Plenary Topics: An Introduction

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Abstract

This section is meant to complement the already extensive collection of articles classified in the following topical sections. In particular, additional applications of computational methods are discussed, which we believe will be of general interest to readers. They focus on different materials – ranging from graphene to titanium oxide to novel superconductors to cement to titanium alloys to glassy oxides and polymers – and/or critical material processes such as defect diffusion and fracture propagation, leading to degradation and failure. We will point out that some chapters can be related to several others across the sections of this part of the handbook (*ACE*) and add new information and perspectives. Connections with those of the companion set (*MTM*) will also be pointed out.

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1 Introduction

This is a brief overview of contributions collected in a special *ACE* section that – as its counterpart in *MTM* – is intended to complement the others, each focused on one specific theme, and also offer additional perspectives.

Most of the plenary topics, it is hoped, will be of general interest to the reader. For example, some chapters deal with materials, such as titanium alloys, cement, titania, and graphene, which are of outstanding relevance for a variety of applications. In particular, the importance of graphene has emerged during the last 15 years (see, e.g., Geim and Novoselov 2007) and thus was not part of the first issue of this handbook. Others focus on topics that did not fit into one of the following sections, for example, superconducting materials. Also in this case, reliable computational approaches have become available only in the last decade or so.

2 Brief Chapter Overviews

This section opens with Payne's view of materials modeling in/for industry, in particular in the UK (Payne, ▸ Chap. 3, "The Industrial Impact of Materials Modelling"). A report is given of recent initiatives in Europe to connect the academic community of computational physicists in the field of materials science to industrial partners. The problems responsible for the fact that materials modeling has so far played a minor role (if any) in industry are clarified. Nevertheless its use has increased over the years at all length and time scales. We refer the reader to a chapter in this same section (Xu et al., ▸ Chap. 7, "Titanium Alloys: From Properties Prediction to Performance Optimization") for a thorough description of how several different approaches can be relevant to the various stages of product design in industry. Payne also provides a thoughtful discussion of the needs that industries will nevertheless continue to have for modeling results, (acquisition of) expertise, and/or tools, depending, in particular, on the size of the company.

One should remark that many academy-industry collaborations exist worldwide – although not systematically – and also that research centers at IBM and at chemical industries such as BASF have constantly supported the development of advanced computational methods as well as their application in various domains of materials science, thus generating several patents (for the impact of ab initio simulations see, e.g., Andreoni et al. 2006, 2012, Afyfy et al. 2013, Laino and Weber 2019).

The two following chapters discuss materials of primary importance in contemporary technology: titanium dioxide (titania) and graphene. In both cases, several examples show how computer simulations have been able to complement and aid in understanding and also predicting the results of experimental investigation.

The chapter on titanium oxide (Selloni, ▸ Chap. 4, "Titania and Its Outstanding Properties: Insights from First Principles Calculations") illustrates how a series of ab initio calculations have been able to elucidate the complex nature of TiO_2 surfaces. For example, their physical properties and chemical reactivity depend on

the specific polymorph, on the specific surface and its structure, on the unavoidable presence of point defects such as oxygen vacancies, and on the exposure to water. It is also clear that the ab initio approach to different situations is not "standard" but special attention must be paid to the methodology to be applied. Indeed real-world applications primarily refer to reduced TiO_2. Thus, modeling imposes the need to go beyond the generalized gradient approximation (GGA) to the DFT exchange-correlation functional so as to reduce its intrinsic self-interaction error. Therefore PBE-DFT was augmented either with a (semiempirical) Hubbard (U) term or with a fraction of exact-exchange term as in the hybrid PBE0 exchange-correlation functional.

The chapter on graphene (Yazyev, ▸ Chap. 5, "Modeling Disordered and Nanostructured Graphene") focuses on the modeling of its peculiar characteristics and the calculation of their effects on a variety of physical properties that are crucial for any of the diverse applications of this material. In particular, an outstanding achievement of computations was the prediction of the structure of topological defects (dislocations and grain boundaries) prior to experiment that has confirmed those results. Key ingredients were the construction of ingenious structural models and subsequent ab initio calculations for the investigation of the electronic properties as well as for the determination of the most energetically favorable defect configurations. Calculations have also revealed the dependence of the electronic properties of nanostructured graphene on the nature of the edges, i.e., armchair or zigzag or chiral. We note that a complementary account of computational studies – also linked to experiment – of graphene nanoribbons can be found in ▸ Chap. 31, "Electronic Structure of Atomically Precise Graphene Nanoribbons," by Talirz and Pignedoli.

One of the greatest challenges for electronic structure calculations has long been that of approaching the physics of superconductors and determining in particular the critical temperature T_c. This "dream" has become reality – within the framework of density functional theory – only recently, after the seminal paper by Lüders et al. (2005). Boeri, ▸ Chap. 6, "Understanding Novel Superconductors with Ab Initio Calculations," guides the reader through the main steps leading to this achievement and subsequent successes of theory and computations for conventional superconductors. State-of-the-art calculations are not only able to contribute to the understanding of mechanisms leading to superconductivity but also to quantitatively characterize superconductive phases and predict the transition temperature. On the other hand, the case of unconventional superconductors like the high-T_c cuprates is not approachable yet with available methods.

The next chapter (Xu et al., ▸ Chap. 7, "Titanium Alloys: From Properties Prediction to Performance Optimization") presents an exhaustive and detailed review of the application of computational tools to the design and optimization of titanium-based alloys. The specific role of different methods at different length scales in this complex process is elucidated. They comprise electronic structure calculations and atomistic simulations for an early screening of fundamental material properties, mesoscale approaches for an understanding of microstructure evolution under specific processing and operational conditions, as well as finite element methods

for the simulation of various manufacturing processes and the final optimization of the material performance. Not only successful applications of the above protocol are described, but also difficulties are pointed out as well as important challenges for future progress. In particular, the aid of artificial intelligence strategies based on "big data" is called for. Connections of this chapter are evident with the *MTM* set of this handbook covering all the above-mentioned methodologies. Moreover, we remark that the example of titanium alloys is extremely interesting in view of their relevance in diverse industries and applications. Namely, depending on their composition, they are used in aerospace, marine, and biomedical applications.

The following articles are concerned with the study of specific and critical material processes via modeling at multiple scales.

The next chapter (Kamrin, ▸Chap. 8, "Quantitative Rheological Model for Granular Materials: The Importance of Particle Size") deals with a class of complex systems – dense granular flows – whose understanding is still limited. This chapter provides an overview of granular material modeling at diverse levels and especially an insightful analysis of the constitutive behavior of dense granular matter through the development of a nonlocal continuum model of fluidity (the nonlocal granular fluidity (NGF) model). Several applications demonstrate, in particular, the importance of grain size effects on the flow properties. We remark that dense granular flows are common in countless natural processes (e.g., rock avalanches) and industrial applications (e.g., in the pharmaceutical and agricultural sectors). In the effort to describe, predict, and thus control their behavior, modeling and numerical approaches play a special role.

The section proceeds with a chapter (Masoero, ▸Chap. 9, "Mesoscale Mechanisms of Cement Hydration: BNG Model and Particle Simulations") focused on cement – the most widely used man-made material in the world and in particular on the formation of its fundamental constitutive unit, calcium-silicate-hydrate (C-S-H). Linking the kinetics of the evolution of this process to the chemical (microscopic) characteristics of the original compounds, and eventually to the structural properties and mechanical behavior of the material, is one of the most critical and still largely open issues. This part of the handbook (*ACE*) dedicates specific chapters to the physical, chemical, and mechanical properties of cement, describing the results of computational methods and their performance relative to experiment (Ioannidou, ▸Chaps. 71, "Mesoscale Structure and Mechanics of C-S-H"; Qomi et al., and ▸72, "Nanoscale Composition-Texture-Property Relation in Calcium-Silicate-Hydrates"). Masoero's plenary topic article can be considered a complement to those chapters. It deals with a relatively simple and very instructive scheme, the model of boundary nucleation and growth (BNG). It is an attempt to provide an approximate description of the early controlling step of hydration that is physically based and amenable to quantitative analysis. In particular, it shows how kinetic Monte Carlo simulations of nanoparticle aggregation can be exploited to improve on the parameters governing the BNG model and especially to provide an insight into their physical meaning.

The next chapter (Ciccotti and George, ▸Chap. 10, "In Situ AFM Investigations and Fracture Mechanics Modeling of Slow Fracture Propagation in Oxide and Polymer Glasses") constitutes an exception because it mainly describes experimental

techniques and observations. It offers an insightful account of how slow fracture propagation can be quantitatively studied using the combination of in situ atomic force microscopy and phenomenological multiscale modeling. While it is focused on oxide and polymer glasses, the results discussed therein have significant and general implications for all time-dependent deformation processes in brittle materials. This detailed and extensive description of the experimental results should be seen as a source of inspiration for the development of computational methods for the simulation of fracture propagation and also other multiscale phenomena. We remark that the use of inserts to explain various key concepts in the subject matter offline from the main text is effective and it is hoped will be helpful to the reader.

Extended defects such as dislocations are ubiquitous in real crystalline materials and influence a variety of physical properties. Diverse examples of modeling and multiscale simulations are currently helping to understand, e.g., the origin of a dislocation or the way it propagates and affects the mechanical properties of a given material (see, e.g., the *MTM* section on "Crystal Plasticity: From the Atomic Scale to the Macroscale" – Editors: Cai and Ghosh). The next chapter (Fan and Cao, ▸ Chap. 11, "Long Time-Scale Atomistic Modeling and Simulation of Deformation and Flow in Solids") is concerned with the onset and propagation of dislocation-driven deformation and flow in crystals (specifically bcc metals) and glasses. These are processes that involve time scales well beyond the reach of classical molecular dynamics of atomistic models. In the *MTM* set of this handbook, we have presented methods allowing to access longer time scales, both those using direct acceleration techniques (see the section "Long Time-Scale Simulation Methods," Editors: Perez and Uberuaga) and those circumventing the time constraints with the aid of advanced enhanced sampling approaches (see the section "Atomistic Simulations," Editors: Andreoni and Yip). Application of the latter is not possible yet, given the complexity and size scale of the systems under investigation. A simpler but efficient alternative is applied instead, the autonomous basin climbing (ABC) algorithm, which allows one to explore and characterize the potential energy surface of a given system by coupling minimum energy pathway methods, kinetic Monte Carlo and transition state theory. We remark that the ABC method was originally employed to investigate viscous flows and the origin of the glass transition in supercooled liquids (Kushima et al. 2009). Note also that related issues are discussed in one of the chapters of the "Plenary Topics" part in *MTM* (Rizzo, Chap. 9, "Critical Phenomena in Glasses").

Dislocations are known to influence not only the mechanical response of a given material but also many other characteristics and functionalities. Understanding and predicting the effects of a dislocation on, e.g., electronic, optical, magnetic, or thermoelectric properties requires a quantum-based approach. To this end, a completely new full quantum theoretical framework has very recently been introduced by Li et al. (in a series of articles starting in 2017) and constitutes the subject of the last chapter of this section (Li et al., ▸ Chap. 12, "Quantized Dislocations for Functional and Quantum Materials"). In this theory a dislocation is quantized ("dislon" is the name of the basic quantum). Starting from a 1D approach to describe quantized single dislocations, these authors have shown that an extended (3D) scheme can be used to describe the electron and phonon interactions with multiple dislocations.

Several examples are presented. Benefits of this framework are claimed also for explicit calculations. Moreover, other implications can be envisaged.

3 Conclusions

A plenary topic is expected to be of general interest to a varied audience of readers. We think that each chapter of this section deserves to be classified in this way. In fact, for example, as we have pointed out, most of the chapters can be related to others across the parts of *MTM* or *ACE* and/or refer to themes (materials or processes) of very particular relevance.

The main messages arising from a careful reading concern, on the one hand, the value that state-of-the-art modeling and simulations have in tackling complex problems related to real materials and, on the other hand, the need to extend their reach through the development of multiscale methods and their integration in the design and optimization process.

In this respect, we underline Payne's contribution that is explicitly concerned with the possible impact of materials modeling in the realm of industry. Beyond that, we wish to call attention to the existence of a natural, cultural gap between the scientific community in the role of "producers" of modeling and simulation tools and society at large in the role of "users" of the science and technology. Bridging this gap is a long-standing challenge to both sides. The most promising solution is bound to involve hands-on collaboration among all the stakeholders. Still, we can conclude that – as illustrated also in this section – in the last decade, many opportunities have flourished for computational materials science to contribute at least to the understanding of problems of relevance to technology and societal needs.

References

Afyfy N, Andreoni W, Curioni A, Khomyakov P, Kim J, Sadana DK. Photovoltaic device with band-stop filter, US Patent Application Publication Number 2013-0312828, published on November 28, 2013

Andreoni W, Curioni A, Shevlin SA (2006) Dielectric materials. US Patent 7,057,244, issued on June 6, 2006

Andreoni W, Callegari AC, Cartier EA, Curioni A, D'Emic CP, Gousev E, Gribelyuk MA, Jamison PC, Jammy R, Lacey DL, McFeely FR, Narayanan V, Pignedoli CA, Shepard JF Jr, Zafar S (2012) Method of forming metal/high-κ gate stacks with high mobility. US Patent 8,153,514, issued on April 10, 2012

Geim AV, Novoselov KS (2007) The rise of graphene. Nature Mater 6:183

Kushima A, Lin X, Li J, Eapen J, Mauro JC, Qian X, Diep P, Yip S (2009) Computing the viscosity of supercooled liquids. J Chem Phys 130:224504

Laino T, Weber V (2019) Sodium ion solid-state conductors with sodium oxoferrate structure. US Patent Number 10,170,790, issued on January 1, 2019

Lüders M, Marques MAL, Lathiotakis NN, Floris A, Fast L, Continenza A, Massidda S, Gross EKU (2005) Ab-initio theory of superconductivity – I: density functional formalism and approximate functionals. Phys Rev B 72:024545