Foreword

First I would like to stress that the main authors of this monograph – Jürn W.P. Schmelzer and Ivan Gutzow – are renowned experts on properties of glasses, relaxation and phase formation processes in glasses that include glass transition, liquid–liquid phase separation, crystal nucleation, crystal growth and overall crystallization processes. In the present book, their attention is concentrated on the description of glasses and glass transition. In analyzing this circle of problems, of special relevance is their strong background on thermodynamics; they always bring their research projects into a solid thermodynamic framework. Their new monograph *Glasses and the Glass Transition* is no exception; it could be also be named, for instance, *Thermodynamics of the Vitreous State*. In this book, they review, organize and summarize – within a historical perspective and discussing alternative approaches – the results of their own publications on different thermodynamic aspects of the vitreous state performed after the publication of their book, *The Vitreous State: Thermodynamics, Structure, Rheology, and Crystallization* published by Springer in 1995.

After the introduction, in Chapter 2, Schmelzer and Gutzow disclose their ideas on the nature of glasses through an overview of the basic laws of classical thermodynamics, the description of nonequilibrium states, phase transitions, crystallization, viscosity of glass-forming systems, thermodynamic properties of glass-forming melts, glass transition, and on the overall thermodynamic nature of the glassy state. Most of the presented concepts are discussed within a thermodynamic perspective.

In Chapter 3, they present and discuss in detail a "generic theory of vitrification of liquids" and explain the application of thermodynamics of irreversible processes to vitrification. Then, the authors review relaxation of glass-forming melts, define the glass transition, comment on the entropy at very low temperatures, the Kauzmann paradox, the Prigogine–Defay ratio – including several quantitative estimates of this parameter – the concept of fictive temperature as a structural order parameter, the viscosity and relaxation time at T_g, and finally frozen-in thermodynamic fluctuations. Once more, all these important characteristics of the vitreous state are discussed within thermodynamic insights. These concepts are developed in more detail in the application to relaxation and the pressure dependence of the viscosity in Chapter 4, and an analysis of systems with a glass-like behavior in Chapter 5.

In order to apply thermodynamic methods, in general, and to glasses and glass transition, in particular, the thermodynamic properties of the respective systems, such as the equations of state, must be known. In order to give an overview on the present state in this direction, the book also comprises two special chapters: Chapter 6, authored by Oleg Mazurin on the collection and analysis of glass property data; and Chapter 7, written by Alexander Priven, discusses the available models to correlate certain glass properties to their chemical composition.

Mazurin was the head of the famous Laboratory of Glass Properties of the Grebenshchikov Institute of Silicate Chemistry of the Russian Academy of Sciences in the former USSR, for almost 40 years. Then he retired and dedicated his efforts to his present passion: collection and critical analysis of glass property data. He worked intensively and published numerous papers on many types of glass properties, and perhaps most importantly, from the early stages he started to collect property data from his own group and from published literature to finally mastermind the assembly of an impressive and most useful glass database – SciGlass – which currently contains the properties of more than 350 000 glass compositions. In my opinion this database is a must in the library of any active glass research group in the world. I am particularly proud to say that my students and I have been using the SciGlass database for several years from its very beginning. In this chapter, Mazurin discusses the power of SciGlass, which is regularly updated on an annual basis, and its multiple utilities. The author emphasizes how one can and should use SciGlass to compare the values of properties measured by any author against all the available data. He also stresses a nasty and frequent problem; that is, the poor quality of data published by some research groups.

Having at one's disposal such a comprehensive overview on existing experimental data on glass properties, the next question arises whether it is possible to theoretically predict – based on such knowledge – some properties of glass-forming systems, for which experimental data are not available. This task is reviewed in the chapter written by Priven. It is probably fair to say that Priven dedicated almost his entire career to this very important scientific and technological theme: development and testing of models to predict the compositional dependence of important glass properties, such as density, thermal expansion coefficient, refractive index, liquidus and viscosity, to their chemical composition. Priven has been involved in the arduous and complex quest of what he calls the "silver bullet." Although I never carried out any specific research on this particular subject, I have always been a keen user of Appen's model, and lately of Priven's model, to calculate glass properties from chemical composition for the development of new glasses and glass-ceramics (which always have a residual glass matrix). Priven discusses the strengths and weaknesses of several available models, for example, Winkelman and Schott's, Gelhoff and Thomas's, Gilard and Dubrul's, Huggins and Sun's, Appen's, Demkina's, Mazurin's, Fuxi's, Lakatos's and of his own model. He also discusses the numerous difficulties to develop an accurate model due to the nonexistence of data for many compositions and nonlinear effects, such as the anomalous effects of boron and alumina, which fortunately have been already solved by some of these models. At present one can use Priven's model and some others for surprisingly good predictions (say within 5–10%) of several properties of glasses containing up to 30 elements. But the "silver bullet" – to accurately predict the properties of all possible glasses with combinations of all the 80 "friendly" elements of the periodical table – is far from being found (please check the Zanotto paper on this topic published in the *Journal of Non-Crystalline Solids*, 347 (2004) 285–288).

After completion of the general task, that is, the thermodynamic description of glasses and the glass transition, the overview on existing data on glasses and the methods of prediction of glass properties, Schmelzer and Gutzow go over to a more detailed discussion of some peculiar properties of glasses and glass-like systems and their possible technological applications. Chapter 8 deals with "glasses as accumulators of free energy, of increased reactivity and as materials with unusual applications," whereas Chapter 9 is devoted to the third law of thermodynamics and its application to the vitreous state. It is usually stated that the third law is not applicable to glasses as they never reach equilibrium for temperatures tending to zero. Therefore, their entropy has to be larger than zero for $T \to 0$. The authors present a detailed historical development, describe the application of thermodynamics to nonequilibrium states, show some thermodynamic and kinetic invariants at T_g and give an extended discussion on the current controversial issue of zero-point entropy of glasses. The book is completed by an interesting analysis of the etymology of the word "glass."

Summarizing, the present book presents a thorough discussion about the nature of glass, with a rich historical background (a characteristic of Ivan Gutzow) on the most basic properties of glasses including vitrification kinetics, relaxation and glass transition. It cites more than 650 articles. This book will certainly be a very useful reference for experienced researchers as well as for post-graduate students who are interested in understanding the nature of glass and the application of the laws of thermodynamics to nonequilibrium materials such as glasses.

Edgar D. Zanotto
August 2010

Head of the Vitreous Materials Laboratory
Federal University of São Carlos, Brazil
Member of the Brazilian Academy of Sciences
Member of the World Academy of Ceramics
Fellow of the British Society of Glass Technology

Preface

Nearly all authors of modern science-based books aspire to write the definitive summary of a chosen subject, a field of inquiry, or the history or future of an emerging discipline. Books such as the *Theory of Metals and Alloys* by N. Mott and H. Jones, *Introduction to Solid State Physics* by C. Kittel, and *The Nature of the Chemical Bond* by L. Pauling readily come to mind in this regard. This book, more correctly a treatise, by Jürn W.P. Schmelzer and Ivan S. Gutzow, with collaboration by Oleg V. Mazurin, Alexander I. Priven, Snejana V. Todorova, and Boris P. Petroff, rises to this level in its comprehensive summary of the field of glass science. Drawing heavily on thermodynamics, kinetic theory, and the physical sciences, virtually all aspects of the material glass including the transition of an undercooled melt to the glassy state, are summarized in an authoritative, scholarly, and convincing manner. Not only is the scope and volume of material examined for this treatise impressive, so is the way in which it was compiled. That is, the compilation was made through an exhaustive, comprehensive review and evaluation of the major literature on this subject from the present day contributions back to the beginning of the last century.

The authors were aided immeasurably by a facility to read articles as they appeared in their original language thereby helping to gain special and even essential historical insight into the value and scientific correctness of the material being reviewed. This in turn allowed a more global approach in direct support of producing an authoritative discourse on glass and the glass transition. Worthy of exceptional praise is their discussion of glass and third law of thermodynamics found in Chapter 9. It gives credence to accepting glass science as a major field in its own right and the need for nearly all theorists to understand what glass is.

The completion of this task is, in fact, a life-long labor of love for these authors, one which could only be undertaken by a handful of scientists across the globe who have shared a similar devotion to this subject throughout their professional lives. In short, they have accomplished their intended purpose in preparing this treatise: writing the definitive description of glass and the glass transition. It holds potential to be recognized as a remarkable milestone.

And what might be the expected outcomes of this Herculean task? As a university professor, I use to make sure my students understood that the penultimate essence of science is to predict – to predict facts that are known and can be measured, to predict those that are unknown, and make sure the predictions are quantitative.

That is, science must be quantified through mathematical treatment. Through the authors' mathematical description of the material of glass and its properties including the glass transition, practicing glass scientists and engineers will find this book invaluable in helping them understand and predict the behavior of glass in a wide range of settings and applications. It will no doubt be a springboard to the development of advanced and possibly even more mathematically rigorous theories of the vitreous state as new observations are recorded, and their meaning explored.

Additionally, it will be difficult to prepare a manuscript or professional presentation on glass or the glass transition without understanding or referencing this contribution to the scientific literature. In a similar way, countless students engaged in thesis work on glass will surely become familiar with this treatise, if their academic work involves fabrication, characterization, or application.

For all of these reasons, it is confidently predicted this treatise will gain international recognition – not only across the entire materials spectrum – but also in the broader fields of physics and chemistry. And for this potential, the authors and their collaborators should take a well-deserved bow.

L. David Pye
August 2010

Professor of Glass Science, Emeritus, Alfred University, USA
Past President of the International Commission on Glass
Past President of the American Ceramic Society
Honorary Member of the German Society of Glass Technology
Honorary Fellow, the British Society of Glass Technology