A divergent correlation length in off-equilibrium glasses

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In off-equilibrium dynamics we define a dynamical correlation length which is proportional to the size of the region in which the atoms move in a correlated way. General arguments indicate that this dynamical correlation length diverges at large times in the glassy phase. Numerical simulations for binary mixtures point toward the correctness of this prediction.

The glass transition has many puzzling features, one being the presence of a divergent time scale without a corresponding divergence of the correlation length as measured by considering equilibrium correlations. In this letter we will show that a divergent correlation length may be identified in the glassy phase, below the glass transition point, if we study the off-equilibrium correlation functions.

The basic idea is quite simple. In a glass atoms are usually frozen in some position. If they try to move, the other atoms push them in the original position. This cage effect is at the origine of the glass transition. At low temperatures, but still in the liquid phase, the viscosity is finite (albeit very large) and some movements are still allowed. In many theoretical approaches these movements correspond to the formation of relatively large fluidified domains. All the particles in the domain move of a certain amount and the radius of the domain diverges when we approach the transition. The Vogel-Fulcher law may be obtained if the volume of these fluidified domains diverges at $(T - T_K)^{-1}$ and the process is controlled by the energy activation which should be proportional to the volume. The existence of processes involving a large number of particles in the liquid phase near the glass transition has been recently shown in [1].

When we decrease the temperature, the number of particles involved increases; these processes involve the crossing of higher and higher barriers and they are extremely hard to observe in equilibrium simulations [3]. Here we study similar processes which are present when we quench the system from an high temperature to a temperature well below $T_g$ [4-6]. The dynamics of systems going toward equilibrium has been the subject of a wide theoretical interests [7]. In the high temperature phase, the energy usually approaches equilibrium exponentially when we approach the transition. The Vogel-Fulcher law gives the overlap $q(i) = \sigma(i)\tau(i)$. The quantity $q$ plays the same role of the magnetization in ferromagnets: the susceptibility associated to $q$ diverges at the critical point; the statistical expectation value of $q(i)$ is equal to $m(i)^2$ and it may different from zero only below the transition. The dynamical correlation function of $q$ gives important information on the dynamics. In this case the theoretical understanding is not as good as in the case of ferromagnets; however intensive numerical simulations [8] show that (in three dimensions) the dynamic correlation length diverges as a power of the time and that the $q$-correlation function has a behaviour which is qualitatively similar to that of a ferromagnet:
among spin glasses and ferromagnets are: (a) the presence of the prefactor $r^{-\omega}$ ($\omega \approx .5$); (b) the value of the exponent $z$, which is approximately given $z_c T/T_c$ ($z_c \approx 7$ and $T_c$ is the critical temperature). Also the relation among $z(T)$ and $\lambda(T)$ is different from that of ferromagnets: the energy approaches the equilibrium value with an exponent $\lambda(T) \approx 2.5 z(T)^{-1}$, which is proportional to the temperature.

Summarizing ferromagnets and spin glasses show a clear cut behaviour characterized respectively by entropic and energetic barriers. Which are the theoretical expectations for structural glasses? We can answer to this question if we assume that the mean field for some generalized spin glasses can be applied also to structural glasses $^{11,12}$. This conjecture can be considered as a rationalisation of the Gibbs Di Marzio approach; as a byproduct it implies the correctness of the mode coupling theory in an appropriate time-temperature window $^{13}$.

In this approach the decay of the energy has a rather interesting behaviour. In the mean field theory there are two time windows. In the first one, at relative short times, the approach to equilibrium is dominated by entropic barriers and the value of the exponent $\lambda(T)$ is roughly independent from the the temperature. At larger times the approach to equilibrium is dominated by crossing of energy barriers; in this regime the time evolution strongly depends on the temperature. Numerical simulations (done both with Hamiltonian and dissipative dynamics $^{33}$) for structural glasses are consistent with this picture. Here we will show that in the first (entropy dominated) regime there is dynamic correlation length which increases as power of time.

We present the results of a simulation for binary fluids. We consider a mixture of soft particles of different sizes. Half of the particles are of type $A$, half of type $B$ and the interaction among the particles is given by the Hamiltonian:

$$ H = \sum_{i<k} (d(i) + d(k))^{12} |\mathbf{x}_i - \mathbf{x}_k|^{-12}, $$

where the radius ($d$) depends on the type of particles. This model has been carefully studied in the past $^{14,15}$. The choice $d_B/d_A = 1.2$ strongly inhibits crystallisation and the system goes into a glassy phase when it is cooled. Using the same conventions of previous investigators we consider particles of average radius 1 at unit density. It is usual to introduce the quantity $\Gamma \equiv \beta Z$. For quenching from $T = \infty$ the glass transition is known to happen around $\Gamma_c = 1.45$ $^{14}$. For computational reasons we have slightly modified this model by introducing a cutoff, i.e. we have put to zero the interaction when $|x_i - x_k|^2 > 3$. The differences in various thermodynamic quantities with the original model are of the order of $1\%$.

Our simulation are done using a Monte Carlo algorithm, which is more easy to deal with than molecular dynamics, if we change the temperature in an abrupt way. Each particle is shifted by a random amount at each step, and the size of the shift is fixed by the condition that the average acceptance rate is about $4$. Particles are placed in a cubic box with periodic boundary conditions and at the end of each Monte Carlo sweep all the particles are shifted of the same vector in order to keep the center of mass fixed $^{3}$. We have done simulations for system of many sizes. Here we present the results for systems with 27000 particles, which correspond to a box of size 30. We need to use large systems in order to avoid finite volume effects $^{16}$ (the size of the system must be much larger than the dynamical correlation length we study). The value of $\Gamma$ is 1.8, which is deep in the glassy region (it corresponds to a temperature three times smaller that the transition temperature $^{14}$).

Let us recall the results for the density-density correlation function ($g(r)$) at equal time at equilibrium after a rapid quench. The correlation function is shown in fig. $^\text{9}$ at distances greater than 1.6; in this region it can be fitted as

$$ g(r) = 1 + Ar^{-\alpha} \exp(-r/R_g) \sin(2\pi r/d + \phi), $$

which correspond to a pair of complex singularities in momentum space (simple poles for $\alpha = 1$). The fitted value of $R_g$ strongly depends on $\alpha$; we find $R_g = 1.29$ and 2.13 respectively for $\alpha = 0$ and $\alpha = 1$. A fit done only at large distance (in the region $r > 4$) is better and gives similar values of $R_g$ ($1.88$ and $1.41$). The value of the correlation length often strongly depends on the power in the prefactor and, unless one has extremely good data,
it is difficult to determine both the power of the prefactor and the rate of the exponential decay.

In order to verify the phenomenon of aging we have introduced the quantity $q(t_w, t)$ defined as

$$q(t_w, t) \equiv N^{-1} \sum_i q_i(t_w, t),$$

$$q_i(t_w, t) \equiv \sum_k w(x_i(t + t_w) - x_k(t_w)), \quad (6)$$

where the sum over $k$ is done over particles of the same type of $i$. We have chosen the function $w$ in such a way that it is very small when $x >> a$ and it is near to 1 for $x < a$, i.e. $w(x) = a^{12}/(x^{12} + a^{12})$, with $a = 22$. The value of $q$ will thus be a number very near to 1 for similar configurations (in which the particles have moved of less than $a$) and it will be much smaller ($O(10^{-1})$) for unrelated configurations; using the terminology of spin glasses $q$ can be called the overlap of the two configurations. In fig. 2 we plot the overlap as function of $s \equiv t/t_w$ at different values of the waiting time, i.e. $t_w = 2^9, 2^{13}$ and $2^{17}$. The data weakly depend on the waiting time. It is possible to assume that $q$ goes to limit when $t_w \to \infty$ at fixed $s$, this limit being reached from above at small $\epsilon$ and from below at large $\epsilon$. This way of approaching the asymptotic limit is quite a common feature in other systems, e.g. spin glasses.

Our aim is to study the correlations of the particles which have moved in a sizable way when the time changes form $t_w$ to $s t_w$. These particles, unless they have exactly replaced other particles, contribute to the decrease of the value of $q$ and have a correlation in in position space which strongly depends on waiting time. To evidenziate this effect, for each particle and pairs of configuration at time $t_w$ and $s t_w$ we define the quantity:

$$\sigma_i(t_w, s t_w) = 2(q_i(t_w, s t_w) - q(t_w, s t_w)). \quad (7)$$

In this way $\sum_i \sigma_i = 0$. When the average value of $q$ is not far $1/2$, this procedure corresponds to put $\sigma_i \approx 1$, if the particle has moved less than $a$, and $\sigma_i \approx -1$, if the particle has moved more than $a$. Movements which correspond to an interchange of particles of the same type have no effect on $\sigma$.

We now we define the function $f(r, t_w)$ as the correlation of the particles at time $s t_w$, where the contribution of two particle is weighted by a factor $\sigma_i \delta_k$. Equivalently, we can define the function $\mu(x) = \sum_i \delta(x-x_i(t_w))\sigma_i(t_w)$, which is the local density $\rho(x)$ multiplied by $\sigma$. In this way we can write $f(r) = (\mu(x)\mu(y))$, where $|x - y| = r$.

The correlation $f(r)$ go to zero at large distances, by construction. We expect also that the values of $r$ at which $f(r)$ is sizable different from zero correspond to the values of distance of particles which move in a correlated way.

The results for the correlation $f(r, t_w)$ computed with $s = 3$ are shown in fig. 3, where we plot $c(r, t_w) \equiv f(r, t_w)/g(r)$ (we have divided the data for $f(r, t_w)$ by $g(r)$ in order to eliminate a natural oscillatory effect). At short times the correlations are present only at short distances, when the time increases they extend on a much larger region. We have analyzed the data by fitting $c(r, t_w)$ as

$$c(r, t_w) = \exp(-r/R(t_w))(c_1 + c_2 r^{-1} \sin(2\pi r/d + \phi)), \quad (8)$$

where we have taken the value of $d$ from the previous fit of the correlation function $g(r)$. (The same qualitative dependence of the dynamic correlation distance $R(t_w)$ is obtained also using other fitting procedures; the precise value of $R(t_w)$ being also here quite sensitive to the introduction of a power decaying prefactor).

In fig. 4 we show the dynamic correlation distance as function of time. We see that the behaviour of $R(t_w)$ is well approximated by a power of time, the exponent
correspond to the rearrangements of regions of size larger and larger as function of the time. Events that happen on a spatial scale which becomes carefully.

An other interesting quantity is \( I(t_w) \equiv \int d^3x f(x, t_w) \) that is the equivalent of a susceptibility (it is equal to \( N((q(t_w, s t_w)^2) - \langle q(t_w, s t_w) \rangle^2) \)). Roughly speaking it is proportional to the number of particles which move in a correlated way. If the typical event correspond to the formation of a fluidified domain of radius of order \( R(t_w) \), \( I(t_w) \) should be proportional to \( R(t_w)^3 \). The corresponding exponent for \( I \) is about 0.52 (a similar conclusion was reached in \( \square \) by an analysis restricted to much smaller samples, \( N \leq 258 \)). It would be tempting to speculate that the exact exponents are 1/6 and 1/2.

We have also similar data also for different values of \( s \), i.e. \( s = 1.5 \) and \( s = .375 \). The dependence on \( s \) of \( R(t_w) \) is mild and the analysis of these data leads to similar conclusions. The data for \( f(r, t_w) \) at different \( s \) are indeed rather similar and there is mainly a difference in the absolute normalization. This fact is consistent with the possibility that the correlated movements of a large number of particles happen in a time interval which is much smaller of \( t_w \) (this point should be studied more carefully).

Our data indicate that the process of rearrangements of the systems happens on a spatial scale which becomes larger and larger as function of the time. Events that correspond to the rearrangements of regions of size \( R \) have a characteristic time which diverge approximately as \( R^3 \). A comparison with the data of \( \square \) shows that in our simulations we have explored a region of time where the relaxation of energy indicates that the approach to equilibrium is dominated by crossing of entropic barriers. For values of time near to the largest ones used in our simulations the energy relaxation enter in a new regime \( \square \), which is quite likely dominated by energetic barriers. It would be extremely interesting to extend these studies to longer times and larger systems, to see if there is any change in the behaviour of \( R(t_w) \) when we enter in this new regime.

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