

Glass and Jamming Transitions

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1 Introduction

Glasses are one of the materials most known and used by humans. Obsidian—a volcanic glass—was used for prehistoric tools and weapons. Now we easily design glasses with desired mechanical or optical properties on an industrial scale; glasses are widely present in our daily life and even used to create art objects, such as Murano glasses. Yet, a microscopic understanding of the glassy state of matter remains a challenge for statistical physicists. Glasses share similarities with crystalline solids, they are both mechanically rigid, but also with liquids since they both have similar disordered structures at the molecular level. In 1995 P.W. Anderson wrote that, *the deepest and most interesting unsolved problem in solid state theory is probably the nature of glass and the glass transition*. The aim of this article is to give an introduction to this problem, describe the mysteries related to it, show the reasons why it is so much studied by theoretical physicists and, finally, explain a theory that can possibly lead to its solution.

Since this is still an unsolved problem there are several—at least apparent—contradictions in the literature, and several debated questions and biases in interpreting the experimental results, and even in deciding which ones are important and which ones are not. In order to convey the state of the art and some of the debated questions, I will make use both of the usual presentation style of physics papers but also of a dialogue format between two characters: Salviati, a theoretical physicist, and Cleverus, a laymen—but a very clever one!¹

2 Basic facts

The usual way to obtain a glass consists in cooling a liquid. The quench must be fast enough in order to avoid the standard first order phase transition towards the crystalline phase. The metastable phase reached in this way is called ‘supercooled phase’. In this regime the viscosity and the relaxation timescale, e.g the decorrelation time of the density field, increase by more than 14 orders of magnitude: from picoseconds to hours. This is a quite unusually broad range for a condensed matter system. Depending on the cooling rate, typically of the order of 0.1 – 100 K/min, and the the patience of the people carrying out the experiment, typically hours, the

¹As the reader certainly knows, such dialogues are not new in the physics literature. Even some characters, like Salviati, appeared already several times [1, 2]. Of course, I have no ambition whatsoever to share anything with the great scientists that wrote those dialogues, except maybe the fun in writing them.

supercooled liquid falls out of equilibrium at a certain temperature, called the glass transition temperature T_g , and becomes an amorphous rigid material—a glass.

This experimental glass ‘transition’ is clearly *not* a thermodynamic transition at all, since T_g is only empirically defined as the temperature below which the material has become too viscous to flow on a ‘reasonable’ timescale. Pragmatically, it has been agreed upon a common definition of T_g such as the temperature at which the shear viscosity is equal to 10^{13} Poise (also 10^{12} Pa.s). In order to grasp how viscous this is, recall that the typical viscosity of water at ambient temperature is of the order of 10^{-2} Pa.s. How long would one have to wait to drink a glass of water with a viscosity 10^{14} times larger?

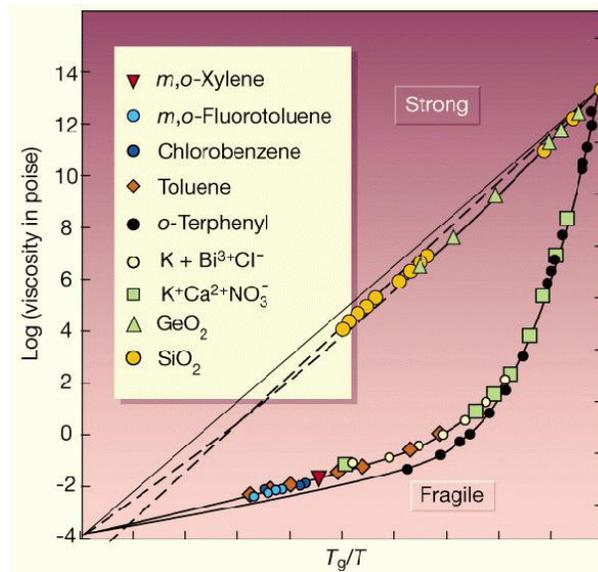


Figure 1: Arrhenius plot of the viscosity of several glass-forming liquids approaching the glass transition temperature T_g . For ‘strong’ liquids, the viscosity increases in an Arrhenius manner as temperature is decreased, $\log \eta \sim E/(K_B T)$, where E is an activation energy and the plot is a straight line, as for silica. For ‘fragile’ liquids, the plot is bent and the effective activation energy increases when T is decreased towards T_g , as for ortho-terphenyl. Note that there exists a continuous range of liquids from very fragile to very strong. By plotting their corresponding data one would fill the gap between the two curves in the figure above.

The increase of the relaxation timescale of supercooled liquids is remarkable not only because of the large number of decades involved but also because of its temperature dependence. This is vividly demonstrated by plotting the logarithm of the viscosity (or the relaxation time) as a function of T_g/T , as in Fig. 1 [3]. This is called the ‘Angell’ plot and is very helpful in classifying supercooled liquids. A liquid is called strong or fragile depending on how the viscosity changes as a function of T_g/T in the Angell plot. Straight lines correspond to ‘strong’ glass-formers and to an Arrhenius behaviour. In this case, one can extract from the plot an effective activation energy, suggesting quite a simple mechanism for relaxation by ‘breaking’ locally a chemical bond. The typical relaxation time is then dominated by the energy barrier to activate this process and, hence, has an Arrhenius behaviour. Window glasses fall in this category. The terminology ‘strong’ and ‘fragile’ is not related to the mechanical properties of the glass but to the evolution of the short-range

| Substance | o-terphenyl | 2-methyltetra-hydrofuran | n-propanol | 3-bromopentane |
|-----------|-------------|--------------------------|------------|----------------|
| T_g | 246 | 91 | 97 | 108 |
| T_0 | 202.4 | 69.6 | 70.2 | 82.9 |
| T_K | 204.2 | 69.3 | 72.2 | 82.5 |
| T_K/T_0 | 1.009 | 0.996 | 1.028 | 0.995 |

Table 1: Values of glass transition temperature, VFT singularity and Kauzmann temperatures T_K for four supercooled liquids [4].

order close to T_g . Strong liquids, such as SiO_2 , have a locally tetrahedric structure which persists both below and above the glass transition contrary to fragile liquids whose short-range amorphous structure disappears rapidly upon heating above T_g . If one tries to define an effective activation energy for fragile glass-formers using the slope of the curve in Fig. 1, then one finds that this energy scale increases when the temperature decreases, a ‘super-Arrhenius’ behaviour. This increase of energy barriers immediately suggests that the glass formation is a collective phenomenon for fragile supercooled liquids: many degrees of freedom have to move cooperatively to make the system relax and this leads to growing energy barriers. Support for this interpretation is provided by the fact that a good fit of the relaxation time or the viscosity is given by the Vogel-Fulcher-Tamman law (VFT):

$$\tau_\alpha = \tau_0 \exp \left[\frac{DT_0}{(T - T_0)} \right], \quad (1)$$

which suggests a divergence of the relaxation time and of the effective barrier $DT_0T/(T - T_0)$ and, hence, a phase transition of some kind at a temperature T_0 . A smaller D in the VFT law corresponds to a more fragile glass. Note that there are other comparably good fits of these curves, such as the Bässler law,

$$\tau_\alpha = \tau_0 \exp \left(K \left(\frac{T^*}{T} \right)^2 \right), \quad (2)$$

that only leads to a divergence at zero temperature but still implies a divergent effective energy barrier, $K(T^*)^2/T$, and hence some kind of growing cooperativity. Actually, although the relaxation time increases by 14 orders of magnitude, the increase of its logarithm, and therefore of the effective activation energy is modest, and experimental data do not allow one to unambiguously determine the true underlying functional law beyond any reasonable doubt. For this and other reasons, physical interpretations in terms of a finite temperature phase transition must always be taken with a grain of salt.

However, there are other experimental facts that shed some light and reinforce the use of eq. (1). Among them, there is an empirical connection found between kinetic and thermodynamic behaviours. Consider the part of the entropy of the liquids, S_{exc} , which is in excess compared to the entropy of the corresponding crystal, and plot it as a function of T . As for the relaxation time one cannot follow this curve below T_g in thermal equilibrium. However, extrapolating the curve below T_g apparently indicates that the excess entropy vanishes at some finite temperature, called T_K ². The big surprise is that T_K is generically very close to T_0 , the temperature

²The sub-index K stands for Kauzmann, who first discussed the possible existence of T_K .

at which a VFT fit diverges. This coincidence is quite remarkable: for materials with glass transition temperatures that vary from 50 K to 1000 K the ratio T_K/T_0 remains close to 1, up to a few percents. Examples reported in Ref. [4] are provided in Table 1. This link between kinetics and thermodynamics appears also in the empirical relation found by Adam-Gibbs, which connects the relaxation time to the excess entropy mentioned above, and reads: $\ln \tau(T) \propto [TS_{xs}(T)]^{-1}$. The Adam-Gibbs relation holds reasonably well both for single liquids as temperature is varied, and cross-sectionally for different liquids. Were this relation exact, it would indeed imply that the temperature at which the relaxation time diverges must coincide with the one at which the the excess entropy vanishes.

But where this empirical relations, in particular the one between T_0 and T_K , come from? This is a first mystery to elucidate. Note that the 'coincidence' between T_0 and T_K strongly suggests that some kind of phase transition may well take place at $T_0 = T_K$. This underlying "ideal glass transition"³ would be the phenomenon responsible for the physical behavior of supercooled liquids and for the glass transition seen in experiments. But what kind of transition is this? And why the excess entropy is an important quantity anyway? Goldstein introduced a physical picture that has been indeed very instrumental in our understanding of the glass problem. He assumed—and this was later verified numerically—that approaching T_g the system of N particles (or molecules) forming the super-cooled liquid explores a part of the energy landscape (or configuration space) which is full of minima separated by barriers that increase⁴ when temperature decreases. In the Goldstein's scenario the dynamic evolution in the energy landscape would then consist in a rather short equilibration inside the minima followed by 'jumps' between different minima. At T_g the barriers have become so large that the system remains trapped in one minimum, identified as one of the possible microscopic amorphous configurations of a glass. Following this interpretation, one can split the entropy into two parts. A first contribution is due to the fast relaxation inside one minimum, a second counts the number of metastable states, $S_c = \log N_{\text{metastable}}$, which is called the 'configurational' entropy. Assuming that the contribution to the entropy due to the 'vibrations' (or coarse-grained vibrations) around an amorphous glass configuration is not very different from the entropy of the crystal, one finds that $S_{\text{exc}} = S_{\text{liquid}} - S_{\text{crystal}} \approx S_c$. Within this approximation, T_K corresponds to a temperature at which the configurational entropy vanishes. Concomitantly, the properties of the energy landscape visited by the system change drastically, since below T_K the system becomes stuck into an handful of low-lying states. Assuming that S_c vanishes linearly as suggested by extrapolations of S_{exc} and using the thermodynamic relation $T \frac{dS}{dT} = C_p$, one finds a downward jump of the specific heat C_p at T_K and therefore a truly thermodynamic phase transition.

At this point the reader might have reached the conclusion that the glass transition may not be such a difficult problem: there are experimental indications of a diverging timescale and a concomitantly singularity in the thermodynamics. It simply remains to find static correlation functions displaying a diverging correla-

³It is called ideal because, if it exists, it would be a true phase transition, compared to the cross-over taking place at T_g , and it could be reached only if one were able to equilibrate the systems on arbitrary large, meaning in practice unattainable, timescales.

⁴Note that the energy landscape does not change with temperature. The regions of the landscape sampled by the system, instead, do depend on temperature. At low temperature, the sampled regions are characterized by higher barriers in the Goldstein's scenario.

tion length related to the emergence of ‘amorphous order’. This would allow us to classify the glass transition as a standard second order phase transition. Remarkably, this remains an open and debated question despite several decades of research. Simple static correlation functions are quite featureless in the supercooled regime, notwithstanding the dramatic changes in the dynamics. A simple static quantity is the structure factor defined by

$$S(q) = \left\langle \frac{1}{N} \delta\rho_{\mathbf{q}} \delta\rho_{-\mathbf{q}} \right\rangle, \quad (3)$$

where the Fourier component of the density reads

$$\delta\rho_{\mathbf{q}} = \sum_{i=1}^N e^{i\mathbf{q}\cdot\mathbf{r}_i} - \frac{N}{V} \delta_{\mathbf{q},0}, \quad (4)$$

with N is the number of particles, V the volume, and \mathbf{r}_i is the position of particle i . The structure factor measures the spatial correlations of particle positions, but it does not show any diverging peak in contrast to what happens, for example, at the liquid-gas tri-critical point where there is a divergence at small \mathbf{q} . A snapshot of a supercooled liquid configuration in fact just looks like a glass configuration, despite their widely different dynamic properties. What happens then at the glass transition? A more refined understanding can be gained studying dynamic correlations or

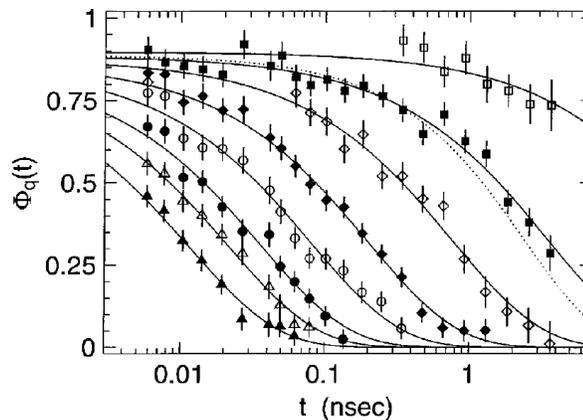


Figure 2: Temperature evolution of the intermediate scattering function normalized by its value at time equal to zero for supercooled glycerol [5]. Temperatures decrease from 413 K to 270 K from right to left. The solid lines are fit with a stretched exponential with exponent $\beta = 0.7$. The dotted line represents another fit with $\beta = 0.82$.

response functions.

A dynamic observable studied in light and neutron scattering experiments is the intermediate scattering function,

$$F(\mathbf{q}, t) = \left\langle \frac{1}{N} \delta\rho_{\mathbf{q}}(t) \delta\rho_{-\mathbf{q}}(0) \right\rangle. \quad (5)$$

Different $F(\mathbf{q}, t)$ measured by neutron scattering in supercooled glycerol [5] are shown for different temperatures in Fig. 2. These curves show a first, rather fast,

relaxation to a plateau followed by a second, much slower, relaxation. The plateau is due to the fraction of density fluctuations that are frozen on intermediate timescales, but eventually relax during the second relaxation. The latter is called ‘alpha-relaxation’, and corresponds to the structural relaxation of the liquid. This plateau is akin to the Edwards-Anderson order parameter, q_{EA} , defined for spin glasses which measures the fraction of frozen spin fluctuations. Note that q_{EA} continuously increases from zero below the spin glass transition. Instead, for structural glasses, a finite plateau appears above any transition.

Many other remarkable phenomena take place when a supercooled liquid approaches the glass transition. I presented above some of the most important ones, but many others have been left out for lack of space.

To sum up, approaching the glass transition a liquid remains stuck for a very long time in an amorphous configuration. It eventually evolves but this takes such a long time that below a certain temperature this regime cannot be probed anymore. As a matter of fact, the number of microscopic configurations in which the glass can get stuck is exponentially large as shown by the value of the configurational entropy at T_g : a few k_B per particle. There seems to be a very large degeneracy in the ways molecules can arrange themselves such as to form mechanically stable, amorphous patterns around which they vibrate without exploring all the other stable patterns. The way in which this degeneracy decreases with temperature seems to be tightly connected to the way the relaxation times increases. Possibly, an ideal glass transition takes place at $T_0 = T_K$. At this temperature the configurational entropy, a measure of this degeneracy, would vanish and the relaxation timescale would diverge. This exponential degeneracy of the “phases” towards which the liquid can freeze is a feature that classical theories of phase transitions cannot easily handle, and that requires new tools. At the same time, this feature seems to be the very essence of glassiness: in order to prevent fast crystallisation, the interaction between molecules must be able to generate enough “frustration” to make the energy landscape rough and rocky and trap the system in a configuration not very different from an arbitrary initial configuration of the liquid.

3 The Jamming-Glass transition of colloids and grains

Colloidal suspensions consist of big particles suspended in a solvent. The typical radii of the particles are in the range $R = 1 - 500$ nm. The solvent, which is at equilibrium at temperature T , renders the short-time dynamics of the particles Brownian. The microscopic timescale for this diffusion is given by $\tau = R^2/D$ where D is the short-time self-diffusion coefficient. Typical values are of the order of $\tau \sim 1$ ms, and thus are much larger than the ones for molecular liquids (in the picosecond regime). The interaction potential between particles depends on the system, and this large tunability makes colloids very attractive objects for technical applications. A particularly relevant case, on which we will focus in the following, is a purely hard sphere potential, which is zero when particles do not overlap and infinite otherwise. In this case the temperature becomes irrelevant, apart from a trivial rescaling of the microscopic timescale. Colloidal hard spheres systems have been intensively studied in experiments, simulations and theory varying their density ρ , or their volume fraction $\phi = \frac{4}{3}\pi R^3\rho$. Hard spheres display a fluid phase from 0 to intermediate volume fractions, a freezing-crystallisation transition at $\phi \simeq 0.494$, and a melting

transition at $\phi \simeq 0.545$. Above this latter value the system can be compressed until the close packing point $\phi \simeq 0.74$, which corresponds to the FCC crystal. Interestingly, a small amount of polydispersity (particles with slightly different sizes) suppresses crystallization. In this case, the system can be more easily ‘supercompressed’ above the freezing transition without nucleating the crystal, at least on experimental timescales. In this regime the relaxation timescale increases very fast. At a packing fraction $\phi_g \simeq 0.58$ it becomes so large compared to typical experimental timescales that the system does not relax anymore: it is jammed. This ‘jamming transition’ is obviously reminiscent of the glass transition of molecular systems and indeed several studies have shown that the phenomenon that take place increasing the volume fraction are analogous to the ones seen in molecular supercooled liquid: the relaxation timescales increases very fast and can be fitted by a VFT law in density as in Eq. (1), dynamical correlation functions display a broad spectrum of timescales and develop a plateau as in Fig. 2, no static growing correlation length has been found, etc. Also the phenomenon of dynamic heterogeneity that we will address later is present in both cases.

It is important to stress that the super-compressed state of colloids is really akin to the super-cooled state of molecular liquids: it is metastable with respect to the crystal but otherwise at equilibrium. We will not address here problems in which the colloid ages or is compressed extremely fast.

In theoretical studies of the jamming-glass transition it is customary to neglect the hydrodynamics effects and focus on hard spheres mixtures undergoing a Brownian dynamics. It is a well known result that the probability distribution at long times for such a system converges to the equilibrium Boltzmann distribution.

As a summary, comparing the jamming-glass transition of colloids to the glass transition of liquids one finds several astonishing similarities, despite the fact that the systems are rather different in nature: for the former the dynamics is Brownian and the order parameter of the Jamming-Glass transition is the density, whereas for the latter the dynamics is Newtonian and the order parameter is the temperature. Another major important difference is that experiments in colloids can only track the first 5 decades of slowing down because the microscopic timescale for colloids is very large. An important consequence is that the comparison between the glass and colloidal transitions must be performed by focusing in both cases on the first 5 decades of the slowing down, which corresponds to relatively high temperatures in molecular liquids.

Understanding how much and to what extent the glassiness of colloidal suspensions is related to the one of molecular liquids is an active domain of research.

Another class of systems that display a Jamming-Glass transition which shares very similar properties with the glass transition of molecular liquids are driven granular media. If colloids can be thought as siblings of molecular liquids, grains must be thought as some more distant relatives, let’s say cousins. The reason is that grains are macroscopic objects and, as a consequence, do not have any thermal motion. A granular material is therefore frozen in a given configuration if no energy is injected into the system. However, it can be forced in a steady state by an external drive, such as shearing or tapping. An example of an experimental setting studied in the group of O. Dauchot at CEA Saclay is shown in Fig. 3. It consists in a bi-dimensional and bi-disperse granular material, which is quasi-statically sheared in an horizontal deformable parallelogram. The dynamics in the steady state is quite different in na-



Figure 3: A bi-dimensional, bi-disperse granular material, composed of about 8.000 metallic cylinders of diameter 5 and 6 mm in equal proportions, is sheared quasi-statically in an horizontal deformable parallelogram. The shear is periodic, with an amplitude $\theta_{max} = \pm 5^\circ$. The volume fraction ($\phi = 0.84$) is maintained constant by imposing the height of the parallelogram. The dynamics of 2818 grains located in the center of the device is followed by a High Resolution Digital Camera which takes a picture each time the system is back to its initial position $\theta = 0$. The microscopic unit of time is one cycle, a whole experiment lasting 10.000 cycles. Experiments with this setting have been performed and analyzed in publications by Dauchot et al.

ture from both the equilibrium dynamics of colloids and molecular liquids: energy is continuously injected into the system and subsequently dissipated. Time-averaged observables cannot be obtained from an equilibrium Boltzmann measure. Actually, the steady state probability distribution is generally unknown. Despite these facts, steady state dynamics of granular systems at high density show remarkable similarities with the ones of colloids and molecular liquids. First, the timescales for relaxation of the density field and for diffusion of a tagged particle increase very fast when density is increased, without any noticeable change in structural properties. It is now established that many phenomenological properties of the glass transition also occur in granular assemblies. Going beyond the mere analogy and understanding how much these different physical systems are related is a very active domain of research. Actually, since the underlying dynamics and microscopic properties are so different between liquids and grains, it would be highly non trivial to find that the microscopic mechanism responsible for the corresponding glass transitions are the same or even very similar. We will discuss some very recent and astonishing results at the end of this paper.

4 First dialogue

Here we present a first dialogue about the glass transition between two characters: Salviati, a theoretical physicist, and Cleverus, a very clever laymen. Cleverus is just back from a cruising trip around the globe with his sail boat, while Salviati has been

actively working on the glass transition lately⁵.

Cleverus: Hi Salviati, long time no see. How're you doing? I'm just back from a long sailing trip. As you know I like to bring some scientific stuff to read during these trips. This time I brought with me several papers and books on the glass transition. It looks like an hot topic. Recently, there was even an article about it on the New York Times! Well, finally, I didn't have much time. I read some stuff though. I didn't understand much and I have a lot of questions. First, why you guys are so much interested in this problem? Liquids stop to flow at low enough temperature and become glasses. So what? It looks like a very boring problem to me. Why is this phenomenon difficult to explain?

Salviati: Hi Cleverus, I see you are fine and provocative as usual. You asked many questions already, let me start from the last one. In order to answer it, let me quote the Nobel laureate P.W. Anderson: "We are so accustomed to the rigidity of solid bodies—the idea, for instance, that when we move one end of a ruler the other end moves the same distance—that it is hard to realize that such an action at a distance is not built into the laws of nature except in the case of the long-range forces such as gravity and electrostatics." We understand why crystals are rigid. This is related to the spontaneous symmetry breaking of translation invariance: particles arrange on a periodic lattice and is the lattice that transmits the force. Of course this reasoning works for crystal, but why liquids become amorphous *rigid* materials at the glass transition? Is there a related spontaneous symmetry breaking transition? As Anderson put it: "We are so accustomed to this rigidity property that we don't accept its almost miraculous nature, that is an "emergent property" not contained in the simple law of physics, although it is a consequence of them". Why glasses are rigid is a very difficult question.

Cleverus: I see, when you are in trouble you start quoting Anderson. I still don't get it. If I consider the strong liquids you were describing before, then it looks clear to me why they become rigid: each particle has to jump a barrier in order to move. When the temperature becomes much less than the barrier the time for this process is of the order of the age of the universe, so all particles are stuck in their positions and the material is a solid. Concerning rigidity, well, the barriers for motion are there, because particles are arranged on an amorphous lattice and the interaction with their almost fixed neighbours creates a barrier for motion for a given particle. So, the reason of rigidity is the same than for crystals.

Salviati: Yes, you might be right for strong liquids. But there are still several mysteries related to the process of glass-formation. First, even if your explanation might work for strong glasses, it does not for fragile ones. In those systems, the barrier *is increasing* with temperature. Why is it so? Furthermore, you seems to accept disingenuously that the low temperature phase of the liquid is a broken symmetry state, where particles are arranged in an amorphous way. But this is something completely new in physics! As for the emergence of chaos from purely deterministic dynamics, here we have low disordered energy states that emerge cooling a completely homogeneous high temperature liquid. Imagine, that a thermodynamic transition takes place what kind of transition would it be? Moreover, the number of amorphous configurations in which the glass can be stuck is huge. That is something

⁵Of course, Salviati does not represent the author. Resemblances to well-known scientists are coincidental, except for the ones you find out.

unheard of in usual theories of phase transitions.

Cleverus: OK, right, I start to see why the problem is difficult and even why *you* are interested. Maybe it's a new kind of phase transition that you cannot handle and understand with the usual theory of phase transitions. But, still, why should it be interesting for a laymen like me. I tried to understand it from the New York Times article. I read a lot of amusing quotes but still didn't find a reason to be interested.

Salviati: Maybe, another reason to find it interesting is that glasses are the archetype of complex systems. Their understanding, or more generally the research on glassy systems, could lead to several spin-offs in other fields like computer science, finance, biology.

Cleverus: Mhmm, don't look at me with your wide blue eyes as the snake in the Walt Disney's "Jungle Book". Maybe doing that and saying "Bzzzzz Glasses Bzzzzz Complex Bzzzzzz Interesting" works with your friends. It does not with me, pal. So you've got to explain me a little better. By the way I thought you guys used the words "complex systems" just in your grant proposals. Do you really mean it when you say that glasses are complex systems? What does it mean "complex system" anyway?

Salviati: I won't try to give a general definition of what is a complex system. That looks like a difficult thing to do. I would say, as the Supreme Court justice Potter Stewart that didn't know how to define pornography: I don't know how to define it but I know it when I see it.

Cleverus: Uhh, is that a joke? I would have indeed trouble defining "complex systems" but pornography...

Salviati: Cleverus, com'on, stop teasing me. I would say that glassy liquids are complex because the properties of their low energy states are extremely difficult to obtain, in particular by a dumb and local optimization procedure. Imagine that you want to find the most compact structure for hard spheres. Yes, don't look me that way, I know that is just a crystal. But forget it for a moment and think what a local optimization procedure would do or, even better, what a particle subject to thermal noise would do. The particle would try to pack close to itself as many neighboring spheres as possible. And its fellow spheres would do the same. Well, doing this, one does not end up with a crystal on large scale in three dimension⁶ but in a relatively loose packing. Imagine now that you want to obtain very compact amorphous packings, which is the counterpart of a "low energy state" for hard spheres. Then you have to optimize the way in which particles are packed together on a large scale. And in this case you don't know how to do it a priori contrary to the crystal case. If you wait that the system does it by itself just by thermal fluctuations, then you have to wait an extremely long time since many particles have to rearrange cooperatively.

This kind of difficulty in finding low energy states is common to many other problems in science where many degrees of freedom, agents, boolean variables interact in a contradictory way (we use the term *frustration* to denote this phenomenon). In those cases the macroscopic properties that emerge are very much unexpected and very often impossible to predict from heuristic or simple arguments. And, by the way, I wasn't trying to selling you an old car when I talked about spin-offs in other branches of science. For example, a central problem in computer science, random K-SAT, was recently analyzed in full detail with techniques developed for glassy systems. The

⁶It does in two dimension because there is no *frustration*.

authors even showed that random K-SAT is characterized by a glass transition [14]!

Cleverus: OK, I understand a little bit better your point now. I would have many questions on complex systems in finance and biology but let's stick to glasses. I don't understand why you made all that fuss about the behavior of fragile liquids. Maybe the explanation is just the same one I gave you for strong glasses, except that the *local* barrier increases approaching T_g .

Salviati: As I told you, there appears to be evidences that the barrier is actually diverging. Our experience taught us that this may happen only when there is some kind of collective phenomenon. A local barrier cannot diverge. You should read the paper by Montanari and Semerjian [13], they proved that a diverging timescales at finite temperature is necessarily related to a diverging length.

Cleverus: Actually, it was among the papers I brought with me. But, oh boy, it's difficult for me. I tried hard for two days. One night, while I was sailing in the arctic ocean, I was so focused on it, or maybe I fell asleep I don't remember, that I almost crushed my boat against an iceberg. Ending my trip in a Titanic way didn't sound like a good idea, so I decided to wait and ask you for a full explanation. Please, go to the blackboard and explain.

Salviati: Well, ehm, it would take some time. I will give you now an imprecise poor man's explanation—*un argument à deux balles*—as the french say. I strongly suggest you to read their paper afterwards. Imagine that you have a system characterized by a diverging relaxation time. If there is no growing cooperation between particles, or no growing correlation lengths whatsoever, then the system can be thought of as formed by independent pieces. Each small microscopic sub-system would then relax independently and have the same diverging relaxation time. On the other hand a finite system, as a rule of thumb, cannot have a relaxation time larger than e^{aN} where N is the number of its degrees of freedom and a is a constant. Thus, if you start from the hypothesis that the relaxation time is diverging at finite temperature then you are borne to conclude that there must be some kind of cooperativity such that the macroscopic system cannot really be considered the union of many microscopic independent parts.

Cleverus: Alas, my dear Salviati, you don't know whether there is an ideal glass transition and the time is really diverging. You just see it increasing. So, although I like your explanation, you cannot really use it to prove that the glass transition is not a just a complete local phenomenon. So, all your mumbo jumbo about a new kind of phase transition, collective phenomena, etc. could well be plain wrong.

Salviati: OK, you are right to be skeptical. But now we know for sure that the glass transition is not just a completely local phenomenon. In the last decades the research has focused on what we call the real space properties of the dynamics. We have found that dynamical processes leading to relaxation are correlated on length-scales that increase approaching the glass transition. Let me explain this in detail because it is a very important point.

5 Dynamical heterogeneities and dynamical correlations

A common feature of the way particles, grains or molecules move in glassy liquids is the so called "cage effect". This is shown in Fig. 4 and means that dynamical trajectories become very intermittent temporally: a particle typically rattles for a long time inside a "cage" formed by its neighbors and then it moves abruptly to a

new position, around which starts to rattle again. In order to show that the glass

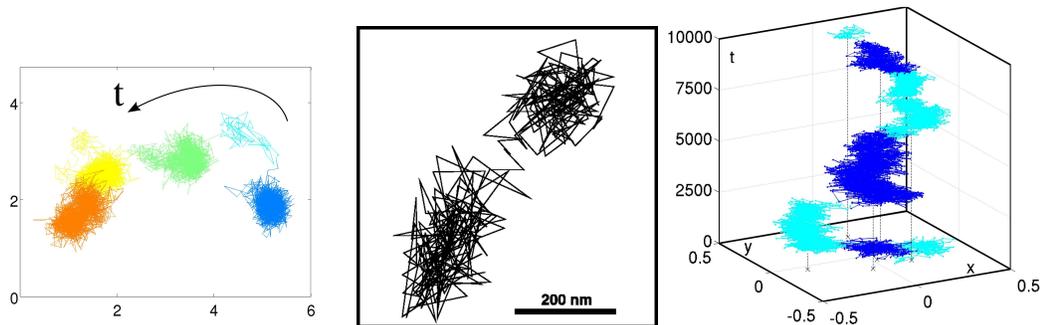


Figure 4: These are three examples of the cage effect in glassy dynamics. The three figures show typical particle trajectories approaching the glass and jamming transitions for a liquid (left: obtained by simulation [6]), a colloid (center: obtained by experiments [7]) and a granular system (right: obtained by experiments [8]). In all cases the size of the "cage" is some tenth of the average interparticle distance. Different colors are used to highlight different cages.

transition is not just a complete local phenomenon one has to study the way in which these "jumps out of the cage" (or cage jumps) are organized in space-time. In particular, are they correlated or completely independent, as would be the case for a completely local process? To answer this question, let us directly focus on their correlation or, more generally, on the correlation of local dynamical relaxations. In order to do that, let us write a global correlation $C(0, t)$ as a sum of local terms:

$$C(0, t) = \frac{1}{V} \int d^3r c(\mathbf{r}; 0, t), \quad (6)$$

where V is the volume of the system. $C(0, t)$ could be the intermediate scattering function considered previously or could be a measure of mobility: $C(0, t) = \frac{1}{N} \sum_i Q_i(t) = \frac{1}{N} \sum_i e^{-[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 / (2a^2)}$. In the latter case

$$c(\mathbf{r}; 0, t) = \frac{V}{N} \sum_i \delta(\mathbf{r}_i - \mathbf{r}) e^{-[\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 / (2a^2)},$$

where a is equal to the particle distance or, alternatively, some fractions of it. The correlations in the dynamics can be probed by using the correlation function:

$$G_4(\mathbf{r}; 0, t) = \langle c(\mathbf{0}; 0, t) c(\mathbf{r}; 0, t) \rangle - \langle c(\mathbf{0}; 0, t) \rangle \langle c(\mathbf{r}; 0, t) \rangle, \quad (7)$$

Since $c(\mathbf{r}; 0, t)$ is generally a two point function, G_4 is a four point function. This is the reason of the the sub-index 4. Direct numerical studies in glass-forming liquids and experimental studies in granular systems have shown that this function, evaluated at t equal to the relaxation time, becomes more and more long ranged approaching the glass or the jamming transition. However, these measurements are difficult and extracting precisely a length ξ_d from G_4 is complicated. The majority of works have focused instead on its integral, which is called $\chi_4(t)$. This is akin to a standard dynamical susceptibility in usual critical phenomena if one interprets $C(0, t)$ as the order parameter for the glass transition. It reads:

$$\chi_4(t) = \rho \int d^3r G_4(\mathbf{r}; 0, t) = N \langle [C(t, 0) - \langle C(t, 0) \rangle]^2 \rangle, \quad (8)$$

This function show a very similar behavior in molecular liquids, hard spheres and

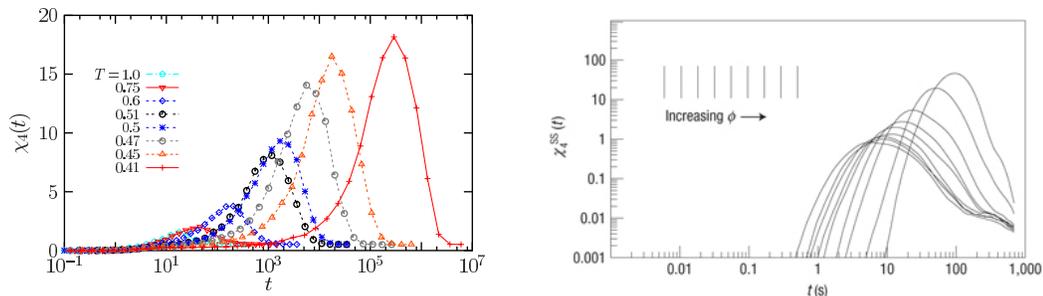


Figure 5: Time dependence of $\chi_4(t)$ quantifying the spontaneous fluctuations of the intermediate scattering function in a Lennard-Jones supercooled liquid [9] and in a granular system consisting in air-driven steel spheres [10]. The peak of $\chi_4(t)$ increases by lowering the temperature in the former case, and increasing the density in the latter one. This reveals that the glassy dynamics becomes more and more correlated approaching the glass and jamming transition.

grains. We show in Fig. 5 the typical shape and the typical evolution of χ_4 for liquids and granular media (hard spheres behave similarly). As a function of time $\chi_4(t)$ first increases, it has a peak on a timescale that tracks the structural relaxation timescale and then it decreases. The peak value, which measures the volume on which the structural relaxation processes are correlated, is found to increase approaching the glass and jamming transitions. Note that if the dynamically correlated regions were compact, the peak of χ_4 would be just proportional to ξ_d^3 in three dimensions.

A visual characterization of dynamical correlations can be obtained plotting a color map of $Q_i(\tau^*)$ where τ^* is the relaxation time of the system. In Fig. 6 we plot this map for a two dimensional glass-forming liquid (right) and a two dimensional granular system close to jamming (left). There are clearly well formed spatial structures. Their extension is what is probed by G_4 and χ_4 . This phenomenon has been called dynamical heterogeneity. Note that independent local relaxations would instead lead to a homogeneously blurred figure displaying no spatial structure.

In molecular liquids, contrary to the other glassy systems, $\chi_4(t)$ has been measured only by numerical simulations and far from the glass transition because probing G_4 or χ_4 in experiments is beyond current capabilities. The reason is that one can track the particle positions for colloids and grains. This is instead impossible for molecular liquids. There are two ways to overcome this difficulty. First, it has been argued that non-linear responses should be directly related to χ_4 and these have been measured recently in the group of D. L'Hôte in CEA Saclay. Second, one can obtain by fluctuation-dissipation relations and rigorous inequalities a relationship between the way the relaxation timescale increases and the growing of dynamical correlations. The main idea is to obtain a rigorous lower bound on $\chi_4(t)$ using the Cauchy-Schwarz inequality $\langle \delta H(0) \delta C(0, t) \rangle^2 \leq \langle \delta H(0)^2 \rangle \langle \delta C(0, t)^2 \rangle$, where $H(t)$ denotes the enthalpy at time t . By using fluctuation-dissipation relations the previous inequality can be rewritten⁷ as [11]

$$\chi_4(t) \geq \frac{T^2}{C_P} [\chi_T(t)]^2, \quad (9)$$

⁷Henceforth we will take $k_B = 1$.

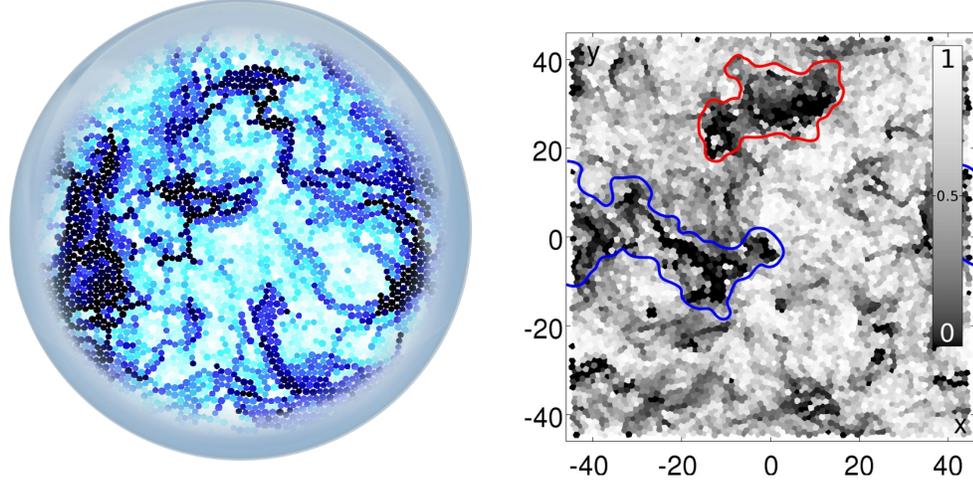


Figure 6: Color map of $Q_i(\tau^*)$ for: (Right) a 2D non-equimolar binary mixture of particles interacting via purely repulsive potentials of the form $u_{ab}(r) = \varepsilon(\sigma_{ab}/r)^{12}$ and (Left) the two dimensional granular system described in Fig. 3. Lowest values of $Q_i(\tau^*)$ correspond to particles that have already relaxed on the time τ^* and to darker colors.

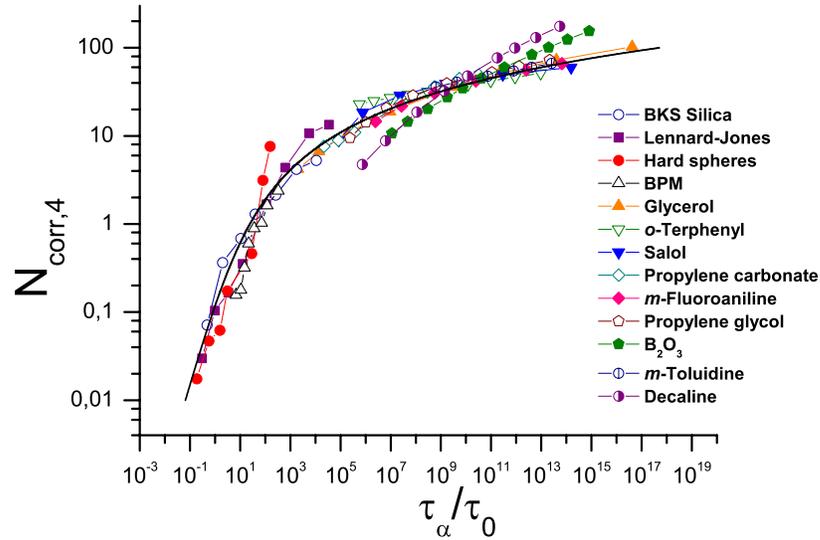


Figure 7: Universal dynamic scaling relation between number of dynamically correlated particles, $N_{\text{corr},4}$, and relaxation timescale, τ_α , for a number of glass-formers [12], determined using Eq. (9).

where the multi-point response function $\chi_T(t)$ is defined by

$$\chi_T(t) = \left. \frac{\partial F(t)}{\partial T} \right|_{N,P} = \frac{N}{T^2} \langle \delta H(0) \delta C(0, t) \rangle. \quad (10)$$

As a consequence, one can obtain a lower bound on the increase of dynamical correlations from the way the correlation function changes with temperature. This is

useful for two reasons. First, it is easy to check⁸ that it implies that a diverging timescale at a finite temperature must be accompanied by a diverging χ_4 . Second, it actually provides a quantitative way to estimate via a lower bound dynamical correlations in glass-forming liquids close to their glass transition. Using this method, Dalle-Ferrier *al.* [12] have been able to obtain the evolution of the peak value of χ_4 (or more precisely its estimation by the lower bound⁹) for many different glass-formers in the entire supercooled regime. In Fig. 7 we show some of these results as a function of the relaxation timescale. The value on the y -axis, the peak of χ_4 , is a proxy for the number of molecules, $N_{\text{corr},4}$ that have to evolve in a correlated way in order to relax the structure of the liquid. Note that χ_4 is expected to be equal to $N_{\text{corr},4}$, up to a proportionality constant which is not known from experiments, probably explaining why the high temperature values of $N_{\text{corr},4}$ are smaller than one. Figure 7 also indicates that $N_{\text{corr},4}$ grows faster when τ_α is not very large, close to the onset of slow dynamics, and a power law relationship between $N_{\text{corr},4}$ and τ_α is good in this regime ($\tau_\alpha/\tau_0 < 10^4$). The growth of $N_{\text{corr},4}$ becomes much slower closer to T_g . A change of 6 decades in time corresponds to a mere increase of a factor about 4 of $N_{\text{corr},4}$, suggesting logarithmic rather than power law growth of dynamic correlations.

6 Second Dialogue

Cleverus: Glassy dynamics have indeed a lot of interesting and remarkable real space properties. I agree now that any explanation of the glass transition in terms of a purely local process is bound to fail. Something I really find puzzling is the apparent similarity between liquids, colloids and grains. They are really different microscopically and yet... You didn't seem to be very much surprised. Do all these glass-jamming transitions are the same?

Salviati: You are right, I didn't stressed enough this similarity. Actually, I find it very remarkable too. As I said, one has to be careful not comparing apples to oranges: in colloids and grains one can probe only the first decades of slowing down. Thus, we don't really know whether their behavior is similar to the one of molecular liquids close to their glass transition, since there the relaxation time has grown of 14 or more decades. Still, at least in the first regime of slowing down of the dynamics, they really are similar and this is remarkable. I have to admit that we don't have a clear idea of why this is so. We have just indications by analytical [15] and numerical approaches [17] that indeed the glass transitions of hard spheres and molecular liquids may be driven by the same mechanism. We have to work more.

Cleverus: From your explanation on the real space properties of the dynamics I got that the dynamical slowing down is accompanied by a growing *dynamical* correlation length. This seems to suggest that the ideal glass transition—if such a thing exists—is purely dynamical; no thermodynamic transition, right?

Salviati: This is a tricky point [16]. Let me again quote Anderson and not because I feel in trouble! Already in 1983 he wrote: "This has, however, become a very knotty question. Some—but not all—transitions to rigid, glasslike states, may

⁸In order to do that, assume that the correlation function has a scaling behavior $f(t/\tau(T))$ and that $\tau(T)$ diverges at a finite temperature T_0 . Plugging this expression into eq. (9) one finds that the lower bound diverges and this implies a diverging χ_4 at T_0 .

⁹Numerical analysis suggested that the lower bound provides a rather good estimation of χ_4 approaching the glass transition.

entail a hidden, microscopic order parameter which is not a microscopic variable in any usual sense, and describes the rigidity of the system. This is the fundamental difficulty of the order-parameter concept: at no point can one be totally certain that one can really exclude a priori the appearance of some new hidden order.” He was right and well ahead of his time—as in many other cases. Only recently, we started to understand what this static correlation length could be. As a matter of fact, in the Montanari and Semerjian work we discussed before, they prove that the length which has to diverge together with the relaxation time is a *static one*!

Clevers: Ahhh, I’ve got your point—I think. There could be a *static* correlation length, and the fact that you don’t see it easily does not mean that is not there. One has to be careful. But then, what is the relationship between the dynamic length you see, cf. your previous explanations, and the static one you don’t?

Salviati: First, we have now direct evidences that there is a static growing length, I can tell you more later. As for your question on the relation between static and dynamic lengths, we didn’t make up our minds. We tend to believe that if particles are correlated statically on a length ξ_s , then they will be dynamically correlated on a length that is at least equal, but possibly larger, than ξ_s . Actually, it is simple to construct models in which the dynamical length ξ_d is much larger than the static one. However, we don’t have any definite proof that $\xi_d \geq \xi_s$, so it is probably better not to make any categorical or dogmatic statement.

Clevers: I see. But do you guys have some hints of what is the theoretical explanation of the glass transition? I mean, if you don’t even know whether it is static or purely dynamic...

Salviati: Well, don’t be too negative. Of course, since the problem of the glass transition is not solved there are many different theoretical approaches, different schools of thought,...

Clevers: Ah, there was a funny quote on the New York Times article. D. Weitz said: ”There are more theories of the glass transition than there are theorists who propose them”. Bravo, your experimental colleagues have a very good opinion of you.

Salviati: Mhmm, it is true that there are possibly 1001 derivations of the Vogel-Fulcher law. However there are very few real theories, meaning based on solid microscopic basis and able to explain a lot of properties of glassy liquids.

Clevers: Why you cannot sort out which is the right one?

Salviati: The main difficulty is that all these theories are based on some kind of critical phenomenon. That’s reasonable since there are indeed growing correlation lengths at the glass transition. The trouble is these lengths are not very large! You saw that the dynamical correlation length takes, at best, a value of 10 at the glass transition. The static lengths are probably smaller. This means that we are still rather far from the critical point, whatever it is. Hence, in order to obtain quantitative predictions that can be tested in experiments and to contrast theories, critical and universal results are not enough. One should be able to compute pre-asymptotic corrections. This is a fundamental difficulty of the glass transition: the relaxation timescale increases so fast that one cannot get close to the transition. This does not happen in standard critical phenomena because the timescale diverges as power law of $T - T_c$.

Clevers: OK, well, you cannot compute pre-asymptotic effects. I hope you are at least able to compute the asymptotic ones.

Salviati:...it depends on the theory.

Cleverus: Oh com'on, stop to be so balanced and sphinxish in your answers. Tell me what theory you think is right and why.

Salviati: I have different reasons to believe that the most promising theory, at least the one which is the correct starting point, is the Random First Order Transition Theory.

Cleverus: Ah, the RFOT theory! I tried to read many papers during my sailing trip. Oh boy, it was a nightmare. I had to choose between some that do awkward computations on very weird models: completely connected mean-field models with quenched disorder and multiple spins interactions. Why these models should be related to glasses anyway? And others, with no computation at all. At first sight, I was happy with the latter, but then I found them full of so many, how do you call them—ah right—hand-waving arguments...One night after reading one of those papers, I dreamt to have the Hindu goddess Kali in front of me waving all her hands and explaining RFOT. It was a mesmerizing experience. But, it didn't help with RFOT. So, please, go ahead, explain it to me if you can.

7 The Random First Order Transition Theory Part I: Mean Field Theory

Historically, the origin of RFOT lies in the study of mean-field disordered systems and starts with pioneering works by Kirkpatrick, Thirumalai and Wolynes. Indeed the Random Energy Model of Derrida contains in a nutshell already many important aspects of RFOT. Many workers in the field of the glass transition often criticizes RFOT on the basis that is not clear why mean-field spin systems with quenched disorder have anything to do with glass-forming liquids, which are formed instead by interacting particles and devoid of quenched disorder. They are right. These systems are microscopically extremely different. However, they are possibly related in the same way liquids close to the liquid-gaz transition are related to spin systems close to the ferromagnetic transition. They belong to the same universality class at least in mean-field theory. Nevertheless, it is clear that analyzing these spin models and, then, applying directly the results to real liquids can be baffling for researchers that want to understand how particles moves and rearrange in real systems and are not used to mean-field disordered systems. At the very end, if RFOT is the Theory of the glass transition, we must be able to explain it without making a long detour on quenched disordered systems. In the following, I shall endeavor to do that. As a consequence, alerted and knowledgeable readers may find that I'm starting from the end instead that from the beginning and, at the same time, sweeping some difficult technical points under the rug. They are right.

7.1 A chaotic free energy landscape

We saw that close to T_g a liquid remain stuck in an amorphous configurations and that the number of these is exponentially large in the system size. A mean-field theory of the problem should therefore be able to: (1) capture this kind of symmetry breaking (2) deal with an exponential number of states. As usual, the first approach to follow in order to get an handle on the physics, at least qualitatively, is mean field theory. As for ferromagnets the first step is studying the evolution of the free-energy landscape. In the Curie-Weiss approach one compute the free-energy as a function

of the global magnetization by a mean field approximation. However, computing the free energy as a function of the global energy or density won't be enough for the glass transition. One has to be able to deal with the fact that the system can be stuck in many different amorphous configurations. As a consequence one is borne to compute the free-energy F as a function of the entire density field. F is defined using the Legendre transform. Consider for simplicity an interacting particle lattice model, the generalization to continuum systems is straightforward. In the lattice case a given configuration is determined by the number of particles, n_i , on every site i . In order to define F , one first introduces the thermodynamic 'potential'

$$W(\{\mu_i\}) = -\frac{1}{\beta} \log \sum_{\{n_i\}} \exp \left(-\beta H(\{n_i\}) + \sum_i \beta \mu_i n_i \right) \quad (11)$$

The free energy function $F(\{\rho_i\})$ is then defined as

$$F(\{\rho_i\}) = W(\{\mu_i^*\}) + \sum_i \mu_i^* \rho_i \quad (12)$$

where the μ_i^* s satisfy the equations $\frac{\partial W}{\partial \mu_i} + \rho_i = 0$ and, hence, are functions of all ρ_i s. This is often called the TAP free energy because Thouless Anderson and Palmer introduced it to study mean field spin glasses. The generalization to continuum systems can be also performed by replacing the discrete variable n_i by a continuum density field $\rho(x)$. In this case F is called density functional.

The free energy landscape is the hyper-surface generated by scanning F over all possible values of $\{\rho_i\}$. Its critical points, in particular the minima, play a crucial role. In fact by deriving the previous equation with respect to ρ_i one finds

$$\frac{\partial F}{\partial \rho_i} = \mu_i^*$$

Thus, when there are no external fields (or local chemical potentials) the solutions of these equations are all the stationary points of the free energy landscape¹⁰.

What are the main features of F for a system approaching the glass transition? This question of course cannot be answered exactly for a three dimensional systems. One has either to make use of approximations (as in the Curie-Weiss description of ferromagnets) or focus on mean-field lattices like Bethe lattices, which often provide a good approximation to the finite dimensional ones. Furthermore, continuum systems are quite complicated, let us first focus on simple but reasonable lattice models.

A concrete example is given by 'lattice glass models'. These are models containing hard particles sitting on the sites of a lattice. The Hamiltonian is infinite if there is more than one particle on a site or if the number of occupied neighbors of an occupied site is larger than a parameter, m , and is zero otherwise. Tuning the parameter m , or changing the type of lattice, in particular its connectivity, yields different models. Lattice glasses are constructed as simple statmech models to study the glassiness of hard sphere systems and they have been shown by simulation to reproduce correctly the physics of glass-forming liquids (at least on the timescales

¹⁰For particle systems there is always a global chemical potential μ fixing the number of particles. In this case, one includes the global term $\mu \sum_i n_i$ in the definition of F so that all μ_i^* are zero.

accessible to simulations). The constraint on the number of occupied neighbors mimics the geometric frustration encountered when trying to pack hard spheres in three dimensions. Other models, which have a finite energy and, hence, are closer to molecular glass-formers, can be also constructed. The technical study of their free-energy landscape is quite involved. Here we will only discuss the main results and consider temperature as a control parameter. The generalization to models where the density or the chemical potential are the control parameters is straightforward.

The main result of the study of the free energy landscape is that it becomes ‘rugged’ at low temperature and characterized by many minima and saddle points. Actually, the number of minima is so large that in order to count them one has to introduce an entropy, called configurational entropy or complexity, $s_c = \frac{1}{N} \log \mathcal{N}(f)$, where $\mathcal{N}(f)$ is the number of free-energy minima with a given free energy density f . The density profile corresponding to one given minimum is amorphous and lacks any type of periodic long-range order, and different minima are ... very different. This is a first result, which is very welcome. Glasses freeze in an exponential number of different amorphous configurations, and within the mean-field approximation of simple but reasonable lattice models we indeed find a lot of amorphous free energy minima at low temperature. Assuming that all the minima are mutually accessible, one can compute the thermodynamic properties, i.e. the partition function by summing over all states with their Boltzmann weights. Formally, one can introduce a free-energy dependent complexity, $s_c(f, T)$, that counts the number of TAP minima with free-energy density f at temperature T . The partition function of the system then reads:

$$Z(T) = \int df \exp \left[-\frac{Nf}{T} + Ns_c(f, T) \right]. \quad (13)$$

For large N , one can as usual perform a saddle-point estimate of the integral, that fixes the dominant value of f , $f^*(T)$, that obeys:

$$T \left. \frac{\partial s_c(f, T)}{\partial f} \right|_{f=f^*(T)} = 1 \quad (14)$$

The temperature dependent complexity is in fact defined by: $s_c(T) \equiv s_c(f^*(T), T)$. The free energy of the system is $f_p(T) = f^* - Ts_c(T)$. The typical shape of the configurational entropy as a function of f and a graphic solution of eq. (13) are plotted in Fig 8. The analysis of the configurational entropy, or complexity $s_c(T)$, reveals that there is a temperature T_K below which $s_c(T)$ vanishes and that $s_c(T)$ increases by increasing the temperature above T_K . There exists a second, higher temperature that we call $T_d > T_K$ (for reasons that will become clear below) above which $s_c(T)$ drops discontinuously to zero again. There is just one minimum¹¹ above T_d and it corresponds to the homogeneous density profile of the high temperature liquid. The situation below T_K and above T_d is very different. At these two temperatures the part of the free-energy landscape relevant for the thermodynamics change drastically in two very different ways. At T_d the homogeneous liquid state fragments in an exponential number of states, or minima. At T_K the number of minima is no more exponential in the system size, $s_c(T < T_K) = 0$. Surprisingly $f_p(T)$ is not singular at T_d . This is one of the most unexpected result emerging from the analytical solution. It suggests that at T_d the liquid state fractures in an

¹¹ Actually things are slightly more complicated than this but this is irrelevant for the present discussion.

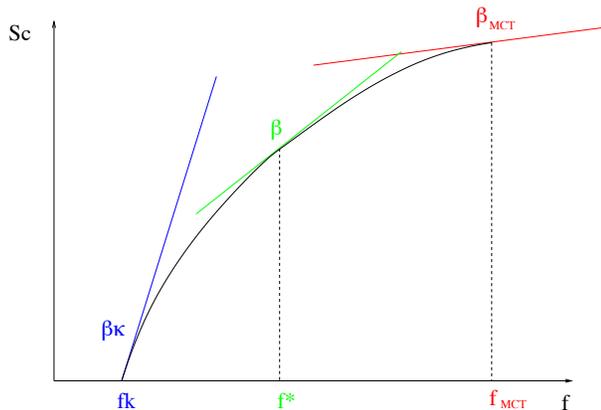


Figure 8: Typical shape of the configurational entropy, Σ , as a function of free energy density, f in the range $T_k < T < T_d$ for random first order landscapes. A graphic solution of Eq. (13) is obtained by finding the value of f at which the slope of the curve is $\beta = 1/T$. Note that s_c is also a function of temperature, so this curve in fact changes with T . T_d is indicated as T_{MCT} for the reasons explained in the text.

exponential number of amorphous states and that this transition is only a dynamical phenomenon with no consequences on the thermodynamics. At T_K instead a thermodynamic phase transition takes place since the contribution to the entropy coming from the configurational entropy disappears¹² and, hence, the specific heat makes a jump downward.

In order to understand what's going on at T_d one has to study the dynamics. Such an analysis shows that a typical time dependent correlation function, e.g. $\sum_i \langle n_i(t)n_i(0) \rangle$, develops a plateau as a function of time, t , and has a shape which is very much reminiscent of experimental curves, like Fig. 2. Within mean-field theory the barriers between states diverge with N and hence at T_d there is a purely dynamical ergodicity breaking¹³.

In summary, the mean field analysis of the free energy landscape leads to many interesting results. There is a first temperature T_d at which many different amorphous states appears and the "liquid state" fragments into all of them below T_d . A detailed analysis close to T_d shows that they disappear discontinuously: they melt because of thermal fluctuations in a spinodal-like way, which means that they loose their stability. Several arguments suggest, and we shall show it directly later on, that all the states we found between T_d and T_K become metastable in finite dimension. As a consequence, the temperature T_d is expected to become a cross-over in finite dimension. Instead, at T_K , a thermodynamic transition at which the configurational entropy vanishes takes place. This would lead to a downward jump of the specific heat, to a thermodynamic phase transition and hence, generically, to the divergence of the relaxation time. Clearly, we are finding several features displayed by experiments: (1) the existence of metastable states that make the dynamics slows down below some temperature (2) a possible ideal glass transition where the configurational entropy and the relaxation time diverge. However, a complete explanation is

¹²The configurational entropy vanishes linearly at T_K .

¹³This result can be obtained in full detail for mean field disordered systems only. For more realistic but still mean-field systems, one can either perform a Landau like expansion or numerical simulations. Both strongly support the existence of the dynamical transition discussed in the main text.

still lacking. At this point it is not clear yet how the relaxation time diverges and why this is related to the vanishing of the configurational entropy.

It is important to stress that these results are general in the sense that they emerge generically in mean-field treatments of models of glasses, both in the case of liquids approaching the glass transition and hard spheres approaching the glass-jamming transition. However, in practice, performing the analysis of the free energy landscape is already technically quite difficult for lattice glass models on Bethe lattice. As a consequence, more realistic continuum models of interacting particles cannot be analyzed in full detail. Some numerical and analytical studies of the density functional of more realistic models, such as hard spheres, have been performed though. They have indeed revealed that an amorphous minimum emerges at low energy and high density. In order to compute approximately the properties of the metastable states and the configurational entropy one has to use different tools. These are explained below and consist in a replica theory for models without quenched disorder.

7.2 Boundary Pinning Field and Replicas

In the following we shall describe an approach based on the replica method which, although more abstract than the one described above, has the clear advantage that analytical mean-field computations for finite dimensional systems, even realistic ones such as hard spheres or binary Lennard-Jones mixtures, becomes feasible, although quite involved. Readers allergic to replica or not interested in the formalism can skip this section without any harm: it is not necessary to understand the rest of the paper.

To understand how replicas come about in a model without disorder, let us assume that the system is in a regime of temperatures where there are indeed many very long-lived metastable states and that the Gibbs-Boltzmann measure is distributed over all of them, as found in the previous section. In order to study the statistical property of a typical metastable state and the number of such states, we focus on a very large cavity of radius R , carved in an otherwise infinite (or much larger) system. The basic idea is to apply a suitable boundary external field in an attempt to pin the system in one of the possible metastable states¹⁴. Contrary to simple cases, e.g. the ferromagnetic transition for which a positive or negative magnetic field selects states, the external “field”, or analogously the boundary condition one has to impose to select a given amorphous state, is as unpredictable as the state one wants to select. To overcome this difficulty one can take an equilibrium configuration α , freeze the position of all particles outside the cavity, and use this as a boundary condition. If the system is a thermodynamic glass characterized by many metastable states then this boundary condition should force the system inside the cavity to be into the same metastable state as the equilibrium configuration α .

Concretely, the procedure consists in computing the cavity partition function, for a fixed α :

$$Z_\alpha(R) = \sum_{\mathcal{C}} \exp(-\beta H(\mathcal{C})) \delta(q^{out}(\mathcal{C}, \mathcal{C}_\alpha) - 1) \quad , \quad (15)$$

where $q^{out}(\mathcal{C}, \mathcal{C}_\alpha)$ is a suitably defined overlap that measures the similarity between density configuration \mathcal{C} and that of the α state in the space outside the cavity. When the overlap equals one the two configurations are the same outside the cavity. In

¹⁴Our presentation is different from that of the original papers but based on the same ideas

the large R limit, the intensive free energy of the metastable state, obtained by taking the logarithm of the partition function, is expected to be self-averaging and independent of \mathcal{C}_α . Physically, this means that the overwhelming majority of the metastable states sampled by the equilibrium Boltzmann measure are characterized by the same intensive free energy.

Although, we started from a problem without quenched disorder, we find that the analysis of the metastable states leads us to a problem where the configuration \mathcal{C}_α plays the role of a (self-induced) quenched disorder. In order to proceed further and compute the intensive free energy of a typical metastable states we have therefore to average over \mathcal{C}_α with the Boltzmann weight $\exp(-\beta H(\mathcal{C}_\alpha))$. As usual for quenched disorder problem, one can make use of the replica trick:

$$\langle \ln Z_\alpha \rangle_\alpha = \lim_{m \rightarrow 1} \frac{\ln \langle Z_\alpha^{m-1} \rangle_\alpha}{m-1} \quad (16)$$

In order to compute the average $\langle Z_\alpha^{m-1} \rangle_\alpha$ one can introduce replicated configurations and write:

$$\langle Z_\alpha^{m-1} \rangle_\alpha = \frac{\sum_{\mathcal{C}_\alpha; \mathcal{C}_1 \dots \mathcal{C}_{m-1}} \exp(-\beta H(\mathcal{C}_\alpha)) \prod_{a=1}^{m-1} [\exp(-\beta H(\mathcal{C}_a)) \delta(q^{out}(\mathcal{C}_\alpha, \mathcal{C}_a) - 1)]}{\sum_{\mathcal{C}_\alpha} \exp(-\beta H(\mathcal{C}_\alpha))} \quad (17)$$

As usual with replicas one computes the above sum for integer and positive values of $m-1$ and then makes an analytical continuation to make the $m \rightarrow 1$ limit. It is important to notice that the average in the numerator of the previous expression can be rewritten as the partition function of m replicas constrained to be identical outside the cavity but free to fluctuate inside since in the above expression \mathcal{C}_α is no longer different from the other replicas.

Let us denote the logarithm of the partition function of the m constrained replicas as $-\beta F_m$. Once this quantity is known, one can compute the partition function of the large cavity as:

$$\mathcal{F} \equiv -T \langle \ln Z_\alpha \rangle_\alpha = \lim_{m \rightarrow 1} \frac{(F_m - F_1)}{m-1} = \left. \frac{\partial F_m}{\partial m} \right|_{m=1} \quad (18)$$

This gives the free energy of one typical state inside the cavity. Since we are interested in thermodynamic quantities, henceforth we will consider R to be very large. If there are many states, i.e. an exponential number in the size of the system, then the free energy of the cavity \mathcal{F} may be different from the unconstrained one F_1 . This can be seen by rewriting the replicated partition function as a sum over all states with their Boltzmann weight. If the constraint is strong enough to force the replicas $a = 1, \dots, m-1$ to fall into the same state as α itself, then:

$$\frac{F_m}{N} = -T \frac{\ln \sum_\alpha e^{-\beta f_\alpha m N}}{N} = -T \frac{\ln \int df \exp(N[-\beta f m + s_c(f, T)])}{N} = f^* m - T s_c(T), \quad (19)$$

where f^* is the free energy density that maximizes the argument of the exponential, $s_c(T) = s_c(f^*, T)$ and N is the number of particles inside the cavity. Using Eq. (18), one immediately finds that $f^* = \mathcal{F}/N$ is the intensive free energy of a typical metastable state. But the free energy of the system without constraint is $F_1 = f^* - T s_c(T)$ that contains the configurational entropy contribution. The replica method

allows one to obtain both quantities, which yields the configurational entropy:

$$s_c(T) = -\beta F_1 + \beta \left. \frac{\partial F_m}{\partial m} \right|_{m=1} = \beta \left. \frac{\partial}{\partial m} \left[\frac{F_m}{m} \right] \right|_{m=1} \quad (20)$$

Hence, we have found that computing the statistical properties of metastable states reduces to the computation of the thermodynamics of $m \rightarrow 1$ replicas with the constraint that the overlap outside a spherical cavity of radius R is equal to one. In practice one has to do a computation for m replicas and take the space dependent overlap $q_{a,b}(r)$ between them in the bulk of the cavity as an order parameter. Hence, one has to compute as accurately as possible the free energy as a function of the overlap $q_{a,b}(r)$, and then find the stationary points.

One always finds a trivial solution with uncoupled replicas, i.e. $q_{a,b}(r) = 0$ for $a \neq b$. This is expected since if it was not for the boundary condition the replicas would be indeed completely uncoupled. If this is the only solution then $F_m = mF_1$, and $s_c = 0$ as it should be in a case without metastable states. One has therefore to inspect whether another solution exists. If it is the case then the constraint outside the cavity plays the role of a boundary condition for $q_{a,b}(r)$ and selects this coupled replica solution.

The approach outlined above is the starting point for several quantitative mean-field investigations of realistic glass-formers [18, 19, 15]. It allows one to compute the property of typical metastable states, the configurational entropy and the characteristic temperatures T_K and T_d for realistic systems. The strategy consists in obtaining an expression as accurate as possible the m -replica free energy as a function of the overlap $q_{a,b}$ and then in studying its stationary points and in computing all the physically interesting quantities. Actually, some successful approaches are close in spirit to what I described above but quite different in the details [18].

8 Third dialogue

Cleverus: There are several things I find strange in the mean field theory you explained before. Why do you sum over all states in eq. (13) if there are infinite barriers between them, as you have stated?

Salviati: The reason lies in what we think is the generalization of RFOT in finite dimension beyond the mean-field approximation. It is clear that the finding so many states with infinite lifetime is an artifact of mean-field theory. For instance, it is impossible for a system to display two thermodynamic states with different *intensive* free energies, because if the system sits in the highest free-energy one, it will eventually nucleate the other, thus showing that the initial one didn't have an infinite life-time. We expect that all the states found in mean field theory between T_K and T_d will acquire a finite life time in a correct treatment. That is the reason why we sum over all of them in eq. (13).

Cleverus: OK, well, you will have then to explain me what the dynamics between metastable states is, because there lies the final explanation of the glass transition if RFOT is right.

Salviati: Yes, sure.

Cleverus: But, before, I have still some questions on RFOT: part I. You seemed to be happy of finding T_K and T_d . T_K , I understand, based on what you explained before, but what about T_d ?

Salviati: Yes, I didn't have time to discuss this point, which is interesting. The physical properties of the dynamical transition taking place at T_d coincide with the ones found for the so called Mode Coupling Transition Theory (MCT) of glasses. This is a self-consistent approach for the dynamics of dense and low temperature liquids that was developed by Gotze and coll.. It has been already tested a lot in simulations and experiments and, indeed, it seems that there is a characteristic temperature where a dynamical cross-over takes place and that this is rather well described by MCT.

Cleverus: Really? I didn't have this impression reading some papers about MCT.

Salviati: You are right, maybe I'm a bit biased. The problem is that the dynamical transition becomes just a cross-over. And a cross-over is difficult to test in a clear cut way. Furthermore, even theoretically, we don't understand well the properties of this cross-over yet.

Cleverus: I have a final question about grand-mothers.

Salviati: Uh?

Cleverus: Yes! In the papers I brought with me, I often read strange sentences stating that even a grand-mother would have a glass transition with your approximations. This apparently shows two things: first, you guys don't respect much grand-mothers, which is bad, and second, that what you find is just due to the approximations you have done.

Salviati: Well, yes and no. No, we respect grand-mothers, this was just a joke. Yes, what we find is due to the approximations but we think that a correct treatment would change somehow the results without jeopardizing the whole scenario.

Cleverus: Is this wishful thinking or is it based on some concrete analysis?

Salviati: In the last years indeed we have found ways to perform concrete analysis and even test our ideas in numerical simulations. I can explain if you want.

Cleverus: Sure! Keep in mind that the things I would like to know are: (1) what happens in real space within the RFOT scenario. You discussed a lot the importance of understanding the glass transition in real space in Section 5, but in your previous sections about RFOT real space was completely out of the game. (2) Why and how the relaxation time diverges at T_K within RFOT?

9 The Random First Order Transition Theory Part II: Beyond mean-field theory and the real space description

9.1 The Mosaic State

We have discussed already that the multiple states found in mean-field theory must become metastable, i.e. with a finite lifetime, in a correct treatment. As Cleverus correctly pointed out, understanding how this comes about and how the dynamics between metastable states takes place is central for the application of RFOT to real glass-formers and hard spheres systems.

In a pioneering work Kirkpatrick, Thirumalai and Wolynes [20] proposed that liquids must become a mosaic of mean-field states with a typical "tile" size of the order of $l^* \propto 1/(T - T_K)$. As before, we shall not reproduce the original arguments but present more recent (and at least to our eyes clearer) ones [21].

Consider the following *Gedanken* experiment. Suppose we could identify one of the exponentially numerous TAP state relevant at a given temperature T , which we call α , and characterize the average position of all the particles in that state.

We shall first establish that there exists a length scale above which the assumption that this TAP state has an infinite lifetime is inconsistent. In order to do this, we freeze the motion of all particles outside a spherical cavity of radius R and focus on the *thermodynamics* of the particles inside the sphere, $\mathcal{S}(R)$, that are free to move but are subject to the boundary conditions imposed by the frozen particles outside the sphere. Because of the ‘pinning’ field imposed by these frozen particles, some configurations inside $\mathcal{S}(R)$ are particularly favored energetically. When $s_c(T)R^d$ is much larger than unity there are many metastable states accessible to the particles in the cavity. The boundary condition imposed by the external particles, frozen in state α , act as a random boundary field for all other metastable states except α itself, for which these boundary conditions perfectly match. Any other metastable state γ has a positive mismatch energy. We assume this interface energy can be written as $\Upsilon_0 R^\theta$. We first imagine that we wait long enough so that the cavity embedded in state α is fully equilibrated. The partition function Z_α can then be decomposed into two contributions:

$$\begin{aligned} Z_\alpha(R, T) &= \exp[-\Omega_d R^d \frac{f_\alpha}{T}] + \sum_{\gamma \neq \alpha} \exp \left[-\Omega_d R^d \frac{f_\gamma}{T} - \frac{\Upsilon_0 R^\theta}{T} \right] \approx \\ &\approx \exp[-\Omega_d R^d \frac{f_\alpha}{T}] + \int_{f_{\min}}^{f_{\max}} df \exp \left[\frac{(T s_c(f, T) - f) \Omega_d R^d - \Upsilon_0 R^\theta}{T} \right] \end{aligned} \quad (21)$$

where f_γ is the excess free energy per unit volume of state γ , Ω_d the volume of the sphere with unit radius in dimension d^{15} . We focus on the case T close to T_K where R is large, allowing one to invoke saddle point arguments. We focus on a typical state α at that temperature, i.e. a state with the free energy f^* that dominates the integral over f above, such that $T \partial s_c / \partial f = 1$. The partition function of the cavity embedded in the α state becomes independent of α and reads:

$$Z(R, T) \approx \exp[-\Omega_d R^d \frac{f^*}{T}] \left(1 + \exp \left[\Omega_d R^d s_c(T) - \frac{\Upsilon_0 R^\theta}{T} \right] \right). \quad (22)$$

The above expression is central to our argument. It points out the existence of a cross-over length ℓ^* :

$$\ell^* = \left(\frac{\theta \Upsilon_0}{d \Omega_d T s_c(T)} \right)^{\frac{1}{d-\theta}}. \quad (23)$$

When R is smaller than ℓ^* but still large, the second term is exponentially small even if an exponentially large number of terms contribute. The mismatch energy dominates and the state α favored by the boundary conditions is the most probable state, even if the particles inside the cavity are free to move. In this sense, the cavity is in a glass phase, where only one (or a few) amorphous configurations, selected by the boundary conditions, are relevant. When $R > \ell^*$, on the other hand, the second term becomes overwhelming. There are *so many* other states to explore that it becomes very improbable to observe the α state. There is ‘‘entropic melting’’ of the cavity. Note that approaching T_K , $s_c(T) \rightarrow 0$ and the length ℓ^* diverges.

The main conclusion is that a TAP state does not make sense on scales larger than ℓ^* . The arguments above strongly suggest that if one starts from the mean-field free energy and add all fluctuations needed to recover the correct result then one

¹⁵Here and below, all lengths are in units of the interparticle distance a .

would obtain the following: For lengths $R < \ell^*$ there is a set of boundary conditions indexed by α such that the true free energy—not the one computed within the mean field approximation—has one different minimum for each boundary condition. Each minimum corresponds to a density profile which is very close to the one, called α , obtained by analyzing the mean field free energy. Instead, for $R \gg \ell^*$, there is just one minimum, or analogously, the density profile at the minimum is just the flat liquid one and is insensitive to the boundary conditions, whatever they are. One therefore identifies the scale ℓ^* as the one over which the liquid can be considered as formed by independent pieces or sub-systems¹⁶. A sketchy representation of this state is a *mosaic* composed by tiles which are the different TAP states that exists on the scale ℓ^* . The free-energy of the liquid is therefore, up to a subleading contributions:

$$f_{liq} \approx f^*(T) - T s_c(T), \quad (24)$$

which is formally identical to the mean field result but very different in terms of the real space interpretation. Approaching T_K the mosaic tiles increase in size and at T_K there is a spontaneous symmetry breaking of translation invariance toward states with amorphous long range order.

Let us now discuss the dynamics. Since the picture we ended up is one where the liquids is composed by a mosaic of different states on the scale ℓ^* , it is natural to expect that the relaxation time of the system is the relaxation time, $\tau(\ell^*)$, of a finite size region of the system of size ℓ^* . Contrary to mean-field theory barriers are now finite, hence T_d is no more a true transition. Focusing for the time being on the dynamical evolution close to T_K , it is natural to assume that the dynamical process leading to relaxation of the cavity is thermal activation over energy barriers which are supposed to grow with size as ξ^ψ , as in disordered systems. One predicts finally that:

$$\log \left(\frac{\tau_\alpha}{\tau_0} \right) = c \frac{\Upsilon_0}{T} (\ell^*)^\psi = c \frac{\Upsilon_0}{T} \left(\frac{\Upsilon_0}{T s_c(T)} \right)^{\psi/(3-\theta)}, \quad (25)$$

where c is a constant. Kirkpatrick, Thirumalai and Wolynes argued that $\psi = \theta = 3/2$, and hence $\psi/(3-\theta) = 1$, thus recovering the Adam-Gibbs law, at least close enough to T_K . This is one of the main result of RFOT: the decrease of the configurational entropy and the increase of the effective barrier are linked together: the latter has to diverge when the former vanishes. Furthermore, with $\psi/(3-\theta) = 1$ one indeed recovers the Vogel-Fulcher law and obtain the identity $T_0 = T_K$.

This is certainly very impressive. However, we are still far from having this theory and, hence, these results lying on a firm ground. In fact, the previous argument is a phenomenological one. However, it has been backed up by microscopic computations based on the replica formalism discussed in a previous section[22, 23]. These analysis have indeed confirmed the existence of the length ℓ^* . Technically, they found an instability length of the homogenous strongly coupled replica solution using instanton techniques. However, the exponent θ that has been found is equal to two and not $3/2$. As for the exponent ψ , there is no reliable computation yet. We are at a stage where we don't know how to compute reliably the exponents and, it is not clear yet that the victory claimed by Wolynes and collaborators is the final word. More work is ahead.

¹⁶Using the concept of "generalized rigidity" of Anderson, one would say that above ℓ^* the system is no more rigid.

9.2 Dynamics close to T_d

We have found that in mean-field theory amorphous states lose their stability in a spinodal-like way close to T_d . Approaching T_d from below the frozen part of density fluctuations, called Edwards-Anderson parameter in the spin-glass jargon, does not go to zero although the states become unstable just above T_d . This means that approaching T_d from above dynamical two point correlation functions must show a plateau whose value converges at T_d toward the Edwards-Anderson parameter of the TAP states. Above T_d , one expects a behavior of the type found in experiments, see Fig. 1: first a relaxation toward a plateau and then a relaxation away from it.

As we have shown, TAP states are unstable in a correct-beyond mean-field-treatment. As a consequence, at T_d there is no dynamical transition, but instead possibly a cross-over. Understanding this cross-over is still an open problem, but one can already obtain many interesting results on the real space dynamics pretending that the transition is real. Of course, it is a crucial issue understanding how much these results persist in a correct treatment where the transition is replaced by a cross-over. In the following we shall list some of the main properties of the dynamics close to T_d that one can obtain within the mean-field approximation. Note that, contrary to what happens below T_d , where mean-field results on the dynamics are completely changed in a correct treatment, we expect that this shouldn't be the case above T_d at least not too close to T_d .

First, mean-field theory leads to specific predictions on the form of the dynamical correlation function, which has been tested during the last decades, because they coincide with the ones obtained from MCT. They are qualitatively correct and quantitative in rather good agreement both for models of glass-formers and for hard sphere systems. Unfortunately, the existence of the cross-over makes any precise test difficult if not impossible.

Furthermore mean field theory correctly reproduces qualitatively the vast majority of the phenomena discussed in Section V under the name of dynamical heterogeneity and dynamical correlations. One obtains from first principle computations a diverging χ_4 and a diverging dynamical correlation length at T_d . Physically, this is due to the fact that TAP states become unstable at T_d because of the emergence of amorphous soft modes that make the system yield above T_d . The dynamics above T_d takes place mainly along these soft modes and is therefore correlated on a large scale. The quantitative predictions for dynamical correlations and dynamical heterogeneity are under current investigation. The evolution of χ_4 is quite in agreement with simulation results, although of course it does not diverge at T_d since the transition is avoided. Actually, one finds results that deviate very close to T_d . Instead the agreement for the growing correlation length is under debate because it appears very difficult to extract reliably the precise values of ξ_d in simulations.

10 Fourth and final dialogue

Cleverus: I see that you still have to wave many hands, but I understand your theory—more or less. There are many loose ends though. You have work to do!

Salviati: Yes, right.

Cleverus: Your Gedanken experiment is nice but couldn't you test it at least in a simulation?

Salviati: This has been done actually in [24] for a model of glass-forming liquids: the authors froze a liquid equilibrium configuration and re-equilibrated the cavity. They found that after re-equilibration the configuration at the center of the cavity becomes independent of boundary conditions only for radii larger than a typical length ℓ^* , which increases approaching the glass transition. They also found that the relaxation time changes from the bulk behavior for radii smaller than ℓ^* .

Cleverus: Interesting. This indicates that maybe you are on the right track. It also shows that, again, a complete local explanation of the dynamical slowing down is completely hopeless. But what about other theories? I guess that their advocates wouldn't be so satisfied with RFOT as you are.

Salviati: You bet! They wouldn't certainly be. There are indeed other theories whose advocates also claim at least partial victory. I think we are still a bit far from the final solution. Our current most important challenge is to nail down what is the closest starting point to the Theory of the glass transition. I believe this is RFOT for several reasons that I partially try to explain before: In particular it's what it comes out naturally from mean field theory and when one tries to correct mean-field theory one ends up with results that are physically sound.

Cleverus: Yes, but for example you don't know how to compute the exponents θ and ψ . Maybe a correct computation would show that $\theta = 0$, so states are unstable, or that $\psi/(3 - \theta)$ is very far from one, so bye bye RFOT!

Salviati: Yes, dear Cleverus, it's indeed a possibility. However, look at the good side of it: there is a clear route to follow, ahead of us, in order to prove whether the theory is right or wrong and many highly non-trivial tests to do to reinforce and eventually validate or disprove RFOT. Note, for example, that the simulations of [24] was indeed already a very important test to pass.

Cleverus: I see...you are viciously implying that this is not the case for the other theories.

Salviati: Nah, not all theories at least. Anyway, I am confident that in few years from now we will be at a stage where it will be clear beyond any reasonable doubt which theory is the good starting point.

Cleverus: All the discussion about the dynamical transition looked fishy: you seems to claim victory saying that it works, and when it does not, you say it is because of the cross-over. Isn't it a bit too easy?

Salviati: Well, yes and no. No, there are some qualitative results of the mean-field theory that are really non-trivial and that one finds in simulations of glass-formers. These results just come straight from first principle computations, they could have been very different, you know. For example, no growing dynamic correlations or growing in a weird way and then, bye bye, mean field theory. However, yes, you are right, the lack of a good description of the cross-over close to T_d is a weak point.

Cleverus: But, physically, you said that it should be related to the emergence of soft modes in the states and that the dynamical relaxation should mainly take place along them. This is something it should be possible to test in simulations.

Salviati: Actually, yes! This has been done for example in [25] for glass-formers and also in [26] for hard spheres.

Cleverus: OK. So, finally, tell me your view on how glassy relax—not the balanced one you write in papers but the wild guess.

Salviati: Mhmm, ok. I think that close to T_d the dynamics is a mix of activation

combined with relaxation along the soft modes. There, the dynamics is characterized by small clusters of particles, which relax by activation and cooperatively. And this triggers an avalanche process along soft modes or regions that are soft. Actually, some of what I am saying has been found in simulations [6] of glass-formers and in experiments of granular systems [8]. Decreasing the temperature, the importance of the soft modes decreases, cooperative clusters increases in size and the relaxation time is determined by some variants of the RFOT argument described before.

Cleverus: Two final questions. From the point of view of RFOT hard sphere colloids and molecular liquids display the very same transition. But what about granular systems, they are phenomenologically very similar but you cannot describe them in terms of Boltzmann equilibrium, they are in an out of equilibrium steady state.

Salviati: You are right. This is puzzling and very fascinating. Could it be that despite the important physical differences, the glass transitions of liquids and grains are driven by the same underlying critical phenomenon? One experiment I would love to see is the Gedanken one for a granular system. Maybe, it would show that the very same kind of subtle amorphous *static* correlations develops also in a granular system despite the stationary distribution is not Boltzmann.

Cleverus: Final question or comment: you swept the crystal problem under the rug. But in general there is an underlying crystal, so the super-cooled liquid state is not a true equilibrium state and the glass transition cannot be a true phase transition.

Salviati: Com'on Cleverus...I got the same comment from Simplicius.

Cleverus: OK, right, it was just to tease you. Thank you very much for all the explanations. No way, I could have understood all this alone during my sailing trip. It was good to see you. By the way, you cited a lot Anderson, but you never quoted the last sentence of his famous article on glasses: "The solution of the more important and puzzling glass problem may also have a substantial intellectual spin-off. Whether it will help make better glass is questionable." Bye Bye.

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Some References

Below I will list some papers that may be useful for a reader that wants to know more about the topics treated in this paper. In the main text I almost didn't cite any paper besides very few random exceptions. I owe an apology to all my colleagues that are not finding their works cited. A complete reference list will be added in the final version of the paper that will appear in 2010.

Sections 1-5

L. Berthier and G. Biroli, *A Statistical Mechanics Perspective on Glasses and Aging* Encyclopedia of Complexity and Systems Science, Springer (2009).

P.G. Debenedetti and F. H. Stillinger, *Nature* **410** (2001), 259.

Section 7-9

- T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, *Phys. Rev. A* **40** (1989), 1045.
 J.-P. Bouchaud and G. Biroli, *J. Chem. Phys.* **121** (2004), 7347.
 A. Cavagna, *Supercooled liquids for pedestrians*, *Physics Reports* **476** (2009), 51.

References

- [1] G. Galilei, *Dialogue Concerning the Two Chief World Systems*.
- [2] S. Coleman, *Aspects of Symmetry*, Cambridge University Press, 1985.
- [3] P.G. Debenedetti and F. H. Stillinger, *Nature* **410** (2001), 259.
- [4] R. Richert and C. A. Angell, *J. Chem. Phys.* **108** (1998), 9016.
- [5] J. Wuttke, W. Petry, and S. Pouget, *J. Chem. Phys.* **105** (1996), 5177.
- [6] R. Candelier, PhD Thesis, Univ. Paris VI (2009).
- [7] E.R. Weeks, J.C. Crocker, A.C. Levitt, A. Schofield, and D.A. Weitz, *Science* **287** (2000), 627.
- [8] R. Candelier, O. Dauchot, and G. Biroli, *Phys. Rev. Lett.* **102** (2009), 088001.
- [9] L. Berthier and G. Biroli, *A Statistical Mechanics Perspective on Glasses and Aging* *Encyclopedia of Complexity and Systems Science*, Springer (2009).
- [10] A. S. Keys, A. R. Abate, S. C. Glotzer, and D. J. Durian, *Nature Physics* **3** (2007), 260.
- [11] L. Berthier, G. Biroli, J.-P. Bouchaud, L. Cipelletti, D. El Masri, D. L'Hôte, F. Ladieu, and M. Pierno, *Science* **310** (2005), 1797.
- [12] C. Dalle-Ferrier, C. Thibierge, C. Alba-Simionesco, L. Berthier, G. Biroli, J.-P. Bouchaud, F. Ladieu, D. L'Hôte, and G. Tarjus, *Phys. Rev. E* **76** (2007), 041510.
- [13] A. Montanari, G. Semerjian, *J. Stat. Phys.* **125** (2006), 23.
- [14] F. Krzakala, A. Montanari, F. Ricci-Tersenghi, G. Semerjian, L. Zdeborova, *Proc. Natl. Acad. Sci.* **104** (2007), 10318.
- [15] G. Parisi and F. Zamponi, arXiv:0802.2180.
- [16] L. Santen and W. Krauth, *Nature* **405** (2000), 550.
- [17] L. Berthier and T. A. Witten, *Phys. Rev. E* **80** (2009), 021502.
- [18] M. Mézard and G. Parisi, *Phys. Rev. Lett.* **82** (1999), 747.
- [19] S. Franz, M. Cardenas, G. Parisi *J.Phys. A: Math. Gen.* **31** (1998), L163.
- [20] T. R. Kirkpatrick, D. Thirumalai, and P. G. Wolynes, *Phys. Rev. A* **40** (1989), 1045.
- [21] J.-P. Bouchaud and G. Biroli, *J. Chem. Phys.* **121** (2004), 7347.

- [22] S. Franz, A. Montanari *J. Phys. A: Math. and Theor.* **40** (2007), F251.
- [23] M. Dzero, J. Schmalian, and P. G. Wolynes, *Phys. Rev. B* **72** (2005), 100201.
- [24] G. Biroli, J.-P. Bouchaud, A. Cavagna, T. S. Grigera, P. Verrocchio, *Nature Physics* **4** (2008), 771. C. Cammarota, A. Cavagna, G. Gradenigo, T. S. Grigera, P. Verrocchio, arXiv:0904.1522; Chiara Cammarota, Andrea Cavagna, Giacomo Gradenigo, Tomas S. Grigera, Paolo Verrocchio, arXiv:0906.3868.
- [25] A. Widmer-Cooper, H. Perry, P. Harrowell and D.R. Reichman, *Nature Physics* **4** (2008), 711.
- [26] C. Brito, M. Wyart, *J. Chem. Phys.* **131** (2009), 024504.