

Asymptotic aging in structural glasses

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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 $0.89T_{\text{MC}}$ (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 $R(t_w, t+t_w) \equiv \delta\langle A(t+t_w)\rangle / \delta h(t_w)|_{h=0}$] 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 form⁵

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

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 $t_w \rightarrow \infty$ with t/t_w fixed has not been carefully studied (except for spin-glasses). For example, in glycerol¹³ 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,

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

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 $q_{\text{EA}}(T)$ (called the Edwards-Anderson parameter) and $X(C)=x(t_w) < 1$ for $C < q_{\text{EA}}(T)$. 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 $T_{\text{eff}}(t_w) \equiv T/x(t_w)$, 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 $T_{\text{eff}}(t_w)$ as $t_w \rightarrow \infty$ (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 $0.53 T_{\text{MC}}$ (T_{MC} is the mode-coupling²⁰ 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 glasses⁸), and where FDT violations are independent of the dynamics and of the age of the system.

We have simulated the soft-sphere binary mixture²² [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 $0.89T_{\text{MC}}$ 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 glasses²³). 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

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

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 $\lambda N A$ was added to the Hamiltonian, with $\lambda \equiv h k_B T$ (h is dimensionless). We considered the correlation $C(t_w, t_w+t) \equiv \langle NA(t_w)A(t_w+t) \rangle$, where $\langle \dots \rangle$ means average over both thermal histories and the ϵ_α , together with the integrated response $k_B T \chi(t_w, t_w+t) \equiv \langle A(t_w+t) \rangle / h$.²⁴

With SMC we can equilibrate the system down to $T=0.89T_{\text{MC}}$. 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 auto-correlation 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 $0.89T_{\text{MC}}$ 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 $T=0.53T_{\text{MC}}$ (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 $t_w=5$

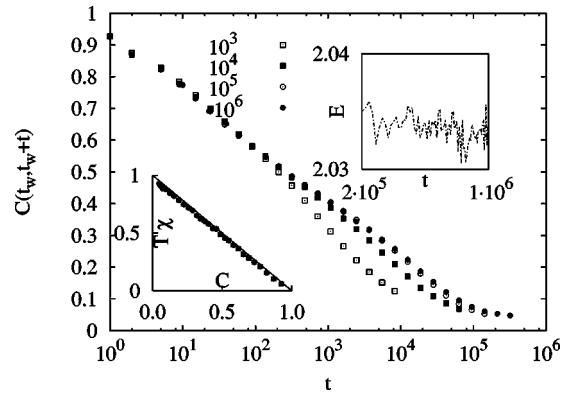


FIG. 1. Correlation function $C(t_w, t_w+t)$ vs t for $T=0.89T_{\text{MC}}$ at $t_w=10^3, 10^4, 10^5, 10^6$ (24 samples). Bottom, left: integrated response $T\chi$ vs correlation function C at $t_w=10^6$. Top, right: Energy per particle E vs t during a SMC quench with $p=0.1$. Error bars are of the order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

$\times 10^5, 5 \times 10^6$ 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 hold⁹ 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.

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 $T=0.89T_{\text{MC}}$ during aging and up to

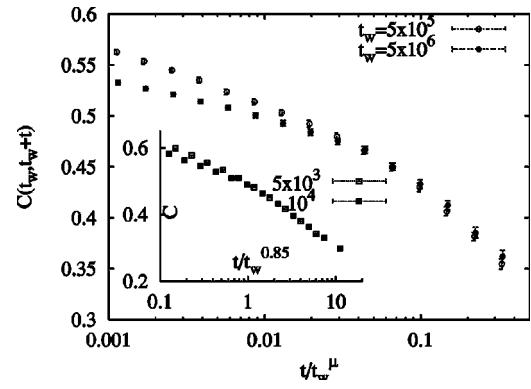


FIG. 2. C vs t/t_w^μ , $\mu=1.05(6)$, for $t_w=5 \times 10^5, 5 \times 10^6$ at $T=0.53 T_{\text{MC}}$ from SMC runs (24 samples). Inset: C vs $t/t_w^{0.85}$ for $t_w=5 \times 10^3, 10^4$ (48 samples).

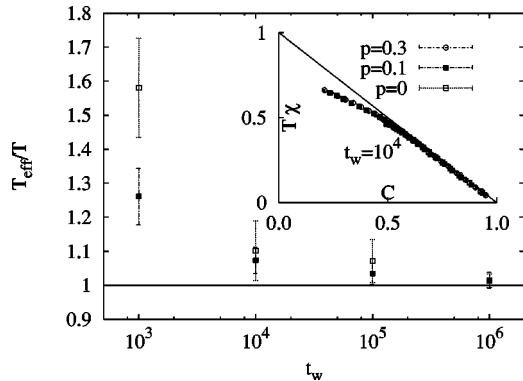


FIG. 3. T_{eff}/T vs t_w for SMC and LMC runs at $T=0.89T_{\text{MC}}$ (16 samples), obtained by a linear fit of the points of the parametric $T\chi$ vs C plots deviating from the FDT line. Errors were estimated with the jackknife method (Ref. 25). Inset: $T\chi$ vs C for $t_w=10^4$ at $T=0.53T_{\text{MC}}$ 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 $T=0.53T_{\text{MC}}$ 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 $T=0.53T_{\text{MC}}$. In Fig. 4 we plot T_{eff} at $t_w=5 \times 10^3$, 10^4 , 5×10^5 , and 5×10^6 as a function of the instantaneous inherent structure (IS) energy $E_{\text{IS}}(t_w)$. We also plot T_{eff} computed according to the IS approach,¹⁸ $T_{\text{eff}}^{-1}=\partial\Sigma/\partial f$, 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 $t_w \rightarrow \infty$ limit of T_{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.

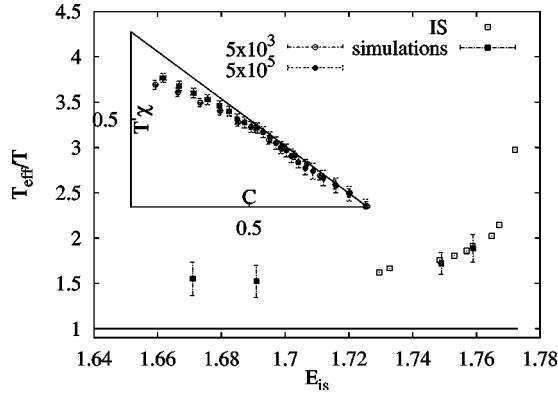


FIG. 4. T_{eff}/T for $T=0.53T_{\text{MC}}$ vs the instantaneous IS energy $E_{\text{IS}}(t_w)$ measured in SMC runs. $E_{\text{IS}}(t_w)$ is found by energy minimization starting from 50 instantaneous configurations within a small time window ($\ll t_w$) around t_w . We also show the T_{eff} predicted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

The limiting value of T_{eff} as $t_w \rightarrow \infty$ is of great theoretical interest. If the system eventually equilibrates, then $T_{\text{eff}} \rightarrow T$, as we have found for $T=0.89T_{\text{MC}}$. 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 order²⁷) 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 $T_{\text{eff}} \rightarrow T$ (Ref. 6)], while below the FDR it should remain nontrivial and T_{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 $T_{\text{eff}} \rightarrow \infty$.

Our results for $0.53T_{\text{MC}}$ 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 $t_w=5 \times 10^5$ and $t_w=5 \times 10^6$ (E_{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 $T_{\text{eff}} \rightarrow T$, but it looks less likely if we note that extrapolating $E_{\text{IS}}(t_w)$ to $t_w \rightarrow \infty$ with a power law gives an asymptotic $E_{\text{IS}}=1.642$. In the first approximation the RSB approach predicts that T_{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_{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 non-local 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 finding³⁰ 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 asymptotic T_{eff} , which is accessible to experiments, and the order parameter, which is not.³¹ The FDR's measured in experiments^{14,15} and simulations¹⁸ 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_{eff} has no noticeable time dependence. Interestingly enough, it coincides with the full-aging regime. At the lowest temperature, the T_{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 ($T_{\text{eff}} \rightarrow T$) or the growth of a crystal phase ($T_{\text{eff}} \rightarrow \infty$) 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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