Proceedings of the ESF Exploratory Workshop on Glassy Liquids under Pressure: Fundamentals and Applications (Ustroń, Poland, 10–12 October 2007)

2008 J. Phys.: Condens. Matter 20 240301

(http://iopscience.iop.org/0953-8984/20/24/240301)

J. Phys.: Condens. Matter **20** (2008) 240301 (5pp) doi:10.1088/0953-8984/20/24/240301

PREFACE

Proceedings of the ESF Exploratory Workshop on Glassy Liquids under Pressure: Fundamentals and Applications

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This preface focuses on the importance of pressure studies for explaining the glass transitions puzzle. Subsequently, some issues related to the European Science Foundation Exploratory Workshop (ESF EW) Glassy Liquids Under Pressure: Fundamentals and Applications (Ustroń, Poland, 10–12 October 2007) are recalled.

Most liquids crystallize on 'normal' cooling at the melting temperature T_m. However, some liquids can skip crystallization and undergo supercooling down to glass temperature T_g. Turnbull [1] proposed an empirical link between these temperatures indicating good glass forming ability (GFA) for $T_g/T_m \leqslant 2/3$. Values of the GFA factor $T_g/T_m \to 1/2$ were suggested for 'poor' glass formers, where crystallization is difficult to avoid. Recently, the significance of the pressure dependence of the GFA factor was also noted [2]. Reaching the glass transition is associated with a series of phenomena, namely [3]: (i) the thermal expansion coefficient at constant pressure changes smoothly from values common for a liquid to those of a crystal, showing anomalous behaviour near T_g, (ii) viscosity reaches a value of $\eta = 10^{13}\,P$ and the structural relaxation time $\tau \approx 100$ s, (iii) the specific heat drop occurs, giving rise to the famous Kauzmann paradox.

On cooling towards glass transition, the 'pretransitional' behaviour can be observed for dynamic properties even well above $T_g + 100$ K [3]. This includes the non-Arrhenius evolution of such magnitudes as viscosity, primary (structural-, α-) relaxation time, electric conductivity or diffusion coefficient associated with increasingly non-Debye distribution of relaxation times [3]. Such behaviour is associated with short-time scale relaxation processes. The most characteristic is the secondary (β-) relaxation [4, 5] which merges with the 'structural' dynamics near $\tau(T_B) = 10^{-7\pm1}s$, the hypothetically universal (magic) time-scale [6]. Below T_B the split in the evolution of the translation and orientation related properties occurs [4, 5]. It is worth stressing that these features seem to be universal, shared by various systems, despite their fundamentally different microscopic basis [3–6]. It is probable that the latter fact caused the long-standing interest in glass transition phenomenon. It can be said that the puzzling artifacts matched with the intuitive hypothetical universality of the given phenomenon have always attracted the attention of researchers. The modern concept of critical phenomena, developed three to four decades ago, serves as an excellent example [7, 8].

Society-relevant applications of the knowledge gained from studies on the vitrification phenomenon are of great significance for material engineering such as rewritable data storage, pharmacy industry, geophysics, biotechnology, etc [3, 9–13]. Glass transition physics also constitutes one of the reference points for the novel category of complex liquids/soft matter systems [13].

One of the basic hallmarks of the hypothetically universal dynamics on approaching glass transition is the Angell plot [14, 15], $\log_{10}\tau$ or $\log_{10}\eta$ versus T_g/T, collecting 'dynamic' data for different systems with the so called fragility as a classifying metric. The latter was introduced as the slope at $T_g/T = 1$ in the Angell plot.
Fragile liquids (large values of m) are linked to the strongly nonlinear dependence in this plot. The so called strong liquids (glassy systems) are characterized by small values of m. For the latter the most linear, Arrhenius-type behaviour takes place. In subsequent years several other measures of fragility were proposed. Fragility became one of the key concepts for glass transition physics [3, 16–20].

Despite extensive experimental findings, numerical results and theoretical concepts [3, 16–20], a breakthrough in explaining the glass transition mystery has not yet been reached. The ultimate model ought to describe vitrification with the use of well defined physical parameters and yield output relations enabling simple and unambiguous experimental tests. Such a model should describe all puzzling dynamical, thermodynamic and structural features as well as identify the origins and the range of the hypothetical universality. Therefore, why are pressure studies so important?

Compressing is another way of vitrifying a system without the necessity of changing the temperature. In temperature studies on glass transition both density and thermal effects are involved [3]. Comprehensive temperature and pressure studies make it possible to separate these contributions and consequently to understand their role [3, 16, 20]. Pressure dependences of various relaxation processes (α-, β-, etc) differ significantly. Hence, pressurization can separate these processes [17]. This is hardly possible in temperature investigations under atmospheric pressure. Dynamic 'equation of states' employing data from the pressure-temperature plane may also offer a qualitatively new tool for testing the validity of the existing theoretical models. This has already been used for the study of free volume models, Adam-Gibbs model or mode coupling theory [16–18]. Let's present some further possible problems associated with pressure and glass transition: (i) the origin of universal phenomena (ii) the ultimate description of the relaxation time or viscosity versus P and T (iii) the proper description of $T_g(P)$, $T_0(P)$, $T_C^{MCT}(P)$, evolution (iv) explaining the possible role of the negative pressures domain (v) the mystery of the pre-vitrification behaviour for systems characterized by $dT_g(P)/dP > 0$ and $dT_g(P)/dP < 0$ (vi) the answer to the question 'does fragility depend on pressure?' (vii) understanding the role of volume in vitrification (viii) β- process related questions (ix) the mode-coupling theory predictions for the pressure path: this includes the 'universality' or 'non-universality' of the power exponent describing the evolution of $\tau(T)$ or $\eta(T)$ (x) the appearance of dynamic hetergeneities on pressuirization, (xi) the decoupling between rotational and translational degrees of freedom (xii) the vitrification-related behaviour at extreme pressures in the multi-GPa domain.

All these problems show that pressure studies on supercooled liquids and glassy systems can shed new light on properties observed under atmospheric pressure. In our opinion comprehensive pressure and temperature research, supported by PVT measurements and matched with sophisticated state-of-the-art modern techniques, may deliver qualitatively new input data for numerical analysis as well as for verification and construction of theoretical models. All these can form a milestone for reaching a long expected breakthrough in glass transition physics.

We would like to stress the interdisciplinary significance of high pressure studies on glass forming materials. They are important not only for condensed matter and soft matter physics but also for tailoring new materials, for biotechnological issues or for deep Earth and planetary sciences [3, 9–13, 16–18]. This poses an additional challenge for glassy liquids under pressure studies.

This issue contains the majority of results presented at the European Science Foundation Exploratory Workshop (ESF EW) 'Glassy Liquids Under Pressure', Ustrón, Poland, 10–12 October, 2007 (convenors: Aleksandra Drozd-Rzoska (Poland) and Josep Ll Tamarit (Spain)).
Aleksandra Drozd-Rzoska belongs to the group (together with Sylwester J Rzoska, Marian Paluch Paluch, Jerzy Zioło, Sebastian Pawlus, Michał Mierzwa and the staff of PhD students) from the Department of Biophysics and Molecular Physics, Institute of Physics, Silesian University, Katowice, Poland), which began pressure studies in liquids almost three decades ago. First, these investigations focused on critical mixtures and liquid crystals [21–24]. On the basis of experimental solutions developed in that period, pressure studies of dielectric relaxation in supercooled, vitrifying systems began a decade ago [18, 25–27]. Results associated with these studies are recalled in some of the papers presented in this issue.

Josep Ll Tamarit is the coordinator of the Group of Characterization of Materials at the Department of Physics and Nuclear Engineering, Universitat Politécnica de Catalunya, Barcelona. Over the last 20 years the group has conducted thermodynamic and structural studies on several series of compounds and on their mixed crystals [28–33]. They invariably involve orientationally disordered phases. For such materials, also known as plastic crystals, the average positions of the centers of mass of the molecules form a regular high-symmetry lattice while the orientations are dynamically disordered. It is well known that the dynamics of (canonical) glasses is almost completely controlled by orientational degrees of freedom [34] and thus, vitrifying orientationally disordered crystals can yield materials with a reduction of complexity. This can be important for reaching a better insight into the glass state and vitrification in general.

The European Science Foundation Exploratory Workshop (ESF EW) is a brainstorming panel for the best specialists in the given field of science. Participants of the ESF EW 'Glassy Liquids Under Pressure' arrived at the Institute of Physics, the Silesian University, Katowice, Poland on 10 October 2007. Katowice is the capital of Upper Silesia and of the metropolitan area of Silesia (population $\approx 4\,000\,000$)—the most industrial area of Poland. The conference coach took participants to the Jaskółka Hotel in Ustrón, a tourist resort situated in the beautiful valley at the foot of the Beskidy mountains (a part of West Carpaty), 80 km south from Katowice. The picturesque surroundings together with the delicious local cuisine created a stimulating atmosphere for the three days of lectures and discussions.

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