrical conductance, based on density functional theory (DFT), were in their infancy. Although significant challenges remain, recent advances in the field have resulted in theories that provide reliable predictions for nanoscale conduction. These theories have been compared to accurate, well-characterized experiments for a broad class of molecules where amine-links provide reliable single molecule circuit formation with gold electrodes (Venkataraman et al. 2006a; Quek et al. 2007). In particular, the use of static DFT within standard approximations for exchange and correlation is insufficient for computing conductance and current, even in the linear response case. Direct incorporation of correlation effects in the junction conductance is essential, e.g., with a new, practical first-principles approach, DFT+Σ (Quek, Choi et al. 2009).

In an example probing novel functionality in a single molecule circuit, recent experiments showed that gold-bipyridine-gold junctions could be mechanically switched between two states, simply by pushing and pulling the junction (Figure 1.6; Quek, Kamenetska et al. 2009; Kamenetska et al. 2010). Using the DFT+Σ approach, the conductance was accurately calculated, and the conductance switching was understood to arise from controllably altering the pyridine-gold link structure. Owing to these and related advances, experiments probing molecular conductance are much more reproducible and simulations are much more predictive than they were 10 years ago.

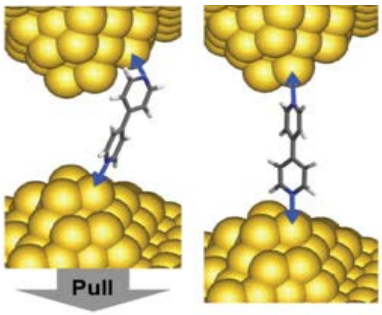

Figure 1.6. New developments in the theory of molecular conduction have resulted in quantitative simulations of molecular junctions. A joint theory and experiment collaboration showed that electrical conductance of a bipyridine-Au molecular junction can be turned "on" or "off" simply by pushing or pulling on the junction. (from Quek, Kamenetska et al. 2009).

1.8.2 Controlling Individual Electrons in Quantum Dots

Contact person: Michael Stopa, Harvard University

Quantum dots can be used as artificial atoms fabricated within a semiconductor heterostructure whose state can be controlled by metallic gates, voltage biases applied to source and drain contacts, and externally applied magnetic fields. These dots, which represent isolated puddles of electrons *inside* the solid, can be fabricated in groups, producing artificial molecules typically, though not exclusively, in a two-dimensional arrangement. Theory and modeling of quantum dots has taken major strides in the past decade, leading to predictions of phenomena such as: (1) single electron devices like diodes (Stopa 2002), (2) artificial molecular electronic structure (Rontani et al. 2004), and (3) the possible realization of quantum computation (Loss et al. 1998). The primary objectives of all

of these applications have been to prepare, manipulate, and measure the state of one or several electrons in one or several dots.

In the early 2000s, semiconductor quantum dots had evolved to a stage where the electron number on a single dot could be tuned down to one and then zero reproducibly. Experiments involved measuring a current *through* the dot and varying it with source-drain biases, external voltages on gates and a magnetic field. Principally, control of the electron state in artificial atoms was achieved through the Coulomb blockade phenomenon, whereby addition of an electron to a dot required a single electron charging energy cost to be paid either by varying a gate voltage or a source-drain voltage.

Two major advances have occurred (both elucidated by close experiment-modeling synergy) that have enhanced the control over these systems. First, the use of "listening" devices—essentially tiny variable resistors that can sense the presence of one electronic charge on a nearby dot—were perfected (Barthel et al. 2010). Second, the phenomenon of the "Pauli blockade"—whereby electrons in the same spin could not occupy the same spatial state—was discovered and elucidated (Figure 1.7; Ono et al. 2002). These two phenomena, together with gate control for shuttling electrons back and forth between members of complexes of dots, allowed for exquisite probing of the single or many-electron state of dots, including spin information, and for the exploration of coherent evolution of those states. Various sequences of prepare-evolve-measure the quantum state, which are the building blocks of quantum computation, have been perfected.

The ultimate goal of scalable quantum computation with its exponential speedup of the solution of several problems is still far off, though it has been made closer. Also, considerable light has been thrown on the many-body problem, the interaction of electrons and nuclei and coherent time-dependent behavior of the many-body system through these advances.

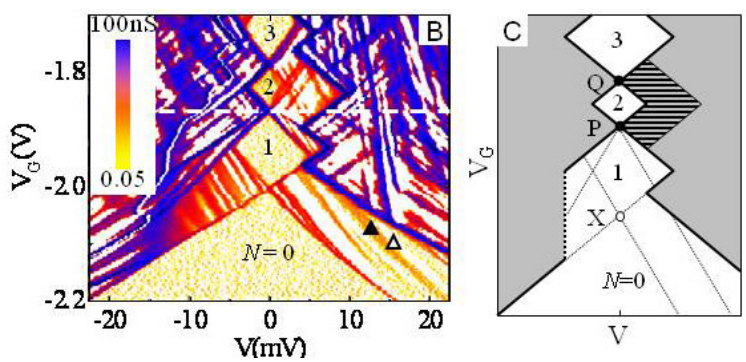

Figure 1.7. "Coulomb diamond" stability diagram showing, as a function of a gate voltage and a source-drain voltage, the current through the double-dot. Where the current is small, particular charge states are stable (diamonds labeled 1, 2, and 3). The extended region on the right of the two-electron dot is a region where a particular spin state (the two-electron singlet) is the stable ground state (from Ono 2002).

1.8.3 Electronic Recognition of DNA Sequence using a Nanopore

Contact persons: A. Aksimentiev, University of Illinois Urbana-Champaign
G. Timp, University of Notre Dame

High-throughput technology for sequencing DNA has already provided invaluable information about the organization of the human genome and common variations of the genome sequence among groups of individuals. To date, however, the high cost of whole-

genome sequencing limits widespread use of this method in basic research and personal medicine. Using nanopores for sequencing DNA may dramatically reduce the costs of sequencing, as they enable, in principle, direct read-out of the nucleotide sequence from the DNA strand via electrical measurement (Branton et al. 2008).

The first experiments demonstrating the possibility of detecting DNA sequences using nanopores employed a biological channel (alpha-hemolysin) suspended in a fragile lipid bilayer membrane (Kasianowicz et al. 1996). Recent advances in nanofabrication technology have allowed nanometer-size pores to be manufactured in thin synthetic membranes, offering superior mechanical stability and the potential for integration with conventional electronics. However, the question remains on how to use such pores to read out the sequence of a DNA molecule.

Using molecular dynamics simulations as a kind of a computational microscope, several plausible strategies for sequencing DNA have been devised (Sigalov et al. 2008; Payne et al. 2008; Timp et al. 2010). One such method is illustrated in Figure 1.8. The key component is a nanometer-diameter pore in a thin capacitor membrane that consists of two conducting layers (doped silicon) separated by a layer of insulator (silicon dioxide). An external electric bias is applied across the membrane to drive a single DNA strand back and forth through the pore, while the electric potentials induced by the DNA motion are independently recorded at the top and bottom layers (electrodes) of the capacitor membrane. Another possible sequencing method exploits the unique mechanical properties of double-stranded DNA, which permit a DNA molecule to be threaded through a nanopore smaller in diameter than the canonical DNA double helix (Timp et al. 2010). The ability of atomic-scale simulations to provide realistic images of DNA conformations in synthetic nanopores and to relate such conformations to experimentally measured quantities has been of critical importance to the development of these sequencing methods. When implemented technologically, nanopore sequencing of DNA molecules will offer an affordable research tool to benchtop scientists across a broad range of disciplines and enable the use of whole-genome sequencing as a routine screening and diagnostics method, opening the door to personalized medicine.

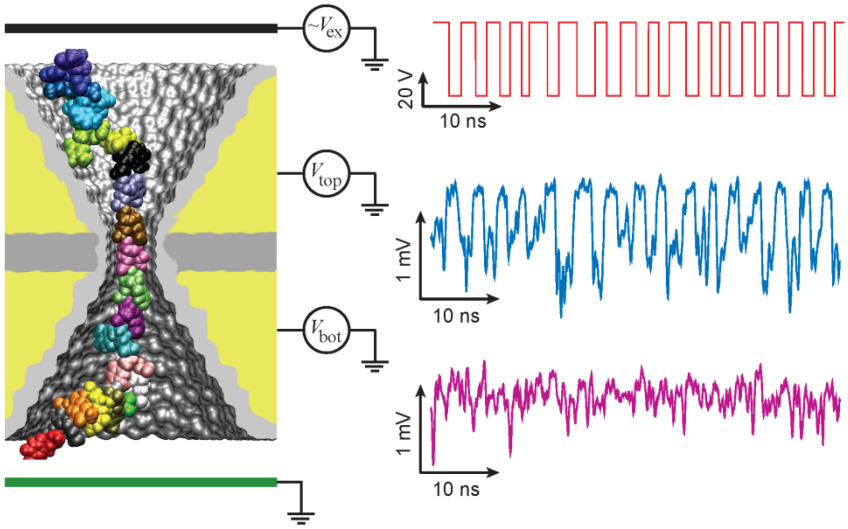

Figure 1.8. Driven by an external electric field, a DNA molecule permeates a nanometer-size pore in a multilayer semiconductor membrane. The nucleotide sequence of the DNA molecule is recorded as the change of the electrostatic potential in the capacitor (from Sigalov et al. 2008).

1.8.4 Modeling and Simulation of Spin-Transfer Torque (STT) Devices

Contact persons: Sayeef Salahuddin, University of California, Berkeley
Stuart Parkin, IBM Almaden Research Center

A decade ago, the only way to switch the magnetization of a magnet was with an applied magnetic field. In 1996, Slonczewski and Berger independently predicted that switching might be possible in a nanoscale magnet by means of a spin-polarized current (Slonczewski 1996; Berger 1996). The essential idea is that when spin polarized electrons flow through a nanoscale magnet, they transfer their spin angular momentum and thereby align the magnet in the direction of the polarized spins. Subsequently, this prediction was experimentally demonstrated by the Ralph and Buhrman groups (Katine 2000) at Cornell University, and the effect is currently being considered as a candidate for a memory that is fast as well as nonvolatile, often called a universal memory.

Nonetheless, we are still at a very early stage of understanding the device physics. For example, direct measurement of spin angular momentum being transferred to the magnet (referred to as the spin torque) has been performed only very recently. The behavior of spin torque shows rich dependence on device geometry and external stimuli like voltage and magnetic field. Recently, a simulation methodology that explains the underlying physics in a simple manner suitable for device design has been developed (Salahuddin 2007). The ferromagnet is modeled using a free electron model and the insulating material as a tunneling barrier. This description of magnetic tunneling junctions is not new; the advance lies in the fact that the transverse modes arising from a large cross section in an experimental device can now be included, and the measured torque dependence can be quantitatively explained.

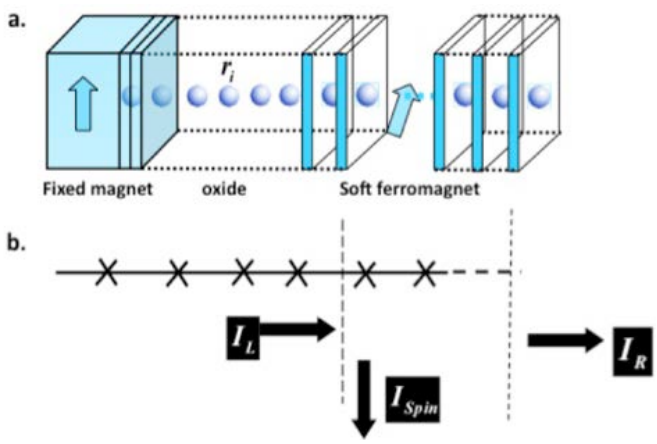

Figure 1.9. (*a*) Schematic of an STT device. An insulator is sandwiched between two ferromagnets. The magnetization of the fixed magnet is kept unchanged. On the other hand, the magnetization of the soft ferromagnet can be changed by applying a spin polarized current through it. (*b*) A simple depiction of underlying physical mechanism. The difference between the spin angular momentum at the left and right interfaces of the soft ferromagnet is absorbed by the magnet itself. This subsequently tries to realign the magnetic orientation to the direction of polarized spins (from Salahuddin et al. 2007).

STT devices are a unique example where TM&S has guided every step of development starting from the initial conception to material optimization. Recent advances provide us with a quantitative tool to analyze experiments and design devices. STT devices are currently also fueling exciting research for a new class of devices where magnetization may be switched just

by applying an electric field (Figure 1.9). Using current to switch the state of a magnet is a new paradigm for electronic devices.

1.8.5 New Materials Based on DNA-Linked Gold Nanoparticles and Polymers: A Theoretical Perspective

Contact person: George C. Schatz, Northwestern University

Gel-like materials derived from DNA-linked nanoparticles, polymers, or molecules are a new class of materials that have emerged in the last 15 years as a result of advances in synthetic methods, including the ability to routinely synthesize oligonucleotides with specified base-pair sequences, and the ability to chemically tether oligonucleotides to metal (typically gold or silver) particles or to organic molecules. The development of these materials has also been stimulated by theory and computation. Shown below (Figure 1.10) is a schematic of these materials, with a DNA-functionalized gold nanoparticle shown on the left and the corresponding DNA-linked nanoparticles on the right.

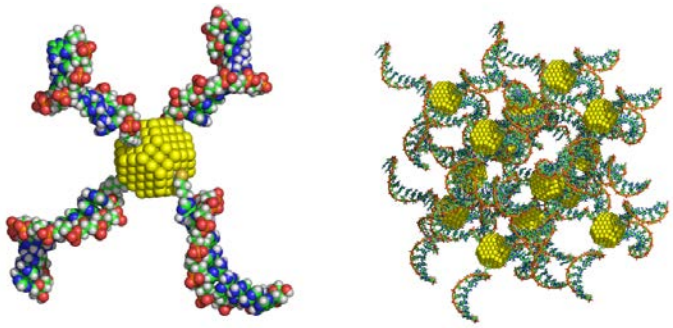

Figure 1.10. *Left panel*: theoretical model of DNA-functionalized gold nanoparticle. *Right panel*: model of DNA-linked gold nanoparticle crystal (adapted from Lee and Schatz 2009).

These materials have quickly demonstrated their usefulness for DNA and protein detection using optical and electrical methods, and there is recent interest in using the functionalized nanoparticles for therapeutic applications, such as for siRNA delivery. Moreover a new generation of DNA-linked materials chemistry is starting to appear with the recent discovery that crystalline rather than amorphous structures can be produced when DNA links the particles together, and that the properties of these crystalline materials can be varied over a wide range by varying DNA length, base-pair sequence, and nanoparticle size and shape (Park et al. 2008).

The properties of these materials have been of great interest to theorists, but predicting these properties is a huge challenge due to the complexity of the structures. When the first DNA-linked gold nanoparticle aggregates were synthesized in the mid-1990s, it was quickly discovered that the thermal melting (dehybridization) transitions in these materials were quite different from the corresponding transitions for the same DNA structures in solution. This behavior also occurs for DNA-linked polymers, but not all DNA-linked structures show this. This work led to the development of a number of theoretical models that can roughly be grouped according to whether they treat the problem as an aggregated material that undergoes a bulk-like phase transition or as the cooperative melting of pairs of particles within an aggregate that are linked by several DNA structures.

Interest in separately observing these two mechanisms has stimulated additional experiments and the development of new classes of materials, including (1) DNA structures

that can partially melt without unlinking, (2) PNA/DNA linked materials (PNA = peptide nucleic acid), and most recently, (3) DNA-linked molecular dimers, in which two organic molecules are linked by three DNA nanoparticles. The dimer experiments cleanly show that cooperative melting can occur, and a molecular dynamics study based on a newly developed coarse-grained DNA model (Lee et al. 2009) has provided an interpretation of these experiments, showing the importance of rigidity of the structure on entropy release in producing cooperativity. Theory has also provided much of the motivation for the development of DNA-linked nanoparticle crystals.

The structural properties of the DNA-functionalized and DNA-linked particles are also surprising. For example the maximum density of ss-DNA that can be attached to gold particles using thiol linkers is amazingly high (compared to DNA-functionalized silica particles, or compared to DNA-functionalized flat gold surfaces), and has been found to depend on particle diameter, being largest for the smallest-diameter particles. In addition, the length of DNA, which is either attached to just one gold particle, or through which hybridization chemistry links two particles together, is apparently much shorter than in conventional Watson-Crick DNA, and it has been proposed that perhaps the DNA structure is A-form rather than B-form in these structures. Although there has been progress with modeling these properties using atomistic molecular dynamics, there are unresolved issues that are at the limit of current simulation technology.

1.8.6 Performance Limit and Design Modeling for Nanoscale Biosensors

Contact person: Muhammad Alam, Purdue University

Biosensors based on silicon nanowires (Si-NW), silicon nano-cantilevers, and composites of carbon nanotubes (CNT) promise highly sensitive, dynamic, label-free, electrical detection of biomolecules with potential applications in proteomics and genomics (Hahm et al. 2004; Star et al. 2006; Gupta et al. 2006). In a parallel array configuration, each individual pixel (sensor) can first be functionalized with specific capture molecules. Once the analyte molecules are introduced to the sensor-array, they are exclusively captured by pixels with complementary probes. The conjugations are reflected in changes of the conductivity (DG) or that of the resonant-frequency (dw) (for cantilever sensors) of the corresponding pixel. The differential map of electrical conductivity before and after conjugation identifies the molecules present in the analyte.

The basic function of the nano-biosensor, as described above, is intuitively obvious and has been extensively verified by many research groups (Zheng et al. 2005; Gao et al. 2007; Stern et al. 2007; Kuznezow et al. 2006; Li et al. 2004). Key challenges now include (1) the minimum detectable limit of analyte concentration by nano-biosensors (current estimates vary from nanomolar to femtomolar), (2) the proper design of sensitive biosensors (as a function of diameter, length, and doping, and fluidic environment, etc.), and (3) the limits of selectivity (i.e., ability to avoid false positives) of a sensor technology. During the past few years, a new theoretical framework to systematically address the above-mentioned questions and consistently interpret apparently contradictory data has been developed. In this regard, theoretical concepts of "geometry of diffusion," "screening-limited response," and "random sequential absorption" have made fundamental contributions to the understanding of biosensors.

To address the first question of minimum detection limits of nano-biosensors (for a given measurement window), a simple analytical model based on reaction diffusion theory can predict the tradeoff between average response (settling) time (t_s) and minimum detectable

concentration (r_0) for nano-bio and nano-chemical sensors. The model (Nair 2006) predicts a scaling relationship $\rho_0 t_s^{M_D} \sim k_D$ where M_D and k_D are dimensionality dependent constants for 1D (planar), 2D (nanowire/nanotube: NW/NT), and 3D (nano-dot) biosensors (see Figure 1.11). Surprisingly, this model suggests that the improvement of the sensitivity of NW/NT sensors over planar sensors arises not because the geometry of the electrostatics, but rather due to the geometry of diffusion. The model also predicts that "femtomolar" detection, a theoretical possibility advanced by some groups, may actually be difficult for any practical measurement time.

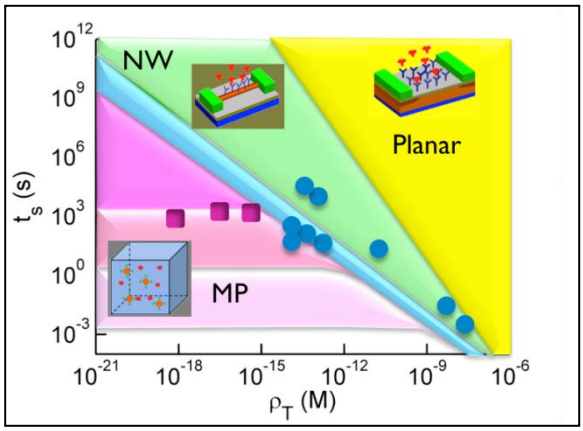

Figure 1.11. Phase space of biosensor response. The different regions show the analyte concentration (ρ_T) that can be measured in a given sampling time (t_S). Classical planar sensors require more time to detect a given analyte concentration. Planar, nanowire (NW), and magnetic particle (MP) sensors behave differently due to their different diffusion characteristics. The enhanced sensitivity of MP bio-barcode sensors is due to a reduction of the diffusion bottleneck by dispersing the "sensors" with the volume of the analyte. (Symbols denote sources of experimental data: NW (*dots*) from Zheng et al. 2005; Gao et al. 2007; Stern et al. 2007; Kusnezow et al. 2006; Li et al. 2004; MP (*squares*) from Goluch et al. 2006; Nam et al. 2004; Nam et al. 2003).

Regarding the second question of electrostatic design of highly sensitive nano-biosensors, one finds that the role of screening is critical in dictating the response of biosensors, and the sensitivity of the biosensor is a nontrivial function of doping, device geometry, and fluidic environment (Nair 2008). For example, simple electrostatics calculations suggest that reduced doping would improve modulation of conductivity (for a given adsorbed charge from a biomolecule), yet device-to-device random dopant fluctuation may actually make the operation of such low-doped sensors difficult and expensive.

Finally, the problem of selectivity can be understood within the framework of random sequential absorption of capture molecules (Nair 2010). Since the theoretical maximum of RSA surface coverage is 54%, one can show that long incubation time and surface passivation by molecules (e.g., PEG) much smaller than the target molecule is the only viable approach to high selectivity. Each of these predictions has now been confirmed by numerous experiments.

1.8.7 First-Order Phase Transition to an Ordered Solid in Fluids Confined to the Nanoscale

Contact person: Peter T. Cummings, Vanderbilt University/Oak Ridge National Laboratory

As we shrink the size of mechanical devices to nanoscopic dimensions—such as hard disk drives, where the distance between the read head and the spinning platter is already less than 10 nm and going down exponentially—the lubrication of these systems becomes an increasingly pressing issue. Some experiments have suggested that a typical lubricant fluid becomes a solid when the distance between the surfaces confining the fluid become nanoscopic, thus rendering the lubricant useless, while other experiments contradict this finding. For over two decades, intense debate about whether or not nanoscale confinement of a fluid can induce a first order phase transition to an ordered solid structure has been an enduring controversy in nanoscience.

Clearly at the heart of the debate over the effect of nano-confinement is the inability to observe directly, via experiment, the structural changes that occur when a fluid is nanoconfined. Molecular simulations can be performed that mimic the experimental system, in which two molecularly smooth mica surfaces are gradually brought to a separation on the order of several nanometers while immersed in the fluid to be studied, and can be used to gain insight into the atomic level structural changes underlying this complex behavior. Such simulations were first attempted in the early 2000s for n-dodecane ($C_{12}H_{26}$) nanoconfined between mica-like surfaces using a united atom (UA) approach and showed a first-order phase transition to a layered and herringbone-ordered structure. Though these simulations provided valuable insight into the effects of nanoconfinement, they were based on several simplifying assumptions (driven by the available computational resources), particularly in the description of the mica surfaces. Due to major advances in both computational hardware and algorithms, these shortcomings have been eliminated and fully detailed atomistically, molecular dynamics simulations have now been performed (Docherty et al. 2010; Cummings et al. 2010) that are faithful to the corresponding experimental systems in a way not previously possible and provide compelling evidence supporting the existence of a phase transition.

The key results are typified by Figure 1.12; specifically, the simulations show that upon sufficient confinement, a range of fluids (from linear to cyclic alkanes) undergo a first-order phase transition to a layered and ordered solid-like structure.

The remarkable finding of this work is that even though the fluids are nonpolar (or very weakly polar), it is nevertheless the *electrostatic* interactions between the fluid and the ions in the mica that drive the fluid-solid transition—an insight that was missing from earlier simulations because the simplified models used did not involve electrostatic interactions.

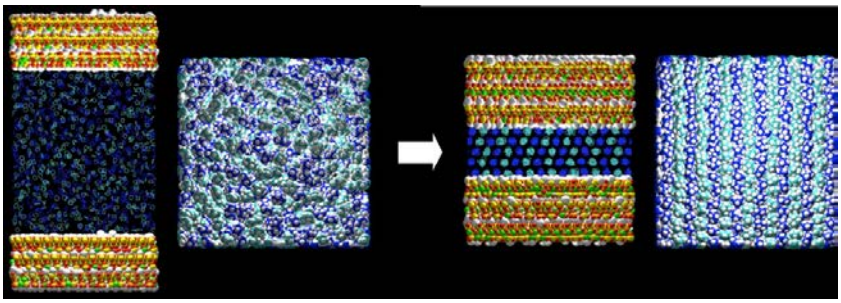

Figure 1.12. Upon sufficient nanoconfinement, cyclohexane undergoes a rapid and abrupt transition to a layered and hexagonal ordered, solid-like structure. In the configurations, the mica sheets are shown and the cyclohexane rendered in stick form on the left, so that it is easy to see through the confined fluid; the confined fluid, rendered in full size without mica, is shown on the right, looking down from above. Cyclohexane molecules (H atoms white, C atoms shades of blue) are colored in two different shades of gray, making the resulting order apparent (from Docherty et al. 2010).

1.8.8 Single-Impurity Metrology through Multi-Million-Atom Simulations

Contact persons: Gerhard Klimeck, Purdue University
Sven Rogge, Delft University of Technology, The Netherlands

Improvements in electronic devices have marched along Moore's law (the doubling of the number of transistors on a chip each technology generation) for the past 40 years, reaching the ultimate limit of atomic-scale devices, high power density, and unscalable economics. To enable further computing capability advancements a replacement concept is needed. Just over 10 years ago Kane proposed a quantum computer based on hydrogen-like quantum states of individual phosphorus impurities in silicon (Kane 1998). Quantum Bits (qbits) are to be encoded in the quantum states of the individual impurities and the associated electrons and manipulated through proximal electronic gates. The concept was based on known bulk concepts, but no theory or experiment existed on gated single donors.

Early hydrogenic models were built at the University of Melbourne (UM), followed by effective mass models by various authors. Even though a single impurity serves as qbit host, the confined electron experiences the presence of around a million atoms around it (Figure 1.13). A detailed understanding of the complex silicon band structure became necessary leading to a band minimum model (BMB) at UM and multi-million-atom simulations powered by NEMO3D at Purdue. The first gated single impurity spectra (see coulomb diamond streaks in Figure 1.13) were measured at Delft University of Technology in experimental devices built at IMEC. Experimental evidence combined with multi-million atom simulations demonstrated the emergence of a new type of hybrid molecule system (Lansbergen, Rahman et al. 2008).

Ultra-scaled FinFET transistors bear unique fingerprint-like device-to-device differences attributed to random single impurities (Lansbergen, Chen et al. 2008). Through correlation of experimental data with multimillion atom simulations (Klimeck 2007), one can now identify the impurity's chemical species and determine their concentration, local electric field and depth below the Si/SiO_2 interface. The ability to model the excited states enabled a new approach to impurity metrology critical for implementations of impurity-based quantum computers.

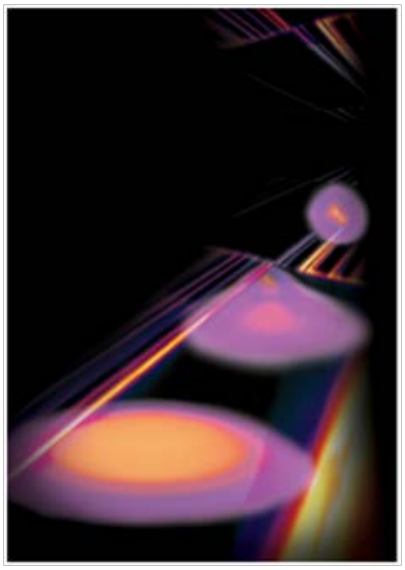

Figure 1.13. Conductance spectroscopy through a nano-scaled transistor dominated by a single impurity. One of several measured Coulomb diamonds is depicted in the background with three different date-field-dependent single-electron wave functions bound to a single impurity (after Lansbergen, Rahman et al. 2008).

1.9 INTERNATIONAL PERSPECTIVES FROM SITE VISITS ABROAD

Four workshops, the first in the United States followed by workshops in Europe, Japan, and Singapore, provided global perspectives on TM&S. A broad consensus on past successes and priorities for the future emerged, but each workshop also highlighted specific challenges and opportunities. In Europe, the need for a unified computational framework to support multiscale, multi-phenomena simulation was identified. Also identified were the strong opportunities for nanotechnology in biology and medicine and the need for user-friendly software designed for non-experts to support design and manufacturing in small and medium sized enterprises. The workshop in Japan stressed the need for improved human interfaces, including visualization, to support the broader application of simulation beyond the TM&S community. The power of simulation and visualization to promote public understanding of nanotechnology was also highlighted. The workshop in Singapore pointed out that multiscale modeling and simulation has not yet realized it potential and that it should be the focus in the next decade. The need for programs that develop long-term dialog between TM&S experts and experimentalists and application engineers was discussed. Finally, the importance of a considerable investment to re-think simulation algorithms and methods and to revise existing software in order to take advantage of the power of new computing architectures (e.g., GPU chips) was stressed.

A common theme that emerged from the workshops is the need for stronger collaborations, between TM&S experts and experimentalists, academia, and universities—and international collaboration and cooperative programs as well. Brief reports of the three overseas workshops follow.

1.9.1 United States-European Union Workshop (Hamburg, Germany)

Panel members/discussants

Lars Pastewka (co-chair), Fraunhofer Institute for Mechanics of Materials (IWM), Germany
Mark Lundstrom (co-chair), Purdue University, United States
Wolfgang Wenzel , Karlsruhe Institute of Technology (KIT) Institute of Nanotechnology, Germany
Costas Kiparissifdes, Aristotle University of Thessaloniki, Greece Alfred Nordman, Technical University of Darmstadt, Germany

TM&S provides insights that are impossible to obtain with current experimental means. Even more important is its use for design and engineering.

Methods for nanoscale TM&S, which require an explicit incorporation of the atomic structure, have evolved over the last 20 years. A wide range of nanosystems have been studied, typically in the gas phase without interaction with the environment. For catalytic activity of nanoparticles on surfaces or nanoscale building blocks for electronic systems, for example, recent calculations now go beyond a gas-phase approximation and routinely include the crucial influence of the support. During the next ten years, such methods need to be advanced in order to model nanosystems in liquid (e.g., during their synthesis or for biological applications) and solid environments (e.g., composite materials). Simulations will go from a basic understanding of clean systems towards real-world applications.

TM&S has advanced significantly over the past ten years. Besides the approximately 1000-fold increase in computing capabilities, advanced theoretical methods have been developed. A partial list includes: (1) advanced sampling techniques for free-energy calculations, (2) methods for electronic transport in realistic systems, and (3) higher accuracy exchange-correlation functionals for density functional theory. The first linear scaling O(N) quantum chemistry methods have been demonstrated, quantum/atomistic and atomistic/classical coupling has been advanced further, and reactive interatomic potentials have been developed for a large number of chemical elements. TM&S has been an enabling technology for the downscaling of MOSFETs, tailoring of multi-layer optical structures, metamaterials, and spectroscopy, among other examples.

TM&S will progress by expanding existing techniques to broader length and time scales. Methods will become more fail-safe so that a deployment to non-experts and hence a pervasive use of TM&S where appropriate can happen. Exploration of hundreds of design alternatives will be enabled. Simulation tools will be deployed to industry, in particular to small- and medium-sized enterprises where TM&S currently finds limited use.

Further progress in TM&S requires the wide deployment of multiscale, multi-phenomena approaches. Different length scales effectively decouple, so application of theories with validity on different scales becomes possible. The interfaces between these scales need to be defined. Here, individual efforts need to occur on different physical regimes, in particular in the electronic regime, the morphological regime, and the electromagnetic regime.

Multiscale/multi-phenomena solutions to some specific “grand-challenge” problems should be funded. Such a funding strategy combines methodological advancements with specific applications. To minimize the overhead spent in developing multiscale methods and software, coordinated international action for the development of a unified computational multiscale framework should be explored. These new computational TM&S tools should make use of recently emerged and emerging computing architectures, such as computing on graphic processors and cloud computing. Specific funding to support this work needs to be available.

The interaction of nanomaterials with biological systems and in medical applications is an area of opportunity for TM&S. TM&S also has huge potential to help in the design of catalysts, composite materials, lithium ion batteries, and solar cells. TM&S will enable the design of novel hybrid nanomaterials e.g., by self-assembly of binary supercrystals, combining magnetic, optical, and electronic properties in novel ways. It will also aid the search for new high Tc superconductors, help to tailor the interface between "man-made" and biological materials, give insights into the working of tribological contacts and other buried interfaces, and advance the field of quantum computing. Smart use of multiscale methods coupled with advances in computing will greatly expand the size of problems that can be addressed.

The enabling character of TM&S and its pervasive application will lead to significantly shorter design cycles, with the obvious impact on society. For example, the 1000-fold increase of computational capacity over the last ten years was catalyzed itself by the use of TM&S as a design tool. In return, it catalyzed TM&S by providing ever-increasing computational capacity, and additionally transformed our society radically due to the ubiquitous presence of computers.

1.9.2 United States-Japan-Korea-Taiwan Workshop (Tokyo/Tsukuba, Japan)

Panel members/discussants

Akira Miyamoto (co-chair), Tohoku University, Japan
Stuart Wolf (co-chair), University of Virginia, United States
Nobuyuki Sano, University of Tsukuba, Japan
Satoshi Watanabe, University of Tokyo, Japan
Ching-Min Wei, Academia Sinica, China

Long-term impacts and future opportunities for nanotechnology in the field of TM&S are increasing rapidly. This is possible because of significant progress in multiscale, multiphysics simulations with sufficient informatics, human interface (visualization), and integration of experiments/measurements. The main scientific/engineering advancements in the last ten years in the field of TM&S are summarized as follows:

- Development of highly efficient density functional theory (DFT) codes, improved DFT theory. and highly accurate QM electronic structure calculations using quantum Monte Carlo and other hybrid functionals
- Large scale simulations that include many body effects and that model the interplay between electron-phonon-atom dynamics in non-equilibrium systems
- Reactive force fields for simulations of materials growth and assembly processes
- Modeling of synthesis and assembly, and programmed materials that make use of self-assembly
- Effective screening medium approach for interfaces (e.g., Pt/water)
- Conceptual and computational tools for quantum transport including NEGF (non equilibrium Green's function technique as well as extensions to NEGF such as combining *ab initio* molecular dynamics (MD) with NEGF, and merging NEGF with the top-down, MC approach for transport, and modeling transient transport/AC transport
- Progress on mesoscale simulations using multiscale, multiphysics approaches
- Simulating integrated functional nanoscale systems
- Real-time processing technologies for huge amounts of experimental data (e.g., data from light sources)

The goal of TM&S for the next 5–10 years is to realize multiscale, multiphysics simulations with sufficient informatics, human interface (visualization), and integration of experiments and/or measurements that can contribute to the progress of a variety technologies with very high social value such as a high-performance Li-ion batteries, solar cells, a polymer electrolyte fuel cell (PEFC), a solid electrolyte fuel cell (SOFC), advanced tribological technologies, and next-generation automotive catalysts.

To realize the computational capacity needed for multiscale simulation, traditional CPUs must be augmented with the new capabilities of GPUs. TM&S infrastructure should also be created to realize more dynamic collaborations between experiment and simulation for solving realistic problems in technology and society. R&D investments should be directed to promote strong coupling to industry.

During the past ten years, nanotechnology was mainly for experts in academia or industry. The steady progress in the past ten years summarized above, especially computer simulation coupled with a human interface (e.g., 3D visualization), will in the next ten years have a big impact on industry and society in general. This progress also promotes societal understanding that leads to political understanding of the breadth of this technology, which is essential for the further progress and funding for nanotechnology. Although the societal understanding of the value of various technologies is considered to be a barrier for these technologies, advanced multiscale, multiphysics simulation with a sufficient human interface can promote the understanding of these technologies.

1.9.3 United States-Australia-China-India-Saudi Arabia-Singapore Workshop (Singapore)

Panel members/discussants

Julian Gale (co-chair), Curtin University, Australia
Mark Lundstrom (co-chair), Purdue University, United States
Michelle Simmons, University of New South Wales, Australia
Jan Ma, Nanyang Technological University, Singapore

TM&S provide insight and rationale for observations and increasingly serve as predictive tools for design and manufacturing. As recognized in the first IWGN report (Dixon, Cummings, and Hess 1999), modeling and simulation face challenges involving length scale, time scale, and accuracy. The past ten years has seen significant progress, not just through increased computing power, but also through the development of the underlying techniques. Key developments include:

- *Linear-scaling quantum mechanics:* Although many of the foundations were laid during the 1990s, advances continued in areas such as purification theory (Niklasson 2002) and new boundary conditions for divide and conquer (Wang et al. 2008). Density functional calculations for thousands of atoms are now routine.
- *Reactive force-fields:* The ReaxFF method (van Duin et al. 2001) saw the advent of an integrated reactive force-field that describes both multiple bond-order contributions as well as variable charge electrostatics and van der Waals terms. This was an important advance beyond the REBO model (Brenner et al. 2002) that had been widely used for nanostructured carbon materials.
- *Simulation of nanostructured materials:* It has become possible to create polycrystalline materials (Sayle et al. 2005) with complex interfacial structure, as well as to study the properties of extended defects (Walker et al. 2004). Coupling different computational techniques has made it feasible to simulate the reactions of nanoparticles, as

demonstrated by the oxidation of an aluminum nanometer-sized cluster (Vashishta 2006). Approaches to extending length and time scales in simulations of crystal growth from solvents have been developed (Piana et al. 2005).

- *Enhanced sampling of free energy surfaces:* One of the greatest challenges in simulation is to reliably search the conformational space to find the configurations that are important for a given system. Advances in this field include metadynamics (Lian and Gervasio 2008), which increases the rate of exploration, though at the expense of time-correlation information. Similarly there have been improvements in methods for determining rate constants (van Erp et al. 2003).
- *Quantum mechanical methods beyond density functional theory (DFT) for condensed phases:* While standard DFT (LDA/GGA) is computationally efficient, it suffers from several limitations. Although methods for obtaining improved reliability have long been known, the application to the solid-state, particularly with systematic basis sets, has only recently begun to become more widespread (Pisani et al. 2008; Hafner 2008).

Although there has been progress in multiscale/multiphysics TM&S, genuine multiscale modeling and simulation (spanning more than two scales or techniques) has yet to realize its full potential. While high-level coupling of models is routinely possible (for example via passing continuum properties or rate constants), more dynamic transfer of information remains challenging. There are emerging protocols for representation of physical metadata (e.g., Murray-Rust and Rzepa 1999), but most software currently will only output, but not read and utilize, this information. Furthermore, the structure of most codes is not designed to facilitate direct coupling of different methods within the same software.

A significant barrier to the wider development of multiscale/multiphysics modeling is the need to develop a long-term dialogue between different disciplines spanning science and engineering. To effectively couple techniques requires experts from both sides to acquire knowledge of the other side, which can take considerable time. Current funding models require short-term achievement, which makes it difficult to engage in such long-term objectives. The geographic dispersity of expertise represents another barrier, both to dialogue between theorists, modelers and simulators, and to experimentalists seeking solutions to multiscale problems.

Proposed goals and strategies for TM&S are as follows:

- *Establish a virtual international centre for grand challenges in TM&S:* A virtual network should be established to focus on the solution of defined grand challenge problems. It would create a focal point for establishing strong links with leading experimental groups. Examples of the challenges that would benefit from such an approach including a) determination of whether a sub-5 nm silicon transistor is operable, b) design of a thermoelectric material with a figure of merit greater than 3, and c) design of an organic photovoltaic cell with an efficiency of greater than 20%.
- *Achieve automated, dynamic tools for multiscale and multiphysics TM&S:* Current software typically requires considerable human effort to establish a pre-determined set of couplings. However, more effective achievement of technological outcomes would be possible by artificially intelligent linking of physics theories, models, and simulations, such that the level of the algorithm can be dynamically adjusted "on the fly" in order to achieve the solution with a target accuracy in the minimum computational time. A first step towards this goal would be real-time interactive simulation, with immersive visualization to permit human manipulation of the model.
- *Improve methods for excited states in nanotechnology:* While linear-scaling DFT allows us to describe the electronic ground state of nanodevices, many technological properties

depend on the excited states of the system. Often these are more delocalized and not as readily amenable to linear-scaling theory. Efficient methods are therefore required for going beyond ground state DFT, including determining energy levels accurately for use in coupled molecular dynamics/electron transport calculations.

To achieve the above goals a significant increase in computing power will be required. For example, the increased use of quantum mechanical methods will require the evaluation of Hartree-Fock exchange to improve accuracy. Assuming a linear-scaling approach is employed, the calculation of the electronic structure of a 10 nm quantum dot would using HF exchange will need an increase in computing power by approximately a factor of 10,000—well beyond the factor of 100 anticipated from advances in computing hardware.

Given the likely change in computing architectures to more complex mixtures of energy efficient, limited instruction co-processors (e.g., GPUs) with conventional cores, and the need for massively parallel applications to exploit increased number of processors (order 10^6 per machine for top 500 in 10 years), the challenge will be to rethink algorithms to best exploit these heterogeneous systems (de Jong 2010). Without considerable investment in scientific tools (e.g., optimized math libraries, etc.), our ability to harness such machines may limit progress.

1.10 REFERENCES

Anderson, J. and S.C. Glotzer. 2010. *Applications of graphics processors to molecular and nanoscale simulations.* Preprint.

Barthel, C., J. Medford, C.M. Marcus, M.P. Hanson, and A.C. Gossard. 2010. Interlaced dynamical decoupling and coherent operation of a singlet-triplet Qubit. *Phys. Rev. B* 81:161308(R).

Berger, L. 1996. Emission of spin waves by a magnetic multilayer traversed by a current. *Phys. Rev. B* 54:9353–9358.

Branton, D., D. W. Deamer, A. Marziali, H. Bayley, S.A. Benner, T. Butler, M. Di Ventra, S. Gara, A. Hibbs, X. Huang, S.B. Jovanovich, P.S. Krstic, S. Lindsay, X.S. Ling, C.H. Mastrangelo, A. Meller, J.S. Oliver, Y.V. Pershin, J.M. Ramsey, R. Riehn, G.V. Soni, V. Tabard-Cossa, M. Wanunu, M. Wiggin, and J.A. Schloss. 2008. The potential and challenges of nanopore sequencing. *Nat. Biotechnol.* 26:1146–1153.

Brenner, D.W., O.A. Shenderova, J.A. Harrison, S.J. Stuart, B. Ni, and S.B. Sinnott. 2002. A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons. *J. Phys. Condens. Matter* 14:783.

Cao, Q., H.-S., Kim, N. Kim, N. Pimparkar, J.P. Kulkarni, C. Wang, M. Shim, K. Roy, M.A. Alam, and J. Rogers. 2008. Medium scale carbon nanotube thin film integrated circuits on flexible plastic substrates. *Nature* 454:495–500.

Cao, Q., J. Rogers, M.A. Alam, and N. Pimparkar. 2009. Theory and practice of 'striping' for improved on/off ratio in carbon nanotube thin film transistors. *Nano Res.* 2(2):167–175.

Csányi, G., G. Albaret, G. Moras, M.C. Payne, and A. De Vita. 2005. Multiscale hybrid simulation methods for material systems. *J. Phys. Condens. Matter* 17:R691, doi: 10.1088/0953-8984/17/27/R02.

Cummings, P.T., H. Docherty, C.R. Iacovella, and J.K. Singh. 2010. Phase transitions in nanoconfined fluids: The evidence from simulation and theory. *AIChE J.* 56:842–848, doi: 10.1002/aic.12226.

Cummings, P.T., and S.C. Glotzer, 2010. *Inventing a new America through discovery and innovation in science, engineering and medicine: A vision for research and development in simulation-based engineering and science in the next decade.* Baltimore, Md.: World Technology Evaluation Center, Inc.

Datta, S. 2005. *Quantum transport: Atom to transistor.* Cambridge, U.K.: Cambridge University Press.

De Jong, W.A. 2010. Utilizing high performance computing for chemistry: Parallel computational chemistry. *Phys. Chem. Chem. Phys.* 12:6896, doi: 10.1039/c002859b.

Dixon, D.A., P.T. Cummings, and K. Hess. 1999. Investigative tools: Theory, modeling, and simulation. Chap. 2.7.1 in *Nanotechnology research directions: IWGN workshop report. Vision for nanotechnology in the next decade,* ed., M.C. Roco, S. Williams, and P. Alivisatos. Dordrecht, The Netherlands: Kluwer Academic Publishers.

Docherty, H., and P.T. Cummings. 2010. Direct evidence for fluid-solid transition of nanoconfined fluids. *Soft Matter* 6:1640–1643.

Gao, Z.Q., A. Agarwal, A.D. Trigg,N. Singh, C. Fang, C.-H.Tung, Y. Fan, K.D. Buddharaju, and J. Kong. 2007. Silicon nanowire arrays for label-free detection of DNA. *Anal. Chem.* 79(9):3291-3297, doi: 10.1021/ac061808q.

Garland, M., S. Le Grand, J. Nickolls, J. Anderson, J. Hardwick, S. Morton, E. Phillips, Y. Zhang, and V. Volkov. 2008. Parallel computing experiences with CUDA. *IEEE Micro.* July–Aug:13–27.

Goddard, W.A., A. van Duin, K. Chenoweth, M.-J. Cheng, S. Pudar, J. Oxgaard, B. Merinov, Y.H. Jang, and P. Persson. 2006. Development of the ReaxFF reactive force field for mechanistic studies of catalytic selective oxidation processes on $BiMoO_x$. *Top. Catal.* 38:93–103, doi: 10.1007/s11244-006-0074-x.

Goldenfeld, N., and L.P. Kadanoff. 1999. Simple lessons from complexity. *Science* 284:87–89.

Goluch, E.D., J.-M. Nam, D.G. Georganopoulou, T.N. Chiesl, K.A. Shaikh, K.S. Ryu, A.E. Barron, C.A. Mirkin, and C. Liu. 2006. A bio-barcode assay for on-chip attomolar-sensitivity protein detection. *Lab on a Chip* 6(10):1293–1299.

Gupta, A., P.R. Nair, D. Akin, M.R. Ladisch, S. Broyles, M.A. Alam, and R. Bashir. 2006. Anomalous resonance in a nanomechanical biosensor. *Proc. Natl. Acad. Sci. U. S. A.* 103(36):13362–13367.

Hamming, R.W. 1971. *Introduction to applied numerical analysis* (from the introduction), New York: McGraw-Hill.

Hafner, J. 2008. *Ab-initio* simulations of materials using VASP: Density-functional theory and beyond. *J. Comput. Chem.* 29:2044, doi: 10.1002/jcc.21057.

Hahm, J., and C.M. Lieber. 2004. Direct ultrasensitive electrical detection of DNA and DNA sequence variations using nanowire nanosensors. *Nano Lett.* 4(1):51–54.

Heinze, S., J. Tersoff, R. Martel, V. Dercycke, J. Appenzeller, and P. Avouris. 2002. Carbon nanotubes as Schottky barrier transistors. *Phys. Rev. Lett.* 89:106801, doi:10.1103/PhysRevLett.89.106801.

Izvekov, S., M. Parrinello, C.J. Burnham, and G.A. Voth. 2004. Effective force fields for condensed phase systems from ab initio molecular dynamics simulation: A new method for force matching. *J. Chem. Phys.* 120:10896, doi:10.1063/1.1739396.

Javey, A., J. Guo, Q. Wang, M. Lundstrom, and H. Dai. 2003. Ballistic carbon nanotube field-effect transistors. *Nature* 424:654–657.

Kamihara, Y., T. Watanabe, M. Hirano, and H. Hosono. 2008. Iron-based layered superconductor $La[O_{1-x}F_x]FeAs$ (x = 0.05-0.12) with T_C = 26 K. *J. Am. Chem. Soc.*130:3296–3297, doi:10.1021/ja800073m

Kamenetska, M., S.Y. Quek, A.C. Whalley, M.L. Steigerwald, H.J. Choi, S.G. Louie, C. Nuckolls, M.S. Hybertsen, J.B. Neaton, and L. Venkataraman. 2010. Conductance and geometry of pyridine-linked single molecule junctions. *J. Am. Chem. Soc.* 132:6817.

Kane, B.E. 1998. A silicon-based nuclear spin quantum computer. *Nature* 393:133.

Kasianowicz, J.J., E. Brandin, D. Branton, and D.W. Deamer. 1996. Characterization of individual polynucleotide molecules using a membrane channel. *Proc. Natl. Acad. Sci. U. S. A.* 93:13770–13773.

Katine, J.A., F.J. Albert, R.A. Buhrman, E.B. Myers, and D.C. Ralph. 2000. Current-driven magnetization reversal and spin-wave excitations in Co/Cu/Co pillars. *Phys. Rev. Lett.* 84:3149–3152, doi:10.1103/PhysRevLett.84.3149.

Klimeck, G., S. Ahmed, H. Bae, N. Kharche, R. Rahman, S. Clark, B. Haley, S. Lee, M. Naumov, H. Ryu, F. Saied, M. Prada, M. Korkusinski, and T.B. Boykin. 2007. Atomistic simulation of realistically sized nanodevices using NEMO 3-D: Part I—models and benchmarks. *IEEE Trans. Electron. Device*s 54:2079–2089, doi:10.1109/TED.2007.902879.

Kocabas, C., N. Pimparkar, O. Yesilyurt, S.J. Kang, M.A. Alam, and J.A. Rogers. 2007. Experimental and theoretical studies of transport through large scale, partially aligned arrays of single-walled carbon nanotubes in thin film type transistors. *Nano Lett.* 7:1195–1204.

Kusnezow, W., Y.V. Syagailo, S. Rüffer, K. Klenin, W. Sebald, J.D. Hoheisel, C. Gauer, and I. Goychuk. 2006. Kinetics of antigen binding to antibody microspots: Strong limitation by mass transport to the surface. *Proteomics* 6(3):794–803.

Lansbergen, G.P., R. Rahman, C.J. Wellard, P.E. Rutten, J. Caro, N. Collaert, S. Biesemans, I. Woo, G. Klimeck, L.C.L. Hollenberg, and S. Rogge. 2008. Gate induced quantum confinement transition of a single dopant atom in a Si FinFET. *Nat. Phys.* 4:656.

Lansbergen, G.P., C.J. Wellard, J. Caro, N. Collaert, S. Biesemans, G. Klimeck, L.C.L. Hollenberg, and S. Rogge. 2008. Transport-based dopant mapping in advanced FinFETs. *IEEE IEDM,* San Francisco, Calif, USA, Dec. 15–17, 2008, doi: 10.1109/IEDM.2008.4796794.

Lee, O-S., and G.C. Schatz. 2009. Molecular dynamics simulation of DNA-functionalized gold nanoparticles. *J. Phys. Chem. C.* 113:2316, doi:10.1021/jp8094165.

Li, Z., Y. Chen, X. Li, T.I. Kamins, K. Nauka, and R.S. Williams. 2004. Sequence-specific label-free DNA sensors based on silicon nanowires. *Nano Lett.* 4:245–247, doi: 10.1021/nl034958e.

Li, Z., B. Rajendran, T.I. Kamins, X. Li, Y. Chen, and R.S. Williams. 2005. Silicon nanowires for sequence-specific DNA sensing: Device fabrication and simulation. *Appl. Phys. A Mater. Sci. Process* 80:1257, doi: 10.1007/s00339-004-3157-1.

Liao, A., and F.L. Gervasio. 2008. Metadynamics: A method to simulate rare events and reconstruct the free energy in biophysics, chemistry and material science. *Rep. Prog. Phys.* 71:126601, doi: 10.1088/0034-4885/71/12/126601.

Loss, D., and D. DiVincenzo. 1998. Quantum computation with quantum dots. *Phys. Rev. A* 57:120, doi: 10.1103/PhysRevA.57.120.

Lundstrom, M., and Z. Ren. 2002. Essential physics of carrier transport in nanoscale MOSFETs. *IEEE Trans. Electron. Dev.* 49:133–141.

Maier, T.A., D. Poilblanc, and D.J. Scalapino. 2008. Dynamics of the pairing interaction in the Hubbard and *t-J* models of high-temperature superconductors. *Phys. Rev. Lett.* 100:237001, doi:10.1103/PhysRevLett. 100.237001.

Murray-Rust, P., and H.S. Rzepa. 1999. Chemical markup, XML, and the worldwide web. 1. Basic principles. *J. Chem. Inf. Comput. Sci.* 39:928, doi: 10.1021/ci990052B.

Nair, P.R., and M.A. Alam. 2006. Performance limits of nano-biosensors. *Appl. Phys. Lett.* 88:233120.

——————. 2007. Dimensionally frustrated diffusion towards fractal absorbers. *Phys. Rev. Lett.* 99:256101, doi:10.1103/PhysRevLett.99.256101.

——————. 2008. Screening-limited response of nanobiosensors. *Nano Letters* 8(5):1281–1285.

——————. 2010. A theory of "Selectivity" of label-free nanobiosensors: A geometro-physical perspective. *J. Appl. Phys.* 107:064701, doi :10.1063/1.3310531.

Nam, J.-M., C.S. Thaxton, and C.A. Mirkin. 2003. Nanoparticle-based bio-bar codes for the ultrasensitive detection of proteins. *Science* 301(5641):1884–1886, doi: 10.1126/science.1088755.

Nam, J.-M., S.I. Stoeva, and C.A. Mirkin. 2004. Bio-bar-code-based DNA detection with PCR-like sensitivity. *J. Am. Chem. Soc.* 126(19):5932–5933.

National Research Council Committee on Modeling, Simulation, and Games. *The rise of games and high performance computing for modeling and simulation*. Washington, D.C.: The National Academies Press, ISBN: 978-0-309-14777-4.

Niklasson, A.M.N. 2002. Expansion algorithm for the density matrix. *Phys. Rev. B* 66:155115, doi: 10.1103/PhysRevB.66.155115.

Ono, K., D.G. Austing, Y. Tokura, and S. Tarucha. 2002. Current rectification by Pauli exclusion in a weakly coupled double quantum dot system. *Science* 297:1313–1317, doi:10.1126/science.1070958.

Owens, J.D., H. Houston, D. Lubeke, S. Green, J.E. Stone, and J.C. Phillips. 2008. GPU Computing. *Proc. IEEE.* 96:879–899, doi: 10.1109/JPROC.2008.917757.

Park, S.Y., A.K.R. Lytton-Jean, B. Lee, S. Weigand, G.C. Schatz, and C.A. Mirkin. 2008. DNA-programmable nanoparticle crystallization. *Nature* 451: 553–556.

Papavasiliou, A., and I.G. Kevrekidis. 2007. Variance reduction for the equation-free simulation of multiscale stochastic systems. *Multiscale Model Simul.* 6:70–89.

Payne, C.M., X.C. Zhao, L. Vlcek, and P.T. Cummings. 2008. Molecular dynamics simulation of ss-DNA translocation between copper nanoelectrodes incorporating electrode charge dynamics. *J. Phys. Chem. B* 112:1712 –1717.

Peumans, P., A. Yakimov, and S.R. Forrest. 2003. Small molecular weight organic thin-film photodetectors and solar cells. *J. Appl. Phys.* 93:3693, doi:10.1063/1.1534621.

Piana, S., M. Reyhani, and J.D. Gale. 2005. Simulating micrometer-scale crystal growth from solution. *Nature* 438:70, doi: 10.1038/nature04173.

Pisani, C., L. Maschio, S. Casassa, M. Halo, M. Schutz, and D. Usvyat. 2008. Periodic local MP2 method for the study of electronic correlation in crystals: Theory and preliminary applications. *J. Comput. Chem.* 29:2113, doi: 10.1002/jcc.20975.

Quek, S.Y., L. Venkataraman, H.J. Choi, S.G. Louie, M.S. Hybertsen, and J.B. Neaton. 2007. Amine-gold linked single-molecule circuits: Experiment and theory. *Nano Lett.* 7:3477–3482.

Quek, S.Y., H.J. Choi, S.G. Louie, and J.B. Neaton. 2009. Length dependence of conductance in aromatic single-molecule junctions. *Nano Lett.* 9:3949.

Quek, S.Y., M. Kamenetska, M.L. Steigerwald, H.J. Choi, S.G. Louie, M.S. Hybertsen, J.B. Neaton, and L. Venkataraman. 2009. Dependence of single-molecule junction conductance on molecular conformation. *Nat. Nanotechnol.* 4:230.

Reith, D., M. Pütz, and F. Müller-Plathe. 2003. Deriving effective mesoscale potentials from atomistic simulations. *J. Comput. Chem.* 24:1624–1636, doi: 10.1002/jcc.10307.

Roco, M.C., R.S. Williams, and P. Alivisatos, P. eds. 1999. *Nanotechnology research directions: IWGN [NSTC] workshop report: Vision for nanotechnology R&D in the next decade.* Baltimore, Md.: International Technology Research Institute at Loyola College. Available online: http://www.nano.gov/html/res/pubs.html.

Rontani , M., F. Troiani, U. Hohenester, and E. Molinari. 2001. Quantum phases in artificial molecules. *Solid State Commun.* 119:309.

Salahuddin, S., D. Datta, P. Srivastava, and S. Datta. 2007. Quantum transport simulation of tunneling based spin torque transfer (stt) devices: Design trade-offs and torque efficiency. *IEEE Electronic Devices Meeting,* 2007:121–124, doi: 10.1109/IEDM.2007.4418879.

Sayle, T.X.T., C.R.A. Catlow, R.R. Maphanga, P.E. Ngoepe, and D.C. Sayle. 2005. Generating MnO_2 nanoparticles using simulated amorphization and recrystallization. *J. Am. Chem. Soc.,* 127:12828–12837.

Schulz, R., B. Lindner, L. Petridis, and J.C. Smith. 2009. Scaling of multimillion-atom biological molecular dynamics simulation on a petascale supercomputer. *J. Chem. Theory Comput.* 5:2798–2808.

Sigalov, G., J. Comer, G. Timp, and A. Aksimentiev. 2008. Detection of DNA sequences using an alternating electric field in a nanopore capacitor. *Nano Lett.* 8:56–63.

Slonczewski, J.C. 1996. Current-driven excitation of magnetic multilayers. *J. Magn. Magn. Mater.* 159:L1–L7.

Star, A., E. Tu, J. Niemann, J.-C.P. Gabriel, C.S. Joiner, and C. Valcke. 2006. Label-free detection of DNA hybridization using carbon nanotube network field-effect transistors. *Proc. Natl. Acad. Sci. U. S. A.* 103:921–926, doi:10.1073/pnas.0504146103.

Stern, E., J.F. Klemic, D.A. Routenberg, P.N. Wyrembak, D.B. Turner-Evans, A.D. Hamilton, D.A. LaVan, T.M. Fahmy, and M.A. Reed. 2007. Label-free immunodetection with CMOS-compatible semiconducting nanowires. *Nature* 445(7127):519–522.

Stopa, M., 2002. Rectifying behavior in coulomb blockades: charging rectifiers. *Phys. Rev. Lett.,* 88:146802.

Timp, W., U.M. Mirsaidov, D. Wang, J. Comer, A. Aksimentiev, and G. Timp. 2010. Nanopore sequencing: Electrical measurements of the code of life. *IEEE Transactions on Nanotechnology* 9:281–294.

Tsoi, M., A.G.M. Jansen, J. Bass, W.-C. Chiang, M. Seck, V. Tsoi, and P. Wyder. 1998. Excitation of a magnetic multilayer by an electric current. *Phys. Rev. Lett.* 80:4281–4284, doi: 10.1103/PhysRevLett.80.4281.

Van Duin, A.C.T., S. Dasgupta, F. Lorant, and W. A. Goddard III. 2001. ReaxFF: A reactive force field for hydrocarbons. *J. Phys. Chem. A* 105:9396–9409.

Van Erp, T.S., D. Moroni, and P. G. Bolhuis. 2003. A novel path sampling method for the calculation of rate constants. *J. Chem. Phys.* 118:7762–7775, doi:10.1063/1.1562614.

Vashishta, P., R.K. Kalia, and A. Nakano. 2006. Multimillion atom simulations of dynamics of oxidation of an aluminum nanoparticle and nanoindentation on ceramics. *J. Phys. Chem. B.* 110:3727-3733, doi: 10.1021/jp0556153.

Venkataraman, L., J.E. Klare, C. Nuckrolls, M.S. Hybertsen, and M.L. Steigerwald. 2006a. Dependence of single-molecule junction conductance on molecular conformation. *Nature* 442:904–907.

————. 2006b. Single-molecule circuits with well-defined molecular conductance. *Nano Lett.* 6:458–462.

Walker, A.M., B. Slater, J.D. Gale, and K. Wright., 2004. Predicting the structure of screw dislocations in nanoporous materials. *Nat. Mater.* 3:715–720, doi:10.1038/nmat1213.

Wang, L.-W., Z. Zhao, and J. Meza. 2008. Linear-scaling three-dimensional fragment method for large-scale electronic structure calculations. *Phys. Rev. B* 77:165113, doi: 10.1103/PhysRevB.77.165113.

Zhang, Z., P. Fenter, L. Cheng, N.C. Sturchio, M.J. Bedzyk, M. Predota, A. Bandura, J. Kubicki, S.N. Lvov, P.T. Cummings, A.A. Chialvo, M.K. Ridley, P. Bénézeth, L. Anovitz, D.A. Palmer, M.L. Machesky, and D.J. Wesolowski. 2004. Ion adsorption at the rutile-water interface: Linking molecular and macroscopic properties. *Langmuir* 20:4954–4969.

Zheng, G.F., F. Patolsky, Y. Cui, W.U. Wang, and C.M. Lieber. 2005. Multiplexed electrical detection of cancer markers with nanowire sensor arrays. *Nat. Biotechnol.* 23(10):1294–1301.