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Introduction

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The present book is devoted to the ways of formation, to the analysis of the properties and to the theoretical description of matter in a very particular state: in the vitreous state. In such a state, as it is usually assumed, amorphous solids may exist with a kinetically frozen-in, rigid structure and correspondingly frozen-in thermodynamic and mechanical properties. In technical applications and in every-day life as materials, in solid state physics, in scientific literature and also in the title of the present book these amorphous solids are called glasses. Glasses are formed in a process, which is also very particular in its physics, in its kinetics and thermodynamics, in the process of glass transition or vitrification. The reverse process is denoted as devitrification, and is frequently but not always accompanied by crystallization processes. Definitions of both these notions are given in this book, accounting for present-day results of structural analysis, statistical physics and especially of thermodynamics of glasses, since thermodynamics is the science that decides over the states of matter.

It turns out that many solids, even with a partly crystalline structure, behave in their properties and thermodynamic state-like glasses: such solids with a frozen-in defect crystalline structure (e.g., defect molecular crystals) are sometimes called glass-like, or even glassy crystals. It is shown in one of the following chapters, that highly oriented liquids, so-called liquid crystals, also form glasses, corresponding to the particular structure of the precursor liquid. Another very particular class of solids with usually crystalline structure but with glass-like magnetic properties are the spin glasses.

The process of glass transition has general, characteristic and remarkable features, which are observed not only in the vitrification of glass-forming melts and in other processes of glass formation to be discussed in details in the present book (e.g., vapor quenching in the formation of amorphous layers or electrolytic deposition of metallic alloy glasses), but also, according to some authors, in quite different events, for example, in cosmic processes. There are also many models in statistical physics, the solution of which leads to virtual systems with glass-like thermodynamic or kinetic properties; or on the contrary, to solutions of the theory developed,

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which against the expectations of their authors, are far from the behavior of real (or "common, molecular or laboratory") glasses.

Out of many possible real or imagined glassy or glass-like systems of different solids with amorphous or defect crystalline frozen-in structure, are the common glasses of every-day life, in particular the technical glasses, who give well-known and best studied examples of the process of glass transition and of the properties of vitreous states. Besides systems with inorganic composition (silicates, phosphates, halides, elemental glasses, etc.), what must also be included are the numerous representatives of organic chemistry (polymers, molecular glasses), aqueous solutions, metal alloys: practically representatives of any known structure and chemical composition. There are, as we have discussed in several publications, serious expectations, based on well-founded kinetic and structural criteria, that almost any substance could be vitrified at appropriately chosen conditions. These expectations are substantiated in our foregoing monograph [1] also devoted to the vitreous state.

However, the best known representatives of vitreous solids still remain the "common" inorganic glasses, which in their composition are oxides and especially silicates. The properties of these silicate, phosphate, borate, and so on, oxide glasses are summarized in a series of monographic reference books and the database organized by Mazurin and his collaborators [2, 3] discussed in detail in one of the chapters of the present book.

Silicate glasses belong with pottery, ceramics and bronze to the oldest materials employed by man. This early widespread application of glasses is in some respect also due to their broad distribution in nature. As an example, magmatic rocks can be mentioned, which to a large degree consists of vitreous silicates, or completely amorphous natural glasses such as obsidian or amber. It is well-known that the natural glass obsidian served as a material for the preparation of the first cutting tools of primitive men. Obsidian remained in the ancient cultures of Central America as the material for objects not only of art but also for the horrible ritual knives of the high priest of these Native American societies. Amber is most probably the first organic glass to be appreciated and used by mankind: impressive with both its beauty and for its unusual dielectric properties, known from ancient times in Greek natural philosophy.

The wide distribution of glasses in nature is not due to chance. The inner part of the Earth, characterized by very high values of pressure and temperature, is most probably itself an enormous reservoir of highly pressurized glass-like or glass-forming melts. Processes of crystallization and glass-formation connected with the eruption of volcanoes and the more or less abrupt cooling and even quenching processes of parts of this melt determine to a large degree the course of geological processes and the structure and properties of the lithosphere. Natural glasses are widespread not only on Earth but also on the Moon as it became evident from the investigation of samples of lunar rocks brought to Earth by the lunar expeditions in the mid-1970s.

Of particular interest is also the vitreous form of water. In this respect it is also worth mentioning that according to estimates made by some authors (see [4, 5]) water in the universe as a whole appears to be practically 99.9% in this vitreous form. In its vitreous form water is the main constituent of comets (of the comet "head"). At earth conditions, glassy water or aqueous solutions can be vitrified only by superfast quenching methods (described in its principle features in Chapter 2) or (as thin layers) by water vapor quenching on cold substrates (held below 120 K). On the possible role of vitreous water in the dissemination of life in the universe (the panspermian hypothesis of Hellenistic philosophy) see the considerations given below and in Chapter 8 of the present book.

The first applications of natural glasses in primitive societies for a limited number of purposes were followed by the beginning of glass production in Mesopotamia, Egypt and ancient Rome, by medieval European and Middle East glass-making and then by a long evolution to the modern glass industries and to glass science. From the point of view of the variety of properties of glasses and of the spectrum of possible applications, the significance of the vitreous state in its different forms in present-day technology and the technical importance of different glasses can hardly be estimated. The validity of this statement becomes evident if one tries to imagine for a while things surrounding us in every day life without the components made of vitreous materials. Technical glasses (like chemically resistant glasses) or optical glasses are well-known to everyone. Imagine, for example, a chemical plant, a physical laboratory, a car or a dwelling house without glasses or let us think about the importance of silicate glasses and optical glasses (with their complex compositions) in general for optical devices, and in particular, in microscopy and astronomy.

In addition to the classical oxide and particularly silicate glasses in the last decades of the twentieth century new structural and chemical classes of vitreous materials gained scientific and technical importance. They consist, as said at the beginning of this introduction, of substances of any class, or of mixtures and solutions of different substances, for which the possibility of existence in the vitreous state at these times was thought as being exotic or even impossible. One example in this respect are metallic glasses which are formed usually in processes, connected with hyper-quenching rates (e.g., in splat-cooling, to be discussed in Chapter 2) of metallic or metal-semi-metal alloy systems. Metallic glasses, first synthesized in the early 1960s, in a period of about ten to twenty years were transferred from a stage of exotic research to the stage of production and world-wide technological application. Similar examples are supplied by glassy polymers or vitreous carbon, glass-forming chalcogenide or glassy halide systems. The development of modern methods of information technology, for example, cable TV is also based on glass: on defect-free, extremely translucent glassy fibers with appropriate optical characteristics.

With the dramatic increase of the number of substances obtained in the vitreous state, the variety of properties and possible applications of glasses has also increased. Beyond the traditional applications in technology and science glassy materials are also used as substitutes for biological organs or tissues, for example, as prostheses (as vitreous carbon in heart transplants, as bio-glass ceramics in bone operations) and even in ophthalmology. Glass-forming aqueous solutions with biologically relevant compositions are used as a carrier medium for the freezing-in of biological tissues. Thus, it seems that even life can be frozen-in to a glass solving the problems of absolute anabiosis within the vitreous state. Life, frozen-in to a glass, supports the already mentioned idea of Hellenistic philosophy for the spreading of life from planet to planet. This ancient hypothesis, further developed at the beginning of the twentieth century by Arrhenius [6], was exploited not only in science fiction, but also in more or less, still fantastic proposals to guarantee immortality. The survival of animals (insects, reptilian, etc.) and of marine life at the polar regions of the Earth is also due to controlled crystallization or to the vitrification of cellular biological liquids [7–9]. Freezing-in of domestic animal sperms at liquid nitrogen temperatures to a glassy aqueous solution is for many years a known practice in present-day veterinary zoo-techniques. Porous silicate glasses are used to supply nutrient solutions to microbial populations and slowly soluble glasses containing exotic oxides are used as an ecologically compatible form of micro-element fertilization. These are only a few examples of the biological significance of vitreous materials.

Besides pure glasses, glass ceramics, like Pyroceram, Vitroceram, various sitals, that is, partially crystalline materials formed via the induced devitrification of glasses and glass-forming melts, are also gaining in importance in modern technology, architecture and in the immobilization of ecologically hazardous waste materials. A well-known example of the last mentioned application gives the vitrification of radioactive waste, originating from the nuclear fuel cycle and from nuclear weapons reprocessing. In this way dangerous radioactive materials are immobilized and stored as insoluble glasses, stable for millennia to come.

In glass-ceramic materials the transformation of the melt into the desired vitrocrystalline structure is initiated by a process of induced crystallization usually caused by the introduction of insoluble dopants (more or less active "crystallization cores") or of appropriate surfactants into the melt. As a result heterogeneous materials are formed in which the properties of both glasses and crystals are combined. In this way, an astonishing variety of new products with extreme properties and unusual possibilities of application is obtained. Classical enamels of every-day cooking ware, the mentioned glass-ceramic materials and so-called glass ceramic enamels for high temperature applications give additional examples in this sense. The physics and the physical chemistry of these materials, the kinetics and the various methods of their formation and the employment of glass ceramics, only mentioned here, is described in detail in many books and review articles and also the previous monograph of Gutzow and Schmelzer [1].

The widespread application and development of different vitreous materials and their production was connected with a thorough study of related scientific and technological aspects, resulting in the publication of a number of monographs, devoted to special classes of vitreous materials or special technological processes like the technology of silicate glasses, glassy polymers, metallic glasses, and so on. In these books specific properties of various vitreous materials are not only discussed in detail, but the attempt is also made to point out the fundamental properties and features which are common to all glasses, independent of the substance from which they are formed and the way they are produced. Latter topic is the focus of the present book. Therefore, particular attention is directed to the specification of the thermodynamic nature of any glass, regardless of its composition or other specific properties. Special glasses or the particular technologies connected with their production are discussed here only so far as it is desirable as an illustration of general statements or conclusions.

We are interested in the present book mainly in finding and describing in an appropriate way the common, general features of glasses. This refers to any of the following chapters and especially to Chapters 2, 3 and 4. There we have tried to elucidate the main, the most characteristic properties of glass-forming substances, common to all or at least to all real, physical glass-forming systems as yet known. In Chapter 2 the thermodynamically significant experimentally known properties of glasses are summarized and compared with the properties of the other forms of existence of matter. Glass transition is paralleled with phase transitions and the similarities and differences are reviewed. In Chapter 3 an attempt is made to correlate in the framework of a generic and generalized phenomenological approach both the kinetics of glass transition and its thermodynamic description. In the same chapter, following the same general approach, developed mainly by its authors in collaboration with several colleagues [1, 10–12], the thermodynamic nature of glasses is analyzed and defined. In doing so the general formulations of the thermodynamics of irreversible processes are applied and developed in a form, first proposed by De Donder [13] and Prigogine [14, 15], convenient to treat glasses as representatives of nonequilibrium systems with frozen-in structure. In Chapter 4 the same approach is used to analyze from a thermodynamic point of view the main kinetic characteristics of glasses: their rheology and viscous flow in particular. Particular emphasis is given in both chapters on the description of viscosity of nonequilibrium systems: here again a proposal by Prigogine [16] is followed in a generic approach, developed by Gutzow, Schmelzer *et al.* in [1, 17], as it follows from the derivations of Chapters 3 and 4. It is shown in Chapter 5 that many of the common properties of typical glasses are repeated or mimicked in a particular way by many other solids with frozen-in defect structures: even by those, which are crystalline.

A detailed analysis of the experimental results and their initial phenomenological interpretation, given in Chapter 2, leads to the conclusion that from a thermodynamic point of view glasses are frozen-in nonequilibrium systems. The detailed thermodynamic description of such states and their specific thermodynamic and kinetic properties are outlined in Chapters 3, 4 and 5. The respective discussion is based on the general postulates of thermodynamics of irreversible processes and, in particular, on the method of description of nonequilibrium states, developed by De Donder [13], Prigogine [14, 15], Glasstone, Laidler, and Eyring [18], Davies and Jones [19, 20] and many following authors as this is given in detail in Chapters 3, 4, 5, 8 and 9.

In Chapters 6 and 7, O.V. Mazurin and A.I. Priven explain and elucidate another problem of present-day glass science: which are the most reliable and convenient ways to collect and preserve, to calculate and to predict the most significant properties of single and multi-component glasses using existing experimental data, summarized in current literature and databases, as it is given the already cited series of reference monographs devoted mainly to silicate and other oxide glass-forming systems.

In Chapter 8 an attempt is made to summarize results on properties of glasses which from the standpoint of every day users are unexpected: their vapor pressure, solubility and electrochemistry. These properties not only illustrate some of the most significant features connected with the thermodynamic nature of glasses, but also give some indications of new and unexpected applications of the different substances in vitreous form. These applications include the usage of glasses as accumulators of hidden potential, of energy, and increased reaction power and (very unusual but possible, e.g., with metallic glasses) as electrochemical power sources. In this chapter also the possibilities of glassy states as a medium of frozen-in life and as promising soluble micro-fertilizers are discussed together with possible employment of soluble glasses in solving some medical problems.

Finally, in Chapter 9 the properties of glasses at extremely low temperatures are considered in detail. In doing so the authors of this chapter were mainly interested in elucidating a very general thermodynamic problem: what would be the most appropriate formulation of the third principle of thermodynamics for nonequilibrium systems, transferred into the vicinity of absolute zero of temperatures. The respective considerations require an analysis of the classical, sometimes already forgotten, formulations of this law as developed by the greatest representatives of classical thermodynamics at the beginning of the twentieth century, like Nernst, Einstein and Planck. Thus, Chapter 9 shows how glass science in its general formulations can give new visions in treating nonequilibrium systems, in general. Glasses, it turns out, are simply the best known representatives of the great class of systems in nonequilibrium. With Chapters 8 and 9 opening new horizons of applications of the vitreous states, the present book deviates from most existing monographs on glass science, treating glasses mostly in their common uses and classical ways of theoretical analysis.

The transformation of more and more substances into the frozen-in, nonequilibrium state of a glass is connected also with a substantial change in the meaning of the word "glass." Originally under the term glasses only amorphous (in the sense of nonstructured) frozen-in nonequilibrium systems were understood. At present every frozen-in nonequilibrium state (nonamorphous systems included) is denoted sometimes as a glass, for example, frozen-in crystals, crystalline materials with frozen-in magnetic disorder (spin glasses) and so on. The etymology of the word glass in its conventional use is given here in the concluding Chapter 10.

Despite its mentioned distinguishing features, the present book is in many respects a direct continuation and development of ideas formulated and exploited in several preceding books by the present authors which, to their satisfaction, were met with interest by the glass community. These publications are firstly the already mentioned collection of available data of Mazurin and colleagues on the properties of oxide glasses (and of silicate glasses in particular) [2, 3]. Secondly, the present book incorporates the concepts from the book by Gutzow and Schmelzer [1] in which the basic ideas on the phenomenology of glass transition, on simple glass models, on molecular statistics and on the crystallization of glass were summarized, corresponding to the state of knowledge at the time of its publication. In its phenomenological aspect this monograph by Gutzow and Schmelzer [1] is to a great extent based on an approximate way of treating the thermodynamics of glasses, proposed many years ago by Simon [21–23]. This fruitful but nevertheless approximate approach is brought in the mentioned monograph to its completion and many useful results are obtained in its framework. Moreover, ways are initiated there, based on the thermodynamics of irreversible processes, to develop a more general approach in the kinetics of glass transition and on the relaxation of glasses, which are developed here to a new level of understanding and application in Chapters 3 and 4. These new ideas are developed in the mentioned parts of the present book in the form of a new generic description on the kinetic processes, connected with glass formation and glass stabilization, as glass relaxation is also called. In doing so we have tried to take account of the whole development in this field of glass science, and especially in what was called in Russian literature the kinetic theory of glass transition; in fact, new thermodynamic foundations are given to this approach in both mentioned chapters of the present book. Moreover, out of it a full generic thermodynamic theory of glass transition is derived there in the frameworks of the thermodynamics of irreversible processes and the course of thermodynamic functions upon which glass transition is constructed. In treating technological problems in the already mentioned multi-volume monograph and reference book, compiled and edited by Mazurin *et al.* [2, 3], also opened are new, empirical and theoretical ways in predicting glass properties: by establishing connections, property vs. composition, to predict the properties of still not synthesized multi-component glasses out of their composition.

As it is seen from the above summary, the present book is directed towards the fundamental problems of glass science which are important for understanding the properties of glasses as a particular state of matter. In this discussion of the basic ideas concerning the vitreous state the historic course of their evolution is also briefly mentioned. In this discussion, a chronologically exact or comprehensive description is not attempted, but a characterization of the inner logics of the historical evolution, the interconnection of different ideas within it. This approach implies that in addition to the most fruitful concepts, which revealed themselves as real milestones in the evolution of glass science, proposals were also analyzed, which already at the time of their formulation or by the subsequent developments, were shown to be incorrect or even misleading, at least, as far as it is known today. It is the opinion of the authors that only by such an approach can a correct picture be given of the evolution of science as a struggle between different or even contradicting ideas. On the other hand, the detailed analysis of different proposals and the proof that some of them are not correct or even misleading is of an undoubted heuristic value. Such an approach can, the present authors hope, also prevent an over-enthusiasm with respect to insufficiently substantiated new or super-new hypotheses or to old, already refuted ideas presented in a modern form.

In the list of literature the interested reader may search for ideas and developments, results and interpretations, which could not be included in this volume. The present authors had to concentrate on those problems and solutions that formed the main roots of development of the knowledge of the vitreous state into a new well-founded science. As far as the present authors took an active part in this development, their results and publications are in many cases discussed in detail. In the theoretical interpretations in the present volume, as already mentioned, the phenomenological approach and the thorough comparison with experimental data is preferred: in this way, at least serious mistakes, common in the history of glass science will hopefully not be repeated. Where possible, as given in Chapters 6 and 7, a general survey of existing experimental data in glass science literature as a method of prediction and scientific prognosis and further development should be recommended. Several statistical model considerations are also introduced here in Chapters 3, 4, 8, and 9; although, from previous developments it is known that theoretical modeling can be sometimes dangerous. That is, in many cases it is not sufficiently evident, as to what extent inevitable approximations change the real picture of the systems investigated. In this sense phenomenology in many cases has been proven to be a more simple tool in glass science, especially when thermodynamics of irreversible processes is used: glasses are nonequilibrium systems and have to be treated accordingly, even classical thermodynamics may here also be misleading.

The present book represents again an attempt to take up Tammann's approach, made in his book *Der Glaszustand* [24] and repeated by two of the present authors in their preceding monograph [1]: to summarize the basic ideas of glass science, including the newest developments, remaining in the framework of only one volume. Many important topics, they initially wanted to include, could not be incorporated due to the lack of space. Other topics – new problems, theoretical approaches and complicated new attempts at a structural or general statistical description – seemed to us to be too complex to be included into one volume, directed not only to the well-established glass scientist, but also to the newcomers to a new and exponentially developing science. To simplify things, in many cases only reviews of new developments are given, in order to find a compromise. Hereby we tried to follow – hopefully successfully – the advice given by Einstein: "Everything should be done as simple as possible but not simpler."