

On the structural heterogeneity of supercooled liquids and glasses^(a)

GIANCARLO JUG¹ , ALOIS LOIDL² and HAJIME TANAKA³

¹ *DiSAT, Università dell'Insubria - Via Valleggio 10, 22100 Como, Italy*

² *Institute of Physics, University of Augsburg - 86159 Augsburg, Germany*

³ *Institute of Industrial Science, University of Tokyo - 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan*

Introduction. – Amorphous solids are ubiquitous in the technical sciences and their applications, as well as in Nature. Understanding the glassy state and the basic principles for modelling the physics of glasses and glass-forming liquids remains one of the outstanding problems of condensed-matter physics. Over the last century or so, the widely used scenario of the continuous random network (for network glasses) [1,2] and the Bernal model (for metallic glasses) [3] has taken a firm hold in the glass science community. In this context, glasses were seen as homogeneous liquids that have become dynamically arrested by the divergence of the structural relaxation time τ and of the viscosity η supposed proportional to it. While a uniformly disordered scenario remains a useful starting point, a century-long [4,5] controversy has been in existence as to whether a more appropriate heterogeneity-based scenario should replace the homogeneous one for the accurate modelling of real glasses and amorphous films.

After all, for glass-forming liquids, the present consensus is that dynamic heterogeneities characterise the supercooled-liquid state [6]. Therefore, it would seem natural that the heterogeneous scenario, somewhat more static below glass formation, should also hold in the solid state for real glassy systems, especially when they are multi-component in composition [7]. However, this extended scenario would change the mathematical modelling and statistical mechanics approach to the description of glasses and amorphous films considerably [8].

Recent experiments and numerical simulations, and the theoretical interpretation thereof, have, in fact, indicated that the heterogeneous scenario is a more realistic starting point for laboratory systems. The new picture emerging [8] is that glasses are made up of a jammed, closed-packed ensemble of solid-like regions of nanometric size that hold up in their “voids” some fluid-like particles behaving somewhat collectively in each void. Moreover, the solid-like regions, though not fully crystalline, do show some quasi-order [9,10] that is related to the symmetry of the putative stable crystal phases of the substance. This type of modelling has proven to be successful for

^(a)Contribution to the Focus Issue *Progress on Statistical Physics and Complexity* edited by Roberta Citro, Giorgio Kaniadakis, Claudio Guarcello, Antonio Maria Scarfone and Davide Valenti.

interpreting a number of experiments [8,11,12] and represents, in the glassy solid state, the natural continuation of what has been established to happen close to the glass formation region in the supercooled liquid state [6].

It is the purpose of this article to outline the recent advances that have led to such an alternative scenario, which is a deeply revised edition of the old “crystallite” model of glasses [4,5] implementing knowledge about the supercooled state [6]. In no way do we wish to contribute to the 100-years old [4] homogeneous-network/crystallite controversy [5]; we argue that the heterogeneous scenario holds —when needed— a better chance for explaining experiments and simulations on real glassy systems. Decades ago, the extensive imaging of single- and multi-component real glasses by means of HRTEM investigations conducted by Vogel [13,14] and Zarzycky [15] have indicated that most real glasses are indeed better characterised by a grainy or cellular type mesoscopic structure, whether for bulk- or thin-splinter in terms of samples. Therefore, the basis for the alternative structural scenario we propose has been laid long ago, and we merely build upon it by specifying what seems to remain in the cell-cell voids. Images similar to the one in Vogel’s book [14] are also seen for metallic glasses [16,17], making the cellular structure a rather generic one for multi-component glasses. We note that such heterogeneities may involve mesoscopic phase separation.

The paper is organised as follows: first, the evidence will be briefly reviewed that the heterogeneous description with fluid-like particles in the voids is very useful for understanding anomalies in the cryogenic properties of glasses [8]. This requires specifying the solid-like and liquid-like organisation of the glassy structure in a mathematical model that allows for the description of the cryogenic anomalies that are not explained by the standard two-level systems tunnelling model (which relies on the homogeneous scenario). Next, we discuss spatial heterogeneity not involving phase separation in supercooled liquids. The evidence from extensive numerical simulations will be briefly reviewed [9,10] that in model systems and just above glass formation, the solid-like regions have a degree of quasi-order. This is affine to the phases of the putative crystal structure, and presumably, when the solid-like regions jam together to begin to form the glassy solid, this quasi-order continues to characterise the structural heterogeneities of the solid. Finally, some evidence is provided from experiments involving broadband dielectric spectroscopy [11,12] that the heterogeneous picture emerging does play an essential role in the proximity of the glass transformation range.

All together, these separate research activities add confidence that the homogeneous scenario for the medium-range structure should be superseded and that the heterogeneous one forms a better basis for the systematic understanding of the physical properties of glasses.

Heterogeneities in glassy solids as perceived from the cryogenic anomalies. –

The STM and its shortcomings. The cryogenic anomalies in glasses (temperatures $T < 4\text{K}$) have been studied since the 1970s within the framework of the Standard Tunneling Model (STM) [18]. This assumes the existence of two-level systems (2LS) distributed throughout the mass of the solid taken as a homogeneously disordered medium [19]. Though the atomic nature of the 2LS is not clear yet, this description makes use of effective particles coupling to the environment and has the well-known, simple mathematical description that affords a near complete understanding of the low-temperature properties. However, there are important deviations in the data from the STM predictions, notably the $-2:1$ slope ratio (a $-1:1$ ratio is observed, typically) in the dielectric constant’s $\log(T)$ anomaly [20]. Moreover, the heat capacity anomaly is often not simply linear in temperature, but a “hump” is observed at the lowest temperatures in most real glasses [21]. When multi-component systems are studied in the presence of a magnetic field, moreover, a whole new phenomenology has been observed [22,23], which cannot be explained through the ordinary STM. An extended STM has been proposed, including the indirect coupling of the nuclear spin to the magnetic field through those chemical elements characterised by a non-zero nuclear electric-quadrupole moment itself coupled to the STM’s 2LS [24]. Though the nuclear explanation does explain some of the experiments in a field, not all the magnetic anomalies can be understood in this framework, and in particular, the order of magnitude of the electric magneto-capacitance anomaly turns out to be far too weak from the nuclear coupling alone [25].

The heterogeneous extended model. All observed deviations from the STM predictions, including all of the magnetic effects, can be explained by considering the cellular heterogeneous structure re-proposed in the Introduction. The idea is [8,21,23] that the 2LS correspond to ions that are trapped between neighbouring solid-like cells and that the new phenomenology derives from the liquid-like species trapped in the cell-cell “voids”. Due to the size of the solid-like cells, the number of mobile particles in the voids can be large, order 50 to 500, and the only other assumption is that they move in a coherent way in such confined spaces. This results in the tunnelling motion of effective particles with heavily renormalised electric charge and tunnelling parameters. This may come as follows, *e.g.*, for silicate glasses. The most active ions should be O^- dangling ions adsorbed on the cells’ surfaces, which act as an effective particle subject to the surrounding forces in the confined space. The shape of the effective potential, for tetrahedral-type voids, is bound to have triangular topology due to the three neighbouring solid-like cells for each of the four effective particles in a void. In fig. 1 is a 2D cartoon of the situation extrapolated from the morphology proposed by the heterogeneous idea, where mobile but

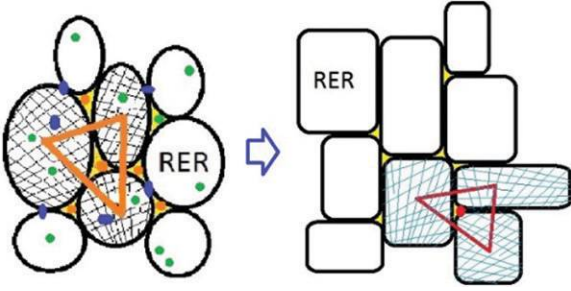


Fig. 1: A 2D cartoon of the model structure for a typical glass. Left: closer to T_g the ovals (RER) are compact solid-like regions characterised by quasi-order, the voids in-between containing new tunnelling species (orange, 3LS, while the blue are 2LS and the green impurities). The solid-like RER become more compact at the lower temperatures (right) [8].

localised charged species are added in the voids or pores between the solid-like cells. In the 3D environment, each effective particle is subjected to a potential of unknown form, which however should display a distorted triangular topology. Owing to the quasi-order within the neighbouring cells, the energy asymmetries' distribution for the collective tunnelling of each effective particle should be favouring near-degeneracy (though not complete degeneracy due to morphological disorder). These extra local degrees of freedom, three-level system (3LS) type, resident in the cell-cell voids, require extra mathematical description [21]. A single 3LS should correspond to a three-well tunnelling Hamiltonian (in a field):

$$H = \sum_a E_a C_a^+ C_a + D_o \sum_a e^{i\varphi/3} C_{a+1}^+ C_a + \text{h.c.},$$

where the C_a^+ are single-well ($a = 1, 2, 3$) particle-creation operators and φ (proportional to the magnetic flux through a single 3LS potential triangular loop) is the orbital-coupling magnetic phase. The E_a are energy asymmetries, and D_o is the tunnelling parameter between a triangular well and its neighbour, these parameters being taken within a distribution imposing near-degeneracy (N_{3LS} being the 3LS density):

$$P(\{E_a\}, D_o) = N_{3LS} / \{(E_1^2 + E_2^2 + E_3^2) D_o\}.$$

The three-level systems and their role. The above heterogeneous picture is the minimal model needed and affords the complete understanding of the low-temperature phenomenology not explained by the STM [8,23]. In the absence of a magnetic field, the $-1:1$ slope ratio for the dielectric anomaly is explained, as well as the hump in the heat capacity, through an extra contribution coming from the 3LS on top of that well understood from the standard 2LS [20,23]. The dependence of these non-STM anomalies on the composition x of two-component mixed glasses $A_x B_{1-x}$ has also been understood within this picture [20]. Likewise, the magnetic anomalies can be understood through the contribution from the extra 3LS implied

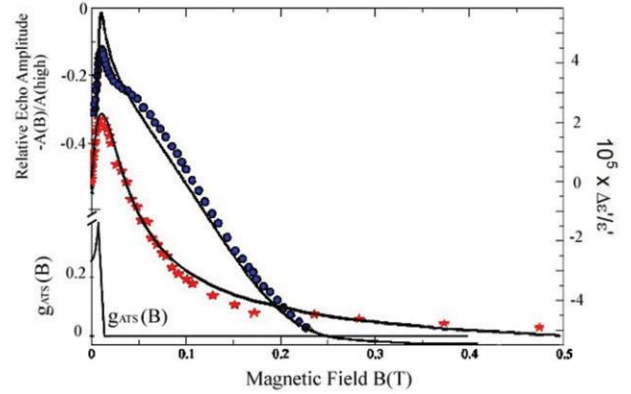


Fig. 2: The DOS $g_{3LS}(B)$ of the 3LS (also called ATS) as a function of the magnetic field B is shown to be responsible for the generic shape of the magnetic response. Data are for the relative change of the (real part ϵ') dielectric constant (red) [22] and (minus) the change of the peak of the polarisation echo (blue) [24]. The continuous lines result from the 3LS theory [8,21,23,26].

by the heterogeneous morphology of fig. 1 [8,21,23,26]. As it turns out, the observed magnetic contributions derive all, as a function of the field, from the behaviour of the 3LS density of states as a function of the field [8]. In this respect, the so-called isotope effect in the polarisation echo experiments is also explained through the competition of the driving microwave frequency and a characteristic oscillation frequency that depends on the elemental tunnelling ion's mass [26].

In fig. 2, the magnetic field dependence of two key experiments' response is reproduced for a single silicate glass (composition $\text{BaO-Al}_2\text{O}_3\text{-SiO}_2$) and compared with the behaviour of the 3LS density of states, $g_{3LS}(B)$. The comparison shows the common origin of the magnetic effects. It is to be remarked that the extended model introduces new adjustable parameters pertinent to the 3LS. However, for a given glassy substance, the values of these parameters as deduced from best fits to experimental data are practically the same in every experiment. Remarkably, the size of the solid-like cells as deduced from the 3LS density compares well with that of the typical observations from HRTEM [8] for multi-component glasses.

In summary, the extended tunnelling model proposed appears to explain all the low-temperature deviations from the STM predictions. It can be best justified through the heterogeneous structure scenario rendered in fig. 1. This has important implications for the physics of glasses at higher temperatures, too [27].

Static and dynamic heterogeneities of a supercooled liquid and their link to slow glassy dynamics. – In this section, we focus on the drastic slowing down of the liquid dynamics towards glass transition. Dynamic heterogeneity (DH) is one of the very robust features of supercooled liquids exhibiting slow glassy dynamics [6,28]. Thus, we discuss the origin of the DH and its relation to

slow glassy dynamics. One critical question is whether the DH has a static structural origin or not. We consider this fundamental question for two extreme cases [9], very fragile hard-sphere-like liquids with isotropic interactions and strong liquids with directional interactions, such as silica and water.

Systems with isotropic interactions. Most theoretical studies on the glass transition focus on the super-Arrhenius behaviour of the structural relaxation time τ_α , which is known to be characteristic of fragile liquids [29]. A hard-sphere liquid is a typical example of such fragile liquids. The most fundamental question concerning the dynamical behaviour of these systems is why the drastic slowing down can take place without significant change in the liquid structures, *e.g.*, measured by scattering experiments. The crucial fact is that the structure of a liquid has been seen mainly through two-body density correlation both experimentally and theoretically.

It has recently been shown that three-body or higher-order correlations can detect the growth of significant development of angular order in a liquid upon cooling [9,30,31]. For example, for weakly polydisperse hard-sphere liquids, it was found that the DH mirrors structural heterogeneity, which can be detected by crystal-like bond-orientational order [32]. Such a link between glassy structural order and crystal-like order is seen only for systems suffering from weak frustration against crystallisation. For strongly frustrating cases, such as binary mixtures and systems suffering from large polydispersity, the glassy structural order does not link to the crystal orientational order but is still characterised by its high packing capability, *i.e.*, high entropy [10,33]. On noting that structures with high crystal-like bond orientational order also have high entropy, structural ordering towards high local entropy (*i.e.*, low free energy) is generic to systems with isotropic interactions [9,30–33].

Furthermore, structures with high packing capability or high vibrational entropy should have slow dynamics (see figs. 3(a) and (b)) since particles' motion in such structures should be highly correlated. Thus, the growth of the correlation length of such glassy structural order in a supercooled liquid is expected to increase the activation energy E . Numerical simulations showed that the static correlation length of glassy order grows with decreasing the temperature T as $\xi \sim (T - T_0)^{-(2/d)}$, where T_0 is the ideal glass transition temperature, and the activation energy grows as $E \propto \xi^{d/2}$. Interestingly, these relations lead to the Vogel-Fulcher-Tammann law [9,29–34]. These relations were mostly confirmed above (or around) the mode-coupling critical temperature T_c due to limited computational power [30–33].

The same relation $E \propto \xi^{d/2}$ is also predicted by the random first-order transition (RFOT) theory [29,35], one of the most popular theories of glass transition. However, the RFOT theory also predicts that the static and dynamic lengths should be decoupled at least above the

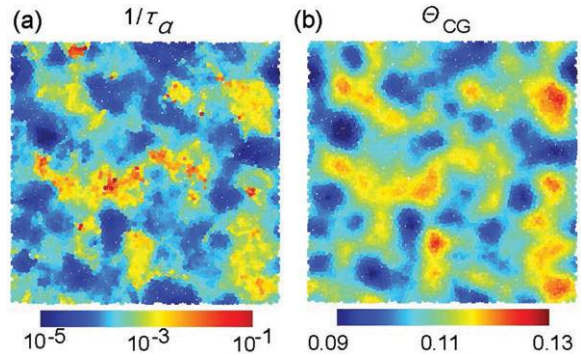


Fig. 3: Structural and mechanical heterogeneities in glass-forming materials. Spatial distributions of microscopic structural relaxation time of each particle, $1/\tau_\alpha$ (a) and coarse-grained packing capability, Θ_{CG} (b) for 2D polydisperse harmonic particles (polydispersity = 13%). Reproduced with permission from ref. [33].

mode-coupling T_c . This prediction was confirmed [36] by the decoupling between the so-called point-to-set length [29] and the dynamic correlation length. However, it was pointed out that the standard point-to-set length may pick up only translational correlation but cannot detect orientational correlation, *i.e.*, high-entropy structures [10,37]. Thus, which scenario captures the nature of slow glassy dynamics is debated and has to be studied carefully.

Systems with strong directional bonding. Strong liquids are another important class of glass-forming materials. The most typical examples are silica and water, which have strong directional bonds (covalent and hydrogen bonds, respectively). These liquids show the Arrhenius behaviour near the glass transition temperature T_g , unlike the fragile liquids discussed above. It was recently found [38–40] that they exhibit the so-called fragile-to-strong transition far above T_g , which was characterised as the crossover from the power-law divergence towards the mode-coupling T_c to the Arrhenius behaviour.

However, a different scenario, *i.e.*, the non-Arrhenius-to-Arrhenius transition, was recently proposed based on the two-state model [41]. These liquids with directional bonding were found to be characterised by the formation of locally favoured tetrahedral structures. Since such local structure formation is energetically favoured but entropically disfavoured, a high-temperature liquid has few such structures, whereas a low-temperature liquid contains plenty of such structures. Thus, the fraction of structures with slow dynamics ψ increases from zero to 1 with decreasing the temperature. Ordered stable structures have a higher activation energy than disordered structures by ΔE . Thus, the effective activation energy is a function of ψ and $E(\psi) = E_0 + \Delta E\psi$. Since the structure formation is local, the DH should have a maximum when ψ becomes 0.5, which was confirmed for water [41].

The above comparison of fragile and strong liquids tells us that the difference comes from the spatial extendibility

of structural order [9,31]. In fragile liquids, the correlation length of low-free-energy local structures grows at deeper supercooling, and the cooperativity in motion in these structures leads to the increase in the activation energy. On the other hand, in strong liquids, the size of local structures shows little change, but their fraction increases, which leads to an increase in the activation energy [41]. For a liquid with intermediate fragility, the structural ordering is expected to be induced both energetically and entropically [9]. Further careful study is necessary to reveal the physical origin of the slow glassy dynamics unambiguously.

Finally, we note that this tendency of structural ordering upon cooling is memorised in glass structures upon freezing and may be responsible for the structural heterogeneity of glasses.

Evidence for a link between vitrification and crystallisation. As mentioned above, in systems suffering from little frustration against crystallisation, structural order related to crystal orientational symmetry develops upon cooling. It was further revealed that such preordering acts as precursor upon crystallisation [42,43]. This indicates that unlike classical nucleation theory and density functional theory, crystal ordering in systems interacting with isotropic interactions starts with orientational ordering rather than translational ordering. Furthermore, it was shown that glass-forming ability is controlled by the degree of crystal-like orientational order developed in a supercooled state [44]. If a liquid structure has local orientational order similar to the crystal, it reduces the crystal-liquid interface tension, promoting crystallisation; in the opposite case, crystallisation tends to be prohibited, leading to high glass-forming ability. These facts indicate a close link between vitrification and crystallisation, both controlled by local structural ordering in liquids as indeed confirmed for realistic materials [45,46].

Static heterogeneities of glasses. As discussed above, a supercooled liquid has dynamically fluctuating structural heterogeneities, whose characteristic size and lifetime increase upon cooling. Below the glass transition, they are practically frozen. Thus, glasses should have static structural heterogeneities, which may play a crucial role in the properties of a glass and the response to an external field [8]. It was also shown that local softness is a crucial feature of glasses [47,48]. In relation to it, we note that mechanical self-organisation also plays a critical role besides structural self-organisation below the glass transition, and structural and mechanical heterogeneities have different physical origins [49–51].

Dynamic heterogeneities studied by linear and non-linear dielectric spectroscopy. – Despite extensive theoretical and experimental studies, the glass transition remains a mystery. At low temperatures glassy matter exhibits mechanical rigidity similar to that observed in crystalline materials. However, glasses exhibit liquid-like short-range order only and glassy rigidity

cannot result from structural long-range order. The question arises, if a hidden order, driven by an amorphous order parameter, characterises the glassy state and it seems natural to search for increasing length scales of cooperativity. In addition, the glass transition is a purely dynamic phenomenon and the enormous slowing down of viscosity follows a super-Arrhenius behaviour, which possibly implies a critical temperature. This fact confronts us with a further open question, if the glass transition is driven by an underlying phase transition, located well below the glass temperature, where the system falls out of thermodynamic equilibrium. The relaxation dynamics of glassy matter is strongly non-exponential (in the time domain) or strongly non-Debye (in the frequency domain). In the time domain relaxation functions are fit to a Kohlrausch-Williams-Watts or stretched exponential functions, with a stretching exponent $\beta < 1$, which usually decreases with temperature. Non-exponential relaxation can result from the fact that either each molecular entity relaxes non-exponentially, or rather from a broad distribution of relaxation times due to an inhomogeneous material with relaxation times depending on the local environment. There is ample evidence from four-dimensional NMR [52], dielectric hole burning [53], and direct probing of structural fluctuations at nanoscale utilising atomic-force microscopy [54] that the latter is the case and glasses show characteristic structural heterogeneities, which exist at least on the time scale of the experiment [6,55]. Lifetimes and sizes of these dynamic heterogeneities (DH) usually are not known and are the focus of recent research. Broadband linear dielectric spectroscopy [56] and non-linear dielectric spectroscopy [57,58] are ideal for studying a number of fundamental phenomena, like DH, increasing length scales, or hidden phase transitions.

Super-Arrhenius relaxation, cooperatively rearranging regions, and their relation to dynamic heterogeneity. Dielectric spectroscopy can be utilised to determine the T -dependence of the mean relaxation time τ , which is directly related to the viscosity, spanning an enormous frequency window. In most cases, the temperature dependence of glassy relaxation is governed by super-Arrhenius behaviour, which usually can be satisfactorily described by the time-honoured Vogel-Fulcher-Tammann (VFT) law, with $\tau = \tau_0 \exp[DT_{VF}/(T - T_{VF})]$. Here D is the so-called strength parameter, and T_{VF} is the Vogel-Fulcher temperature, where the relaxation times would diverge, in the case the system did not fall out of thermal equilibrium. Small values of D imply strong deviations from the Arrhenius behaviour. Such glass formers are termed “fragile”, in contrast to so-called “strong” glass formers whose relaxation time closely follows a simple Arrhenius law [59]. In a naive interpretation, super-Arrhenius behaviour is thought to follow from significant temperature dependence of the activation energy, which results from an increasing size of cooperatively rearranging regions (CRRs). With decreasing temperature, an increasing number of

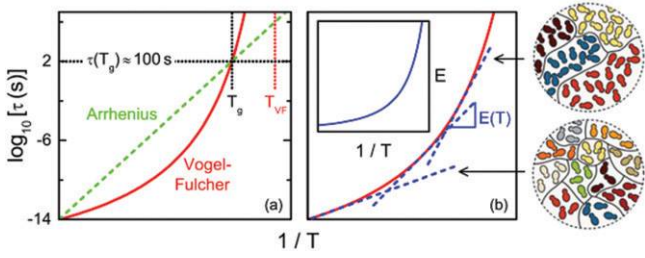


Fig. 4: (a) Arrhenius representation of the temperature-dependent relaxation time for Arrhenius (dashed line) and VFT behaviour (solid line). For the Arrhenius case, the activation energy is proportional to the slope in this plot. (b) A possible explanation of the non-Arrhenius behaviour: an increase of the size of CRRs (schematically indicated by molecules of the same colour) leads to an increase of apparent energy barriers (inset). The latter are proportional to the slopes within the Arrhenius plot, $\log \tau$ vs. $1/T$ (dashed lines). Reprinted figure from ref. [58], with kind permission from *The European Physical Journal* (EPJ).

molecules have to move cooperatively, which explains the increase in hindering barrier and the strong non-Arrhenius type of behaviour of the temperature dependence of the mean relaxation times. This is schematically shown in fig. 4. The existence of CRRs was already proposed more than 50 years ago by Adam and Gibbs [60]. There have been some attempts to estimate the size of CRRs at the glass transition from thermodynamic parameters, which were found to be of nanometer size in a variety of materials [61]. It is also clear that there must be a relation of CRRs to the DH. Usually, it is thought that the length scale of the DH, ξ_{het} , provides an upper limit of CRRs, ξ_{CRR} [52]. So far nothing can be said concerning the size distribution or the temperature dependence of these length scales. In addition, a precise relation between CRRs and DH has still to be formulated.

Non-linear dielectric spectroscopy to search for growing length scales and hidden phase transitions. During the last decades, it was evidenced that higher-order harmonic susceptibilities in the dielectric response can provide detailed information on specific correlations governing glass formation. Growing or even diverging non-linear susceptibilities have been documented for a variety of disordered systems, including spin glasses, orientational glasses, colloidal systems, and molecular glass formers [57]. In the frequency regime, non-linear dielectric susceptibilities, e.g., third-order χ_3 or fifth-order χ_5 susceptibilities, exhibit a significant and characteristic hump close to the structural relaxation frequency, anomalously increasing on decreasing temperatures. It has been shown that from the T -dependence of this hump, it is possible to determine the increasing number of correlated particles N_{corr} . [12,57,62].

Figure 5 shows the temperature dependence of the normalised correlated number of particles N_{corr} for a variety of glass-forming materials, including the canonical molecular glass formers glycerol, propylene carbonate

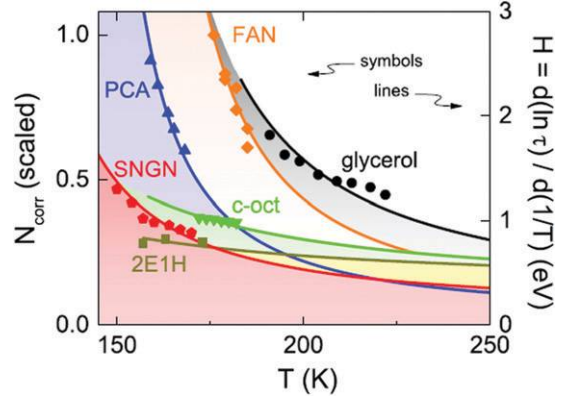


Fig. 5: Comparison of activation energies and the number of correlated particles N_{corr} as determined for a number of glass-forming materials: Glycerol, propylene carbonate (PCA), 3-fluoroaniline (FAN), 2-ethyl-1-hexanol (2E1H), cyclo-octanol, and succinonitrile/glutaronitril mixtures (SNGN). Lines indicate effective activation energies H determined from the derivatives of the temperature-dependent relaxation times (right scale). The symbols show N_{corr} , as determined from χ_3 (left scale). Reprinted figure from ref. [58], with kind permission from *The European Physical Journal* (EPJ).

(PCA), and 3-fluoroaniline (FAN), the mono-hydroxy alcohol 2-ethyl-1-hexanol (2E1H), as well as the plastic crystals cyclo octanol (c-oct) and mixtures of succinonitrile and glutaronitril ((60SN-40GN) [58]. For all these glassy systems N_{corr} increases with decreasing temperature, implying a significant growth of correlation lengths on decreasing temperatures. This increase of correlation lengths is consistent with a phase-transition-related origin of the glass transition. The temperature dependence of the number of correlated particles can be perfectly scaled with the increase of activation energies as determined from the relaxation times (solid lines in fig. 5). Propylene carbonate and 3-fluoroaniline exhibit the strongest temperature dependence, while the temperature dependence is weakest for 2E1H and cyclo-octanol. Obviously, these differences are fully correlated with the different fragilities of these systems.

Hence, dielectric measurements of higher harmonic susceptibilities revealed an increasingly cooperative motion of molecular entities. In this way, even strong hints on a hidden unconventional thermodynamic phase transition were obtained [12]. However, it is still a matter of debate if the number of correlated particles as determined from higher-order harmonics can directly be compared with length scales of the DH or CRRs. It seems natural to assume that in real systems at temperatures below the hidden phase transition, the growth of length scales is interrupted and the DH transform into static disorder.

Summary. – Here we discussed two types of spatial heterogeneities of glassy systems and their link to the physical properties below and above the glass transition. We hope that this article will stimulate further research on

the impact of heterogeneity on glassy materials' physical properties.

HT acknowledges grants-in-aid for Scientific Research (A) (JP18H03675) and Specially Promoted Research (JP25000002 and JP20H05619) from the Japan Society for the Promotion of Science (JSPS).

REFERENCES

- [1] ZACHARIASEN W. H., *J. Am. Chem. Soc.*, **54** (1932) 3841; *J. Chem. Phys.*, **3** (1935) 162.
- [2] WARREN B. E., *Phys. Rev.*, **45** (1934) 657.
- [3] BERNAL J. D., *Proc. R. Soc. A*, **280** (1964) 299.
- [4] LEBEDEV A. A., *Trud'i Gos. Opt. Inst.*, **2** (1921) 1 (in Russian).
- [5] PORAI-KOSHITS E. A., *J. Non-Cryst. Solids*, **123** (1990) 1.
- [6] EDIGER M. D., *Annu. Rev. Phys. Chem.*, **51** (2000) 99.
- [7] WRIGHT A. C., *J. Non-Cryst. Solids*, **401** (2014) 4.
- [8] JUG G., *The Polycluster Theory for the Structure of Glasses: Evidence from Low Temperature Physics*, in *Modern Problems in Molecular Physics: Selected Reviews*, edited by BULAVIN L. A. and CHALYI A. V. (Springer International Publishing AG, Berlin) 2018, Chapt. 13.
- [9] TANAKA H. *et al.*, *Nat. Rev. Phys.*, **1** (2019) 333.
- [10] TONG H. and TANAKA H., *Phys. Rev. X*, **8** (2018) 011041.
- [11] LUNKENHEIMER P. *et al.*, *Contemp. Phys.*, **41** (2000) 15.
- [12] ALBERT S. *et al.*, *Science*, **352** (2016) 1308.
- [13] VOGEL W. *et al.*, *J. Non-Cryst. Solids*, **49** (1982) 221.
- [14] VOGEL W., *Structure and Crystallisation of Glasses* (Pergamon Press, Oxford) 1971.
- [15] ZARZYCKY J., *Glasses and the Vitreous State* (Cambridge University Press, Cambridge) 1991.
- [16] BAKAI A. S., *The Polycluster Concept of Amorphous Solids*, in *Metallic Glasses III*, edited by BECK H. and GUNTERODT H.-J., *Topics in Applied Physics*, Vol. **72** (Springer-Verlag, Berlin, Heidelberg) 1994, pp. 209–255.
- [17] HIROTSU Y. *et al.*, *J. Appl. Phys.*, **59** (1986) 3081.
- [18] PHILLIPS W. A. (Editor), *Amorphous Solids: Low Temperature Properties* (Springer, Berlin, Heidelberg) 1981.
- [19] PHILLIPS W. A., *Rep. Prog. Phys.*, **50** (1987) 1657.
- [20] JUG G. and PALIENKO M., *EPL*, **90** (2010) 36002.
- [21] JUG G., *Philos. Mag.*, **84** (2004) 3599.
- [22] STREHLOW P. *et al.*, *Phys. Rev. Lett.*, **84** (2001) 1938.
- [23] JUG G. *et al.*, *Philos. Mag.*, **96** (2016) 648.
- [24] WURGER A. *et al.*, *Phys. Rev. Lett.*, **89** (2002) 237601.
- [25] BODEA D. and WURGER A., *J. Low Temp. Phys.*, **136** (2004) 39.
- [26] JUG G. *et al.*, *J. Non-Cryst. Solids*, **401** (2014) 66.
- [27] JUG G., arXiv:1909.04086.
- [28] WOCHNER P. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **106** (2009) 11511.
- [29] BERTHIER L. and BIROLI G., *Rev. Mod. Phys.*, **83** (2011) 587.
- [30] TANAKA H., *Eur. Phys. J. E*, **35** (2012) 113.
- [31] TANAKA H., *J. Stat. Mech.*, **2020** (2020) 034003.
- [32] TANAKA H. *et al.*, *Nat. Mater.*, **9** (2010) 324.
- [33] TONG H. and TANAKA H., *Nat. Commun.*, **10** (2019) 5596.
- [34] LANGER J. S., *Rep. Prog. Phys.*, **77** (2014) 042501.
- [35] KIRKPATRICK T. R. *et al.*, *Phys. Rev. A*, **40** (1989) 1095.
- [36] KOB W. *et al.*, *Nat. Phys.*, **8** (2012) 164.
- [37] RUSSO J. and TANAKA H., *Proc. Natl. Acad. Sci. U.S.A.*, **112** (2015) 6920.
- [38] ITO K. *et al.*, *Nature*, **398** (1999) 492.
- [39] SAIKA-VOIVOD I. *et al.*, *Nature*, **412** (2001) 514.
- [40] XU L. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **102** (2005) 16558.
- [41] SHI R. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **115** (2018) 9444.
- [42] KAWASAKI T. and TANAKA H., *Proc. Natl. Acad. Sci. U.S.A.*, **107** (2010) 14036.
- [43] RUSSO J. and TANAKA H., *J. Chem. Phys.*, **145** (2016) 211801.
- [44] RUSSO J. *et al.*, *Phys. Rev. X*, **8** (2018) 021040.
- [45] LEINES G. D. and ROGAL J., *J. Phys. Chem. B*, **122** (2018) 10934.
- [46] BECKER S. *et al.*, *Phys. Rev. B*, **102** (2020) 104205.
- [47] MANNING M. L. and LIU A. J., *Phys. Rev. Lett.*, **107** (2011) 108302.
- [48] DING J. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **111** (2014) 14052.
- [49] YANAGISHIMA T. *et al.*, *Nat. Commun.*, **8** (2017) 15954.
- [50] TONG H. *et al.*, *Phys. Rev. Lett.*, **122** (2019) 215502.
- [51] TONG H. *et al.*, *Nat. Commun.*, **11** (2020) 4863.
- [52] TRACHT U. *et al.*, *Phys. Rev. Lett.*, **81** (1998) 2727.
- [53] SCHIENER B. *et al.*, *Science*, **274** (1996) 752.
- [54] RUSSELL E. V. and ISRAELOFF N. E., *Nature*, **408** (2000) 695.
- [55] BÖHMER R., *Curr. Opin. Solid State Mater. Sci.*, **3** (1998) 378.
- [56] LUNKENHEIMER P. and LOIDL A., in *The Scaling of Relaxation Processes, Advances in Dielectrics*, edited by KREMER F. and LOIDL A. (Springer International Publishing) 2018, p. 23.
- [57] ALBERT S. *et al.*, in *Nonlinear Dielectric Spectroscopy, Advances in Dielectrics*, edited by RICHERT R. (Springer International Publishing) 2018, p. 219.
- [58] LUNKENHEIMER P. *et al.*, *Eur. Phys. J. ST*, **226** (2017) 3157.
- [59] ANGELL C. A., in *Strong and fragile liquids*, in *Relaxations in Complex Systems*, edited by NGAI K. L. and WRIGHT G. B. (Naval Res. Lab.) 1984, p. 3.
- [60] ADAM G. and GIBBS J. H., *J. Chem. Phys.*, **43** (1965) 139.
- [61] DONTH E., *J. Non-Cryst. Solids*, **53** (1982) 325.
- [62] CRAUSTE-THIBIERGE C. *et al.*, *Phys. Rev. Lett.*, **104** (2010) 165703.