Configurational entropy and the one-step RSB scenario in glasses

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Abstract. In this talk we discuss the possibility of constructing a fluctuation theory for structural glasses in the non-equilibrium aging state. After reviewing well known results in a toy model we discuss some of the key assumptions which support the validity of this theory, in particular the role of the configurational entropy and its relation to the effective temperature. Recent numerical results for mean-field finite-size glasses agree with this scenario.

I THE GLASS STATE

A theoretical understanding of the physical mechanisms behind the glass transition remains an open problem [1]. What is commonly understood as a glass (for instance, window glass) is a metastable phase, with free energy higher than that of the crystal obtained by the continuation of the liquid line below the melting transition temperature $T_M$. Such a glassy state may be experimentally achieved by cooling the liquid fast enough. Glasses share physical properties common to liquids and solids making difficult to decide in which phase (if any) they are. On the one hand, atom positions are randomly located in the glass much alike a liquid and apparently there is no long-range order. On the other hand, under compression glasses behave like a solid showing a very low mobility. Glasses constitute a state of matter in between liquids and solids, not completely classifiable as any of them, which show the following generic features:

• The viscosity anomaly. Glasses show a very rapid increase of the viscosity $\eta$ in a relatively narrow range of temperatures. For instance, in window glass the viscosity increases over nearly 20 orders of magnitude by changing the temperature in a range within a 10% of the value of the melting transition temperature. This increase is often well fitted by the Vogel-Tamman-Fulcher law, $\eta \sim \exp(\Delta/(T - T_0))$ where $T_0$ and $\Delta$ are free parameters. Fragile glasses
are those where \( T_0 \) is finite while for strong glasses \( T_0 \) is small (compared to \( T_M \)) and the viscosity displays Arrhenius behavior. By convention the glass transition temperature \( T_g \) is defined such that \( \eta(T_g) = 10^{13} \) Poise which for many liquids corresponds to a relaxation time of several minutes.

- **Two-step relaxation.** In the undercooled regime glasses show relaxation functions with a characteristic two-step form. Intermediate scattering functions show a first decay to a plateau (\( \beta \)-process) followed by a secondary and slower relaxation (\( \alpha \)-process) which defines the longest activated time. Although both processes are activated their characteristic times turn out to be well separated below the mode-coupling transition temperature.

- **Aging.** Suppose a glass is quenched to a temperature \( T_f \) below the glass transition temperature \( T_g \). If one were able to measure the viscosity as a function of time one would observe that it grows with time \( t \) according to the approximate law: \( \eta \sim \eta_0 + at \) where \( \eta_0 \) is the initial value reached soon after the quenching and \( a \) is a temperature dependent parameter \( a \sim \exp(-B/T_f) \) where \( B \) is an activation barrier. This growth can be extremely slow since \( a \) can be very small depending on the value of the ratio \( B/T_f \). The growth of the viscosity manifests itself as a dependence of intermediate scattering functions on the time of the measurement (usually called waiting time \( t_w \)) where the longest decorrelation time depends on the value of the viscosity \( \eta \) at \( t_w \). The dependence of the response of the system in the presence of an external perturbation, which softens as time goes by, is commonly referred as aging.

**II A SIMPLE SOLVABLE MODEL OF A GLASS**

Before describing the key assumptions to understand glasses it is convenient to consider an instructive example. One of the simplest solvable models which shows key features of structural glasses is the oscillator model with parallel dynamics introduced by one of us in [2]. This model contains some essential features of non-equilibrium thermodynamics applied to glassy systems. The model is defined by a set of non-interacting \( N \) harmonic oscillators with energy:

\[
E = \frac{K}{2} \sum_{i=1}^{N} x_i^2, \quad -\infty < x_i < \infty
\]

where \( K \) is a coupling constant. An effective interaction between oscillators is introduced through a parallel Monte Carlo dynamics characterized by small jumps \( x_i \rightarrow x'_i = x_i + \frac{r_i}{\sqrt{N}} \), \( 1 \leq i \leq N \) where the variables \( r_i \) are extracted from a Gaussian distribution \( P(r) = \frac{1}{\sqrt{2\pi\Delta^2}} \exp(-r^2/(2\Delta^2)) \). At each Monte Carlo step all oscillators are updated following the previous rule and the move is accepted according to the Metropolis algorithm with probability \( W(\Delta E) = \min[1, \exp(-\beta \Delta E)] \) where
\[ \Delta E = E(\{x'\}) - E(\{x\}). \] The smallness of the jumps in the variables \(x_i\) is required in order to give a finite change in the energy so the acceptance does not vanish in the \(N \to \infty\) limit.

This model (as well as some modifications proposed afterwards [3]) has been extensively studied and shows the following scenario. Because of the finiteness of the moves the ground state cannot be reached in a finite amount of time. Despite the absence interactions in the Hamiltonian, the Monte Carlo dynamics induces entropy barriers corresponding to the flat directions in energy space that the system hardly finds when the acceptance is low. A simple calculation at finite temperature shows activated behavior for the relaxation time \(\tau_{\text{relax}} \sim \exp(\frac{\Delta E}{kT})\) despite the absence of energy barriers in the model (the potential is a single well in \(N\) dimensions) making the dynamics of this model quite reminiscent (but simpler) of that of the Backgammon model [4].

The interesting dynamics in this model is found when studying the relaxation after quenching to zero temperature. In what follows we summarize the main findings for this case: [2]:

- **Slow decay of the energy:** The evolution equation for the energy is Markovian. This simplicity allows for an asymptotic large-time expansion. The energy asymptotically decays logarithmically \(E(t) \sim 1/\log(t)\) and the acceptance ratio decays faster \(A(t) \sim 1/(t \log(t))\).

- **The effective temperature.** The fluctuation-dissipation (FDT) ratio [5] can be exactly computed and depends only on the lowest time. At zero temperature one gets in the large \(s\) limit,

\[
T_{\text{eff}}(s) = \frac{\partial C(t, s)/\partial s}{G(t, s)} \to \frac{2E(s)}{N} \tag{2}
\]

i.e., equipartitioning is obeyed off-equilibrium allowing to define an effective temperature in terms of the FDT ratio.

- **The role of the configurational entropy.** The effective temperature previously obtained allows for a definition of a time dependent configurational entropy. At time \(t\) the number of configurations explored by the system is given by the surface of an \(N\)-dimensional sphere of radius \(R = E^{\frac{1}{2}}\) where \(E\) is the energy at time \(t\). The configurational entropy is then given by \(\Omega \sim R^{N-1} = E^{\frac{N-1}{2}}\) leading to an extensive configurational entropy \(S_c = \log(\Omega) = \frac{N}{2} \log(E)\) which satisfies, using (2), the canonical thermodynamic relations,

\[
\frac{\partial S_c}{\partial E} = \frac{N}{2E} = \frac{1}{T_{\text{eff}}} \tag{3}
\]

- **Heat-flow driven by the effective temperature.** Following [6] we can obtain the resulting heat-current by coupling two identical harmonic oscillator systems with a term \(\epsilon x_i y_i\) and measuring the energy flow to order \(\epsilon^2\). One gets [7],
\[ J(t) = \lim_{t \to s} \left( \frac{\partial Q(t, s)}{\partial t} - \frac{\partial Q(t, s)}{\partial s} \right) \] (4)

with \( Q(t, s) = \frac{1}{N} \sum_{i=1}^{N} x_i(t) y_i(s) \). If one of the two systems acts as a thermometer with characteristic frequency \( \omega \gg 1/t \) then the measured temperature coincides with the effective temperature and the Onsager relation is satisfied,

\[ J = L_{QQ} \nabla \left( \frac{1}{T} \right) \] (5)

with \( L_{QQ} \simeq 1/(t \log(t)) \) and \( \lambda \approx \log(t)/t \) for the thermal conductivity [7]. This example generalizes the Fourier law (and by extension, all linear relations between fluxes and forces initially derived in the vicinity equilibrium [8]) to the case where fluctuations are present around the off-equilibrium aging state.

### III THE CANONICAL THERMODYNAMIC SCENARIO FOR GLASSES

In the previous example we have seen how equipartitioning in the off-equilibrium state is satisfied when the acceptance rate is small. This can be easily understood: at zero temperature only configurations with the same or lower energy are accepted. Because the size of the moves \( \Delta \) is finite the system samples all the configurations of equal or lower energy with the same probability. Being their number a monotonically increasing function of the energy and because the energy cannot increase at \( T = 0 \) we conclude that the relevant fluctuations are those which explore the constant energy surface. After quenching to \( T = 0 \) and for long times, the probability to explore a different state with energy \( E < E^* = E(t) \) is uniform for all states with a given energy and given by,

\[ P \sim \Omega(E) = \exp(N S_c(E)) \sim \exp \left( \frac{N}{2} \log(E) \right) = \exp \left( \frac{N}{2} \log(E^*) + \frac{N}{2E^*}(E - E^*) \right) \propto \exp(\beta_{\text{eff}}(E - E^*)) \Theta(E^* - E) \] . (6)

Fluctuations are then described in terms of an effective temperature given by the configurational entropy as described in eq.(3). In the last years Th. M. Nieuwenhuizen, inspired by results for this oscillator model as well as for the \( p \)-spin spherical spin glass has proposed that a similar scenario could apply for generic glassy systems [9]. Although it is not clear in what conditions these results are valid for realistic systems the idea is suggestive enough to merit a more detailed investigation. A more elaborate picture along the same line has been presented by Franz and Virasoro who, using well known results from spin glasses and assuming a separation of timescales, have proposed that a modified version of the Onsager hypothesis
should put the configurational entropy into the game [10]. Although their analysis is based on some mean-field models it can be probably extended to realistic systems under some general mild assumptions.

The idea goes as follows. Imagine a glass that is obtained by quenching the liquid to a temperature $T_f$ below $T_g$. As already discussed, one of the main experimental facts regarding relaxational processes (for which mode-coupling theory gives a fairly good description in a large range of temperatures) is the emergence of well separated timescales (the $\alpha$ and $\beta$ processes). Dynamics can then be viewed as if the system were jumping among different metastable states or basins, each basin defined as the set of configurations explored by the system during a time $t^*$ of the order of the relaxation time itself. The definition of the precise value of $t^*$ does not matter as soon as the timescales separation becomes very strong, a condition which emphasizes the robustness of the present scenario. Fluctuations around a given configuration have two contributions: 1) Thermal fluctuations within a basin, i.e., typical fluctuations occurring on a timescale less than $t^*$ and driven by the temperature $T_f$ and 2) Activated jumps between different basins typically occurring for times larger than $t^*$. If basins with a given free energy are more or less similar (they are not too big or too small) then their typical lifetime is of order $t^*$ implying that the probability to visit them at subsequent times $t > t^*$ is simply proportional to their number $\exp(S_c(F))$ where $S_c(F)$ defines the configurational entropy,

$$P(F) \propto \Omega(F) = \exp\left(S_c(F)\right) = \exp\left(S_c(F^*) + \left(\frac{\partial S_c(F)}{\partial F}\right)_{F=F^*}(F - F^*)\right) + O(F - F^*)^2 \propto \exp\left(\left(\frac{\partial S_c(F)}{\partial F}\right)_{F=F^*}(F - F^*)\right)$$

(7)

where $F^*$ is the threshold value of the free energy, i.e., the free energy of the basins at time $t$. Note that the present threshold we define here is conceptually different from that defined in mean-field $p$-spin models since now $F^*$ is a time dependent quantity. From (7) we can infer that the probability distribution for basin-to-basin fluctuations is given by the configurational entropy $S_c(F)$ which satisfies the relation,

$$\frac{1}{T_{\text{eff}}} = \left(\frac{\partial S_c(F)}{\partial F}\right)_{F=F^*}$$

(8)

and defines an effective temperature for interbasin fluctuations. The essentials of the physics contained in eq.(7) is the same as that contained in eq.(6) for the oscillator model with the difference that in the oscillator model fluctuations above the threshold $E^*$ are forbidden because $T_f = 0$ while now fluctuations are dominated by jumps to basins with free energies around the threshold $F^*$ and differing by a finite amount. We must stress that eq.(7) gives a good description of the fluctuations when $T_f$ is much smaller than $T_{\text{eff}}$, otherwise thermal activation driven by $T_f$ will modify the simple entropic contribution entering in (7). Biroli and Kurchan [11] have recently addressed the notion of configurational entropy in the framework
of the Gaveau-Schulmann formalism showing that $S_c$ is a time-dependent quantity. This is in complete agreement with the present scenario: basins with free energies $F$ above the time-dependent threshold $F^*$ are completely washed out as time goes leading to the appearance of a time-dependent cutoff $S_c(F) = S_c(F^* \quad F < F^* \quad S_c(F) = -\infty \quad F > F^*$ with $S_c(F)$ a monotonous increasing function of $F$. This keeps the full meaning of (8).

The conclusion of this discussion is that, as soon as the formula (7) gives a faithful description of basin-to-basin fluctuations occurring beyond a timescale $t^*$ (which changes itself as a function of time), then it is possible to write down a dynamical free energy which controls both fast and slow processes:

$$F_{dyn} = F_{basin} - T_{eff} S_c(F).$$

Keeping in mind that both terms contribute to physically different processes occurring in different (well separated) timescales this corresponds to the formula obtained in the framework of $p$-spin models. We must stress that in models where free energy basins are not uniformly sampled the simple results (8,9) cannot hold. Examples of such a class of systems are generic coarsening models into a finite number of absorbing states [12].

This formula has been recently checked in finite-size mean-field models for glasses where activated processes occur with finite probability [13,14]. One can evidenciate the presence of an activated regime different from that observed in the $N \to \infty$ where ergodicity breaks below the threshold. To verify the above scenario is necessary to estimate the configurational entropy. A good recipe to do that is to partition the phase space into basins by counting the number of energy minima. These are also called inherent structures and were proposed by Stillinger and Weber as a powerful tool to investigate the landscape energy surface of liquids [15]. The above scenario has been verified in the ROM model [16] which is a faithful microscopic realization of the random energy model introduced by Derrida [17]. In this model, $F_{basin} \approx E_{basin}$ because the intra-basin entropy is very small ($q_{EA} \sim 0.96$ for the metastable states) and the effective temperature can then be obtained using eq. (8) with $S_c(F) \approx S_c(E)$. The results for the configurational entropy and the effective temperature (obtained through FDT plots) are shown in figure (1), panels (a) and (b) respectively. The agreement between equation (8) and the numerics is excellent. Recent results [18] in the case of Lennard-Jones glasses, where the contribution $F_{basin}$ turns out to be important, also confirm these results.

The simplicity of the hypothesis presented here suggests that some generic and simple principles are behind the statistics of fluctuations around the aging state for structural glasses. Surely we will see fast developments in the forthcoming years which will show to what extent these hypothesis are correct.

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FIGURE 1. (a) Configurational entropy as a function of energy. The data are temperatures $T = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0. The line is the quadratic best-fit from Ref. [13]. (b) FDT plot for the ROM model (Integrated response function as a function of IS correlation function). The dash line has slope $\beta_f = 5.0$, while the full lines is the prediction $S_c(E)$ from Ref. [14]: $T_{\text{eff}}(2^{11}) \approx 0.694$, $T_{\text{eff}}(2^{16}) \approx 0.634$ and $T_{\text{eff}}(2^{19}) \approx 0.608$. The dot-dashed line is $\beta_{\text{eff}}$ for $t_w = 2^{11}$ drawn for comparison.

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