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Ordering and structural changes at the glass–liquid transition

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ABSTRACT

Ordering types of amorphous solids and structural changes which occur at glass–liquid transition are discussed focusing on configuron percolation theory (CPT) of glass transition. The glass transition temperature can be calculated using bond thermodynamic parameters e.g. enthalpy H_d and entropy of formation S_d. Explicit equations have been derived to assess H_d and S_d from available data on viscosity of amorphous materials using the CPT viscosity equation. A universal equation for the variable activation energy of viscous flow $Q(T)$ has been found. The glass–liquid transition is accompanied by formation of a percolation macroscopic cluster made up of broken bonds – configurons – which are dynamic in nature. The characteristic linear size of dynamic clusters formed is given by correlation length which universally depends on formation Gibbs free energy of configurons $G_d = H_d - TS_d$ and becomes macroscopic at glass transition. Fractal-type medium range order (MRO) is revealed at correlation length sizes and homogeneous and isotropic disordered state (DS) characteristic for macroscopic sizes larger than the correlation length. The reduction of topological signature (Hausdorff dimensionality) of disordered bonding lattice from 3 for glass to fractal $D_f = 2.4 - 2.8$ for melt is the main signature change to explain the drastic changes of material behaviour at glass transition.

1. Background

The interest to glasses and glass–liquid transition is within a growing attention of many researchers [1–6] with important results obtained on the nature of glassy state and processes at glass transition [7–20]. Glasses are typically formed on rapid cooling of melts so avoiding crystallisation since little time is allowed for the ordering processes. Whether a crystalline or amorphous solid forms on cooling depends also on the ease with which a random atomic structure in the liquid can transform to an ordered state. Most known glassy materials are characterised by atomic or molecular structures that are relatively complex and become ordered only with some difficulty. Therefore it has long been assumed that the glassy state is characteristic of special glass-forming or network materials such as covalent substances which exhibit a high degree of structure organisation at length scales corresponding to several atomic separations. However, after the discovery of metallic glasses it was realised that any substance melt, if cooled sufficiently fast, could be obtained in the glassy state [21]. Nowadays the glassy state is acknowledged as one of most important not only for the inorganic matter but also for living species e.g. arctic fish use antifreeze proteins, whereas arctic insects and arctic frogs use sugars as cryoprotectants to reduce ice formation [22,23].

Glasses are solid amorphous materials. The internal structure of glasses is represented by a topologically disordered three-dimensional lattice — network of interconnected microscopic structural blocks. Glasses transform into liquids upon heating through the glass transition e.g. the solid-like behaviour of amorphous materials at low temperatures (glasses) is separated from liquid-like behaviour at high temperatures (melts) by the glass transition temperature, T_g. Moreover the glass transition is similar to a second-order phase transition in the Ehrenfest sense with continuity of volume and entropy, but discontinuous changes of their derivatives [6]. Very often the liquid–glass transition is regarded as a transition for practical purposes rather than a thermodynamic phase transition e.g. it is considered that a liquid on being cooled becomes practically a glass when the viscosity equals 10^{12} Pa s which enables calculation of many glass parameters and designing of proper glass materials [24,25]. However rearrangements that occur in an amorphous material at glass transition lead to characteristic jumps of derivative thermodynamic parameters such as the coefficient of thermal expansion or the specific heat. Moreover these discontinuities allow to detect experimentally the T_g. Because of that the liquid–glass transition has been considered as a second order (or second order like) phase transition in which a supercooled melt yields, on cooling, a glassy structure and properties similar to those of crystalline materials e.g. of an isotropic solid material [26]. It has been however shown that glass transition is rather a percolation-type phase transformation which demonstrates both kinetic and thermodynamic characteristics [27]. Indeed the glass transition shows distinctly thermodynamic phase transition features, however, being a kinetically controlled phenomenon the glass transition exhibits a range of T_g which depends on the cooling rate with maximal T_g at highest rates of cooling [28–30]. Although T_g depends on the rate of cooling it can be roughly assessed from Kauzmann's relation $T_g \approx 2T_L/3$ where T_L is the liquidus temperature at which a phase diagram shows a crystal-free melt.

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Amorphous oxide materials have an internal structure made of a 3-D network of interconnected structural blocks via chemical bonds. It has been noted that glass transition may arise due to the high degree of polymerisation in the glass which makes it prone to deformation and movement of the polymerised rings with respect to each other, once sufficient thermal vibration energy is available locally [31]. In addition to that different partial ordering of the glass has been found at glass interfacial systems [32]. Chemical bonds can be either intact or broken e.g. due to thermal fluctuations. Each broken bond in an amorphous material is treated as an elementary configurational excitation — configuron [33,34]. A configuron is formed by breaking of a chemical bond followed by the associated strain-releasing local adjustment of centres of atomic vibration. Both glasses and liquids are isotropic, e.g. the translation–rotation symmetry of particles is unchanged at the glass–liquid transition. However glasses have elastic properties of isotropic solids which are qualitatively different compared liquids. The difficulty to understand the glass–liquid transition is because of almost undetectable changes in the structure of amorphous materials in contrast to qualitative changes in characteristics and extremely large change in the time scale of relaxation processes. We discuss herein ordering types in the disordered structure of amorphous solids (glasses) and structural changes which occur at glass–liquid transition. This reveals ranges of sizes with medium range order (MRO) and reduction of topological signature (Hausdorff dimensionality) of disordered bonding lattices at glass transition.

2. Structural features of glasses and melts

Although amorphous both glasses and melts possess short-range order (SRO) with a typical radius about several angstrom. SRO structural groups in commercial glasses are usually tetrahedral Si, B, Al, Fe, P surrounded by 4 oxygen atoms (tetrahedral coordination) or B surrounded by 3 oxygen atoms (trigonal coordination). Moreover glasses are typically named based on predominant tetrahedral species such as borosilicate glasses which have primarily B and Si species. The tetrahedra and trigonal species in glass link to each other via bridging oxygen bonds (BO). The remaining non-bridging (NBO) atoms effectively carry a negative charge and ionically bond positively charged cations such as Na^+ or Ca^{+2} [35]. The atomic structure of oxide glasses is most exactly represented by Greaves' modified random network model [36] which has two interlacing disordered sublattices: one is the network region and another consists of regions comprised of large concentrations of atoms which do not enter in the network e.g. network modifiers. These may form percolating channels at higher concentrations of network modifiers. The tetrahedra define the network regions, while NBO atoms define depolymerised regions that can form percolation channels. Percolation channels are defined by the NBO atoms at the edges of the highly ordered network regions, which ionically bond to the alkali, alkaline earths or other modifier species in a glass. Moreover these channels can be revealed as they act as ion-exchange paths for elements that are less well bonded to the NBO [36]. It has been also found that for small length scales the alkali pathways are fractal in structure with Hausdorff dimensionality d_f in the range from 1.5 to 2.0 whereas on macroscopic scales the d_f rapidly increases to three-dimensional $d_f = 3$. This structural feature of oxide glasses explains the well-known mixed alkali effects in glasses as caused by the blocking by immobile unlike cations. It has been revealed that blocking effect is highly effective namely due to low dimensionality (<3) pathways on local length scales [37].

Summarising, the structurally oxide glasses can be characterised as follows: (i) SRO with molecular type units such as tetrahedral structures in silicates, at atomic size range; (ii) MRO which extends from second- and third-neighbour environments to percolating and fractal structures at a larger size range; (iii) disordered state (DS) which is homogeneous and isotropic at macroscopic sizes. Notable that such type of structure of glasses e.g. SRO–MRO–DS results from the configuron percolation theory (CPT) of glass transition which is briefly discussed below.

3. Structural changes at glass transition

Transformation of a liquid on cooling into a glass (i.e. glass transition) can take place at melt cooling rates rapid enough that crystallisation is kinetically avoided. Liquid-glass transition phenomena are observed universally; moreover all liquids can be in practice vitrified provided that the rate of cooling is high enough to avoid crystallisation. Because of almost undetectable changes in the structure of amorphous materials at glass transition it is difficult to understand the nature of glass transition. It is known however that on cooling structural changes occur in liquids such as formation of clusters e.g. it has been revealed that an array of fractal aggregations, known as Fischer clusters, forms as a liquid is cooled [38]. Fig. 1 shows that schematically — at higher temperatures liquids contain clusters which become larger at lower temperatures.

Earlier it has been suggested that on further cooling glass formation is caused by the formation of solid-like percolation clusters made of high-density atomic configurations [39]. These ideas have been further developed by Wool who has developed the twinkling fractal theory (TFT) and has shown that it results in explanation of relaxation phenomena on glass transition [11,40,41]. TFT assumes development of percolating solid fractal structures near T_g, which are said to be in dynamic equilibrium with the surrounding liquid. Indeed clusters in liquids become larger at lower temperatures until they form a macroscopic percolating structure which has been recently proved experimentally via AFM-visualisation of fractal structures near the glass–liquid transition temperatures [11]. Successive two-dimensional height AFM images reveal that the percolated solid fractal clusters exist for longer time scales at lower temperatures and have lifetimes that are cluster size dependent. The computed fractal dimensions, ≈ 1.88, are shown to be in excellent agreement with the theory of the fractal nature of percolating clusters.

4. Configuron percolation theory (CPT) of glass transition

In contrast to TFT, the CPT of glass transition considers changes that occur in the solid state — glass on approaching the glass transition temperature [15]. Melting of a solid occurs because of vibrational instability, e.g. when the average amplitude of thermal vibrations of atoms is high compared with interatomic distances: $<\delta u^2>^{1/2} > \delta_L R_s$, where δu is the atomic displacement e.g. the Lindemann parameter $\delta_L \approx 0.20$–0.25 and R_s is a half of the inter-atomic distance. Hence on increase of temperature more and more bonds are broken (see Fig. 1 at low temperatures) until percolation occurs via broken bonds. For an amorphous material that opens a possibility of easier deformation via the backbone of the percolation cluster formed.

Whether a material is liquid or solid depends primarily on the connectivity between its elementary building blocks so that solids are characterised by a high degree of connectivity whereas structural blocks in fluids have lower connectivity. Melting of an amorphous material can be considered as a percolation via broken bonds which occurs when the configurons form a percolation cluster [15,27,42]. Note that the percolation via broken bonds used within CPT formally differs from that of rigid-floppy percolation model of Thorpe and Phillips [43–46]. The idea of Thorpe and Phillips is that a threshold should appear when the number of degrees of freedom of building units of the network becomes equal to the number of constraints imposed on it. Moreover both rigid and the floppy clusters may play the key role e.g. solid electrolytes have a percolating rigid skeleton and at the same time have high conductivity controlled by the floppy cluster that also percolates [17]. Notable recent works involved temperature dependent constraint theory, where bonds/constraints are broken as temperature increases, which have resulted in a natural explanation for the presence of the constant T_g regime observed in alkali borate systems [24,25]. The CPT assumes