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Application of computational modeling methods to metallic phenomena

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Abstract

Computational modeling techniques are becoming increasingly useful for studying a wide array of metallic properties at all length scales as the complexity of materials increases and the requirements for their application becomes more stringent. The development of algorithms for individual size and time domains is central to this area of research. An overview of various modeling methods is presented in this paper, categorized by their size domains, as well as their current applications in research on metallic phenomena. The methods described are Finite Element Analysis and Finite Volume Analysis on the macroscale, Cellular Automata and Monte Carlo methods on the microscale, and Molecular Dynamics and Density Functional Theory on the atomistic scale.

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1. Introduction

The search for novel materials has typically been done in physical labs with repeated cycles of synthesis and characterization, which is a slow process if done naively. There are also limits to the information that can be characterized in physical labs. Computational methods focus on simulating the behavior of materials without performing the experiment physically, allowing for expedited materials research and discovery [1, 2]. The focus of this paper will be on computational methods as they apply to metals.

Metallurgy is a field that has benefited greatly from the introduction of computational material methods [1, 3-10]. Metals are of great importance to the modern world, and there are a variety of phenomena that can be observed in metals at different length scales. Each scale presents its own limitations, so a wide range of simulation techniques is required for proper investigation.

The first step in creating a computational model for a material is to determine the appropriate length scale, anywhere from the atomic scale (~Å) to the industrial production scale (~m). This selection is necessary because it is much easier to design a model that fits one scale than it is to create one that spans the entire range [3]. Atomic scale models are almost universally more accurate and can provide a larger variety of information than their large scale counterparts, but the downside is increased computational cost [3-5]. Supercomputers are usually a requirement even for relatively small atomic systems [1, 3, 6]. The trade-off between accuracy and computational cost is the key driver of simulation design. This barrier has driven innovation in computational materials for decades. Every area of application requires the development of a model that is well suited for that specific purpose. This paper will overview a selection of common computational methods, ordered by decreasing length scales.

Methods that operate on the macroscale often assume that the material is continuous and ignore the effects of individual atoms and are thus called continuum methods. Finite Element Analysis and Finite Volume Analysis are two examples of continuum methods. Mesoscale methods add in discrete elements, but don't directly consider the behavior of individual atoms. Two examples are Cellular Automata and the Monte Carlo methods. Models on the nanoscale predict the behavior of individual atoms and are thus called atomistic methods, two examples being Molecular Dynamics and Density Functional Theory.

2. Continuum Methods

Starting at the largest scales are the continuum methods, which assume materials are perfectly continuous. Doing so allows for arbitrary subdivision of the system in question. For example, a simple system like a square sheet can be broken into a 10 by 10 grid, resulting in 100 square subdivisions. All properties are considered identical throughout each subdivision and are solved for through mathematical relationships with the properties in neighboring subdivisions [11]. The large assumptions and the relatively small number of variables make continuum methods the least computationally costly and allow them to be easily applied to macroscopic systems. They also handle complex shapes well for the same reasons. These methods are also heavily dependent on previously collected experimental data [3].

2.1 Finite Element Analysis

One method of note is Finite Element Analysis (FEA), which is frequently used in mechanical design. FEA takes the object under study and subdivides it into elements of constant mass that can transfer force and energy to its neighboring elements. These quantities are related to each other by PDE's which can be solved statically or dynamically [12]. The objects under study are most commonly metallic since metals are often the most common materials used in mechanical design.

The most common application of FEA is in stress/strain analysis of parts to test their mechanical properties without the need for physical prototyping. This is usually visualized as a 3D model of the part with a color map on the surface showing the magnitude of the internal stress. To ensure the highest accuracy, the size and shape of the finite elements must be converged. More complex shapes require a greater mesh density than simple ones, which requires more computational power [12].

2.2 Finite Volume Analysis

A similar but less common method is Finite Volume Analysis (FVA). FVA subdivides space into regions of constant dimensions through which quantities like mass, energy, etc. can transfer [11]. The transport equations can be solved through time to predict the evolution of the system. FVA finds its use in systems that have strong flow, and as such it is considered a fluid dynamics method. The approach of averaging a continuum (instead of a system of discrete particles) across a representative volume is called the Eulerian approach to volume averaging [11].

FVA is currently used to model industrial-scale metal solidification. Of importance to industry is the ability to cast molten metal in large containers, thus understanding the phenomena on the largest length scales is a requirement. Unfortunately, it would be incredibly expensive to model an entire cast with microscale crystal growth and phase transformation, which would be the most accurate option [6]. The challenge is balancing accuracy and cost.

Researchers have developed and are improving upon a method that can add features of small scale modeling to FVA methods [3]. Firstly, the solid particles in the system are treated as their own continuum, or more precisely, as multiple continua since different phases can form [3]. These continua overlap with the liquid continuum. Secondly, the interactions between continua must be considered. A second level of modeling for crystal growth can be added in to supplement the continuum, of which there are many options. An example of crystal growth model is discussed in the following section 3.1. on cellular automata. By cleverly combining elements of models at different scales, a more optimal balance between accuracy and cost can be achieved.

3. Mesoscale Methods

The term "mesoscale" eludes an exact definition but is used to describe methods of intermediate scale or those that do not fit well into other categories. They tend to be modeling phenomena between the nanoscale and microscale and are distinguished from continuum methods by the introduction of discrete elements and values. Because of the open-ended nature of these elements, mesoscale methods can be more specific to the target application. For example, dislocations can be modelled as discrete states that move through a material. In essence, many mesoscale methods often track small patterns in an object, since dislocations are not physical objects but are instead disruptions in the material.

3.1 Cellular Automata

One such mesoscale model uses the concept of cellular automata (CA) [7]. This method describes the system as finite cubic cells with a finite number of discrete states. The subsequent state of a cell is determined by its current state and the states of its nearest neighbors. Every cell has the same rules and acts only with information about its immediate surroundings during every time iteration, which is where the name "cellular automata" is derived. This method varies from FVA in that there are not quantities being averaged over continua; there are finite states a cell can be in. A simple 2D application of this method is Conway's famous Game of Life. [13] This game has incredibly simple rules, but CA simulation in general has no limit on the complexity of the interactions, and researchers have found use for this method in simulating crystal growth.

Recently, Gu et. al. [7] developed a multicomponent CA model that simulates dendritic growth during solidification of an Al-Si-Mg-Fe-Mn quinary alloy. The goal was to match the accuracy of previous models that only worked on binary alloys and extend that accuracy to more complicated systems. The rules of interaction were derived from equations for preferential crystal growth. This model was compared to previous models with a binary system instead of a quinary system to determine its effectiveness, but it had the capacity to extend beyond its predecessors. The initial state of the system is a seed crystal that is placed in the calculation domain, surrounded by cells entirely in the liquid state. They found that the steady-state growth velocity of the dendrites converged as they decreased cell size [7]. This kind of convergence is often a sign that a model is working well. The discrete states found in CA are unphysical and exist to make modelling faster and less complicated. By reducing the cell size, the model approaches the real system. This CA model differed from the current analytical model in its growth rate over time, showing an asymptotic approach to a steady state. They concluded that this arose from the CA model accounting for the local solute concentrations, which the analytical model did not do. The specific quinary alloy was predominately aluminum, and so the other elements can be considered solute elements. The solid phase has a lower concentration of solute than the surrounding liquid material in this case, and so the solid/liquid interface must have an increased concentration. The simulation was also run with columnar dendritic growth to model solidification near the container walls. These walls act as heat sinks and show preferential crystal formation. The resulting microscale structure was confirmed by experimentalists [7].

3.2. Monte Carlo Methods

Monte Carlo (MC) simulation involves the prediction of deterministic problems using randomness and probability [14]. Given an arbitrary probability distribution for an event and the current state of the system, the subsequent states can be randomly generated, and the results can be interpreted using statistics. The complexity of these models is lower than their counterparts that operate on the same length scales and they are easily parallelizable by modern computing software, since different random options are independent and can be explored at the same time [1, 14]. A simple example is the MC method for calculating the value of π (**Figure 1**). Random points are plotted with a uniform probability distribution, and the number of points inside the circular region can be used to calculate π since the probability that a point is inside the circular region is related to the respective areas of the circular region and the square. A problem this simplistic would not normally warrant the use of MC methods, but it is useful in demonstrating that problems without inherent randomness, like calculating the value of π, can be solved by artificially inserting randomness into the system and then using statistical laws to make claims.

The basis of statistics that MC methods rely on makes it well suited for problems in statistical thermodynamics. Of note is its frequent use in studying the behavior of quasicrystals and crystallized nanoparticles [8-10, 15, 16]. Quasicrystals are structures that can tile space, but without translational periodicity [8]. Such materials were thought to be impossible until Dan Schetman observed that Al-Mn alloys could be made with 5-fold symmetry, which is impossible for a perfectly regular tiling of space [16]. The discovery earned Schetman the Nobel Prize in Chemistry in 2011 [17]. This opened a new area in crystallography and has since been combined with the field of nanoparticles to create higher-order lattice structures [10]. By applying MC methods to isochoric and isobaric systems, scientists can simulate the preferred structure of particles in an arbitrary system [8, 15-16]. Quasicrystal stability can be observed by modeling atoms as hard spheres with a square-shoulder potential [8]:

$$V_{HCSS}(r) = \begin{cases} \infty, & r \leq \sigma \\ \epsilon, & \sigma < r < \delta\sigma, \\ 0, & r \geq \delta\sigma \end{cases} \tag{1}$$

where σ is the radius of the particle and ϵ and δ are the height and width of the potential barrier. Tuning these parameters can produce a quasicrystalline system. Since these are essentially fitting parameters, they do not automatically have physical meaning, but can still be used to explore all the possibilities of the system. Matching the behavior of such a system to a physical one can allow for its intricate study. Recently, scientists have moved beyond modeling the arrangement of atoms in lattice structures. With the increased ability to produce nanocrystals of specific shapes [15-16], the same thermodynamic MC methods are being applied to nanocrystal superlattices, or lattices with constituents of nanosized polyhedra, structures which could provide increased control of electronic and optical properties [10]. A comprehensive study on the formation of superlattices simulated 145 convex polyhedra and categorized the resulting structures, similarly to how normal lattice structures are categorized into Bravais lattices. They were modelled as hard polyhedra, meaning there was no deformation in their shape and were not a particular material, but such nanocrystals are almost always made of metal alloys. Notably, tetrahedral shapes preferred quasicrystal structures. An investigation into the tetrahedra showed that despite the densest known packing of the solid shape being around 85.63%, such an arrangement is most stable at the limit of

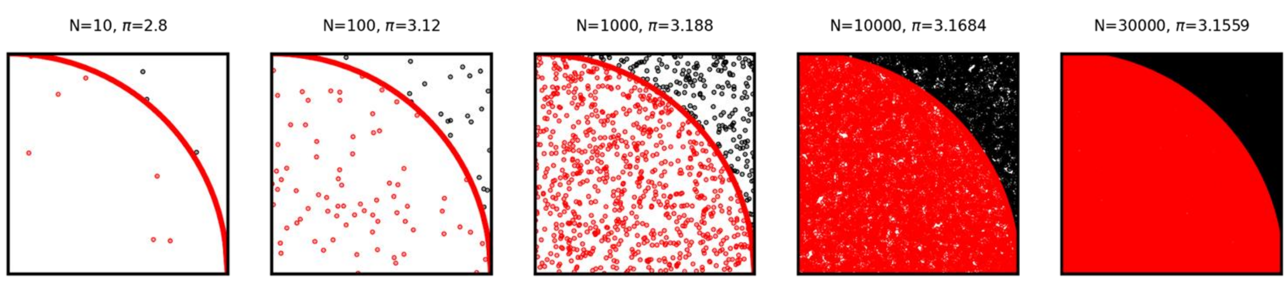

Figure 1. Approximation of π with an MC method

infinite pressure, and without that pressure the tetrahedra tended towards a dodecagonal quasicrystalline structure with a packing density of closer to 50% [16].

4. Atomistics Methods

4.1 Molecular Dynamics

To improve upon the assumptions made by mesoscale methods, scientists can model the individual atoms in a system [4]. The benefit of using such atomistic methods is the reduction of assumptions by using more fundamental and better understood scientific principles, such as forces between individual atoms. By calculating these forces, the motion of each atom can be found using Newtonian physics and numerical integration [4]. This last step requires an incredible amount of computing power, which is why the relatively cheap mesoscale and continuum models are used before MD models.

This is not to say that approximations are not made for MD methods. There are various ways to define the equations for the electric potential from which interatomic forces can be generated, and multiple sets of boundary conditions exist for each simulation problem. Each one makes different approximations and ignore some phenomena. These challenges must be tackled when performing atomistic modeling of nanoindentation of metals [4-5]. Instead of using the standard indenter sizes for testing hardness, nanoscale indenters can be used. Such a small device is helpful in researching dislocation motion in metals but using simulation techniques would allow for time-dependent analysis of the system. The challenges for nanoindentation simulation are due to the limits on the time and length scales for such models [5]. Firstly, by trying to decrease the time interval over which the model operates, the computational cost increases. This creates a lower bound on the speed with which the indenter can be applied, around 1 m/s, whereas experimental methods operate at speeds lower than 25 μm/s. Researchers believe that since both speeds are much lower than the speed of sound in solid-state materials, MD simulations can dissipate the propagation wave fronts that come from the motion of the indenter itself using more complicated boundary conditions. This can mitigate the effects caused by the speed of the indenter if applied properly. Length scales will also affect how the system operates. In this case, it is the total system dimensions that are a problem. For small systems, unrealistic processes can occur at the boundaries of the system, such as the disappearance of dislocations. Luckily, MD simulations have been able fix this issue purely with computational power and optimization, allowing for systems with billions of atoms [5]. Lastly is the question of interatomic potentials. The range of current potential equations can account for a wide range of interactions, but only independently. A single potential that can describe all the interactions of interest does not exist and finding even suitable equations is a time-consuming process. One common improvement is to shift away from empirical potential equations towards the most fundamental calculations contemporary physics has to offer: quantum mechanics.

4.2 Ab initio Methods

In this context, *ab initio* means “from first-principles”, which indicates that no higher-order material properties nor experimental data are required. It is entirely theoretical in nature, dealing with the electronic structure of atoms. The current quantum mechanical wavefunction cannot be solved directly for a system with an arbitrary number of particles (N), so theoretical approximations must be made. Despite this, the produced results are incredibly accurate. One method that has seen high usage in solid-state physics is density functional theory (DFT) [5, 19-23]. In short, DFT does not deal directly with the wavefunction, which is a function of 3N variables, but instead uses electron density, which is a function of only three variables in the ground-state (x, y, and z in space). The Hohenburg-Kohn principle states that electron density can be used to determine the ground-state electronic properties of the system [18]. These properties are then used to investigate a material’s electronic and functional properties [19-21]. Often, these *ab initio* methods are not programmed from scratch and are instead put into open-source packages for scientific use. One such package is called Quantum Espresso [23], which uses various DFT methods to make predictions about a system. There are several related packages that complement each other using different techniques and data manipulation / visualization tools. *Ab initio* methods do not have to stand on their own; they can be combined with higher-order methods by providing energetic properties that large scale calculations can use. For example, to extend the length scales for nanoindentation simulations, DFT can be combined with finite element (FE) methods. [5] In most cases, the relationships of the finite elements are determined from experimental data, but by integrating DFT, the relationships can be generated theoretically, providing increased accuracy and adaptability [5].

4.3 Atomistic Drawbacks

Atomistic systems provide incredible accuracy with the tradeoff of extremely limited scale in both time and space. *Ab initio* methods like DFT are also limited to ground-state electronic properties, which makes investigating mechanical or energetic behavior difficult and imprecise. Even analyzing the data on a microscale is challenging [4-5]. If a simulation is using a mesoscale method that essentially tracks patterns, like when dislocation motion is monitored, extracting and analyzing that data is relatively simple, but recognizing these patterns from purely atomic or electronic data is much more complex. Several post-processing tools are required for data extraction and analysis, and even more for data visualization

[4]. Usability and interpretability play a role in the selection of simulation methods.

5. Conclusions

This review attempts to summarize a selection of computational modeling methods from a wide range of scales and discuss their application to metal research. There are constraints for any phenomena that often determine the kinds of methods available. Continuum methods find frequent use in industrial scale applications, *ab initio* methods shed light on fundamental science and provide unparalleled accuracy, and mesoscale methods fill the space to connect lab work to industry. As computational power continues to increase, simulation will increasingly become a vital tool in materials synthesis and characterization.

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Conflict of Interest

The author has no conflict of interest.

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