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The glassy state — Magnetically viewed from the frozen end

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ABSTRACT

It is argued that the structure of real glasses, especially the multi-component ones, can be investigated at low temperatures by exploiting the existence of tunneling systems (TSs) in the glass which can be described by a suitable extension of the standard tunneling model (STM) as was proposed by one of us. Even the simplest glass – as already argued in 1921 and in 1937 by A.A. Lebedev – is likely to contain elementary crystallites (not yet crystals) embedded in a random network, and our work has shown that this statement is even more true in the case of phase-separating, multi-component glasses, solids containing network-modifying components in their chemical make-up. Using the concept of TSs specifically nesting within the crystallites, we describe how our extended TM can explain puzzling experiments in glasses at low temperatures and in the presence of a magnetic field for a variety of amorphous insulators. The success of the theoretical analysis of a large number of experimental data confirms the crystallite hypothesis, clarifies the nature of the TS and opens the way to a possible new form of spectroscopy for the amorphous solid state in which the TSs play the role the atomic nuclei play in NMR spectroscopy.

1. Introduction — The atomic structure of glasses

The nature of the glass transition and of the precise microscopic structure of glasses determining their physical properties remains to this day issues of considerable intellectual challenge in physics [1]. Glasses are normally regarded as fully homogeneously-disordered amorphous systems, much alike liquids except for the glassy arrested dynamics close and below the glass transition temperature T_g. Nevertheless homogeneity is most probably only a useful idealization, for real glasses must always contain some small (in ceramic glasses not so small) concentration of tiny, ordered or nearly-ordered regions of variable size with the atoms, ions or molecules in these regions characterized by their own frozen dynamics. Indeed the thermodynamically stable phase of an undercooled liquid would be the perfect crystal, thus most substances in approaching the crystallization temperature T_c ($T_c > T_g$) from above would spontaneously generate local regions of enhanced regularity (RERs) much like a substance approaching the critical temperature is known to develop regions (droplets) resembling the ordered low-temperature phase. In the case of a first-order phase transition (e.g. at T_c, given enough time to crystallize) the process of nucleation consists exactly in this type of mechanism and thus it would seem natural that glasses should contain RERs or micro-crystals to some extent. These RERs are of course to be distinguished from the concept of short-ranged atomic order which is typical of ideal glasses and is restricted to the first few atomic spacings. We are considering in this paper realistic glasses in which a degree of *devitrification* has naturally occurred in the quench. The size and concentration of these RERs will depend, e.g., on the rapidity of the quench leading to the formation of the glass, but also on the chemical composition of the substance, the presence of impurities and so on. On general grounds, however, even the purest of glasses should contain RERs in non-zero concentration and size.

Indeed in the early 1930s, with the development of X-ray spectroscopy, Randall imagined glasses like pure a-SiO_2 made up of tiny true micro-crystals of the dominant crystalline phases [2], a vision that was soon replaced by Zachariasen's concept of random network [3] which could explain both rounded X-ray spectra from glasses and their bulk thermal properties. This remains the currently accepted view, but in the words of Hunklinger and Arnold [4]: “the possibility cannot be excluded, however, that some parts of the network can have ordered regions of larger dimensions forming isolated micro-crystallites”. In other words, one must also account for tiny crystal-like structures to exist in an amorphous solid, somehow embedded in an otherwise disordered (random-networked) amorphous medium. This was in fact A.A. Lebedev's view, developed phenomenologically in 1921 [5] and then from analyzing X-ray spectra [6]. Lebedev coined the word “crystallites”, meaning regions that only just started to resemble micro-crystals. The discussion about crystallites in glasses continued well into the 1970s and 1990s [7] and, as can be learnt from A.C. Wright's contribution to this Conference, it continues to this day. Fig. 1 depicts the evolution of these ideas for a simplified 2D representation of

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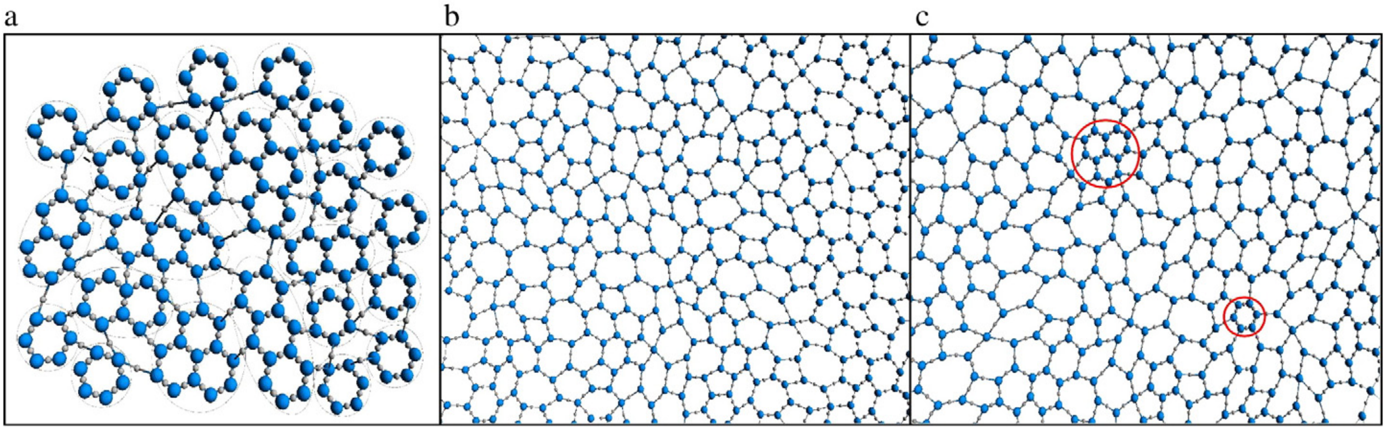

Fig. 1. Chronological evolution of ideas about the nature of the atomic structure of vitreous SiO_2 (schematic). (a) Randall [2], (b) Zachariasen [3], and (c) Lebedev [5,6].

vitreous SiO_2. Presently, the RERs (or crystallites, or crystal-embryos, or crypto-crystals as one may want to call them) are described by the term *cybotactic groupings* by X-ray spectroscopists, meaning regions of the amorphous mass which may have very complicated morphologies and in which the atomic constituents are more ordered than the rest. These are indeed our RERs, which one of us found [8] to be at the basis of the most rational and comprehensive explanation of many rather puzzling magnetic effects discovered in the late 1990s and early 2000s in the low-temperature properties of multi-silicate and organic glasses.

On the other hand, the formation of structures going under the name of dynamical heterogeneities (DHs) [9] or continuously rearranging regions (CRRs) [10] has been firmly established in computer simulations of supercooled liquids. In these structures, the existence of constituent particles with an intermittent partly-frozen dynamics has been ascertained; it seems natural to us that if the quench continues well into the glassy solid phase these structures will eventually come to form our RERs, or crystallites, in the frozen solid. Fig. 2 exemplifies, in a Molecular Dynamics computer simulation, the frozen dynamics of some of the model glass' particles just above T_g.

That single-component glasses indeed contain crystallites or RERs has been demonstrated recently for the structure of the metallic glass $Zr_{50}Cu_{45}Al_5$ [11], where a combination of fluctuation electron microscopy and hybrid reverse Monte Carlo simulation has revealed the presence of crystal-like regions of sub-nanometer size embedded in an otherwise homogeneously amorphous mass of the same composition (Fig. 3). Similar conclusions have been reached for amorphous Si, using combined electron diffraction and fluctuation electron microscopy [12]. Here the experimental data can be reproduced well by a model in which paracrystalline inhomogeneous structures are present and contain local cubic ordering at the 10 to 20 Å length scale beyond which the structure is truly disordered. It is to be expected that other metallic and covalent glasses should present similar structural features and thus – on general grounds – one would expect that non-metallic window glasses too, like pure SiO_2 and all the more so the commercial multi-silicates of complex chemical composition, should present a multi-phased structure with the size and concentration of the near-crystalline regions, or RERs, depending (e.g.) on composition, quench rate and the presence of impurities acting as nucleation centers for the RERs. Indeed, materials of the general composition $(MgO)_x(Al_2O_3)_y(SiO_2)_{1-x-y}$ (MAS, in short) are termed *ceramic glasses*. These materials are known to contain micro-crystals embedded in an otherwise homogeneously amorphous matrix [13]. This is not surprising, for materials made up of a good glass-former and good

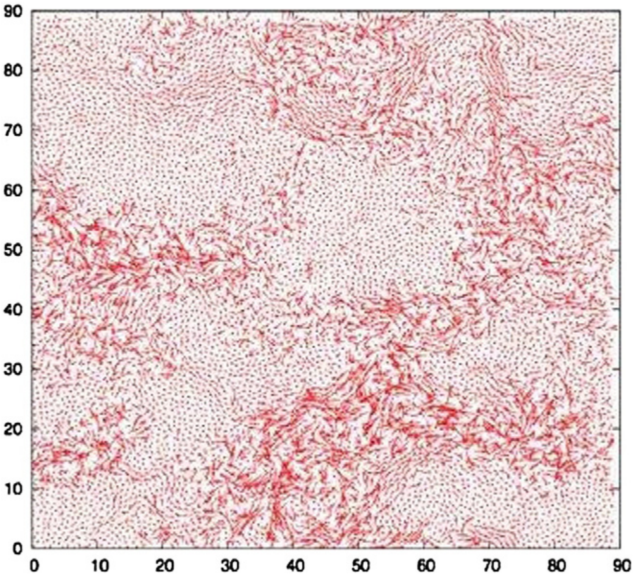

Fig. 2. A time-sequenced mapping of the positions and velocities of individual atoms in a (binary mixture) Lennard–Jones supercooled liquid (from [9]) showing regions (dynamical heterogeneities, DHs) which are slower and better ordered than the surrounding fluid.

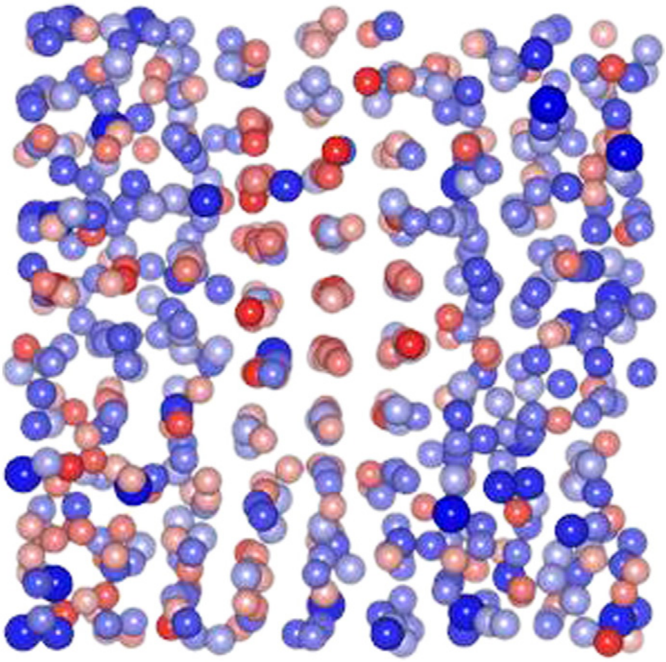

Fig. 3. The first picture/simulation of a crystallite in a metallic glass (from Ref. [11]).