Materials by numbers: Computations as tools of discovery

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Current issues pertaining to theoretical simulations of materials, with a focus on systems of nanometer-scale dimensions, are discussed. The use of atomistic simulations as high-resolution numerical experiments, enabling and guiding formulation and testing of analytic theoretical descriptions, is demonstrated through studies of the generation and breakup of nanojets, which have led to the derivation of a stochastic hydrodynamic description. Subsequently, I illustrate the use of computations and simulations as tools of discovery, with examples that include the self-organized formation of nanowires, the surprising nanocatalytic activity of small aggregates of gold that, in the bulk form, is notorious for being chemically inert, and the emergence of rotating electron molecules in two-dimensional quantum dots. I conclude with a brief discussion of some key challenges in nanomaterials simulations.
ticle interactions or of response characteristics), and other simplifying assumptions. This “noncompromising” nature of computer-based simulations, applied to well posed models, endows them with the ability to unveil, in certain cases, new, emergent (5) behavior that may be regarded as arising from a higher level of organization and complexity than that which may be predicted, or explained (through common methods of analysis), from the primary simulation model or found through the use of simplified analytical approximations. Furthermore, such theoretical experiments, when used with adherence to strict standards pertaining to the range of validity and faithfulness of the simulated model, can serve as numerical microscopies of reliable descriptive and predictive power. Moreover, in certain circumstances, the results of a computer simulation may serve as theoretically generated data (i.e., as a substitute to laboratory recorded results when such are lacking), which may be used as the basis for the formulation, development, and testing of analytical theories.

Small Is Different: Physical and Chemical Phenomena in Nanoscale Systems

Characterization and elucidation of size-dependent patterns of the properties of finite materials’ aggregates exhibiting discrete quantized energy level spectra and specific structures and morphologies, investigations of the unique properties of finite-size materials clusters, and studies of the nature of the evolution of materials’ properties from the molecular and cluster regimes to the bulk phase are among the major challenges of modern materials science, and as such, these issues have been the subject of intensive research endeavors.

In many instances, it has been found that, for larger materials’ aggregates, the deviation of the properties from the bulk limit scales with the size of the aggregate. However, in many cases, at sufficiently small sizes (often in the nanoscale regime), the dependence of the material property on size becomes non-scalable; at this point, small is different in an essential way, with the physical and chemical properties becoming emergent in nature, i.e., they can no longer be deduced from those known for larger sizes (6–10).

In most cases, when the nonscalable regime is approached, the physical size of the system along at least one of the coordinate axes becomes comparable to a phenomenon-dependent characteristic length; examples include: conductance quantization occurring when the diameter of the constriction (e.g., a nanowire) approaches the electronic Fermi-wave-length (typically 0.5 nm in metals), i.e., “when the electron feels the boundary”; transport in a wire becoming ballistic (rather than diffusive) when the length of the wire is shorter than the electron mean-free-path (11); a column (or a jet) of invicid fluid becoming unstable when its length equals approximately nine times its radius (this length equals the wavelength of the fastest growing viscous instability mode, known as the Rayleigh instability; ref. 12); and the mechanical response and deformation modes of nanocrystals becoming dislocationless when their physical dimensions are comparable to the dislocation core size, resulting in enhanced mechanical strength of nanoscale crystallites and nanowires (13, 14), as well as mechanical reversibility (14) and absence of work-hardening.

Here, I highlight certain developments in areas pertaining to physical and chemical materials phenomena, focusing on theoretical simulations of systems with nanometer dimensions. This article is not intended as a review. Instead, I summarize my experience and view point on the subject, and use examples from my own work as illustrations; however, this does not imply in any way that other appropriate examples cannot be found.

Case Studies: New Behavior, Surprises, and Emergent Phenomena Revealed Through Simulations

The eternal mystery of the world is its comprehensibility. The fact that it is comprehensible is a miracle.

Albert Einstein

Formation and Breakup of Nanojets: The Use of Simulations as Theoretical Experiments

Liquid jets of macroscopic dimensions and their breakup into drops have been the subject of active scientific (12, 15, 16), as well as technological, interest. As the transverse length-scale (i.e., diameter) of the jet approaches the molecular scale, the validity of commonly used continuum fluid dynamics treatments, including Rayleigh’s (12) original linear stability analysis of invicid fluids and its extensions (15), as well as computational fluid dynamical simulations of the Navier–Stokes equations and treatments based on the so-called lubrication equation (LE) (sometimes called the “slenderness approximation,” ref. 15) in which averaging over the lateral cross-section of the jet is performed, become questionable (16, 17). In particular, because of the reduced dimensions, the behavior of such systems involves large spatio-temporal variations and fluctuations of the liquid properties (such as temperature gradients and liquid density changes caused by viscous heating and evaporative cooling), requiring the development of physically reliable and accurate atomic-scale simulations. In light of these considerations, the first issue that needs to be resolved pertains to the very existence and stability of contiguous elongated liquid structures (e.g., liquid bridges or jets) of nanometer dimensions.

Results from MD simulations (16), performed for a common fuel (propane, C3H8) as a fluid confined and injected into vacuum through a nozzle of 6 nm diameter, are shown in Figs. 1 and 2. Generation of the nanojet required the application of a back pressure of 500 MPa, with the exterior surface of the gold nozzle heated to the boiling temperature of propane (230 K) to prevent condensation of thick blocking films...
(alternatively, the outer surface of the nozzle could be coated by a film that is not wetted by the jet fluid). Under these conditions, steady-state flow was achieved after 1 ns (see Fig. 2 Left) and the nanojet propagated with a velocity of 200 m/s.

Spontaneously developing fluctuations destabilize the jet, leading to formation of droplets. The Fig. 2 Left Inset shows the time evolution of the intact jet length \( L \) at selected times (0.1 ns < \( t < 2 \) ns). Steady state is achieved for \( t > 1 \) ns. (Right) Results for the time evolution of the intact jet length \( L \) (Upper) and for the minimal jet radius \( h_{\text{min}} \) (Lower), obtained from MD, LE, and SLE simulations (distinguished by color). Each of the saw-tooth discontinuities in \( L \) and the corresponding sharp dips in \( h_{\text{min}} \) are associated with a breakup event resulting in formation of a drop. Note the remarkable agreement between the MD and SLE results. This figure was modeled after ref. 16.

Fig. 2. Propagation and breakup of a nanojet. (Left) Evolution of the propane nanojet along the direction of propagation (z axis) at selected times (0.1 ns < \( t < 2 \) ns). Steady state is achieved for \( t > 1 \) ns. (Right) Results for the time evolution of the intact jet length \( L \) (Upper) and for the minimal jet radius \( h_{\text{min}} \) (Lower), obtained from MD, LE, and SLE simulations (distinguished by color). Each of the saw-tooth discontinuities in \( L \) and the corresponding sharp dips in \( h_{\text{min}} \) are associated with a breakup event resulting in formation of a drop. Note the remarkable agreement between the MD and SLE results. This figure was modeled after ref. 16.

To resolve this problem and extend the LE continuum approach to the nanoscale regime, Moseler and Landman (16) derived a stochastic version of the MD simulations (see ref. 16), insulating the time evolution of and the intact-length (\( L \)) of the jet, and its smallest diameter (\( h_{\text{min}} \)) along the propagation axis shown in Fig. 2 Right. Moreover, in separate MD simulation, it has recently been determined (W. Kang and U.L., unpublished data) that the time-evolution of the minimum width of a collapsing 6-nm diameter bridge of liquid propane (referred to the breakup time, \( t_0 \)) obeys the relation \( h_{\text{min}} = h_0 (t - t_0)^\gamma \), with \( \gamma = 0.418 \). This result agrees with that predicted recently (19) from analysis of the SLE equations, lending further support to the applicability of the stochastic formulation (16).

**Nanowires.** The propensity of materials systems of reduced size to undergo self-selection of size and shape, as well as their ability to spontaneously adopt optimal configurations by self-organization, are among the unique properties of nanoscale materials systems. Examples include magic number sequences that reflect enhanced stabilities of particular sizes [e.g., number of cluster atoms (20–22) or radii of nanowires (23–25)] originating from electronic shell effects (a concept familiar from nuclear structure studies) and/or from particular geometrical atomic packing arrangements; shape deformations effects (21, 22), akin to Jahn–Teller distortions (familiar in molecular and nuclear systems) that lift spontaneous symmetry-lowering (or breaking); and self-assembly processes underlying formation of nanostructures and nanoparticle arrays (10, 26–30).

These self-selection processes are portrayed in systematic size-dependent patterns characterizing the properties of nanoscale structures, including cluster abundances, single-particle and collective excitations (i.e., ionization potentials, electron affinities, optical absorption spectra, and plasmon excitations), odd–even variations of the properties of metal clusters (particularly, simple sp-bonded metals) (20–22),
magnetic properties (31–33), charging characteristics, fragmentation barriers and fission dynamics of charged clusters (6, 21, 34–37), chemical adsorption and reactivities of free (gas-phase) and surface-supported clusters (38–46), and correlated force oscillations and conductance quantization steps in nanowires (13, 14, 23, 25, 47–49).

As an example of a nanostructure formed through atomistic self-assembly and self-organization processes, Fig. 3 shows a nanowire discovered through early MD simulations that were part of an effort aimed at understanding the atomic origins of frictional processes (7–9, 13, 50). The nanowire junction shown in Fig. 3 formed (at room temperature) during an adiabatically slow separation of the contact between a nickel tip and a gold surface. This mechanism is portrayed in oscillations of the force required to elongate the wire, with a period that equals approximately the interlayer spacing. Moreover, the critical resolved yield stress of gold nanowires has been estimated (13, 14) to be 3–4 GPa, which is over an order of magnitude larger than that of bulk gold, and is comparable to the theoretical (“ideal”) value for Au (1.5 GPa) in the absence of dislocations. The predicted dislocationless mechanical response originates from the fact that, for a typical metallic nanoscale junctions (e.g., with a radius of 1 nm), the pressure needed to generate a loop dislocation (of that radius) is over an order of magnitude larger than the macroscopic yield stress. Therefore, in such nanowires, plastic deformation is expected to occur without dislocations.

These predictions, as well as anticipated electronic conductance properties (that is, point contact characteristics and conductance quantization in units of the conductance quantum $g_0 = 2e^2/h$, $g_0^{-1} = 12.9$ k$\Omega$), have been corroborated in a number of experiments using scanning tunneling microscopy and force microscopy (47–49, 51), controllable break junction (49), and pin-plate (14) techniques, carried out at ambient environments, as well as under ultrahigh vacuum and/or cryogenic conditions.

Atomically thin nanowires developing at the ultimate stages of the elongation process, which may act as atomic-scale contacts or switches (13, 52, 53), have been observed in the aforementioned early simulations of gold nanowires (13), as well as in later ab initio simulations (54) of sodium nanowires (55). More recently, atomically thin gold nanowires [pulled from a surface by a STM tip (56), or bridging perforated gold membranes (56, 57)], have been imaged by high-resolution transmission electron microscopy.

Results from ab initio MD simulations, coupled with calculations of the electronic conductance in the wire as a function of the distance between the two opposing tip-electrodes (58), are shown in Fig. 4. Elongation-induced variations of the conductance are illustrated in Fig. 4a, and portraits of the two eigen-conductance channels (the functions that diagonalize the scattering matrix, see ref. 58), corresponding to the elongation stage with $G \approx 2g_0$, are displayed in Fig. 4b. Further elongation results in a single-strand wire with a single conductance channel. The structure of a single-strand nanowire is shown in Fig. 4c, illustrating formation of a gold dimer, with the highest occupied molecular orbital (i.e., the Fermi-level) exhibiting a pronounced d-orbital character (see Fig. 4d) resulting from the strong relativistic effect in gold that enhances s–d hybridization (between the atomically fully occupied 5d shell and the singly occupied 6s).

Finally, in the context of the effect of chemical interactions on the structural and electrical properties of nanowires, Fig. 4e shows the structure of a single-strand nanowire with an adsorbed methyl thiol. Along with the marked effect on the wire conductance, this study (59) suggested that certain high-resolution transmission electron microscopy observations (56) of anomalously large intergold distances are likely
Gold Nanocatalysis. Unlike supported particles of larger size or extended solid surfaces (61), small metal clusters adsorbed on support materials were found to exhibit unique properties that originate from the highly reduced dimensions of the individual metal aggregates (32, 38–46). In particular, investigations on size-selected small gold clusters, Au₇₈ (20 ≤ n ≤ 20), soft-landed (62) on a well characterized metal-oxide support [specifically, a MgO (001) surface, with and without oxygen vacancies, or F-centers], revealed (40) that gold octamer (Au₈) clusters bound to F-centers of the magnesia surface are the smallest known gold heterogeneous catalysts that can oxidize CO into CO₂ at temperatures as low as 140 K. The same cluster adsorbed on a MgO surface without oxygen vacancies is catalytically inactive for CO combustion (40).

Quantum mechanical ab initio simulations (including scalar relativistic corrections; refs. 63 and 64), in juxtaposition with laboratory experiments, led us to conclude (40, 43, 46) that the key for low-temperature gold catalysis in CO oxidation is the binding of O₂ and CO to the supported gold nanocluster, which activates the O–O bond to a peroxy-like (or superoxy-like) adsorbate state. Charging of the metal cluster, caused by partial electron transfer from the substrate F-center into the deposited cluster (see Fig. 5), underlies the catalytic activity of the gold octamers (Au₈), as well as that of other small gold clusters (Auₙ, 8 ≤ n ≤ 20). These investigations predicted that (i) oxygen vacancy (F-centers) on the metal-oxide support surface play the role of “active-sites” (a concept that has been central to the development of heterogeneous catalysis); (ii) these sites serve to anchor the deposited clusters more strongly [binding energy, E Binding = 3.44 eV for Au₈ to MgO(FC)] than sites on the undefective surface (E Binding = 1.22eV), thus inhibiting their migration and coalescence; and most importantly, (iii) these active sites control the charge-state of the gold clusters, thus promoting the activation of adsorbed reactant molecules (i.e., formation of the aforementioned peroxy or superoxy species; refs. 40, 43, and 46).

The correlation diagram in Fig. 6 shows that the local density of states projected on the adsorbed oxygen molecule in the reaction complex overlaps with the entire d-band of the Au₈ cluster (see Fig. 6 Center in the range of −10 eV ≤ E ≤ E F, where E F is the Fermi energy). The antibonding 2π* states of O₂ are pulled below E F, and thus the full spin manifold of these states is populated in the reaction complex (resulting in the aforementioned partial excess charge on the adsorbed molecule). The occupation of the antibonding level results in strong weakening (activation) of the O–O bond that is reflected in a significant increase of its length (1.43 Å, compared to that of the free oxygen molecule, 1.25 Å). Accompanying the activation process is a change in the spin state of the molecule from a triplet state in the gas phase to a peroxy-like adsorbed state with a zero net spin.

A different scenario is found for smaller gold clusters, as well as for gold clusters adsorbed on a perfect magnesia surface (that is, with no F-centers). In these cases, we find a smaller projected density of states on the adsorbed gold cluster near E F, leading to a weaker (or no) resonance with the antibonding orbitals of the adsorbed reactant molecules, thus resulting in weak binding of the molecule to the cluster with a consequent small degree of activation and reduced chemical reactivity; these results have indeed been observed experimentally under these situations.

Symmetry Breaking in Quantum Dots (QDs): Electron Molecules. Two-dimensional QDs, created at semiconductor interfaces through the use of lithographic and gate-voltage techniques, with refined control of their size, shape, and...
number of electrons, are often referred to as "artificial atoms" (65, 66). These systems are expected, with the use of applied magnetic fields, to have future applications as logic gates in quantum computing and as nanoscale switching devices. As indicated above, certain analogies have been made between these man-made systems and their natural counterparts, suggesting that the physical nature of electrons in the former is similar to that underlying the traditional description of natural atoms, containing particularly to electronic shells and the Aufbau principle in atoms (where electrons are taken to be moving in a spherically averaged effective central mean-field potential).

The above analogy has been challenged recently (67, 68) on the basis of calculations that showed evidence for formation (under conditions that are readily achievable in the laboratory) of "electron molecules," which are alternatively called Wigner molecules after the physicist who predicted formation of electron crystals in extended systems (69). The mean-field spin-and-space (sS) unrestricted Hartree–Fock (UHF) calculations used here (denoted as sS-UHF) for electrons confined by a parabolic potential in 2D QDs led to the discovery of spontaneous symmetry breaking (that is, the spontaneous reduction in the symmetry of a system that is driven by the stability thus acquired; ref. 6), manifested by the appearance of spatial interelectronic (crystalline) correlations (even in the absence of magnetic fields).

Symmetry breaking (at the mean-field level of the calculation, see below) may indeed be expected, based on the interplay between the interelectron repulsion, \( Q \), and the zero-point kinetic energy, \( K \). Taking \( Q = \frac{e^2}{\kappa \alpha_0} \) and \( K = \hbar \omega_0 \) where \( \alpha_0 = \hbar (m^* \omega_0)^{1/2} \) is the spatial extent of an electron in the lowest state of the parabolic confinement; \( m^* \) is the electron effective mass, \( \kappa \) is the dielectric constant, and \( \omega_0 \) is the frequency that characterizes the parabolic confining potential, the Wigner parameter is defined as \( R_W = Q/K \). Symmetry breaking may be expected when the interelectron repulsion dominates, i.e., for \( R_W \geq 1 \). Under such circumstances, an appropriate approximate (mean-field) solution of the Schrödinger equation necessitates consideration of wave functions with symmetries that are lower than that of the circularly symmetric QD Hamiltonian. Such solutions may be found through the use of the sS-UHF method, where all restrictions on the symmetries of the wave functions, as well as the double occupancy requirement (which is inherent to the restricted HF, i.e., RHF, method) are lifted. From the above, we note that the state of the system may be controlled and varied through the choice of materials (i.e., \( \kappa \)) and/or the strength of the confinement (\( \omega_0 \)), because \( R_W \approx 1/(\kappa \sqrt{\omega_0}) \).

Formation of "electron molecules" has been investigated through exact calculations for two-electron confined parabolically in a QD (70); for exact diagonalization of the Hamiltonian for three electrons in a parabolic QD with \( B = 0 \), see ref. 71. For the two electron case, the terms in the Hamiltonian corresponding to the center-of-mass and the interelectron relative degrees of freedom are separable. The spectrum obtained for large values of \( R_W \) exhibits features that are characteristic of a collective rovibrational dynamics, akin to that of a natural "rigid" triatomic molecule with an infinitely heavy middle particle representing the center of mass of the two-electron system (71). The solutions to the Schroëdinger equation must have good approximations for these states to be stable (75). The rotations stabilize the electrons on each ring rotating coherently (75). The rotations stabilize the ground state and its angular momentum to change. The cusp states have been long recognized (80) as the finite-N precursors of the fractional quantum Hall effect states in extended systems. In particular, the fractional fillings \( \nu \) (defined in the thermodynamic limit) are related to the magic angular momenta of the finite-N system as \( \nu = (N - 1)/2L \).

Recently derived parameter-free wave functions corresponding to the RWM picture in QDs, characterized by prominent crystalline correlations, have been shown to provide a simple, improved, and consistent description of the cusp states, superior to the liquid-like characteristics obtained through wave functions developed in the context of the fractional quantum Hall effect (82, 83) (particularly for high angular momenta, corresponding to low fractional fillings \( \nu \); refs. 72 and 73). The ground-state crystalline arrangements of the electron (Wigner) molecules were found (72–75) to consist of concentric polygonal rings rotating independently of each other (see in particular the CPDs for the two rings shown for \( N = 9 \) in Fig. 7), with the electrons on each ring rotating coherently (75). The rotations stabilize the RWM relative to the static one; namely, the projected (symmetry-restored) states (that are multideterminantal) are lower in energy compared to the broken-symmetry ones (the single determinantal sS-UHF solutions).

Formation of electron molecules is enhanced for nonspherical confining potentials (76). Indeed, evidence for formation of a two-electron molecule has been inferred most recently from transport measurements on elliptic 2D
Among the many challenges facing computational investigations of materials, I selected here certain issues that arise when attempting to extend the spatial dimensions and time intervals of dynamical simulations of materials. Many of the research activities involving materials systems of highly reduced (nanoscale) dimensions are focused on identification and elucidation of the unique behavior of materials in the non-scalable size regime. Stated in an alternative fashion, investigations of nanoscale materials respond to the quest to identify and understand size-dependent patterns that underlie the evolution of materials' properties, starting from the atomic and molecular regime, proceeding to small clusters, nanoscale aggregates, and mesoscopic materials, and ultimately arriving to the bulk condensed phase domain. The search for size-evolutionary patterns requires the development of an arsenal of theoretical methodologies and techniques appropriate for treating materials systems with varying sizes and dimensionalities.

Common to the above issues is the need to extend the simulations to larger systems. Methodologies that aim at this goal (although direct MD simulations, i.e., direct integration of Newton's equations of motion for a system consisting of multimillion interacting particles, are possible; refs. 87 and 88) are commonly referred to as multiscale modeling methods, and they include (i) procedures for embedding atomistic regions in continuum environments (such as in treatments of mechanical properties and response of materials, indentation, fracture, crack initiation and propagation, and film growth processes) (89, 90) and (ii) methods for embedding regions that are treated quantum mechanically (QM) in environments that are treated classically (with atomic resolution) (91, 92); the latter embedding scheme is often referred to as QM/MM, where MM stands for molecular mechanics, although the MD method is used in most modern applications. We note that, in recent years, efforts have been invested also in combining the entire multiscale spectrum (classical continuum, classical atomistic, and QM) into a single simulation (90).

The key to the success of embedding schemes is the formulation and implementation of “seamless” interfaces that couple the various regions (e.g., QM, classical-atomicistic, and continuum). As an illustration of the results of a QM/MM simulation, Fig. 8 shows results for the ionization hole in DNA (93) taken from a most recent investigation of the reaction of water with ionized DNA (R. N. Barnett, A. Bon-giorno, C. L. Cleveland, A. Joy, U.L., and G. B. Schuster, unpublished data, and refs. 94 and 95). For other recent studies employing the QM/MM methodology, see refs. 96 and 97.

An alternative approach to the simulation size problem is offered by coarse-grain models, reviewed recently in ref. 98. In these methods, which have found

**Fig. 7.** CPDs at high B, evaluated for parabolic quantum dots through (i) the two-step procedure of symmetry breaking and subsequent restoration, resulting in RWM (Left), and (ii) exact diagonalization (Right). The angular momentum values and corresponding values of the fractional filling are given on the left. The optimal polygonal structure for a given N is given by \((n_1, n_2)\) with \(n_1 + n_2 = N\). For \(N = 7, 8,\) and 9, these arrangements are \((1, 6), (1, 7),\) and \((2, 7)\), respectively. The reference point for the calculation of the CPD is denoted by a filled dot. Note in particular the two CPDs shown for \(n = 9\), illustrating that, for a reference point located on the outer ring, the inner ring appears uniform, and vice versa for a reference point located on the inner ring (Bottom). These results illustrate that the rings rotate independently of each other. This figure was modeled after ref. 75.

**Fig. 8.** QM/MM calculation of the ionization hole in a 14-bp oligomer of B-DNA d(5′-AAGGGAAGGAAAGGG-3′), where the bold letters denote the region treated quantum mechanically (QM). The atoms in the QM region are shown in color, and those in the classical MM region are depicted in blue-gray; the classically treated H\(_2\)O molecules are depicted as a background shadow. The hole density (electron density difference between the neutral and ionized system, both calculated for the same geometry) is superimposed on the QM region, and it appears as the light blue iso-surfaces localized on the GG doublet. There are 3,105 atoms in the MM region (12 base pairs, 775 water molecules, and 22 Na ions), and the QM region contains 221 atoms (two base pairs (G-C) linked by sugar-phosphate groups, 28 water molecules, and four Na atoms). A total of 680 valence electrons were included in the QM calculation. In the QM region, the color assignments are as follows: P, yellow; C, green; N, blue; O (base), red; O (phosphate), red; O (H\(_2\)O), orange; H (H\(_2\)O), small blue spheres; Na, purple. Note that most of the counterions are located in the vicinity of the phosphate groups, with one of the counterions in the QM region residing in the major groove. The QM/MM method used here was developed by A. Bongiorno, S. B. Suh, R. N. Barnett, and U.L. (unpublished data). The QM calculations were performed by using the method described in ref. 54, with generalized gradient corrections (GGA) (94) and a plane-wave basis with a 62 Ry kinetic-energy cutoff. In the classical (MM) region, the AMBER 96 potentials (95) were used.
applications mainly in soft-matter simulations, a coarsened model of the simulated system is constructed and parameterized, with coarse-grained particles (“superatoms”) representing groups of (real) atoms or whole molecular segments.

Another set of challenges arise in connection with the time-scale gap; i.e., issues pertaining to limitations in the accessible simulation time intervals for which the dynamical evolution of materials systems may be simulated. Of particular interest are systems and processes that are characterized by the presence of different relevant time scales (a chemical reaction where the reaction time may be larger by orders of magnitude than the period of molecular vibrational is an example of a system with a separation of time scales). Issues pertaining to limitations of the time scales accessible to dynamical simulations remain serious problems that are not likely to be solved (merely) by progress in computational hardware because of the sequential (time-step-by-time-step) nature of the solution of the classical equations of motion. Currently, the methods that have been proposed for “boosting” the simulated time span address, mainly, processes characterized by infrequent events (e.g., bulk and surface diffusion of atoms or clusters; ref. 99).

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