Preface

The first edition of the present monograph was met with interest by the glass science community, and at the end of 1996, it was practically already completely sold out and, thus, open for preparation of a second edition. However, in the following 15 years to come, we, both authors of the first edition, were involved with a variety of projects connected with experimental applications and even with the technical realization of some of the ideas developed in our book. Particular attention was given also by both of us to further theoretical generalizations of the results already achieved. In particular, both authors were involved with the study and with the development of problems, connected with the very essence of the theory forming the basis for the understanding of the glass transition, of the apparent kinetic stability, and of segregation processes and crystallization of glass-forming systems. In some respect, these were projects connected with the application of glasses as a very specific material and particular physical state of matter.

In the first edition of the present book, already the conviction was expressed that common, e.g. silicate glasses are only the most popular, the experimentally most frequently investigated, and, in many respects, the theoretically best-known representatives of matter in this particular state, the vitreous state. This notion was one of the leading ideas in writing the first edition of our book: analyzing the state of common glasses supplies us simultaneously with valuable information on many other systems in which matter exists as a particular frozen-in immobilized state. Thus, it was to be expected that results, obtained on common glasses, could be of use in many other fields of science. In this respect, the evidence obtained with technical glasses and especially with simple model glasses could and can be, so we hope, applied also to the vitreous-like states of matter in cases, when experimental analysis and theoretical modeling are more difficult or even impossible. Here we have first to mention the particular cases of unusual glasses, like vitreous ice, or of aqueous solutions with particular biological properties, allowing even life to be frozen-in into the vitreous-like state of absolute anabiosis. It is well known that there are even proposals to consider cosmic objects like black holes or the excited state of light in lasers like being in physical situations similar to those existing in common glasses. Let us mention also the case of comets: according to present-day
knowledge, the kernel of comets is constituted of vitreous ice. If this is so, it would turn out that 99.9% of water in the universe as a whole is not to be found in the form of the common water of our oceans but exists as vitreous ice. In speaking about such seemingly extreme cases of systems with vitreous-like behavior or vitreous-like states, it becomes evident how significant in fact can be the knowledge and especially the lack of knowledge in investigating glasses and glassy systems.

The years after 1995 have been a time in which many well-known specialists in the field of glass science devoted their efforts to the development of ideas or models to describe vitreous states in a general way. Here first we have to mention ideas based on modeling glass-like systems in terms of statistical mechanics, for example, based on general concepts like mode-coupling theory, energy landscape approaches, models based on extended lattice hole approaches (with nonsymmetric two-minima energetic wells), and many others. The results obtained with most of these statistical physics models were however in many respects disappointing: some of the results even contradicted experiment; others gave only commonly known information. This is the reason why the efforts of several scientific groups were mainly concentrated on the development of ideas connected with the phenomenology, that is, with thermodynamics and overall kinetics of glass transition in terms of the more general formulation of thermodynamics, especially of the thermodynamics of irreversible processes in its simplest, linear formulations. Out of the cooperation of both authors of the present monograph in the time elapsing between 1995 and 2012, more than 40 common publications have been developed. They have been published in the international literature, and most of them are devoted to the analysis of the thermodynamic state, the structure, and the crystallization of glass-forming systems. We have prepared in the same time (in cooperation with two Russian colleagues, Oleg V. Mazurin and Alexander I. Priven, and two Bulgarian coworkers, Boris P. Petroff and Snejana V. Todorova) also a second monograph (J. W. P. Schmelzer and I. S. Gutzow, “Glasses and the Glass Transition”, Wiley-VCH, 2011) where the interested reader can find summarized and further developed many of the problems initiated and formulated in the first edition of the present book. A brief account of these new developments, going at part widely beyond the results presented in latter monograph, can be found here in Chap. 14 and in several footnotes to the text of the present second edition. Particular efforts of both authors were also concentrated on the development of thermodynamic problems connected with phase formation in glass forming systems; in the framework of this subject, one of the present authors (J.W.P.S.) developed an approach, to which particular attention is given in the second part of the above-mentioned Chap. 14.

Thermodynamics is the science which has to decide where to put and how to describe any state of matter. This is the reason why this great phenomenological approach is used in the present book. However, thermodynamics was classically derived as a science describing only systems in equilibrium and in predicting changes, which can and have to take place between different equilibrium states, for example, when one of them is more stable than the other. On the other hand, vitreous states, as proven already by the first investigations of the thermodynamics of glasses, are nonequilibrium states: this is their particular and most striking
characteristics. Sometimes this particular feature of glasses is expressed in terms of ergodicity and none-ergodicity: in the sense that glasses are non-ergodic systems. However, in doing so, it is usually forgotten that even the definition of ergodicity is at present open to discussion: this is why the use of the more generally defined notion of equilibrium and nonequilibrium seems to be more appropriate to the present authors at least to define a particular state in terms of properly understood, defined, and accepted notions. It is known and discussed in details in Chap. 5 of the first edition of our monograph that the investigations, which led to the conclusion that glasses are nonequilibrium, systems that is, non-thermodynamic bodies were reached in the beginning of the 1920s in connection with the efforts to verify Nernst’s heat theorem and the third principle of thermodynamics by several of the most outstanding representatives of twentieth century classical thermodynamics. This problem is also summarized in Chap. 14, and its development represents an exciting scientific story retold by the present authors in two contributions cited there. It was F. Simon who proposed a remarkable approximation which has given the possibility to describe for a number of purposes with sufficient accuracy both glass transition and the thermodynamic properties of glasses. This approximation, governing the development of ideas and their treatment and development into what can be called the initial phenomenological theory of glass, was for more than 90 years adopted in glass science. This approximation of F. Simon was taken as a leading tool and the main idea in writing the first edition of the present book and in developing the ideas described there. We hope that this development, we decided to perform beginning with the 1990s, showed the really great advantage of Simon’s approximation. We described in its framework the glass transition itself, vapor pressure and solubility of glasses, influence of the conditions of vitrification on glass properties, relaxation, stabilization, and crystallization of glass-forming systems: all this is given in the first edition of our book.

But the reader will also see how our efforts also indicated the deep limitations of Simon’s approximation, the estimate of errors, introduced by it in both scientific thinking and prediction: to this is devoted a particular publication of both authors, also mentioned in Chap. 14. It turned out that the development of the basic idea of Simon’s approximation also brought with it the further developments out and beyond of it, to which the efforts of the present authors lead as a logical consequence. And this consequence was that the second phenomenological stage in the theory of glass transition and in the description of glasses has to be the generic application to this problems of the following, the nonequilibrium stage of thermodynamics itself, of the development of thermodynamics, already several times mentioned in the present preface, into the thermodynamics of irreversible processes, as it was developed by scientists like De Donder, Prigogine, de Groot, and many others.

As indicated with the title of our book, our intention was and is also to continue the idea of another great scientist of mid twentieth century, Gustav Tammann, who proposed to treat glasses out of mysticism as a physical state, although as a particular physical state, and this was what also gave the title to his little famous booklet with the German title Der Glaszustand. We tried with the first edition of our
monograph to continue not only a tradition introduced by Tammann in the title of our book, but also to follow a remarkable idea formulated by this great scientist.

In adopting this idea and assuming irreversible thermodynamics to be the key, allowing one to open a new way of the description of glass transition and description of glasses, we had also to introduce into our book a generalized summary of essential basic thermodynamics in the form we thought that it is most convenient to be applied to glass science. It is introduced in the first chapters of the first edition of our book and gives not only essentials of thermodynamics, but also, what seemed to be even more necessary to the present authors, the direct applications of classical thermodynamics in the form of Simon’s approximations to vitreous states and the necessary preparation for the second step: to go beyond classical thermodynamics. From the point of view of classical thermodynamics the kinetics of nucleation, of crystallization, and of phase transitions in glasses were treated in great details. The strict employment of thermodynamics led us to a further development of Gibbs model of the thermodynamics of nucleation. In this respect, we would like to acknowledge the close cooperation, in particular, of V. V. Slezov, A. S. Abyzov (Kharkov, Ukraine), V. G. Baidakov, G. Sh. Boltachev (Yekaterinburg, Russia), V. M. Fokin (St. Petersburg, Russia), and E. D. Zanotto (Sao Carlos, Brazil). Treating both vitrification and stabilization of glasses and the crystallization of glass-forming systems strictly and consequently in the framework of thermodynamics – in both its classical and newer formulations – is one of the features, in which most probably our book differs from most textbooks and monographs devoted to glass science.

In trying to open thermodynamic thinking and application of thermodynamics to glasses even to beginners in glass science, we introduced in the first two chapters of the book a thermodynamic introduction beginning with the essentials of classical thermodynamics and continuing further on to what we thought was necessary for the next and decisive step of any-one interested in glass science, including the thermodynamics of nonequilibrium. This basic idea was noticed by our readers and, we may even say, appreciated by many of our colleagues. In Chap. 3 of our book moreover, a direct introduction is given into the thermodynamics of irreversible processes: at least into the essentials we considered necessary to understand vitreous state and vitrification from this enlarged standpoint of thermodynamics. In this way from a beginning with the essentials of glass science and irreversible thermodynamics as they are introduced in Chap. 2 of our book and in developing ideas and methods to the third chapter, the present authors also enlarged their own possibilities to treat and analyze vitrification in the specific features of thermodynamics of irreversible processes. Beginning in 1996, both authors made the necessary efforts to develop their ideas on glass science in connection with the basic principles of thermodynamics of irreversible processes.

It is also to be noted that the first edition of this book published in 1995 was born in two series of lectures on the fundamentals of glass science given by one of the present authors in a series of courses in Bulgarian universities (at the Assen Zlatarov Technical University in Bourgas, 1985–1995 in collaboration with Dr. B. Bogdanov) and then (in 1996–2002 at the Chemical Technical University
in Sofia with Dr. I. Gugov) and after that in a joint lecture course of the two present authors at the Physical Institute of Rostock University in Germany at the beginning of the 1990s. In 1996–1999, this course of lectures was continued by I. S. Gutzow in collaboration with Prof. L. D. Pye at the Alfred College of Glass and Ceramics of the State University of New York (USA) and in 1995 also at the Federal University of Sao Carlos in Brazil. In all these lecture courses, the thermodynamic accent was always of significance in order to bring glass science to students of both theoretical physics and in engineering chemistry and ceramic materials. The generalized treatment of glasses in terms of the thermodynamics of irreversible processes was initiated by the same author (I.S.G.) by a course he had to give as several lectures at a Black Sea conference on the theory of amorphous states and the structure of glasses held in the little town of Sozopol in 1996. A resume of his lectures was published as two overview contributions given as references in Chap. 14 of the present second edition. The title of one of these papers was formulated as *The generic phenomenology of glass formation*. This title was proposed by the conference proceedings editor, a well-known American colleague, Prof. P. Boolchand.

Of even greater significance in preparing several of the publications of both authors in employing thermodynamics of irreversible processes to describe glasses and glass transitions were the conferences and lecture courses organized by one of the present authors (J. W. P. Schmelzer) annually for more than 15 years, now, at the Bogoliubov Laboratory of Theoretical Physics of the Joint Institute for Nuclear Research in Dubna (Russia), under the title *Nucleation Theory and Applications*. The presence at these conferences and the benefit of discussions with our colleagues including outstanding well-known scientists like W. Ebeling, D. H. E. Gross, V. P. Skripov, V. V. Sle佐v, V. G. Baidakov, V. P. Koverda, A. M. Gusak, B. M. Smirnov, A. P. Grinin, A. K. Shchekin, G. E. Norman, G. T. Guria, R. Feistel, S. A. Kukushkin, V. S. Balizkij, and colleagues from the St. Petersburg glass school like I. G. Polyakova, V. M. Fokin, B. Z. Pezvner, V. K. Leko, L. Landa, and many others were of greatest significance because practically any new idea developed by the authors was first discussed and partly even published as preprints in the proceedings of these conferences (available as pdf files via Internet at http://theor.jinr.ru/meetings/2012/nta/) and then adopted and included in following scientific publications and in the present book. In fact, several of the considerations of both authors connected with the thermodynamics of glasses were initiated by their analysis of the most significant peculiarities of crystallization of glass-forming melts discussed in the course of these conferences. It is also a great pleasure to acknowledge the financial support from the DFG, the DAAD, the Heisenberg-Landau program of the BMBF, QSIL Langewiesen (Dr. F.-P. Ludwig), the Leibniz Institute for Tropospheric Research Leipzig (Dr. O. Hellmuth), the Russian Foundation for Basic Research, and other sponsors of our activities as well as the hospitality and support of the Joint Institute for Nuclear Research in Dubna, Russia (Dr. V. I. Zhuravlev, Mrs. G. G. Sandukovskaya, Mrs. E. N. Rusakovich). We would like to express here our particular gratitude to the DFG for long-standing financial support both of the stays of J. W. P. Schmelzer in Sofia and I. S. Gutzow in Germany. One
of the authors (J.W.P.S.) would like to express his deep gratitude to the Institute of Physical Chemistry in Sofia for long-standing hospitality and for electing him as an Institute Associate Member and to the Bulgarian Academy of Science for decorating him with the Marin Drinov Medal of Honour acknowledging the very fruitful cooperation over a period of more than three decades. The other author (I.S.G.) would like to express his deep gratitude to the Alexander von Humboldt Foundation for the Humboldt Research Prize 2002–2003 assigned to him and for the possibilities it opened to him for his work at German universities. Thanks are to be expressed as well to the same organization for the grant given to Dr. J. Möller for a stay in Sofia in 2005 allowing him to perform joint work with both authors at the Institute of Physical Chemistry of the BAS. This prize allowed also one of the authors to perform joint research with Prof. C. Ruessel at the Otto-Schott Institute of the Friedrich-Schiller University in Jena. In particular, it allowed I. Gutzow et al. to perform investigations with DARA in Cologne on crystallization experiments under cosmic conditions discussed in details in Chap. 14. Here particular thanks are to be expressed to DARA for the financial support for this cosmic project. Also of significance for the development of the thermodynamic aspects of glass science problems treatment were the three Glass and Entropy Workshops, organized in 2008, 2009, and 2012 by our colleagues L. Wondraczek and R. Conradt initiated by discussions at the 21st ICG Congress in Strasbourg in 2007. In these discussions, the significance of thermodynamic thinking was brought to its full development, especially when it turned out necessary to be used in analyzing and even in rejecting not sufficiently founded opinions. J.W.P.S. would like to express his particular gratitude to the highly interesting cooperation with BASF Ludwigshafen (Dr. H. Baumgartl) on technological problems of production of polymeric foams, to Dr. F.-P. Ludwig (QSIL Langewiesen) for long-standing scientific cooperation including the analysis of a variety of problems of the technology of silicate glass production, and to Dr. O. Hellmuth for the cooperation on different aspects of the physics of the atmosphere and the influence of phase formation processes on its dynamics.

The evolution of ideas themselves, the developing knowledge of the authors in cooperation and discussion with their protagonists or antagonist gave impetus to new developments: development new to both authors and to their colleagues in many parts of glass science. This development as it took place in the last 15 years is summarized here in Chap. 14 of the present second edition of our monograph. The first publications, in this new direction were a series of papers beginning in 2000 by one of the present authors and his Bulgarian colleagues and continued in collaboration of both present authors. In the framework of these first publications we have to mention our Bulgarian colleagues V. Yamakov, F. Babalievski, and D. Ilieva and in particular our American colleague, Prof. L. David Pye. In the following period of joint developments, we have especially to mention the contributions of J. Möller, B. Petroff, S. Todorova, and I. Avramov. In this time, we had to introduce into the treatment of vitrification one of the most specific notions of thermodynamic of irreversible processes: the entropy production accompanying any irreversible process. This analysis was then continued in a series of papers by J.W.P. Schmelzer
with his German colleagues from the Polymer Physics Laboratory of C. Schick in Rostock in cooperation with T. V. Tropin from Dubna, Russia, and then with R. Pascova and quite recently in application of thermodynamics of glasses to problems of electrochemistry with L. Wondraczek and N. Jordanov. Finally, we would like to acknowledge the support of A. S. Abyzov in the course of the preparation of the present book and to N. Jordanov for similar assistance and especially in writing of Chap. 14.

In this way, the present two authors hope to have initiated and brought to a new, higher level of understanding the analysis of vitrification and of the properties of glasses in the most natural way possible: in the framework of thermodynamics of irreversible processes. It turned out that the process of glass transition can be described in a generic way out of first principles of thermodynamics of irreversible processes without introducing additional approximations. For many years, the peculiarities of glass and especially the complicated nature of its thermodynamics led many authors into the belief that new and more new glassy models are necessary in order to describe glass and improve the level of its understanding. Our experience shows that in fact it is not the development of more and more new models but a better understanding of the existing sound thermodynamic basis in the form of the thermodynamics of irreversible processes which is of major significance in developing a new understanding of glass science.

For several years, we performed intensive work trying to reorganize our first monograph: we tried to add several new topics and to introduce new ideas and the concepts of the thermodynamics of irreversible processes in a more advanced form into the original structure of the first edition. The realization of this task turned out to be a very difficult problem not solved by the present authors. So we tried to bring to the attention of the devoted readers of our book on the thermodynamics and the kinetics of the vitreous state in its initial formulation, adding in Chap. 14 and in several footnotes a brief account of these new developments which followed since 1996 both from our own work and in the publications of colleagues who worked in the same field of science. We have tried to summarize also in our already-mentioned second monograph most of the ideas developed in the time 1996–2010.

We hope that this way of preparing the second edition of this monograph is the most appropriate one and that most colleagues, who would like to try to begin and continue study of glasses, would like to have the original form of our first book as an introduction into thermodynamics in its essentials and especially also the application of thermodynamics and kinetics to the processes of crystallization of glasses in the form as they are given in the first edition. So following this believe and the outspoken advise of several colleagues, we decided to prepare the second edition of our book preserving its original kernel, however, extending it in adding the following parts: (i) in Chap. 14, the development of the generic way of treating glasses and glass transition in the way this was done mainly by the present authors is reviewed briefly including also new developments in the theory of phase transformation processes in glass-forming systems. (ii) With footnotes, some necessary corrections and new developments are introduced which have become apparent 15 years after the first publication. (iii) The main text is reprinted in an widely identical form as in
the first edition except minor corrections, for example, of several misprints. (iv) In the second edition, we have provided our book with an index.

We hope that in such a combination the interested reader will find the optimal way to follow the developments as they have been initiated and performed by the present authors and may be even of help to find better ways of further developing the science of glass. In this way, we hope to bring to the attention of our colleagues interested in the theory and the application of glasses a book which can be used as a bridge between classical thermodynamics and the classical way of treatment of the theory of glasses in an approximative approach following the new ideas and possibilities opened by the thermodynamics of irreversible processes. This science in the opinion of the present authors is the only theory, which indicates new ways in which all these strange physical states denoted as vitreous or glassy states may be treated from a simple and sound theoretical standpoint. For many years, glass science is never any more the story about the Egyptian queen Hatseputh (1500 BC) and the glassy beads of her necklace nor the story of fine wine glasses and even not of optical glasses: it is now more and more the new material in sun-energy convertors, of glassy quick-dissolving medicines, of frozen-in life and anabiosis, and even of a variety of processes taking place in the universe. Time has come to understand that although glass is not the fourth state of matter as proclaimed by enthusiastic glass researchers of the 1920s, it is one of the most interesting physical states, in which matter can exist. We hope that the renewed second edition of our book will help both people, experienced in glass and its problems, and newcomers, even students in materials science, in physics and in physical chemistry, to learn something new about one of the oldest materials mankind has ever employed.

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