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Advancing glasses through fundamental research

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Abstract

Fundamental research is critical for enabling future breakthroughs in glass science and technology. This is especially true as we approach a new decade of glass research, when addressing technological challenges will require an unprecedented knowledge of structure–property relationships and of the thermodynamics and kinetics of the glassy state. Proper understanding of these issues can be gained only through advances in our knowledge of the physics and chemistry of the glassy state.

Recent advances in modeling and simulation have enabled researchers to study glass physics and chemistry at the atomic level. Molecular dynamics and Monte Carlo simulations have proved invaluable for understanding the relationships between glass structure and properties. More recently, a master equation approach has been applied in the energy landscape framework to allow for direct simulation of glass transition range behavior on a laboratory time scale.

Furthermore, recent experimental studies have led to a great growth in our understanding of pressure effects in glass. In particular, distinct types of glassy phases can be produced using the same composition but different pressure conditions. This effect, dubbed "polyamorphism," has provided a new depth to our understanding of the thermodynamics and statistical mechanics of glass.

Keywords: Glass; Modeling; Glass transition; Pressure

1. Introduction

In 1995, Nobel laureate Philip W. Anderson (Nobel prize in physics, 1977) wrote that the nature of glass and the glass transition may be "the deepest and most interesting unsolved problem in solid-state theory" and predicted that "this could be the next breakthrough in the coming decade" [1]. In 1999 poll by *Physics World* magazine among 250 physicists from around the world, the subject of the glass transition scored among the top-10 problems for future research in condensed matter physics [2]. Since then roughly a decade has passed, and although significant progress has been made on a number of different topics [3], new questions have been raised and many other questions remain unanswered. Anderson's statement certainly is no less true in the year 2008, since clarifying the nature of the glass transition [4] remains the Holy Grail in glass science.

The phrase "advancing glasses" in the title of this paper may have very different meanings for physicists, chemists, materials scientists, and process engineers. As we try to illustrate in Table 1, most engineers and materials scientists will likely focus on: (a) creating new markets with new glass products, (b) increasing existing market share by replacing other materials with glass, or (c) increasing the overall market size. These goals can be achieved by discovering new applications for glass or improving upon existing glass properties or processing. For example, the invention of low-expansion glass ceramics in the late 1960 s was based on fundamental research into the use of TiO_2 as a nucleation agent in specific glasses [5]. The invention of glass–ceramics enabled a new generation of cooking devices that in the following replaced many gas or electrically heated kitchen stoves [6].

Progress in glass technology is based on both material and process-related innovations. In the case of long-haul optical telecommunication fibers, which replaced copper wires in the 1980s, the invention of a process for making ultra-high purity glass preforms proved the key enabler for achieving very low optical loss [7]. Together with the invention of the erbium-doped fiber amplifier [8,9], this led to a revolution in

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Table 1
Areas for advancing glasses 3

Progress in . . .	Subject	Examples
Market share	Material ↓ Process	Low-expansion glass ceramics [122] long-haul telecommunication fiber [7] photonic crystal fiber [10]
Market size	Material	Bendable fiber [13]
New market	Material process	Bioactive glass [14] display glasses [16]
Knowledge	Research education	Glassy water [4] TC23 [123]
Sustainability	Materials ↓ Process	As-free display glasses [16] nuclear waste vitrification [17] submerged combustion melting [18]

worldwide communication and can be considered one of the greatest achievements in glass technology. The story continues with the invention of hollow-core photonic crystal fiber [10], which may enable further market gains if process improvements result in significant decrease in the fiber loss value (today's reported record is 1.2 dB/km [11]). In addition to process improvements, advances in photonic crystal fiber technology can be made through better understanding of the nanometer-scale roughness of glass surfaces [12]. Very recently, the development of a new "bendable fiber" [13] promises to create a significant increase in market size by enabling the use of optical fiber within residential buildings. In a similar way, new materials (e.g., bioactive glass [14]) or new processes (e.g., the overflow process for producing thin glass sheet with very high surface quality [15]) have enabled totally new markets for glass, e.g., tissue engineering or flat panel displays, respectively. Finally, we note in Table 1 that sustainability is another important aspect driving advances in glass technology. Examples include the development of new glasses without any toxic species (e.g., as fining agents [16]), recycling and immobilization of waste [17], and new processing techniques that may save energy [18].

It is thus apparent that research can be classified into three categories:

1. Materials design and engineering, including the discovery of new materials (glasses), bulk or surface modification (e.g., glass ceramics, coated glasses), and physical and/or chemical characterization;
2. Research into the properties, structure–property relations and underlying mechanisms (e.g., fracture behavior, nucleation processes, corrosion or other interface reactions, optical properties); and
3. Fundamental description of the glassy state (statistical mechanics, thermodynamics of irreversible processes, kinetics, etc.).

Today, glass researchers have access to sophisticated technical databases such as SciGlass [19,20] and Interglad [21] that offer fast access to physical and chemical properties of hundreds of thousands of glass compositions, including virtually all oxide glasses that have ever been studied, and an ever-growing number of non-oxide glasses. These tools have greatly simplified the design of experimental plans for the development of new glass compositions. Although existing databases do not yet link all important properties of a given glass composition, it seems only a matter of time until the development of new glasses will be dominated by pen, paper, and databases. As a result, practically any research into new applications now touches research into structure–property relationships, surfaces and coatings, nucleation and crystallization mechanisms, nanostructures, etc.

Fig. 1 illustrates the distribution of recent research symposia focusing on different aspects of glass science and technology. Here, the number of symposia that were held on a specific topic during 16 large International Conferences (with glass as the overall topic) between 2004 and 2008 are plotted. This is used as a rough estimate of the individual impact of each topic during this time. It does not, however, illustrate trends. If one assumes that each symposium contributed equally to the progress of its respective field, one might conclude that during the considered time period, the biggest progress was made in the field of optical, electronic, magnetic and electro-optical properties of glasses, and the least on refractories. (Whether or not this is true will need a deeper analysis.) At least one may conclude that fields that ranked higher received more interest from the research community, while lower-ranked fields where either less hot or based on a smaller subset of the community.

In the following, we offer focused reviews on two specific areas of fundamental glass research and try to identify the major questions on those areas with respect to scientific and technological progress: (1) computational simulation and modeling of glass at the atomic level and (2) the effect of pressure on the glass transition and polyamorphism. These two topics touch some of today's most cited questions in glass science. While modeling and computational simulations start to replace purely experimental studies into the nature of the glassy state, experimental examination of the impact of pressure on the structure and dynamics of glasses and melts is gaining growing interest, and recent progress in the field is remarkable.

2. Modeling

While laboratory experiments are essential for confirming or refuting any theory, often more physical insight may be gained through modeling and simulation. In particular, atomistic models have proved invaluable for determining the structure of a wide assortment of glasses and glass-forming liquids. Computational power has increased exponentially over the past several decades, enabling researchers to simulate larger systems over longer time scales. In addition, new simulation techniques have enabled the calculation of many thermal, mechanical, and kinetic properties of glass. Indeed, modeling has proved essential for developing a fundamental understanding of structure–property relationships, and it promises to play an even larger role in the development of new glass compositions with the desired combination of property values.

In this section, we review several techniques for numerical modeling of glass at the atomistic level. We provide brief overviews of molecular dynamics, Monte Carlo, and master equation techniques, discuss their application to various glassy systems, and offer some thoughts about the future promise of

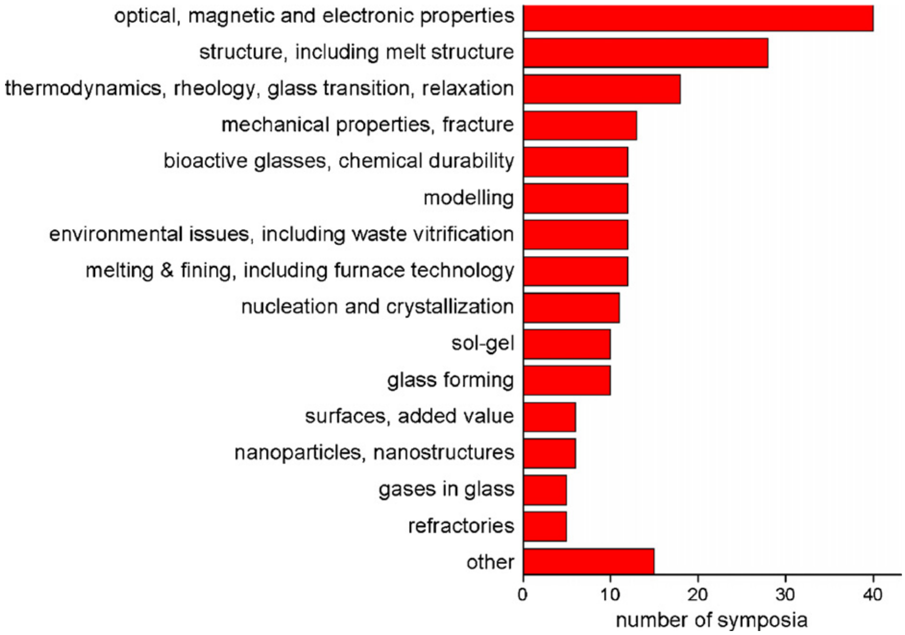

Fig. 1. Number of symposia that were held to a specific topic cumulated from 16 large International Glass Conferences between 2004 and 2008, including the International Congress on Glass, The Conference of the European Society of Glass, The Meeting of the Glass and Optical Materials Division of the American Ceramic Society, The Conference Series on the Physics of Non-Crystalline Solids.

these techniques for tackling even more complicated problems. While quantum mechanical techniques such as molecular orbital theory and density function theory have also proved extremely valuable in the modeling of glass, here, for the sake of brevity, we focus on classical modeling techniques only. Excellent reviews of quantum-level modeling techniques are available elsewhere [22–25].

We would like to stress that there is no “one size fits all” technique for modeling of glassy systems. Different problems call for different simulation techniques, depending on the particular properties of interest and systems under study.

2.1. Molecular dynamics

The molecular dynamics technique, pioneered by Alder and Wainwright [26], Rahman [27], and Verlet [28], is currently the most popular method for modeling glassy systems at the atomic level. With molecular dynamics, each atom is treated as an individual point particle. The atoms interact with each other based on pairwise, and sometimes higher order, interatomic potentials. These interatomic potentials can be determined empirically to reproduce known experimental data, or they can be derived from quantum mechanical simulations. With the molecular dynamics technique, the interatomic potentials are used to compute force vectors on each atom. Dividing the force by the mass of the atom yields an acceleration, which is integrated in order to update the atomic velocities and positions. A thermostat is typically employed to maintain a specified temperature through adjustment of the atomic velocities [29].

In the glass science community, molecular dynamics was first applied in 1976 by Woodcock et al. [30] to investigate the structure of vitreous silica. Within a few years, the approach had been extended by Soules [31] and Soules and Varshneya [32] to multicomponent silicate glasses. Since then, researchers have introduced many new and more accurate sets of interatomic potentials for silicate glasses [33–36] and applied the technique to compute a wide variety of properties, including elastic coefficients [35], diffusivity [36], and surface interactions [37,38]. Molecular dynamics has also offered insight into ion transport mechanisms [39] and shed much light on the so-called “mixed alkali effect” in silicate glasses [40,41]. Very recently, molecular dynamics has been applied to the study of collective motions and dynamical heterogeneities in glass [42–44]. In addition, molecular dynamics has been used to investigate the structure of non-oxide glasses such as metallic glasses [45].

The molecular dynamics technique faces two main challenges to addressing more complicated problems in glass science. Firstly, since the integration time step is on the order of 10^{-15} s, molecular dynamics cannot access the long-time scales necessary for modeling realistic glass transition range behavior. As a result, molecular dynamics cannot account directly for realistic thermal history effects as observed in experiment. Secondly, molecular dynamics can simulate only a relatively small number of atoms (currently no more than about 10^6 atoms). As such, the impact of trace dopants and phase separation cannot be captured. Both the length and time scales of molecular dynamics simulations can be extended through increased computer power and parallelization [46] as well as algorithms for accelerated dynamics [47]. Another possibility for extending molecular dynamics is through the use of coarse-graining, where groups of atoms (for example, a Si-centered tetrahedron in SiO_2) are treated as a single rigid unit with effective interactions between these larger units rather than between individual atoms. While each of these approaches would extend the length and time scales accessible by molecular dynamics, other techniques are capable of accessing even larger scales.

2.2. Monte Carlo methods

Whereas molecular dynamics provides a deterministic method for following atomic trajectories in time, the Metropolis Monte Carlo technique is a stochastic method that avoids computation of forces and integration of the equations of motion. Instead, it relies on generating random configurations of atoms in phase space and using special criteria for determining whether to accept each new configuration [48]. In fact, the name "Monte Carlo" was coined by Metropolis [49] owing to the technique's extensive use of random numbers.

With Metropolis Monte Carlo, the atoms undergo a series of random trial displacements. The potential energy of the system is calculated both before and after the trial displacement. If the final energy is less than the initial energy, then the trial displacement is accepted and the atom stays at its new position. If the displacement results in an increase of potential energy, then a probability of acceptance is computed following a Boltzmann distribution [50,51]. This procedure is repeated for each trial displacement until the potential energy has converged and the detailed balance condition is satisfied. By relying on scalar energy rather than vector force calculations, Metropolis Monte Carlo can provide an accurate glass structure with much less computation time than traditional molecular dynamics. Another advantage of Metropolis Monte Carlo is that it can be trivially adapted to run under constant pressure rather than constant volume conditions [52].

While the first application of Metropolis Monte Carlo in the glass science community followed molecular dynamics by only a few years [53], the technique has not received nearly as widespread adoption by the glass science community. This is surprising given the efficiency of Monte Carlo for computing static properties such as glass structure. Currently, most Monte Carlo modeling of glass has involved chalcogenide systems [54–58], including calculation of bulk and surfaces structures, rigidity percolation behavior, and incipient plasticity. We believe that the Metropolis Monte Carlo technique holds much promise for computing the structure of other glass compositions, particularly where a large number of atoms is required (e.g., glasses with low concentrations of certain elements such as fining agents). While Metropolis Monte Carlo does not offer any information on the dynamics of the system (since there is no time variable in the calculations), the glass structure computed with Monte Carlo can be used as a starting configuration for subsequent molecular dynamics simulations. As with molecular dynamics, parallelization techniques [59,60] can be implemented to increase further the number of atoms simulated.

Three other Monte Carlo techniques are worthy of note here. The first, simulated annealing [61,62], is a simple extension of Metropolis Monte Carlo where the simulation starts at some high temperature, which allows for a greater fraction of trial displacements to be accepted. As the simulation proceeds, the temperature is gradually lowered to some desired final temperature, where fewer trial displacements are accepted. By allowing for a more efficient sampling of configurational phase space, the simulated annealing technique enables a faster convergence to the final glass structure compared to standard isothermal Monte Carlo.

Reverse Monte Carlo is a stochastic modeling approach where the atoms in a system undergo trial displacements while seeking to minimize the difference between the simulated glass structure and that measured experimentally [63,64]. Reverse Monte Carlo has been applied to a variety of glass compositions, including silicates, germanates, and metallic glasses [65–70]. The main advantage of reverse Monte Carlo is that it does not require any interatomic potentials: no energy calculations are performed since the atomic positions are optimized against experimental data only. Of course, since the experimental data must be known beforehand, reverse Monte Carlo does not offer predictive calculations on new glass compositions.

Finally, the kinetic Monte Carlo technique [71] offers the ability to incorporate dynamics (i.e., time data) into Monte Carlo simulations. With kinetic Monte Carlo, activations barriers are computed for a set of possible transitions. One of these transitions is selected randomly based on a Boltzmann distribution, and the simulation time variable is increased by a mean first passage time over that barrier, typically following transition state theory. Since the simulation time is connected to the height of the activation barriers and the temperature of the simulation (rather than a fixed integration time step) kinetic Monte Carlo simulations can access much longer time scales than molecular dynamics. The most challenging aspect of kinetic Monte Carlo is determination of the set of possible transitions and their associated activation barriers. This can be accomplished using eigenvector-following [72,73] or a number of other techniques [74]. The kinetic Monte Carlo technique has only recently been applied to glassy systems by Wales and coworkers [75,76]. Because of its ability to access long-time scales and infrequent transition events, kinetic Monte Carlo offers great possibilities for future modeling of glass-forming systems.

2.3. The master equation approach

The master equation approach [77], as applied to glass-forming systems [78,79], involves constructing a set of rate equations for modeling the departure of an equilibrium liquid system into the glassy state upon cooling with some temperature path. This approach is similar to kinetic Monte Carlo in that it can access long time scales by mapping the system to a discrete set of stable configurations called "inherent structures," corresponding to minima in the energy landscape [80–83], and the transition barriers connecting these minima. The key advantage of the master equation approach over kinetic Monte Carlo is that is offers built-in ensemble averaging for property calculation [78,79]. With kinetic Monte Carlo, such averaging requires the use of multiple simulations with different random seeds. Also, the master equation approach offers a simplified way to account for entropic effects [84,85] and broken ergodicity [86]. The main disadvantage of the master equation approach is that it requires prior computation of inherent structure and transition point distributions. (With kinetic Monte Carlo, the transition points can be computed "on the fly" at each step of the simulation.) Fortunately these initial computations only need to be performed once for any given composition. The same inherent structure and transition point distributions can be used in conjunction with any temperature

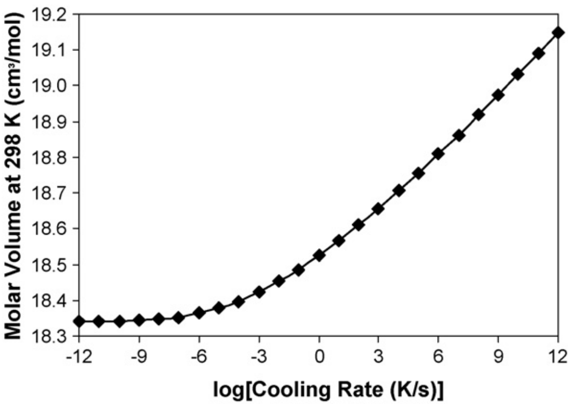

Fig. 2. Molar volume of selenium after cooling from the melting temperature (490 K) to room temperature (298 K) with linear cooling rates ranging from 10^{-12} to 10^{12} K/s. For extremely slow cooling rates ($<10^{-9}$ K/s), the system never departs from the equilibrium.

path, and the master equations themselves can be solved efficiently using the "metabasin" approach of Mauro, Loucks, and Gupta [84].

Recently, the master equation approach has been applied to study the glass transition range behavior of selenium [87]. Using the technique of Ref. [84], the molar volume of selenium glass could be computed for cooling rates covering 25 orders of magnitude. Fig. 2 plots the final molar volume as a function of cooling rate, where the systems are linearly cooled from the melting temperature of selenium (490 K) to room temperature (298 K). For the very slow cooling rates ($<10^{-9}$ K/s), the system remains a supercooled liquid; glasses form for all of the faster cooling rates. The results show an Arrhenius dependence of molar volume with respect cooling rate, in excellent agreement with the experimental findings of Moynihan et al. [88]. The complete volume–temperature curves for three of the cooling rates (10^{-12}, 1, and 10^{12} K/s) are plotted in Fig. 3. Using the master equation technique described above, the computation time is approximately equal for all cooling rates. While thus far the master equation approach has been applied only to selenium, it certainly holds much promise for other compositions. This technique is currently the only way to compute suitably averaged properties such as molar volume, enthalpy, and entropy, for realistic glass-forming systems with an arbitrary thermal history.

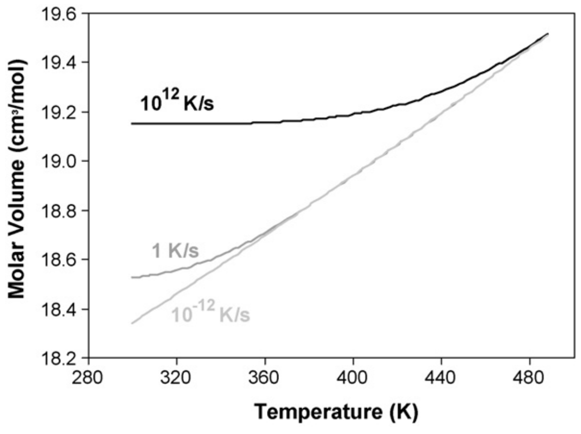

Fig. 3. Volume–temperature diagrams for three selenium systems cooled from the melting temperature (490 K) to room temperature (298 K) at rates of 10^{12}, 1, and 10^{-12} K/s.

3. Pressure and the glass transition

In the previous section we illustrated how modeling has become an essential tool in fundamental glass research. Indeed, laboratory experiments and computational simulation started to switch roles in many aspects of glass science, partly due to steadily increasing availability of computational resources and partly due to the simple fact that some questions cannot presently be answered by experimental means. For example, computer modeling has become the major research method in addressing problems related to the glass transition. However, experimental studies will remain of paramount importance.

On the other hand, the question of how inorganic glasses and melts behave under high pressure is a topic where most recent progress has been made through experimental studies. This topic has been a traditional area of interest in geosciences for decades: since pressure increases towards the interior of the earth and approaches several GPa already in the upper earth mantle, knowledge about the genesis, phase stability, and flow behavior of mineralic melts is of crucial importance to understand geologic processes [89]. Employing the falling-sphere technique at temperatures well above T_g, the pressure dependence of viscosity has been studied as early as in the 1970 s [90,91]. Several still unresolved peculiarities such as negative viscosity–pressure dependencies have been observed in multiple materials (e.g., [92,93]). Only recently, Behrens and Schulze reported on a technique that enabled *in situ* parallel-plate viscosity measurements under high pressure, close to T_g, that they employed to confirm a transition from positive to negative viscosity–pressure dependence on the compositional join diopside-albite [92]. As of today, negative viscosity–pressure dependencies cannot reliably be predicted from computational simulation.

Pressure and temperature are important thermodynamic variables that determine structure, dynamics and macroscopic properties of glasses and liquids. Just as pressure and temperature control the stability fields of different polymorphs of the same chemical composition in crystalline materials, the existence of thermodynamically distinct liquid or glassy phases of equivalent composition, i.e., the phenomenon of pressure-induced polyamorphism became highly debated in recent years [94]. First-order entropy- or density-driven liquid–liquid phase transitions have been suggested in multiple glass-forming materials, e.g., water [95], elemental liquids [96,97], metallic glasses [98] and more complex systems [99,100]. As of today, however, literature is primarily focused on phenomenology. Nature and eventual generality of polyamorphic transitions remain far from understood. A comprehensive review of the topic is given by McMillan et al. [101].

Studies that relate to the phenomenon of polyamorphism are usually performed at pressures of several GPa up to tens of GPa and rely on the use of so-called multi-anvil presses. This restricts experiments to relatively small samples, typically of poor homogeneity. In addition, if melts need to be cooled down to room temperature in order for further *ex situ* analyses, this is typically done with high cooling rates and/or in an uncontrolled way. As a consequence, the properties of the derived glass originate from a convolution of fast cooling and high generic pressure. This may have undesired consequences for the interpretation of the derived results. For example, Du et al. [102] evidenced a dependence of boron coordination in borosilicate glasses on pressure: increasing pressure favours tetrahedrally oriented boron while at lower generic pressures, a higher concentration of trigonal boron can be found. The effect became visible at pressures of several GPa. On the other hand, boron coordination in such glasses is well known to also depend on thermal history [103,104], but in an inverse way: higher cooling rates lead to higher concentrations of trigonal boron, and the dependence on cooling rate is usually much stronger than that on pressure [105]. If compressed melts are cooled slowly, one can easily observe the reported pressure sensitivity at pressures as low as a tenth of a GPa [106]. This example illustrates significant consequences for concrete technical problems, e.g., anisotropic glasses and glass fibers [107,108]. Production of glass fibers usually involves high tensile and/or shear stresses, leading to structural anisotropy (birefringence). In addition, very high cooling rates result in relatively high fictive temperatures. Knowledge of the structural origin of the anisotropy may significantly improve understanding of the fiber's mechanical, chemical and thermo-mechanical properties, and may also enable drawing advantage from the phenomenon, e.g., for optical applications: From a previous study, Stebbins et al. [109] concluded for E-glass that structural anisotropy is not related to short-range structural changes. However, analyses of slowly cooled anisotropic glasses [110] might very well reveal a different picture in the future.

Such examples illustrate that technical relevance of pressure-related phenomena in glasses, in the regime of some 100 MPa, may be found on different fields, ranging from injection moulding [111] and pressure-assisted sintering, to fiber development and processing.

Experimentally, this regime is becoming more and more accessible with the help of internally or externally heated autoclaves [105,106,112,113]. Such facilities offer the additional advantage of relatively large sample chambers, high versatility with respect to the experimental atmosphere that can range from deeply reducing to oxidizing, and the possibility of controlled cooling at comparably low rates.

Speaking in terms of energy landscapes [114] the energetic state of a liquid is made up by two contributions: configurational and vibrational energy. Under isobaric conditions, the configurational energy may be described by the fictive temperature, the vibrational energy by the real temperature. Both temperatures decouple when liquid undercools and becomes a glass [115]. The macroscopic fictive temperature [116] is thus the temperature that corresponds to the fictive enthalpic equilibrium between glass and melt [117]. In non-isobaric transitions, fictive and real pressures become additional parameters. For this case, the term *apparent fictive temperature* has been introduced [113] to describe contributions from both cooling rate and pressure-of-freezing. Deviation of the apparent fictive temperature from the fictive temperature of a glass is a result of non-equivalence between fictive pressure [118,119,105] and real pressure, and 'deviation from equilibrium' [120] of a glass on a (p, V, T, t)-landscape can formally be separated in two contributions: a part that depends on cooling rate and a second part that depends on pressure of freezing [105]. For a full thermodynamic treatment [121], ideally, an experiment must therefore provide a glass that was cooled under pressure at a given cooling rate, and a glass that was cooled under a reference (ambient) pressure with the same cooling rate. Only then one can clearly distinguish between pressure and cooling-rate-induced changes in the structure and thermodynamic state of the considered system.

Coming back to the phenomenon of polyamorphism, today it is difficult to anticipate concrete technical relevance. However, the connection between phenomena that are observed under very high pressures, observations from the intermediate pressure regime and deeper understanding of the flow behavior may enable further progress in the aforementioned fields.

4. Conclusions

The topics of atomistic modeling and pressure effects in glass are just two areas where fundamental research has provided deeper insights into the nature of glass. As findings from fundamental physics and chemistry continue to be harvested, a fuller understanding of the glassy state will be obtained, increasing our ability to solve difficult problems in materials science and engineering. These advancements in fundamental research will assuredly lead to a number of significant technological breakthroughs in the coming decade.

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