MIRACLE OF REINFORCED STATES OF MATTER
Glasses: ancient and innovative materials for the third millennium[*]

J. Šesták

Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10, 16253 Praha and Institute of Fundamental Studies of the Charles University, Legerova 63, 11000 Praha Czech Republic

Abstract

Besides a short introduction to historical data on inorganic and polymeric glasses, some aspects of the glassy-state are analyzed: particularly, induced entropy changes, characteristics of the glass transformation and a novel anharmonicity vibrational approach. The horizons and scientific prospects for the nano- and non-crystalline states are discussed.

Introduction

Controlled combination of atoms and molecules in large segregations in ways that endow the resulting compounds with desired properties depends, not only on the chemical nature of atomic and molecular constituents, but also on the degree of their interactions, organization and reinforcement (freeze-in phenomena). The greatest flexibility for such combinations exists in the field of non-equilibrium states of solids called glasses. The traditional concept of what material science is, and what role it

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should play in solid-state chemistry and physics, is being reshaped by consideration of modern aspects of structure focused on ordering and/or disordering phenomena. Controlled, as well as unintentional, thermal treatment and analysis has been a unifying motive in the historical development of such materials and has played an essential role in the tailoring of the properties of innovative materials.

Besides its long-lasting status in the sphere of beauty [1–3], glass is a remarkable technical material [4], customarily made from the simplest and easily available raw inorganics. Mimicking evolution, however, new families of a wide variety of glasses have gradually appeared through human creativity, particularly during the last hundred years, where the process of rapid extraction of heat has led to successful quenching processes (restrained thermal treatments) [5, 6]. This has assisted physicists to prepare glassy-states from different sorts of inorganic materials, in comparison with the traditional chemical approach which sought only appropriate compositions that would vitrify under self-cooling.

Glasses exhibit a rather curious but apparent degree of similarity with biopolymers (genes) [7, 8]. Both are in a reinforced (thermodynamically unstable) state formed due to kinetic reasons, which exists until glasses transform into stable structures (crystals or liquids with lowest free energy), or biopolymers (occurring as parts of living organisms) stop their biological activity (life). Both glasses and biopolymers adapt to their environment and previous history and there is an almost limitless range of compositions of glasses and countless numbers of different living species, each family having particular molecular building blocks and structural rules (some compositional restrictions of glasses were gradually overcome). Although the origin of glass is lost in prehistoric obscurity, all imaginable glasses can be synthesized, thus making natural and manmade glasses indistinguishable. Another intriguing parallel can be drawn in the apparently spontaneous emergence of new phyla, or groups of species, involving both the (disordered) glasses and (highly ordered) biopolymers in often remarkable states existing outside of equilibrium. The structure and properties of these materials are understood and subjected to monitoring in ways that were unheard of decades ago, although such materials have been central to the growth, prosperity, security and quality of life of humans since the beginning of history. Despite all the similarities, one difference is fundamental: life forms are self-replicable and living organisms cannot be created in the laboratory yet. Attempts to produce even a simple protein macromolecule have not succeeded. All cells contains proteins and protein synthesis requires enzymes. So how biosynthesis could begin without enzymes is the question to be resolved. This dilemma may involve our better understanding of possible convergence of glass and genes assuming known bioactivity (of certain inorganic glasses capable of binding their specific compositions to living tissues [7, 8]). This is one of the most challenging fields of modern biochemistry and forms grounds for the concept that ordered proteins could be formed on such bioactive inorganic substrates. Nevertheless, the major difference should be remembered to be the lowered entropy content which is installed in living genes, while glasses have their higher entropy residue mechanically frozen in. We are, however, not going into more detail, because the goal of this survey is to focus attention on

more fundamental aspects of the understanding and progress made in the field of inorganic and partly polymeric glasses (and related structures) and the horizons for their future advancement.

Short history of inorganic glasses

The first natural glasses were formed as the earth cooled and, therefore, predate creation of living organisms by about 1.5 billion years. Such primordial glasses were limited in composition and versatility, as were the first primitive unicellular organisms (bacteria). However, some compositions (in an unstable state of glass) have survived unchanged for enormously long times (similarly to certain strains of bacteria). It is worth noting that the extent of natural glass on earth is in the range of a tenth of a percent, with the ratio of about 3450 minerals to 5 types of natural glass, while on the moon it is possible to exhibit a mere 60 minerals *vs*. 35 glasses, the frequency of glass deposits being at least one order of magnitude higher than that on the earth. As a matter of interest we can mention that Southern Bohemia is known as a tektite-strewn field, famous for deeply sculptured pieces of olive-green, usually rapidly frozen, droplets of meteoritic origin, called Moldavites [9] (Fig. 1).
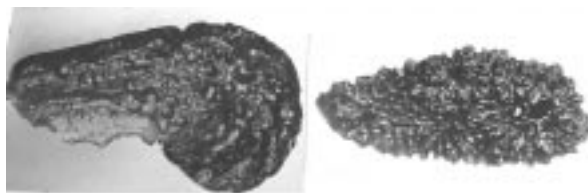

Fig. 1 Moldavites, greenish natural glasses named according to their deposits, located near the south part of the major Bohemian river Moldau (Vltava), length of each about 5 cm

The diversification of glasses has been known since humans learned how to control fire, roughly a few hundred thousand years ago. The first artificial glasses were synthesized unintentionally by the fortuitous smelting of sand and alkaline plant flux by fire about ten thousand years ago. Some glasses were created by accidental action of sparks and tektites (natural acidic silicate glasses [9] with a high melting point) were formed by terrestrial impact volcanism and have attracted the attention of men since prehistoric times, having been used as cutting instruments, amulets or cult objects. Manmade glasses passed through two general streams [10], one based on ancient Syria, where glass was made from sand, rich in shells (CaO), smelted with ash of desert plants (Na_2O) and often transported for final melting to Egypt. Similar compositions were later exploited in Rome, producing a rather stable glass to survive environmental corrosion, almost resembling today's table glasses. The second stream was based on glass batches enriched by PbO, due to additions of the mineral galenite. Such an easily melting composition was later renowned in old Russia (icons) and yet later rediscovered in medieval England. The middle European glass modifications, however, were never so fine and flexible as Roman (Venice) type glass, which was

more suitable for forming fantastically shaped vessels because it was rich in soda from sea plants. On the other hand, beech (and also less-suitable oak) wood used for firing and its refined ash, rich in lime and potash, common additives of chalk and the country's quality siliceous sand contributed to the greater purity of the famous Bohemian glass, which was mainly composed of potassium calcium silicate. Hard, clear glass which resembled natural rock crystal, generally called (Bohemian) mountain glass, was suitable for engraving, but distinctly corrosive due to too high a content of CaO and K_2O. It is worth noting that the consequential hollow glass of the 14th century already manifested a long-standing production tradition with its refined shapes and difficult and complicated hand-executed decorations. The most typical glass products of the Czech environment were flute-shaped glass beakers, tall slender goblets called the 'Bohemian type' (Fig. 2).

Fig. 2 Left – Flute-shaped glass of the so-called Bohemian type, with minor stuck-on decoration dating from about the 14th century; Right – Cut goblet made from Bohemian rock crystal (with slight ruby strings in the stem) engraved with the wine-picking motive (around 1700)

Several notable milestones of more modern science depended on the availability of glass as a preeminent choice of alchemists for their apparatus. Relatively unstable and fragile glass was always essential for many chemical operations in early times. Dissatisfied with the chemical durability of glass, glass properties were modified by adjusting the composition. This could not, however, have been done properly, because chemistry was still on a mystical basis and the techniques of analysis that would be needed did not exist. Important cornerstones were Galileo's work on the motion of planets, based on glass lenses in astronomical telescopes, as well as Newton's pioneering work in optics (1666) requiring, in addition, prisms and mirrors. Other basic investigations required glass apparatus to describe the properties of gases, introduce thermometry, barometry and to develop microscopy. The first reasonably-documented description of glass-making procedures is associated with the invention of lead glass around 1676. The most influential books appeared to be Neril's 'L'Arte Vetraria' (1612) and Kuncel's 'Ars Vitraria Experimentalis' (1679) which were translated into other languages (as well as many others such as the Ency-

clopedia in 1765, etc.). All of them remained, however, no more than recipe manuals. In the seventeenth century a proper understanding of heat was lacking. First only three degrees of heat sensed were recognized and heat was treated more as a kind of chemical element, even with a negative mass. From the work of the Bohemian educator, Comenius, up until the Scottish scientist, Black, temperature and heat became very slowly distinguished, so that melting, solidification and glass formation were not properly understood. The only important glass properties, well-defined and easily measurable, were then density and refractive index.

Since medieval times, manual skill allowed the making of window glass by the crown process (forming a shallow bowl and, after reheating, spinning to make it open into almost a flat circular disc) and by the cylinder process (blowing a cylinder, cutting off the ends and cracking it longitudinally) often mentioned as '*procede de Boheme*'.

One of the most significant scientific achievements was Griffith's theory of the strength of brittle materials (1920). X-ray diffraction analysis was a particularly exciting field having enormous impact on glass science in the first quarter of the century. It led Zachariasen to develop his principles on how bonding requirements were met, and nearest neighbor coordination maintained, without imposing an exact long-range order. Since the 1930s, regular conferences on oxide glasses have been accompanied by searches for glasses with properties not previously known or studied. This has resulted in the introduction of novel families of unconventional glasses. First to be mentioned are the non-oxide glasses of chalcogenides [11] which exhibit many general features shared with oxide glasses. Conferences on chalcogenide glasses were started in the fifties and the most widespread ones came later with the development of xerography, electrophography and lithography. Quite unexpected inorganic systems followed, of which halide and metallic glasses [12] are the most notable, with conferences specializing in metallic glasses starting in the sixties.

Halide glasses have potential applications as ultra low-loss optical fibers operating in the mid-IR and for non-linear optics, while 'metglasses' and, nowadays, nano-crystalline 'finemetals' have already found their place in various magnetic applications. Worth noting also is the preparation of glass-like carbon achieved by solid carbonization of thermosetting resins in the 1960s (once used for bio-inert implants) which appeared in the same year as the first Au–Si alloy glass. There was, however, an almost parallel development of individual descriptions of vitrification and crystallization, based on the theories of nucleation and crystal growth, which applied not only to oxide glasses [13, 14], but also to the frequently separately treated organic and polymeric glasses. Nowadays the theories have marched to unification [6, 15].

Material progress in terms of polymers

It is often noted that we are now in the epoch of polymers that has certainly had a rich history, too. Prehistoric men were probably first attracted by amber [16], a fossil resin produced in the Oligocene age by exudation from a now extinct species of pine. Although amber was rarely recognized as a plastic, it has roused both historical and ety-

mological interest. Its chemical nature is very complex and not fully elucidated. The largest surface deposits of these hydrocarbons, varying in the sizes of the molecules, have been located in Northern Alberta, where aboriginal people prized this gem material for many millennia and were, probably, the first who actively used the solid–liquid transition while heating tar sand for the purposes of impregnation. Another historically important natural material was shellac, a refined form of the secretion of the lac-insect parasitic on certain trees in India. The hand process for producing shellac has been used since ancient times and is carried on largely as a cottage industry. Thermally processed shellacs were greatly favored for (78 rev/min) gramophone records. Although ignored in the plastic literature, the bituminous compounds have still been of interest. Where the bitumens are associated with mineral matter, the mixture is referred to as native asphalts. The term is applied to petroleum distillation residues which are complex mixtures of paraffinic, aromatic and naphthenic hydrocarbons.

Most important, however, is natural rubber [17–19]. Latex was used by the South American Indians for long time before the arrival of the first European and was named Cau-Uchu which means 'crying wood'. If such a product is precipitated by formic acid, or heated on a fire, it converts to the state of an elastic liquid, characterized by high mobility of its chains. The material can, however, be stabilized in its shape by the process of vulcanization (introduced independently by Goodyear and by Hancock in 1844). Such a restriction of chain motions by extensive crosslinking provides the level of modulus characteristic of a glassy-state. On reacting rubber with melted sulfur, a rigid resin is formed, called ebonite (having up to 30% S) and a glass–rubber transition temperature, T_g, around 100°C. Distillation of latex was later shown to yield a pure liquid substance called isoprene which was also shown to be capable of polymerizing to form a synthetic resin (Williamson, 1880). Together with knowledge of latex balata (from Venezuela trees), latex provided the basis for massive production of polybutadiene-type resins at the begining of the 20th century. A similar extensive rise in the production of phenolic resins followed the 119 patents of Baekelend who invented phenol-formaldehyde plastics in 1907.

A similar resin, known as Gutta Percha [17], is a rigid crystalline substance at room temperature, with melting point of 60°C, although obtained from comparable latex of plants and their leaves grown in Malaysia. As an excellent insulator, it made the laying of the transatlantic undersea cable connection possible. Natural rubber (*cis*-1,4 polyisoprene) and Gutta Percha (*trans*-1,4 polyisoprene) are good examples of differences between the glassy and crystalline states of substances that have the same monomer as the basic structure backbone. Below the T_g of natural rubber (–78°C), both substances have similar values of modulus ($E > 10^9$ N m^{-2}). On the microlevel, natural rubber contains disoriented polyisoprene chains, while Gutta Percha contains an ordered (crystalline) chain structure capable of maintaining the modulus until 60°C. It follows that, for polymeric materials, the chain mobility on the microlevel seems be the major feature characterizing the solid and the liquid-states [20]. The rubber-like state is somehow equivalent to the liquid-state on the microlevel also with respect to the chain mobility. The liquid areas can also form

bridges between the rigid island, either for glassy or crystalline states, and the study of heterogeneity is important. From the point of view of organic chemists, the glassy-state is therefore considered in terms of both very high viscosity and elastic moduli. The individual particles forming the glassy rigid body are irregularly separated and long-range order is non-existent. The glassy state, however, may also exist at the level of microdomains combined either with nanocrystallites, liquids or with rubber-like states [21].

At the present time of Hi-Tech materials and technologies, glasses are usually formed by crosslinking of various monomers, often based on aromatic epoxies and aromatic hardeners. Methylene dianiline with vinylcyclohexane dioxide is employed for manufacturing of parts for jet fighters, and poly(ether ketone) has found application as high-performance wiring in aviation and computer industries, because it exhibits outstanding thermal stability amongst melt-processable thermoplastics (T_{melt} about 400°C). Other high-performance polymers are, for example, aromatic polysulphones which show exceptional resistance to creep, good rigidity, transparency and self-extinguishing characteristics, without any tendency to crystallize.

A very broad interplay of the properties of highly viscous crosslinked liquids, on one hand, and rigid glasses on the other hand, is illustrated in the development of contact lenses. The idea of correcting eye astigmatism was first mentioned in 1827 by the British physicist, Herschel, but was only realized in practice in 1887 by the eye-glass craftsman, Muller, using very well cut and polished pieces of inorganic glasses. The Czech physician, Teissler, replaced rigid oxide glass by a rubbery material based on celluloid foil as early as 1935. The major disadvantage, i.e., the difference between the mechanical properties of the lenses and the cornea, was not overcome until the 1952 invention of Wichterle, who proposed the use of hydrophilic gels to match, not only the mechanical properties of the cornea, but also to make a free exchange of biological liquids and oxygen possible. Trial materials were first prepared by radical polymerization of methacrylesters of ethylene glycol, yielding poly(2-hydroxyethyl methacrylate), abbreviated as poly(HEMA). This can easily become swollen with water, while remaining mechanically applicable. The preparation of optically well-defined lenses was, however, the major problem because of the difficulty of mechanical working. This was overcome by rotatory casting and the Czech patented process has been applied in various countries including the USA. Nowadays this type of material is used, not only for interocular lenses, but also for other organs such as blood vessels etc.

Entropy considerations

Let us reflect generally on the total entropy changes involved, assuming first-order transformations only and an uncomplicated system convenient for simple illustration. According to the third law of thermodynamics, when the temperature approaches absolute zero, entropy diminishes. However, it was experimentally shown that, for certain inorganic molecules, exemptions can exist for a particular modification, such as that for N_2O, which can have either $S=0$ or $S=5.76$ J K^{-1}, both at $T=0$ K. When, for example, ice is

heated, it first melts, then boils, and on further heating it provides steam. On the other hand, if we cool ice to absolute zero, where entropy is supposed to become zero, reaching an ideally ordered crystal with no thermal vibrations, its energy cannot be decreased by further withdrawal of heat. There, however, remains conspicuous information about its perfect structure, its occupation of space, and there is no theoretical reason why one may not supposedly assume yet a further 'decrease' of entropy by a certain hypothetical 'addition of spatial information', entering the strictly forbidden world of 'negentropy' [22, 23] so far familiar only for living organisms. This becomes intuitively apparent when one compares such a single crystal of ice with that of DNA. We can imagine that, at any comparable temperature below its melting or dissociation (including 0 K), the DNA will supposedly contain more information than simple ice. We can also visualize a force field which could 'freeze' the constituents to total immobility at higher temperatures. In fact, we can actually identify such a phenomenon when approximating an imaginary force field to hold atoms in a relatively immobile state at elevated temperatures. We can recall certain organic molecules in which the resonating 'pi' clouds of electrons act as an interatomic force stabilizing the positions of atoms. The best examples, however, can be met in all biological systems where, for example, the heat is absorbed not merely to provide energy, but to maintain a stable temperature so as to diminish externally induced entropy changes. Whether looking at DNA molecules and related genetic or metabolic systems, cellular organization, the evolution of organisms, or ecosystems, the process is the same. There is an installed modification of entropy reduction by 'inserting information' as the simple systems become more complex and differentiated, ordered and integrated, both within the internal organization and with the environment outside the system, evolving itself to become thermodynamically increasingly improbable.

The difference in entropy between a perfect crystal of ice at 0 K (S=0), and its vapour-state (S_{vap}) at the boiling point (373 K) is about 200 J K^{-1} mol^{-1} of H_2O. Using the relationship between information and entropy (and Boltzmann's constant k=1.38·10^{-23} J K^{-1}) we can obtain I=I_o exp(–1.45·10)^{25} or, in the binary base, I=I_o 2–(2.1·10)^{25}. (Note that the increase in entropy is shown by a negative sign in the exponent indicating a loss of information.) Because the exponent is to the base 2, we can assume that this exponent may be stated as a bit and then, by contrast, the information needed to organize a mole of steam into a perfect crystal of ice would require an input of 10^{25} bits, or an average of about 35 bits per single molecule. It covers, however, a complicated process of trapping gaseous molecules existing in a 'cloud' state by means of a complex arrangement of electric and magnetic fields. The randomly moving molecules become fixed by the force fields into a regular array. This is a general characteristic for formation of the crystalline state and there is a spectrum of crystalline states, ranging from a powder up to a perfect crystal, usually classified by their X-ray diffraction patterns.

Biological systems also fit into the category of order/disorder transformations which are characteristic of life and involve the equivalent of nucleation of DNA within a cell. The growth of any organic nuclei is metabolic, interstitial and extremely complex [24, 25]. There are 21 amino acids which form proteins. Nucleic acids have only four base-pairs that store genetic information via DNA, with two additional

pairs to transfer information via RNA. The self-assembly of these building blocks into a myriad of structures follows stringent rules and results in species as diverse as man and amoebas. The sequences of base pairs in the double helical structure of DNA provide the detailed information for replicating the organism, as well as maintaining its vitality. We can envisage that such a complicated structure, thermodynamically as improbable as a perfect crystal at absolute zero, can be created to exist at room temperature in the form of a perfectly organized organic crystal. Restricting our protein to being composed of the 21 essential amino acids only, we arrive at 21^{200} possible primary structures. This is equivalent in binary terms to approximately 878 bits per molecule. (In comparison, if language consisted of only ten-letter words, the total vocabulary available would amount to 26^{10}, requiring a mere 47 bits per word.) The entropy change for denaturation of a molecule of enzyme from biologically active to inactive states can also be measured and involves about 900 J K^{-1}. The exponent of the information ratio can be interpreted again to represent an information change of 155 bits per molecule. If these assumptions concerning information are correct, then the lost bits per molecule, when a perfect ice crystal is vaporized (=35), or when a trypsin molecule is inactivated (=155), show the different levels of entropy involvement. In addition to destructive denaturation, there is considerable biological interest in transitions. Several conformations of DNA, other than the classical double helical forms, exist: for example, the right-handed B-DNA and the left-handed Z-DNA. Transitions are dependent on temperature, ionic conditions (heavy metals), non-aqueous solvents and the presence of peptide or other ligands. The transition enthalpy for one mole of the base pair may vary from -4.8 kJ mol^{-1} (so-called 'entropy driven') up to $+8.4$ kJ mol^{-1} (in the presence of Mg^{2+}). This gives, not only an approximate length of a cooperative unit of 110 base pairs (at $\Delta H = -530$ kJ mol^{-1}), but also shows the important variability in the order of these transitions.

What is the glass transition?

Any of the above mentioned biological processes aims to gain negentropy to enable ordering outside of equilibrium. When dealing with glasses, however, a discrete part of the disorder is supposed to be mechanically preserved by a temperature imposed halt (entropy freeze-in) of constituent motion (e.g. viscosity, molecular rotations). According to some scientists, the explanation of all phenomena associated with such an enforced (second-order-like) transformation, is one of the most necessary tasks of modern physics of fluids and solids. Consensus in the terminology has not yet been reached and there are inconsistent meanings for 'glassy-state' and (routinely synonymous) 'amorphous state' in relation to solids. The latter is frequently employed by physicists to describe particular materials as highly non-equilibrated structures of quenched metals and semiconductors, while the 'glassy-state' is preferred by chemists in the traditional field of self-cooled silicates (and related oxide and other anionic melts). The terms can be better distinguished by recognizing that amorphous solids are often prepared by any generalized process of chemical and/or physical disordering (to exhibit generally an overlap of crystallization with the glass transformation).

This is somewhat different from the 'thermodynamically better characterizable state' of glasses [26], which is only attainable by the repeatable process of vitrification through the (often rapid) cooling of the liquid. This state should always be accompanied by a more-or-less discriminative temperature effect, called the glass transformation region, T_g, which is thus assumed to be a general characteristic of the glassy-state. The physical appearance of a (thermodynamically unstable) glassy and/or amorphous solid looks, however, more stable than that of an (thermodynamically metastable) undercooled liquid, the latter being more instantly convertible to the nearest stable state of crystalline solid, by a slight action to surmount the energy barrier to nucleation, than a rigid, extremely viscous glass.

The term 'solid' can also be discussed in relation to the term 'vitroids' [15, 26, 27] within the framework of rheology. This latter term would be more appropriate for glass because a vitroid changes with time and the observation time is involved in detecting the extent of change. In this light a Deborah number [28] is sometime quoted to express the ratio between the time of glass relaxation and that of its observation (recalling the prophetess Deborah's song 'the mountains flowed before the Lord').

Three types of glasses [29] can be distinguished by their precursor matter and ranked into glassy liquids, glassy (molecular) crystals and glassy liquid crystals, characterized by their own transformation regions related to dissipation of a certain 'freedom' of constituent motion. In this view, amorphous solids actually belong to a fourth limiting case, which depends on the execution of the crystal disordering process itself [15] (intensive milling, etc.). In this category we can also consider the formation of low-dimensional structures, submicron colloids and sol-gels, the latter being subject to yet further classification due to their habitual inability to clearly involve the glass transformation phenomenon. The viscosity of liquid can be regarded as a measure of the relation between the thermal energy available at a given temperature and the strength of the forces pulling the species together and restructuring their position to a given volume within which molecular rearrangement can occur. The possible rate of these rearrangements rapidly decreases with decreasing volume within which the species are packed. The volume is determined by the strength of the attractive forces and reflected in the characteristic temperatures (melting, critical points, etc.). The more strongly the components of the mixture interact, the more rapidly the freezing point of the solvent is depressed and the viscosity is increased, consequently slowing and perturbing nucleation [26]. These effects should not, however, be strong enough to generate a new competing crystalline phase. The famous Zachariesen rules can now be understood as predicting low melting points relative to the forces acting between species (although some newly developed glasses may violate these predictions).

Let us make some energy considerations for inorganic mixtures. At the melting point the liquid and the solid have equal Gibbs energies, but differ in their enthalpy and entropy contents. Upon cooling below the melting point, the entropy of the undercooled liquid decreases more rapidly than that of a stable solid. Examining these different rates of entropy loss, we can determine a point where the entire entropy of melting would be diminished, resulting in the entropy of both phases becom-

ing identical at a temperature, called the 'pseudocritical' temperature, T_o, still above absolute zero [30]. The liquid loses entropy at a faster rate than the solid and, if the liquid maintains configurational equilibrium on very slow cooling to the region where it attains high viscosity, it would reach a lower entropy than the solid. Such a state, however, is unattainable and the equilibrium-like liquid must therefore transform into a rigid glass in what resembles a second-order transformation. This critical role of entropy is not always sufficiently understood because such a prior intersection by the liquid vitrification, where the heat capacity of the liquid changes abruptly to a value close to that of a corresponding solid, preserves the excess entropy characteristic of the glassy state alone. However, an unsolved question remains as to what would happen if such an iso-entropic temperature of the so-called ideal glass transformation were to be attained by a hypothetical infinitesimally slow cooling rate (thereby avoiding the occurrence of the irreversible freeze-in). Although it is an imagination game, there would appear to be a kind of higher-order transition possible where the heat capacity of the undercooled liquid changes to that of the congruous stable crystalline solid and this could be regarded as an additional 'state of matter'.

Anharmonicity vibrational approach

Correlations between the characteristic temperatures and glassforming ability have been anticipated theoretically in the form of reduced quantities (r). A simple ratio between T_g and T_{melt} (=T_{gr}) should hold as approximately 2/3, but could fall as low as 1/2 [26, 27] and the ratio of T_o/T_{melt} (=T_{or}) can behave similarly. Assuming hypothetically that the entropy difference [31] frozen-in due to vitrification at T_g is about 1/3, then we can estimate further apparent changes (e.g. the reduced C_{pr} should be zero at T_{or}=0, but should rise to the range from 1.65 to 0.96 for T_{gr} falling between 2/3 and 1/2). Such observations evidently stem from overemphasis of the significance of the configurational and/or conformational part of entropy [32, 33] in the equation $S=k\ln W_{conf}+k\ln W_{therm}$ where k stands for the Boltzmann constant and W for the number for possible arrangements. At the moment of glass transformation, one can either assume that W_{conf} becomes equal to unity (S=0, because only one arrangement is available due to the already fixed solid-state) or admit that, even if the rigid state exists, there are still more ways how to realize the inherent species disordering (as experimentally proved in studies on amorphous silicon or gels, where S>0). Although the first approach has recently been more widely accepted, it is still a matter of instinctive perception that some residual entropy must be accounted for as a consequence of the freeze-in phenomena. It is a future task for thermal analysis and calorimetry, as well as for deeper thermodynamic and theoretical authentication.

A simple model of T_g was described by the statistical mechanics of a set of non-interacting particles [34], each of them being able to assume either of two energy levels under consideration. T_g was also assumed to be a result of increasing cluster-size, where the apparent surface-to-volume ratio involved means that the cluster interior is ordered, while the surface layers remain disordered. The once popular 'hole theory' of the liquid-state [35, 36] was used to elucidate glass-formation: a quasi-crystalline lattice with a considerable fraction of vacant sites or holes was imagined and the number of holes

was taken to be a function of temperature. Hole theory has been neglected but was recently restored in the anharmonicity vibrational approach.

In the theory by Hlaváček [37–39], it is supposed that the glass transition is connected with the release of motion of monomer (or dimer) units in the rotational sense as, for example, the spinning of a benzene ring around the vinyl group in a polystyrene chain, or the diffusional action in inorganic glasses when the liberation of the substructure of SiO_4 tetrahedra can occur. As shown above, the explanation of T_g was for a long time presumed to be mainly related to the relationship of entropy to $\ln W_{conf}$. It is necessary to concentrate our effort on the clarification of the glass transition through the anharmonic vibrations and volume growth, assuming that S is related only to $\ln W_{therm}$. Let us thus presuppose an intrinsic, isolated and non-linear oscillator which can reveal the double frequencies and pulses. If the serial oscillators can individually interact on similar frequencies, then the particular particles can undergo a discontinuity in amplitudes (so-called amplitude jumps). Related to a liquid-state, such an amplitude jump of a monomer/dimer unit would push aside the particles in its vicinity forming a vacancy space (hole). In practice the enlargement of the amplitude can be detected by means of neutron scattering [40] which can provide the information about the average vibrational amplitude (*cf.* the Debye–Waller factor).

Occasional misapprehensions have their source in disregarding a proper definition of thermal expansion, α, known through traditional studies in solid-state physics. The so-called Kauzman paradox [30] of negative entropy (the entropy crisis) can thus never occur, because one part of the configurational entropy, S_{conf}, would just disappear. For polymers, the value of the heat capacity, c_p, per atom is approximately k or $2k$ and forms a sort of analogy to the Dulong–Petit rule for metals. The potential valley, in which the individual particle is supposed to undergo a vibrational motion, can be written in the form of a second-order differential equation [37–39] and this type of potential valley is generally considered in the basic physics of inorganic glasses. Various authors do not consider, however, any possible interactions of particles with the particles in the neighbourhood. Such interactions with a nearby resident can bring the isolated particle to a completely different vibrational level, in comparison with that if the particle is left isolated and it can become associated with a different anharmonicity level. Such a non-linearity [39] can also be taken into account through the variation of coefficients of the differential equation under the above considerations. By using mathematical manipulations [38], the non-linear system of the second-order differential equation can be turned into two separate differential equations of the first-order and, subsequently, even the time dependence can be eliminated. Neutron scattering data [41] present the most convincing evidence of the average amplitude rise in the vicinity of T_g. The average amplitude of vibrations starts to rise slowly and, at the so-called crossover temperature ($\approx 1.2\ T_g$), a constant slope of the average amplitude rise is established. Then we can assume that the vacancies are created in the liquid matrix through a high amplitude motion of the particles. In such a case, the vibrating particle is capable of pushing aside the nearest neighbouring particles, as experimentally evidenced for *cis*-1,4-poly(butadiene) [42].

The basic conclusion of this theory [37–39] is that the amplitude change would play the governing role in the definition of a liquid-state and in its transition into the solid or the glassy-state. It is assumed that voids are created in the liquid matrix through the high amplitude motion of the particles later responsible for liquid/solid volume enlargements. These expansions can proceed either through continuous changes, or through a sharp discontinuity. In such a way, the non-linear, mutually interactive, system of oscillators can successfully cope with first-order, as well as with second-order, transitions.

The science and horizons of nano- and non-crystalline states

Yet further study [43] should be directed to ascertain the near-glass-transformation and pseudo-glass-transformation processes, in order to study intermediate states between amorphous and glassy solids in the sub-glass transformation region. Such states include order/disorder changes of deposited tetrahedral and amorphous carbon, and pronounced short and medium ordering in as-quenched and amorphised alloys. Progress in the study of the vibrational states of silicon in the crystalline and amorphous forms, as well as the associated void formation, is important for a better understanding of the higher densities of the amorphous forms. It would also be of value to determine the kinetics of valence alternating reactions (which effect the whole electronic system) in which the local bonding configuration of the dopants and defect sites is changed. As already mentioned, neutron scattering data can present the most convincing evidence of the average amplitude of a particle's vibrations, which start to rise slowly until the discontinuity at the melting point. Inelastic neutron scattering can also be of assistance in observing the nature of hydrogenated amorphous silicon when investigating, e.g., the bond type (so far single, double, but not triple) of hydrogenated and deuterated samples, as well as the effect of hydroxylation. An attempt at forming a nano-crystalline theory of photoluminescence is also foreseen as being a guide to technologists in preparing a comparable material by controlled nucleation of laser glazed surfaces, or even sol-gel precursor samples. There is hope for tailoring multilayer silicon-silica sandwiches instead of using conventional electrolysis by discharge of high voltages.

Interest is expected to continue in the study of the intermediate states between glass, liquid and crystal, i.e., the architecture of ordered crystallites at a nanocrystalline scale, relevant thus to the medium-range order that exists in the glassy-state (and which likely serve as prenucleation stages in generalized precursor liquids). Such studies can be continued using anomalous small/wide angle X-ray diffraction (ASAXS and AWAXS) and NMR for insight into the medium-range ordering and microscopic mechanism of diffusion and viscous flow in precursor melts. This could provide a better understanding of the bonds between cations and anions. The spectroscopy of substructures (using the still traditional concept of bridging, half- and non-bridging oxygen) could be used, for example, in closer analysis of the background of bioactivity, or the interaction of metallic and metalloid species in metglasses, to possibly explain the role of thermal history, recreated medium-range

order and the effects of modifying admixtures. The assistance of theoretical treatises, based on classical molecular dynamics and dynamic stimulation of electronic ground states and of topological restructuring (low-temperature annealing process), will remain inevitable (ab-initio molecular dynamic technique, reverse Monte Carlo, etc.).

For successful tailoring [44] of magnetic as well as of mechanical, ferroelectric and dielectric properties, attention needs to be paid again to the medium-ordering states, because, for example, the extent of magnetic exchange interactions is effective across a given width of magnetic domain walls, and the disordered nano-crystallites of a subcritical domain size ('finemetals') would thus appear as magnetically disordered in a similar way to truly non-crystalline yet classical glasses ('metglasses'). It may similarly bring new dimensions to non-linear optoelectronics, where non-crystalline waveguides can eventually play an important role in infrared optics. Silica glass fibers alone can cause frequency doubling of infrared laser beams, suggesting that even non-crystalline solids can have large second-order susceptibilities. Such oxide glasses can also serve as useful transparent matrices for semiconductor nanocrystallites to form nanocomposites (formerly known as colloids, e.g., ruby glass) with large third-order susceptibilities. Controlled uniform size distribution of such ('quantum') dots is needed for non-linear devices and soliton switching, as well as for waveguide lasers, while non-uniformity is required in applications for optical data storage. Oxide gels and organically modified silicate gels ('ormosils') can also serve as hosts for such semiconductor nano-crystallites, as well as for other various inorganics and polymers. Submicron-sized halides in composite glassy electrolytes can essentially increase ionic conductivity, and nanometric ('pinning') centers improve superconductivity of complex cuprates. Nano-crystallization of porous silicon can play an important role in the better management of photoluminiscence. The separating interfaces of silicon grains were recently shown to be responsible for the blue photoluminescence. The quality was dependent on the nanosized separating layers which remain, according to the early studies carried out on inorganic and organic silanes.

In the important area of superalloys, we can briefly cite the importance of inhibition of any subcritical formation of nuclei. Similar considerations apply to embryos in such a diverse spheres as growth of viruses and/or disease faults (cancer) in preventive medicine, as well as creation of smog, rain, snow in environmental sciences. Self-protection of plants *vs.* freezing of aqueous low molecular mass carbohydrates (sugar) solutions also belongs to this category and is accomplished by increasing their body's liquid supersaturation to high viscosity which is then capable of undergoing vitrification [45]. Formation of a glassy (freeze-concentrated) phase may thus greatly improve the stability of frozen food [6] and is equally important in the cryopreservation of human implants in liquid nitrogen, and for shelf-life in general. Stability can be improved by the addition of cryoprotectors to avoid damage caused by both inappropriate cooling (at slow rates, cells can be killed by too high a salt concentration, owing to intracellular water loss as a result of osmosis and, at fast rates, cells can be destroyed by intracellular ice formation due to insufficient water outflow), or the undesirable phase separation of lipids and proteins in membranes (protecting their mesomorphic liquid-crystalline state which is capable of commencing a glass transition).

Biological materials from both human and nonhuman synthetic sources have medical applications. These include processed tissue from porcine heart valves, bovine carotid arteries, human umbilical veins, hyaluronic acid or chitosans, and are complemented by wide range of synthetic non-degradable, bioabsorbable and soluble polymers which yet require deeper study of the effects of enzymes and other biologically active materials, absorbability, degradability and degradation products. Such studies are equally important for inorganic metals, ceramics and glasses that exhibit some phenomena which meet the criteria for biomedical use. Their use introduce additional questions of electrochemical corrosion, durability of passive layers and their self-production on certain surfaces (growth of TiO_2 layers capable of biocompatibility), ability to elicit immune and hypersensitive reactions, interactions with biological pathways, processing and sterilization on biodegradation, or self-sterilization effects (TiO_2-treated surfaces under ultraviolet light). Another impressing sphere could be found in substituting attempts to the courageous replacement the eye retina by amorphous silicon chips as an 'active' inorganic implant.

Order/disorder phenomena in systems with lower dimensions are another separate and emerging category, which provides new boundary problems, such as nanometer range phase separation in the thin amorphous films prepared by CVD, as is known, for example, for germanium. It also touches upon non-stoichiometric semiconductors prepared via non-equilibrium MBE (molecular beam epitaxy) or MOCVD (metal-organic vapor phase epitaxy). Such a matrix can be generally understood as being a submerged disordered system of defects with nano-crystalline dimensions. When one characteristic dimension of a system is comparable with the electron wavelength, the quantum electron phenomena (i.e. dimensional absence of electron resistance) become of importance and are known as quantum wells, wires and/or dots. If for an appropriate thickness of a semiconductor layer, the disorder of the interface is controlled by remote doping, a high-mobility transistor function can

Fig. 3 Left – Gel eye-lenses, invented and developed in the former Czechoslovakia and produced by the ophthalmological center of the Prague Institute for Macromolecular Chemistry (Czech Academy of Sciences); Right – Endosteel dental implants manufactured from the biocompatible Ti_6Al_4V alloy, coated either with a titanium oxide microsurface, or with a thick layer of white hydroxyapatite (developed by the Prague Glass and Ceramic Laboratory, LASAK, courtesy of Prof. Z. Strnad)

be achieved. Quantum dots can also be conventionally formed by dispersion in a suitable matrix. Their optimum size can be estimated on the basis of the ratio of the material permittivity to the effective mass. Such a field, apparently remote from a traditional glass framework, may become a boundary area for theoreticians when the assumption is made that, even during very slow cooling of a single crystal, non-equilibrium and relatively large-scale fluctuations can be created. Even such highly ordered structures (with a low concentration of dopants) can show localization that is somewhat comparable with the modulated structures studied in non-crystalline materials (Fig. 4).
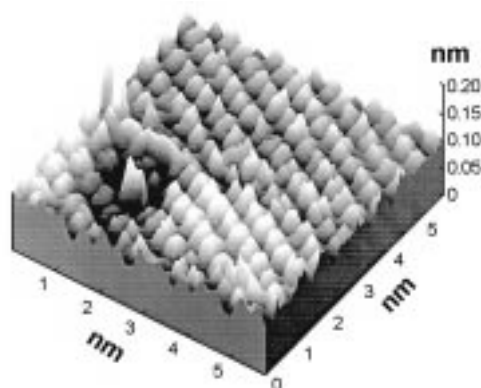

Fig. 4 The STM (scanning tunneling microscopy) image of the As sublattice in the (110) surface of a GaAs single crystal (Molecular beam epitaxy done and scanned at the Institute of Physics, courtesy of Dr. O. Pacherova). This is an example of the low-dimensional case of disorder-in-order, showing the single Si dopant atom sitting in the Ga site (see left corner)

The functional utility of such newly ranked materials may not be immediately appreciated before their properties are adequately characterized. Already common rapid solidification has played a key role in the discovery of quasicrystals, a class of materials neither exactly crystalline nor non-crystalline, where the symmetry of the order is not consistent with the heretofore accepted rules defining the allowable symmetries of crystals. This has led to an ongoing re-examination of the basic principles of crystallography, a science that now will have to be reformulated in a more general framework, not knowing yet whether these new phases will have interesting and useful properties. Closely related are stereochemical models, where so-called order within disorder is a reliable approach when considering modulus as a probable measure of structural order, thus questioning the classical models of crystallography *vs*. non-crystallographic disorder.

Conclusions

Breakthroughs, such as the recent discovery of the Hall quantum effect, or high-temperature superconductivity, cannot be predicted or planned for the next millennium, and the case is similar for prospects of the above discussed branches of material science of glasses related to non-crystalline and low-dimensional structures. In spite of that, conventional, and also non-traditional, thermal treatment and analysis will remain a useful tool to continue development successfully. This can be done, for example, by advanced laser surface glazing, so as to tailor thin glassy layers that improve the properties of materials, or by studying intimate surface structures by such a unique simultaneous TA technique as atomic force microscopy fitted with an ultra-miniature temperature probe.

Understanding the mechanisms underlying the mystery of order-disorder transitions from non-living to living offers hope for prolonging the quality of life by, e.g., helping to design therapeutic treatments for diseases of the skeletal system, or, perhaps, even dietary supplements which will inhibit the onset of diseases. An important step is seen in the ostogenic properties of the bioactive glasses capable of releasing soluble hydrated silicon, which can activate bone cells to produce growth factors. Formation of ordered proteins and DNA structures on inorganic bioactive substrates cannot be solved by mere entropy concepts, but such ideas may indicate possible mechanistic solutions to the order-disorder paradox of life [46]. For example, hydrated three-membered silica rings can be easily formed on activated silica surfaces (fractures or bio-stimulated) creating penta-coordinated silica atoms in a metastable transition state due to an amino acid interaction with a trisiloxane ring. Such a Si–OH complex can act like an inorganic enzyme by providing a favorable reaction pathway for polypeptide synthesis [47].

Besides its firm, long-lasting position in the world of elegance, glass was gradually put to practical use in chemistry as containers, or in physics as insulators. Yet, half a century ago, nobody would have assumed that metals could be vitrified, chalcogenide glasses be used for semiconductor devices, or that artificial glass-ceramic materials would not provoke antigenic rejection responses. The transparency of silica glass improved only slowly over centuries, until studies on optical fibers were begun in earnest. The transparency then increased by orders of magnitude within just a few years. The traditional scope of oxide, chalcogenide, metallic and halide glasses yet owes many answers to the question 'why?', e.g., UV-illuminated TiO_2 layers can exhibit antibacterial effects or glassy beryllium or MoRePB-based glasses can display superconductivity, etc. In this light, glass is surely a fascinating state of matter although not yet fully understood, thus still leaving space for our followers and their further research, as well as for creative hypotheses. It is clear that beside the traditional artistic magnificence and high technical usefulness, glass has definitely gained its scientific beauty, too.

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Many individuals played an essential and unforgettable role in giving glass its pronounced charm and deeper technical importance. Among many others, let us mention the late Emeritus Professor Norbert J. Kreidl, Austrian born (1904) and of pre-war Czechoslovakian origin, who lived in the US until his death in 1994, and gave to both glass science and human relations a desired new dimension. He also passed his very important messages to many of us through his constant effort over many years to find and motivate glass scientists young and old. This article has been written under the financial support of grants agencies of the Czech Republic and the author is indebted to Professor Michael E. Brown (Rhodes University, Grahamstown, South Africa) for his comments and critical reading of the manuscript. As well as backing by the TC7 committee of ICG.

Prof. Norbert J. Kreidl (middle) with his former postdoctorants (UMR 1970), i.e., from left: Dr. Peter C. Schultz (President, Heraeus Amersil, Buford, GA), Prof. J. Šesták (Vice Director, Institute of Fundamental Studies of the Charles University) and Dr. Edward N. Boulos (Head Scientists of Glass Division, Ford, Dearborn, MI) celebrating the Kreidl's nineties during the Kreidl's Symposium on the Present State and Future Prospect of Glass Science and Technology (Lichstein 1994)

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