The quest for a transition and order in glasses

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June 1, 2013

Abstract

The physics of glasses is rather special, in that we have to stop often and ask what we are really looking for. Unlike other branches of physics, we have very good microscopic models exhibiting the correct phenomenology, and we have access to most of the experimental facts we need – but probably are still missing some insights.

The basic question is: how is it possible that a supercooled liquid develops, upon cooling a few degrees, an enormous increase in the viscosity; and we do not see any obvious microscopic organization to explain this. A second, perhaps more relevant, yet less explored question is to find a description that is suitable and generalizes thermodynamics for the out of equilibrium situation glasses are in.

1 Introduction

Ever since childhood we are taught that heat is motion, and that the constant collisions keep molecules from sticking together, and are responsible for the pressure exerted by a fluid. When a system is cooled to sufficiently low temperatures, we thus expect it to 'collapse': molecules becoming more densely packed, leading to a form of matter that does not flow easily which we call a solid.

We then become aware of a fact that is commonplace and yet astonishing: in general molecular crowding is not a continuous process, but what happens rather is that upon cooling, all of a sudden the system arranges itself in an ordered manner, all particles performing their thermal motion around average positions disposed regularly, in a periodic arrangement.

Crystallization is indeed the first inherently collective phenomenon we become aware of, because we soon realize that the question whether a collection of twenty molecules is a solid or a liquid is meaningless.

There are however exceptions to this miracle of crystalisation, in which systems upon cooling seem to behave in the most naive manner, gradually becoming solid-like, with particles just moving slower and in a more constrained manner, but with no evident spatial order emerging: we then say that we have formed a glass. This at first sight most unremarkable behavior where apparently nothing collective is happening is, strangely enough, the one we understand the least.

The viscosity of a glass-former liquid (a substance able to avoid crystalisation) increases upon cooling without any important change in structure, but still in an explosive way: many orders of magnitude in only a few degrees Celsius. How are we to explain this, in the absence of anything sudden or remarkable happening to the arrangement of the particles (see Fig. 1)? Having avoided the obvious miracle of ordering, glass formers present us with the mystery of their sudden change of behavior, leaving us to wonder if there is a hidden form organization of matter, or an avoided 'nearby' sharp transition, which we have yet to discover.

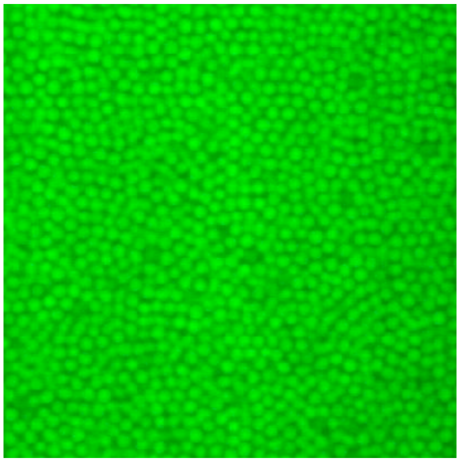

Figure 1: A confocal microscopy of a colloidal glass (from Bonn et al.). No obvious order may be seen.

The following six lectures try to give a first look at these problems, and a biased introduction to some of the currently discussed questions. They are a modified and expanded version of a lecture given in Seminaire Poincare in November 2009 (see http://www.bourbaphy.fr/novembre2009.html).

2 What is a solid?

Being a solid is very much like being a ferromagnet: a conspiracy of simple elements yielding a long-range order. Just as a finite number of spins cannot have true ferromagnetic order, a finite number of particles at finite pressure cannot form a solid.

When we cool a liquid, crystalisation may occur all of a sudden. The energy then jumps to a lower value (Fig 2)– we say the system loses its latent heat – and from the microscopic point of view the system is now organized (Fig 3). The same situation arises with hard particles, with the volume and the inverse pressure playing the role of energy and temperature $(V, P^{-1}) \leftrightarrow (E, T)$.

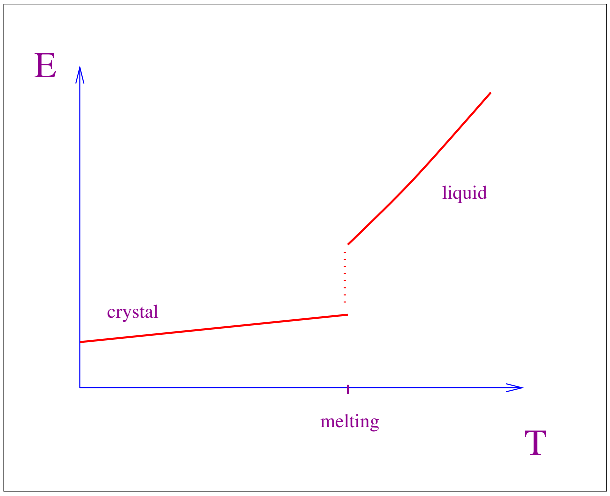

Figure 2: Energy versus temperature – or volume versus 1/(pressure).

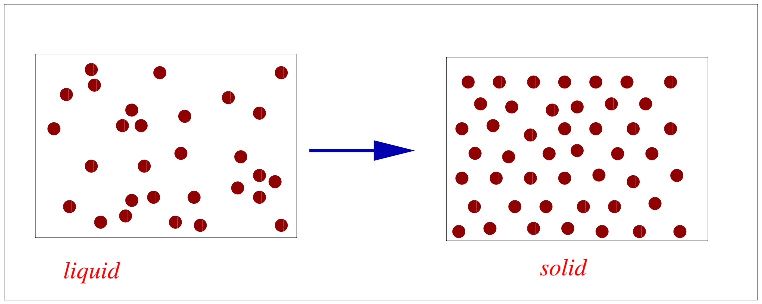

Figure 3: Ordering as the system jumps from a liquid (left) to a crystalline configuration (right).

A periodic distribution of matter has a spatial Fourier spectrum composed of delta contributions: these are the Bragg peaks (Fig. 4). They are directly observable with diffraction measurements. Except at zero temperature, the instantaneous location of particles fluctuates around their truly ordered positions. For a crystal, these fluctuations do not affect the notion of order, since even in their presence there are Bragg peaks – and what is more, they pose no problem for our eye to recognise periodicity either.

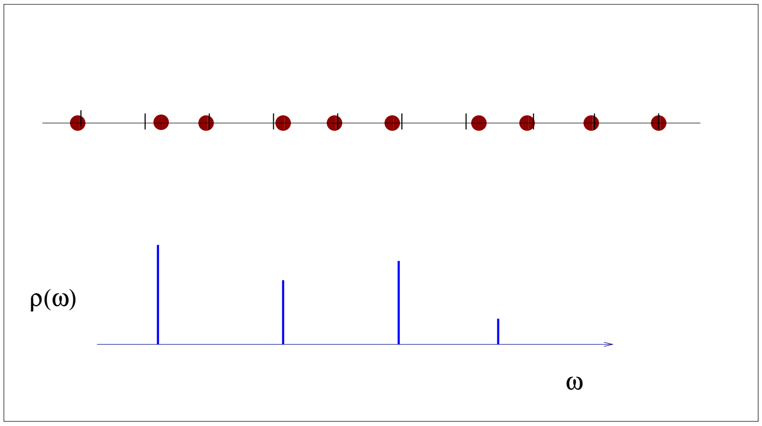

Figure 4: Periodicity, fluctuations and a Bragg peak

Because we shall need to consider cases in which there is no periodicity, and no tool playing the role of a Fourier transform, it is convenient to detect order in an alternative fashion. The fact that there is an average density modulation can be directly seen from the fact that the time-average density (Fig. 5)):

$$\bar{\rho}(x) = \tau^{-1} \int_0^\tau dt \; \rho(x,t) \; = \frac{1}{N\tau} \int_0^\tau dt \; \Sigma_a \; \delta[x_a(t) - x] \tag{2.1}$$

has a non-constant limit as $\tau \to \infty$ (taken *after* the thermodynamic limit).

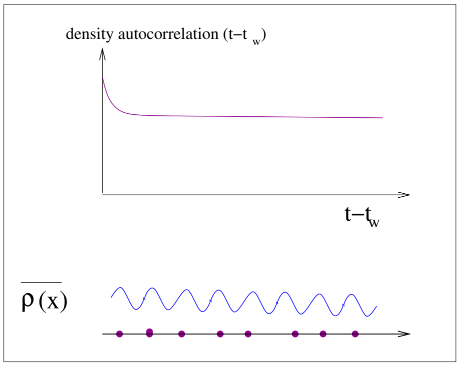

Figure 5: A sketch of the situation in a crystal. At finite temperatures, particles are not in periodic positions. However, the average density, defined by performing an infinite time average, is indeed periodic. In this case, we also have the possibility of averaging over spatial repetitions, a procedure automatically performed by the Fourier transform. The density-density correlation function has a plateau in time, which lasts forever if there is positional order.

Another useful way of conveying the same information, is to consider a two-time autocorrelation function, as in figure 6:

$$C(t, t_w) = V^{-1} \int dx \; [\rho(x,t)\rho(x,t_w) - \rho_o^2] \tag{2.2}$$

In terms of $t - t_w$, there is a fast relaxation, corresponding to the rapid motion including the phonons, but the correlation saturates to a plateau $C = V^{-1} \int dx \; [\bar{\rho}(x) - \rho_o]^2$

2.1 Collective nature of solidity

The popular, generic term *jamming* as applied to solidification [1] may be suggestive of rigidity arising from hard constituents in contact with one another, each one blocking its neighbour. However, it is important to bear in mind that rigidity is, at least for crystals and glasses, a collective phenomenon that does not require hard constituents at all, and does not imply or require that any individual one be blocked. The crystal example allows us to discuss in a very simple manner what being a solid does, and what it does not mean. The property of having a permanent (average) density modulation is one characteristic defining a solid. Another, more explicit one, is the fact that they do not flow when subjected to *infinitesimal* stress [2, 3] (about which, more below).

Consider first the case of soft particles (without a hard core) at finite temperatures, as in figure 7. It is clear that any particle may exchange its position with a neighbouring one with finite probability, so that there is no order in the

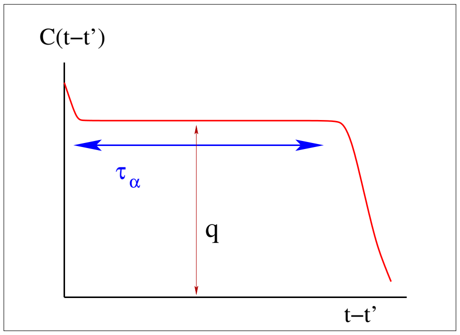

Figure 6: A sketch of the autocorrelation function with a two-step relaxation, plotted in logarithmic scale for the times. There is a rapid decrease into the a plateau, whose value is by definition the Edwards-Anderson parameter, followed by a fall to zero at a longer time scale τ_α. The slow timescale τ_α for an equilibrium system depends on the temperature, and grows as the glassy phase is approached. Out of equilibrium, τ_α grows with the 'waiting' time after preparation, and saturates if and when equilibrium is reached.

particle positions, if they are distinguished. Order is then a property of the density modulation, just as an army has permanent rank order independent of the changing names of soldiers and generals. Another important point is that there can be no order in a *finite* system, since for such a system there will be a finite probability of being in any configuration, having started from any other. The same can be said for a system of hard spheres (Fig. 8), at finite pressure, because particles can always 'make way' for others to rearrange. And yet, we know that infinite systems of this kind – soft spheres, hard particles at densities such that they do not touch – *do* form solids in the thermodynamic limit.

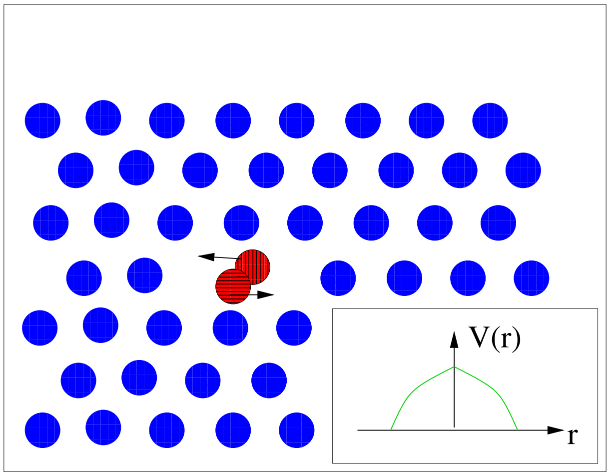

Figure 7: Permuting soft particles.

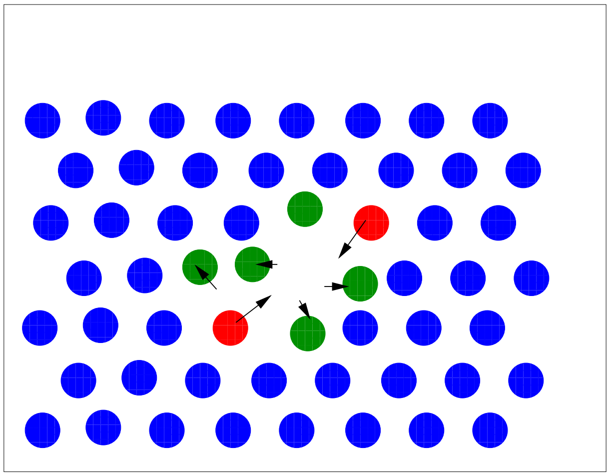

Figure 8: Permuting hard particles

Two further examples may be instructive. Consider the ferromagnetic Ising model at $T = T_c/10$. Equilibrium is given by a state with positive and one with negative magnetisation. The fact that an infinite system has a permanent magnetisation, and that symmetry is broken, relies on the impossibility of the magnetisation flipping. However, it is easy to find a path of constant energy leading from a typical configuration of the positive magnetization state to a typical configuration of the negative magnetization state. It suffices (Fig. 9) to 'herd' the minority down spins into a large stripe, and then grow laterally this stripe a constant energy. The barrier is entropic in nature: it takes many simultaneous things to happen in order to assure the passage, and the probability of all of them occurring, though finite in a finite sample, becomes zero in the thermodynamic limit.

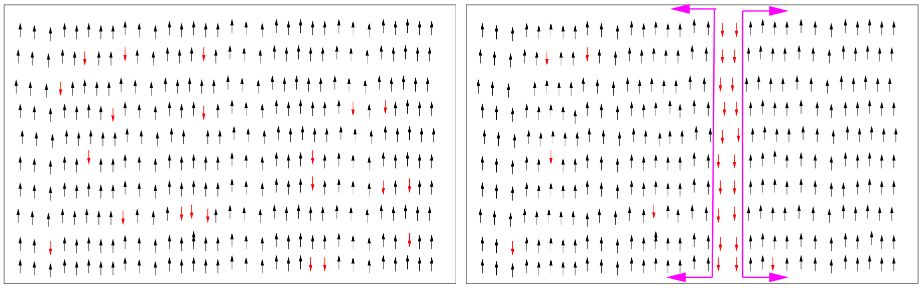

Figure 9: A collective, entropic, infinte barrier

Going back to the soft-sphere crystal, a spontaneous deformation like that of Figure 10, has an infinite energy barrier, because it involves an infinite amount of overlaps in the thermodynamic limit. Infinite entropic or energetic barriers are, in all these cases, collective phenomena.

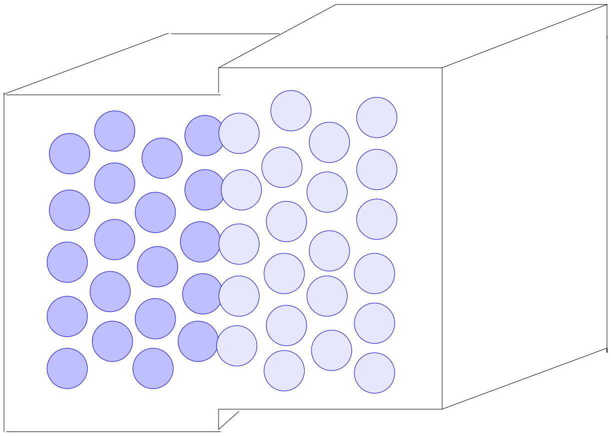

Figure 10: A collective, energetic, infinite barrier.

In contrast with the previous examples, one may have systems that are only solid because already its individual constituents are. In that case, even a finite version may be solid. Simple examples of this are depicted in figure 11, where the spheres are assumed to be hard, or if they are not, the temperature is assumed to be zero.

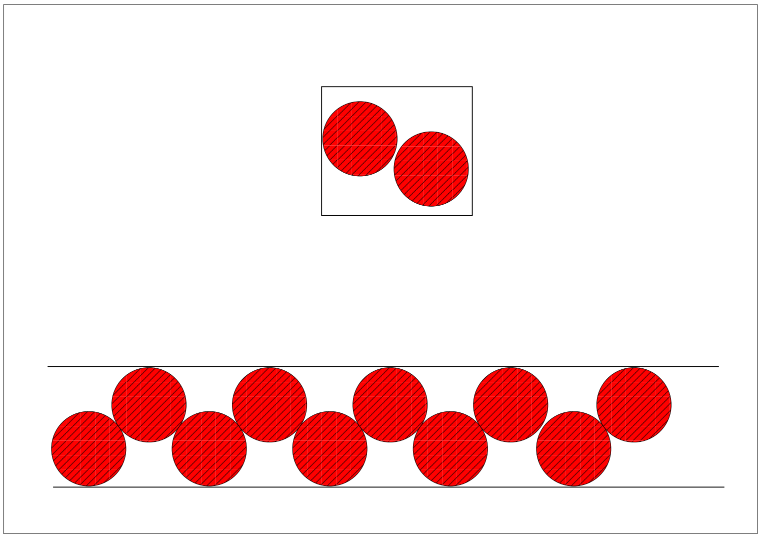

Figure 11: Non-collective rigidity.

A more subtle example of the same thing are the *kinetically constrained models* [4]. These are lattice models in which the particles have some forbidden moves. For example if their number of neighbors is higher than a certain number, the particle is immobile. The restriction play, in this case, a role analogous as the hard constraints of Fig 11: as soon as they are partially lifted, infinite timescales and permanent modulations dissapear.

In the situations in which rigidity and permanent modulations of density do not have a collective origin, for example in the case of *finite* systems, the timescales grow as $T \to 0$ or $P \to \infty$ in an typical activated (Arrhenius) manner. This is clear, because there is a finite barrier that takes more to cross at lower temperatures. On the other hand, a collective system in the thermodynamic limit may have timescales that diverge at finite temperatures (e.g. the Ising model), or at any rate grow faster than with an exponential Arrhenius law. What we have just said can be made rigorous [5]: a system having a timescale that grows faster than exponentially *necessarily* has some equilibrium coperativity length that diverges when the timescale diverges. We shall come back to this several times below.

2.2 Short disgression: the nucleation argument

Before continuing, it is useful to recall the nucleation argument, which allows us to conclude that for finite dimensional systems at non-zero temperature, with short range interactions and soft potentials – these are all we consider here – a phase with a free energy density higher than the equilibrium one *cannot be stable*. This means that true stable states have a free energy that exceeds the equilibrium one at most by a *subextensive* amount.

One considers two phases **a** and **b** with free energy densities $f_a > f_b$ (Fig. 12). In the phase **a**, a droplet of radius r of the phase **b** costs at most a surface energy σr^{d-1}, with $\sigma \leq 0$, and involves a gain $-(f_a - f_b)r^d$. In terms of r, we have:

$$\delta f(r) = \sigma r^{d-1} - (f_a - f_b)r^d \tag{2.3}$$

which has a maximum $\delta f(r^*)$ at a critical radius r^* :

$$r^* = \frac{(d-1)\sigma}{d(f_a - f_b)} \quad \rightarrow \quad f(r^*) \propto \frac{\sigma^d}{(f_a - f_b)^{d-1}} \tag{2.4}$$

The droplet growth is activated up to r^*, with Arrhenius probability $\sim e^{-\delta f(r^*)/T}$, and then proceeds downhill until the phase **b** prevails. We have found a path leading from state **a** to phase **b** with a finite free energy barrier requiring a finite number of moves: it is perhaps not the best path, but it gives an upper bound on the probability of nucleation. The only way in which the droplet will not unstabilise **a** is that either $\sigma = \infty$ (which requires hard, or long-range interactions), or that $(f_a - f_b) \rightarrow 0$ as $N \rightarrow \infty$.

The nucleation argument is stronger than this: it implies that the state **a** cannot have *any* sub-region of extensive volume having a free energy density larger than the corresponding one of the state **b**.

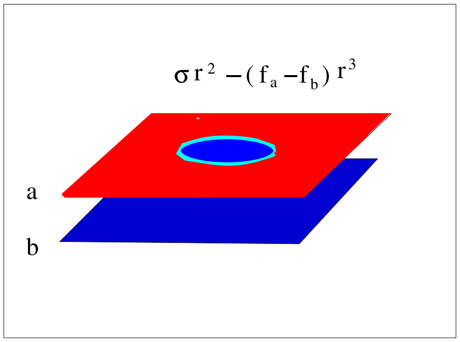

Figure 12: A droplet of the blue phase will always be favorable beyond a critical radius, if the red and blue phases' free energy difference is extensive

2.3 Do solids flow?

When we say that a glass behaves as a solid, the seemingly more natural way to think of this is by imagining the sample subjected to stress, and proposing that it does not flow.

One has to be careful, however, since in fact all solids at positive temperature and finite pressure flow, when subjected to a macroscopic stress [3]. To see this, we apply the argument above concerning the nucleation of metastable phases.

Consider a solid of size L^3,it could be an equilibrium phase such as a crystal, a quasi-crystal or a ideal glass. We apply a very small but macroscopic shear stress, as in Fig. 13. After a very rapid equilibration time the sample will deform elastically, by a finite amount $\gamma = \sigma/G_P$ (this is what we understand by 'macroscopic'), where G_P is referred to in practical applications as the elastic shear modulus. This deformation leads to an increase in the free energy of the system that according to elasticity theory is $L^3\sigma^2/2G_P$. The deformed solid has a free energy extensively higher than the one of the equilibrium undeformed state and is thus in a metastable state. According to what was discussed above, the deformed state necessarily has a finite life-time. To see this, let us concentrate on a cavity of radius R inside the deformed solid, and consider reshuffling all particles inside the cavity from the deformed to the undeformed configuration as in Fig 14. Clearly, we are in a situation like the one of Figure 12: the cost of deforming back the cavity is proportional to the area of the interface, while the gain in free energy is proportional to the volume. Of course, this is only an upper bound, but it suffices in order to show that there is a finite barrier to nucleation of the undeformed state.

As a consequence, after a certain time, the deformed solid goes back to the undeformed state. If, however, the external shear stress is continuously applied, the solid deforms again and the entire process repeats, creating a net flow.

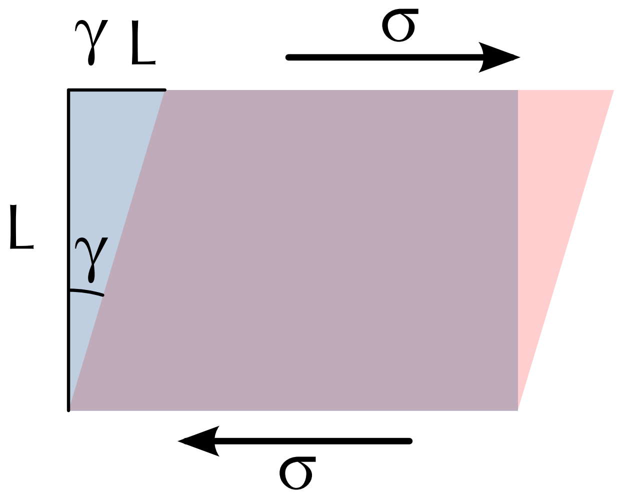

Figure 13: Shearing a solid

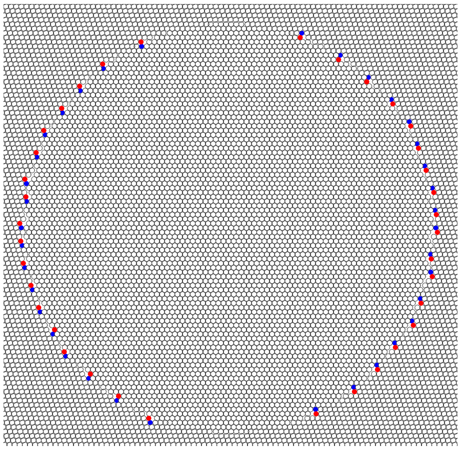

Figure 14: The nucleation argument as applied to a sheared solid

3 From supercooled liquids to glasses : general phenomenology

A liquid may be cooled in such a way as to avoid crystallization. What one observes then is a spectacular increase of the viscosity, that is not concomitant with any obvious change in structure. The phenomenology of this *glass transition* (an already loaded name) is very similar for substances that may have widely different elementary constituents, such as hard spheres and polymers.

The increase in the viscosity may go as an Arrhenius law $\eta \sim e^{A/T}$ or a super-Arrhenius law, such as $\eta \sim e^{A/T^2}$. or $\eta \sim e^{A/(T-T_o)}$. Although in practice the difference may seem barely detectable, for physicists, it is of considerable importance. The reason is that a super-Arrhenius behavior implies a new physical phenomenon, characterized by some hidden form of long range order between particles.

Let us now turn to the situation when crystalisation does not happen. One can cool a liquid in such a way that the crystalline phase does not have the oportunty to nucleate. How easily this is done depends on the cooling protocol and on the nature of the liquid – a 'good' glass-former is a poor crystalisor, and vice-versa.

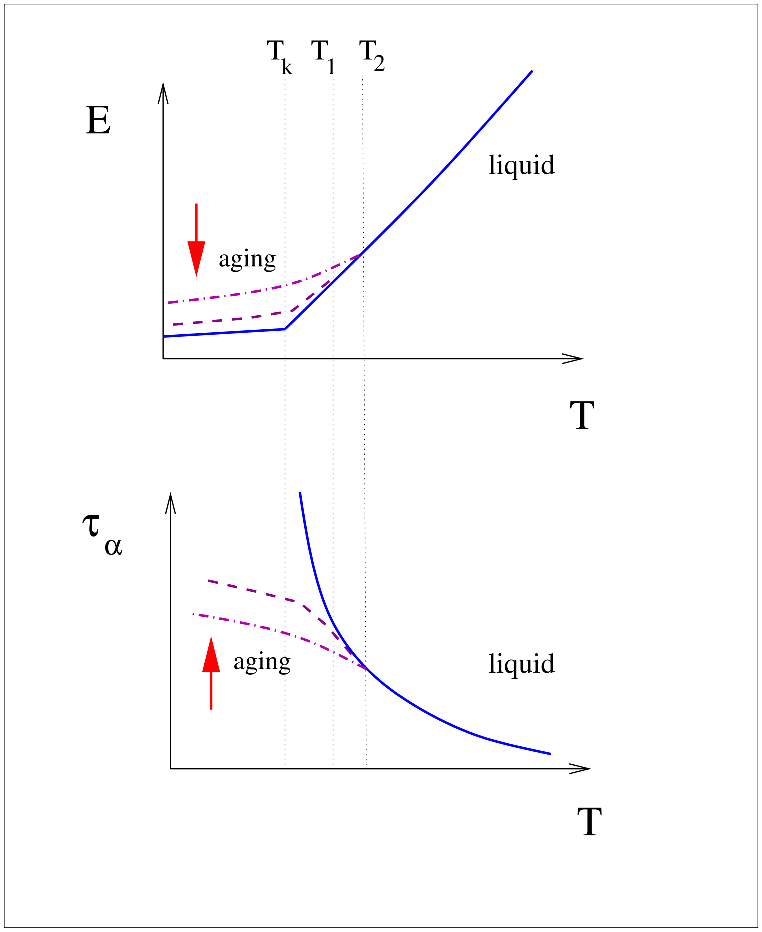

Figure 15: Different annealing speeds. The dashed lines indicate out of equilibrium situations, and are necessarily evolving in time. The full line is the result of infinitely slow cooling: energy has a nonanaliticity, and the relaxation timescale τ_α a divergence, if there is a true phase transition.

The supercooled liquid just below the melting temperature is metastable, but in an innocent way: it can be considered to be in 'local' equilibrium: if the temperature is not changed, the macroscopic observables do not evolve, and the equilibrium theorems (Fluctuation-Dissipation, Onsager reciprocity) hold. In other words, the supercooled liquid phase is in a situation similar to that of diamond, a mixture of oxygen and hydrogen at room temperature, or a current-carrying superconductor; which for all practical purposes ignore the possibility of nucleating graphite, water, or a lower supercurrent, and may be treated as equilibrium systems.

Upon cooling further, the viscosity grows dramatically, and the liquid reaches a point in which it falls out of equilibrium – but this time in a serious way. We can tell this because energy and viscosity now start depending on the cooling speed, and even if the temperature is held constant, they continue to evolve – as do all other macroscopic observables. This situation is completely unrelated to the existence of the cristal and very different from the innocent metastability of diamond or the oxygen-hydrogen mixture. The system is now in a situation in which something is constantly evolving so that, as we shall see, one can determine experimentally its 'age' since it fell out of equilibrium and it became a glass.

Cooling a system as in Figure 15, we see that for a fast cooling, the energy ceases to have its equilibrium value at a temperature T_2, and for a slower process, this happens at a lower temperature T_1. We recognize the equilibrium energy vs. temperature curve as the envelope beyond which all slower annealing protocols coincide. What we have said about energies can be said about the viscosities, or the relaxation times τ_α. Let us focus on an autocorrelation function, for example (Fig. 2.2). In the supercooled liquid phase, the autocorrelation falls in two steps: first to a plateau, and the second, in a much longer time τ_α, to zero, just as in Fig 6 . The first drop to the plateau is analogous to the one observed in a crystal (Fig. 6), and is a consequence of rapid vibrations, while the second drop – entirely absent in a crystal – reflects the large rearrangements that a liquid can afford to make. A direct way to picture the α relaxation is to consider, as in Figure 16, the analogue of Fig. 6: averaging out the rapid vibrations, as we did in the crystalline case, we obtain an amorphous density profile that does not last forever, but takes a time $\sim \tau_\alpha$ to evolve. Within (metastable) equilibrium, τ_α is growing rapidly as the temperature is decreased, reflecting the increase in the viscosity (Fig. 17, right). When the system is further cooled and falls out of equilibrium, the autocorrelation function is no longer an exclusive function of temperature, but depends also on history via the 'waiting' time t_w (Fig. 17, left): in particular, the system needs time to become more viscous. This is the 'aging' phenomenon. Still, at a temperature T_1 (Fig. 17, top), eventually τ_α reaches its equilibrium value, although this may take so long to do so, that we only observe aging.

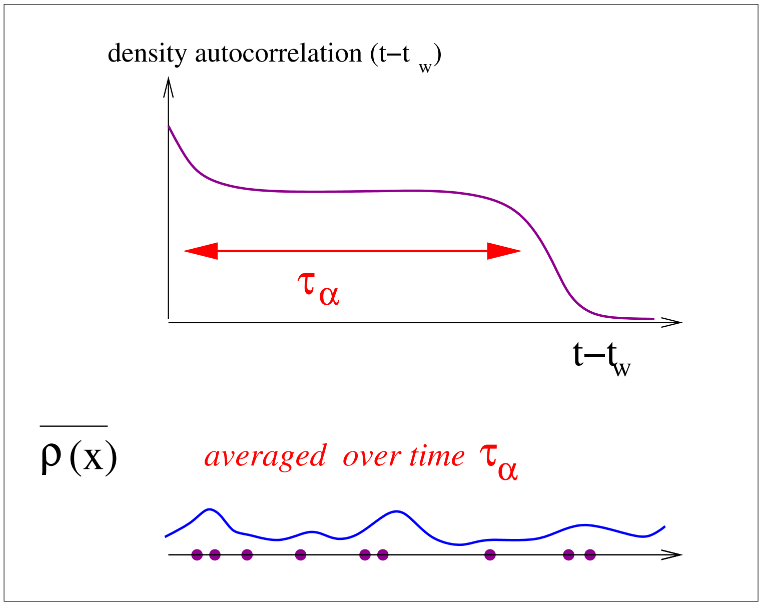

Figure 16: Density profile in an α scale.

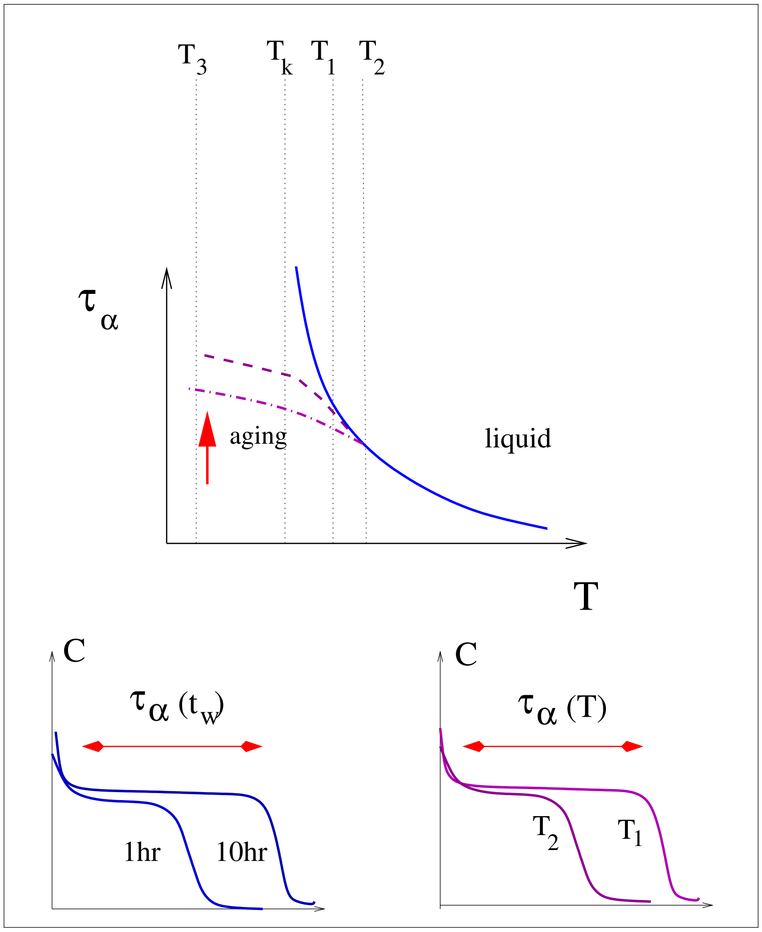

Figure 17: α time relaxation depends on temperature in equilibrium, and on the waiting time out of equilibrium.

3.1 Ideal glass. Arrhenius versus non-Arrhenius

This is how glasses present themselves to us in real, experimental life. We may still be curious to know whether there is a temperature T_K below which aging lasts forever, equilibrium is never achieved, and the timescale τ_α becomes infinite. If this were the case, one could ideally consider samples with a permanent, amorphous, averaged density profile $\bar{\rho}(x)$, a solid just like a crystal in all but the spatial periodicity. The discussion above about collective rigidity implies that if such states with permanent spatial modulation of density exist at finite temperature, then necessarily they involve a coherent behaviour of particles that only exists rigorously in the thermodynamic limit, and requires the divergence of some correlation length. This is even the case if $T_K = 0$, but τ_α grows faster than an Arrhenius law $\tau_\alpha \sim e^{b/T}$, for example as $e^{A/T^2+B/T}$ [6].

In a word, whenever there is a faster-than-Arrhenius law of growth of timescales, something non-trivial is happening: particles are moving in a more and more coordinated way as temperature goes down and pressure goes up. The Angell plots (Fig. 18), are specially designed to see the departure from Arrhenius behavior *in an equilibrium liquid*: one picks a (rather arbitrary) empirical glass temperature T_g, and plots the logarithm of the viscosity versus T_g/T, so that Arrhenius corresponds to a straight line. When this is the case, we say that the glass is 'strong', and when it is not, we say that it is 'fragile'.

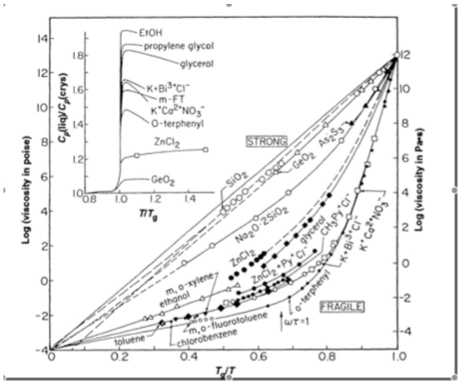

Figure 18: Visualizing the non-Arrhenius nature with an Angell plot

As all the questions in glass physics, the classification gets weakened by relativism: there is always the doubt that at longer timescales everything always becomes Arrhenius.

3.2 States

Within an α scale, we can classify configurations as in Figure 19: two configurations are considered to be in the same metastable state if the density profiles obtained starting from either one, and averaging over a time τ_α, coincide up to, say, $\tau_\alpha^{-1/2}$ (i.e. within the statistical error). This is sometimes depicted in a 'landscape' picture (Fig 19, right). All the configurations that yield the same profile constitute a 'state', and their number yields the entropy within that state. More importantly, the logarithm of the number of states (per unit volume) is by definition the *complexity* Σ [7].

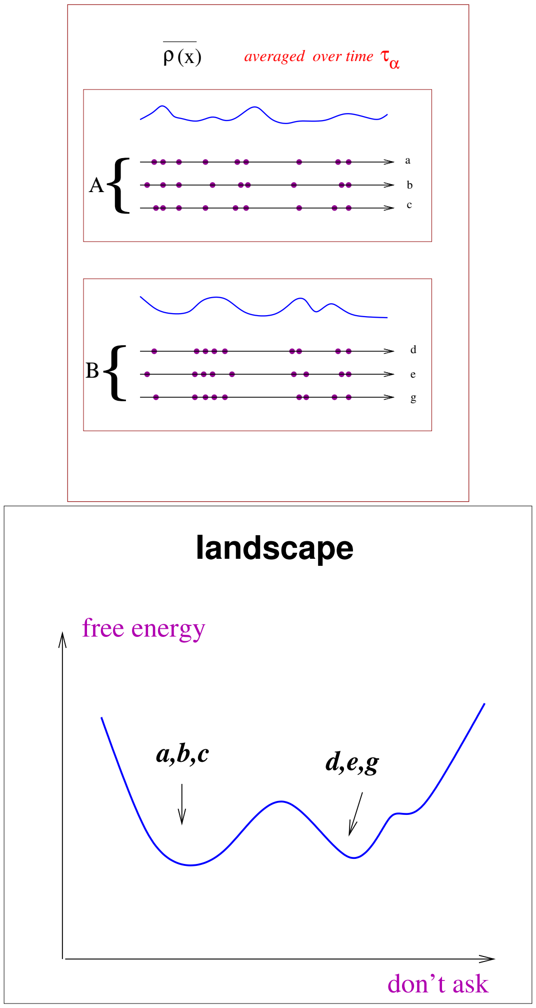

Figure 19: States as density profiles, and within a *free energy landscape* picture

4 Equilibrium versus non equilibrium

In real life glasses are out of equilibrium, so, strictly speaking, they escape the field of statistical mechanics. Even the ”temperature of a piece of glass” is an ill-defined concept! One may ask: is there anything generic one can still say, under these conditions?

In the real world, glasses know nothing about an ideal transition, they are just systems slowly working their way to equilibrium, insensitive to whether such an equilibrium is eventually reachable or not. It would seem that the phenomenology of such a situation would be all but universal, and that a theory of such a situation is hopeless. This turns out not to be quite the case.

As mentioned above, in the aging phase the α relaxation time increases with time, as does the viscosity [1]. When stress is applied to a plastic bar below the glass transition, the contraction happens in two steps: a fast elastic step followed by a slow 'creep' motion [8]. Figure (20) shows the classical experiments by Struik, where the creep motion as a function of time is measured for a sample at different 'waiting' times after it was quenched below the glass transition (the first, rapid part of the relaxation is not visible in the plot). Remarkably, the creep step takes a time roughly proportional to the waiting time, and this in a range from minutes to years. Clearly, no equilibrium theory can explain this behaviour, which has been obtained in a variety of glassy systems: plastics, colloids, spin glasses, etc.

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[1] Note that this would happen also in an imperfect crystal which is gradually healing its defects.

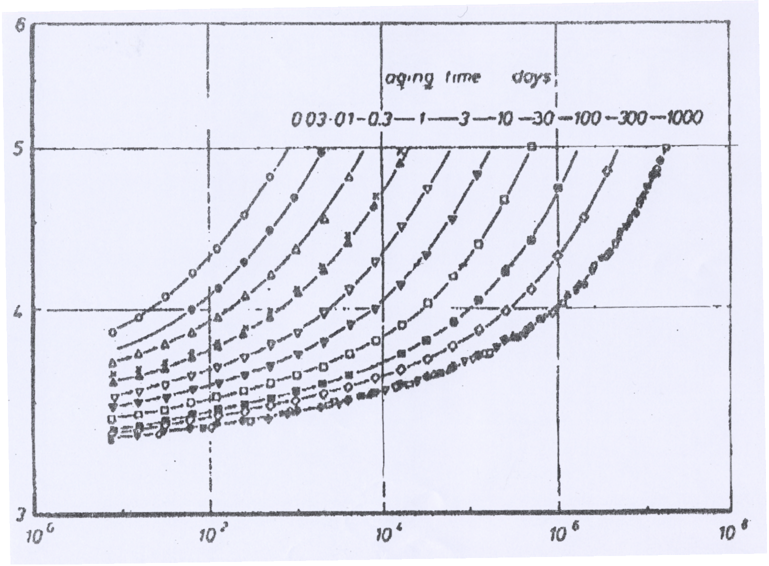

Figure 20: Struik's classical experiment

These experiments concern a *response* to a field. Similar curves are obtained when one considers a *correlation* (Fig. 21).

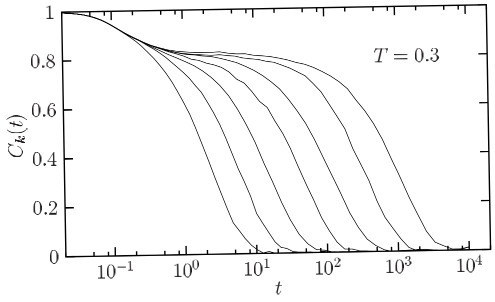

Figure 21: Autocorrelation decay for different values of the waiting time for a Lennard-Jones system (taken from Kob and Barrat)

In equilibrium, these two a related by the fluctuation-dissipation relation (Fig. 22), which states that the response of an average value $\chi(t, t_w) = \frac{\delta\langle X\rangle}{\delta h_Y(t_w \to t)}$ to a field that acts on Y from time t_w up to time t, is given in terms of the correlations as:

$$T\chi(t, t_w) = \langle X(t)Y(t)\rangle - \langle X(t)Y(t_w)\rangle = C(t, t) - C(t, t_w) \tag{4.1}$$

That such a relation should exist is not really surprising: the amplitude of the spontaneous fluctuations are related to the 'softness' of the equilibrium situation, as is the susceptibility to a perturbation (Fig. 22).

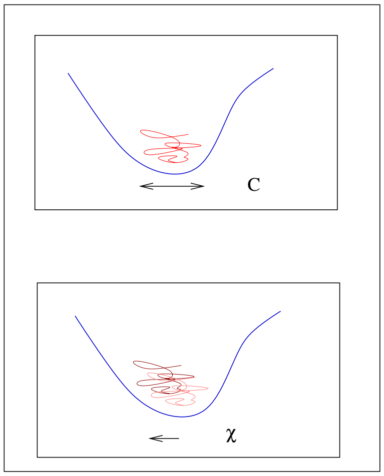

Figure 22: The fluctuation-dissipation theorem states the fact that spontaneous and induced fluctuations are not independent, in equilibrium.

In equilibrium, a χ versus C plot, parametric plot of all (t, t_w) then yields a straight line with slope $-1/T$ (Fig. 23).

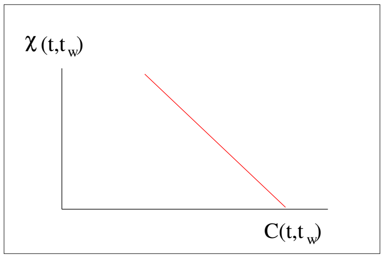

Figure 23: An FDT plot for an equilibrium system

A very different thing happens when we consider [9] the correlation and response of an aging glass (Fig. 24). All points fall on a line, which is now composed of two segments, one straight, and the other that may be curved or straight. For t close to t_w, corresponding to high frequencies, one obtains a line with gradient $-1/T$ as in equilibrium, but for t and t_w farther apart – precisely in the range where the response is the creep motion – one may obtain a different line with slope, say, $-1/T_{eff}$. The remarkable fact is that T_{eff} is the same (for the same time regime), for many different observables, suggesting that T_{eff} is a genuine temperature. Indeed, one can show that this is what a thermometer coupled to the slow degrees of freedom would measure [9], as we shall discuss below.

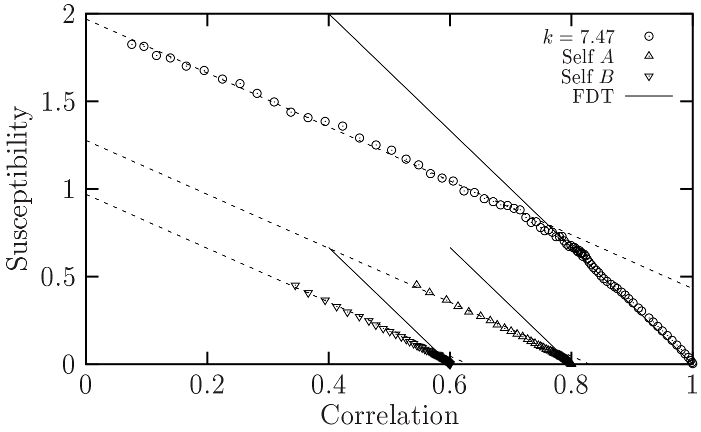

Figure 24: Effective temperatures: Response versus correlation for a binary mixture glass. The three lines correspond to density autocorrelations, and to diffusion versus mobility for each kind of particle. The autocorrelation curve shows the two-temperature behaviour, while the diffusion only the effective temperature, since it is a low-frequency quantity. The effective temperatures seem to coincide, as witnessed by the fact that the segments are parallel. Taken from Berthier and Barrat [10]

This way of approaching the effective temperature comes to us from the analytic solution of the aging dynamics of the Random First Order theory (RFOT, see below), but it seems to be the same kind of idea proposed at a phenomenological level many years ago by Tool [11]. What we know is that it is rigorously true for models within RFOT, but for realistic situations we are left with simulations, as in Fig 24, or with experiments, as the one performed by Oukris and Israeloff [12], see Figure 25

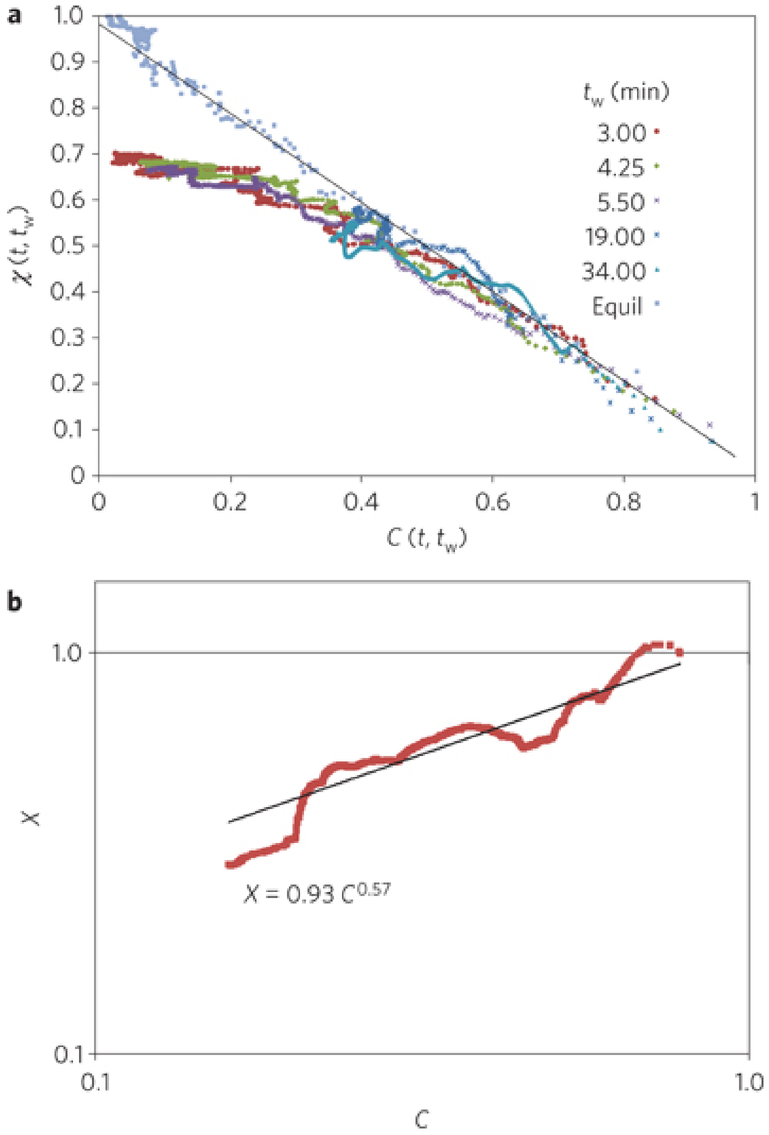

Figure 25: Effective temperatures: experimental response versus correlation for a polymer system. Taken from Oukris and Israeloff [12]

One should beware of simplistic explanations: what is most important to keep in mind is that these effective temperatures are *not* due to some structure that has remained frozen at the configuration it had when the system crossed the glass temperature: since that time the system has decorrelated substantially, and the identity of the particles responsible for the aging motion and the effective temperature *is constantly changing.*

4.1 Measuring effective temperatures

The fluctuation-dissipation theorem says something important about thermalization and about thermometry .

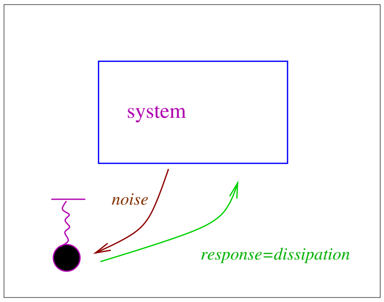

Figure 26: The fluctuation-dissipation theorem guarantees that a thermometer will measure the correct temperature in a system at equilibrium

Consider a thermometer made of a harmonic oscillator, coupled to a macroscopic observable of the system, for example a Fourier component of the density fluctuations (Figure 26):

$$\rho_k(t) = \int dx\ cos(kx)\rho(x,t)$$

The oscillator exchanges energy with the system: it gains energy from the noise (fluctuations), and looses it through dissipation. By reading the energy of the of the oscillator we may infer the temperature: the balance between fluctuation and dissipation guarantees equipartition *in equilibrium.* Let us see how this comes about. The energy of system and thermometer is:

$$E^* = E + x\rho_k + \frac{p_x^2}{2} + \frac{\omega^2 x^2}{2}$$

and the equation of motion of the oscillator and system is:

$$\ddot{x} = -\omega x - \rho_k \qquad but \qquad \rho_k = \underbrace{[\rho_k]_o}_{bare} + \underbrace{\int_\infty^t dt'\ \frac{\partial \chi(t,t')}{\partial t'} x(t')}_{back\ reaction}$$

where we have computed the influence of the thermometer on the system using linear response. We then have that the oscillator evolves with:

$$\ddot{x} = -\omega x + [\rho_k]_o + \int_\infty^t dt'\ \frac{\partial \chi(t,t')}{\partial t'} x(t')$$

This is of the form of a Langevin equation, which acts as a thermal bath of temperature T provided that:

$$\langle [\rho_k]_o(t)[\rho_k]_o(t')\rangle = -T\frac{\partial\chi(t,t')}{\partial t'}$$

Now, if at the frequency of the oscillator, the fluctuation-dissipation relation is valid with a factor T_{eff}, the oscillator will be thermalized with that temperature, and this will be true for any thermometer exchanging energy at that frequency.

A concrete example of coupling of an oscillator and a system for a magnetic system (Figure 27) was proposed in [9], and was actually performed experimentally by Grigera and Israeloff [13]:

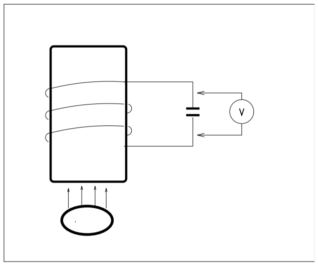

Figure 27: Measuring an effective temperature: the Grigera-Israeloff experiment.

5 A zoo of models

Do we have a realistic and relatively simple microscopic model of a glass? Yes indeed: a system of hard spheres under pressure is a perfectly good candidate. Then: why look for other models?

Glass physics is particular, in that we have canonical models – hard spheres, or particles interacting with Lennard-Jones interactions – that have all the microscopic elements. The problem is that we cannot solve exactly these models; and, although we can realize them experimentally and simulate them, the kind of questions we wish to answer would require unrealistically long times. (One may wonder, of course, why so much emphasis on questions, such as existence of a true glass transition, that are irrelevant for experiments.)

Because realistic models defy solution, there has been quite an intense activity on the construction of models that are easily solvable, and illuminate at least some partial aspect of glassy physics. Before discussing some of them, it is important to distinguish two common uses of the word 'glassy"; which may be taken to mean: *i)* anything with slow dynamics, or *ii)* the precise manner of slowing down of systems of particles, with its apparently non-Arrhenius behavior.

Let us list some examples of the first kind:

- **'Dirty' versions of ordered systems** such as ferromagnets, vortex lattices, crystals: any system that has an ordered symmetry-breaking phase, and some form of spatially random perturbation, will tend to have slow phase-ordering kinetics [14]. The classical example is a ferromagnet subject to a weak spatially random field: following a quench, ferromagnetic domains grow, but the domain walls are pinned by the random fields and growth proceeds by activated depinning – which becomes extremely slow.

- **Spin glasses** These are spin systems with interaction having spatially random signs. They are rather simpler than particle systems, but their phenomenology is quite different. They have been fully solved within mean field [15], but the question whether this solution applies to finite dimensions is not yet settled.

- **The trap model** The trap model [16] assumes that the system chooses sequentially randomly chosen traps in phase-space. Each one of these traps has a typical residence time. What one can show is that if these 'trapping' times are randomly distributed with a wide (Lévy) law, then the system tends to be, at longer times, in deeper traps: a form of aging.

- **Backgammon [17], Car Parking [18], ...**

These are extremely schematic models. In the Backgammon model, particles move randomly between a number of sites, and there is an energetic preference for the particles piling on the same site. Because there is no external field that decides which site will be the meeting point, the system tends to spend a long time making and unmaking partial piles of particles.

In the Car-Parking models, extended particles ('cars') are sequentially added, avoiding superpositions. The dynamics gets slower as the 'parking space' becomes more limited.

- **Kinetically constrained models [19, 20, 21]**

  When one looks in detail at the dynamics of a supercooled liquid, one sees that the important rearrangements – those that are not mere back and forth motion – tend to be localized in space. Active regions shift over space, but in an epidemic manner. Kinetically constrained models are an idealization of this, where everything else is abstracted. Consider, for example, the Kob-Andersen model [20]. The system consists of N particles in a cubic lattice of side L, ($V = L^3$) with periodic boundary conditions. There can be at most one particle per site. At each time step a particle and one of its neighboring sites are chosen at random. The particle is moved if the three following conditions are all met: (i) the neighboring site is empty; (ii) the particle has less than four nearest neighbors; (iii) the particle will have less than four nearest neighbors after it is moved. The rule is symmetric in time, detailed balance is satisfied and the allowed configurations have equal probability in equilibrium. In this model the dynamics becomes slower and slower as the particle density ρ increases. A density close to one, particle diffusion stops almost completely.

- **The special case of spin glasses with multi-spin interactions**

  Spin glasses have random interactions $J_{i_1,\ldots,i_p}$, yielding an energy

  $$H = \sum_{i_1,\ldots,i_p} J_{i_1,\ldots,i_p} s_{i_1} \ldots s_{i_p} \tag{5.1}$$

  The original spin-glass models had only two-spin interactions J_{ij}, but soon after systems with $p > 2$ spin interactions where studied, and found to have, at the mean-field (fully connected) level rather different properties. It was Kirkpatrick, Thirumalai and Wolynes who realized [27] that in fact the models with $p > 2$ could be considered as mean field versions of structural (rather than 'spin') glasses, thus giving birth to the Random First Order theory (about which, more below).

  Frustratingly enough, finite-dimensional versions of p-spin models have up to now eluded the structural glass behavior.

- **Frustration-limited domain theory of supercooled liquids [25].**

  The motivation for these models starts from the observation that spheres have an icosahedral arrangement that is favorable at short distances, but does not pay at the largest distances. In a schematic way, this may be symbolized by a system with short-range ferromagnetic interactions, frustrated by an antiferromagnetic interaction acting strongly only in the long range. Thus, a ferromagnetic transition is approached but eventually hampered by the antiferromagnetic term. The idea is that something similar may happen with icosahedral order in liquids.

- **Particles on trees**

  One way to implement mean-field is to put particles on a Cayley tree, allowing them to interact with their neighbors along the branches. The Biroli-Mezard [22] model allows each site to be occupied by at most one particle, and any particle may have at most **l** occupied nearest neighbors. Another strategy is to put particles in ordinary space, but making them interact with only a restricted subset of others [23] In this way, some of the characteristics of finite dimensions are retained, while still having the mean-field property that allows to solve the model.

- **High dimensions**

  The statics of the liquid phase of spheres in high dimensions has been studied long ago. It is only recently [24] that the possibility of a glassy phase has been discussed in analytic terms. Work is still in progress, in particular concerning the dynamics in the supercooled and glassy phase (see [26]).

6 The ideal glass state (why do we care so much?). Correlation lengths.

Are glasses true solids? Or rather: would they be, if given an opportunity? A related question: is there a correlation length of some kind that would diverge, if the liquid were annealed sufficiently slowly?
These questions have obsessed many physicists for a long time, even if they may have little practical importance.

6.1 Point to set correlations

If a system with short-range, smooth interactions has a timescale that diverges faster than with an Arrhenius law, there is a lengthscale that must diverge. Physically this is clear because, as mentioned in several places above, the only way that $T \times \ln(timescale)$ – the effective barrier – might grow, is through increasing cooperativity.

There are several results in the mathematical literature proving this rigorously. Montanari and Semerjian have shown [5], for lattice systems with discrete variables, the following: Consider an equilibrium liquid, and within it a closed volume. We ask if the configuration on the surface is correlated with the one in the center (a point-to-set correlation). In other words, if we fix the configuration on the boundary of the volume, to what extent does the probability distribution of the configuration in the center change? This, of course, depends on the size of the enclosed region; there will be maximal radius r_{max} up to which the influence of the boundary in the center will be larger than a given threshold (see Figure 6.1). One can prove that r_{max} diverges if a timescale diverges: the only way that the system may generate infinite timescales, is by influences of boundaries that propagate through infinite distances.

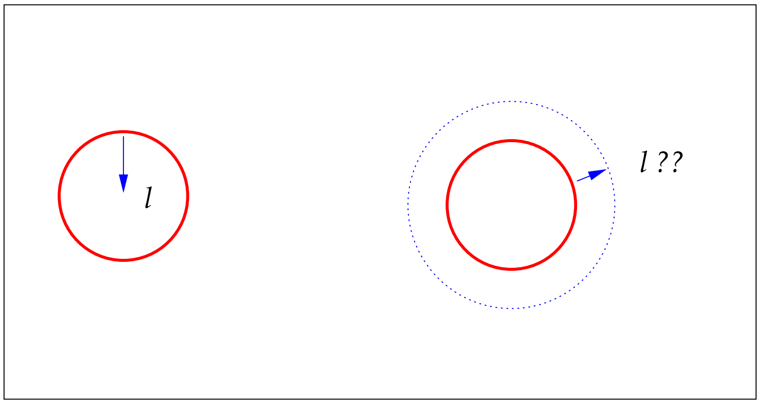

Figure 28: Fixing a boundary in an equilibrium configuration may constraint all the configuration inside, up to a radius which is, by definition, the correlation length

This result is essentially model-independent. The precise manner of this divergence is, on the contrary, dependent on the system considered. Building on the *Mosaic Picture* – a finite-dimensional incarnation of the mean-field Random First Order scenario (see next section), Biroli and Bouchaud [29] derived the precise dependence $r_{max}(T)$ within that scenario.

6.2 Reading the complexity and a coherence length from the average density profile $\bar{\rho}(x)$

Another divergent length that may be read directly from a time-averaged configuration is the following [30]: given an infinite system, we choose a block of size ℓ, and see how far we have to go in order to find – within a certain precision – a block with the same configuration of $\bar{\rho}(x)$ (see Figure 29) . This length is exponential of the volume ℓ^d in a truly random density configuration, but will be subexponential in a crystal, a quasicrystal, and more general objects with hidden forms of order. The distance of patch-repetition gives a direct measure of the complexity: if a patch repeats every $e^{\ell^d \Sigma}$ (for large ℓ), then Σ is the complexity and $\ell_o \sim \Sigma^{1/d}$ is a length. Note that $\Sigma \to 0$ implies a diverging length.

Let us make this more precise. First, we recognize that order concerns the time-averaged density, which is insensitive to fast excitations such as vibrations, particle-vacancy excitations, or isolated spin flips. This is true as well for crystals, which are only truly periodic at finite temperature once such excitations are averaged out. As was mentioned above, in a non-crystalline system, there is a multitude of possible average density profiles (the '*states*'). The logarithm of this number is the *complexity* Σ. We now consider a sample of very large size $\mathcal{V}$, and 'patches' of volume $V \ll \mathcal{V}$ belonging to it. The fact that the number of

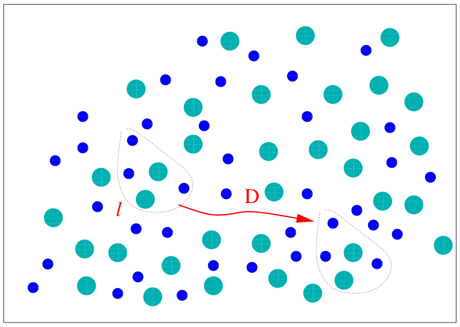

Figure 29: Looking for a patch that is the same, up to a certain precision, and allowing for rotations.

density profiles in a solid is subexponential implies that patches of configurations of volume V repeat more often than exponentially in V, so that their number $\mathcal{N}(V)$ obeys $\ln(\mathcal{N}(V)) < O(V)$. On the contrary, within the liquid phase, or in a defective (nonequilibrium) glass, the system breaks into uncorrelated regions, and we have, for large V, $\ln(\mathcal{N}(V)) \sim VK$, with K being the complexity per unit volume in the large V limit ($\lim_{V\to\infty} K^V$), with the statistics taken over patches belonging to the (much larger) volume $\mathcal{V}$.

Suppose we have a region of volume V with a configuration A. To what extent does A determine the configuration (say, B) of a neighboring region, also of size V? The typical number of repeats of configurations of volume V (or rather, its typical logarithm) is $\ln \mathcal{N}(A) \sim \ln \mathcal{N}(B) \sim -K_V$. Clearly, if A and B appeared independently, the repetition probability of the pair $A + B$ would be $\ln \mathcal{N}(A + B) = \ln \mathcal{N}(A) + \ln \mathcal{N}(B) \sim -2VK_V$, while in general it will be some number $\ln \mathcal{N}(A + B) \sim -VK_{2V}$. The patches will then not be independent if $K_{2V} < 2K_V$, or, in other words, if the entropy of patches of size V is subextensive. In that case, the knowledge of the configuration in a volume V gives information on that of an adjoining patch.

A system with subextensive patch entropy K will then have an infinite length - in this sense, it is *ordered*. Now, let us start from such an ordered system, and fracture it into pieces of typical size V_c. Let us now reassemble these pieces at random to form a new system of large size. In this case,we expect patches smaller than V_c will be found often, and those larger than V_c will be exponentially rare, as in Fig. 30. We are led then to the definition of the following types of length for an amorphous system:

- **Complexity length**: $\ell_1 = K^{-\frac{1}{d}}$, measures the frequency with which a *typical* patch repeats.
- **Crossover length**: If patches with volumes smaller than $V \ll V_c$ repeat often, while larger ones $V_c \ll V$ are exponentially rare, we define a crossover length as $\ell \sim V_c^{\frac{1}{d}}$.

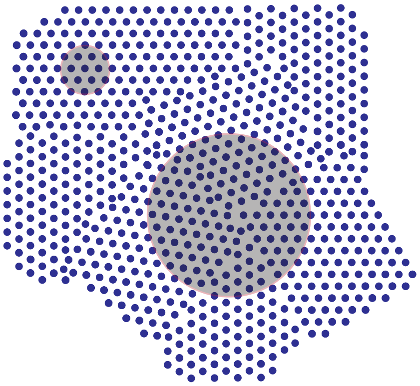

Figure 30: Two patterns, one smaller and one larger than the crystallite length. The small pattern will recur with high frequency, but the large one will be rare, because it requires recurrence of the crystallite boundaries within a patch, which is random event. Patches that are very large with respect to the crystallite volume occur with multiplicity exponential in the number of defects per volume, of the order of the number of microcrystallites contained.

These measures may be understood easily in the case of a microcrystalline system, as sketched in Figure 30.

Let us start from a density profile $\rho(\mathbf{r})$ that has averaged out – to the extent possible – all rapid degrees of freedom:

$$\rho(\mathbf{r}) = \lim_{\tau_\rho \to \infty} \frac{1}{\tau_\rho} \int_0^{\tau_\rho} dt\; \rho(\mathbf{r}, t) \qquad with \quad \rho(\mathbf{r}, t) \equiv \sum_a \delta\left(\mathbf{r} - \mathbf{r_a}(\mathbf{t})\right) \tag{6.1}$$

Our problem now is how to identify and count the resulting continuous profiles, a tricky question given that two continuous objects never really coincide. This situation is already familiar in a different context: it arises when we wish to determine the entropy of trajectories of a dynamical system, in which setting it has been well discussed both in principle and in practice. In the case of dynamical systems, we first discretize phase-space in cubes of size ϵ and time in intervals τ. We consider pieces of trajectories d time-intervals long, and define the Kolmogorov-Sinai entropy on the basis of the probability $P_\epsilon(i_1, ..., i_d)$ that at time τ the trajectory lies in the cube i_1, at time 2τ it lies in the cube i_2, ..., and at time $d\tau$ it lies in cube i_d, as [31]:

$$K = -\lim_{\tau\to 0}\lim_{\epsilon\to 0}\lim_{d\to\infty}\frac{1}{\tau d}\sum_{i_1,\dots,i_d} P_\epsilon(i_1,...,i_d)\ln P_\epsilon(i_1,...,i_d) \tag{6.2}$$

Note that d goes to infinity *before* ϵ and τ go to zero, a fact that shall turn out to be important.

In practice, one may proceed as proposed by Grassberger and Procaccia [32]: we consider a very long sequence of M times, and for every patch of length d labeled by its starting point i (Fig. 32) , we count the number of patches $n_i^{(d)}(\epsilon)$ that coincide with it – up to precision ϵ. The entropies are estimated by

$$K \sim -\lim_{\tau\to 0}\lim_{\epsilon\to 0}\lim_{d\to\infty}\frac{1}{\tau d}\left\{\frac{1}{M}\sum_i \ln[n_i^{(d)}]\right\} \tag{6.3}$$

This way of putting the problem is practical, because we may extrapolate the results from finite ϵ (for which we have many coincidences) to smaller ϵ. This is illustrated in Fig. 32 (a sketch).

The fact that an entropy may be defined and computed may be understood if we assume that [31] the dependence on ϵ (for small ϵ) is subdominant in d:

$$\frac{1}{M}\sum_i \ln[n_i^{(d)}] \sim e^{\tau dK}\epsilon^{\phi(q)} = e^{\tau dK+\phi\ \ln\epsilon} \tag{6.4}$$

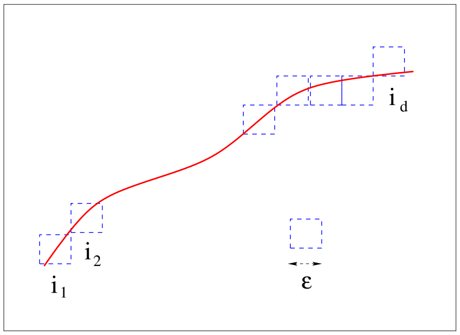

Figure 31: Counting trajectories in a discretized space and time.

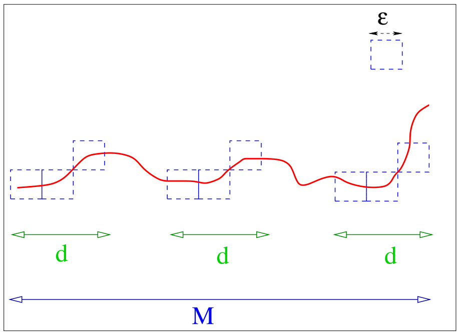

Figure 32: Discretization of trajectories. A sequence is repeated three times at this level of precision, but each one will be counted as distinct at a smaller ϵ.

We may easily adapt this procedure for counting density profiles. We consider average profiles $\rho(\mathbf{r})$ in D-dimensional space (Fig. 33). We discretize space in some manner, with a typical grid spacing Δ playing the role of the time-interval τ in a dynamic system, and we also discretize ρ in intervals of precision ϵ. Here again, we may proceed as follows. We consider a large sample containing M different patches $\mathbf{a_1}, ..., \mathbf{a_M}$ each of volume V. We look for the number of coincidences between a patch and all others, centered about any site and allowing for rotations. Two patches coincide if all the differences in the value of ρ between corresponding sites is smaller than ϵ. Denoting by $n_a^{(V)}(\epsilon)$ the number of patches that coincide in this way with the patch $\mathbf{a}$, we have:

$$K \sim - \lim_{\Delta \to 0} \lim_{\epsilon \to 0} \lim_{V \to \infty} \frac{1}{V} \left\{ \frac{1}{M} \sum_i \ln[n_a^{(V)}(\epsilon)] \right\} \tag{6.5}$$

Here and in what follows we shall for (conceptual, though not practical) simplicity keep the limits $\Delta \to 0$ and $\epsilon \to 0$, although they are probably unnecessary provided that one takes $V \to \infty$.

6.3 The point to set and the patch-repetition length should be infinite (i.e. $\Sigma = 0$), in an ideal glass.

As we have mentioned above, if there is a timescale that diverges – as there has to be, in a true solid — the point-to-set correlation length must diverge. On may argue in the same manner that the patch-repetition length should also diverge, or, equivalently, that the configurational entropy should vanish. Let us make a simple argument for the latter question: if we wish to concentrate on a truly solid phase, in which a density profile lasts forever, the number of different possible density profiles cannot be exponential in the volume, or, to be more precise, the complexity cannot be extensive. This is because if there

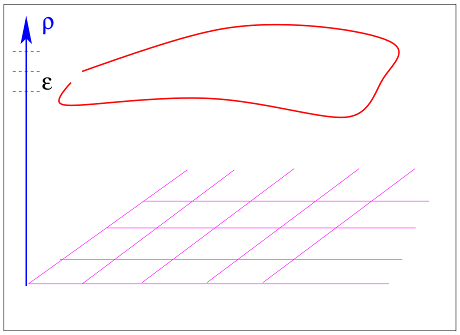

Figure 33: The analogue of a trajectory is the density profile. The density plays the role of the position in a dynamical system, and space the role of time.

are exponentially many metastable states in competition, a simple nucleation argument suggests that they cannot all have infinite lifetime; starting from any particular state, some other state will nucleate in finite time.

That multiplicity of barriers should help nucleation seems rather mysterious, because after all the system takes only one path, ignoring all others. In order to clarify this, consider a simple situation in a potential V as in Fig 34 in d dimensions.

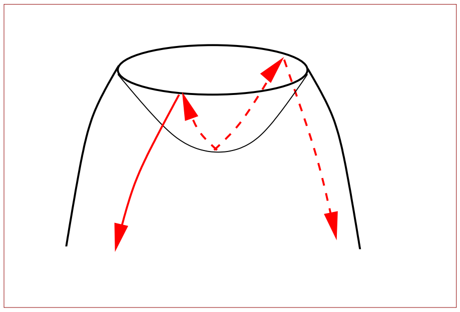

Figure 34: Many routes of escape lower the effective barrier.

Going to spherical coordinates, one can easily show that the system evolves in an effective one-dimensional potential $V(r) - T(d-1)\ln r$. The second term in this effective potential derives from the multiplicity of states: $(d-1)\ln r$ is the the logarithm of the volume of a shell of radius r. We thus conclude that the multiplicity of states has the effect of lowering the barrier against nucleation. In particular, with very small T, but with $T\,d = O(1)$ such that $V(r) - T(d-1)\ln r$ is monotonic decreasing, the particle will escape in finite time.

An intuitive way of understanding this result is as follows: At low temperatures, for every trajectory that escapes, there are many unsuccessful trials which just fall short of escaping, and return to the center. Although still extremely rare, trials reaching, say, 90% of the barrier height are exponentially more common than those which actually escape. Their frequency is, however, proportional to the surface of the 90% energy level: because of the separation of timescales, a barrier-crossing problem has to be thought of as a 'parallel' sampling of all possible paths.

The situation for one out of an exponential number of metastable states is very similar. The nucleation of a droplet of any state of volume V will cost a free energy at most proportional to the surface. However, there are $e^{V\Sigma(f)}$ options of different droplets of free energy density f, and they will be accessed with total frequency $\int df \; e^{V[\Sigma-\beta\Delta f]}$ (where Δf is the free-energy price paid to nucleate the new phase). These need not be grown simultaneously, but the many unsuccessful attempts in which a droplet grows and collapses will be helped by the multiplicity of possible states. The usual nucleation argument then tells us that if Δf is only a surface term, the volume term Σ will sooner or later overcome it, and the system will leave the original state if there is an extensive complexity $\Sigma(f) > 0$ of states with the same free energy density f.

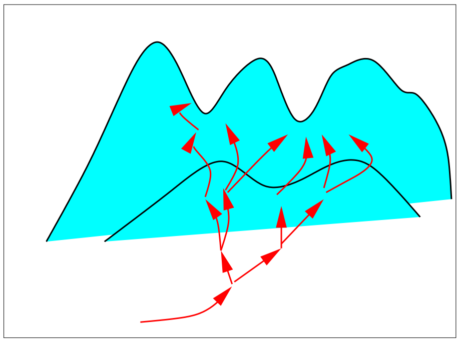

Figure 35: Entropic pressure to cross a mountain range with exponentially many passes

7 A brief overview of the Random First Order (mean-field) description of glasses

The Random First Order theory [27, 28] is perhaps the first theoretical construction that has some of the desirable features of a physical theory: it predicts, it constraints and (sometimes) it surprises. There is however, a long way to go...

Local mean-field.

Landau theory involves writing a (mean-field) free energy in terms of a space-dependent order parameter. This free energy functional contains an entropic term that takes into account all the rapid thermal fluctuations, and temperature enters only as a parameter. The order parameter itself represents the time-average of the microscopic variables, for example the magnetization is the time-average of the spins. For simple forms of order, although we know that the theory is not exact, and in general leads to the wrong exponents, it gives a satisfactory qualitative picture. Phase transitions appear when the minima of the free energy functional are a set of symmetry-breaking solutions related between one another by the symmetry operation.

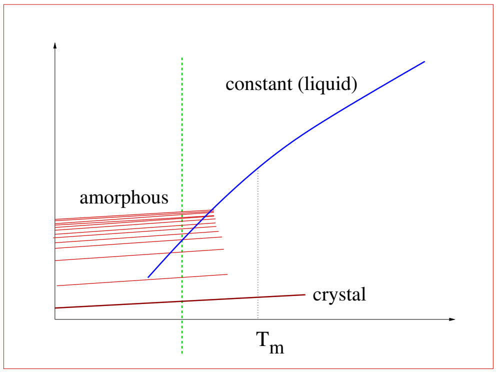

Figure 36: Complexity Σ versus free energy f.

In glassy systems, when we attempt such a mean-field approach, for example the Thouless-Anderson-Palmer (TAP [33]) approach to spin glasses, we find that at low temperatures the free energy functional has an exponential number of solutions, rather than two as a ferromagnet. For the case of a liquid, the analogue of the local magnetization is clearly our time-averaged density $\bar{\rho}(x)$, and an approach closely related to the TAP formalism is the so-called density functional theory. We are given a free energy functional in d-dimensional space [34]:

$$F[\rho(\mathbf{x})] = \int d^d\mathbf{x}\ \rho[\ln\rho(\mathbf{x}) - 1] - \frac{1}{2}\int d^d\mathbf{x}\ d^d\mathbf{x}'\ [\rho(\mathbf{x}) - \rho_o]C(\mathbf{x} - \mathbf{x}')[\rho(\mathbf{x}') - \rho_o] \tag{7.1}$$

Here $C(\mathbf{x} - \mathbf{x}', \rho_o)$ is the liquid direct correlation function at average density ρ_o computed within a some, such as the Percus-Yevick, approximation. For short range interactions, $C(x)$ is short ranged. We look for the 'local' free energy minima that satisfy:

$$\frac{\delta F[\rho(\mathbf{x})]}{\delta\mathbf{x}} = \ln\rho(\mathbf{x}) - \int d^d\mathbf{x}'\ C(\mathbf{x} - \mathbf{x}', \rho_o)[\rho(\mathbf{x}') - \rho_o] = 0 \tag{7.2}$$

At low average densities ρ_o, the spatially constant 'liquid' solution dominates. As the density increases, a periodic, 'crystalline' solution appears. What is interesting from the glassy point of view [35], is that in the high density regime, there appear also many non-periodic 'amorphous' solutions,each one a local minimum of (7.1) satisfying (7.2 (Figure 36). Each one of these is supposed to represent a metastable glassy state, as described in the previous section.

Now, as we have seen, the nucleation argument implies that as soon as we go beyond the mean-field approximation and add fluctuations to this picture, solutions with free-energy density $O(1)$ above the lowest are destabilized. We already know that if the crystal has lower free energy, everything is metastable with respect to it, and we have argued that we could ignore this. But we have also argued above, because of the entropic pressure for nucleation, in fact essentially all solutions schematized in Fig 36 are metastable: *even if we neglect the crystal*, they will nucleate one onto the other and only the lowest of the amorphous ones are truly stable – or only unstable with respect to crystal nucleation (which takes an altogether different scale).

We are now embarrassed: we have claimed that the amorphous solutions of (7.2) represent a glass, but in fact, since all but the very lowest are metastable: *they correspond to the liquid phase.* Worse of all, we have now *two different* representations of the liquid phase, one as a constant solution, and one as a set of metastable amorphous solutions.

A sum rule.

Let us be more precise: consider all amorphous solutions at temperature T, summed with the Boltzmann weight:

$$Z = \Sigma_{solutions}\quad e^{V[\Sigma(f) - \beta f]} \tag{7.3}$$

This sum is dominated by the saddle point, yielding:

$$\frac{d\Sigma}{df} = \frac{1}{T} \tag{7.4}$$

The solution of this equation is obtained with a tangent construction as in Figure 36 (right). For sufficiently high temperatures, the saddle-point free energy corresponds to solutions that are well above the lowest, so that the Boltzmann weight is dominated by an exponential number of metastable states with a finite lifetime. The question is now: who is the true representative of the supercooled liquid, these states or the constant solution? The answer is quite surprising: it turns out that within the models for which a full solution is available, there is a range of temperatures where *both results coincide*, so that the liquid is given *twice*, once by a constant profile and once as a packet of amorphous solutions. The latter give us the metastable states characteristics, such as one observes in that regime within the α scale. This sum rule has not been, to the best of my knowledge, discussed or tested within these approaches 'with space'.

The transition.

What happens within this approximation when we lower the temperature? Just looking at Figure 36 (right), we see that if the Σ versus f curve reaches zero with a finite gradient equal to, say, β_c, then below $T_K = 1/\beta_c$ the equilibrium distribution freezes in the lowest amorphous states. These are the ones that *are stable* (except for crystal nucleation), and they represent the true glass phase. Hence, we have obtained the glass transition as a condensation into a handful of low-lying density profiles, coming from a supercooled liquid made of similar, though metastable, states states representing the liquid. This is the Kauzmann scenario [36].

If, on the contrary, $\Sigma(f)$ reaches zero with infinite slope (a possibility advocated in [37]), we have that the glass transition temperature is zero. Note again that this will not make it more trivial, since the vanishing of entropy, even at $T = 0$, implies some form of order.

7.1 A model for which all this may be calculated

The mean-field with spatial dependence above is rather hard to solve exactly. It turns out that one may find a family of models that play the role for glasses analogous to the one played by the Curie-Weiss model for ferromagnets: all spatial dependence is gone, but we may solve the problem in every detail.

The first and simpler member of this family is a version of (Eq. (5.1), but with continuous spins satisfying a spherical constraint: $\sum_i s_i^2 = N$. Almost every feature of a liquid has been discarded, but the very abstract model that is left has a solution that is the paradigm of all mean-field models with space. The question that remains is whether the mean-field solution is just a metaphor of the true finite-dimensional situation, or it remains essentially true in this case.

7.2 The mosaic picture

The mosaic picture [39, 29, 28] is a phenomenological attempt to transpose what we know from mean-field models without space, or with a very primitive way of including space, to the true physical situation with non mean-field fluctuations. It postulates that in a supercooled liquid, the space is tiled by patches (mosaics) of pure states. The tiles reorganize constantly, and there is a competition between the price paid by the mismatching of tiles and the multiplicity of possibilities. This competition determines the size of the mosaics, which ultimately diverges at the transition.

7.3 Is mean-field circumstantial or essential?

Let us recap. We start out trying to explain why is it that a liquid may become essentially solid by changing by a few degrees the temperature, with barely any detectable change in its structure.

Clearly, the question whether there is a diverging timescale, or rather, whether the longest (α) timescale is as long as it could be – that is, equal to the time of nucleation of a crystal and not shorter – is one which we may ask without an approximation scheme in mind. However, in attempting an explanation we introduce notions such as metastable state, complexity, mosaic, effective temperature. We are limited in our analytic powers, and we resort to mean-field like approximations, or diagrammatic resumations [2] in order to obtain results.

The question we may ask is whether the concepts themselves are inherently mean-field in nature. Clearly, this is the case of finite free-energy density metastable states, and hence the complexity: once we step outside mean-field we need to specify a lifetime above which we call a state a state. Similarly, mosaics carrying a state label which has a meaning locally in space (rather than globally for the whole system) are also mean-field constructs, and so on. Even the definition of 'activated' processes is also related to an approximation, since at the end of the day they are defined as being non-analytic corrections in the mean-field parameter.

If it turned out that our mental constructs are inherently mean-fieldy, this could pose a problem in cases that are far removed from being exactly of that kind, but they could still provide the best (approximate) approach to thinking of the glass transition. This situation would not be without parallel in other branches of physics: for example superconductivity [40], superfluidity [41], elasticity [42] and rigidity [3] are in principle, but not in practice, undermined by activation.

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[2] I assimilate diagrammatic resumations with mean-field treatments because one can always find a model for which the resumation is exact, and can be thought of as some form of mean-field disordered system [38]

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