Modeling Materials

Material properties emerge from phenomena on scales ranging from ångstroms to millimeters, and only a multiscale treatment can provide a complete understanding. Materials researchers must therefore understand fundamental concepts and techniques from different fields, and these are presented in a comprehensive and integrated fashion for the first time in this book.

Incorporating continuum mechanics, quantum mechanics, statistical mechanics, atomistic simulations, and multiscale techniques, the book explains many of the key theoretical ideas behind multiscale modeling. Classical topics are blended with new techniques to demonstrate the connections between different fields and highlight current research trends. Example applications drawn from modern research on the thermomechanical properties of crystalline solids are used as a unifying focus throughout the text.

Together with its companion book, *Continuum Mechanics and Thermodynamics* (Cambridge University Press, 2012), this work presents the complete fundamentals of materials modeling for graduate students and researchers in physics, materials science, chemistry, and engineering.

Ellad B. Tadmor is Professor of Aerospace Engineering and Mechanics, University of Minnesota. His research focuses on the development of multiscale theories and computational methods for predicting the behavior of materials directly from the interaction of the atoms.

Ronald E. Miller is Professor of Mechanical and Aerospace Engineering, Carleton University. He has worked in the area of multiscale materials modeling for over 15 years and has published more than 40 scientific articles in the area.

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Continuum, Atomistic and Multiscale Techniques

ELLAD B. TADMOR
University of Minnesota, USA

RONALD E. MILLER
Carleton University, Canada

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Preface

Studying *materials* can mean studying almost anything, since all of the physical, tangible world is necessarily made of *something*. Normally, we think of studying materials in the sense of materials science and engineering – an endeavor to understand the properties of natural and man-made materials and to improve or exploit them in some way – but even this includes broad and disparate goals. One can spend a lifetime studying the strength and toughness of steel, for example, and never once concern oneself with its magnetic or electric properties. At the same time, *modeling* in science can mean many things to many people, ranging from computer simulation to analytical effective theories to abstract mathematics. To combine these two terms "modeling materials" as the title of a single book, then, is surely to invite disaster. How could it be possible to cover all the topics that the product *modeling* $\times$ *materials* implies? Although this book remains true to its title, it will be necessary to pick and choose our topics so as to have a manageable scope. To start with, then, we have to decide: what models and what materials do we want to discuss?

As far as *modeling* goes, we must first recognize the fact that materials exhibit phenomena on a broad range of spatial and temporal scales that combine together to dictate the response of a material. These phenomena range from the bonding of individual atoms governed by quantum mechanics to macroscopic deformation processes described by continuum mechanics. Various aspects of materials behavior and modeling, which tend to focus on specific phenomena at a given scale, have traditionally been treated by different disciplines in science and engineering. The great disparity in scales and the interdisciplinary nature of the field are what makes modeling materials both challenging and exciting. It is unlikely that any one researcher has sufficient background in engineering, physics, materials science and mathematics to understand materials modeling at every length and time scale. Furthermore, there is increased awareness that materials must be understood, not *only* by rigorous treatment of phenomena at each of these scales alone, but rather through consideration of the *interactions* between these scales. This is the paradigm of *multiscale modeling* that will also be a persistent theme throughout the book.

Recognizing the need to integrate models from different disciplines creates problems of nomenclature, notation and jargon. While we all strive to make our research specialties clear and accessible, it is a necessary part of scientific discourse to create and use specific terms and notation. An unintended consequence of this is the creation of barriers to interdisciplinary understanding. One of our goals is to try to facilitate this understanding by providing a unified presentation of the fundamentals, using a common nomenclature, notation and language that will be accessible to people across disciplines. The result is this book on *Modeling Materials* (MM) and our companion book on *Continuum Mechanics and Thermodynamics* (CMT) [TME12].

The subject matter in MM is divided into four parts. **Part I** covers continuum mechanics and thermodynamics concepts that serve as the basis for the rest of the book. The description of continuum mechanics and thermodynamics is brief and is only meant to make MM a stand-alone book. The reader is referred to CMT for a far deeper view of these subjects consistent with the rest of MM. **Part II** covers atomistics, discussing the basic structure and symmetries of crystalline materials, quantum mechanics and more approximate empirical models for describing bonding in materials, and molecular statics – a computational approach for studying static properties of materials at the atomic scale. **Part III** focuses on the atomistic foundations of continuum concepts. Here, using ideas from statistical mechanics, connections are forged between the discrete world of atoms – described by atomic positions, velocities and forces – and continuum concepts such as fields of stress and temperature. Finally, the subject of molecular dynamics (MD) is presented. We treat MD as a computational method for studying dynamical properties of materials at the atomic scale subject to continuum-level constraints, so it is yet another unique connection between the atomistic and continuum views. **Part IV** on multiscale methods describes a class of computational methods that attempt to model material response by simultaneously describing its behavior on multiple spatial and temporal scales. This final part of the book draws together and unifies many of the concepts presented earlier and shows how these can be integrated into a single modeling paradigm.

By bringing together this unusual combination of topics, we provide a treatment that is uniquely different from other books in the field. First, our focus is on a critical analysis and understanding of the fundamental *assumptions* that underpin these methods and that are often taken for granted in other treatments. We believe that this focus on fundamentals is essential for anyone seeking to combine different theories in a multiscale setting. Secondly, some of the topics herein are often treated from the perspective of the gaseous or liquid states. Here, our emphasis is on solids, and this changes the presentation in important ways. For example, in statistical mechanics we comprehensively discuss the subject of the stress tensor (not just pressure) and the concept of a restricted ensemble for metastable systems. Similarly, we talk at length about constant stress simulations in MD and how to correctly interpret them in a setting of finite deformation beyond that of simple hydrostatic compression. Third, while covering this broad range of topics we strive to regularly make connections between the atomistic, statistical and continuum worldviews. Finally, we have tried to create a healthy balance between fundamental theory and practical "how to." For example, we present, at length, the practical implementation of such topics as density functional theory, empirical atomistic potentials, molecular statics and dynamics, and multiscale partitioned-domain methods. It is our hope that someone with basic computer programming skills will be able to use this book to implement any of these methods, or at least to better understand an implementation in a pre-existing code.

Although the modeling methods we describe are, in principle, applicable to any material, we focus our scope of materials and properties on those that we, the authors, know best. The answer to "What materials?" then is crystalline solids and their thermomechanical (as opposed to electrical, optical or chemical) properties. For the most part, these serve as examples to illustrate the application and usefulness of the modeling methods that we

describe, but we hope that the reader will also learn something new regarding the materials themselves along the way.

Even starting from this narrow mandate we have already failed, to some degree, in our goal of putting all the fundamentals in one place. This is because the binding of these subjects into a single volume becomes unwieldy if we wish to maintain the level of detail that we feel is necessary. To make room in this book, we sacrificed coverage of continuum mechanics, leaving only a concise summary in Chapter 2 of the key results needed to make contact with the rest of the topics. CMT [TME12], the companion volume to this one, provides the full details of the continuum mechanics and thermodynamics that we believe to be fundamental to materials modeling.

Both books, MM and CMT, are addressed to graduate students and researchers in chemistry, engineering, materials science, mathematics, mechanics and physics. The interdisciplinary nature of materials modeling means that researchers from all of these fields have contributed to and continue to be engaged in this field. The motivation for these books came from our own frustration, and that of ours students, as we tried to acquire the breadth of knowledge necessary to do research in this highly interdisciplinary field. We have made every effort to eliminate this frustration in the future by making our writing accessible to all readers with an undergraduate education in an engineering or scientific discipline. The writing is self-contained, introducing all of the necessary basic concepts and building up from there. Of course, by necessity that means that our coverage of the different topics is limited and skewed to our primary focus on materials modeling. At the end of each chapter, we recommend sources for further reading for readers interested in expanding their understanding in a particular direction.

Acknowledgments

One of our favorite teachers when we were graduate students at Brown University, Ben Freund, has said that writing a book is like giving birth. The process is long and painful, it involves a lot of screaming, but in the end something has to come out. We find this analogy so apt that we feel compelled to extend it: in some cases, you are blessed with twins.[1] As we initially conceived it, our goal was to have everything in a single volume. But as time went on, and what we were "carrying" grew bigger and bigger, it became clear that it really needed to be two separate books.

Since the book has been split in two, we choose to express our gratitude twice, once in each book, to everyone who has helped us with the project as a whole. Surely, thanking everyone twice is the least we can do. Some people helped in multiple ways, and so their names appear even more often. Our greatest debt goes to our wives, Jennifer and Granda, and to our children: Maya, Lea, Persephone and Max. They have suffered more than anyone during the long course of this project, as their preoccupied husbands and fathers stole too much time from so many other things. They need to be thanked for such a long list of reasons that we would likely have to split these two books into three if we were thorough with the details. Thanks, all of you, for your patience and support. We must also thank our own parents Zehev and Ciporah and Don and Linda for giving us the impression – perhaps mistaken – that everybody will appreciate what we have to say as much as they do.

The writing of a book as diverse as this one is really a collaborative effort with so many people whose names do not appear on the cover. These include students in courses, colleagues in the corridors and offices of our universities and unlucky friends cornered at conferences. The list of people that offered a little piece of advice here, a correction there, or a word of encouragement somewhere else is indeed too long to include, but there are a few people in particular that deserve special mention.

Some colleagues generously did calculations for us, verified results, or provided other contributions from their own work. We thank Quiying Chen at the NRC Institute for Aerospace Research in Ottawa for his time in calculating UBER curves with DFT. Tsveta Sendova, a postdoctoral fellow at the University of Minnesota, coded and ran the simulations for the two-dimensional NEB example we present. Another postdoctoral fellow at the University of Minnesota, Woo Kyun Kim, performed the indentation and thermal expansion simulations used to illustrate the hot-QC method. We thank Yuri Mishin (George Mason

[1] This analogy is made with the utmost respect for our wives, and anyone else who *actually has* given birth. Assuming labor has units of power, then we feel that the integral of this power over the very different timescales of the two processes should yield quantities of work that are on the same order of magnitude. Our wives disagree, no doubt in part because some of the power consumed by book-writing indirectly comes from them, whereas our contribution to childbirth amounts mainly to sending around e-mail photos of the newborn children.

University) for providing figures, and Christoph Ortner (Oxford University) for providing many insights into the problem of full versus sequential minimization of multivariate functions, including the example we provide in the book. The hot-QC project has greatly benefited from the work of Laurent Dupuy (SEA Saclay) and Frederic Legoll (École Nationale des Ponts et Chaussées). Their help in preparing a journal paper on the subject has also proven extremely useful in preparing the chapter on dynamic multiscale methods. Furio Ercolessi must be thanked in general for his fantastic web-based notes on so many important subjects discussed herein, and specifically for providing us with his molecular dynamics code as a teaching tool to provide with this book.

Other colleagues patiently taught us the many subjects in this book about which we are decidedly *not* experts. Dong Qian at the University of Cincinnati and Michael Parks at Sandia National Laboratories very patiently and repeatedly explained the nuances of various multiscale methods to us. Similarly, we would like to thank Catalin Picu at the Rensselaer Polytechnic Institute for explaining CACM, and Leo Shilkrot for his frank conversations about CADD and the BSM. Noam Bernstein at the Navy Research Laboratories was invaluable in explaining DFT in a way that an engineer could understand, and Peter Watson at Carleton University was instrumental in our eventual understanding of quantum mechanics. Roger Fosdick University of Minnesota discussed, at length, many topics related to continuum mechanics including tensor notation, material frame-indifference, Reynolds transport theorem and the principle of action and reaction. He also took the time to read and comment on our take on material frame-indifference.

We are especially indebted to those colleagues that were willing to take the time to carefully read and comment on drafts of various sections of the book – a thankless and delicate task. James Sethna (Cornell University) and Dionisios Margetis (University of Maryland) read and commented on the statistical mechanics chapter. Noam Bernstein (Navy Research Laboratories) must be thanked more than once for reading and commenting on both the quantum mechanics chapter and the sections on cluster expansions. Nikhil Admal, a graduate student working with Ellad at the University of Minnesota, contributed significantly to our understanding of stress and read and commented on the continuum mechanics chapter, Marcel Arndt helped by translating an important paper on stress by Walter Noll from German to English and worked with Ellad on developing algorithms for lattice calculations, while Gang Lu at the California State University (Northridge) set us straight on several points about density functional theory. Ryan Elliott, our coauthor of the companion book to this one, must also be thanked countless times for his careful reading of quantum mechanics and his many helpful suggestions and discussions. Other patient readers to whom we say "thank you" include Mitch Luskin from the University of Minnesota (numerical analysis of multiscale methods and quantum mechanics), Bill Curtin from Brown University (static multiscale methods), Dick James from the University of Minnesota (restricted ensembles and the definition of stress) and Leonid Berlyand from Pennsylvania State University (thermodynamics).

There are a great many colleagues that were willing to talk to us at length about various subjects in this book. We hope that we did not overstay our welcome in their offices too often, and that they do not sigh too deeply anymore when they see a message from us in their inbox. Most importantly, we thank them very much for their time. In addition to

those already mentioned above, we thank David Rodney (Institut National Polytechnique Grenoble), Perry Leo and Tom Shield (University of Minnesota), Miles Rubin and Eli Altus (Technion), Joel Lebowitz, Sheldon Goldstein and Michael Kiessling (Rutgers),[2] and Andy Ruina (Cornell University). We would also be remiss if we did not take the time to thank Art Voter (Los Alamos National Laboratory), John Moriarty (Lawrence Livermore National Laboratory) and Mike Baskes (Sandia National Laboratory) for many insightful discussions and suggestions of valuable references.

There are some things in these books that are so far outside our area of expertise that we have even had to look beyond the offices of professors and researchers. Elissa Gutterman, an expert in linguistics, provided phonetic pronunciation of French and German names. As neither of us is an experimentalist, our brief foray into pocket watch "testing" would not have been very successful without the help of Steve Truttman and Stan Conley in the structures laboratories at Carleton University. The story of our cover images involves so many people, it deserves its own paragraph.

As the reader will see in the introduction to both books, we are fond of the symbolic connection between pocket watches and the topics we discuss herein. There are many beautiful images of pocket watches out there, but obtaining one of sufficient resolution, and getting permission to *use* it, is surprisingly difficult. As such, we owe a great debt to Mr. Hans Holzach, a watchmaker and amateur photographer at Beyer Chronometrie AG in Zurich. Not only did he generously agree to let us use his images, he took over the entire enterprise of retaking the photographs when we found out that his images did not have sufficient resolution! This required Hans to coordinate with many people that we also thank for helping make the strikingly beautiful cover images possible. These include the photographer, Dany Schulthess (www.fotos.ch), Mr. René Beyer, the owner of Beyer Chronometrie AG in Zurich, who compensated the photographer and allowed photographs to be taken at his shop, and also to Dr. Randall E. Morris, the owner of the pocket watch, who escorted it from California to Switzerland (!) in time for the photo shoot. The fact that total strangers would go to such lengths in response to an unsolicited e-mail contact is a testament to their kind spirits and, no doubt, to their proud love of the beauty of pocket watches.

We cannot forget our students. Many continue to teach us things every day just by bringing us their questions and ideas. Others were directly used as guinea pigs with early drafts of parts of this book.[3] Ellad would like to thank his graduate students and post-doctoral fellows over the last five years who have been fighting with this book for attention; specifically Nikhil Admal, Yera Hakobian, Hezi Hizkiahu, Dan Karls, Woo Kyun Kim, Leonid Kucherov, Amit Singh, Tsvetanka Sendova, Valeriu Smiricinschi, Slava Sorkin and Steve Whalen. Ron would likewise like to thank Ishraq Shabib, Behrouz Shiari and Denis Saraev, whose work helped shape his ideas about atomistic modeling. Harley Johnson and his 2008–2009 graduate class at the University of Illinois (Urbana-Champaign) used the book extensively and provided great feedback to improve the manuscript, as did Bill

[2] Ellad would particularly like to thank the Rutgers trio for letting him join them on one of their lunches to discuss the foundations of statistical mechanics – a topic which is apparently standard lunch fare for them along with the foundations of quantum mechanics.

[3] Test subjects were always treated humanely and no students were harmed during the preparation of this book.

Curtin's class at Brown University in 2009–2010. The 2009 and 2010 classes of Ron's "Microstructure and properties of engineering materials" class caught many initial errors in the chapters on crystal structures and molecular statics and dynamics. Some students of Ellad's continuum mechanics course are especially noted for their significant contributions: Yilmaz Bayazit (2008), Pietro Ferrero (2009), Zhuang Houlong (2008), Jenny Hwang (2009), Karl Johnson (2008), Dan Karls (2008), Minsu Kim (2009), Nathan Nasgovitz (2008), Yintao Song (2008) and Chonglin Zhang (2008).

Of course, we should also thank our own teachers. Course notes from Michael Ortiz, Janet Blume, Jerry Weiner and Tom Shield were invaluable to us in preparing our own notes and this book. Thanks also to our former advisors at Brown University, Michael Ortiz and Rob Phillips (both currently at Caltech), whose irresistible enthusiasm, curiosity and encouragement pulled us down this most rewarding of scientific paths.

We note that many figures in this book were prepared with the drawing package Asymptote (see http://asymptote.sourceforge.net/), an open-source effort that we think deserves to be promoted here. Finally, we thank our editor Simon Capelin and the entire team at Cambridge, for their advice, assistance and truly astounding patience.

Notation

In a book covering such a broad range of topics, notation is a nightmare. We have attempted, as much as possible, to use the most common and familiar notation from within each field as long as this did not lead to confusion. However, this does mean that the occasional symbol will serve multiple purposes, as the tables below will help to clarify. To keep the amount of notation to a minimum, we generally prefer to append qualifiers to symbols rather than introducing new symbols. For example, $\boldsymbol{f}$ is force, which if relevant can be divided into internal, $\boldsymbol{f}^{\rm int}$, and external, $\boldsymbol{f}^{\rm ext}$, parts.

We use the following general conventions:

- Descriptive qualifiers generally appear as superscripts and are typeset using a Roman (as opposed to Greek) nonitalic font.
- The weight and style of the font used to render a variable indicates its type. Scalar variables are denoted using an italic font. For example, T is temperature. Array variables are denoted using a sans serif font, such as A for the matrix A. Vectors and tensors (in the technical sense of the word) are rendered in a boldface font. For example, $\boldsymbol{\sigma}$ is the stress tensor.
- Variables often have subscript and superscript indices. Indices referring to the components of a matrix, vector or tensor appear as subscripts in italic Roman font. For example, v_i is the ith component of the velocity vector. Superscripts are used as counters of variables. For example, $\boldsymbol{F}^e$ is the deformation gradient in element e. Superscripts referring to atoms are distinguished by using a Greek letter. For example, the velocity of atom α is denoted $\boldsymbol{v}^\alpha$. Iteration counters appear in parentheses, for example $\boldsymbol{f}^{(i)}$ is the force in iteration i.
- The Einstein summation convention is followed on repeated indices (e.g. $v_i v_i = v_1^2 + v_2^2 + v_3^2$), unless otherwise clear from the context. (See Section 2.1.1 for more details.)
- One special type of superscript concerns the denotation of Bravais lattices and crystals. For example, the position vector $\boldsymbol{R}^{[\boldsymbol{\ell}\lambda]}$ denotes the λth basis atom associated with Bravais lattice site $\boldsymbol{\ell}$. (See Section 3.6 for details.)
- A subscript is used to refer to multiple equations on a single line, for example "Eqn. $(2.66)_2$" refers to the second equation in Eqn. (2.66) ("$a_i(\boldsymbol{x},t) \equiv \ldots$").
- Important equations are emphasized by shading.

Below, we describe the main notation and symbols used in the book, and indicate the page on which each is first defined. We also include a handy list of fundamental constants and unit conversions at the end of this section.

Mathematical notation

Notation	Description	Page
$\equiv$	equal to by definition	28
$:=$	variable on the left is assigned the value on the right	24
$\forall$	for all	28
$\in$	contained in	28
iff	if and only if	28
$O(f)$	terms proportional to order f	188
$O(n)$	orthogonal group of degree n	31
$SO(n)$	proper orthogonal (special orthogonal) group of degree n	31
$\mathbb{R}$	set of all real numbers	26
$\mathbb{R}^n$	real coordinate space (n-tuples of real numbers)	27
$\lvert \bullet \rvert$	absolute value of a real number	28
$\lVert \bullet \rVert$	norm of a vector	28
$\langle \bullet, \bullet \rangle$	inner product of two vectors	28
$\langle \bullet \vert \bullet \rangle$	inner product of two vectors (bra-ket notation)	161
$\langle \bullet \vert \bullet \vert \bullet \rangle$	bra-operator-ket inner product	163
$[uvw]$	direction in a crystal ($u\boldsymbol{a} + v\boldsymbol{b} + w\boldsymbol{c}$)	125
$\langle uvw \rangle$	family of crystal directions	125
(hkl)	Miller indices denoting a crystallographic plane	150
$\{hkl\}$	family of crystallographic planes	151
$\{M \mid C\}$	a set of members M such that conditions C are satisfied	245
$\overline{\bullet}$	time average of a quantity	388
$\langle \bullet \rangle$	phase average of a quantity	391
$\langle \bullet; f \rangle$	phase average of a quantity relative to distribution function f	391
$\Pr(O)$	probability of outcome O	395
$\mathrm{Var}(A)$	variance of A: $\mathrm{Var}(A) = \langle A^2 \rangle - (\langle A \rangle)^2$	396
$\mathrm{Cov}(A, B)$	covariance of A and B: $\mathrm{Cov}(A, B) = \langle AB \rangle - \langle A \rangle \langle B \rangle$	461
$\mathrm{Cov}_\chi(A, B)$	covariance of A and B in a restricted ensemble	577
$\widehat{f}(\boldsymbol{k})$	Fourier transform of $f(\boldsymbol{x})$	166
$\underset{\sim}{f}(s)$	Laplace transform of a $f(t)$	684
$\bullet^*$	complex conjugate	161
$\boldsymbol{A}^T$	transpose of a matrix or second-order tensor: $[\boldsymbol{A}^T]_{ij} = A_{ji}$	25
$\boldsymbol{A}^{-T}$	transpose of the inverse of$\boldsymbol{A}$: $\boldsymbol{A}^{-T} \equiv (\boldsymbol{A}^{-1})^T$	35
$\boldsymbol{a} \cdot \boldsymbol{b}$	dot product (vectors): $\boldsymbol{a} \cdot \boldsymbol{b} = a_i b_i$	28
$\boldsymbol{a} \times \boldsymbol{b}$	cross product (vectors): $[\boldsymbol{a} \times \boldsymbol{b}]_k = \epsilon_{ijk} a_i b_j$	30
$\boldsymbol{a} \otimes \boldsymbol{b}$	tensor product (vectors): $[\boldsymbol{a} \otimes \boldsymbol{b}]_{ij} = a_i b_j$	33
$\boldsymbol{A} : \boldsymbol{B}$	contraction (second-order tensors): $\boldsymbol{A} : \boldsymbol{B} = A_{ij} B_{ij}$	36
$\boldsymbol{A} \cdot\cdot \boldsymbol{B}$	transposed contraction (second-order tensors): $\boldsymbol{A} \cdot\cdot \boldsymbol{B} = A_{ij} B_{ji}$	36
$\lambda_\alpha^{\boldsymbol{A}}, \boldsymbol{\Lambda}_\alpha^{\boldsymbol{A}}$	αth eigenvalue and eigenvector of the second-order tensor $\boldsymbol{A}$	38
$I_k^{\boldsymbol{A}}$	kth principal invariant of the second-order tensor $\boldsymbol{A}$	38
$\det \boldsymbol{A}$	determinant of a matrix or a second-order tensor	26
$\mathrm{tr}\, \boldsymbol{A}$	trace of a matrix or a second-order tensor: $\mathrm{tr}\, \boldsymbol{A} = A_{ii}$	25

$\nabla\bullet$, grad $\bullet$	gradient of a tensor (deformed configuration)	40
$\nabla_0\bullet$, Grad $\bullet$	gradient of a tensor (reference configuration)	45
curl $\bullet$	curl of a tensor (deformed configuration)	41
Curl $\bullet$	curl of a tensor (reference configuration)	45
div $\bullet$	divergence of a tensor (deformed configuration)	41
Div $\bullet$	divergence of a tensor (reference configuration)	45
$\nabla^2\bullet$	Laplacian of a tensor (deformed configuration)	41
$\vec{d}$	inexact differential	81
$\boldsymbol{r}^{\alpha\mathring{\beta}}$	position vector to closest periodic image of β to atom α	326
$\mathring{\alpha}$, $\overset{\#}{\alpha}$	unit cell and sublattice of atom α in a multilattice crystal	564

General symbols – Greek

Symbol	Description	Page
Γ	phase space	382
$\boldsymbol{\Gamma}$, Γ_i	set of extensive kinematic state variables	63
$\boldsymbol{\Gamma}_i$	wave vector of the ith DFT plane wave basis function	211
$\boldsymbol{\gamma}$, γ_i	set of intensive state variables work conjugate with $\boldsymbol{\Gamma}$	78
γ	damping coefficient	511
γ_{s}	surface energy	340
γ_{GB}	grain boundary energy	346
γ_{SF}	stacking fault energy	357
δ_{ij}	Kronecker delta	25
ϵ	energy of an electron	164
$\boldsymbol{\epsilon}$, ϵ_{ij}	small strain tensor	49
ϵ_{ijk}	permutation symbol	26
ζ_i^α	fractional coordinates of basis atom α	142
$\kappa^{\alpha\beta\gamma\delta}$	scalar atomistic stiffness term relating bonds α–β and γ–δ	297
Λ	de Broglie thermal wavelength	241
Λ_i	projection operator	162
λ	Lamé constant	105
λ	plane wave wavelength	164
μ	shear modulus (solid)	105
$\mu(m)$	mth moment of a function	230
ν	Poisson's ratio	105
ν_e	number of atoms associated with element e in QC	612
Π	total potential energy of a system and the applied loads	107
$\boldsymbol{\Pi}^\alpha$, Π_i^α	pull-back momentum of atom α	452
ρ	mass density (deformed configuration)	52
ρ	electron density	188
ρ_0	mass density (reference configuration)	52
ρ^{pt}	pointwise (microscopic) mass density field	468

ρ^α	total electron density at atom α in a pair functional	263
$\Sigma(E;\Delta E)$	hypershell in phase space with energy E and thickness ΔE	404
$\boldsymbol{\sigma}$, σ_{ij}	Cauchy stress tensor	56
$\boldsymbol{\sigma}^{\rm inst}$, $\sigma_{ij}^{\rm inst}$	instantaneous atomic-level stress	457
$\boldsymbol{\sigma}^{\rm pt}$, $\sigma_{ij}^{\rm pt}$	pointwise (microscopic) Cauchy stress tensor	470
$\boldsymbol{\sigma}^{\rm pt,K}$, $\sigma_{ij}^{\rm pt,K}$	kinetic part of the pointwise (microscopic) Cauchy stress	471
$\boldsymbol{\sigma}^{\rm pt,V}$, $\sigma_{ij}^{\rm pt,V}$	potential part of the pointwise (microscopic) Cauchy stress	471
$\boldsymbol{\varphi}$, φ_i	deformation mapping	43
$\phi(r)$	pair potential as a function of distance r	251
φ	electron wave basis function	173
$\varphi^{\alpha\beta}$	scalar magnitude of force on atom α due to presence of atom β	291
χ	general, time-dependent electronic wave function	163
χ	characteristic function in restricted ensemble	554
ψ	specific Helmholtz free energy	95
ψ	general, time-independent electronic wave function	165
$\psi^{\rm sp}$	single-particle, time-independent electronic wave function	194
Ω	volume of a periodic simulation cell in a DFT simulation	210
Ω_0	nonprimitive unit cell volume in reference configuration	124
$\widehat{\Omega}$	volume of the first Brillouin zone	208
$\widehat{\Omega}_0$	primitive unit cell volume in reference configuration	122
$\Omega(E;\Delta E)$	volume of hypershell $\Sigma(E;\Delta E)$ in phase space	404
ω	plane wave frequency	164

General symbols – Roman

Symbol	Description	Page
$\mathcal{A}$	macroscopic observable associated with phase function $A(\boldsymbol{q},\boldsymbol{p})$	387
$A(\boldsymbol{q},\boldsymbol{p})$	phase function associated with macroscopic observable $\mathcal{A}$	387
$\boldsymbol{A}_1$, $\boldsymbol{A}_2$, $\boldsymbol{A}_3$	reference *nonprimitive* lattice vectors	123
$\hat{\boldsymbol{A}}_1$, $\hat{\boldsymbol{A}}_2$, $\hat{\boldsymbol{A}}_3$	reference *primitive* lattice vectors	120
$\boldsymbol{a}$, a_i	acceleration vector	50
$\boldsymbol{a}_1$,$\boldsymbol{a}_2$,$\boldsymbol{a}_3$	nonprimitive lattice vector (deformed configuration)	561
$\mathcal{B}$	the first Brillouin zone	212
B	bulk modulus	112
$B(\boldsymbol{x};\boldsymbol{u},\boldsymbol{v})$	bond function at $\boldsymbol{x}$ due to the spatially averaged bond $\boldsymbol{u}$–$\boldsymbol{v}$	479
$\boldsymbol{B}_1$, $\boldsymbol{B}_2$, $\boldsymbol{B}_3$	reciprocal reference lattice vectors	147
$\boldsymbol{B}$, B_{ij}	left Cauchy–Green deformation tensor	47
BO	bond order	272
$\boldsymbol{b}$, b_i	body force (spatial description)	55
$\boldsymbol{b}$, b_i	Burgers vector	351
$\boldsymbol{b}^{\rm pt}$, $b_i^{\rm pt}$	pointwise (microscopic) body force field	470
$\mathcal{C}$	the DFT simulation cell	210

C_v	molar heat capacity at constant volume	69
$\boldsymbol{C}$, C_{IJ}	right Cauchy–Green deformation tensor	47
$\boldsymbol{C}$, C_{IJKL}	referential elasticity tensor	101
c_v	specific heat capacity at constant volume	70
c_I, c_{Ij}, c_{iI}^{α}	Ith eigenvector solution and its components (associated with plane wave j or orbital i on atom α)	176
$\boldsymbol{c}$, c_{ijkl}	spatial (or small strain) elasticity tensor	102
$\mathbf{c}$, c_{mn}	elasticity matrix (in Voigt notation)	104
$D(E)$	density of states (statistical mechanics)	405
$D(\epsilon)$	electronic density of states	230
D_i^{α}	electronic density of states for orbital i on atom α	230
$\boldsymbol{D}$, D_{iJkL}	mixed elasticity tensor	102
$\boldsymbol{d}$, d_{ij}	rate of deformation tensor	50
$\mathcal{E}$	total energy of a thermodynamic system	68
E	Young's modulus	105
$E_{\text{free}}(Z)$	energy of a free (isolated) atom with atomic number Z	247
E_{coh}, E_{coh}^0	cohesive energy and equilibrium cohesive energy	332
$\boldsymbol{E}$, E_{IJ}	Lagrangian strain tensor	48
$\boldsymbol{e}_i$	orthonormal basis vectors	27
$\boldsymbol{F}^{\text{ext}}$	total external force acting on a system	54
$\boldsymbol{F}$, F_{iJ}	deformation gradient	46
f	occupancy of an electronic orbital	208
$f(\boldsymbol{q},\boldsymbol{p};t)$	distribution function at point $(\boldsymbol{q},\boldsymbol{p})$ in phase space at time t	391
$f_{\text{mc}}(\boldsymbol{q},\boldsymbol{p};E)$	microcanonical (NVE) distribution function	407
$f_{\text{c}}(\boldsymbol{q},\boldsymbol{p};T)$	canonical (NVT) distribution function	427
$\boldsymbol{f}^{\alpha}$, f_i^{α}	force on atom α	54
$\boldsymbol{f}^{\alpha\beta}$, $f_i^{\alpha\beta}$	force on atom α due to the presence of atom β	289
$\boldsymbol{f}^{\text{int},\alpha}$, $f_i^{\text{int},\alpha}$	internal force on atom α	289
$\boldsymbol{f}^{\text{ext},\alpha}$, $f_i^{\text{ext},\alpha}$	external force on atom α	289
$\mathbf{f}$	column matrix of finite element nodal forces	603
$\boldsymbol{G}^{\alpha}$, G_i^{α}	stochastic force on atom α	511
g	specific Gibbs free energy	96
$g(r)$	electron density function in a pair functional	264
$\mathcal{H}$	Hamiltonian of a system	159
$\boldsymbol{H}$, H_i	angular momentum	58
$\mathbf{H}_0$	matrix of periodic cell vectors (reference configuration)	326
$\mathbf{H}$	matrix of periodic cell vectors (deformed configuration)	326
$\hat{\mathbf{H}}$	matrix of reference primitive lattice vectors	120
$\boldsymbol{I}$	identity tensor	34
$\mathbf{I}$	identity matrix	25
J	Jacobian of the deformation gradient	46
$\mathcal{K}$	macroscopic (continuum) kinetic energy	68
$\mathbf{K}$	stiffness matrix or Hessian	312
$\boldsymbol{k}$	wave vector and Fourier space variable	146

$\mathcal{L}$	Lagrangian function	158
$\boldsymbol{L}$, L_i	linear momentum	54
$\boldsymbol{L}$, $\boldsymbol{L}_i$	vectors defining a periodic simulation cell (reference)	325
$\boldsymbol{l}$, l_i	vectors defining a periodic simulation cell (deformed)	563
$\boldsymbol{l}$, l_{ij}	spatial gradient of the velocity field	50
M	total mass of a system of particles	380
M_{cell}	mass of a unit cell	567
$\boldsymbol{M}^{\text{ext}}$	total external moment acting on a system	58
M	finite element mass matrix	660
m, m^α	mass, mass of atom α	54
$\mathcal{N}^\alpha$	set of atoms forming the neighbor list to atom α	324
N	number of particles/atoms	54
N_{B}	number of basis atoms	142
$\hat{N}_{\text{B}}$	number of basis atoms in the primitive unit cell	140
N_{lat}	number of lattice sites	563
n_{d}	dimensionality of space	22
$\mathcal{P}^{\text{def}}$	deformation power	86
$\mathcal{P}^{\text{ext}}$	external power	85
$\boldsymbol{P}$, P_{iJ}	first Piola–Kirchhoff stress tensor	59
$\boldsymbol{\mathfrak{P}}^\alpha$, $\mathfrak{P}_i^\alpha$	reference momentum of atom α	452
p	pressure (or hydrostatic stress)	57
$\boldsymbol{p}^\alpha$, p_i^α	momentum of atom α	54
$\boldsymbol{p}_{\text{rel}}^\alpha$	center-of-mass momentum of atom α	380
$\boldsymbol{p}$, p_i	momentum of an electron or atom	164
$\boldsymbol{p}$, p_i	generalized momenta in statistical mechanics	382
$\Delta\mathcal{Q}$	heat transferred to a system during a process	68
$\mathbf{Q}$,$\mathsf{Q}_{\alpha i}$	orthogonal transformation matrix	31
$\boldsymbol{q}$, q_i	spatial heat flux vector	87
$\boldsymbol{q}_0$, q_{0I}	reference heat flux vector	88
$\boldsymbol{q}$, q_i	generalized positions in statistical mechanics	382
$\bar{\boldsymbol{q}}$, $\bar{q}_i$	generalized mean positions in restricted ensemble	556
$\mathcal{R}$	rate of heat transfer	85
$\boldsymbol{R}$, R_{iJ}	finite rotation (polar decomposition)	47
$\boldsymbol{R}^{[\ell\lambda]}$	reference position of the λth basis atom of lattice site ℓ	141
$\boldsymbol{R}$, R_i	center of mass of a system of particles	380
$\boldsymbol{R}^\alpha$, R_i^α	reference position of atom α	242
r	spatial strength of a distributed heat source	87
r_0	reference strength of a distributed heat source	88
$\boldsymbol{r}^\alpha$, r_i^α	spatial position of atom α	54
$\bar{\boldsymbol{r}}^\alpha$, $\bar{r}_i^\alpha$	mean position of atom α in restricted ensemble	556
$\boldsymbol{r}_{\text{rel}}^\alpha$	center-of-mass coordinates of atom α	380
$\mathcal{S}$	electronic orbital overlap	225
$\mathcal{S}$	entropy	73
$\mathcal{S}^\lambda$	set of all atoms belonging to sublattice λ in a multilattice	564

S^I	shape function for finite element node I	602
S_E	hypersurface of constant energy E in phase space	382
$\boldsymbol{S}$, S_{IJ}	second Piola–Kirchhoff stress tensor	60
s	specific entropy	88
$\boldsymbol{s}$, s_{ijkl}	spatial (or small strain) compliance tensor	103
$\bar{\boldsymbol{s}}^\lambda$, $\bar{s}_i^\lambda$	shift vector of basis atom λ	560
$\mathcal{T}$	instantaneous microscopic kinetic energy	158
$\mathcal{T}^{\rm vib}$	microscopic (vibrational) kinetic energy	379
$\mathcal{T}^{\rm el}$	instantaneous kinetic energy of the electrons	190
$\mathcal{T}^{\rm s}$	instantaneous kinetic energy of the noninteracting electrons	192
T	temperature	65
$\boldsymbol{T}$, T_i	nominal traction (stress vector)	60
$\boldsymbol{t}$, t_i	true traction (stress vector)	56
$\bar{\boldsymbol{t}}$, $\bar{t}_i$	true external traction (stress vector)	55
$\mathcal{U}$	internal energy	68
$\mathcal{U}$	potential energy of a quantum mechanical system	169
$U(\rho)$	embedding energy term in a pair functional	263
$U(z)$	unit step function (Heaviside function)	404
$\boldsymbol{U}$, U_{IJ}	right stretch tensor	47
u	spatial specific internal energy	85
u_0	reference specific internal energy	88
$\boldsymbol{u}$, u_i	displacement vector	48
$\widetilde{\boldsymbol{u}}$, $\widetilde{u}_i$	finite element approximation to the displacement field	602
$\mathbf{u}$	column matrix of finite element nodal displacements	601
$\mathcal{V}$	potential energy of a classical system of particles	158
$\mathcal{V}^{\rm int}$	internal (interatomic) part of the potential energy	240
$\mathcal{V}^{\rm ext}$	total external part of the potential energy	240
$\mathcal{V}^{\rm ext}_{\rm fld}$, $\mathcal{V}^{\rm ext}_{\rm con}$	potential energy due to external fields and external contact	240
V_0	volume (reference configuration)	46
V	volume (deformed configuration)	46
V_0^α	volume of atom α (reference configuration)	457
V^α	volume of atom α (deformed configuration)	457
V_R	volume of region R in phase space	384
$\boldsymbol{V}$, V_{ij}	left stretch tensor	47
$\boldsymbol{v}$, v_i	velocity vector	50
$\boldsymbol{v}^{\rm pt}$, $v_i^{\rm pt}$	pointwise (microscopic) velocity field	468
$\boldsymbol{v}^\alpha$, v_i^α	velocity of atom α	54
$\boldsymbol{v}^\alpha_{\rm rel}$, $v^\alpha_{{\rm rel},i}$	velocity of atom α relative to center of mass	471
$\mathbf{v}$	column matrix of finite element nodal velocities	660
$\Delta\mathcal{W}$	work performed on a system during a process	67
$\mathcal{W}$	virial of a system of particles	422
W	strain energy density function	96
$w(\boldsymbol{r})$, $\hat{w}(r)$	spatial averaging weighting function (general and spherical)	476
$\boldsymbol{w}$, w_{ij}	spin tensor	50

$\boldsymbol{w}^\alpha$, w_i^α	displacement of atom α relative to its mean position	556
$\boldsymbol{X}$, X_I	position of a point in a continuum (reference configuration)	43
$\mathbf{X}$	column matrix of finite element nodal coordinates	601
$\boldsymbol{x}$, x_i	position of a point in a continuum (deformed configuration)	43
$\boldsymbol{x}$, x_i	position of an electron	156
Z	atomic number	176
Z	partition function	426
Z^{K},Z^{V}	kinetic and potential parts of the partition function	427
$\hat{\boldsymbol{Z}}^\alpha$	position of basis atom α relative to the Bravais site	141
z	valence of an atom (or charge on an ion)	198

Fundamental constants

Avogadro's constant (N_{A})	6.0221×10^{23} mol^{-1}
Bohr radius (r_0)	0.52918 Å
Boltzmann's constant (k_{B})	1.3807×10^{-23} J/K
	8.6173×10^{-5} eV/K
charge of an electron ($\tilde{e}$)	1.6022×10^{-19} C
charge-squared per Coulomb constant ($\tilde{e}^2/4\pi\epsilon_0 \equiv e^2$)	14.4 eV · Å
mass of an electron (m^{el})	9.1094×10^{-31} kg
permittivity of free space (ϵ_0)	8.8542×10^{-12} C^2/(J · m)
Planck's constant (h)	6.6261×10^{-34} J · s
	4.1357×10^{-15} eV · s
Planck's constant, reduced ($\hbar = h/2\pi$)	1.0546×10^{-34} J · s
	6.5821×10^{-16} eV · s
universal gas constant (R_{g})	8.3145 J/(K · mol)

Unit conversion

1 fs	=	10^{-15} s (femto)
1 ps	=	10^{-12} s (pico)
1 ns	=	10^{-9} s (nano)
1 µs	=	10^{-6} s (micro)
1 ms	=	10^{-3} s (milli)
1 Å	=	10^{-10} m = 0.1 nm (ångstrom)
1 eV	=	1.60212×10^{-19} J
1 eV/Å	=	1.60212×10^{-9} N = 1.60212 nN
1 eV/Å^2	=	16.0212 J/m^2 = 16.0212 N/m
1 eV/Å$^{2.5}$	=	1.60212×10^6 N/m$^{1.5}$ = 1.60212 MPa · $\sqrt{\mathrm{m}}$
1 eV/Å^3	=	1.60212×10^{11} N/m^2 = 160.212 GPa
1 amu	=	1.66054×10^{-27} kg = 1.03646×10^{-4}eV · ps^2/Å^2