Asymptotic aging in structural glasses

T. S. Grigera,[1,*] V. Martín-Mayor,[2,3] G. Parisi,[4] and P. Verrocchio[2,3]
[1]*Centro Studi e Ricerche "Enrico Fermi," via Panisperna, 89A, 00184 Roma, Italy*
[2]*Departamento de Física Teórica, Universidad Complutense, Avenida Complutense, 28040 Madrid, Spain*
[3]*Instituto de Biocomputación y Física de Sistemas Complejos (BIFI), Universidad de Zaragoza, 50009 Zaragoza, Spain*
[4]*Dipartimento di Fisica, Università di Roma "La Sapienza," (SMC-INFM unità di Roma–Italy INFN sezione di Roma) P. le Aldo Moro 2, 00185 Roma, Italy*
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Using a nonlocal Monte Carlo algorithm, we study the aging of a fragile glass, being able to follow it up to equilibrium, down to $0.89T_{MC}$ (T_{MC} is the mode-coupling temperature), and up to long waiting times at lower temperatures. We show that the fluctuation-dissipation ratio is independent of the dynamics chosen and is compatible with a phase transition and that the scaling behavior of the aging part of the correlation supports the full-aging scenario.

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Aging is found in many complex systems out of equilibrium, such as supercooled liquids,[1] polymers,[2] colloids,[3] or spin-glasses,[4] and understanding it is a necessary step towards a unified description of such systems.[5,6] After a short transient since preparation, a state is reached in which one-time observables (e.g., energy, enthalpy) vary extremely slowly, while two-time quantities (correlations, susceptibilities) strongly depend on the *age* (or *waiting time* t_w, i.e., the time elapsed since preparation) of the system as well as on frequency ω (or the measurement time t). Despite recent efforts, our knowledge of aging of real materials is scant in the theoretically important regime of large t_w and small frequency, where universal features should show up.[5] Two issues still open are the scaling of correlations and the behavior of the fluctuation-dissipation ratio.

Consider observables A and B (B couples to an external field h). The susceptibility χ [i.e., the time integral of the linear response $R(t_w,t+t_w)\equiv\delta\langle A(t+tw)\rangle/\delta h(t_w)|_{h=0}$] and the correlation function $C(t_w,t+t_w)\equiv\langle A(t+t_w)B(t_w)\rangle$ are expected to be of the form[5]

$$C(t_w,t_w+t)=C_{st}(t)+C_{ag}\left(\frac{g(t_w+t)}{g(t_w)}\right), \tag{1}$$

where $g(t)$ is a monotonic function acting as an "effective" correlation time, and C_{ag} describes the aging of the system.[7] Most published studies focus on the scaling properties of C_{ag}: it is generally a function of t/t_w^{μ}, but there is a lack of universality in the values of the exponent μ, embarrassing in view of the claimed equivalence of complex systems. *Full aging* ($\mu=1$) has been clearly observed so far only in spin-glasses.[8] For colloids, both *superaging*[9] ($\mu>1$) and full aging has been reported.[10] Polymers show rather *subaging* ($\mu<1$),[2,11] as has also been observed in simple liquids.[12] However, the values quoted often correspond to different time regimes, and the regime where $t_w\to\infty$ with t/t_w fixed has not been carefully studied (except for spin-glasses). For example, in glycerol[13] full aging has not been seen either close to the glass temperature T_g (almost at equilibrium) or at lower temperatures T. In both regimes the explored frequencies were much larger than $1/t_w$.

Aging is also characterized by a nontrivial behavior of the fluctuation-dissipation ratio (FDR), namely,

$$X(t_w,t+t_w)=\frac{TR(t_w,t+t_w)}{dC(t_w,t_w+t)/dt_w}. \tag{2}$$

The fluctuation-dissipation theorem (FDT) states that $X=1$ in thermodynamic equilibrium, but this need not be so during aging, and *FDT violations* (i.e., $X\neq 1$) are observed. Experiments,[14,15] mean-field results,[16] and simulations[17,18] suggest that the FDR depends on time only through the correlation function, i.e., $X=X(C(t_w,t_w+t))$. In structural glasses, in which we concentrate from now on, simulations also show that at fixed t_w, X takes essentially two values: $X(C)=1$ for C greater than some $q_{EA}(T)$ (called the Edwards-Anderson parameter) and $X(C)=x(t_w)<1$ for $C<q_{EA}(T)$. Since T/X can be interpreted as an effective temperature T_{eff},[16] it seems that FDT violations in structural glasses can be characterized by a single time-dependent $T_{eff}(t_w)\equiv T/x(t_w)$, related to the slowest degrees of freedom. This lacks experimental confirmation. (Note that other definitions of effective temperatures have been explored.[13,19]) Also open is the issue of the behavior of $T_{eff}(t_w)$ as $t_w\to\infty$ (numerical data available cover only very short waiting times in the sense that one-time quantities are still quickly evolving[12,18]), of great theoretical interest because it is related to the possible *thermodynamic* meaning of T_{eff}.[16]

In this paper we study the aging dynamics down to $0.53\,T_{MC}$ (T_{MC} is the mode-coupling[20] temperature, below which dynamics slows down dramatically), reaching very large waiting times. This can be achieved through the use of a nonlocal algorithm [Swap Monte Carlo or SMC (Ref. 21)], which greatly accelerates the dynamics. We reach an asymptotic regime where the correlation function shows full aging within errors (supporting the analogy with spin glasses[8]), and where FDT violations are independent of the dynamics and of the age of the system.

We have simulated the soft-sphere binary mixture[22] [pair potential $V_{AB}(r)=(\sigma_{AB}/r)^{12}$, diameter ratio 1.2), a simple fragile glass former, using a *nonlocal* Metropolis Monte Carlo algorithm [hereafter SMC (Ref. 21)] which adds swap moves (with probability p) to standard *local* Monte Carlo (LMC). Although swap acceptance is very low ($\approx 3\times 10^{-3}$) the equilibration time is considerably shortened; e.g., at $0.89T_{\mathrm{MC}}$ extrapolations estimate it to be three orders of magnitude larger for LMC than for SMC (note that other nonlocal algorithms have proved useful in simulations of structural glasses[23]). We used the following protocol: Starting from a random configuration, a system of $N=2048$ particles was instantaneously quenched to the final temperature T, and allowed to evolve for t_w steps. This preparation was done with the SMC algorithm with $p=0.1$, which gives the faster equilibration for this system size. After t_w, the correlation and response functions in the presence of an external field h were computed, mostly in SMC runs with $p=0.1$, but also in LMC and SMC runs with different p in order to assess the dependence of the results on the dynamics. Due to the swap moves, particle diffusion is not a convenient observable. Instead, we divided the simulation box in N_c cubic subcells and considered the quantity

$$A(t)=\frac{1}{N}\sum_{\alpha=1}^{N_c}\epsilon_\alpha n_\alpha(t), \tag{3}$$

where $\epsilon_\alpha=\pm 1$ randomly and n_α is the occupation number of subcell α. The side of the subcells was about $0.35\sigma_{AA}$ so that essentially $n_\alpha=0,1$. Note that swap moves do not change $A(t)$. To measure response, a term λNA was added to the Hamiltonian, with $\lambda\equiv hk_BT$ (h is dimensionless). We considered the correlation $C(t_w,t_w+t)\equiv\overline{\langle NA(t_w)A(t_w+t)\rangle}$, where $\overline{\langle\ldots\rangle}$ means average over both thermal histories and the ϵ_α, together with the integrated response $k_BT\chi(t_w,t_w+t)\equiv\overline{\langle A(t_w+t)\rangle}/h$.[24]

With SMC we can equilibrate the system down to $T=0.89T_{\mathrm{MC}}$. The correlation $C(t_w,t_w+t)$ shows aging up to $t_w=10^5$, but does not change between $t_w=10^5$ and 10^6, which is approximately the region where the energy reaches a stationary value (Fig. 1). We conservatively estimate the autocorrelation time as the time τ needed for C to reach the asymptotic value N/N_c (~ 0.04), obtaining $\tau=2\times 10^5$, much smaller than 10^6 (the total length of the simulation). Hence we claim that the system has equilibrated, which is further confirmed by the fact that the FDT holds. In contrast, well below $0.89T_{\mathrm{MC}}$ the system is out of equilibrium up to $t_w=2\times 10^7$ (our largest observational time). A stretched exponential fit of the equilibrium correlation in the late α-relaxation regime yields a stretching exponent $\beta\sim 0.3$. The equilibrium LMC correlation function does not decay to N/N_c within the simulated times; hence it is still an open point whether SMC changes the shape of the correlations in equilibrium, or whether the two dynamics are related by a simple rescaling of time.

We first address the issue of the scaling of the correlation during aging at $T=0.53T_{\mathrm{MC}}$ (in general far below T_g, e.g. for glycerol this corresponds to $T\sim 140$ K, while $T_g\sim 190$ K). With SMC we find (Fig. 2) that the correlations for $t_w=5\times 10^5$, 5×10^6 can be made to collapse by plotting them as a function of t/t_w^μ with $\mu=1.05(6)$, compatible with full aging. The collapse applies to the aging part [C_{ag}, Eq. (1)], which dominates the correlation for $t/t_w>0.1$ ($\omega t_w<10$), as has also been observed in spin glasses.[8] The two shortest t_w's (inset) can instead be scaled with $\mu\sim 0.85$. The same value (within errors) was found in molecular dynamics simulations of the Lennard-Jones binary mixture,[12] so we argue that the accelerated dynamics does not affect the scaling. If one insists on scaling all curves, it can be done reasonably well using $\mu\sim 0.9$, though this is likely an artifact of mixing two different regimes. The relevant point is that $\mu\sim 1$ is seen clearly only for $t_w\gg 1$ and in the $t\sim t_w$ region, which is where it is expected to hold[9] if structural glasses share the dynamic properties of spin-glasses.[5] The failure of full aging for $t/t_w\ll 1$ is hence in agreement with dielectric susceptibility measurements in glycerol.[13] We are not aware of experimental studies in the conditions where we find full aging, but such measurements are clearly needed.

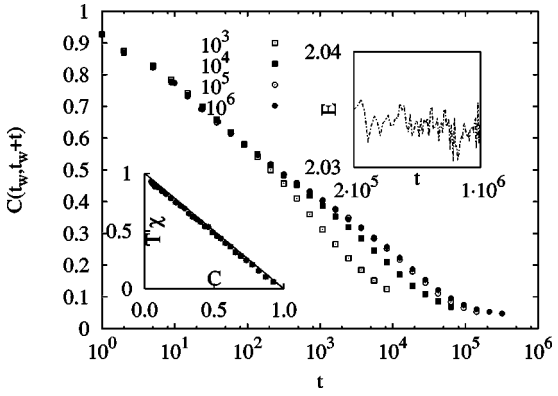

FIG. 1. Correlation function $C(t_w,t_w+t)$ vs t for $T=0.89T_{\mathrm{MC}}$ at $t_w=10^3,10^4,10^5,10^6$ (24 samples). Bottom, left: integrated response $T\chi$ vs correlation function C at $t_w=10^6$. Top, right: Energy per particle E vs t during a SMC quench with $p=0.1$. Error bars are of the order of point size.

A second important result is that although the susceptibility and correlation are affected by the choice of dynamics, the FDR is not. In fact, Fig. 3 shows the ratio T_{eff}/T (i.e., the inverse of the FDR) at $T=0.89T_{\mathrm{MC}}$ during aging and up to

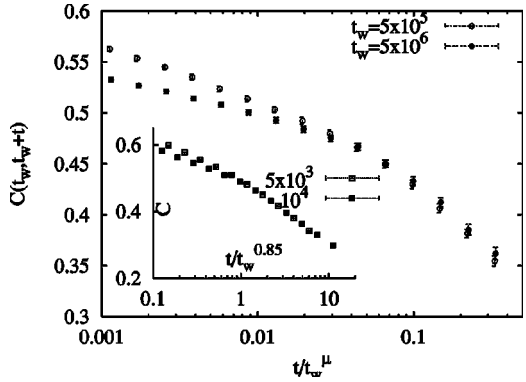

FIG. 2. C vs t/t_w^μ, $\mu=1.05(6)$, for $t_w=5\times 10^5,5\times 10^6$ at $T=0.53\,T_{\mathrm{MC}}$ from SMC runs (24 samples). Inset: C vs $t/t_w^{0.85}$ for $t_w=5\times 10^3,10^4$ (48 samples).

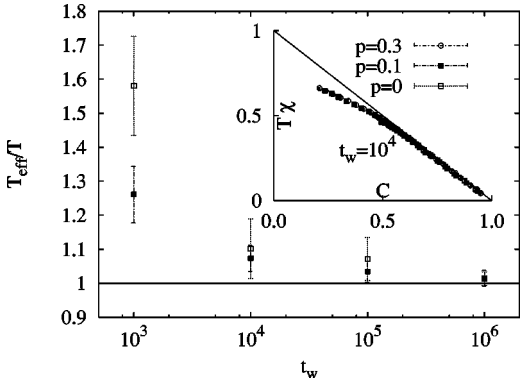

FIG. 3. $T_{\rm eff}/T$ vs t_w for SMC and LMC runs at $T=0.89T_{\rm MC}$ (16 samples), obtained by a linear fit of the points of the parametric $T\chi$ vs C plots deviating from the FDT line. Errors were estimated with the jacknife method (Ref. 25). Inset: $T\chi$ vs C for $t_w=10^4$ at $T=0.53T_{\rm MC}$ for $p=0$ (LMC) and $p=0.1, 0.3$ (SMC), $N=20000$ (8 samples).

equilibration for both SMC and LMC algorithms, obtained measuring the FDR in simulations that used configurations taken along the SMC quench as a starting point. After a short transient ($\sim 10^4$ steps) the FDR's become indistinguishable within errors. At $T=0.53T_{\rm MC}$ and with LMC, we can reach the region of FDT violations only for $t_w=10^4$, so we look at the FDR at fixed t_w for LMC and SMC with $p=0.1$ and 0.3, obtaining a good agreement (Fig. 3, inset).

Finally, we investigate the FDR for large times at $T=0.53T_{\rm MC}$. In Fig. 4 we plot $T_{\rm eff}$ at $t_w=5\times10^3$, 10^4, 5×10^5, and 5×10^6 as a function of the instantaneous inherent structure (IS) energy $E_{\rm IS}(t_w)$. We also plot $T_{\rm eff}$ computed according to the IS approach,[18] $T_{\rm eff}^{-1}=\partial\Sigma/\partial f$, where $\Sigma(f)$ is the logarithm of the number of IS with free energy f, and $\partial\Sigma/\partial f$ is obtained as in Ref. 18. This idea (which makes no prediction about the $t_w\to\infty$ limit of $T_{\rm eff}$) had previously been confirmed only in the very early aging regime by molecular dynamic simulations.[18] Our results show a reasonable agreement even at quite large times.

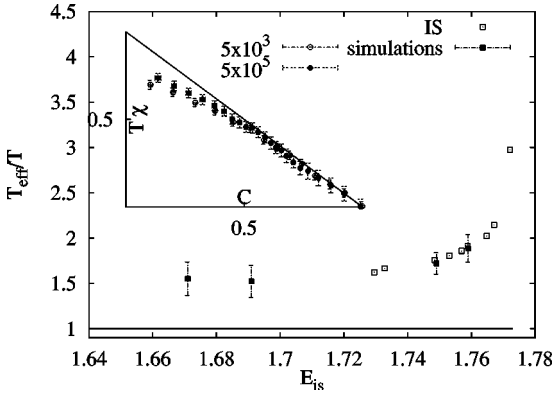

FIG. 4. $T_{\rm eff}/T$ for $T=0.53T_{\rm MC}$ vs the instantaneous IS energy $E_{IS}(t_w)$ measured in SMC runs. $E_{is}(t_w)$ is found by energy minimization starting from 50 instantaneous configurations within a small time window ($\ll t_w$) around t_w. We also show the $T_{\rm eff}$ predicted by the IS approach (Ref. 18). Inset: the $T\chi$ vs C plot for two different t_w.

The limiting value of $T_{\rm eff}$ as $t_w\to\infty$ is of great theoretical interest. If the system eventually equilibrates, then $T_{\rm eff}\to T$, as we have found for $T=0.89T_{\rm MC}$. Approaches that consider aging a result of critical slowing down due to the proximity of a critical point which is never reached (because it is located at $T=0$,[26] or because of the impossibility to establish a "liquid" long range order[27]) predict this to be the case for all temperatures. A different view relates the asymptotic value of the FDR to a thermodynamic transition described by replica symmetry breaking.[28] Above the transition, $X(C)$ is predicted to reach slowly the equilibrium value 1 [so $T_{\rm eff}\to T$ (Ref. 6)], while below the FDR it should remain nontrivial and $T_{\rm eff}$ should tend to a constant $>T$, since the system never equilibrates. In this scenario the asymptotic FDR is claimed to classify complex systems in universality classes.[5,28] A third possibility is that FDT violations are due to nucleation and slow growth of the crystal phase,[29] in which case at long times one expects the coarsening regime to be reached, and so $T_{\rm eff}\to\infty$.

Our results for $0.53T_{\rm MC}$ do not seem to support this last possibility. The data are instead compatible with the presence of a thermodynamic replica symmetry breaking (RSB) transition,[28] since FDR does not seem to change between $t_w=5\times10^5$ and $t_w=5\times10^6$ ($E_{\rm IS}$ are, respectively, 1.691 and 1.671). Note that this is the same regime where the system displays full aging. It cannot be excluded that $T_{\rm eff}\to T$, but it looks less likely if we note that extrapolating $E_{\rm IS}(t_w)$ to $t_w\to\infty$ with a power law gives an asymptotic $E_{\rm IS}=1.642$. In the first approximation the RSB approach predicts that $T_{\rm eff}$ equals the transition temperature, which unfortunately has been only roughly estimated.[28] We just observe the fact that, at the qualitative level, the measured $T_{\rm eff}/T$ in Fig. 4 levels off at a value greater than 1 in the late aging regime supports the RSB scenario.

In summary, we have studied numerically the late aging regime of a simple glass-forming liquid using local and nonlocal Monte Carlo (SMC). We find that the scaling of the correlation functions and the FDR during aging do not depend on the dynamics. This is a strong generalization of the previous finding[30] that equilibrium relaxation in the Lennard-Jones mixture is qualitatively identical under different *local* dynamics (except, as here, for very short times). We have found that correlation functions in the late aging regime show within errors full-aging scaling, suggesting an equivalence between the aging dynamics of structural and spin glasses. This should be searched experimentally at frequencies comparable or shorter than $1/t_w$. We also measured the FDR while taking one-time quantities closer to asymptotic values than in previous studies. FDT violations do not imply a thermodynamic transition. However, if a transition does exist, there should be a correspondence between the asympotic $T_{\rm eff}$, which is accessible to experiments, and the order parameter, which is not.[31] The FDR's measured in experiments[14,15] and simulations[18] up to now depend strongly on the age of the system; hence their utility in investigating the existence of a transition is still an open point.

Here, we have been able to reach a regime where $T_{\rm eff}$ has no noticeable time dependence. Interestingly enough, it coincides with the full-aging regime. At the lowest temperature, the $T_{\rm eff}$ measured over a time window of 3 orders of magnitude approaches a finite value, different from the equilibrium temperature. This seems only slightly compatible with a critical slowing down ($T_{\rm eff} \to T$)) or the growth of a crystal phase ($T_{\rm eff} \to \infty$) and favors instead the phase transition scenario. Our result suggests that the relevant information for an understanding of aging in structural glasses has to be looked for in a regime that so far had not been investigated, either in experiments or in simulations.

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*Present address: Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA, CONICET–UNLP), c.c. 16, suc. 4, 1900 La Plata, Argentina.

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