

A simple picture for structural glasses

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Abstract This paper is an essay on mosaic structures in glasses, and their possible role in relaxation phenomena. (a) Near T_g the fluid is assumed to contain clusters, slightly more compact than the matrix: they cannot grow in size because of frustration effects, as noted by Kivelson and others. (Mode/mode coupling theories cannot describe this, because they do not incorporate frustration.) The size of the clusters corresponds to the Boson peak wavelength. (b) We propose that the standard free volume picture may be transposed: (i) clusters move rather than molecules, (ii) the required cavity space ('vacancy') for cluster motion is not empty, but filled with the low density matrix. (The old criticism against free volume based on pressure effects is thus removed.) (c) To reach one cluster, a 'vacancy' must hop through many 'traps': the distribution of hopping times ultimately leads to a stretched exponential for the relaxation, as argued by Bendler and Schlesinger. *To cite this article: P.-G. de Gennes, C. R. Physique 3 (2002) 1263–1268.*

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Un modèle simple pour les verres structuraux

Résumé Cet article discute certaines structures 'mosaïques' dans les verres minéraux ou organiques : (a) Près de la température de transition vitreuse T_g , le fluide contiendrait des « amas » compacts ; ceux-ci sont limités en taille par des effets de frustration, comme l'ont proposé Kivelson et al. (Les théories de couplage mode/mode ne peuvent pas bien décrire ces effets, car les corrélations à 2 points ne suffisent pas pour la frustration.) La taille des amas correspond à la longueur d'onde du pic de Bosons. (b) Nous proposons de transposer le modèle classique de volume libre : (i) ce sont les amas et non les molécules qui sont l'objet élémentaire, (ii) le volume de cavité nécessaire pour un saut n'est pas vide, mais est rempli par la matrice (de densité un peu plus basse). Les critiques formulées jadis contre le modèle du volume libre, à partir des effets de pression, sont ainsi éliminées. (c) Pour arriver jusqu'à un amas, une lacune doit sauter à travers de nombreux pièges : il y a une distribution des temps de saut qui conduit à une relaxation en exponentielle étirée, comme l'ont montré Bendler et Schlesinger. *Pour citer cet article : P.-G. de Gennes, C. R. Physique 3 (2002) 1263–1268.*

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verres structuraux / frustration / volume libre / inhomogénéités

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Version française abrégée

Différentes expériences suggèrent qu'un verre est localement hétérogène. Il est naturel de penser que des régions compactes (amas) se forment, mais qu'elles ne peuvent pas croître au-delà d'une certaine taille – comme la coordination icosaédrique autour d'une sphère. Notre proposition est de reprendre une forme modifiée du modèle classique de *volume libre*, qui décrit assez bien les effets à l'équilibre et hors d'équilibre. Mais ici, l'unité élémentaire n'est pas une molécule, c'est un amas, et l'espace entre amas n'est pas vide ; il est rempli d'une matière amorphe de densité un peu plus basse.

L'hypothèse centrale qui est faite (décrite sur la Fig. 1) est la suivante : on suppose qu'entre les amas peuvent exister quelques lacunes, de taille assez bien définie (comparable à la taille des amas). C'est le mouvement de ces lacunes qui contrôle la dynamique. Mais, encore une fois, ces lacunes ne sont pas vides : elles sont remplies par la matrice amorphe. On peut ainsi rendre compte de beaucoup de propriétés statiques (comme l'anomalie de chaleur spécifique liée à la fraction matrice) et dynamiques (comme les exponentielles étirées).

1. Introduction

Glass has been produced for more than 3500 years, by melting sand, sea shells and natron (CO_3Na_2). An amazing cascade of inventions followed: ovens, crucibles, and the superb idea of glass blowing – all of them more than 2000 years old. Later, in Europe, the fabrication of flat glass and mirrors in Venice, the discovery of splendid pigments – oxides and metal nanoparticles, up to recent achievements like float glass or optical fibers have advanced the technology.

But all this art grew without a deep understanding of what happens when a liquid cools down into a glass. An important distinction between strong liquids (where activation energies are well defined) and fragile liquids (where the apparent activation energies increase upon cooling) was made many years ago [1]. When some degrees of freedom are left after allowing for covalent bonding, we expect a fragile liquid [2]. Very recently, a geometric interpretation of fragility (from the dependence of typical barrier heights on the system energy) has been suggested in simulations [3]. However, from a spatial point of view, the organisation of fragile glasses remains opaque.

In the present note, we start from the most recent observations on structural glasses (with their fundamental heterogeneity) and we propose one more (tentative) model based on clusters.

All our reflection is purely qualitative. However, the hope is to bring in a real contact between different schools of thought.

2. Mosaic structures

2.1.

The idea of local clusters in glasses has shown up rather early in the crystallographic literature: Greaves's conjecture [4] about SiO_2 regions, surrounded by metal ions is a typical example; the possible role of the outer regions in ionic transport and in fracture propagation has been mentioned.

2.2.

The polarised photobleaching experiments of Ediger and coworkers [5] show that probe molecules (dyes) in a glassy matrix are divided into different populations – some with fast orientational relaxation, some with slow relaxations. And these populations do interchange after a certain (long) time.

2.3.

Dielectric saturation experiments [6] allow one to ‘burn a hole’ in the distribution of dipoles. The hole is not nicely narrow (as it is in NMR experiments on systems with inhomogeneous fields), but it also displays different populations.

2.4.

Similar information (more precise, but more complex) comes from NMR measurements [7].

2.5.

The depolarisation of fluorescence can now be studied on a *single* probe molecule [8]. The conclusions are:

- (a) two different molecules can have different relaxation behaviors;
- (b) one same molecule can switch from a simple (exponential) relaxation to a more complex mode, after a certain time τ_{jump} : the environment has been modified.

All this points clearly to a mosaic structure.

3. The Fischer experiments

3.1.

The coherent light scattering intensity $S(q)$, at small wave vectors q , is anomalous, as recognised first by Fischer [9] on OTP and other molecular glasses.

There is a small angle peak of $S(q)$ (for $q \sim 1/\xi$) which violates the thermodynamic rule relating $S(O)$ to the bulk compressibility. This is seen by light scattering, but (using synchrotron sources) it is possible to show that the X ray curve matches exactly the light curve [10]. The characteristic length ξ is large, >10 molecular sizes, and does not show any critical behavior as a function of temperature.

3.2.

More recently, Fischer has analysed the speckle pattern [11] of the anomalous light scattering: it behaves very much like the pattern of a dense colloidal suspension, with clusters which move by a slow diffusion process. The diffusion constant D is proportional to the α relaxation frequency $D \sim \tau_{\alpha}^{-1}$.

3.3.

By various preparational tricks, the Fischer group has been able to prepare ‘clear’ samples with no anomalous scattering. (These samples regenerate the anomalous scattering, after a long time τ_g .) An important feature of the clear samples (pointed out to me first by C.A. Angell) is that their relaxation is still τ_{α} : the large associations seen by Fischer are *not* the source of the long relaxation times [12]. Fischer set up a picture where primary clusters of small size (some nm) aggregate to build up fractal clumps of size ξ . We return to this notion in more detail in Section 4.

4. The cluster picture

4.1.

Returning to Section 3, it is natural to assume that the mosaic structure is based on *compact primary clusters* (having an internal density larger than average, by a few percent) which roughly correspond in size to the Boson peak [13,14].

4.2.

Why do these clusters retain a finite size b , instead of growing indefinitely? The answer (proposed in particular by Kivelson and coworkers [15]) is that the size is limited by *frustration effects*. The packing involved cannot propagate up to large distances.

At this level, the statement is universal. However, the detailed frustration process will vary from system to system. With Van der Waals spheres, the icosahedral packing has been fully analysed [16,17]. For flexible polymers, the nature of the frustrated packing is unclear (and should be studied by adequate simulations). For systems with charged ions, we might find a form of frustration similar to what is expected in networks of incompatible polymer mixtures [18]. In both cases there is a conflict between ‘charge’ requirements and density requirements.

4.3.

The current attempts to derive the cluster size by general statistical arguments are not very convincing: they do not take into account the frustration properly.

4.4.

A possible weakness of the mode/mode coupling approach [19,20] is the ignorance of geometrical frustration effects. For instance, with spheres, the delicacies of icosahedral packings show up mainly in high order density/density correlations, which are systematically erased in MMC.

4.5.

The simulation approach on clusters is promising, but just starting. What is currently done is to use a mixture of two atom types, with slightly different sizes. This is an excellent way to prevent crystallisation, but the frustration aspects are not deeply controlled. However, Tomida and Egami [21] found icosahedrons which aggregate into larger clusters.

4.6.

The clusters cannot be welded together, because of frustration. One might wonder whether they however attract each other by long range Van der Waals forces, because of the contrast in density with the surrounding matrix. For spherical clusters, a rule of the thumb estimate of the cluster/cluster interaction is:

$$U_{cc} \sim U_{11} \left(\frac{\delta\rho}{\rho} \right)^2 \frac{b}{a}, \quad (1)$$

where U_{11} is the interaction between basic units (‘atoms’ or ‘monomers’) of size a , and $\delta\rho/\rho$ is the density contrast. Eq. (1) usually leads to attractions which are weaker than kT for $T \sim T_g$. However, if the clusters are not spherical (faceted?) the interaction could be larger. These weak interactions may be the source of the correlations observed by Fischer.

4.7.

An open question is the value of the fraction $\psi(T)$ of particles which are in the ‘soft’ matrix.

It is tempting to propose that $\psi(T)$ is proportional to the extra volume $\Delta V(T)$, measured in classical experiment (difference between molar volume and the value extrapolated from low T , with a constant expansion coefficient).

4.8.

The question of how molecular probes (dyes) fit inside or between clusters is entirely open.

5. Returning to classical experiments

5.1.

One approach to the mechanical properties, using clusters, is based on friction between primary clusters, or changes inside a primary cluster [22]: the area involved is of order b^2 , and the resulting activation energies are huge, giving a possible clue to the behavior of viscosities in fragile glasses.

5.2.

Here, we make a different proposal: a transposition of the classical free volume ideas [23]: using *clusters, rather than atoms, as the building blocks*. The cavity volume is now not empty, but filled with the low density compound. Free volume has been questioned because of misfits with pressure effects. But here, if the two phases have very similar densities, the pressure effects should be indeed minor.

5.3.

What is the source of the broad distribution of relaxation times (at one given temperature near T_g) around τ_α ? Our tentative answer here follows the main idea of Bendler and Schlesinger [24]. We assume that a cluster can move (or rotate) only when a ‘vacancy’ (in the sense of 5.2) reaches its neighborhood. There are very few vacancies: thus, to reach one particular cluster, a vacancy must perform many hops, or go through many traps. The traps have various barrier energies: Bindler and Schlesinger have shown that the distribution of hopping times ultimately translates into a stretched exponential relaxation for the cluster.

5.4.

How can we link the dielectric data and the mechanical data? The above model suggests that they involve the same relaxation time $\tau_\alpha(T)$. We can also understand this as follows. Starting from a Kubo formula for the viscosity η , and assuming that the range of mechanical correlations is the cluster size b , we are led to:

$$\eta = \frac{1}{kT} \langle \sigma^2 \rangle b^3 \tau_{\text{rot}}, \quad (2)$$

where σ is a shear stress inside a cluster, and τ_{rot} is a rotational time of the clusters, assumed to be essentially the same as τ_α . A fluctuation theorem gives:

$$\langle \sigma^2 \rangle \sim \mu kT/b^3, \quad (3)$$

where μ is the shear modulus of the hard clusters (and is finite at all temperatures). Then $\eta = \mu \tau_{\text{rot}}$: the rotational properties command both the mechanics and the dielectric properties.

6. The central assumption

We want the soft matrix surrounding the clusters to be able to form ‘vacancies’ in the stacking of clusters as shown on Fig. 1(a). We repeat that the vacancies are not empty: they contain matter with the average density of the soft matrix.

Why should such a vacancy be able to retain its individuality, while hopping around? At first sight, we might fear that the vacancy splits into small pieces, as shown on Fig. 1(b). If this splitting occurs, we lose most of the attractive features: (a) there is no reason to have the Cohen Turnbull exponential, and to recover the WLF laws; (b) the Shlesinger Bendler explanation for stretched exponentials also falls out.

It may be that the attractive forces between clusters (roughly discussed in Eq. (1)) disfavor the conformations of Fig. 1(b), as compared to Fig. 1(a): the clusters want to stick together. What we need is a proof (or disproof) of the existence of durable vacancies: it might be reached by clever spectroscopic measurements on a single molecule.

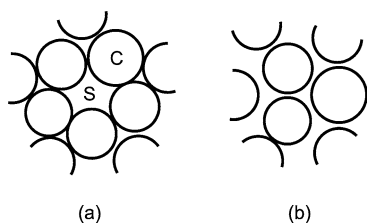


Figure 1. (a) A localised ‘vacancy’ among clusters C (note that the vacancy is not empty, but is filled by the soft matrix S); (b) a distributed vacancy.

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