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Glasses

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Towards a Molecular View of Glass Heterogeneity

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In spite of the technological importance and ubiquity of glasses in our lives, we still lack a clear understanding of what actually happens when a non-crystallizing liquid is cooled down and turns into a disordered solid. As temperature is lowered, the liquid's viscosity increases by several orders of magnitude, and relaxation appears to come to a stop. For practical purposes, the glass-transition temperature T_g is defined as the point where relaxation becomes too slow to measure, when the viscosity reaches about 1 TPa·s. On a logarithmic scale of viscosity, there is no apparent accident or remarkable point on the viscosity curve, only a smooth Arrhenius law for strong glasses, such as silica, or a Vogel–Fulcher law for fragile glasses, such as most molecular glass formers.[1] Combining the material's shear modulus (which characterizes its elasticity) with this viscosity, we can define a characteristic time, which, for a homogeneous medium, is scale-independent. This time, called the alpha relaxation time, can be seen as the reorganization time of the material, down to molecular scales. A characteristic shear modulus of 1 GPa and the glassy viscosity of 1 TPa·s therefore give a relaxation time of 1000 s, the reorientation time of a typical molecule at the glass transition (15 orders of magnitude longer than the relaxation time of a small molecule in the normal liquid phase, 1 ps). The above simple argument relies on the assumption of a spatially homogeneous medium and conveys a picture of the glass as a "liquid in slow motion". However, it has been known for a long time that this naive picture is deeply misleading. Adam and Gibbs have explained why the cooperation of many molecules is necessary to obtain large viscosities,[2] within larger and larger cooperatively rearranging regions (CRRs) as the viscosity increases. Such a highly hierarchical arrangement of molecules is totally incompatible with the structure of the high-temperature liquid, in which all molecular correlations are short-ranged. The structure of a glassy liquid must therefore differ in profound ways from that of the high-temperature liquid. Although glass-forming materials have long been known to present heterogeneity,[3,4] no structural differences spring to the eye from regular ensemble measurements. Presumably, the inhomogeneities responsible for the cooperating rearranging regions are too subtle to show up and are averaged out in most ensemble measurements. Therefore, to understand glassy behavior, one must include heterogeneity as an essential part of the material description.

When honey starts to crystallize, it shows solid-like lumps in a thinner liquid. Such a solid–liquid mixture or slurry may serve as a mundane picture of what a heterogeneous glass-forming liquid might be like. The irregular structures shown in Figure 1 in a thin layer of cottage cheese provide another example from our everyday experience. They arise from the solid-like curd which closely intermingles with liquid-like whey. These examples show the difficulty in quantifying the structure of an inhomogeneous system, even when "curds" and "whey" are made out of the same material. Another approach is to follow what happens to the density fluctuations of a homogeneous liquid when its temperature is lowered. As long as the liquid remains homogeneous, one can derive and apply the equations of motion of density fluctuations. This approach, called mode-coupling theory (MCT),[5] predicts a critical temperature T_c at which one of the liquid's fluctuation modes becomes infinitely slow. The critical temperature should not be identified with the glass transition, though, because the slowing down may concern only a minor fraction of the total volume involved. A similar phenomenon occurs in percolation theory, where the percolating aggregate

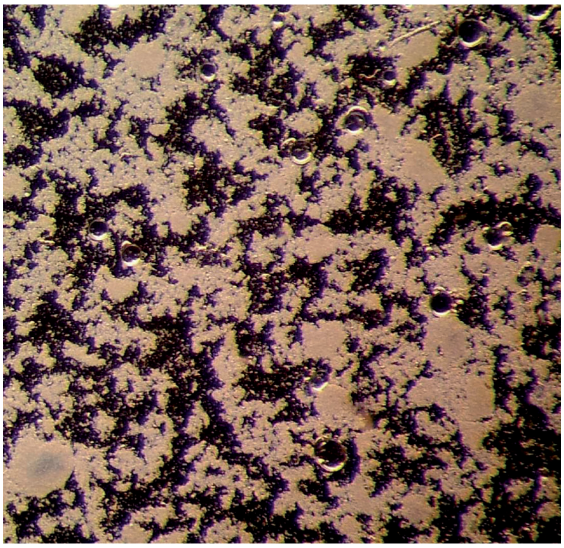

Figure 1. Curds and whey observed by pressing a piece of cottage cheese (Hüttenkäse) between two glass slides. The picture is taken in an optical microscope under white-light illumination. The side of the field is about 1 mm.

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at the critical temperature covers only a vanishingly small part of the total lattice. As soon as the mode becomes slow enough, thermodynamic equilibrium cannot be reached any more: ergodicity is broken. The system's state now depends on initial conditions, themselves possibly varying from point to point in a macroscopic sample. The system therefore has become non-ergodic and inhomogeneous (in particular, mode-coupling theory of course ceases to apply). Note that this transition to non-ergodic behavior happens well above the conventional glass transition, $T_c > T_g$ (for many systems, the critical temperature is estimated to $T_c \approx 1.2\,T_g$). Below T_c, some of the relaxation times of the system much exceed the alpha relaxation time deduced from the homogeneous liquid approximation. However useful mode-coupling theory may be to understand ergodicity breaking, it leaves many questions about the glass unanswered. It is still unclear what the slow mode is, or whether it is the precursor of a solid-like "lump of curd" in the (still) generally fluid material.

Conventional ensemble measurements such as NMR spectroscopy[6] do not provide a molecular view of heterogeneity, because they are often based on two-point correlation functions.[7] Deviations from homogeneity can appear in higher-order correlation functions[8] but access to these complex quantities is fraught with assumptions and experimental difficulties. Light and X-ray scattering experiments provide signals which directly arise from density fluctuations. These experiments have confirmed the inhomogeneity of glass-forming materials and shown that Rayleigh scattering from density fluctuations is much higher than expected from thermodynamic equilibrium.[9] Moreover, the Rayleigh scattering intensity strongly depends on the thermal history of the sample. Since these first results, a new class of experiments has been performed on individual molecules as local reporters in glass-forming materials. These experiments represented a fundamental change in the study of glasses, as the different responses of different individual local probes in the material directly report on heterogeneity and on its spatial dependence. The purpose of this Essay is to summarize these new results, to point out the questions they open, and to indicate possible future experiments to answer them. Much of our discussion will be qualitative and speculative, and is meant to stimulate further thinking and research on glass formation.

The principle of single-molecule optical measurements is to follow local reporters (molecules, nanocrystals, or nanoparticles) at different positions in the material and to compare their responses. This method has been applied to a wide range of materials,[10] in particular organic glass formers: polymers and molecular liquids. The easiest experiment is to follow the polarization of the fluorescence of individual fluorescent molecules, which indicates rotational diffusion of the emitters. Other possible observables are conformational changes of a quenchable probe[11] and translational diffusion. This latter observable has not been often used to date, but it could give a very complementary picture to rotational diffusion now that superresolution techniques provide access to distances as small as some tens of nm.[12] In essence, each individual molecular probe is considered as a small "bobber" driven by thermal fluctuations and measuring the local viscosity. The advantage of molecules of a well-defined compound is that all individuals are absolutely identical. Therefore, any difference from molecule to molecule must come from the local structure of the material.

Hereafter, we briefly summarize published single-molecule observations in glass-forming materials. A common result of all the publications is the heterogeneity of single-molecule responses: different molecules tumble at different rates in glass-forming liquids[13–15] or in polymers.[16–18] In the following, we concentrate on molecular glass-forming liquids, where the host molecules are smaller than the probes. The case of polymers is more complex because of the different length scales of monomer and polymer chain, particularly when the probe is also a polymer.[19] The different experiments appear to agree as to the extent of the heterogeneity. In glycerol, for example, the spread of tumbling times of a large aromatic molecule appears to be almost one order of magnitude at 15 K above the glass transition. Moreover, in some experiments,[13,14] this extent appears to increase when the temperature decreases, as shown in Figure 2. This behavior, which is not always seen,[20] would appear consistent with the mode-coupling theory's picture, because all the different micro-environments should converge to the homogeneous liquid above the critical temperature T_c.

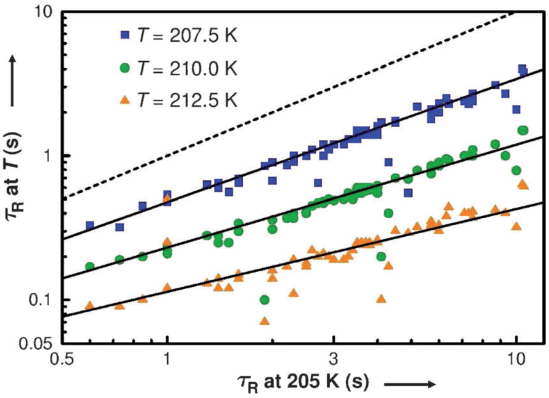

Figure 2. Measured tumbling times of single dye molecules in supercooled glycerol at different temperatures.[14] The tumbling time of each molecule at three temperatures (207.5, 210, and 212.5 K) is plotted against the tumbling time of the *same* molecule at 205 K. The spread of values directly shows heterogeneity. The strong correlation of the times of each molecule at different temperatures shows that there are few environmental exchanges only, with notably more of them at the highest temperature. The decreasing slope of these correlation plots shows that the spread in tumbling times decreases as temperature increases. For a homogeneous environment, above the critical temperature in mode-coupling theory, all the times should be equal, yielding a line with zero slope. The solid lines are guides for the eye, the broken line corresponds to the correlation at the same temperature (slope unity).

Mode-coupling theory suggests that ergodicity is broken below T_c, but does not precisely indicate how this might take place. Is ergodicity strongly broken, with frozen micro-environments, or weakly broken with each molecule having access to only a part of the configuration space? In practice, we can expect that an individual probe may change its dynamic behavior, either by diffusing to a different region of the material, or because the material's local properties may have changed at the molecule's position. These changes of properties are called environmental exchanges, and can be explored by following the statistical properties of rotational diffusion for the same molecules over extended durations. Different experiments have indicated a large spread in the observed environmental exchange times. Typically, ensemble experiments do not see any exchanges.[6] In single-molecule experiments, these exchange times have ranged to some rotational tumbling times[13,15,20] to millions of them or longer.[14] These widely different times may be related to the thermal history of the sample, a parameter that is not always precisely reported in the different papers, and whose importance has been underestimated in the early literature. The experiments of Zondervan et al. were done after long waiting times (up to months) at low temperature,[21] which may have allowed for extended growth of solid-like parts and made relaxation of heterogeneity nigh to impossible.

Collectively, single-molecule experiments point towards the existence and growth of denser or solid-like parts. This property seems to be general, for polymers as well as for small molecular glass formers. Experiments with very long exchange times find stable, but different rotation rates for different molecules. This observation can be rationalized assuming that solid-like walls are isolating liquid lakes with different local properties. This model is consistent with the curds–whey picture, except that the liquid parts appear unable to mix with one another (thus this model is rather one of "curd and wheys"). The structure of the solid-like parts is an open question. For small molecules, such as glycerol, it seems natural that a solid-like cluster would be made of (nano)crystallites, as recently suggested by Stevenson and Wolynes.[22] In polymers, no crystallization being expected, denser solid-like parts could nevertheless form as "lumps of curd". Another important question concerns the distribution of the probe molecules in the heterogeneous liquid. Recent work[20] shows that whether the molecules prefer denser or thinner regions (or alternatively, more or less polar regions in glycerol, a strong hydrogen bonder) depends on their chemical nature as well as on the local structure. One of the main conclusions of these observations is the surprising number and range of questions arising from heterogeneity in a material. Ergodicity breaking implies that thermal history becomes a relevant and even central parameter, which can determine the structure of the material. This fact was already very well established from early experiments, as cooling below T_g is a reliable method to start solidification, even in liquids as difficult to crystallize as glycerol. The complex interplay of nucleation and growth processes explains the complexity and multiplicity of non-equilibrium states, which may depend not only on thermal history, but also on small perturbations, such as impurities and interfaces.

In addition to the single-molecule measurements, some other experiments were done by the author's group in the past few years. We summarize them hereafter and try to see how they may complement single-molecule results to provide a consistent view of glassy materials at the molecular scale.

1) Rheology: The curds-and-whey hypothesis predicts long-range solid-like structures, which should confer a solid-like response to the material, at least for weak deformations. Indeed, flow experiments in the cryostat indicate that a yield–stress behavior develops in the material after aging at low temperatures.[21] Even at a few Kelvin above the glass transition, the solid-like response slowly grows. This experiment was repeated with a more sensitive rheometer.[23] However, this apparatus did not allow for very long aging times and the aging had to be carried out at a higher temperature, 40 K above the glass transition. In these conditions, crystallization was apparent in the sample, although not complete because the material remained very soft. Indeed, the aged sample could be crushed easily at stresses orders of magnitude weaker than those needed to crush the bulk polycrystal. This result suggests the presence of liquid parts even in the crystallized aged sample. The crystalline parts may have been mainly located close to the surface, rather than inside the material.
2) Optical microscopy: observations at micrometer scales with fluorescent dyes show evidence for patterns reminiscent of a phase separation.[24] The dye usually appears to be expelled from possibly denser regions, a few microns in size. These results show that heterogeneity can extend to large distances, depending on aging and thermal history.
3) Neutron scattering: neutron diffraction on glycerol samples aged at a relatively high temperature (50 K above the glass transition) gives sharp Bragg peaks, which are evidence for rather large crystals, at least 40 nm in size.[25] Moreover, the presence of crystals strongly depends on thermal history.

Giving a synthetic view of all these observations is difficult, but some conclusions can be drawn. Heterogeneity has been found in all single-molecule experiments to date, with comparable extents in systems with or without possible crystallization. This may indicate that denser or solid-like structures spontaneously form at a low enough temperature, which provides a natural model for the ergodicity breaking predicted by mode-coupling theory. For molecular glass formers, such as glycerol or *o*-terphenyl, these solid-like structures are probably crystalline or nanocrystalline. For polymers, they are necessarily amorphous. The times for environmental exchanges have been found to differ by orders of magnitude in different experiments on glycerol. We suggest that these differences are related to the different thermal histories that these samples underwent. It would be interesting to search for a similar behavior in polymers, which can't crystallize. If the same trend is also found in polymers, it would mean that the (nano)crystals of glycerol and other small-molecule glass formers are a consequence of glass heterogeneity rather than its primary cause. Beyond demonstrating heterogeneity, a new generation of experiments with local probes will have to characterize it more quantitatively on a wide range of length and time scales. Here are a few suggestions of such experimental directions:

- Translational diffusion could be monitored on sub-micron scales with superresolution techniques. This approach would make the diffusion areas visible and provide answers to such questions as: what is the shape and size of the high-mobility and of the solid-like regions? How do they change with temperature and time? What are the associated dynamic and mechanical properties of the material?

- How does heterogeneity appear upon cooling down? Experiments with long waiting times seem to indicate an increase of heterogeneity when temperature is lowered. Mode-coupling theory suggests that, above the critical temperature, all molecules should tumble in the same way. The appearance of heterogeneity could be explored around the critical temperature, possibly with larger probes which diffuse more slowly than single molecules.

The structure and dynamics of glass-forming materials is surprisingly rich and complex, already well above the glass transition. The complexity of these materials arises from the multiple states they can reach, which depend on thermal treatment, and probably also on weak perturbations such as impurities and interfaces. To explore the rich space of configurations of these complex systems, a new generation of experiments with a range of different local probes is needed. Only then will we have a chance to solve the vexing problem of the glass transition, which has been frustrating experimentalists and theorists for more than a century.

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