A real-space description of the glass transition based on heterogeneities and entropy barriers

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An alternative scenario for the glass transition based on the cooperative nature of nucleation processes and the role of entropic effects is presented. The new ingredient is to relate the dissipation during the relaxation process to the release of strain energy driven by the nucleation of progressively larger cooperative spatial regions. Using an equiprobability hypothesis for the transition between different metastable configurations, we obtain a relation between the free energy dissipation rate and the size of the largest cooperative regions. This leads to a new phenomenological relation between the largest relaxation time in the supercooled liquid phase and the effective temperature. This differs from the classical Adam-Gibbs relation in that it predicts no divergence of the primary relaxation time at the Kauzmann temperature but a crossover from fragile to strong behavior.

Introduction. After many decades of efforts, a complete and unifying description of the glass transition problem is still not available. The standard approaches to the glass transition have been largely based on hydrodynamic (such as MCT\textsuperscript{1}) or thermodynamic entropic theories like that proposed by Adam, Gibbs and Di Marzio (hereafter referred to as AGM) nearly 50 years ago.\textsuperscript{2} Surprisingly, still nowadays the ideal AGM theory remains not accepted nor disproved. A salient outcome of the AGM theory is the prediction of the existence of a second-order phase transition driven by the collapse of the configurational entropy (also called complexity). It is known that an unambiguous definition of the complexity is possible only in the framework of mean-field theories where phase space splits into ergodic components of infinite lifetime. Recent approaches to the glass transition problem from the perspective of disordered systems have, to a large extent, validated this mean-field scenario.\textsuperscript{3} Nevertheless, a complete understanding of the glass transition must go beyond mean field by including nucleation processes into any valuable theory. This poses the question about how the mean-field picture for the glass transition is modified in the presence of real-space effects. In this paper we propose an alternative scenario for the glass transition where spatial effects such as heterogeneities play a crucial role in the theoretical description of the glassy state being also the necessary ingredient to validate and reinforce some aspects of entropic mean-field approaches.

We present a phenomenological real-space description of nucleation processes of cooperative nature in the spirit of the AGM theory. This should complement other approaches such as mode-coupling theory.\textsuperscript{4} The main outcome of our analysis is that the standard relation between the relaxation time and the complexity originally proposed in the AGM theory is modified and the primary relaxation time does not depend directly on the complexity but on the so called effective temperature (to be defined later). This predicts a crossover from fragile to strong behavior and a saturation (and not a divergence) of the effective barrier or primary relaxation time at the Kauzmann temperature.

A phenomenological description of heterogeneities in glasses. One of the most intriguing features in glasses is the existence of heterogeneous structures.\textsuperscript{5} Experimentally these manifest as some set of atoms which have a dynamics manifestly slow when compared to the rest. Although experiments or numerical simulations in this field are very recent, heterogeneities are a direct manifestation of the cooperative nature of nucleation processes.\textsuperscript{6} The basic idea in our approach is to assume that nucleation processes take place everywhere inside the glass when some structures of size $s$ are built up by a cooperative mechanism. To build these structures the $s$ atoms of the cooperative region must coherently move to occupy certain positions which enable that region to release some strain energy. Each of these moves constitutes an elementary activated process, for instance, the exchange between two neighboring particles. Therefore, the heterogeneities observed in the experiments are transient frozen structures which eventually nucleate in time scales larger than the observational time. When a droplet of liquid nucleates it changes to a new locally disordered structure. The local structure of the glass is always that of a liquid and there is no coarsening of a given pattern whatsoever.

In our scenario the time to activate a region of size $s$ is,

$$\frac{\tau(s)}{\tau_0} \propto \left(\frac{\tau^*}{\tau_0}\right)^s = \exp\left(\frac{B_s}{T}\right)$$

(1)

where $\tau^* = \tau_0 \exp(B/T)$ is the activated time to activate one atom, $\tau_0$ being a microscopic time and $B$ the corresponding energy barrier. Let us introduce the quantity $n_s(t)$ as the number of cooperative regions (we will refer to them as domains) of size $s$ at time $t$. Experimentally it is well known that time correlations in the glass state are stretched but decay faster than any power law. According to (1) this means that the distribution $n_s$ must
abruptly fall down beyond a cutoff size \( s^* \) in such a way that long time nucleations occur with a negligible probability. Consequently, \( n_s(t) \) for \( s > s^* \) must be nearly zero. This approach is similar in spirit to the mosaic theory developed by Xin and Wolynes \(^4\) who also considered the existence of a cutoff size \( s^* \). The existence of this cutoff is tightly related to the cooperative character of the dynamics itself eq. \((\ref{eq:1})\) and can be illustrated within a simple domain aggregation model. We note that the model we present here is oversimplified, our aim being only to stress the relation between cooperativeness and the presence of a cutoff size. Let us imagine a liquid that is quenched to a temperature \( T_f \) where equilibration cannot be achieved within the time scale of the experiment. Let us think about the molecules inside the glass as grouped into non-overlapping domains of different sizes \( s \). After nucleating, domains of a given size \( s \) destabilize breaking into smaller domains. In the simplest scenario the aggregation and breaking of domains occurs inside a bath of particles. We assume that, after nucleation of a domain of size \( s \), domains can gain or lose one particle with respective probabilities \( g_s, l_s \) with \( g_s + l_s = p_s \). \( p_s \) is the probability that a nucleation occurs which we take proportional to \( 1/\tau(s) \) where \( \tau(s) \) is given by eq. \((\ref{eq:1})\) with \( B = r_0 = 1 \) and \( T = T_f \). For sake of simplicity we take \( g_s = gp_s, l_s = lp_s \) with \( g + l = 1 \). Consequently, the balance equations involve the following “chemical reactions”: \( D_s \rightarrow D_{s-1} + p \) with rate \( l_s \) and \( D_s + p \rightarrow D_{s+1} \) with rate \( g_s \), where \( D_s \) denotes a domain of size \( s \) and \( p \) a single particle of the bath. The balance equations read \((s \geq 2)\),

\[
\frac{dn_s(t)}{dt} = l_{s+1}n_{s+1}(t) + g_{s-1}n_{s-1}(t) - p_sn_s(t) \quad . \quad \tag{2}
\]

This set of equations must be supplemented with the dynamical equation for the “bath” of particles which is deduced from mass conservation \( \sum_{s=1}^{\infty} sn_s(t) = \text{const.} \) In this simple model there are three parameters \( g, l \) and \( \beta = 1/T_f \) entering the equations. By appropriately rescaling the time only two of them \((\beta, g/l)\) are free parameters. Although all possible values of \( g, l \) are possible the interesting regime is obtained for \( g/l \) small. Physically this means that, during the nucleation, domains have more probability to loose particles than to capture them. This is a very reasonable assumption: just before the nucleation takes place the domain is in an unstable configuration and loosing a particle seems a more probable event. We numerically solved \((\ref{eq:2})\) by numerically integrating them using a second order Euler algorithm. In the left panel of figure 1 we show the time evolution for \( n_s(t) \). At any time it displays a well defined time dependent cutoff value \( s^*(t) \) above which the \( n_s(t) \) drops to zero very fast. From the knowledge of \( n_s(t) \), assuming independent exponential relaxations for the different domains, we can also obtain the two-time correlation function,

\[
C(t, t') = \sum_{s \geq 1} sn_s(t') \exp(-t/\tau(s)) \quad . \quad \tag{3}
\]

where \( t \) denotes the time after the quenching and \( \tau(s) \) is given by expression \((\ref{eq:1})\). The correlations can be excellently fitted by a stretched exponential law with a \( t \)-dependent stretching exponent \( \beta_s, C_s(t') = \exp(-t'/\tau(t)\beta_s(t)) \). In the right panel of figure 1 we show the corresponding correlation functions as well as the best fits. Note that the average relaxation time \( \tau_{av} = \int_0^\infty dt'C_s(t') \) does not necessarily scale like \( t \). A careful examination of the time dependence of the distribution \( n_s(t) \), reveals that it scales like \( n_s(t) = (1/s^*)\tilde{n}(s/s^*) \) with \( t = \exp(\beta s^*) \), \( s^* \) being the time dependent cutoff size. Consequently, relaxation to equilibrium is driven by the growth of the largest domain of size \( s^*(t) \). When a glass is relaxing to equilibrium, the average release of energy to the thermal bath is done by nucleation of the largest domains of size \( s^* \), meaning that the advance motion of the front of \( n_s(t) \) located at \( s = s^* \) is the leading source of energy dissipation. Nucleation processes involving regions of size smaller than \( s^* \) always occur but do not yield a net energy current flow to the thermal bath. Metastable equilibrium is reached when the cutoff size \( s^* \) saturates to a finite value and the net energy flow between the glass and the bath vanishes.

![figure 1](image-url)

FIG. 1. \( n_s(t) \) and \( C(t, t + t') \) for different times \( t = 10^{14} - 10^{33} \) (in dimensional units) for the numerical solution of model \((\ref{eq:2})\) with \( l = 8, g = 1 \) and \( \beta = 2.2 \). The parameter \( \tau(t) \) and the stretching exponent are very well fitted by \( \tau(t) = 2.2t^{0.35}, \beta(t) = 0.34 + 0.45t^{-0.06} \).

Let us now focus our attention in the energy dissipation rate in this relaxation process. This is given by typical free energy variation of the relaxing domains of size \( s^*(t) \) multiplied by their number \( N_{s^*}(t) = \frac{V(t)}{V}n_{s^*}(t) = (V/s^*)\tilde{n}(1) \), divided by their typical nucleation time \( t = \exp(B\beta s^*) \).
\[ \frac{1}{V} \frac{\partial F}{\partial t} \sim \frac{\Delta F^* N_*(t)}{V t} \sim \frac{\Delta F^*}{s^* t}. \]  

(4)

Now, the crucial difference between nucleation processes in glasses and other systems is that nucleation in a glass occurs between metastable liquid drops. The typical release of energy \( \Delta F^* \) released after nucleating a metastable liquid drop of size \( s^* \) into another drop does not scale with its surface (like in coarsening systems) nor its volume (like in standard liquid-solid nucleations) but is finite and independent of \( s^* \) yielding,

\[ \frac{1}{V} \frac{\partial F}{\partial t} \sim -\frac{\Delta F}{s^* t}. \]  

(5)

where \( \Delta F \) is the average free energy change. The growth of \( s^* \) as a function of time is \( s^*(t) \sim T \log(t) \) and stops when \( n_s(t = t_{eq}) \) reaches the stationary distribution. In principle the value of the equilibration time \( t_{eq} \) depends on the particular model under consideration. From a microscopic theory this time can be deduced only from the hydrodynamic equations. We see below how we can circumvent the hydrodynamic description by relating the relaxation time of the supercooled liquid to the complexity.

The fluctuation formula. One of the main problems in the theory of glasses is to define the complexity \( S_c \). In the original AGM theory, \( S_c \) was defined as the configurational part of the entropy obtained by disregarding the kinetic part of the energy. Here we consider a different dynamical definition adapted from concepts developed in spin-glass theory. The key concept in our definition is the concept of conformation or basin: a basin includes those configurations which do not release an extensive (proportional to \( s \)) strain energy to the thermal bath after nucleating a region of size \( s \). Let us consider a relaxing liquid quenched to \( T_f \). We define \( S_c(t, F) \) as the logarithm of the total number of basins with free energy \( F \) which can release strain energy to the thermal bath after nucleating regions of size \( s^* \) at time \( t \). In other words, because \( s^* \) is the maximum size of nucleating regions at time \( t \), \( S_c(t, F) \) counts the number of still not visited conformations at time \( t \). In this scenario regions of size \( s \) which have already nucleated once (i.e., \( s < s^* \)) have already released their strain energy while regions which have not yet nucleated (\( s > s^* \)) still contain some strain energy. Nucleations which do not lead to a new release of strain energy do not yield new conformations.

Each of these conformations at time \( t \) may contain different possible configurations \( C \) which do not contribute to the complexity but contribute to the free energy of the configuration \( B \),

\[ F_B(t, T_f) = -T_f \log(\sum_{C \in B} \exp(-E(C)/T_f)) \]  

where time dependent expectation values of a given observable \( A_B(t, T_f) \) are defined as follows: \( A_B(t, T_f) = \sum_{C \in B} A(C) \exp\left(-\frac{(E(C) - F_B(t, T_f))}{T_f}\right) \).

The liquid character of the glass phase implies that basins with identical free energy \( F_B(t, T_f) \) have reproducible physical properties (i.e., independent of \( B \)). Note that the free energy and the expectation value of any observable \( A \) evaluated at a given conformation \( B \) depend on both \( T_f \) and the quenching time \( t \). The dependence on \( t \) directly appears through the set of configurations \( C \) contained in \( B \). In particular, for large enough times, basins with very high free energy only contain configurations which have been explored several times, hence they do not contribute to the complexity. Contrarily, conformations with very low free energy contain configurations which have still not been reached, hence they contribute to the complexity. This leads to a dynamical complexity \( S_c(t, F) \) which has \( t \)-dependent cutoff value \( F^* \) such that the number of conformations or basins with \( F_B(t, T_f) > F^* \) vanishes. Moreover, the complexity is a monotonous increasing function of the free energy since the number of possible conformations which decrease the energy \( N_*(t) = (V/s^*)\bar{n}(1) \) is larger when nucleating regions are smaller. In the asymptotic large \( t \) limit it takes the form,

\[ S_c(t, F < F^*) = \hat{S}_c(F, T_f); \quad S_c(t, F > F^*) \to -\infty \]  

(6)

Now we can introduce the fluctuation formula and see how the present scenario substantially differs from the classical one by AGM. At time \( t \) after the quenching, nucleation processes inside the glass occur between cooperative regions with a disordered local structure and no characteristic pattern grows with time. This amounts to say that nucleations must be entropically driven meaning that some sort of equiprobability hypothesis for visiting conformations holds. While this is an assumption, its validity must be founded on principles similar to those which justify the equiprobability hypothesis in Boltzmann-Gibbs equilibrium theory. Therefore, the probability to jump from the free energy level \( F^* \) to another conformation with free energy \( F \) is always proportional to the number of configurations with final free energy \( F \),

\[ \mathcal{W}_{F^* \to F} \propto \frac{\Omega(F)}{\Omega(F^*)} \propto \exp(\hat{S}_c(F, T_f) - \hat{S}_c(F^*, T_f)) \quad \text{(7)} \]

Substituting (3) in (6) and denoting \( \delta F = F - F^* \) we obtain for the transition probability,

\[ \mathcal{W}_{\delta F} \propto \exp\left(\beta_{\text{eff}}(F^*) \delta F\right) \theta(-\delta F) \]  

(8)

where we have defined the effective temperature \( T_{\text{eff}}(F^*) = 1/\beta_{\text{eff}}(F^*) \) with \( \beta_{\text{eff}}(F^*) = \left(\sum_{F^*} \frac{\partial \hat{S}_c(F, T_f)}{\partial F} \right)_{F^*} \) being the density of complexity with free energy \( F^* \). This formula establishes the probability of free energy jumps in the aging state. Fluctuations to conformations or basins which increase the free energy are forbidden, simply because they have already nucleated in the past. While fluctuations to very low free energy conformations are entropically suppressed due to the monotonous increasing property of \( \hat{S}_c(F, T_f) \). In the off-equilibrium
state the average rate variation of the free energy at time \( t \) is then given by,
\[
\frac{1}{V} \frac{\partial F}{\partial t} \sim \frac{f_{-\infty}^{\infty} x W_t dx}{t \int_{-\infty}^{\infty} W_t dx} = -\frac{1}{\beta_{\text{eff}}(F^*) t} \tag{9}
\]

We can now establish the connection between equation (9) and the present one. Consistency requires that \( s^* = \Delta F / \beta_{\text{eff}}(F^*) \), i.e. the size of the largest nucleating regions \( s^* \) is directly proportional to the inverse effective temperature \( \beta_{\text{eff}}(F^*) \) evaluated at the time-dependent free energy \( F^* \). After equilibrating at time \( t_{\text{eq}} \), \( F^* \) converges to \( F_{\text{eq}} \) and \( s^* \) has saturated to a value \( s^*(t_{\text{eq}}) \) which determines the new phenomenological relation,
\[
\tau_0 = \tau_0 \exp \left( \frac{B s^*(t_{\text{eq}})}{T_f} \right) = \tau_0 \exp \left( \frac{B \Delta F / \beta_{\text{eff}}(F_{\text{eq}})}{T_f} \right). \tag{10}
\]

We can now compare our prediction with the standard AGM scenario. In that scenario the number of different combinations obtained from the two possibilities (nucleated and not yet nucleated) for the largest nucleating regions \( n_o(t) \). This number is given by \( \Omega = 2^n \) yielding for the complexity, \( S_c(t) = \log(\Omega_t) = V \log(2) s^* \) which relates the size of the cooperative region to the complexity. Using eq.(9) and taking \( t = t_{\text{eq}} \) this yields the famous Adams-Gibbs relation \( \tau_0 = \exp(B \log(2) V / T_f S_c) \). The strong assumption contained in the AGM relation is to suppose that, in the off-equilibrium regime during the relaxation, the glass explores nucleated and not nucleated conformations with the same probability. But this cannot be true if free energy jumps are biased towards lower free energy conformations. Actually, according to AGM, the size of the cooperative region increases with time and diverges at the Kauzmann temperature \( T_K \) while in our theory it saturates to a finite value.

One more consequence of the fluctuation formula (10) concerns the fluctuation-dissipation ratio (FDR) and its one-step characterized. After quenching to \( T_f \) a possible way to quantify violation of FDR is to measure the average value of any observable \( A \) after a perturbation field \( h_A \) conjugated to the observable \( A \) is applied to the system. Due to the disordered structure of the cooperative regions, if the perturbation equally weights all conformations, the entropically driven assumption implies that states with free energy \( F \) are sampled with a probability proportional to their number. In the presence of a field \( h_A \) the complexity must be a function of three variables, \( S_c(F, T_f, A) \). We can simply obtain the average change in the expectation value \( \langle A(t) \rangle \) after switching on the perturbation field \( h_A \) at time \( t_{\text{w}} \). In the linear response regime (11) the Onsager regression principle implies for the transition probabilities \( \tilde{W}_{F_S,A} = A_{\rightarrow A_0} = W_{F_S} \exp(S_c(F, T_f, A) - S_c(F, T_f, A_0)) = W_{F_S} \exp(\frac{\partial S_c(F, A)}{\partial A})_{A_0} \). Using the relation \( \frac{\partial S_c(F, A)}{\partial A} = -\beta_{\text{eff}}(F) h_A \) and expanding for \( h_A \) small we finally get the famous violation FDT expression, \( \frac{\delta A(t)}{\delta h_A(t_{\text{w}})} = \beta_{\text{eff}}(F^*) \langle A(t) - A(t_{\text{w}}) \rangle_{h_A = 0} \). Note that the description of the violation of FDT in terms of a single time scale \( t \) is consequence of the asymmetric shape (i.e. \( W_{F^* > 0} = 0 \)) of \( \delta F \).

**Main implications of the present scenario.** It can be proved \( 4 \) that \( \beta_{\text{eff}}(F) \leq 1 / T_K \) where \( S_c(T_K) = 0 \) at \( T_K \). This implies an asymptotic crossover for all fragile liquids to strong behavior. A strong glass is a fragile one which has exhausted all its complexity and the effective barrier has saturated to its maximum value \( \beta_{\text{eff}} = 1 / T_K \). Instead fragile glasses have high excess complexity and still big variation of \( \beta_{\text{eff}} \) along the supercooled line. The non-trivial temperature dependence of the activation barrier in \( 10 \) through the non-universal quantity \( \beta_{\text{eff}} \) explains why it is so difficult to find a unique empirical law that properly describes the viscosity anomaly of all glasses. The prediction that \( s^* \) saturates to a finite value \( s^* = \Delta F / T_K \) at \( T_K \) is not easy to check experimentally due to the difficulty to cover one order of magnitude in the effective barrier. Yet some experimental results suggest a crossover from fragile to strong behavior.\( 13,14 \)

The present scenario could be also checked doing numerical aging experiments. According to (10) the \( t \) dependent effective temperature \( \beta_{\text{eff}}(t) \) (measured through FDT-violations or the formula (8) should be given by \( \beta_{\text{eff}}(t) \rightarrow (T_f / B \Delta F) \log(t / \tau_0) \) if \( \tau_0(t) \approx t \) and both \( \tau_0 \) and \( B \Delta F \) are nearly \( t \) and \( T_f \) independent. This relation should hold for all \( T_f \) and \( t \) predicting a value for the activation barrier and the cooperative size.\( 10 \)
The experimental confirmation of a saturation of the heterogeneity sizes for not too fragile glasses and the crossover from fragile to strong behavior is probably not out of reach and would be a check of the validity of the present theory.

**Acknowledgments.** We wish to thank suggestions by C. Cabrillo, G. Parisi, F. Sciortino and G. Tarjus. F.R. is supported by the MEC in Spain, project PB97-0971.

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