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Scenarii for slow dynamics and cooperative lengthscales in glass-formers

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Abstract. Glasses are often described as a genuine state of matter. The aim of this paper is to briefly review several ideas, old and new, about what makes glasses so special as a state of matter: glasses are liquids that do not flow, characterized by increasingly cooperative dynamics.

PACS. 61.43.Fs Glasses – 05.20.-y Classical statistical mechanics – 05.50.+q Lattice theory and statistics

1 Introduction

The most salient properties of *fragile* glasses are (a) the non exponential ("stretched"), spatially heterogeneous and temporally intermittent nature of the relaxation; (b) the extremely fast rise of their viscosity η that increases by 15 orders of magnitude as the temperature is decreased by less than a factor 2, and appears to diverge at a finite (Vogel-Fulcher) temperature; (c) the aging and memory effects of the out-of-equilibrium phase, that shows some similarities with spin-glasses. A rather remarkable aspect of the Vogel-Fulcher divergence (b) is that the extrapolated freezing temperature T_{VF} is found to be, for a whole range of materials, rather close to the Kauzmann temperature T_K where the extrapolated entropy of the supercooled liquid becomes smaller than that of the crystal. Assuming that the entropy of a typical metastable state in which the glass can get stuck is close that of the crystal, the difference between the liquid and crystal entropies (aka the configurational entropy) counts approximatively the number of metastable states in which the glass can get stuck. The experimental finding, $T_0 \simeq T_K$, then implies that the divergence of the viscosity is related to a rarefaction of metastable states (also called the entropy crisis phenomenon).

The striking observation that makes the 'problem of glasses' interesting is that very many, totally different materials, exhibit the same properties, pointing to the existence of a somewhat universal mechanism: glassy dynamics is physics more than chemistry.

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2 Mean field: landscapes and MCT

Two apparently quite different frameworks have been discussed in the (fourty years old) literature to account for this phenomenology:

- phase space/energy landscape pictures, where the system is trapped in metastable states of varying depth. The dynamics is made of small harmonic vibrations around each metastable configurations, separated by hops between different minima of energy (or free-energy);
- cooperatively rearranging regions of increasing length. The dynamics becomes sluggish because larger and larger regions of the material have to move simultaneously to allow substantial motion of individual particles.

Although the idea of cooperative dynamics seems most reasonable, its reality has remained elusive until recently: a consistent definition of this growing length, its experimental measurement and its calculation within a theoretical model (even highly simplified) are subjects of topical activity. Interestingly, similar concepts are also relevant for the description of other "jammed" systems, such as dense granular assemblies that flow in a very jerky way.

The landscape picture can be given more flesh within mean-field spin-glass theories. The Random Energy Model, for example, contains already a lot of the glass phenomenology (entropy crisis at T_K, aging..). The analogy with spin-glasses actually helps understanding that the proper order parameter to describe the glassy state is the Edwards-Anderson parameter, which is a measure of the amplitude of density fluctuations which does not decay with time. More elaborate mean field spin-glasses theories lead to dynamical equations that are identical to the "Mode Coupling" theory (MCT) of supercooled liquids.

MCT is considered by many to be the only available first principle theory of the supercooled state, starting from interacting atoms and making its way up to compute the viscosity of the liquid as a function of density and temperature. This theory makes a number of quantitative predictions that can be compared to experiments, some of which in remarkable agreement with observations. This analogy between MCT and mean-field spin-glasses allows one to interpret the MCT scenario for dynamical arrest in a clear fashion: the potential energy landscape has only unstable saddle points above a certain "threshold" energy, around which the system can only pause momentarily before continuing its exploration of phase space. This corresponds to the high temperature liquid phase. Lowering the temperature, the number of unstable directions decreases. At the energy threshold (corresponding to T_{MCT}), the saddles only have marginal (zero curvature) escape directions, responsible for the MCT divergence of relaxation times. For lower energies (temperature) there are only minima where the system gets trapped. The number of these minima is exponential in the size of the system as long as $T_K < T < T_{MCT}$, but the barriers between them are (in mean-field) infinite: once trapped in a minimum, the system remains there forever. These marginal saddles (or minima) also dominate the out of equilibrium dynamics: after a quench below T_{MCT} the system ages due to a never-ending descent toward the threshold states. The system never relaxes to equilibrium because the older it is, the fewer and the flatter the unstable directions and the longer it takes to decrease the energy.

3 Finite dimensions and dynamic heterogeneities

Is this above mean-field picture at all relevant for finite range interactions? Phase-space pictures cannot be directly applied when the dynamics is local: the energy surface must somehow "factorize". "Hops" in phase space should correspond to definite spatial structures (vacancies? strings? fractal clusters?). The observed dynamical heterogeneities, and the corresponding viscosity/diffusion decoupling must be accounted for. Hidden behind phase space pictures, there must thus be a dynamical length scale $\xi(T)$ governing the slowing down of these materials. Contrarily to simple systems where this length scale is the characteristic size over which some order (ferromagnetic, crystalline, etc.) is established, the difficulty of glasses and spin-glasses is that no obvious local order sets in. The definition of a dynamical length scale is more subtle and requires a *four point* density correlation function that attempts to quantify the size of dynamically correlated regions. Since the glass order parameter is already a two-body correlation function, the natural "susceptibility" for the MCT transition is a four-point function. Interestingly, the MCT freezing transition is indeed accompanied by the growth of a dynamic correlation length scale, exactly as usual second order phase transitions are accompanied by the growth of a static correlation length. This dynamic susceptibility is in fact related in a deep way to a dynamical response: if a local perturbation is introduced at point $\boldsymbol{r}$ in space (for example a local excess density), what is the size of the region where the dynamics is significantly affected? This dynamic response can be computed explicitely within MCT, and reveals the existence of a dynamic correlation length that diverges as $(T-T_{MCT})^{-1/4}$. As noted above, the MCT transition can be interpreted as describing the appearance of marginally metastable states that slow down the dynamics. These states are characterized by soft modes that involve a diverging number of particles moving in correlated clusters. A series of precise and non trivial predictions about the scaling of these dynamic clusters can be made close to T_{MCT}, which are in rather good quantitative agreement with simulations in the weakly supercooled region. Some of these predictions are however more general than MCT, such as the link between the four-point susceptibility and the dynamical response. In fact, the integral over space of the dynamic response is related to the derivative of the two-point correlation function with respect to a control parameter, e.g. the temperature, which is easily measured. This leads to a simple and direct way to access dynamic correlation volumes experimentally. In close analogy with spin-glasses, one also expects that the appearance of long-ranged amorphous order in glasses should be signaled by growing non-linear susceptibilities (e.g. non-linear dielectric constant).

Since dynamic fluctuations diverge close to T_{MCT}, one expects that MCT will fail in low enough dimensions. It turns out that below $d_c = 8$, fluctuation effects become dominant and lead in particular to a breakdown of the Stokes-Einstein relation. Therefore, MCT predictions cannot be quantitative in three dimensions very close to T_{MCT}. However, a more essential problem of MCT is that barriers between metastable states must be finite for realistic potentials, even for $T < T_{MCT}$. Therefore, the very divergence of the viscosity at T_{MCT} is smeared out and replaced by a crossover.

What is then the nature of the growing length scale at lower temperatures? Old free volume ideas, recently revived within the context of 'facilitated' models, suggest that mobility defects trigger the dynamics and become more and more dilute as temperature decreases – the length scale is then related to the distance between defects. A more ambitious scenario, proposed by Adam-Gibbs in the 60's and, inspired by mean-field spin-glasses, by Kirkpatrick, Thirumalai and Wolynes in the 80's, relates the size of collectively rearranging regions to the configurational entropy of the glass. The idea is that of entropic melting of frozen clusters: small clusters have few low energy metastable configurations and are pinned in one of them by the external environment; large clusters can explore many configurations and free themselves from any boundary conditions: entropy, which is extensive, wins over the energetic gain due to pinning boundary conditions. On small scales, the dynamics from state to state is fast (low barriers) but leads to nowhere – the system ends up always visiting the same state. For larger scales, the system can at last delocalize itself in phase space and kill

correlations, but this takes an increasingly large time. The crossover scale ξ, determined by the balance between configurational entropy and pinning boundary energy, then sets the relaxation time and diverges when the configurational entropy goes to zero, explaining the deep connection between dynamics and thermodynamics (absent in mobility defect theories). The supercooled liquid is in a *mosaic state*, made up as a patchwork of all possible frozen configurations, with cell size ξ. The dynamics within scale ξ is collective and landscape (trap) pictures should be relevant. For larger scales, however, the dynamics occurs in parallel and global phase space ideas are meaningless. The mosaic state offers a plausible interpretation of the random first order transition to an amorphous solid predicted by mean-field theories. The relevance of this beautiful scenario, where the liquid slows down because of the emergence of a very large number of metastable states that momentarily trap the system, with larger and larger frozen regions as the system is allowed to visit deeper and deeper energies (i.e. more and more jammed states), is however still quite controversial. This theory is certainly still imperfect in many ways: no realistic model where this it can be proved mathematically yet exists. Although its mean field version has been worked out in detail, its finite dimensional extension have still to be put on firm theoretical grounds (some steps on highly stylized models have been made recently). Yet, it has already produced many non trivial predictions, such as the idea of out of equilibrium effective temperatures and scaling of dynamic correlations, and it explains naturally some puzzling experimental facts such as the Adam-Gibbs relation between dynamics and thermodynamics. One of its main asset, compared to many other scenarios of glass transition, is that is firmly based on a well defined microscopic theory.

The same issues in fact exist also for spin-glasses. Parisi's mean-field solution in this case reveals an even richer and more complex landscape structure, with valleys within valleys within valleys, in a hierarchical (fractal) fashion. Although this fractal picture is very helpful to account for example for the memory and rejuvenation effects, the way to reconcile mean-field with real spin-glasses where the dynamics again becomes slow because of the growth of some cooperative length scale is far from settled. A remarkable effect predicted in spin-glasses is their extreme fragility to tiny temperature changes, that may induce large rearrangements in the equilibrium spin configuration. Such a fragility was also discussed in other contexts (pinned vortex lines, dislocations, domain walls; force chains in granular materials). The extent to which this 'temperature chaos' effect also exists in regular glasses and allows one to understand rejuvenation in these materials is an open problem.

4 Some open problems

Some of the outstanding questions that remain before we can say we understand why glasses do not flow are the following:

- How relevant (if at all) are mean-field ideas/models for real glasses (and spin-glasses)? Is cooperativity non thermodynamical as in mobility defect/facilitated models or related to an exponential degeneracy of metastable states, as in mean-field models? Can one make some (controlled) theoretical progress on a non mean-field model of glasses, or at least formulate a Ginzburg-like criterion to understand the parameter region where mean-field models are relevant to describe real glassy materials? Can one describe in detail the crossover between the (high temperature) MCT region and the (low temperature) mosaic/activated region?
- What is the geometry of elementary dynamical excitations in glasses (and spin-glasses): strings, fractal clusters? Is there really, experimentally, a detectable growing dynamical length scale in glassy systems (including jamming granular materials, soft glassy materials, spin glasses) that is the cause of the dramatic slowing down of the dynamics? How large can this length actually grow (experiments suggest roughly 100 correlated particles at T_g). Can this explain the apparent universality of glassy dynamics? Is this length scale important to understand, e.g. anomalous phonon modes or fracture in these materials? Does this length scale measure the size of the cooperative rearranging regions?
- Is there a random matrix like theory of the statistics of energy landscapes, that would make MCT predictions generic? Is the idea of fragility and disorder/temperature chaos, now well established for disordered systems (spin glasses, randomly pinned objects) and possibly related to rejuvenation effects, also relevant for structural glasses?

We hope that the upsurge of theoretical, numerical and experimental activity on dynamical heterogeneities in glasses and disordered materials will help answering some of these questions in the near future.

5 References

We point here toward a restricted list of references that may be useful to know more about some of the issues addressed in this paper. This list is neither exhaustive nor faithful to the historical development of the field, and biased towards our own work.

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