

Chapter 1

Introduction

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Abstract In this chapter, we present the conceptual framework that motivates the development of a predictive multiscale approach to Integrated Computational Materials Science and Engineering. Clear distinction among theories, models, and simulations allow us to categorize the underlying physical principles used, the realization of those principles, and their implementation on a computational architecture. The physical theories that are explored in this volume can be combined into coherent multi-theory constructs that preserve the fidelity of each theory over its range of applicability. Similarly, models of these physical theories, which can be realized in computer simulations, must respect their range of validity over both spatial and temporal scales. The principles and procedures presented in this book promote a clear and concise methodological approach for the creation of predictive multi-theory, multi-model, multiscale simulations.

1.1 Conceptual Framework in Theory, Modeling and Simulation

Over the past few decades, a variety of computational modeling and simulation methods have provided powerful insight into the behavior of materials across the entire process-structure-properties-performance spectrum. These methods have most commonly been used to address materials phenomena at the level of a single scale belonging to the range of electronic, atomic, microstructural, mesostructural and macroscopic scales. However, many materials phenomena are inherently multiscale in both space and time and often it is making a drastic approximation to

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ignore the coupling between phenomena across multiple scales. While computational methods based on the most fundamental theoretical principles have the potential of modeling materials phenomena with a high degree of fidelity at all scales, the sheer computational cost of simulating materials phenomena at the largest spatio-temporal scales renders this approach impractical. Novel multiscale modeling and simulation paradigms are providing the means to bridge different modeling and simulation methods to achieve modeling and simulation capabilities of materials behavior from the atom all the way to the components of an engineered system. The combination of computational materials science and engineering methods with multiscale paradigms is therefore becoming of continually increasing importance for the emergence of a robust and predictive approach to materials design and analysis, namely the approach of Integrated Computational Materials Science and Engineering (ICMSE). The ICMSE approach can be understood by focusing on clear distinctions among Theory, Modeling, and Simulation, and their integration into multiscale methodologies. We address in detail below the Theory-Modeling-Simulation framework on which chapters in this book are based.

1.1.1 Theory

A *Theory* is a set of axioms and interpretative procedures that constitute a predictive mathematical description of the natural world. We will address ICMSE within the context of the theories of (a) non-relativistic quantum mechanics (QM), (b) classical mechanics, and continuum mechanics, (c) statistical mechanics and thermodynamics, (d) classical thermodynamics, etc.

Particles described within the framework of QM obey the time-independent Schrödinger equation and their behavior can be characterized through a physical interpretation of its many-particle wave function solutions. The reformulation of quantum mechanics theory in terms of electron density instead of wave functions forms the foundation of density functional theory (DFT). DFT is motivated by the Hohenberg-Kohn theorems [1] which state that the ground state of a many electron system is uniquely determined by the electron density and that this density minimizes an energy functional (a function of the spatially dependent density). For atom and molecules which include many electrons, and hence for the general many electron problem, DFT reduces the search for a three-dimensional wave function for each electron to that of a single three-dimensional function (electron density) for a given nuclear configuration or external potential.

Lagrange's formalism of classical mechanics finds the trajectory of some particle (position and velocity) in some potential as that which minimizes the action (a temporal integral of the Lagrangian, the difference between the kinetic and potential energy functions). Hamilton's approach replaces, via a Legendre transformation, position and velocities by positions and conjugated momenta as the canonical variables. The Hamilton's formalism constitutes a framework that can provide a deep physical insight into the behavior of dynamical systems.

The Hamiltonian expressing the energy of a system plays a central role in this formalism. The extension of classical mechanics from assemblies of particles to matter distributions and vector (displacement, force) and tensor (strain, stress) fields leads to the theory of continuum mechanics. For instance, linear elasticity theory addresses the deformation of solid continuum materials subjected to stress field that relate linearly to the strain field.

The formalism of the classical theory of continuum mechanics is based on partial differential equations (strain defined in terms of the gradient of displacement, mechanical equilibrium condition expressed in terms of the divergence of the stress field, etc.). The difficulty of defining partial derivatives at singularities such as discontinuities in materials (surfaces, interfaces, etc.) limits the direct application of this theory to materials exhibiting such discontinuous structural features. In contrast, the theory of peridynamics is a formulation of continuum mechanics based on force and displacement fields and integral equations of these fields. The integral equations of peridynamics are mathematically compatible with the structural discontinuities and singularities featured by most materials.

The theories of statistical mechanics and statistical thermodynamics aim at explaining the physical properties of macroscopic systems based on the knowledge of the behavior of their microscopic constituents (particles). QM and classical mechanics provide a framework for the description of systems of particles but have difficulties addressing large assemblies of interacting particles. Statistical theories enable the scale up from microscopic to macroscopic systems where only average values and fluctuations are observed. In the context of the fundamental concept of ergodicity, at equilibrium, the time average of some quantity that varies along the temporal trajectory of a dynamical system of particles is equivalent to a statistical average over a large number of macroscopically identical systems (i.e. a so-called ensemble). In that framework, one may consider the microcanonical ensemble (macroscopic systems with same energy, volume and composition), canonical ensemble (same temperature, volume and composition), and isothermal-isobaric ensemble (same temperature, pressure, composition) among others.

The theory of classical thermodynamics is based on the principle of maximization of the entropy of an isolated system. All macroscopic thermodynamics state variables are related through a fundamental equation. In the entropy representation of the fundamental equation, the equilibrium state of the system is one that maximizes the entropy with respect to the unconstrained state variables. Other representations of the fundamental equation are obtained through Legendre transformations of the entropy form, namely the Helmholtz free energy, Gibbs free energy, and enthalpy representations. The pertinent choice of these representations is made depending upon the convenience of the chosen state variables and the constraint they may be subjected to. The maximum entropy principle translates into a minimization variational principle for these other representations.

1.1.2 *Model*

A *Model* is a prescribed physical description of a real-world system or class of systems formulated within the concepts of a Theory.

Within the framework of DFT, Kohn and Sham [2] have reduced the problem of a many interacting electron system to the more tractable problem of a system composed of non-interacting electrons evolving in an effective potential. This effective potential includes any external potential (e.g. interactions with nuclei), the electron-electron Coulomb interactions and the exchange and correlation interactions. The latter two interactions are modeled via simplified exchange-correlation functionals such as the local density approximation (LDA) that is based on the exchange energy of the uniform electron gas. The kinetic energy is known for non-interacting particles as their wave function can be represented as a Slater determinant of orbitals. In ab initio molecular dynamics the forces acting on a set of nuclei are calculated from the electron densities determined from DFT combined with the nuclear (or ionic) repulsions.

In quantum statistical mechanics, all static properties and dynamic properties of a system of particles in thermal equilibrium are specified from the thermal density matrix. Using the closure conditions of quantum states, the partition function of this system may be expressed in terms of very high temperature thermal density matrices which can be approximated by Gaussian functions of position. This approach parallels the path integral approach to describing quantum systems. Approximate classical model Hamiltonian of systems of quantum particles results from this approach, providing an isomorphism between classical mechanics models and quantum systems. While the dynamics of the model classical system may not be realistic, statistical averages (equivalently time averages, provided the ergodic condition is satisfied) of quantities calculated from the classical Hamiltonian will be representative of the quantum system.

Classical mechanics models of interacting particles use interatomic potentials to describe the potential energy part of the classical Hamiltonian. The precision of atomistic models is dependent on the ability of the governing interatomic potential/force field to model the atomic interactions accurately, which can be achieved by parameterizing the potentials to reflect the underlying electronic effects. While equilibrium properties of materials can be successfully obtained from empirical potentials they cannot be expected to accurately model systems that are far away from equilibrium, such as when the systems are subjected to extreme conditions, where interatomic charge polarization and transfer may become significant. Thus potential formulations such as the ones based on chemical potential equalization and the recently developed charge-transfer embedded atom method (CT-EAM) and chemical environment dependent dynamic charge (EDD-Q) potentials have become extremely useful for modeling interatomic forces away from equilibrium [3]. Of particular interest are the EDD-Q formulations due to their ability to be parameterized based on quantum chemical data in a straight forward way.

A phase field model represents the non-uniformity of polycrystalline or polyphase materials via one or more ad hoc order parameters (phase fields) supplemented by other fields such as compositional, stress/strain fields, etc. An order parameter may model the grain orientation in a polycrystalline material or the different phases in a polyphase material. In this model, interfaces are not atomically sharp but modeled as diffuse continuous variations in an order parameter. The interfacial energy relates to the gradient in the order parameter. The formulation of the phase field model is then based on a free energy functional of the order parameter and other state variable fields (a fundamental equation) that may represent the thermodynamics of the system of interest [4].

The critical difference between the peridynamics approach and other approaches in classical continuum mechanics is that the former is formulated using integral equations as opposed to derivatives of the displacement components, allowing for a straight forward description of properties of materials without resorting to special boundary conditions to avoid singularities [5, 6]. Displacements in the peridynamics formalism are driven by a force which is expressed as a spatial integral of a force density. This force density is a function of the relative position between two points in the continuum and of the relative displacement between these points. Solid bodies in peridynamics are therefore modeled by the pairwise force density function for the “bond” connecting any two points. Discontinuities are easily handled by “cutting” the “bond” between two points across the discontinuity. The force density function requires a small number of materials parameters as input (e.g. elastic modulus, yield strength, critical interaction cutoff or stretch).

1.1.3 *Simulation*

A *Simulation* is the computational realization of a particular model. It consists of a set of algorithms and rules for reliable, refine-able (in the sense of precision) calculation of the properties of models. Improvements in the quality and reliability of computed results are separable in this framework.

Simulation methods enable the sampling of the phase space of Hamiltonian-based models, whether representing truly classical systems such as collections of particles interacting via interatomic potentials or a classical model of quantum systems (Path Integral Classical Isomorphism representation) or a quantum system. Both deterministic and stochastic simulation methods can be used to propagate the system through phase space. Molecular Dynamics (MD) is an example of a deterministic approach whereby one investigates the intrinsic dynamics of the system by integrating numerically in time the equations of motion. There exists a variety of algorithms for the states of the system to march in time. Stochastic methods such as Monte Carlo (MC) methods do not provide dynamical information but only evaluate the configurations of the system. Transitions from one configuration to another are driven by probabilistic evolution schemes such as a Markov process. This approach is therefore also applicable to model systems that may not have intrinsic dynamics.

The natural ensemble for the MD method is the microcanonical ensemble. Extension of the microcanonical MD method to simulating the dynamics of a model system in another ensemble (e.g. such as the canonical ensemble) requires the application of constraints on its degrees of freedom i.e. on its trajectories (e.g. thermostating). In that case, the dynamics of the system may be influenced by the constraint and one may consider that one only evaluates realistically the configurational part of the problem. Stochastic methods do not suffer from these constraints.

For equilibrium, variational methods are applied to the phase field free energy functional, which is minimized with respect to its degrees of freedom: order parameters and other state variable fields. For simulating time-dependent processes, one establishes dynamical equations relating the rate of change of the order parameters and state variables to the driving force (variational derivatives of the free energy functional) through mobility coefficients. Details of these equations may vary depending on the existence or not of conservation laws for the fields. Stochastic fluctuations such as thermal fluctuations may be added by introducing them in the dynamical equations stochastic terms.

The peridynamics model can be suitably discretized to model material properties, where the particle-to-particle (point-to-point in a continuum) interaction is represented via the parameterized force density function. Numerical methods to solve the classical equations of motion of each particle are used to drive the dynamics of the model solid.

1.1.4 Additional Remarks

The quality and reliability of results obtained within the *Theory-Modeling-Simulation* framework can be improved separately. For instance one can adopt a more refined theory that will include a more realistic description of the physical or chemical processes taking place in a natural system. This could be illustrated by employing a quantum mechanical description of a molecular system in place of a classical mechanics description of molecular forces. Another approach would be to adopt a more refined model within a theory. For instance, within the context of classical mechanics description of materials composed of collections of interacting atoms, the utilization of three-body interatomic potentials may enable a better prediction of mechanical properties compared to pair-wise additive potentials. Independently, within a given theory and for a fixed model, one may improve the simulation in two ways. The first one could involve the application of more accurate solvers of differential equations or the use of a smaller time step in solving numerically some equation of motion. The second may concern the adoption of a better thermostat in a canonical ensemble MD simulation.

In no way should the *Theory-Modeling-Simulation* framework allow the exploitation of offsetting errors by one or all of the three categories. What is done in the simulation must not offset limitations implicit in the choices upstream.

The *Model* must not “fix” the *Theory* by reintroducing features not in the theory. The algorithms and rules in the *Simulation* must not offset the intrinsic limits of the *Model* being treated.

Because separability of refinement is coupled with fidelity, the *Theory-Modeling-Simulation* framework explicitly supports systematic, quantitative exploration of the effects of empiricism. Convenient empirical assumptions can be replaced by more realistic ones and the consequences quantified. Moreover, the appraisal of computed data by visualization techniques is disciplined by explicit knowledge of the chain of relationships and assumptions contained in the *Model* and the *Simulation*.

1.2 Multiscale Modeling and Simulation

The Integrated Computational Materials Science and Engineering (ICMSE) paradigm captured in the *Theory*, *Modeling*, and *Simulation* triad is integrated into multiscale approaches.

1.2.1 Multiscale Approaches

To this point we have not mentioned the multiscale aspects of the *Theory*, *Modeling* and *Simulation* paradigm explicitly. For materials science, this is an issue of the desired level of fundamental understanding. Consider the simulation of a material from a quantum mechanical perspective. The limitations of computing power imposed by current computer platforms enable the simulation of systems containing at most a few hundred atoms. This means that this type of simulation cannot account for phenomena with long-range characteristics. Newtonian atomistic models simulated by MD can handle the simulation of systems that may contain billions of atoms thus permitting the investigation of phenomena at scales larger than those possible by a quantum description. However, the reliance on classical interatomic potentials makes the details of the very shortest scale of the atomic bond and related electronic phenomena inaccessible. Even with billions of atoms, very long range phenomena are inaccessible to MD simulations. Simulations of continuum models open a window on very long range scales but distance themselves from phenomena resulting from the discrete nature of matter. While, our argument above is based on the inability of some type of simulation or model to address the complete range of spatial scales that may be needed to truthfully describe a natural system, similar observations can be made concerning temporal scales. For instance, current computing power limits the time over which the dynamics of an atomistic system can be simulated. This makes long-time scale phenomena inaccessible. Again, simulations of coarser models may permit the investigation of a system over

much longer periods of time without however providing access to the detailed processes taking place at very short time scales.

The inability to handle large systems over large periods of time can be viewed as a *Simulation* limitation, not a *Model* limitation. However, as we saw, the adoption of a different *Model*, for example a MD simulation using some interatomic potential versus a quantum level simulation, might be helpful in circumventing the *Simulation* limitations. This choice will have a cost though in the inability, for instance, to handle the electronic phenomena taking place at the level of the bonds. This is a *Model* limitation. Development of multiscale models and the corresponding simulations is a direct consequence of these *Model* limitations.

In the *Theory-Modeling-Simulation* framework, a multiscale model can be defined as one in which more than one theory is incorporated, each corresponding to one of several physically important scales involved in the model.

1.2.2 Serial and Concurrent Multiscale Modeling and Simulation

Most of the modern simulation methods for coupling length scales can be characterized as either serial or concurrent. Within serial methods, a set of calculations at a fundamental level (small length scale) is used to evaluate parameters as input for a more phenomenological model that describes a system at longer length scales. For example the Quasi-continuum (QC) method is a zero temperature technique with a formulation based on standard continuum mechanics (e.g. Finite Element (FE) method) with the additional feature that the constitutive equations are drawn from calculations at the atomic scale [7–10]. In contrast, concurrent methods build around the idea of describing the physics of different regions of a material with different models and linking them via a set of boundary conditions. The archetype of concurrent methods divides the space into atomistic regions coupled with a continuum modeled via FE [11, 12]. Coarse graining has been proposed as a mean to couple seamlessly a molecular dynamics (MD) region to a FE mesh [13]. Coarse-grained MD produces equations of motion for a mean displacement field at the nodes of a coarse-grained mesh partitioning the atomistic system. Other algorithms that allow the coupling between atomistic and continuum regions have been proposed [14–17]. The fundamental issue in multiscale modeling and simulation relates to the nature of the “interface” between the models that are used to bridge their individual ranges of scales. All models must be connected as seamlessly as possible. This is the challenge of “scale-parity” simulation. Successful multiscale modeling and simulation requires treatment of all the relevant scales even-handedly. Scale-parity requires that no one scale be favored. This has led to the development of an approach to multiscale modeling called “consistent embedding” [18].

1.2.3 *Consistent Embedding*

The principle of consistent embedding dictates that the information that comprises a model at a larger spatial or longer time scale be compatible with the model used at a smaller or shorter scale. This principle is essential to the development of predictive theory and modeling, as the materials that exist on either side of a multiscale interface must be physically consistent. For example, if we wish to look at the phenomenon of fracture, then the stress-strain relationship for the model at the shorter length scale should, at the very least, display the same small strain behavior, Young's modulus, as the model used at the longer length scale. Enforcing this kind of constraint, that the Young's modulus of the quantum chemical and atomistic models be equivalent, up to some controllable error, is an example of consistent embedding. Other criteria can be developed, based on the physical properties being modeled, which improve the likelihood that emergent behavior of larger systems is grounded in the theoretical description of the smaller system.

The consistent embedding requirement has led to the development of techniques (e.g. based on wavelet analysis) that enable the mathematically rigorous construction of a multiscale model which range of scales is the union of the scales of the individual models that are integrated [19–25]. These techniques are applicable to serial and current methods and to bridging not only spatial but also temporal scales.

1.2.4 *Multi-theory and Multi-model Approaches*

We have addressed the concept of multiscale approaches in computational simulations in the previous sections. We wish to clarify this concept in the context of our *Theory-Modeling-Simulation* framework by introducing the additional concepts of multi-theory and multi-model approaches.

The three differing concepts of multi-theory, multi-model, and multiscale approaches can occur singly or in combination. An example of a multi-theory approach would be the usual description of quantum chemical theory where the electrons are taken to behave according to quantum mechanics, while the nuclei, or ions, are taken to behave according to classical mechanics.

Another example of multi-theory approach results from the dynamical treatment of some classical mechanics system composed of particles modeled with some interatomic potential model. Using an ergodic sampling of configuration space, the system is then being studied under the rubric of statistical mechanics or thermodynamics, at the level of theory, in addition to the classical mechanics theory that was at the foundation of the model.

Following these examples a little further, we can consider a multi-theory, multi-model description of a material. If considered in the context of dynamics, the system can be comprised of (a) quantum mechanical electrons described within the

framework of DFT and modeled with some specific choice of an approximate density functional, and classical mechanical ions modeled using some interatomic potential. This system falls into the combined theories of QM, Classical Mechanics and Statistical Thermodynamics as well as two distinct models.

A single theory but multi-model example would consist of the description of a system of different particles (say electrons and ions) both in the framework of the theory of QM but the electrons being modeled with DFT and the ions modeled with an approximate classical Hamiltonian of systems of quantum particles derived from the path integral approach.

It is also possible to consider multiscale simulation versions of multi-theory, multi-model approaches. An example might be the use of atomistic and continuum mechanical theories to describe the linear mechanical response of a material (i.e. elastic behavior) in the context of a dynamical simulation. Some portion of the material may be modeled as a combination of classical ions and quantum electrons as illustrated in previous examples while another portion of the same system might be modeled as a set of mesh points using continuum mechanics. The theories used here include quantum mechanics, classical atomic and continuum classical mechanics as well as statistical mechanics. This simulation would then be based on multiple theories captured by multiple models working at distinctive spatio-temporal scales such as a density functional model of the electrons, a classical Hamiltonian model of the ions and linear elastic model of the continuum. The quantum model may be solved statically within the Born-Oppenheimer approximation (electrons always in their ground state relative to atomic motions), while the dynamics of the atomistic region is simulated with MD schemes, the elastic medium is dynamically simulated with a finite difference scheme in the time domain. This type of multi-theory, multi-model and multiscale simulations will be addressed in details in Chap. 6.

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