

Single particle fluctuations dominate the long-time dynamic susceptibility in glass-forming liquids.

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Liquids near the glass transition exhibit dynamical heterogeneity, i.e. correlated regions in the liquid relax at either a much faster rate or a much slower rate than the average. This collective phenomenon has been characterized by measurements of a dynamic susceptibility $\chi_4(t)$, which are sometimes interpreted in terms of the size of those relaxing regions and the intensity of the fluctuations. We show that the results of those measurements can be affected not only by the collective fluctuations in the relaxation rate, but also by density fluctuations in the initial state and by single-particle fluctuations. We also show that at very long times the average overlap $C(t)$ probing the similarity between an initial and a final state separated by a time interval t decays as a power law $C(t) \sim t^{-d/2}$. This is much slower than the stretched exponential behavior $C(t) \sim e^{-(t/\tau)^\beta}$ previously observed at times within one or two orders of magnitude of the α -relaxation time τ_α . We find that for times longer than $10 - 100\tau_\alpha$, the dynamic susceptibility $\chi_4(t)$ is dominated by single particle fluctuations, and that $\chi_4(t) \approx C(t) \sim t^{-d/2}$. Finally, we introduce a method to extract the collective relaxation contribution to the dynamic susceptibility $\chi_4(t)$ by subtracting the effects of single-particle fluctuations and initial state density fluctuations. We apply this method to numerical simulations of two glass forming models: a binary hard sphere system and a Kob-Andersen Lennard-Jones system. This allows us to extend the analysis of numerical data to timescales much longer than previously possible, and opens the door for further future progress in the study of dynamic heterogeneities, including the determination of the exchange time.

I. INTRODUCTION

Glass forming liquids are characterized by a dramatic slowdown of the relaxation dynamics as the temperature is reduced or the density is increased. A common way to probe relaxation is to measure the similarity between states of the system at different times. To do this an often used quantity is the average overlap $C(t) = \langle w(\Delta\vec{r}) \rangle$. Here $w(\Delta\vec{r})$ is an individual particle overlap function that goes from one to zero as the particle displacement $\Delta\vec{r}(t)$ goes from being smaller to being larger than a typical vibrational amplitude [1, 2]. The main timescale describing the slowdown of the dynamics is the α -relaxation time τ_α . This timescale characterizes the decay of an average two-time correlation function, usually the average overlap $C(t)$, or the self part $F_s(\vec{k}, t)$ of the intermediate scattering function [2–4]. The time dependence of the average overlap $C(t)$ for times within one or two orders of magnitude of the α -relaxation time has been found to be well described by a stretched exponential form $C(t) \sim e^{-(t/\tau)^\beta}$ [5].

As the relaxation time of a fragile glass former increases in the vicinity of the glass transition, *dynamical heterogeneity* emerges, i.e. the relaxation becomes much slower or much faster in some regions than in others [3, 4, 6]. The typical distance over which the local relaxation is correlated increases as the glass transition is approached, which, together with other evidence [3, 4, 6], suggests that glassy dynamics is a collective phenomenon [2]. One of the most common approaches to study those correlations is to compute the four-point structure factor $S_4(\vec{q}, t)$, which is the Fourier transformed spatial correlator of the individual particle overlap w [1, 2, 7]. The

dynamic susceptibility $\chi_4(t) \equiv \lim_{q \rightarrow 0} S_4(\vec{q}, t)$ [1, 2, 5, 8, 9] gives a measure of the overall strength of the fluctuations, and its maximum value is sometimes interpreted as being proportional to the typical number of particles in a correlated region [2]. Additionally, a dynamic correlation length $\xi_4(t)$ can be defined by the expansion $S_4(\vec{q}, t) = \chi_4(t)[1 - \xi_4^2(t)q^2 + \mathcal{O}(q^4)]$, valid for small but nonzero q [1, 5, 8, 9].

The dynamical behavior of glassy systems is characterized by several timescales besides the relaxation time τ_α . Some of them, such as the time t_4 when $\chi_4(t)$ reaches its maximum, are typically not far from τ_α [1, 2, 8]. But other timescales may sometimes be much longer. For example, the dynamic correlation length of fluctuations continues to increase after τ_α [2, 5]; and the typical time it takes for a slow region to become fast or viceversa - the exchange time τ_{ex} - may in some cases be much longer than τ_α [3, 10, 11]. However, for times $t > t_4$, little is known theoretically about $\chi_4(t)$ beyond the observed fact that it decreases with time [2, 8]. In the case of $\xi_4(t)$, it is not even clear whether it decreases or not at very long times. Additionally, even though the four point functions $S_4(\vec{q}, t)$ and $\chi_4(t)$ have been the main tool used to analyze numerical data on dynamical heterogeneity, no clear connection has been established between them and the exchange time τ_{ex} characterizing the lifetime of the heterogeneous regions.

The purpose of this work is twofold. First we present evidence that the long time behavior of the average overlap is given by a power law $C(t) \sim t^{-d/2}$, where d is the dimensionality of space. Then we focus on the four point structure factor $S_4(\vec{q}, t)$. We introduce a decomposition of $S_4(\vec{q}, t)$ as the sum of four contributions: (i) S_4^{r} , describing collective relaxation fluctuations; (ii) S_4^{st} , associated with the density fluctuations in the initial state; (iii) S_4^{mc} , due to the interplay of density fluctuations in the initial state with relaxation fluctuations, and (iv) S_4^{sp} , due to uncorrelated *single-particle* fluctuations. As a function of q , $S_4(\vec{q}, t)$ decays to a plateau value $\chi_{4,b} > 0$ [8]

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for $q \ll 2\pi/r_{NN}$, where r_{NN} is the typical nearest neighbor distance. We propose here that this plateau corresponds to the sum of the contributions S_4^{st} , S_4^{mc} , and S_4^{sp} , and show that its time dependence can be well reproduced by a simple expression involving only the overlap $C(t)$ and the static structure factor $S(\vec{q})$. The fact that all contributions except S_4^{cr} are q -independent allows us to introduce a simple method of analysis that separates those contributions, and enables the detailed study of dynamical heterogeneities at timescales much longer than τ_α . We apply this method to simulation data for a binary hard-sphere system and for the Kob-Andersen Lennard-Jones system. We show that for temperatures or densities near the mode-coupling crossover [2, 12], the collective relaxation contribution S_4^{cr} is orders of magnitude larger than the others at $t \sim \tau_\alpha$, but the single particle contribution becomes dominant at $t \gg \tau_\alpha$. In fact, we find that for very long times, $S_4(\vec{q}, t) \approx S_4^{\text{sp}}(\vec{q}, t) \approx C(t) \sim t^{-d/2}$. By subtracting the other three contributions, we isolate the collective contribution $S_4^{\text{cr}}(\vec{q}, t)$, and find that for the systems we simulate it decays as a power law at very long times $S_4^{\text{cr}}(\vec{q}, t) \sim t^{-p}$, with $p > d$, i.e. with an exponent at least twice larger than the one for the single-particle contribution. We also use this decomposition to determine $\xi_4(t)$ for times up to $t \sim 80\tau_\alpha$ in the hard-sphere system, thus showing how to provide an answer to the longstanding question regarding the long time behavior of $\xi_4(t)$.

The rest of this paper is organized as follows. In Sec. II we briefly discuss the simulation details. In Sec. III we show evidence for a power law behavior $C(t) \sim t^{-d/2}$ of the overlap at very long times. In Sec. IV we discuss the decomposition of the four-point functions in terms of four contributions with distinct physical interpretations, and analyze the long time behavior of the single-particle and collective relaxation contributions. Finally, in Sec. V we summarize our results.

II. SIMULATION DETAILS

We simulate two 3D equilibrium glass-forming liquids. The first system is a 50:50 binary mixture of hard-spheres (HARD), with diameters d and $1.4d$. Lengths are measured in units of d , and wavevectors are measured in units of $1/d$. Monte Carlo simulations were performed for $N = 80000$ particles at packing fractions $\phi = 0.50, 0.52, 0.55, 0.56, 0.57$, and 0.58 . For each packing fraction, data were taken for four runs, after the system was well equilibrated, during a time of about $100\tau_\alpha$. The second system is the Kob-Andersen Lennard-Jones (KALJ) [13–15] 80:20 binary mixture with $N = 27000$ particles. Here all lengths are measured in units of σ_{AA} , the characteristic length of the Lennard-Jones potential between A particles, and all wavevectors are measured in units of $1/\sigma_{AA}$. The simulations were performed with Newtonian dynamics for temperatures $T = 0.50, 0.55, 0.60, 0.65, 0.70$, and 0.80 at a density $\rho = N/V = 1.2$. At all temperatures, four runs were performed and data were taken for at least $100\tau_\alpha$ after the system was well equilibrated. More details about the simulation and characterization of the systems can be found in Ref. [5] for HARD and in Ref. [16] for KALJ.

III. SINGLE-PARTICLE DYNAMICS

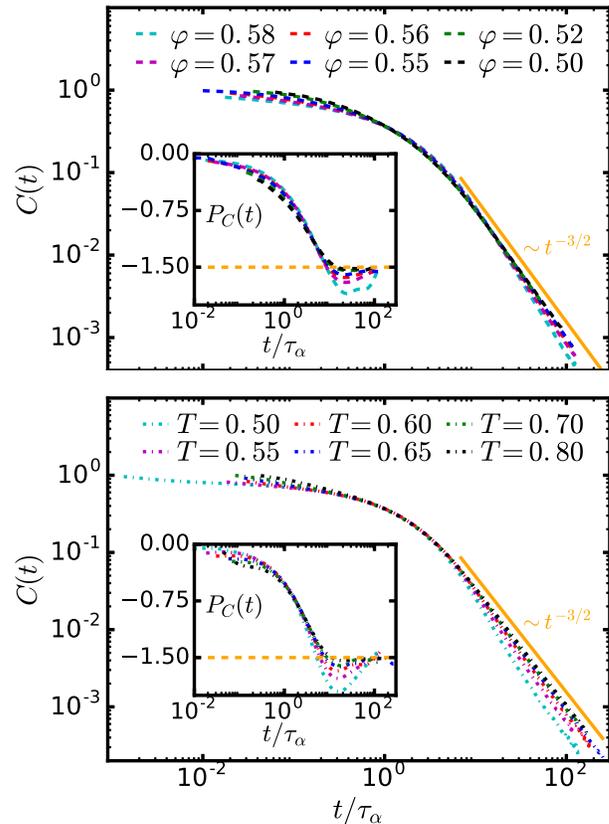


FIG. 1: Two time correlation function $C(t)$ for HARD for packing fractions $\phi = 0.50, 0.52, 0.55, 0.56, 0.57, 0.58$ (top panel) and for KALJ for temperatures $T = 0.80, 0.70, 0.65, 0.60, 0.55, 0.50$ (bottom panel). A $t^{-3/2}$ power-law time dependence is shown for comparison. Insets: Power-law exponent $P_C(t) \equiv d \ln C(t) / d \ln t$ of $C(t)$.

We probe the dynamics by using a microscopic overlap function $w_n(t) = \theta[a - |\mathbf{r}_n(t) - \mathbf{r}_n(0)|]$, where $\theta(x)$ is the Heaviside step function, $\mathbf{r}_n(t)$ is the position of the n -th particle at time t , and a is a characteristic distance that is larger than the typical amplitude of vibrational motion (we take $a = 0.3$ for HARD and $a = 0.25$ for KALJ). For a given time interval t , if a particle moves less than the characteristic distance a , then $w_n(t) = 1$. The average dynamics is characterized by the two-time correlation $C(t) = N^{-1} \sum_{n=1}^N \langle w_n(t) \rangle$ (i.e. the average fraction of particles with displacements $|\Delta \vec{r}| < a$, where $\langle \dots \rangle$ denotes the average over the simulation ensemble [1]). We define the α -relaxation time τ_α by setting $C(\tau_\alpha) = 1/e$. At times of order τ_α , the decay of $C(t)$ follows a stretched exponential form $C(t) \sim \exp[-(t/\tau)^\beta]$ [28].

However, as shown in Fig. 1, at times $t \gg \tau_\alpha$ the decay of $C(t)$ approaches a power law form, both for the HARD and the KALJ systems. The insets of Fig. 1 show that the exponent $P_C(t) \equiv d \ln C(t) / d \ln t$ approaches $-1.5 = -d/2$ at very long times, where $d = 3$ is the dimensionality. A fuller discussion of this limit is given in [17], but we can give a

simple argument to justify this behavior. At time $t \gg \tau_\alpha$, and considering only long lengthscales, we expect the dynamics to be diffusive with self-diffusion coefficient D , and the displacement probability distribution $G_s(\vec{r}, t)$ to be a gaussian with characteristic size $R(t) = (2Dt)^{1/2}$. This corresponds to $G_s(\vec{0}, t) \approx (4\pi Dt)^{-d/2}$, and the probability of being within a region of radius $a \ll R(t)$ in dimension d around the origin to be $C(t) \sim a^d G_s(\vec{0}, t) \sim t^{-d/2}$ [17]. We expect $G_s(\vec{r}, t)$ to approach normal-diffusion-like behavior and $P_C(t)$ to approach $-d/2$ faster for less glassy systems (more weakly interacting, lower ϕ , higher T) and viceversa. Indeed, $P_C(t)$ ‘‘overshoots’’ its asymptotic value of $-d/2$ for $10\tau_\alpha \lesssim t < 100\tau_\alpha$, and this overshooting increases with ϕ for HARD (Fig. 1, top panel inset) and increases at lower T for KALJ (Fig. 1, bottom panel inset).

IV. FOUR-POINT FUNCTIONS: DECOMPOSITION AND LONG-TIME BEHAVIOR

A. Contributions to the Four-Point Functions

To characterize the dynamical heterogeneity, we compute [18] the four-point dynamic structure factor $S_4(\vec{q}, t)$ [1, 7],

$$S_4(\vec{q}, t) \equiv \frac{1}{N} \sum_{n, n'=1}^N \left\langle w_n(t) w_{n'}(t) e^{[i\vec{q} \cdot (\vec{r}_n(0) - \vec{r}_{n'}(0))]} \right\rangle - \delta_{\vec{q}, 0} N C^2(t) \quad (1)$$

The full lines in Fig. 2 show $S_4(\vec{q}, t)$. The two top panels correspond to time around $20\tau_\alpha$ for both systems. Let’s consider intermediate values of q , $\xi_4^{-1} \ll q \ll q_0 \approx 2\pi/r_{NN}$, where q_0 is the location of the main peak of the static structure factor $S(q)$, and r_{NN} is the typical nearest neighbor distance. We find that at $t \approx 20\tau_\alpha$, for $\xi_4^{-1} \ll q \ll q_0$, $S_4(\vec{q}, t)$ decays to a plateau value $\chi_{4,b}$ which is almost half of its maximum χ_4 at the origin. By contrast, at $t \approx \tau_\alpha$, the q -independent background $\chi_{4,b}$ is very small compared to the peak value χ_4 , as shown in the bottom two panels of the same figure. A q -independent background in Fourier space suggests that there are uncorrelated displacements of particles in position space, giving rise to $S_4^{\text{sp}}(\vec{q}, t) \neq 0$. As discussed in [17], $S_4^{\text{sp}}(\vec{q}, t)$ only contains contributions from same particle ($n = n'$) terms in Eq. (1), and by neglecting a small collective relaxation contribution to those terms we obtain

$$S_4^{\text{sp}}(\vec{q}, t) = \chi_4^{\text{sp}}(t) \approx \frac{1}{N} \sum_{n=1}^N \langle (w_n(t) - \langle w_n(t) \rangle)^2 \rangle = C(t) - C^2(t). \quad (2)$$

The initial density contribution $S_4^{\text{st}}(\vec{q}, t)$ is obtained [17] by replacing the microscopic overlap $w_n(t)$ by its average $C(t) = \langle w_n(t) \rangle$ in Eq. (1),

$$\begin{aligned} S_4^{\text{st}}(\vec{q}, t) &\equiv \frac{1}{N} \sum_{n, n'=1}^N C^2(t) \langle e^{[i\vec{q} \cdot (\vec{r}_n(0) - \vec{r}_{n'}(0))]} \rangle - \delta_{\vec{q}, 0} N C^2(t) \\ &= C^2(t) [S(\vec{q}) - \delta_{\vec{q}, 0} N]. \end{aligned} \quad (3)$$

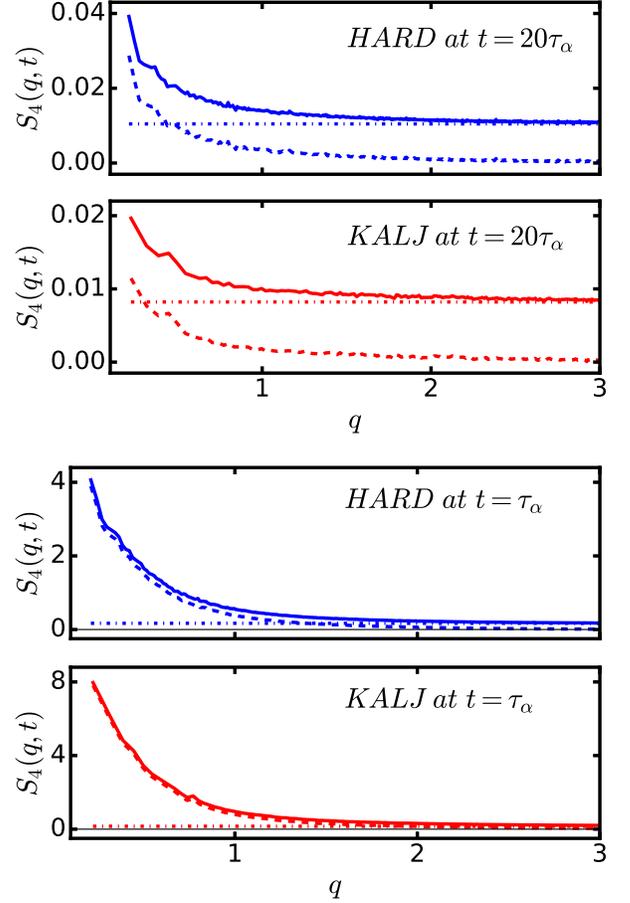


FIG. 2: Decomposition of $S_4(\vec{q}, t)$ (full lines): collective relaxation part $S_4^{\text{cr}}(\vec{q}, t)$ (dashed lines), and background term $\chi_{4,b}(t)$ (dash-dotted lines). First panel from top: HARD at $\phi = 0.57$, with $t = 20\tau_\alpha$. Second panel: KALJ at $T = 0.55$, with $t = 20\tau_\alpha$. Third panel: HARD at $\phi = 0.57$, with $t = \tau_\alpha$. Bottom panel: KALJ at $T = 0.55$, with $t = \tau_\alpha$.

For $q \ll q_0 \approx 2\pi/r_{NN}$, the static structure factor is weakly dependent on q , and $S(q) \approx \lim_{q \rightarrow 0} S(q) = N^{-1} \langle (\delta N)^2 \rangle$. In Reference [17] it is argued that, for $\xi_4^{-1}, q \ll 2\pi/r_{NN}$, the q -dependence of all contributions except S_4^{cr} can be neglected, so that

$$S_4(\vec{q}, t) \approx S_4^{\text{cr}}(\vec{q}, t) + \chi_{4,b}(t), \quad \text{with} \quad (4)$$

$$\begin{aligned} \chi_{4,b}(t) &\equiv \chi_4^{\text{sp}}(t) + \lim_{q \rightarrow 0} S_4^{\text{st}}(\vec{q}, t) + \lim_{q \rightarrow 0} S_4^{\text{mc}}(\vec{q}, t) \\ &\approx C(t) + [N^{-1} \langle (\delta N)^2 \rangle - 1] C(t)^2 \equiv \chi_{4,b}^{(0)}(t). \end{aligned} \quad (5)$$

To extract the collective relaxation part $S_4^{\text{cr}}(\vec{q}, t)$ from the data, we use Eq. (4). Fig. 2 shows this decomposition: $S_4(\vec{q}, t)$ is shown with full lines, the q -independent background $\chi_{4,b}(t)$ is shown with dash-dotted lines, and $S_4^{\text{cr}}(\vec{q}, t)$ is shown with dashed lines.

To characterize the collective relaxation part of the four-point function, $S_4^{\text{cr}}(\vec{q}, t)$, we fitted it with a slightly generalized version of the Ornstein-Zernike functional form, motivated by results from inhomogeneous mode coupling theory [19],

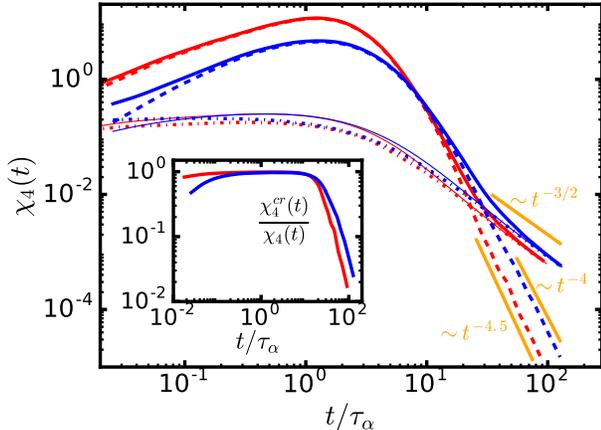


FIG. 3: Dynamic susceptibility decomposition for HARD at $\phi = 0.57$ (blue) and KALJ at $T = 0.55$ (red). Main panel: total dynamic susceptibility $\chi_4(t)$ (solid lines), collective relaxation part $\chi_4^{\text{cr}}(t)$ (dashed lines), background term $\chi_{4,b}(t)$ (dashed-dotted lines), and its leading order approximation $\chi_{4,b}^{(0)}(t)$ (thin full lines). Power law time dependences (orange full lines) shown for comparison with long time asymptotic behavior for: $\chi_{4,b}(t) \sim t^{-3/2}$, $\chi_4^{\text{cr}}(t)$ for HARD ($\sim t^{-4} \ll t^{-3}$), and $\chi_4^{\text{cr}}(t)$ for KALJ ($\sim t^{-4.5} \ll t^{-3}$). Inset: $\chi_4^{\text{cr}}(t)/\chi_4(t)$.

which has been used in [5, 20, 21] (see App. A for more details on the fitting procedure). The fitting form for $S_4^{\text{cr}}(\vec{q}, t)$ reads

$$S_4^{\text{cr}}(\vec{q}, t) = \frac{\chi_4^{\text{cr}}(t)}{1 + [\xi_4^{\text{cr}}(t)]^2 q^2 + [c(t)]^2 q^4}, \quad (7)$$

where $\chi_4^{\text{cr}}(t)$ is the collective relaxation part of the dynamic susceptibility, $\xi_4^{\text{cr}}(t)$ is the four-point dynamic correlation length, and $c(t)$ is an additional parameter characterizing the quartic contribution. From this point on we use the notation $\xi_4^{\text{cr}}(t)$ for this correlation length, to emphasize that it is extracted from the collective relaxation part of the four-point function.

The presence of additional contributions beyond the one due to collective relaxation cannot be ignored, particularly for long times $t \gtrsim 10\tau_\alpha$. It is shown in Appendix B that attempting to fit the data in that time regime without taking into account those additional contributions leads to very poor fits and to substantial systematic errors in the determination of the dynamic susceptibility $\chi_4(t)$ and the dynamic correlation length $\xi_4^{\text{cr}}(t)$.

B. Long-time behavior of the dynamic susceptibility $\chi_4(t)$ and the single particle and collective relaxation contributions

By taking the $q \rightarrow 0$ limit of Eq. (4), we obtain the decomposition $\chi_4(t) \approx \chi_4^{\text{cr}}(t) + \chi_{4,b}(t)$ for the dynamic susceptibility. Fig. 3 shows $\chi_4(t)$ (full lines), $\chi_4^{\text{cr}}(t)$ (dashed lines), $\chi_{4,b}(t)$ (dash-dotted lines), and $\chi_{4,b}^{(0)}(t)$ (thin full lines), in the cases of HARD for packing fraction $\phi = 0.57$ (blue) and

KALJ for temperature $T = 0.55$ (red). For both systems, the collective relaxation part $\chi_4^{\text{cr}}(t)$ of the dynamic susceptibility increases with time to a peak value $\chi_4^{\text{cr,max}}$, which may be interpreted to indicate the maximum correlated volume of the fluctuating region. The approximation $\chi_{4,b}(t) \approx \chi_{4,b}^{(0)}(t)$ (Eq. (6)) becomes asymptotically exact for $t \gg \tau_\alpha$, and the biggest discrepancy between the two quantities is $\chi_{4,b}(t)/\chi_{4,b}^{(0)}(t) \approx 0.7$ when $\chi_4^{\text{cr}}(t)$ is near its peak, i.e. when the collective relaxation corrections neglected in Eq. (6) are largest [17]. For long times, $t \gg \tau_\alpha$, $\chi_4^{\text{cr}}(t)$ decreases as a t^{-3} power law or faster, while $\chi_{4,b}(t)$ - which in this time regime is dominated by $\chi_4^{\text{sp}}(t) \approx C(t)$ - also decreases but as a much slower power law $\sim t^{-3/2}$ [17]. Thus there is a crossover between a shorter time regime where the collective relaxation contribution dominates and a longer time regime where the single particle contribution dominates. We define the crossover time $\tau_{\chi_4^{\text{cr}}/\chi_4=1/2}$ as the time when $\chi_4^{\text{cr}}(t)/\chi_4(t) = 1/2$. We find that $\tau_{\chi_4^{\text{cr}}/\chi_4=1/2} \sim 40\tau_\alpha$ for HARD at $\phi = 0.57$ and $\tau_{\chi_4^{\text{cr}}/\chi_4=1/2} \sim 25\tau_\alpha$ for KALJ at $T = 0.55$. The inset of Fig. 3 shows the ratio $\chi_4^{\text{cr}}(t)/\chi_4(t)$ for the same cases as in the main panel. The ratio is close to unity for times up to about $20\tau_\alpha$ and then it decreases rapidly, becoming roughly two orders of magnitude smaller by $t \sim 100\tau_\alpha$. For other values of the control parameters, as long as the system is close to the mode-coupling crossover, the behavior of $\chi_4^{\text{cr}}(t)/\chi_4(t)$ is very similar [22].

As the system approaches the glass transition at fixed rescaled time t/τ_α , the collective relaxation contribution χ_4^{cr} grows strongly, while the background contribution $\chi_{4,b}$, which, to a good approximation, can be computed in terms of $C(t)$ and $S(q)$ (Eq. (6)), shows little if any change [17]. Thus we expect both the ratio $\chi_4^{\text{cr}}(t)/\chi_4(t)$ at fixed t/τ_α [22] and the rescaled crossover time $\tau_\alpha^{-1} \tau_{\chi_4^{\text{cr}}/\chi_4=1/2}$ (Fig. 4) to increase. Both increases are indeed observed in our data, and in fact we find $\tau_{\chi_4^{\text{cr}}/\chi_4=1/2} \sim \tau_\alpha^{1+p}$, with $p \approx 0.40$ for HARD and $p \approx 0.15$ for KALJ.

C. Long-time behavior of the correlation length $\xi_4(t)$ for the binary hard-sphere system

We now turn to the determination of the dynamic correlation length. The behavior of the dynamic correlation length $\xi_4(t)$ in glass-forming liquids for times $t > \tau_\alpha$ has been controversial. In one early study [1], it was found that the time dependence of the dynamic correlation length roughly follows that of the dynamic susceptibility. Other studies, in a variety of glass-forming models, have found monotonous increasing growth of the dynamic correlation length as time increases [8], possibly with a plateau [23, 24] starting at a time longer than both τ_α and the time when χ_4 reaches its peak. Monotonous growth of the dynamic correlation length with time difference was also found in aging glassy systems [9, 25]. In Fig. 5, we show results for $\xi_4^{\text{cr}}(t)$ as a function of t/τ_α for times up to $80\tau_\alpha$ for the HARD system at packing fractions $\phi = 0.50, 0.52, 0.55, 0.57, 0.58$. As discussed in [5], the dynamic correlation length grows approximately logarithmically

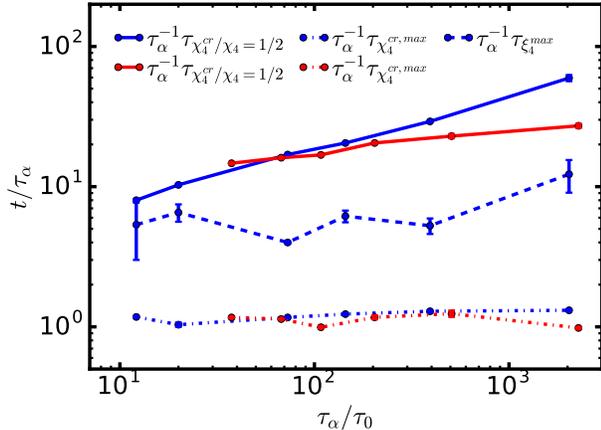


FIG. 4: Rescaled timescales for HARD (blue) and KALJ (red) as functions of the rescaled relaxation time τ_α/τ_0 ([16]): rescaled crossover time $\tau_\alpha^{-1}\tau_{\chi_4^{\text{cr}}/\chi_4=1/2}$ (solid lines); rescaled time $\tau_\alpha^{-1}\tau_{\xi_4^{\text{max}}}$ at which the dynamic correlation length ξ_4^{cr} becomes maximum (dashed lines); rescaled time $\tau_\alpha^{-1}\tau_{\chi_4^{\text{cr,max}}}$ at which the collective dynamic susceptibility χ_4^{cr} becomes maximum (dash-dotted lines). Following Ref. [16], the parameter τ_0 ($\tau_0 = 70$ for HARD and $\tau_0 = 1/15$ for KALJ) is used so that relaxation times can be compared across different systems.

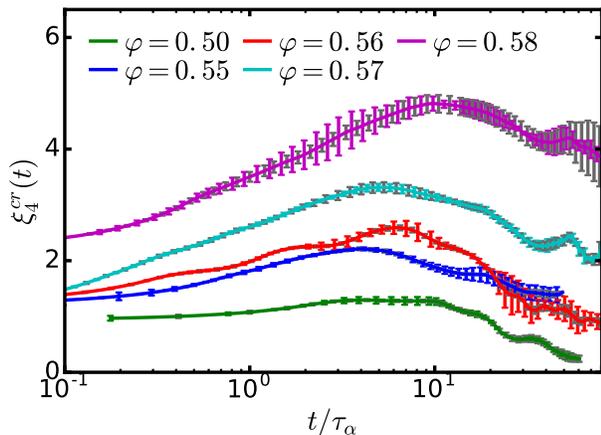


FIG. 5: Correlation length $\xi_4^{\text{cr}}(t)$ as a function of t/τ_α for HARD system at packing fractions $\phi = 0.50, 0.55, 0.56, 0.57, 0.58$. The grey error bars represent statistical errors in the determination of $\xi_4^{\text{cr}}(t)$ for a fixed fitting interval. The error bars in the same color as the curve represent the range of variation in the determination of $\xi_4^{\text{cr}}(t)$ as the fitting interval is changed (see App. A). For clarity, each type of error bar is showed for one out of every 10 data points.

with times and reaches a maximum value $\xi_{\text{max}} > \xi_4^{\text{cr}}(\tau_\alpha)$ at a time $\tau_{\xi_4^{\text{max}}} > \tau_\alpha$. The approach introduced in this work allows us to now explore times $t \gg \tau_{\xi_4^{\text{max}}}$. We find that for $\tau_{\text{max}} < t \lesssim 80\tau_\alpha$, our results for $\xi_4^{\text{cr}}(t)$ are noisy, but they show a general trend to decrease as time increases.

V. SUMMARY

In this paper we have discussed the behavior of the average overlap and of the four-point functions in models of glass-forming liquids, with emphasis on times much longer than the α -relaxation time. We have presented simulation results for two models of 3D glass forming liquids: a binary hard-sphere model and a Kob-Andersen Lennard-Jones model. We have showed that at very long times the average overlap $C(t)$ probing the similarity between an initial and a final state separated by a time interval t decays as a power law $C(t) \sim t^{-d/2}$. This is much slower than the stretched exponential behavior $C(t) \sim e^{-(t/\tau)^\beta}$ previously observed at times within one or two orders of magnitude of the α -relaxation time τ_α .

We have also introduced a decomposition of the four point dynamic structure factor $S_4(\vec{q}, t)$ as the sum of four parts: S_4^{cr} (collective relaxation fluctuations); S_4^{sp} (*single-particle* fluctuations); S_4^{st} (initial density correlations); and S_4^{mc} (interplay between initial density fluctuations and collective relaxation fluctuations). Although valid at all times, this decomposition is particularly useful to enable the study of dynamical heterogeneities at $t \gg \tau_\alpha$. We argued that in this decomposition, all contributions except the collective relaxation one can be approximated as q -independent for $q \ll 2\pi/r_{\text{NN}}$, thus explaining the presence of a flat background term $\chi_{4,b}(t)$ in the q -dependence of the four-point function, as made explicit in Eq. 4. This structure allowed us to subtract the background from $S_4(\vec{q}, t)$ and thus recover the collective relaxation contribution S_4^{cr} . We have also shown that a simple approximate expression depending only on the overlap $C(t)$ and the static structure factor $S(\vec{q})$ reproduces very well the time dependence of the background term, particularly for times $t \gg \tau_\alpha$.

We have found that for higher ϕ (lower T), S_4^{cr} is between one and two orders of magnitude bigger than the other contributions at $t \sim \tau_\alpha$, but for $t \gg \tau_\alpha$ the single particle contribution $S_4^{\text{sp}} \approx C(t) \propto t^{-d/2}$ dominates against all others, because $S_4^{\text{cr}} + S_4^{\text{st}} + S_4^{\text{mc}} \lesssim \text{const } t^{-d}$. We have also used the decomposition of $S_4(\vec{q}, t)$ to address the controversy regarding $\xi_4(t)$ for $t \gg \tau_\alpha$: for a binary hard-sphere mixture, we found that $\xi_4(t)$ is maximum at $t = \tau_{\xi_4^{\text{max}}} \sim 4 - 15\tau_\alpha$ and then generally decreases up to at least $t \sim 80\tau_\alpha$.

The decomposition introduced here enables substantial further progress in the understanding of dynamical heterogeneities in glassy systems. A first application [26] will introduce an explicit formula for $S_4^{\text{cr}}(\vec{q}, t)$ in terms of the average correlation function $C(t)$ and a two-point correlation function $s(\vec{q}, t)$ of the local relaxation rates. This two-point function $s(\vec{q}, t)$ probes the collective relaxation dynamics and makes quantitative the qualitative description of dynamic heterogeneity in terms of slow and fast regions. It also provides a method to obtain τ_{ex} from $S_4(\vec{q}, t)$ [26], and allows to obtain explicit predictions for $\chi_4(t)$ under various assumptions regarding the decay of the relaxation rate fluctuations. Potential applications of the same ideas also include, among others, the introduction of other observables that are better able to probe the relaxation rate fluctuations, and the study of spatiotemporal correlations of local relaxation rates in aging systems.

VI. ACKNOWLEDGEMENT

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Appendix A: Fitting Method

To extract the collective relaxation part of the four-point function, $S_4^{\text{cr}}(\vec{q}, t)$ and the q -independent background $\chi_{4,b}$, we fitted $S_4(\vec{q}, t)$ by combining Eqs. (4) and (7). The complete fitting form for $S_4(\vec{q}, t)$ reads

$$S_4(\vec{q}, t) = \frac{\chi_4^{\text{cr}}(t)}{1 + [\xi_4^{\text{cr}}(t)]^2 q^2 + [c(t)]^2 q^4} + \chi_{4,b}(t). \quad (\text{A1})$$

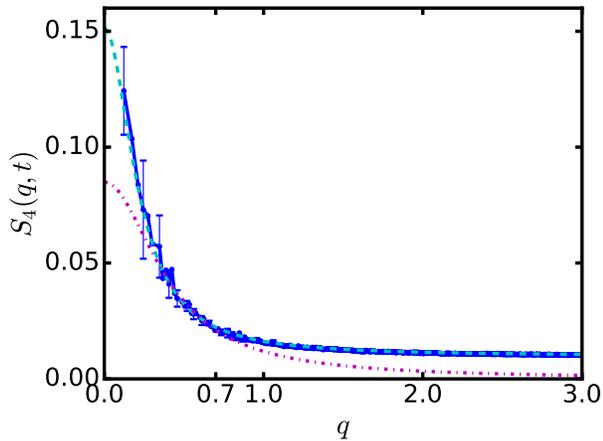


FIG. 6: Effects of allowing for a background contribution to $S_4(\vec{q}, t)$ due to single particle fluctuations and initial density fluctuations. $S_4(\vec{q}, t)$ as a function of q for HARD at $\varphi = 0.58, t = 20\tau_\alpha$: data (symbols with error bars joined by full line), fit allowing for a q -independent background (dashed line), fit not allowing for a background contribution (dot-dashed line).

The form for $S_4(\vec{q}, t)$ is fitted for each time separately in a two-step procedure. In the first step, a wide fitting range is used: $0 < q < q_M$ with $q_M \sim q_0/2 \approx \pi/r_{NN}$. We choose $q_M = 3.0$ and $q_M = 3.5$ for HARD and KALJ respectively. In this first step, the q -independent background $\chi_{4,b}$ is determined. In the second step, a much narrower range $0 < q < q_m \ll q_M$ is used, and $\chi_{4,b}$ is now kept as a fixed value as determined in the first step. The fitting ranges for the second fit are $0 < q < q_m = 0.7$ and $0 < q < q_m = 0.8$ for HARD and KALJ respectively. The four independent simulation runs are fitted separately for each value of the control parameter. The average results and statistical errors of the fits are calculated as the average and the standard deviation of the average from those four fits. The LOESS smoothing technique (Ref. [27]) is used to reduce noise in the reported results for $\chi_4^{\text{cr}}(t)$, $\xi_4^{\text{cr}}(t)$, and $c(t)$. The values of $\xi_4^{\text{cr}}(t)$ for HARD determined with this procedure are somewhat sensitive to the range of wavevectors used in the second step of the fitting procedure. To quantify

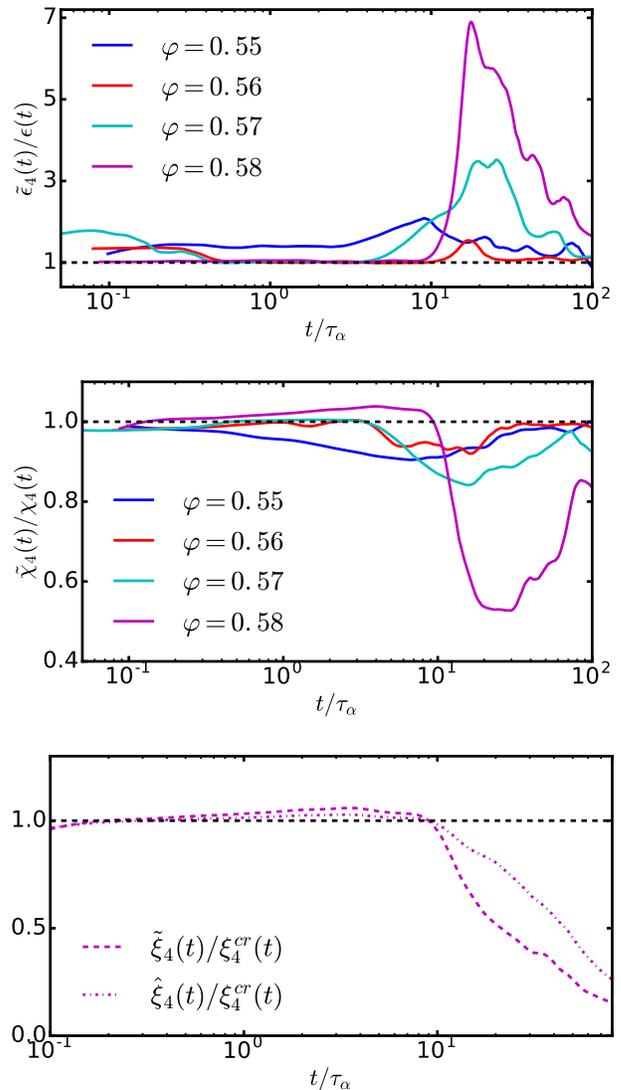


FIG. 7: Effects of allowing for a q -independent background contribution $\chi_{4,b}(t)$ to $S_4(\vec{q}, t)$ due to single particle fluctuations and initial density fluctuations, in the case of HARD. $\chi_4(t)$ [$\tilde{\chi}_4(t)$] is the dynamic susceptibility, $\xi_4^{\text{cr}}(t)$ [$\tilde{\xi}_4(t)$] is the dynamic correlation length, and $\epsilon(t)$ [$\tilde{\epsilon}(t)$] is the rms fitting error per degree of freedom in the interval $0 < q < q_\epsilon = 0.4$, obtained from a fit of $S_4(\vec{q}, t)$ vs q allowing [not allowing] for a background contribution. $\tilde{\xi}_4(t)$ is the dynamic correlation length obtained from the following procedure: first, $\chi_4(t)$ is obtained from a fit allowing for a nonzero background; after that, a fit is performed where $\chi_4(t)$ is fixed to the value obtained before, but the background is constrained to be zero. Top panel: $\tilde{\epsilon}(t)/\epsilon(t)$ vs time t , for $\varphi = 0.55, 0.56, 0.57, 0.58$. Middle panel: $\tilde{\chi}_4(t)/\chi_4(t)$ vs time t , for $\varphi = 0.55, 0.56, 0.57, 0.58$. Bottom panel: $\tilde{\xi}_4(t)/\xi_4^{\text{cr}}(t)$ and $\hat{\xi}_4(t)/\xi_4^{\text{cr}}(t)$ vs time t , for $\varphi = 0.58$.

the size of this effect, the second step discussed above is performed for $q_m \in \{0.6, 0.7, 0.8, 0.9\}$, and the systematic error bars due to the choice of q_m , which are shown in Fig. 5, are evaluated for each time and packing fraction as the standard deviation of the average of $\xi_4^{\text{cr}}(t)$ over those four determina-

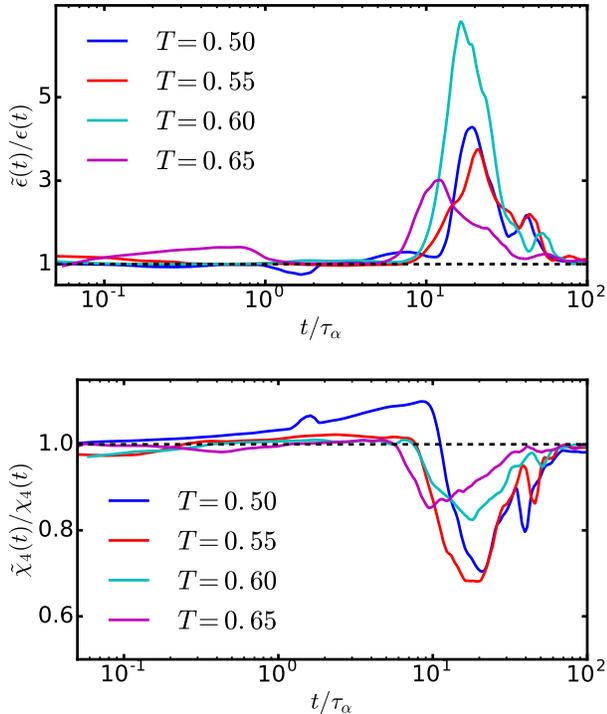


FIG. 8: Effects of allowing for a q -independent background contribution $\chi_{4,b}(t)$ to $S_4(\vec{q}, t)$ due to single particle fluctuations and initial density fluctuations, in the case of KALJ. $\chi_4(t)$ [$\tilde{\chi}_4(t)$] is the dynamic susceptibility and $\epsilon(t)$ [$\tilde{\epsilon}(t)$] is the rms fitting error per degree of freedom in the interval $0 < q < q_\epsilon = 0.55$, obtained from a fit of $S_4(\vec{q}, t)$ vs q allowing [not allowing] for a background contribution. Top panel: $\tilde{\epsilon}(t)/\epsilon(t)$ vs time t , for $T = 0.50, 0.55, 0.60, 0.65$. Bottom panel: $\tilde{\chi}_4(t)/\chi_4(t)$ vs time t , for $T = 0.50, 0.55, 0.60, 0.65$.

tions.

Appendix B: Effects of the presence of the q -independent background $\chi_{4,b}(t)$ on the determination of $\chi_4(t)$ and $\xi_4^{\text{cr}}(t)$

The presence of the background term $\chi_{4,b}(t)$, due mostly to single particle fluctuations and to initial density fluctuations, has a strong effect on the determination of $S(\vec{q}, t)$ for small wavevector q , and consequently on the determination of $\chi_4(t)$ and $\xi_4^{\text{cr}}(t)$. Fig. 6 shows an example of those effects by comparing the determination of $S_4(\vec{q}, t)$ as a function of q for HARD at $\phi = 0.58, t = 20\tau_\alpha$ by using two different methods: one is a fit that allows for a q -independent background $\chi_{4,b}(t) \neq 0$, consistent with the decomposition introduced in this work; the other is a fit that imposes the condition $\chi_{4,b}(t) = 0$. It is clear that outside a narrow range of q values where the two fits are equivalent, the one that allows for a nonzero flat background is a much better representation of the data. Figs. 7 and 8 presents a more systematic demonstration of the effects of the background term, for the hard-sphere system and the Kob-Andersen Lennard-Jones system respectively. In these figures, $\chi_4(t)$ [$\tilde{\chi}_4(t)$] is the dynamic suscepti-

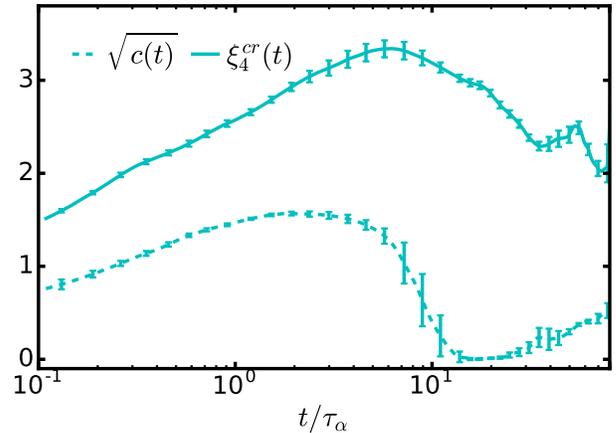


FIG. 9: Time dependence of quartic term coefficient $\sqrt{c(t)}$ in the four-point function fit, for HARD at $\phi = 0.57$. $\xi_4^{\text{cr}}(t)$ is shown for comparison, since both quantities have dimension of length.

bility, $\xi_4^{\text{cr}}(t)$ [$\tilde{\xi}_4(t)$] is the dynamic correlation length, and $\epsilon(t)$ [$\tilde{\epsilon}(t)$] is the rms fitting error per degree of freedom in the interval $0 < q < q_\epsilon$, obtained from a fit of $S_4(\vec{q}, t)$ vs q allowing [not allowing] for a background contribution. In each figure, the first panel from the top shows $\tilde{\epsilon}(t)/\epsilon(t)$ vs t , and the second panel shows $\tilde{\chi}_4(t)/\chi_4(t)$ vs time t . In the case of HARD, there is a third panel that shows $\tilde{\xi}_4(t)/\xi_4^{\text{cr}}(t)$ and $\tilde{\xi}_4(t)/\xi_4^{\text{cr}}(t)$ vs time t , for $\phi = 0.58$. Here $\tilde{\xi}_4(t)$ is the dynamic correlation length obtained from the following procedure: first, $\chi_4(t)$ is obtained from a fit allowing for a nonzero background; after that, $\chi_4(t)$ is kept fixed and a new fit is performed with the background constrained to be zero, which produces the value of $\tilde{\xi}_4(t)$. We notice that in all cases the rms fitting error is either the same or smaller if the background term is allowed. In most cases the difference becomes largest for times t in the interval $10\tau_\alpha < t < 100\tau_\alpha$. For example, the ratio $\tilde{\epsilon}(t)/\epsilon(t)$ is in the range of 2–8 for HARD at $\phi = 0.57, 0.58$ at most times in that interval. For the same time range, the effect on the determination of the dynamic susceptibility is particularly large for HARD at $\phi = 0.58$, namely a reduction of up to a factor of ≈ 2 if the background is assumed to be zero. For KALJ, the effect is strongest in the same time range, with a maximum reduction by a factor of ≈ 1.4 for $T = 0.50, 0.55$. For the correlation length, there is a clear reduction in the value measured if the background is ignored, which starts to be noticeable at $t \approx 10\tau_\alpha$, and becomes gradually stronger as time grows. Although slightly weaker for $\tilde{\xi}_4(t)$ than for $\tilde{\xi}_4(t)$, the effect is very similar in both cases, which shows that it cannot be avoided just by constraining the fit by fixing a better determined value of the dynamical susceptibility.

Appendix C: Quartic term in the generalized Ornstein-Zernicke form.

The quartic coefficient $c(t)$ included in the denominator of the generalized Ornstein-Zernicke fitting form in Eq. 7 allows

the definition of a length $\sqrt{c(t)}$, which turns out to be generally smaller than $\xi_4^{\text{cr}}(t)$, as shown in Fig. 9.

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