Glasses

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1 Introduction

At school we are taught that heat is motion, and that the constant molecular collisions are the explanation why a solid expands, and in general becomes more fluid as it gets hotter. When a system is cooled to sufficiently low temperatures, we thus expect it to collapse: molecules should become densely packed, leading to a form of matter that does not flow easily.

We are later surprised to learn that, in many cases, this 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 spending most of their time around positions disposed regularly, in a periodic arrangement. Crystallisation is the first inherently collective phenomenon we become aware of.

There are however exceptions to this miracle of crystallisation, 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 contrained manner, but with no evident spatial order emerging: we then say that we have formed a glass. This at first sight most unremarkable behaviour is, strangely enough, the one we understand the least.

The viscosity of a glass-former liquid (a substance able to avoid crystallisation) 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 happenning to the arrangement of the particles? Having avoided the obvious miracle of ordering, glass formers present us with the mystery of their sudden change of behaviour, leaving us to wonder if there is a hidden form organisation of matter, or an avoided "nearby" sharp transition, which we have yet to discover.

The problem in glasses, and why we consider it still open, is neither a question of fundamental interactions nor of practical calculations. On the fundamental side, we have plenty of models that exhibit a glass transition, and computers that can simulate by now very respectable times and sizes: they confirm that every microscopic element has already been put in. On the other hand, even if we do have limitations in our ability to compute things analytically, the situation is the same with liquids or dense gases, both subjects that are not usually described as a challenge. Our problem is then one of interpretation: we are trained to believe that for every striking phenomenon there should be a set of ideas that is simple, invokes entities that have a clear definition, lends itself to a mathematical formulation, and is able to surprise us with a new prediction. We are only beginning to envisage such

a theory.

2   Crystallisation

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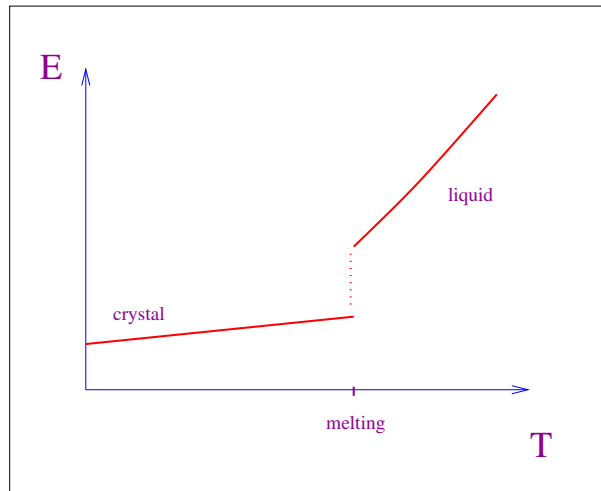

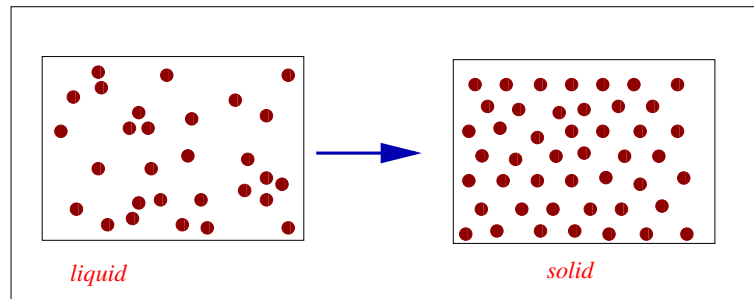Figure 1: Energy versus temperature – or volume versus 1/(pressure).

Figure 2: 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. 3). 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.

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
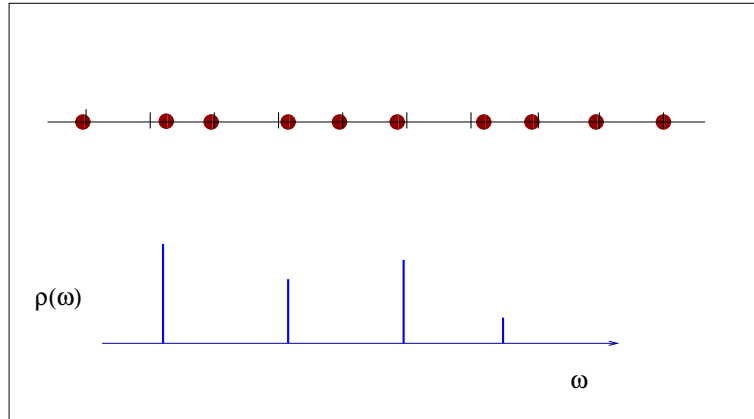
Figure 3: Periodicity, fluctuations and a Bragg peak.

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. 4)):

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

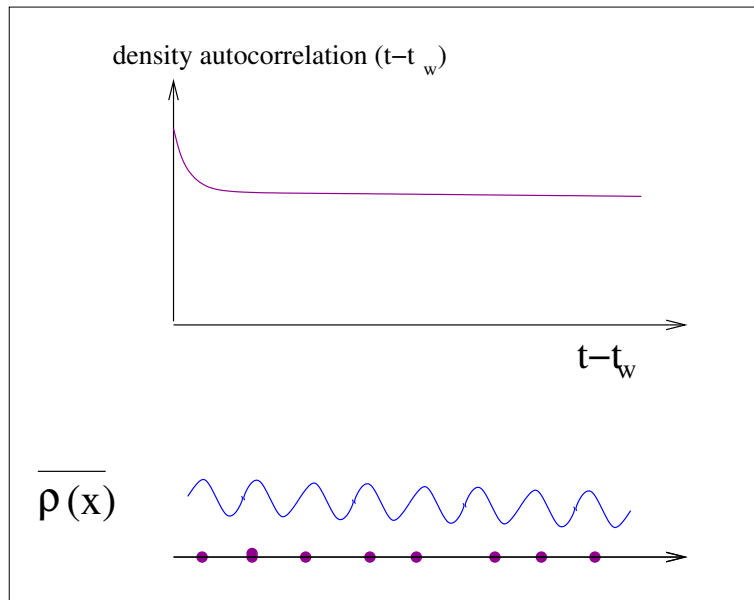has a non-constant limit as $\tau \to \infty$ (taken *after* the thermodynamic limit). Another

Figure 4: Autocorrelation function and time-averaged density $\bar{\rho}(x) = \tau^{-1} \int_0^\tau dt\ \rho(x,t)$.

useful way of conveying the same information, is to consider a two-time autocorrelation function, as in figure 4:

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

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 $C = V^{-1} \int dx \, [\bar{\rho}(x) - \rho_o]^2$

3   Collective nature of solidity: Arrhenius versus Super-Arrhenius

The popular, generic term *jamming* as applied to solidification [2] 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 [1, 29].

Consider first the case of soft particles (without a hard core) at finite temperatures, as in figure 5. 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 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. 6), 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.
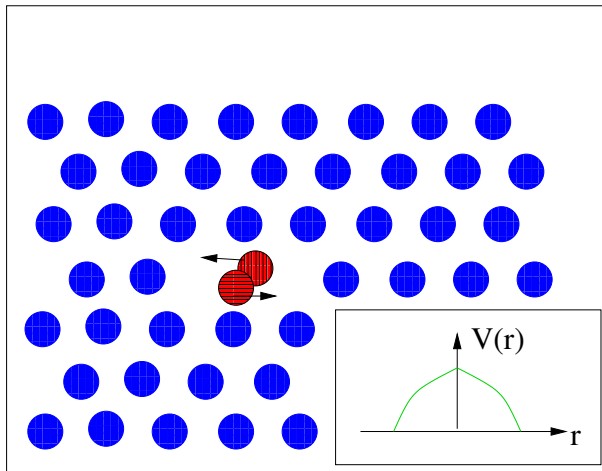

Figure 5: Permuting soft particles.

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
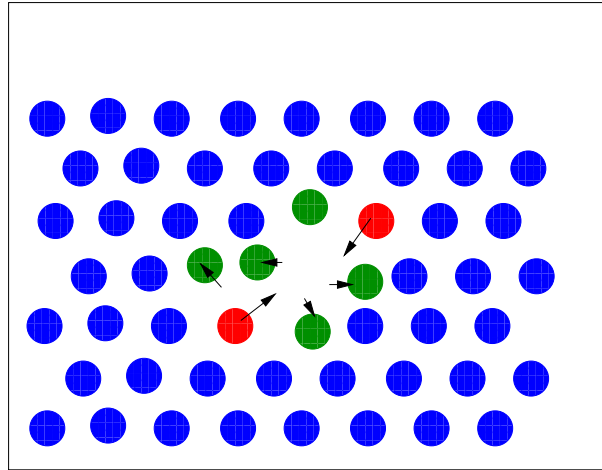
Figure 6: Permuting hard particles.

configuration of the positive magnetisation state to a typical configuration of the negative magnetisation state. It suffices (Fig. 7) 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. Going back to the soft-sphere
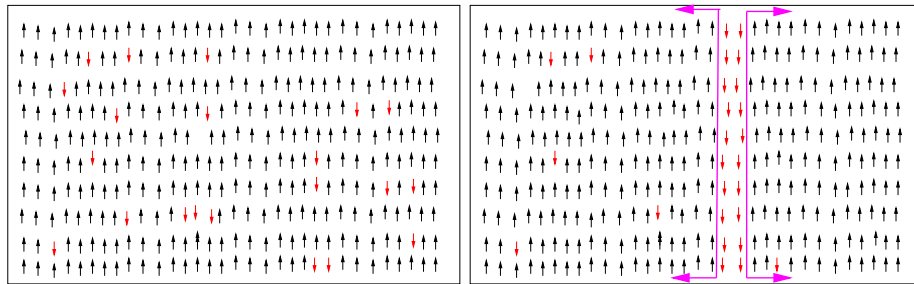

Figure 7: A collective, entropic, infinite barrier

crystal, a spontaneous deformation like that of Figure 8, 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.

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 9, where the spheres are assumed to be hard, or if they are not, the temperature is assumed to be zero.

A more subtle example of the same thing are the *kinetically constrained models* [3]. These are lattice models in which the particles have some forbidden moves. For example if their number of neighbours is higher than a certain number, the particle is immobile. The restrictions play, in this case, a role analogous as the hard constraints of Fig 9: as soon as they are partially lifted, infinite timescales and permanent modulations disappear.
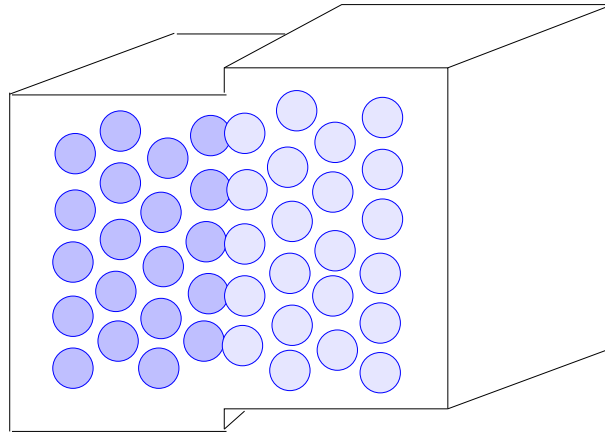
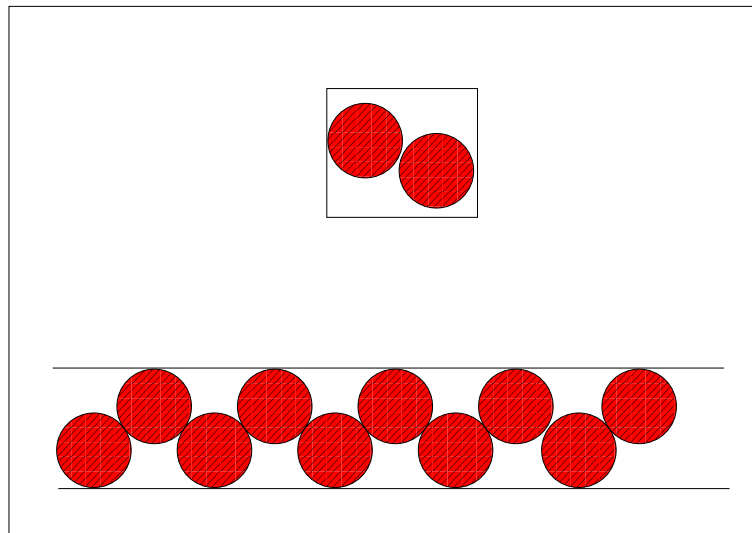Figure 8: A collective, energetic, infinite barrier.

Figure 9: Non-collective rigidity.

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 [4]: a system having a timescale that grows faster than exponentially *necessarily* has some equilibrium cooperativity length that diverges when the timescale diverges.

4   Avoiding crystallisation

Let us now turn to the situation when crystallisation does not happen. One can cool a liquid in such a way that the crystalline phase does not have the opportunity 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 crystallisor, and vice-versa.
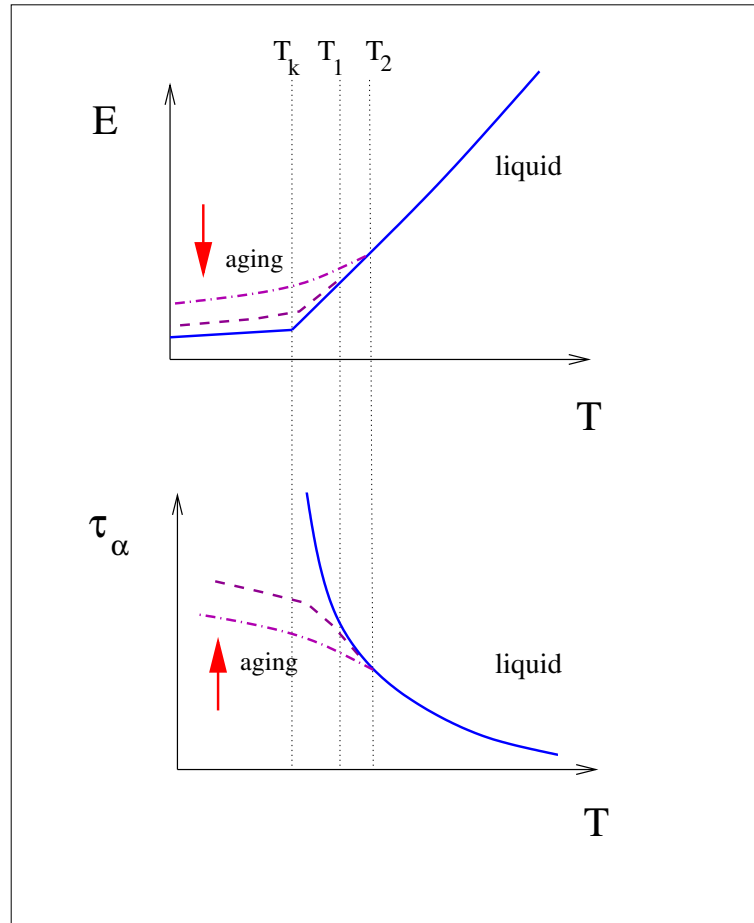

Figure 10: Different annealing speeds. The dashed lines indicate out of equilibrium situations, and are necessarily evolving in time. The full line is the result of infinitely slow cooling: energy has a nonanaliticity, and the relaxation timescale τ_α a divergence, if there is a true phase transition.

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.

Consider the cooling of a system as in Figure 10. For a fast cooling, the energy ceases to have its equilibrium value at a temperature T_2; for a slower process, this happens at a lower temperature T_1. We recognise the equilibrium energy vs. temperature curve as the envelope beyond which all slower annealings coincide. What we have said about energies, can be said about the viscosities, or the relaxation times τ_α. Consider an autocorrelation function, for example (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. The first drop to the plateau is analogous to the one observed in a crystal (Fig. 4), 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 11, the analogue of Fig. 4: 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 increases rapidly as the temperature is decreased, reflecting the increase in the viscosity (Fig. 12, 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. 12, left): in particular, the system needs time to become more viscous. This is the 'aging' phenomenon. Still, at a temperature T_1 (Fig. 12, top), eventually τ_α reaches its equilibrium value, although this may take so long that we only observe aging.
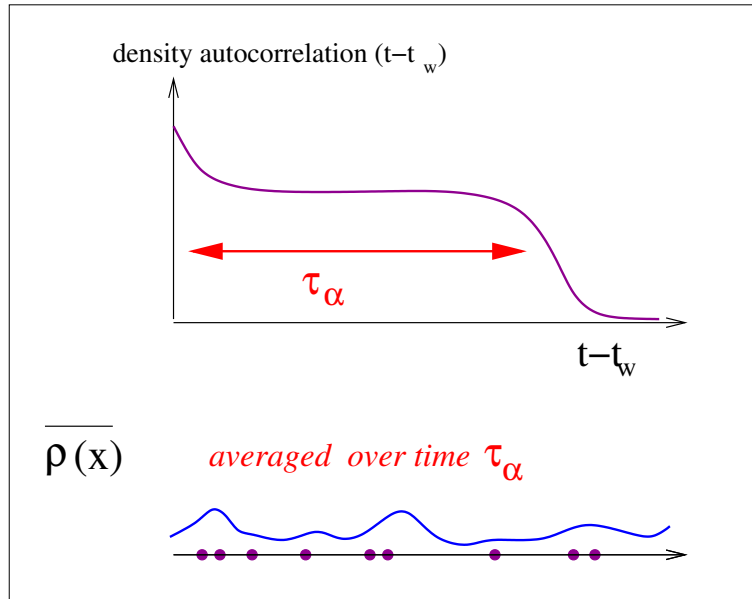
Figure 11: Density profile in an α scale.

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 period-

Figure 12: α time relaxation depends on temperature in equilibrium, and on the waiting time out of equilibrium.

icity. The discussion above about collective rigidity implies that if such states with permanent spatial modulation of density exist at finite temperature, th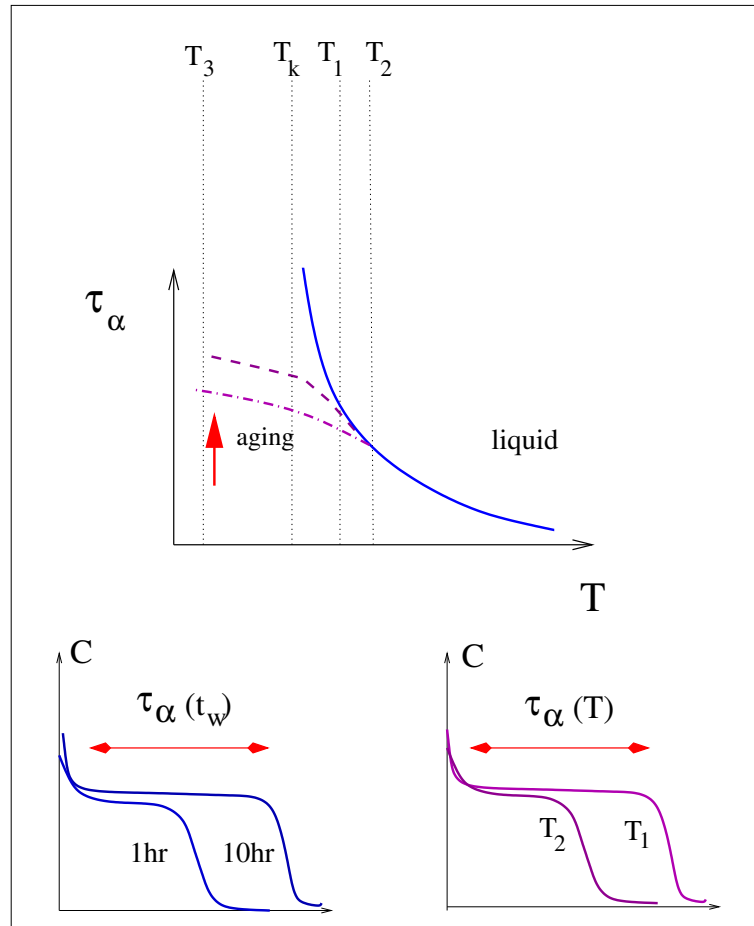en necessarily they involve a coherent behaviour of particles that only exists rigorously in the thermodynamic limit, and requires the divergence of some correlation length. This is even the case if $T_K = 0$, but τ_α grows faster than an Arrhenius law $\tau_\alpha \sim e^{b/T}$ [5].

Within an α scale, we can classify configurations as in Figure 13: 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 13, right). All the configurations that yield the same profile constitute a "state", and their number yields the entropy within the state. More importantly, the logarithm of the number of states (per unit volume) is by definition the *complexity* Σ [6].
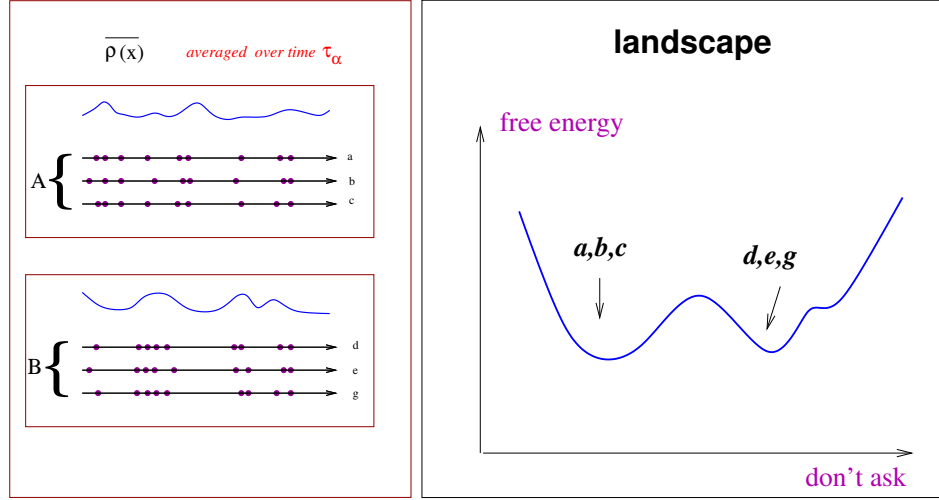
Figure 13: Free Energy Landscape picture.

5 Short digression: the nucleation argument

Two phases

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 to phases **a** and **b** with free energy densities $f_a > f_b$. 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:

$$\delta f(r) = \sigma r^{d-1} - (f_a - f_b)r^d \tag{3}$$

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

$$r^* = \frac{(d-1)\sigma}{d(f_a - f_b)} \quad \rightarrow \quad f(r^*) \propto \frac{\sigma^d}{(f_a - f_b)^{d-1}} \tag{4}$$

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 $(f_a - f_b) \to 0$ as $N \to \infty$.

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**.

Entropic drive

A situation that arises in supercooled liquids is that a system has many options of phases for nucleating. The question then is: does this multiplicity increase the probability of nucleation? The argument against says that it does not, since once one is nucleating one phase, in what does it help the fact that there was another option? Or, put in another way, how can the system know, when it is going somewhere, that there are other options out there?

To clarify the point, best is to do a small calculation. Consider a system at very low temperature, activating its escape out of the spherical crater $V(r)$ in Fig. 14. Starting from a spherical distribution concentrated at the bottom, the particle
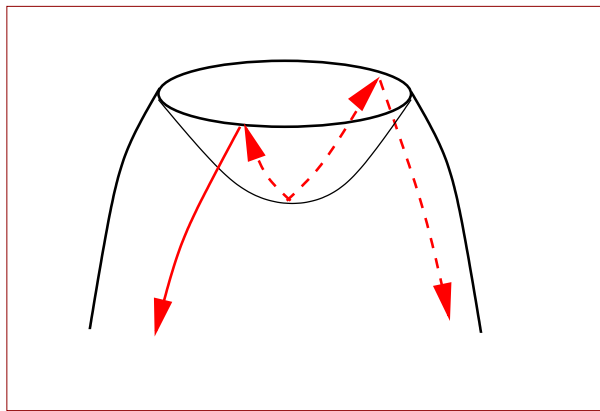

Figure 14: Two trajectories escaping a crater.

follows (say) a Langevin process, and the probability evolves via a Fokker-Planck equation.

$$\dot{P} = \nabla \left[T\nabla + \nabla V \right] P \tag{5}$$

Assuming the distribution was spherically symmetric at the start, it will remain so, and we may go to spherical coordinates:

$$\dot{P} = \frac{1}{r^{d-1}} \left[T\frac{d}{dr}\left(r^{d-1}\frac{dP}{dr} \right) + P\frac{d}{dr}\left(r^{d-1}\frac{dV}{dr} \right) + \frac{dV}{dr}\frac{dP}{dr} \right] \tag{6}$$

Putting $\tilde{P} \equiv r^{d-1}P$ we get the radial diffusion equation

$$\dot{\tilde{P}} = \left[T\frac{d^2}{dr^2} + \frac{d}{dr}\left(V(r) - T(d-1)\ln r \right) \right] \tilde{P} \tag{7}$$

This is the dynamics in a potential V corrected by precisely the entropy(the logarithm of the volume) $(d-1)\ln r$ of a shell of radius r. Indeed, the different possibilities do add, and help lowering the effective barrier. With hindsight, we can justify this even at very low temperatures by noting that before a passage is actually made, many attempts that barely failed have been done – and these take all possible paths. We shall use this in what follows.

6   Configurational entropy and metastale states

Local mean-field.

Landau theory consists of writing a 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 magnetisation 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.
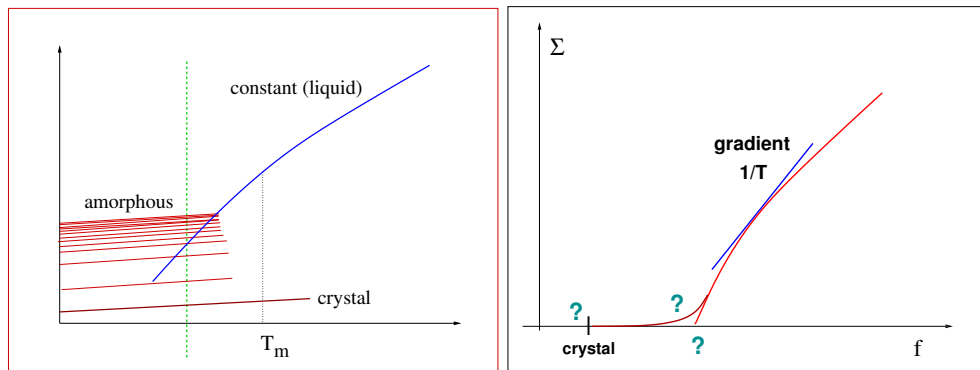

Figure 15: Complexity Σ versus free energy f.

In glassy systems, when we attempt such a mean-field approach, for example the Thouless-Anderson-Palmer (TAP [7]) approach to spin glasses, we find that at low temperatures the free energy functional now has an exponential number of solutions, rather than two as a ferromagnet. For the case of a liquid, the analogue of the local magnetisation is clearly our time-averaged density $\bar{\rho}(x)$, and a closely related approach is the so-called density functional theory. We are given a free energy functional in d-dimensional space [8]:

$$F[\rho(\mathbf{x})]$$
$$= \int d^d\mathbf{x} \, \rho[\ln \rho(\mathbf{x}) - 1] - \frac{1}{2} \int d^d\mathbf{x} \, d^d\mathbf{x}' \, [\rho(\mathbf{x}) - \rho_o]C(\mathbf{x} - \mathbf{x}')[\rho(\mathbf{x}') - \rho_o] \quad (8)$$

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:

$$\frac{\delta F[\rho(\mathbf{x})]}{\delta \mathbf{x}} = \ln \rho(\mathbf{x}) - \int d^d\mathbf{x}' \, C(\mathbf{x} - \mathbf{x}', \rho_o)[\rho(\mathbf{x}') - \rho_o] = 0 \quad (9)$$

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 [11], is that in the high density regime, there appear also many non-periodic "amorphous" solutions, as depicted schematically in Figure 15. Each one of these is supposed to represent a metastable glassy state, as described in the previous section. These states are local minima of (8) satisfying (9).

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 unstabilized. We already know that if the crystal has lower free energy, everything is metastable with respect to it, but we have argued that we could ignore this. Here we are saying that in fact essentially all solutions schematised in Fig 15 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 (9) 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:

$$Z = \Sigma_{solutions} \quad e^{V[\Sigma(f) - \beta f]} \tag{10}$$

This sum is dominated by the saddle point, yielding:

$$\frac{d\Sigma}{df} = \frac{1}{T} \tag{11}$$

The solution of this equation is obtained with a tangent construction as in Figure 15 (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 (more about these later), 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".

An objection may now arise: given that states that dominate in the liquid phase have the same free energy, how do we know that the free-energy barrier separating is not infinite? This is indeed a valid question, since our nucleation argument only showed that barriers are finite between states with a finite free-energy density difference. Here we have to invoke the entropic drive we mentioned above: just like in the escape from a crater, the system has many nucleation paths (roughly $e^{\Sigma r^3}$) leading to different density profiles, and this modifies accordingly the activation time, cfr. Eq. (7).

The transition.

What happens within this approximation when we lower the temperature? Just looking at Figure 15 (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 [9].

If, on the contrary, $\Sigma(f)$ reaches zero with infinite slope (a possibility advocated in [10], 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. We cannot exclude yet other possibilities, and the question marks on Fig 15 are there to express this.

Reading the complexity and a coherence length from $\bar{\rho}$

At any rate, it is interesting to note that as we find deeper and deeper amorphous states, we expect that a correlation (or coherence) length will grow. A concrete realisation of this length is the following [18]: 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 $\bar{\rho}$. This length is exponential in 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 $e^{\ell^d/\Sigma}$, then Σ is the complexity. Note that $\Sigma \to 0$ implies a diverging length.

7   Analogy with – and lessons from – chaotic systems

The equations (9) are analogous to the equations of motion of a dynamical system, with space playing the role of (multidimensional) time. A constant "liquid" solution is then analogous to a stationary point, a crystal to a periodic solution, and amorphous solutions correspond to chaotic orbits. This similarity between dynamical systems that are chaotic in time, and glassy systems that are chaotic in space, was pointed out many years ago by Ruelle [15]. As it stands, the analogy is not perfect, since we demand not only that the density profile be a solution of (9), but that in addition it be a deep minimum of (8). In order to make the analogy closer, we may consider a dynamical system, in which in addition we look for minimal solutions of the action

$$S = \int dt \; L(q, \dot{q}) \tag{12}$$

so that (12) plays the role of (8), and the (Lagrange) equations of motion

$$\frac{\delta S}{\delta q(t)} = 0 \tag{13}$$

play the role of (9). A realisation of this appeared in the theory of charge-density waves [16, 17], in particular in the Frenkel-Kontorova model, for which the local energy minima of the model are given by the trajectories of the 'standard map", which has both regular and chaotic orbits.

In order that the action plays the role of a free energy, we need that the it be bounded from below. This is not in general the case, and one needs for example that the potential be bounded from above. This should not worry us: in fact, one can take

Lagrange's equations (13) as the analogue of (9) and any functional $\mathcal{A} \equiv \int dt\, A(q, \dot{q})$ as the analogue of (8). One is then computing trajectories that are a large deviation of $\mathcal{A}$ [13].

What seems to happen [16, 17, 13] when we look for trajectories that are solution of the equations of motion of a *chaotic* system *and* minimise globally some quantity $(S, \mathcal{A})$ is that the trajectories that dominate are periodic or quasiperiodic, or have in general some form of regularity. In such systems, these trajectories are *not* in a regular region of phase-space, they are unstable and buried in the middle of the chaotic sea.

With this analogy in hand, we now consider again the solutions of (13), but classifying them according to (12) (when possible), or with any other functional $\mathcal{A}$, and the correspondence is:

- Stationary points correspond to the liquid solution.

- Periodic orbits in regular (unstable) regions correspond to a crystal.

- Chaotic trajectories correspond in general to the supercooled liquid phase.

- The glass state corresponds to chaotic solutions that minimise the chosen functional (S or $\mathcal{A}$). These may be *isolated, unstable* periodic or quasiperiodic orbits [13], or have a more subtle form of order [18].

  However, note that *even when they were periodic, these extremal orbits are very different from an orbit of a regular system*, in that they are in the middle of a sea of chaotic solutions, and are dynamically unstable in the sense that a perturbation in the boundaries will change the orbit dramatically.

  An orbit minimising $\mathcal{A}$ but with arbitrary boundary conditions in the coordinates will approach the unstable periodic one, shadow it for most of the time, and then go to the prescribed endpoint.

If we take this analogy seriously, the ideal glass state may well be spatially ordered (periodically, quasiperiodically, or in general with frequent motif repetition), but it would be of a different kind than a crystal or quasicrystal: the density profile would be surrounded by disordered solutions, just as the isolated periodic orbits which exist in purely chaotic systems, intermixed with the chaotic orbits as the rationals are with the reals.

8   Glasses in the real world: aging

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 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

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

slow "creep" motion [14]. Figure (16) 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. 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.
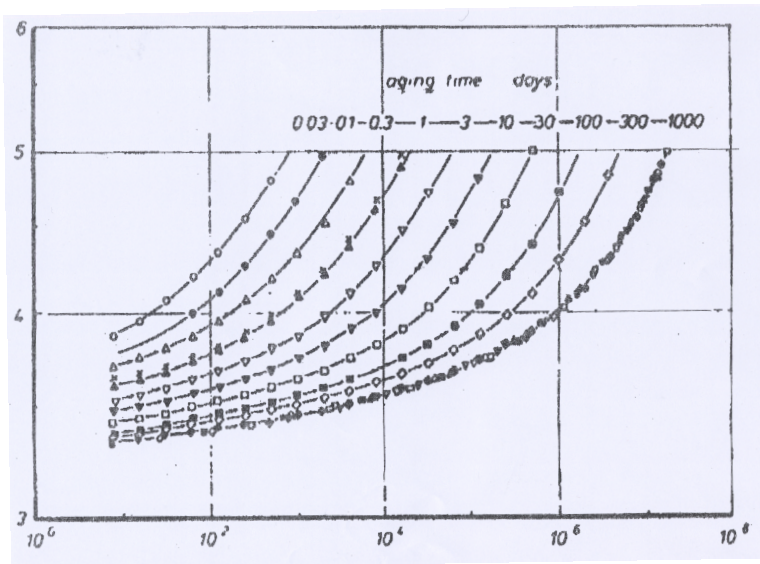

Figure 16: Struik's classical experiment.

These experiments concern a *response* to a field. Similar curves are obtained when one considers a *correlation*. In equilibrium, these to a related by the fluctuation-dissipation relation, which states that the response of an average value $\chi(t, t_w) = \frac{\delta}{\delta \langle X \rangle(t)}$ to a field that acts on Y from time t_w, is given in terms of the correlations as:

$$T\chi(t, t_w) = \langle X(t)Y(t) \rangle - \langle X(t)Y(t_w) \rangle = C(t, t) - C(t, t_w) \tag{14}$$

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

A very different thing happens when we consider [22] the correlation and response of an aging glass (Fig. 17). All points fall on a line, which is now composed of two apparently straight segments. 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 obtains 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 [22]. This way of approaching the effective temperature comes to us from the analytic solution of the aging dynamics of the Random First Order theory (see below), but it seems to be the same kind of idea proposed at a phenomenological level many years ago by Tool [24].
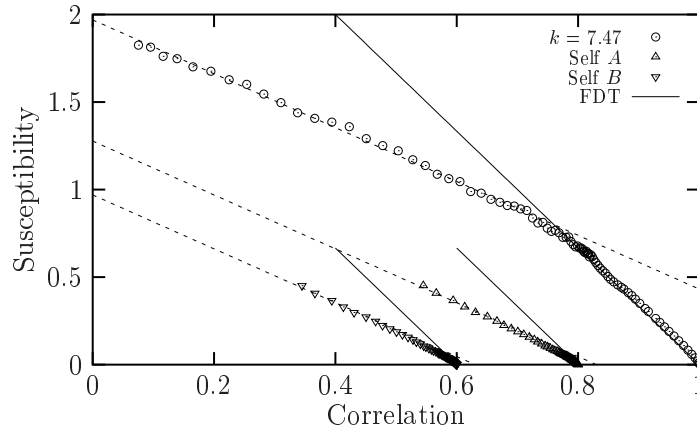
Figure 17: Effective temperatures: Response versus correlation for a binary mixture glass. The three lines correspond to density autocorrelations, and to diffusion versus mobility for each kind of particle. The autocorrelation curve shows the two-temperature behaviour, while the diffusion only the effective 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 [23].

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.*

9   Random First Order theory

Random First order theory is, or starts from, a family of models that are asserted to be for glasses what the Curie-Weiss (fully-connected) models are for a ferromagnet. First, comes the observation [31] that spin models with random disorder of the form

$$E = \sum_{ijk} J_{ijk} s_i s_j s_k \qquad (15)$$

with J_{ijk} random interactions, reproduce some of the phenomenological features of glasses. Models like this have a static transition like Derrida's Random Energy Model (REM) [35]. The mechanism is like the one described in Section 6, where the measure freezes at a certain T_K: this is indeed Kauzmann's scenario [9] for an ideal glass transition, with the random energy levels playing the role of the states.

Next, one can study the relaxational dynamics with this energy function. Remarkably, in the high temperature phase, the dynamics turn out to be exactly described by the Mode-Coupling (MCT) equations [33], which are a widely studied model of the first stages of approach to the glass transition from the liquid side. There is a Mode Coupling Transition at a certain $T_d > T_K$, known to be an artifact

of the approximation, and within the present perspective one can understand easily why the MCT transition has to go away in finite dimensions.

Between T_d and T_K the *sum rule* mentioned in Section 6 is strictly obeyed: the description of the liquid state may be made in terms of many metastable glassy states, or a single high-temperature one, and both descriptions strictly coincide thermodynamically.

You are not forced to restrict the dynamics to the high temperature phase. If you quench the models to low temperatures, it turns out that the system does not equilibrate: it "ages", just like true glasses [21]. When one analyses the properties of observables out of equilibrium, one discovers [22] that the slow fluctuations behave as if they were "thermalized" in an effective temperature T_{eff}. As mentioned above, "fictive temperatures" have been around since the 1940's [24], and it is likely that what one has discovered is precisely a non-phenomenological version of that. One may also study how the system responds to forces that do work on it: one finds the generic phenomenology of "shear thinning" of supercooled liquids, and in some cases you can explain the much more rare "shear thickening" of certain glasses.

One may go back and study the free energy landscape, defined by the TAP [7] equations, something that was not available in a pure mode coupling context. One recovers the main features (importance and location of saddles, marginality, etc) that where discussed many years ago by Goldstein [36] at a phenomenological level.

The next extension of the Random First Order scenario, is getting rid of the quenched disorder (the J_{ijk}), which are artificial and foreign to the problem. This has been done successfully, and by the 90's there was a plethora of fully connected models having the same properties as (15). As in all mean-field situations, we wish to "put some space" into the formalism, in this way getting a Landau theory which, although we know will not capture fully the essence of finite dimensions, it will at least give us a first hint. This was done by Mézard and Parisi [32] within the hypernetted chain and other approximations, and using the replica trick [30]. Approaching the mean-field-with-space approximation with a free-energy TAP [7] rather than a replica formalism, should finally give us a systematic and well controlled way to go back to a density functional formalism like the one described in section 6 – which we now recognise as a form of the "Random First Order" scenario.

As we have seen in section 6, the next big question is how to include fluctuations beyond mean-field, which will inevitably unstabilise metastable solutions, and re-express the liquid in terms of those. This has been argued phenomenologically in the so-called *mosaic picture* [37, 38], with a degree of success [39]. A line that has not, to the best of my knowledge, been followed by many is an analytical study of the constraints of a theory with space. How does one define rigorously the complexity of density profiles, in analogy with the Kolmogorov-Sinai entropy? Are the lowest free energy solutions regular, and what is the correlation length that defines them (see discussion in [18])?. What is the relation between configurations of a crystal with defects and the lowest amorphous ones, do they merge one into the other?

10   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 resummations[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 [26], superfluidity [27], elasticity [28] and rigidity [29] are in principle, but not in practice, undermined by activation.

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