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## Computational Study of Nanomaterials: From Large-Scale Atomistic Simulations to Mesoscopic Modeling

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## Synonyms

[Carbon nanotube materials](#); [Carbon nanotubes](#); [Computer modeling and simulation of materials](#); [Dislocation dynamics](#); [Kinetic Monte Carlo method](#); [Mechanical properties of nanomaterials](#); [Mesoscopic modeling](#); [Metropolis Monte Carlo method](#); [Molecular dynamics method](#); [Multiscale modeling](#); [Nanocrystalline materials](#); [Nanofibrous materials and composites](#); [Nanomaterials](#)

## Definitions

*Nanomaterials* (or nanostructured materials, nanocomposites) are materials with characteristic size of structural elements on the order of less than several hundreds of nanometers at least in one dimension. Examples of nanomaterials include nanocrystalline materials, nanofiber, nanotube, and nanoparticle-reinforced nanocomposites, and multilayered systems with submicron thickness of the layers.

*Atomistic modeling* is based on atoms as elementary units in the models, thus providing the atomic-level resolution in the computational studies of materials structure and properties. The main atomistic methods in material research are (1) molecular dynamics technique that yields “atomic movies” of the dynamic material behavior through the integration of the equations of motion of atoms and molecules, (2) Metropolis Monte Carlo method that enables evaluation of the equilibrium properties through the ensemble averaging over a sequence of random atomic configurations generated according to the desired statistical-mechanics distribution, and (3) kinetic Monte Carlo method that provides a computationally efficient way to study systems where the structural evolution is defined by a finite number of thermally activated elementary processes.

*Mesoscopic modeling* is a relatively new area of the computational materials science that considers material behavior at time- and length-scales intermediate between the atomistic and continuum levels. Mesoscopic models are system-/phenomenon-specific and adopt coarse-grained representations of the material structure, with elementary units in the models designed to provide a computationally efficient representation of individual crystal defects or other elements of micro/nanostructure. Examples of the mesoscopic models are coarse-grained models for molecular systems, discrete dislocation dynamics model for crystal plasticity, mesoscopic models for nanofibrous materials, cellular automata, and kinetic Monte Carlo Potts models for simulation of microstructural evolution in polycrystalline materials.

## Computer Modeling of Nanomaterials

Rapid advances in synthesis of nanostructured materials combined with reports of their enhanced or unique properties have created, over the last decades, a new

active area of materials research. Due to the nanoscopic size of the structural elements in nanomaterials, the interfacial regions, which represent an insignificant volume fraction in traditional materials with coarse microstructures, start to play the dominant role in defining the physical and mechanical properties of nanostructured materials. This implies that the behavior of nanomaterials cannot be understood and predicted by simply applying scaling arguments from the structure–property relationships developed for conventional polycrystalline, multiphase, and composite materials. New models and constitutive relations, therefore, are needed for an adequate description of the behavior and properties of nanomaterials.

Computer modeling is playing a prominent role in the development of the theoretical understanding of the connections between the atomic-level structure and the effective (macroscopic) properties of nanomaterials. Atomistic modeling has been at the forefront of computational investigation of nanomaterials and has revealed a wealth of information on structure and properties of individual structural elements (various nanolayers, nanoparticles, nanofibers, nanowires, and nanotubes) as well as the characteristics of the interfacial regions and modification of the material properties at the nanoscale. Due to the limitations on the time- and length-scales, inherent to atomistic models, it is often difficult to perform simulations for systems that include a number of structural elements that is sufficiently large to provide a reliable description of the macroscopic properties of the nanostructured materials. An emerging key component of the computer modeling of nanomaterials is, therefore, the development of novel mesoscopic simulation techniques capable of describing the collective behavior of large groups of the elements of the nanostructures and providing the missing link between the atomistic and continuum (macroscopic) descriptions. The capabilities and limitations of the atomistic and mesoscopic computational models used in investigations of the behavior and properties of nanomaterials are briefly discussed and illustrated by examples of recent applications below.

## Atomistic Modeling

In atomistic models [1, 2], the individual atoms are considered as elementary units, thus providing the

atomic-level resolution in the description of the material behavior and properties. In classical atomistic models, the electrons are not present explicitly but are introduced through the interatomic potential,  $U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ , that describes the dependence of the potential energy of a system of  $N$  atoms on the positions  $\vec{r}_i$  of the atoms. It is assumed that the electrons adjust to changes in atomic positions much faster than the atomic nuclei move (Born–Oppenheimer approximation), and the potential energy of a system of interacting atoms is uniquely defined by the atomic positions.

The interatomic potentials are commonly described by analytic functions designed and parameterized by fitting to available experimental data (e.g., equilibrium geometry of stable phases, density, cohesive energy, elastic moduli, vibrational frequencies, characteristics of the phase transitions, etc.). The interatomic potentials can also be evaluated through direct quantum mechanics–based electronic structure calculations in so-called first principles (ab initio) simulation techniques. The ab initio simulations, however, are computationally expensive and are largely limited to relatively small systems consisting of tens to thousands of atoms. The availability of reliable and easy-to-compute interatomic potential functions is one of the main conditions for the expansion of the area of applicability of atomistic techniques to realistic quantitative analysis of the behavior and properties of nanostructured materials.

The three atomistic computational techniques commonly used in materials research are:

1. Metropolis Monte Carlo method – the equilibrium properties of a system are obtained via ensemble averaging over a sequence of random atomic configurations, sampled with probability distribution characteristic for a given statistical mechanics ensemble. This is accomplished by setting up a random walk through the configurational space with specially designed choice of probabilities of going from one state to another. In the area of nanomaterials, the application of the method is largely limited to investigations of the equilibrium shapes of individual elements of nanostructures (e.g., nanoparticles) and surface structure/composition (e.g., surface reconstruction and compositional segregation [3]).
2. Kinetic Monte Carlo method – the evolution of a nanostructure can be obtained by performing atomic rearrangements governed by pre-defined

transition rates between the states, with time increments formulated so that they relate to the microscopic kinetics of the system. Kinetic Monte Carlo is effective when the structural and/or compositional changes in a nanostructure are defined by a relatively small number of thermally activated elementary processes, for example, when surface diffusion is responsible for the evolution of shapes of small crystallites [4] or growth of two-dimensional fractal-dendritic islands [5].

3. Molecular dynamics method – provides the complete information on the time evolution of a system of interacting atoms through the numerical integration of the equations of motion for all atoms in the system. This method is widely used in computational investigations of nanomaterials and is discussed in more detail below.

### Molecular Dynamics Technique

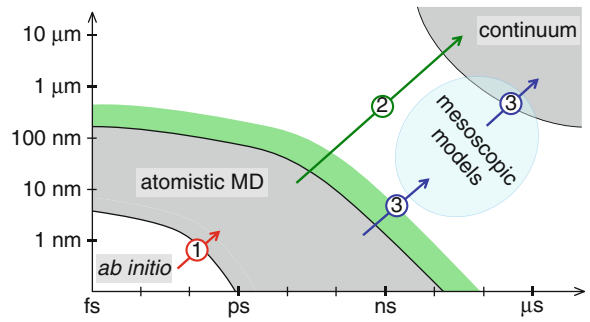
Molecular dynamics (MD) is a computer simulation technique that allows one to follow the evolution of a system of  $N$  particles (atoms in the case of atomistic modeling) in time by solving classical equations of motion for all particles in the system,

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i, \quad i = 1, 2, \dots, N \quad (1)$$

where  $m_i$  and  $\vec{r}_i$  are the mass and position of a particle  $i$ , and  $\vec{F}_i$  is the force acting on this particle due to the interaction with other particles in the system. The force acting on the  $i^{\text{th}}$  particle at a given time is defined by the gradient of the inter-particle interaction potential  $U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$  that, in general, is a function of the positions of all the particles:

$$\vec{F}_i = -\vec{\nabla}_i U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad (2)$$

Once the initial conditions (initial positions and velocities of all particles in the system) and the interaction potential are defined, the equations of motion, (Eq. 1), can be solved numerically. The result of the solution is the trajectories (positions and velocities) of all the particles as a function of time,  $\vec{r}_i(t)$ ,  $\vec{v}_i(t)$ , which is the only direct output of an MD simulation. From the trajectories of all particles in the system, however, one can easily calculate the spatial and time evolution of structural and thermodynamic parameters of the system. For example, a detailed atomic-level analysis of



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**Fig. 1** Schematic representation of the time- and length-scale domains of first-principles (ab initio) electronic structure calculations, classical atomistic MD, and continuum modeling of materials. The domain of continuum modeling can be different for different materials and corresponds to the time- and length-scales at which the effect of the micro/nanostructure can be averaged over to yield the effective material properties. The arrows show the connections between the computational methods used in multiscale modeling of materials: The red arrow #1 corresponds to the use of quantum mechanics-based electronic structure calculations to design interatomic potentials for classical MD simulations or to verify/correct the predictions of the classical atomistic simulations; the green arrow #2 corresponds to the direct use of the predictions of large-scale atomistic simulations of nanostructured materials for the design of continuum-level constitutive relations describing the material behavior and properties; and the two blue arrows #3 show a two-step path from atomistic to continuum material description through an intermediate mesoscopic modeling

the development of the defect structures or phase transformations can be performed and related to changes in temperature and pressure in the system (see examples below).

The main strength of the MD method is that only details of the interatomic interactions need to be specified, and no assumptions are made about the character of the processes under study. This is an important advantage that makes MD to be capable of discovering new physical phenomena or processes in the course of “computer experiments.” Moreover, unlike in real experiments, the analysis of fast non-equilibrium processes in MD simulations can be performed with unlimited atomic-level resolution, providing complete information of the phenomena of interest.

The predictive power of the MD method, however, comes at a price of a high computational cost of the simulations, leading to severe limitations on time and length scales accessible for MD simulations, as shown schematically in Fig. 1. Although the record length-

scale MD simulations have been demonstrated for systems containing more than  $10^{12}$  atoms (corresponds to cubic samples on the order of  $10\ \mu\text{m}$  in size) with the use of hundreds of thousands of processors on one of the world-largest supercomputers [6], most of the systems studied in large-scale MD simulations do not exceed hundreds of nanometers even in simulations performed with computationally efficient parallel algorithms (shown by a green area extending the scales accessible for MD simulations in Fig. 1). Similarly, although the record long time-scales of up to hundreds of microseconds have been reported for simulations of protein folding performed through distributed computing [7], the duration of most of the simulations in the area of materials research does not exceed tens of nanoseconds.

### Molecular Dynamics Simulations of Nanomaterials

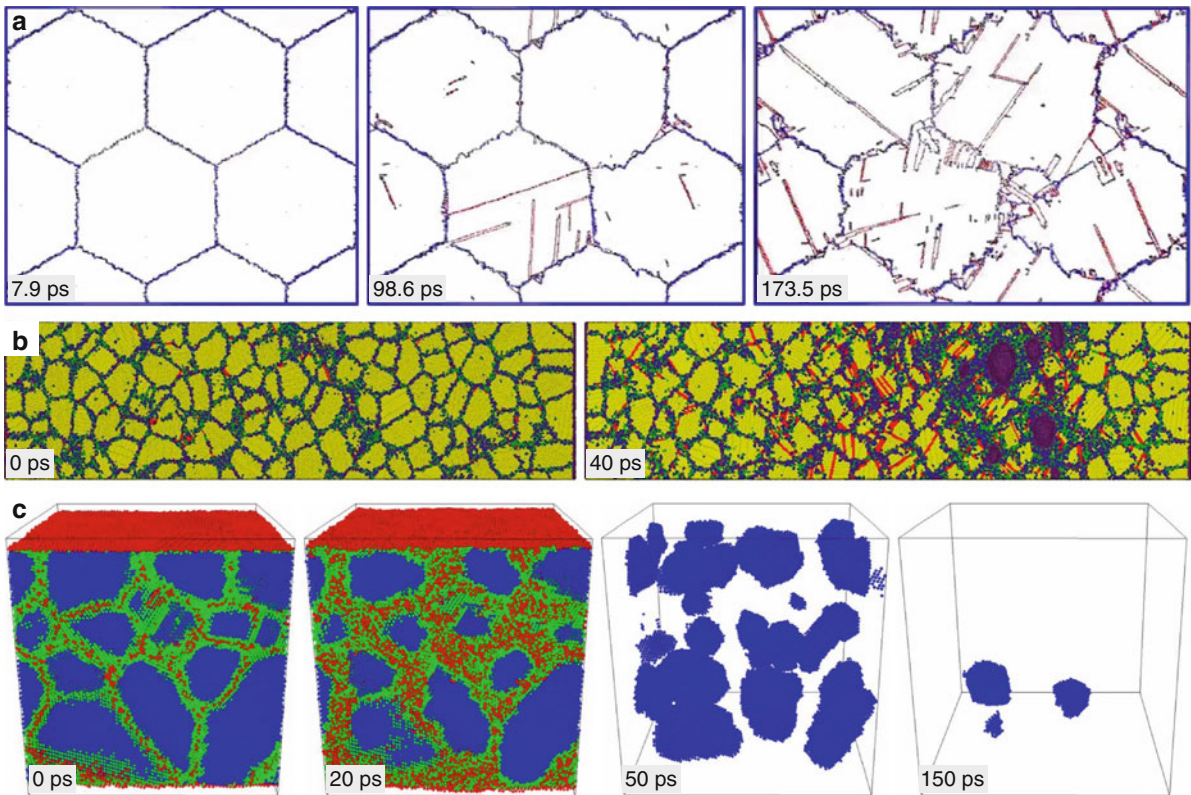
Both the advantages and limitations of the MD method, briefly discussed above, have important implications for simulations of nanomaterials. The transition to the nanoscale size of the structural features can drastically change the material response to the external thermal, mechanical, or electromagnetic stimuli, making it necessary to develop new structure-properties relationships based on new mechanisms operating at the nanoscale. The MD method is in a unique position to provide a complete microscopic description of the atomic dynamics under various conditions without making any a priori assumptions on the mechanisms and processes defining the material behavior and properties.

On the other hand, the limitations on the time- and length-scales accessible to MD simulations make it difficult to directly predict the macroscopic material properties that are essentially the result of a homogenization of the processes occurring at the scale of the elements of the nanostructure. Most of the MD simulations have been aimed at investigation of the behavior of individual structural elements (nanofibers, nanoparticles, interfacial regions in multiphase systems, grain boundaries, etc.). The results of these simulations, while important for the mechanistic understanding of the elementary processes at the nanoscale, are often insufficient for making a direct connection to the macroscopic behavior and properties of nanomaterials.

With the fast growth of the available computing resources, however, there have been an increasing

number of reports on MD simulations of systems that include multiple elements of nanostructures. A notable class of nanomaterials actively investigated in MD simulations is nanocrystalline materials – a new generation of advanced polycrystalline materials with sub-micron size of the grains. With a number of atoms on the order of several hundred thousands and more, it is possible to simulate a system consisting of tens of nanograins and to investigate the effective properties of the material (i.e., to make a direct link between the atomistic and continuum descriptions, as shown schematically by the green arrow #2 in Fig. 1). MD simulations of nanocrystalline materials addressing the mechanical [8, 9] and thermal transport [10] properties as well as the kinetics and mechanisms of phase transformations [11, 12] have been reported, with several examples illustrated in Fig. 2. In the first example, Fig. 2a, atomic-level analysis of the dislocation activity and grain-boundary processes occurring during mechanical deformation of an aluminum nanocrystalline system consisting of columnar grains is performed and the important role of mechanical twinning in the deformation behavior of the nanocrystalline material is revealed [9]. In the second example, Fig. 2b, the processes of void nucleation, growth and coalescence in the ductile failure of nanocrystalline copper subjected to an impact loading are investigated, providing important pieces of information necessary for the development of a predictive analytical model of the dynamic failure of nanocrystalline materials [8]. The third example, Fig. 2c, illustrates the effect of nanocrystalline structure on the mechanisms and kinetics of short pulse laser melting of thin gold films. It is shown that the initiation of melting at grain boundaries can steer the melting process along the path where the melting continues below the equilibrium melting temperature, and the crystalline regions shrink and disappear under conditions of substantial undercooling [11].

The brute force approach to the atomistic modeling of nanocrystalline materials (increase in the number of atoms in the system) has its limits in addressing the complex collective processes that involve many grains and may occur at a micrometer length scale and above. Further progress in this area may come through the development of concurrent multiscale approaches based on the use of different resolutions in the description of the intra-granular and grain boundary regions in a well-integrated computational model. An example of a multiscale approach is provided in Ref. [13], where



**Computational Study of Nanomaterials: From Large-Scale Atomistic Simulations to Mesoscopic Modeling, Fig. 2** Snapshots from atomistic MD simulations of nanocrystalline materials: (a) mechanical deformation of nanocrystalline Al (only atoms in the twin boundaries left behind by partial dislocations and atoms in disordered regions are shown by red and blue colors, respectively) [9]; (b) spallation of nanocrystalline Cu due to the reflection of a shock wave from a surface of the

sample (atoms that have local fcc, hcp, and disordered structure are shown by yellow, red, and green/blue colors, respectively) [8]; and (c) laser melting of a nanocrystalline Au film irradiated with a 200 fs laser pulse at a fluence close to the melting threshold (atoms that have local fcc surroundings are colored blue, atoms in the liquid regions are red and green, and in the snapshots for 50 and 150 ps the liquid regions are blanked to expose the remaining crystalline regions) [11]

scale-dependent constitutive equations are designed for a generalized finite element method (FEM) so that the atomistic MD equations of motion are reproduced in the regions where the FEM mesh is refined down to atomic level. This and other multiscale approaches can help to focus computational efforts on the important regions of the system where the critical atomic-scale processes take place. The practical applications of the multiscale methodology so far, however, have been largely limited to investigations of individual elements of material microstructure (crack tips, interfaces, and dislocation reactions), with the regions represented with coarse-grained resolution serving the purpose of adoptive boundary conditions. The perspective of the concurrent multiscale modeling of nanocrystalline materials remains unclear due to the close coupling

between the intra-granular and grain boundary processes. To enable the multiscale modeling of dynamic processes in nanocrystalline materials, the design of advanced computational descriptions of the coarse-grained parts of the model is needed so that the plastic deformation and thermal dissipation could be adequately described without switching to fully atomistic modeling.

### Mesoscopic Modeling

A principal challenge in computer modeling of nanomaterials is presented by the gap between the atomistic description of individual structural elements and the macroscopic properties defined by the

collective behavior of large groups of the structural elements. Apart from a small number of exceptions (e.g., simulations of nanocrystalline materials briefly discussed above), the direct analysis of the effective properties of nanostructured materials is still out of reach for atomistic simulations. Moreover, it is often difficult to translate the large amounts of data typically generated in atomistic simulations into key physical parameters that define the macroscopic material behavior. This difficulty can be approached through the development of mesoscopic computational models capable of representing the material behavior at time- and length-scales intermediate between the atomistic and continuum levels (prefix *meso* comes from the Greek word μέσος, which means middle or intermediate).

The mesoscopic models provide a “stepping stone” for bridging the gap between the atomistic and continuum descriptions of the material structure, as schematically shown by the blue arrows #3 in Fig. 1. Mesoscopic models are typically designed and parameterized based on the results of atomistic simulations or experimental measurements that provide information on the internal properties and interactions between the characteristic structural elements in the material of interest. The mesoscopic simulations can be performed for systems that include multiple elements of micro/nanostructure, thus enabling a reliable homogenization of the structural features to yield the effective macroscopic material properties. The general strategy in the development of a coarse-grained mesoscopic description of the material dynamics and properties includes the following steps:

1. Identifying the collective degrees of freedom *relevant for the phenomenon under study* (the focus on different properties of the same material may affect the choice of the structural elements of the model)
2. Designing, based on the results of atomic-level simulations and/or experimental data, a set of rules (or a mesoscopic force field) that governs the dynamics of the collective degrees of freedom
3. Adding a set of rules describing the changes in the properties of the dynamic elements in response to the local mechanical stresses and thermodynamic conditions

While the atomistic and continuum simulation techniques are well established and extensively used, the mesoscopic modeling is still in the early development stage. There is no universal mesoscopic technique or

methodology, and the current state of the art in mesoscopic simulations is characterized by the development of system-/phenomenon-specific mesoscopic models. The mesoscopic models used in materials modeling can be roughly divided into two general categories: (1) the models based on lumping together groups of atoms into larger dynamic units or particles and (2) the models that represent the material microstructure and its evolution due to thermodynamic driving forces or mechanical loading at the level of individual crystal defects. The basic ideas underlying these two general classes of mesoscopic models are briefly discussed below.

The models where groups of atoms are combined into coarse-grained computational particles are practical for materials with well-defined structural hierarchy (that allows for a natural choice of the coarse-grained particles) and a relatively weak coupling between the *internal* atomic motions inside the coarse-grained particles and the *collective* motions of the particles. In contrast to atomic-level models, the atomic structure of the structural elements represented by the coarse-grained particles is not explicitly represented in this type of mesoscopic models. On the other hand, in contrast to continuum models, the coarse-grained particles allow one to explicitly reproduce the nanostructure of the material. Notable examples of mesoscopic models of this type are coarse-grained models for molecular systems [14–16] and mesoscopic models for carbon nanotubes and nanofibrous materials [17–19]. The individual molecules (or mers in polymer molecules) and nanotube/nanofiber segments are chosen as the dynamic units in these models. The collective dynamic degrees of freedom that correspond to the motion of the “mesoparticles” are explicitly accounted for in mesoscopic models, while the internal degrees of freedom are either neglected or described by a small number of internal state variables. The description of the internal states of the mesoparticles and the energy exchange between the dynamic degrees of freedom and the internal state variables becomes important for simulations of non-equilibrium phenomena that involve fast energy deposition from an external source, heat transfer, or dissipation of mechanical energy.

Another group of mesoscopic models is aimed at a computationally efficient description of the evolution of the defect structures in crystalline materials. The mesoscopic models from this group include the

discrete dislocation dynamics model for simulation of crystal plasticity [20–22] and a broad class of methods designed for simulation of grain growth, recrystallization, and associated microstructural evolution (e.g., phase field models, cellular automata, and kinetic Monte Carlo Potts models) [21–23]. Despite the apparent diversity of the physical principles and computational algorithms adopted in different models listed above, the common characteristic of these models is the focus on a realistic description of the behavior and properties of individual crystal defects (grain boundaries and dislocations), their interactions with each other, and the collective evolution of the totality of crystal defects responsible for the changes in the microstructure.

Two examples of mesoscopic models (one for each of the two types of the models discussed above) and their relevance to the investigation of nanomaterials are considered in more detail next.

### Discrete Dislocation Dynamics

The purpose of the discrete dislocation dynamics (DD) is to describe the plastic deformation in crystalline materials, which is largely defined by the motions, interactions, and multiplication of dislocations. Dislocations are linear crystal defects that generate long-range elastic strain fields in the surrounding elastic solid. The elastic strain field is accounting for ~90% of the dislocation energy and is responsible for the interactions of dislocations among themselves and with other crystal defects. The collective behavior of dislocations in the course of plastic deformation is defined by these long-range interactions as well as by a large number of local reactions (annihilation, formation of glissile junctions or sessile dislocation segments such as Lomer or Hirth locks) occurring when the anelastic core regions of the dislocation lines come into contact with each other. The basic idea of the DD model is to solve the dynamics of the dislocation lines in elastic continuum and to include information about the local reactions. The elementary unit in the discrete dislocation dynamics method is, therefore, a segment of a dislocation.

The continuous dislocation lines are discretized into segments, and the total force acting on each segment in the dislocation slip plane is calculated. The total force includes the contributions from the external force, the internal force due to the interaction with other dislocations and crystal defects that generate elastic fields, the

“self-force” that can be represented by a “line tension” force for small curvature of the dislocation, the Peierls force that acts like a friction resisting the dislocation motion, and the “image” force related to the stress relaxation in the vicinity of external or internal surfaces. Once the total forces and the associated resolved shear stresses,  $\tau^*$ , acting on the dislocation segments are calculated, the segments can be displaced in a finite difference time integration algorithm applied to the equations connecting the dislocation velocity,  $v$ , and the resolved shear stress, for example, [21]

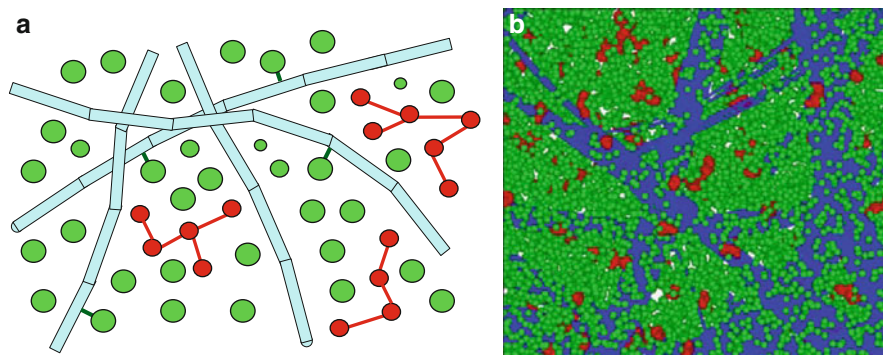
$$v = A \left( \frac{\tau^*}{\tau_0} \right)^m \exp \left( - \frac{\Delta U}{kT} \right) \quad (3)$$

when the displacement of a dislocation segment is controlled by thermally activated events ( $\Delta U$  is the activation energy for dislocation motion,  $m$  is the stress exponent, and  $\tau_0$  is the stress normalization constant) or

$$v = \tau^* b / B \quad (4)$$

that corresponds to the Newtonian motion equation accounting for the atomic and electron drag force during the dislocation “free flight” between the obstacles ( $B$  is the effective drag coefficient and  $b$  is the Burgers vector).

Most of the applications of the DD model have been aimed at the investigation of the plastic deformation and hardening of single crystals (increase in dislocation density as a result of multiplication of dislocations present in the initial system). The extension of the DD modeling to nanomaterials is a challenging task as it requires an enhancement of the technique with a realistic description of the interactions between the dislocations and grain boundaries and/or interfaces as well as an incorporation of other mechanisms of plasticity (e.g., grain boundary sliding and twinning in nanocrystalline materials). There have only been several initial studies reporting the results of DD simulations of nanoscale metallic multilayered composites [24]. Due to the complexity of the plastic deformation mechanisms and the importance of anelastic short-range interactions among the crystal defects in nanomaterials, the development of novel hybrid computational methods combining the DD technique with other mesoscopic methods is likely to be required for realistic modeling of plastic deformation in this class of materials.



**Computational Study of Nanomaterials: From Large-Scale Atomistic Simulations to Mesoscopic Modeling, Fig. 3** Schematic representation of the basic components of the dynamic mesoscopic model of a CNT-based nanocomposite

### Mesoscopic Model for Nanofibrous Materials

The design of new nanofibrous materials and composites is an area of materials research that currently experiences a rapid growth. The interest in this class of materials is fueled by a broad range of potential applications, ranging from fabrication of flexible/stretchable electronic and acoustic devices to the design of advanced nanocomposite materials with improved mechanical properties and thermal stability. The behavior and properties of nanofibrous materials are defined by the collective dynamics of the nanofibers and, in the case of nanocomposites, their interactions with the matrix. Depending on the structure of the material and the phenomenon of interest, the number of nanofibers that has to be included in the simulation in order to ensure a reliable prediction of the effective macroscopic properties can range from several hundreds to millions. The direct atomic-level simulation of systems consisting of large groups of nanofibers (the path shown by the green arrow #2 in Fig. 1) is beyond the capabilities of modern computing facilities. Thus, an alternative two-step path from atomistic investigation of individual structural elements and interfacial properties to the continuum material description through an intermediate mesoscopic modeling (blue arrows #3 in Fig. 1) appears to be the most viable approach to modeling of nanofibrous materials. An example of a mesoscopic computational model recently designed and parameterized for carbon nanotube (CNT)-based materials is briefly discussed below.

The mesoscopic model for fibrous materials and organic matrix nanocomposites adopts a coarse-

material (a) and a corresponding molecular-level view of a part of the system where a network of CNT bundles (blue color) is embedded into an organic matrix (green and red color) (b)

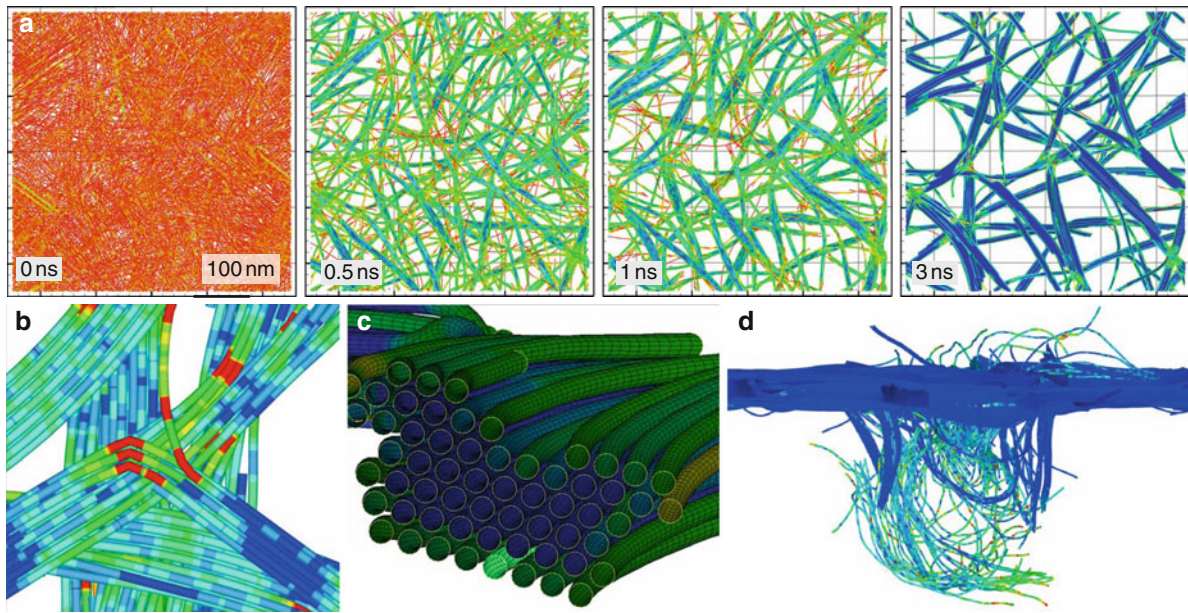
grained description of the nanocomposite constituents (nano-fibers and matrix molecules), as schematically illustrated in Fig. 3. The individual CNTs are represented as chains of stretchable cylindrical segments [19], and the organic matrix is modeled by a combination of the conventional “bead-and-spring” model commonly used in polymer modeling [14, 15] and the “breathing sphere” model developed for simulation of simple molecular solids [16] and polymer solutions [25].

The degrees of freedom, for which equations of motion are solved in dynamic simulations or Metropolis Monte Carlo moves are performed in simulations aimed at finding the equilibrium structures, are the nodes defining the segments, the positions of the molecular units, and the radii of the spherical particles in the breathing sphere molecules. The potential energy of the system can be written as

$$U = U_{T(int)} + U_{T-T} + U_{M-M} + U_{M(int)} + U_{M-T} \quad (5)$$

where  $U_{T(int)}$  is the potential that describes the internal strain energy associated with stretching and bending of individual CNTs,  $U_{T-T}$  is the energy of intertube interactions,  $U_{M-M}$  is the energy of chemical and non-bonding interactions in the molecular matrix,  $U_{M(int)}$  is the internal breathing potential for the matrix units, and  $U_{M-T}$  is the energy of matrix – CNT interaction that can include both non-bonding van der Waals interactions and chemical bonding. The internal CNT potential  $U_{T(int)}$  is parameterized based on the results of atomistic simulations [19] and accounts for the transition to the anharmonic regime of stretching (nonlinear





**Computational Study of Nanomaterials: From Large-Scale Atomistic Simulations to Mesoscopic Modeling, Fig. 4** Snapshots from mesoscopic simulations of systems consisting of (10,10) single-walled carbon nanotubes: (a) spontaneous self-organization of CNTs into a continuous network of CNT bundles (CNT segments are colored according to the local intertube interaction energy) [18]; (b) an enlarged view of

a structural element of the CNT network (CNT segments colored according to the local radii of curvature and the red color marks the segments adjacent to buckling kinks) [26]; (c) a cross-section of a typical bundle showing a hexagonal arrangement of CNTs in the bundle [18]; (d) snapshot from a simulation of a high-velocity impact of a spherical projectile on a free-standing thin CNT film

stress–strain dependence), fracture of nanotubes under tension, and bending buckling [26]. The intertube interaction term  $U_{T-T}$  is calculated based on the tubular potential method that allows for a computationally efficient and accurate representation of van der Waals interactions between CNT segments of arbitrary lengths and orientation [18]. The general procedure used in the formulation of the tubular potential is not limited to CNTs or graphitic structures. The tubular potential (and the mesoscopic model in general) can be parameterized for a diverse range of systems consisting of various types of nano- and micro-tubular elements, such as nanotubes, nanorods, and micro-fibers.

First simulations performed with the mesoscopic model demonstrate that the model is capable of simulating the dynamic behavior of systems consisting of thousands of CNTs on a timescale extending up to tens of nanoseconds. In particular, simulations performed for systems composed of randomly distributed and oriented CNTs predict spontaneous self-assembly of CNTs into continuous networks of bundles with partial hexagonal ordering of CNTs in the bundles, Fig. 4a–c

[18, 26]. The bending buckling of CNTs (e.g., see Fig. 4b) is found to be an important factor responsible for the stability of the network structures formed by defect-free CNTs [26]. The structures produced in the simulations are similar to the structures of CNT films and buckypaper observed in experiments. Note that an atomic-level simulation of a system similar to the one shown in the left panel of Fig. 4 would require  $\sim 2.5 \times 10^9$  atoms, making such simulation unfeasible.

Beyond the structural analysis of CNT materials, the development of the mesoscopic model opens up opportunities for investigation of a broad range of important phenomena. In particular, the dynamic nature of the model makes it possible to perform simulations of the processes occurring under conditions of fast mechanical loading (blast/impact resistance, response to the shock loading, etc.), as illustrated by a snapshot from a simulation of a high-velocity impact of a spherical projectile on a free-standing thin CNT film shown in Fig. 4d. With a proper parameterization, the mesoscopic model can also be adopted for calculation of electrical and thermal transport properties of complex nanofibrous materials [27].

## Future Research Directions

The examples of application of the atomistic and mesoscopic computational techniques, briefly discussed above, demonstrate the ability of computer modeling to provide insights into the complex processes that define the behavior and properties of nanostructured materials. The fast advancement of experimental methods capable of probing nanostructured materials with high spatial and temporal resolution is an important factor that allows for verification of computational predictions and stimulates the improvement of the computational models. With further innovative development of computational methodology and the steady growth of the available computing resources, one can expect that both atomistic and mesoscopic modeling will continue to play an increasingly important role in nanomaterials research.

In the area of atomistic simulations, the development of new improved interatomic potentials (often with the help of *ab initio* electronic structure calculations, red arrow #1 in Fig. 1) makes material-specific computational predictions more accurate and enables simulations of complex multi-component and multiphase systems. Further progress can be expected in two directions that are already actively pursued: (1) large-scale MD simulations of the fast dynamic phenomena in nanocrystalline materials (high strain rate mechanical deformation, shock loading, impact resistance, response to fast heating, etc.) and (2) detailed investigation of the atomic structure and properties of individual structural elements in various nanomaterials (grain boundaries and interfaces, nanotubes, nanowires, and nanoparticles of various shapes). The information obtained in large-scale atomistic simulations of nanocrystalline materials can be used to formulate theoretical models translating the atomic-level picture of material behavior to the constitutive relations describing the dependence of the mechanical and thermal properties of these materials on the grain size distribution and characteristics of nanotexture (green arrow #2 in Fig. 1).

The results of the detailed analysis of the structural elements of the nanocomposite materials can be used in the design and parameterization of mesoscopic models, where the elementary units treated in the models correspond to building blocks of the nanostructure (elements of grain boundaries, segments of dislocations, etc.) or groups of atoms that have some distinct properties (belong to a molecule, a mer unit of

a polymer chain, a nanotube, a nanoparticle in nanocomposite material, etc.). The design of novel system-specific mesoscopic models capable of bridging the gap between the atomistic modeling of structural elements of nanostructured materials and the continuum models (blue arrows #3 in Fig. 1) is likely to become an important trend in the computational investigation of nanomaterials. To achieve a realistic description of complex processes occurring in nanomaterials, the description of the elementary units of the mesoscopic models should become more flexible and sophisticated. In particular, an adequate description of the energy dissipation in nanomaterials can only be achieved if the energy exchange between the atomic degrees of freedom, excluded in the mesoscopic models, and the coarse-grained dynamic degrees of freedom is accounted for. A realistic representation of the dependence of the properties of the mesoscopic units of the models on local thermodynamic conditions can also be critical in modeling of a broad range of phenomena.

In general, the optimum strategy in investigation of nanomaterials is to use a well-integrated multiscale computational approach combining the *ab initio* and atomistic analysis of the constituents of nanostructure with mesoscopic modeling of the collective dynamics and kinetics of the structural evolution and properties, and leading to the improved theoretical understanding of the factors controlling the effective material properties. It is the improved understanding of the connections between the processes occurring at different time- and length-scales that is likely to be the key factor defining the pace of progress in the area of computational design of new nanocomposite materials.

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## Cross-References

- ▶ [Ab initio DFT Simulations of Nanostructures](#)
- ▶ [Active Carbon Nanotube-Polymer Composites](#)
- ▶ [Carbon-Nanotubes](#)
- ▶ [Finite Element Methods for Computational Nanooptics](#)

- ▶ [Mechanical Properties of Nanocrystalline Metals](#)
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- ▶ [Reactive Empirical Bond-Order Potentials](#)
- ▶ [Self-Assembly of Nanostructures](#)
- ▶ [Vertically Aligned Carbon Nanotubes, Collective Mechanical Behavior](#)

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## Computational Systems Bioinformatics for RNAi

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## Synonyms

[Automatic data analysis workflow for RNAi](#); [Systems level data mining for RNAi](#)

## Definition

Computational systems bioinformatics for RNAi screening and therapeutics is defined as complete