An Increasing Correlation Length in Off-Equilibrium Glasses

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In off-equilibrium dynamics we define a dynamical correlation length that 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 are consistent with this prediction, at least in the time window explored in this paper.

A puzzling feature of the glass transition is the presence of a divergent time scale without a corresponding divergence of the correlation length, as measured by considering *equilibrium* correlations.[1] In this paper we will show that an increasing correlation length may be identified below the glass transition point, if we study the *off-equilibrium* correlation functions.

In a glass atoms are usually frozen. If they try to move, the other atoms push them in the original position. This cage effect is at the origin of the glass transition. In many theoretical approaches[1] these movements correspond to the formation of relatively large fluidized domains.[2] All the particles in the domain move 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 fluidized domains diverges at $(T - T_K)^{-1}$ (T_K being the Kauzmann transition temperature, i.e., the temperature at which there is a thermodynamic transition at equilibrium) and the process is controlled by an activation energy that is 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 ref 3.

When we decrease the temperature, the number of particles moved increases; these processes involve the crossing of higher and higher barriers, and they are extremely hard to observe in equilibrium simulations.[4] Here we study similar processes present when we quench the system from a high temperature to a temperature well below T_c[5−7] and quite likely T_K (T_c being defined as the temperature at which the relaxation time becomes rather large and the data for the viscosity can be fitted, for not loo low temperature, as $(T - T_c)^{-\gamma}$, γ being an appropriate exponent).

The dynamics of systems going toward equilibrium has been the subject of wide theoretical interests.[8] In the high-temperature phase the energy usually approaches equilibrium much faster as a power of time (depending on the temperature−time range, the approach to equilibrium may be an exponential or a stretched exponential). In the low-temperature phase the energy has corrections that decrease as a power of time: $E(t) = E_\infty + At^{-\lambda(T)}$. The dependence of $\lambda(T)$ on the temperature is instructive and can be studied in infinite range models. There are two simple possibilities: (a) the approach to equilibrium is dominated by entropic barriers, and the value of the exponent $\lambda(T)$ is roughly independent from the temperature; (b) the approach to equilibrium is dominated by energy barriers (the value of $\lambda(T)$ strongly depends on the temperature and vanishes linearly with the temperature).

In short range models a similar behavior is present:[9,10] the approach to equilibrium is related to the correlated motion of regions that become larger and larger when the time increases. There are domains of typical radius $R(t)$: the system is at equilibrium inside the domain, but some extra energy is concentrated in the interface among the domains. Quite often the radius $R(t)$ has a power-like behavior (i.e., $R(t) \propto t^{1/z(T)}$) although a different behavior is possible (e.g., $R(t) \propto \ln(t/t_0)$). The exponent $\lambda(T)$ is equal to $\Delta/z(T)$, where the value of Δ depends on the nature of the interface among domains and it is often temperature independent. Two well-studied cases, corresponding to the two different behaviors, are the spinodal decomposition[9] and the spin glasses.[10]

If we quench a ferromagnetic Ising system to temperatures much smaller than the critical one, we find bubbles in which the spins have a similar value: their radius increases like $t^{1/z}$ with $z = 2$[9] and it coincides with our dynamical correlation length (this happens for nonconserved order parameter, for conserved order parameter z is supposed to be equal to 3). The persistence time of a bubble of size R is proportional to R^z. Here $\lambda(T) = 1/2 = 1/z$. i.e., $\Delta = 1$. All exponents are temperature independent. A similar behavior is expected for the *XY* ferromagnet in three dimensions, where $z = 2$ and $\Delta = 2$.[9]

An opposite behavior is seen in spin glasses. The local magnetizations ($m(i) \equiv \langle\sigma(i)\rangle$, i being a point of the lattice) fluctuate from point to point with zero average. It is convenient to consider two copies of the same system (σ and τ) and to introduce the overlap $q(i) = \sigma(i)\,\tau(i)$. The quantity q plays the same role of the magnetization in ferromagnets: the statistical expectation value of $q(i)$ is equal to $m(i)^2$, and it is different from zero only below the transition. Intensive numerical simulations[10] show that (in three dimensions) the dynamic correlation length diverges as a power of the time and $z \approx z_c T_c/T$ ($z_c \approx 7$). The energy approaches the equilibrium value with an exponent $\lambda(T) \approx 2.5z(T)^{-1}$, that is proportional to the temperature (i.e., $\Delta \approx 2.5$).

Ferromagnets and spin glasses show a clear-cut behavior characterized respectively by entropic effects and energetic barriers. In the ferromagnetic case there are no energy barriers to be crossed, and the slow dynamics is an effect of the very large phase space. These entropic effects are temperature independent. In spin glasses the dynamics is dominated by

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activated processes at low temperatures and the data (e.g., the remanent magnetization after a large shift in the magnetic field) collapse when the variable $T \ln(t)$ (i.e., the height of a barrier that can be crossed in time t at temperature T) is used.

Which are the theoretical expectations for structural glasses? We can answer this question if we assume that the mean field for some generalized spin glasses can be applied also to structural glasses.[11−13] This conjecture can be considered as a rationalization of the Adam−Gibbs approach: it implies that at low temperatures the phase space of the system breaks down in an exponential large number of different regions, which gives a contribution (the so-called configurational entropy) to the total entropy vanishing at the Kauzmann temperature. The mode coupling theory is correct in an appropriate time−temperature window,[14] i.e., near T_c. In the mean field theory there are two time windows for $T < T_c$. 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[6,7]) for structural glasses are consistent with this picture. Here we will show that in the first (entropy dominated) regime there is a dynamic correlation length that increases as a 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:

$$H = \sum_{i<k} ((d(i) + d(k))^{12} |\mathbf{x}_i - \mathbf{x}_k|^{-12} \qquad (1)$$

where the radius (d) depends on the type of particles. This model has been carefully studied in the past.[5,15,16] The choice $d_B/d_A = 1.2$ strongly inhibits crystallization, and the system goes into a glassy phase when it is cooled. We consider particles of average radius 1 at unit density. It is usual to introduce the quantity $\Gamma \equiv \beta^{1/4}$. A numerical study of the viscosity implies that the glass transition is known to happen around $\Gamma_c = 1.45$.[15] When the system is rapidly cooled, the energy approaches its equilibrium value rather fast for $\Gamma < \Gamma_c$ and a power-like behavior is observed starting from temperatures near Γ_c. A similar value of Γ_c is obtained by monitoring the violations of the fluctuation dissipation theorem.[16]

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 potential is changed only in the region where it is smaller than 10^{-3}. The differences in various thermodynamic quantities with the actual model are of the order of 1%, and we have checked that no nonphysical effects are introduced: all the correlation functions (including the time dependence) are quite similar with and without the cutoff.

Our simulations 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. The initial configuration is random (which corresponds to infinite temperature). 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 0.4. 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.[4] We have done simulations for systems of many sizes. Here we present the results for systems with 27 000 particles, which corresponds to a box of size 30. We need to use large systems in order to avoid finite volume effects[17] (the size of the system must be much larger than the dynamical correlation length we study). The value of Γ that we use is 1.8, deep in the glassy region: the temperature is 2.3 times smaller than T_c.[15]

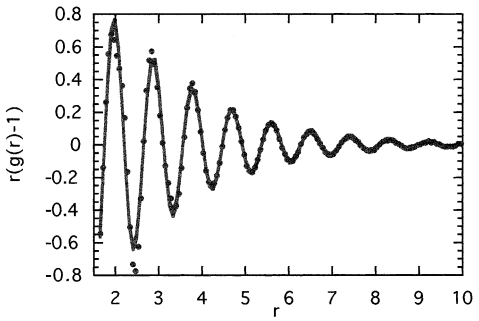

Figure 1. The function $r(g(r) - 1)$ versus r at density 1. The values of the fit parameters (according to eq 2) are for $a = 0$: $R_g = 1.29$, $d = 0.89$, $\phi = -1.15$. Superimposed is an indistinguishable fit with $a = 1$.

The static density−density correlation function ($g(r)$, which is computed for both A and B particles) after a rapid quench is shown in Figure 1 at distances greater than 1.6; in this region it can be fitted as

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

which corresponds to a pair of complex singularities in momentum space (simple poles for $a = 1$). The fitted value of R_g strongly depends on a; we find $R_g = 1.29$ and 2.13, respectively for $a = 0$ and $a = 1$. A fit done only at large distances (in the region $r > 4$) is better and gives similar values of R_g (1.41 and 1.88). 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. The same difficulty if determining the value of the correlation length independently from assumptions on the form of the decay will be present also later.

As a preliminary step, in order to verify if value of the temperature is sufficiently low to be in the glassy region, we have checked if the phenomenon of aging is present in the simulations. At this end we have introduced the quantity $q(t_w, t)$[5] defined as

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

$$q_i(t_w, t) \equiv \sum_k w(x_i(t + t_w) - x_k(t_w)) \qquad (3)$$

where the sum over k is done over particles of the same type of i where the waiting time, t_w, measured in units of Monte Carlo steps, is the time elapsed from the rapid quenching.

We have chosen the function w in such a way that it is very small when $x \gg a$ and it is near to 1 for $x < \delta$, i.e., $w(x) = \delta^{12}/(x^{12} + \delta^{12})$, with $\delta = 0.22$. The value of q will thus be a number very near to 1 for similar configurations (in which the particles have moved less than δ) and it will be much smaller (i.e., $\int d^3x\, w(x) \approx O(10^{-1})$) for unrelated configurations; using the terminology of spin glasses q can be called the overlap of the two configurations. In Figure 2 we plot the overlap as

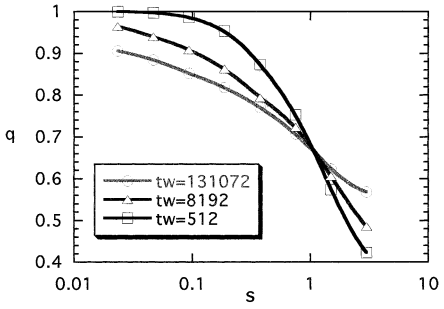

Figure 2. Overlap q as function of $s \equiv t/t_w$ for $t_w = 2^9$, 2^{13}, and 2^{17}, averaged over three initial conditions, the errors being smaller than the points, time being measured in units of one Monte Carlo sweep.

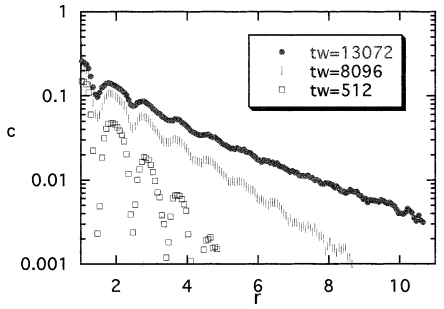

Figure 3. Correlation $c(r,t_w)$ as a function of the distance for $t_w = 2^9$, 2^{13}, and 2^{17}.

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 $q(t_w, t)$ goes to limiting function $Q(s)$ when $t_w \rightarrow \infty$ at fixed s, this limit being reached from above at small s and from below at large s. This way of approaching the asymptotic limit is quite a common feature in other systems, e.g., spin glasses.[18]

Our aim is to study the correlations of the particles that have moved in a sizable way when the time changes from t_w to st_w. These particles, unless they have exactly replaced other particles, contribute to the decrease of the value of q and have a correlation in position space that strongly depends on waiting time. To elucidate this effect,[3,4] for each particle we define the quantity:

$$\sigma_i(t_w,st_w) = 2(q_i(t_w,=st_w) - q(t_w,st_w)) \qquad (4)$$

In this way $\sum_i \sigma_i = 0$. When the average value of q is not far from $^1/_2$, this procedure corresponds to $\sigma_i \approx 1$, if the particle has moved less than a, and $\sigma_i \approx -1$, if the particle has moved more than a. An interchange of particles of the same type has no effect on σ.

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

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

The results for the correlation $f(r,t_w)$ computed with $s = 3$ are shown in Figure 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

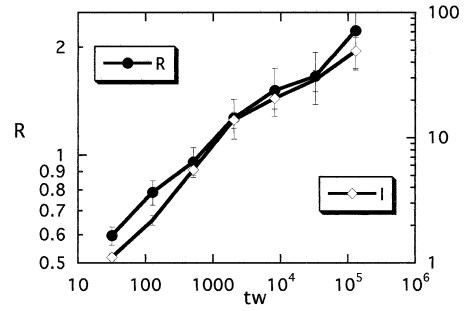

Figure 4. On a double logarithmic scale we find the values of the correlation length ($R(t_w)$, axis on the left) as a function of the waiting time and the values of the integral of the correlation function ($I(t_w)$, axis on the right).

extend to a much larger region. We have analyzed the data by fitting $c(r,t_w)$ as

$$c(r,t_w) = \exp\left(-\frac{r}{R(t_w)}\right)\left(c_1 + c_2 r^{-1} \sin\left(\frac{2\pi r}{d} + \phi\right)\right) \qquad (5)$$

where in order not to increase the number of parameters we have taken the value of d from the previous fit of the correlation function $g(r)$ (nearly the same value of d would have been obtained by leaving it as a free parameter). 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 Figure 4 we show the dynamic correlation distance as a function of time. The behavior of $R(t_w)$ is well approximated by a power of time, the exponent being in the interval 0.1−0.2 (the best fit is $R(t) = 0.47^{0.15}$)). The increase of the value of R is slightly less than 4 if t_w is increased by nearly 4 orders of magnitude, and the maximum value we obtain is about 2. It would be interesting to measure what happens at large times in order to get evidence that the radius R is really divergent.

A stronger effect is observed for the quantity $I(t_w) \equiv \int d^3x\, f(x,t_w)$ which is the equivalent of a susceptibility (it is equal to $N(\langle q(t_w,st_w)^2\rangle - \langle q(t_w,st_w)\rangle^2)$. It is proportional to the number of particles that move in a correlated way. If the typical event corresponds to the formation of a fluidized domain of radius of order $R(t_w)$, $I(t_w)$ should be proportional to $R(t_w)^3$, under the hypothesis that the fluidized domains are compact. If the fluidized domains have fractal dimensions smaller than 3, as suggested in ref 3 above T_c the relationship between R and I should be different; much more precise data on a larger sample and longer times is needed to address this point in a conclusive way. The corresponding exponent for I is about 0.5 (the best fit is $I(t) = 0.28t^{0.46}$). A similar conclusion was reached in ref 5 by an analysis restricted to much smaller samples, $N \leq 258$. Here the time dependence is much more pronounced: the value of I is about 1 at short times (only another particle is on the average involved) and it becomes rather large (about 100) by increasing the time, indicating the presence of collective movements.

We have also similar data also for different values of s, i.e., $s = 1.5$ and $s = 0.375$. The dependence on s of $R(t_w)$ is mild and the analysis of these data leads to similar conclusions. The data suggest that the correlated movements of a large number of particles happen in a time interval that is much smaller than t_w.

Our data indicate that the process of rearrangements of the particles happens on a spatial scale that becomes larger and

larger as a function of time. Events that correspond to the rearrangements of regions of size R have a characteristic time that increases approximately as R^6 (equivalent $R(t) \propto t^{1/6}$). A comparison with the data of ref 7 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 the largest ones used in our simulations, the energy relaxation enters a new regime,[7] which is quite likely dominated by energetic barriers. It would be interesting to extend these studies to longer times and larger systems, to see if there is any change in the behavior of $R(t_w)$ when we enter in this new regime. It is likely that a similar behavior should be observed at higher values of Γ, although this point deserves a careful study.

If the particles are atoms, the time scale of our simulations is quite short, i.e., of the order of the nanosecond (of course, it could much larger, depending on the radius, in the case of colloidal particles) so that a very large gap exists among simulations and experiments. A direct experimental observation of this phenomenon is not simple: the large correlation length appears in the correlation functions of four densities that are notoriously difficult to investigate. The effect could be seen in the video recorder of the motion of large colloidal particles or in the finite size effect on dynamical quantities like viscosity.[17] The study of the diffusion constant as a function of the molecular size may give interesting information. It could also be possible to use the same methodology as in spin glasses where nonlinear effects in the aging regime are used to estimate the dynamic correlation length.[19]

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References and Notes

(1) For review see: Gotze, W. *Liquid, freezing and the Glass transition*; Les Houches, J., Hansen, P., Levesque, D., Zinn-Justin, J., Eds.; North Holland: Amsterdam, 1989. Angell, C. A. *Science* **1995**, *267*, 1924.

(2) Stillinger, F. H. *Science* **1995**, *267*, 1935 and references therein.

(3) Kob, W.; Donati, C.; Plimpton, S. J.; Poole, P. H.; Glotzer, S. C. *Phys. Rev. Lett.* **1997**, *79*, 2827. Donati, C.; Douglas, J. F.; Kob, W.; Plimpton, S. J.; Poole, P. H.; Glotzer, S. C. *Phys. Rev. Lett.* **1998**, *80*, 2338.

(4) Lancaster, D.; Parisi, G. *J. Phys. A.* **1997**, *30*, 5911.

(5) Parisi, G. *J. Phys. A* **1997**, *30*, L765.

(6) Kob, W.; Barrat, J.-L. *Phys. Rev. Lett.* **1997**, *78*, 4581.

(7) Coluzzi, B.; Parisi, G. *On the Approach to the Equilibrium and the Equilibrium Properties of a Glass-Forming Model*, cond-mat/9712261 (submitted to *J. Phys. A*).

(8) Cugliandolo, L. F.; Kurchan, J. *Phys. Rev. Lett.* **1993**, *71*, 1. Franz, S.; Mézard, M. *Europhys. Lett.* **1994**, *26*, 209.

(9) Bray, A. J. *Adv. Phys.* **1994**, *43*, 357.

(10) Marinari, E.; Parisi, G.; Ruiz-Lorenzo, J. J.; Ritort, F. *Phys. Rev. Lett.* **1996**, *76*, 843. Parisi, G.; Ricci-Tersenghi, F.; Ruiz-Lorenz, J. J. *J. Phys. A: Math Gen.* **1996**, *29*, 7943.

(11) Bouchaud, J.-P. *J. Phys. Fr.* **1992**, *2*, 1705.

(12) Kirkpatrick, T. R.; Thirumalai, D.; Wolynes, P. G. *Phys. Rev.* **1989**, *A40*, 1045.

(13) Parisi, G. *Phil. Mag. B* **1995**, *71*, 471. Mézard, M. Parisi, G. *J. Phys. A* **1996**, *29*, 6515. Franz, S.; Parisi, G. *Phys. Rev. Lett.* **1997**, *79*, 2486.

(14) Bouchaud, J.-P.; Cugliandolo, L.; Kurchan, J.; Mézard, M. *Physica A* **1996**, *226*, 243.

(15) Barrat, J.-L.; Roux, J-N.; Hansen, J.-P. *Chem. Phys.* **1990**, *149*, 197. Hansen, J.-P.; Yip, S. *Trans. Theory Stat. Phys.* **1995**, *24*, 1149.

(16) Parisi, G. *Phys. Rev. Lett.* **1997**, *79*, 3660.

(17) Horbach, J.; Kob. W.; Binder, K.; Angell, C. A. *Some Finite Size Effects in Simulations of Glass Dynamics*, cond-mat/9610066.

(18) A. Baldassarri, cond-mat/9607162. H. Yoshino, cond-mat/9612071. E. Marinari, G. Parisi, D. Rossetti, cond-mat/9708025 (submitted to *J. Phys. A*).

(19) R. Orbach, private communication.