

Preface

The purpose of this book is to identify current achievements and properly assess the state of the art in the atomic scale modelling of structurally disordered (glassy) materials. More precisely, we intend to bring to the attention of the readership representative examples of systems for which the structural information provided by molecular dynamics has been instrumental in bringing significant progresses in the area of glass science. The underlying motivation of this collection of contributions rests on the notion that glassy materials are intrinsically devoid of regular structural organization.

Early attempts to extract information on glass structure were based on a combination of indirect experimental evidence (quite often obtained by associating measured spectral features with specific crystalline-like motifs) and phenomenological models. The resulting descriptions of the glass structures were highly qualitative and unable to account for the role of chemical bonding in determining the nature of the structural units, their connectivity as well as the extent of their correlation and order. Advances in algorithms and high performing computer facilities capable of handling realistic models and to extend the size and timescale of dynamical simulations have represented a major step forward in promoting this class of simulations to reliable *virtual* experiments. Indeed, recent years have witnessed the advent of atomic scale modelling as a new approach for understanding the properties of glass. This approach is characterized by a clear distinction between the notion of “glasses” as ideal “statistical mechanics” models and their treatment as real materials of interest in material science and technology. By focusing on real glasses a computational material scientist seeks a precise knowledge of structural properties for a given system by using quantitative tools. This strategy is radically different from qualitative assessments that are equally valid and applicable to any disordered system but do not target any correlation between atomic structure and bonding properties. Investigating glasses in the framework of computational material science is a theoretical strategy legitimated by the increased

reliability of both classical molecular dynamics (CMD) and first-principles molecular dynamics (FPMD). This will be exemplified in this book and it is fully substantiated by the observation that CMD and FPMD are able to produce models more and more realistic, since their predictive power increases at a very fast pace.

To set the scene for a proper account of relevant issues in the area of disordered network, this volume opens with a contribution (by Philip S. Salmon and Anita Zeidler) having a predominant experimental character and yet containing several useful considerations on the role played by atomic scale modelling in the understanding of short and intermediate range order. While the essence of classical molecular dynamics is intuitively accessible to any practitioner willing to model a system by employing a suitable interatomic potential, the concepts inherent in first-principles molecular dynamics are less straightforward to grasp. This is because FPMD requires the knowledge and the control of a specific methodology combining electronic structure concepts and newtonian dynamics. For this reason, a chapter written by Mauro Boero and co. is devoted to this issue. Moving a further step into the methodology to tackle problems related to the glassy state organization, the contribution by the team of Riccardo Mazzarello focuses on metadynamics as a tool to understand nucleation and phase changes involving the disordered state. Moving into actual modelling of glassy materials, the proper description of iono-covalent bonding is extremely challenging within an effective interatomic potential framework. In the first contribution devoted to modelling of glasses within classical (and yet realistic) molecular dynamics, Liping Huang and John Kieffer are able to describe under which conditions potential models can be used to study archetypical, iono-covalent glass formers. Along the same lines, Pedone and Menziani address the issue of the development of reliable and transferable empirical potentials, optimization of the glass forming procedures and experimental validation of the resulting structures. At the crossroad between simulation methodology (applied to amorphous recrystallization) and realistic modelling of interface phenomena, the classical modelling developed by Evelyne Lampin is able to account for the morphology and the dynamics of a crystal/amorphous interface. In his contribution, Jincheng Du addresses the issue of atomic-scale modelling of multicomponent oxide glasses. Once again, the focus is on the capabilities of classical molecular dynamics to model (with no explicit account of the electronic structure) interactions requiring the account of polarizability for systems that can contain several hundred thousand atoms. The team of Monia Montorsi is also very much concerned by this issue, as shown by the quite realistic modelling of complex transition metal oxides. The section of the book devoted to the applications of classical molecular dynamics models and methods ends with a large series of examples (by Mark Wilson) for silica and carbon system, based on highly refined interatomic potentials containing n -body and/or polarization effects. Interestingly, these models turn out to be quite realistic for systems having different dimensionalities. At the crossroad between classical and first-principles molecular dynamics, Antonio Tilocca addresses a very

important issue of glass science, namely the role of these materials in determining and regulating biological functions such as biodegradation. Dynamical effects are nicely highlighted, within the framework of surface reactivity and ion migration. First-principles molecular dynamics (FPMD) is the common ingredient of the last set of contributions, all inspired and nurtured by the predictive power of electronic structure calculations for the potential energy surfaces, combined with newtonian dynamics. For instance, Matthieu Micoulaut establishes the link between the connectivity of such realistic models and the topological constraint theory. The contribution by Assil Bouzid and co. (C. Massobrio/M. Boero team) traces back the modelling of $\text{Ge}_x\text{Se}_{1-x}$ chalcogenides from the early stages until the last realizations, with a focus on the comparison between GeSe_4 and GeS_4 glasses. The peculiar properties of glass surfaces (for silica and chalcogenides) are addressed by Guido Ori and co., with implications for the development of classic force fields based on a consistent definition of charges depending on the local environment. The case of a prototypical network-forming systems based on trigonal units is presented in great detail by Guillaume Ferlat, focussing on the ring structure of glassy B_2O_3 . First-principles molecular dynamics approaches have been widely employed in recent years to gain valuable insight into the properties of a very important class of disordered networks, the so-called phase change materials. These are of great interest for optical recording and memory devices. This book ends with five contributions related to the structural and bonding properties of specific chalcogenide alloys very much employed in this context. As shown by Caravati and co., FPMD can also be used as an input for the creation of smart interatomic potentials (the so-called Neural Network ones) enabling realistic crystallization studies on quite large samples (4000 atoms). Structure and crystallization dynamics are also tackled by Jaakko Akola and co. on the prototypical phase change material (PCM hereafter and in the remainder of the book) $\text{Ge}_2\text{Sb}_2\text{Te}_5$, while a large variety of structural behaviours common to sub-systems inherent in the PCMs are reviewed in the contribution by Jean-Yves Raty and co., with a special emphasis for the criterion of structural stability. Finally, the effect of doping on phase change materials is considered in the contribution of the teams headed by David Drabold and Stephen Elliott, respectively. While both contain information on transition metal doping, the second paper also provides information on carbon and nitrogen doping.

Overall, we are convinced that the research efforts presented in this volume are highly representative of the impact of atomic-scale molecular dynamics modelling towards the understanding of structural and topological features of glass. Whenever it appears possible, sufficiently realistic and convenient, glass can be simulated by using interatomic potential, these tools becoming more and more refined, especially when they are derived from electronic structure potential energy surfaces. For situations where the accuracy of first-principle molecular dynamics is required, glasses are studied via a quantitative account of chemical bonding, through

first-principles molecular dynamics, yielding trajectories that evolve self-consistently as a function of the network topology and of the changes induced by temperature.

Based on the above assertions, we conclude that molecular dynamics applied to glass has evolved from a computer-based tool complementary to experiments to a reliable and authoritative source of atomic-scale information on its own.

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