

Structure Dominates Localization of Tracers Within Aging Nanoparticle Glasses

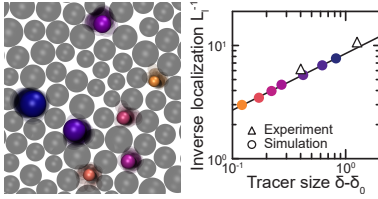
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Abstract: We investigate the transport and localization of tracer probes in a glassy matrix as a function of relative size using dynamic x-ray scattering experiments and molecular dynamics simulations. The quiescent relaxations of tracer particles evolve with increasing waiting time t_w . The corresponding relaxation times increase exponentially at small t_w and then transition to a power-law behavior at longer t_w . As tracer size decreases, the aging behavior weakens and the particles become less localized within the matrix until they delocalize at a critical size ratio $\delta_0 \approx 0.38$. Localization does not vary with sample age even as the relaxations slow by approximately an order of magnitude, suggesting that matrix structure controls tracer localization.



Transport of small molecules, tracers, and particles within disordered glassy matrices can destabilize biological molecules in harsh environments,^{1,2} govern the production of optically active nanoparticles,³ affect the performance of membranes,^{4,5} and introduce functionality in polymer nanocomposites.^{6–12} In each scenario, understanding how matrix structure and dynamics¹³ affect particle transport is essential for predicting the properties of these composite materials. Localization of particles within glasses,¹⁴ for example, depends on particle size^{15–17} as well as on void structure^{18,19} and slow dynamics^{16,20} of the matrix. Because tracer relaxations may occur on significantly shorter timescales than those of the matrix, this localization transition can exhibit strong similarities to dynamic arrest within a random matrix of immobile obstacles.^{21–25}

Fundamental understanding of tracer transport and localization within glassy matrices, however, is complicated by the fact that glasses age over time. Aging is a universal phenomenon in glasses, occurring in metallic and inorganic glasses,^{26,27} polymers,²⁸ and colloids²⁹ and manifesting in macroscopic changes such as shrinkage³⁰ and increases in mechanical properties.³¹ Microscopically, the dynamics in glasses evolve after the sample is quenched out-of-equilibrium, slowing and becoming more heterogeneous with aging time t_w .^{32–34} In the aging regime, heterogeneous stress relaxations^{27,35} often lead to hyperdiffusive matrix dynamics.^{36–38} Surprisingly, the mechanical and dynamical

changes occur with only minor changes in two-body metrics of matrix structure over time.^{34,39,40} Although molecular¹³ or particulate^{40–43} tracers are commonly used to probe glassy behavior, how their dynamics depend on the structure and dynamics of the glassy matrix remains incompletely understood. An aging matrix whose dynamics evolve but whose structure remains effectively constant provides a model system by which to investigate the relative roles of matrix structure and dynamics on transport of tracer particles in heterogeneous complex media.

In this Letter, we investigate the transport and localization of tracer particles in aging glassy nanoparticle matrices, using x-ray photon correlation spectroscopy and event-driven molecular dynamics (MD) to probe a complementary range of time scales. We characterize the dynamics of tracers whose size is smaller than or comparable to that of the matrix particles. In both experiment and simulation the tracer relaxations are hyperdiffusive, suggesting that tracers probe relaxation of internal stresses in the matrix. We observe two distinct aging regimes for both matrix and tracers, indicating that the relaxations of the tracers couple to those of matrix particles. The localization length quantifies the degree of coupling and decreases as the tracer to matrix particle size ratio δ is reduced. This length scale diverges at $\delta_0 \approx 0.38$, near the value at which tracers exhibit anomalous collective transport in glassy matrices,^{16,20} but does not depend on matrix age. The lack of change in the localization length across a range of waiting times relative to relaxation time $10^{-4} \leq t_w / \tau \leq 10^3$ suggests that structure strongly influences the transition from diffusion to localization in glassy materials, even though matrix relaxation enables anomalous diffusive transport of finite-sized tracers. By connecting tracer size to localization, we provide a basis from which to predict transport properties through slowly relaxing and heterogeneous materials.

Polystyrene particles (Thermo-Fisher Scientific) with diameter $\sigma = 60$ nm and polydispersity 10% were acquired as an aqueous suspension with volume fraction $\phi = 0.1$. Silica particles from nanoComposix with nominal diameters σ_{nom} of 20 nm and 60 nm and polydispersities $< 10\%$ were acquired as aqueous suspensions with $\phi = 0.0023$ and 0.0046 , respectively. To account for electrostatic repulsions, which modify the effective particle size,^{44–46} we use the Barker-Henderson formalism to map the tracers onto a hard-sphere model (Supporting Information). This procedure yields effective hard sphere diameters of $\sigma_t = 47 \pm 4$ and 99 ± 2 nm for the nominally sized 20 and 60 nm tracers, respectively. Normalizing these hard-sphere sizes by the polystyrene matrix diameter gives $\delta \equiv \sigma_t / \sigma = 0.78 \pm 0.06$ and 1.65 ± 0.03 , respectively. Polystyrene and silica suspensions were pipetted in appropriate ratios into an Amicon microcentrifuge filter tube

with a 10 kDa cutoff and centrifuged at $3000 \times g$ for 30 minutes. The centrifuge tube was then refilled with additional stock suspensions and centrifuged again to produce a glassy material near random close packing ($\phi \approx 0.64 \pm 0.03$)⁴⁷ (Supporting Information) with silica to polystyrene volume ratio of 0.002. Sample age is characterized by the waiting time t_w , the elapsed duration from the end of centrifugation. The glassy sample was then placed into a 2-mm thick aluminum sample holder, sealed with Kapton windows to prevent evaporation, and attached to a copper block with Peltier to regulate temperature. Small-angle x-ray scattering (SAXS) indicated that the tracers were well dispersed in the glass (Supporting Information). X-ray photon correlation spectroscopy (XPCS) data were collected at a frame rate of 1 s^{-1} on the 8-ID-I beamline at the Advanced Photon Source at Argonne National Laboratory over a wavevector range that depended on scattering intensity so that $0.003 \text{ \AA}^{-1} \leq q \leq 0.009 \text{ \AA}^{-1}$ for nominal 60 nm tracers and $0.006 \text{ \AA}^{-1} \leq q \leq 0.017 \text{ \AA}^{-1}$ for nominal 20 nm tracers.

We also performed complementary event-driven MD simulations to investigate tracer diffusion in aging glass matrices. Fundamental units of σ , m , and $1/k_B$ were adopted in the simulations for length, mass, and temperature respectively. The corresponding unit of simulation time is $t_s \equiv \sigma(m/k_B T)^{1/2}$. The glass matrix was modeled as a 35-component mixture of $N = 2048$ hard-spheres.^{48,49} The composition was chosen to yield a discrete normal distribution of particle sizes (mean 1.0, std. 0.1), matching the ca. 10% polydispersity of the experimental system. Similarly, a three-component mixture of hard-sphere tracers with 5% polydispersity was embedded in the matrix at 0.002 volume fraction, resulting in at least 40 tracers per simulation box. The simulations were performed at $T = 1$, and the mass for matrix particles of average size was set to unity (i.e., $m = 1$), yielding a density $m\sigma^{-3} = 1$. Masses of the remaining matrix species and tracers were scaled to obtain the same mass density for each particle in the system. The matrix was compressed in a cubic simulation cell to achieve a final packing fraction $\phi = 0.59$. Simulations at higher volume fractions did not relax on accessible time scales. We note, however, that aging behavior is qualitatively similar for volume fractions above and below the glass transition.⁵⁰ We correspondingly define t_w as the elapsed duration after end of the compression.^{48,51,52} For each value of $\delta = [0.5, 1.2]$ examined, reported results were averaged over at least 72 independent simulations, each initiated from a new matrix configuration. This range of δ was chosen to extend experimental results towards a critical size $\delta_0 = 0.35 \pm 0.05$ associated with anomalous dynamics.¹⁶

Experimentally, the high scattering contrast of the silica tracer particles in x-rays, relative to the other components, ensures that the intensity correlation function g_2 measures the relaxations of tracer particles within the glassy matrix of polystyrene nanoparticles. The experimental g_2 values and those calculated from simulations decay as a function of time and depend on both δ and t_w (Fig. 1). To quantify the tracer dynamics, we fit experimental data according to $g_2 = 1 + Bg_1^2 + \varepsilon$, where B is the global experimental contrast related to beam geometry and coherency, $g_1 = A(q)\exp[-(t/\tau)^\beta]$ is the self-intermediate scattering function, $A(q)$ is a wavevector-dependent contrast, β is a positive fitting exponent, and ε captures any residual noise. Because g_2 curves from simulations have less statistical noise, we determine $A(q)$ and $\tau = A(q)/e$ by reading

directly from the individual curves.

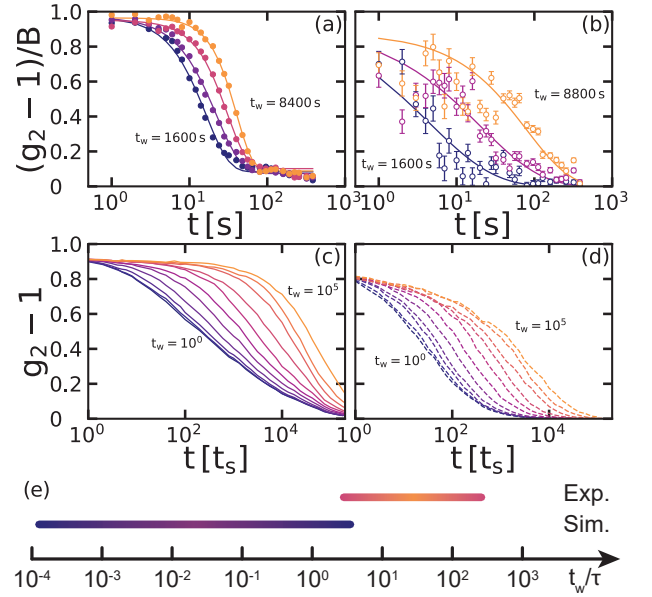


Figure 1. Normalized intensity correlation function $(g_2 - 1)/B$ at a normalized wavevector $q\sigma = 3.5$ as a function of time t for different t_w . (a,b) Experimental data for tracers of size (a) $\delta = 1.65$ and (b) $\delta = 0.78$. (c,d) Simulation data for tracers of size (c) $\delta = 1$ and (d) $\delta = 0.65$. Curves in (a,b) are best fits to stretched exponential functions. (e) Schematic of ratio of waiting time to relaxation time t_w/τ in experiments (yellow) and simulations (blue).

Using simulations and experiments, we measure autocorrelation curves for tracers with various δ across many orders of magnitude in t_w (Fig. 1). In simulation, the computational cost of the calculations limits the maximum time scale that can be explored. In experiment, by contrast, the time necessary to load the sample into the beamline places a lower bound on t_w . Simulation and experiment thus probe complementary ranges of t_w/τ (Fig. 1). As samples age, relaxations in both experiments and simulations become slower, as is common for glassy materials.⁵³ In experiments, the relaxations of the large tracers ($\delta = 1.65$) are compressed with $\beta > 1$, indicating that these large tracers move hyperdiffusively. Hyperdiffusive relaxations are commonly observed in glassy systems with either attractive or repulsive interactions and are attributed to anisotropic stress relaxations^{27,30,35,37,38,54} or to relaxations occurring in regions that are power-law distributed in size.^{55,56} In both experiments and simulations, the relaxations of smaller tracers ($\delta < 1.65$) are stretched with $\beta < 1$ rather than compressed. Experimental g_2 curves for $\delta = 0.78$ are noisier due to lower scattering intensity but still have sufficient signal to noise to quantify tracer dynamics with high reliability. The degree of stretching quantified by β agrees within error for comparably sized tracers in experiments and simulations (Supporting Information). Previous studies^{16,20} found that smaller tracers can exhibit fast and anomalous transport. This fast transport arises from size-dependent coupling of hard-sphere tracer dynamics to relaxations of the surrounding glassy matrix, in which the interplay between void diffusion of the tracer particles and slow relaxations of the matrix led to a broad spread of relaxation times.⁵⁷ Thus, the stretched relaxations of small tracer particles likely also reflect coupling to a wider distribution of relaxation modes than are inaccessible to the larger, hyperdiffusive particles. Additionally, as the samples age, the tracer relaxations typically become

less stretched (β increases) in both simulations and experiments (Fig. 1, Supporting Information). The increase in β with increasing t_w is consistent with previous work on glassy laponite suspensions⁴² and suggests that the tracers access a narrower distribution of relaxation modes as the glass ages.³³

As the samples age, the relaxation times initially increase exponentially for short t_w and then transition into a power-law increase $\tau \sim t_w^n$ with $0 < n < 0.5$ at larger t_w (Fig. 2). Similar two-step aging processes have been observed for glasses and gels.^{27,30,36,50,58,59} In experiments, small tracers relax more slowly than large tracers at large t_w . These slow relaxations likely arise not from the tracer size but rather from small changes in ϕ between samples. Near random close packing, even minor changes in ϕ (Supporting Information) can result in increases in τ of over an order of magnitude.⁶⁰ Indeed, τ increases monotonically with tracer size δ in simulations for which ϕ is precisely controlled. Thus, we focus on the qualitative two-step aging mechanism captured in both simulations and experiments. Although the physics underlying the two aging regimes remains poorly understood, one picture proposes that the exponential increase arises from cage formation before entering the power-law full-aging regime.^{61–63} Within this long-time aging regime, the power-law exponent n is thought to be related to the deepening and shifting of local minima in the underlying free energy landscape over time.^{32,64–66} As the tracer size decreases, n also decreases, indicating that smaller tracers can more easily relax out of these local energy minima and explore the landscape. Additionally, the lower n of small tracers suggest that they may be less spatially localized than larger tracers within the glassy matrix.

Spatial localization manifests as a complex decay in g_2 , with an initial relaxation on very short time scales that corresponds to cage rattling followed by a final relaxation that arises as a particle escapes its localization cage.⁶⁷ Although the short-time relaxation occurs on time scales faster than those accessible in experiments, the short-time plateau $A(q)$ in g_2 is less than one for all tracer particles at all t_w (Fig. 3). This suppressed plateau depends on wavevector q , confirming that the tracer particles undergo an initial relaxation within a localization cage. The localization length L_l was extracted from the plateau's q -dependence according to $A(q) = \exp[-(L_l q)^2/6]$. For experimental measurements, L_l is globally fit across all wavevectors at each waiting time to reduce error associated with determining the intercept for each g_2 curve at a specific q . For simulations, $A(q)$ is extracted directly from the calculated g_2 curves. In both simulation and experiment, L_l does not vary significantly with sample age (Supporting Information) but does depend on particle size (Fig. 4). As particle size increases, L_l decreases monotonically as particles become more strongly caged. The effect of this localization on $A(q)$ depends on the wavevector range over which g_2 is measured. This range is restricted by limitations in scattering intensity in experiments and by computational cost in simulations. Due to these restrictions on the range of accessible wavevectors and to the degree of probe localization, the range of normalized wavevector qL_l is shifted to smaller values for large tracers than it is for small tracers. Thus, even at comparable $q\sigma$, $A(q)$ is more suppressed for small tracers than for large tracers (Fig. 3).

Accounting for delocalization at a finite size δ_0 ^{16,20,68,69} and treating the probe dynamics within a microrheological framework^{70,71} so that localization is determined by the elas-

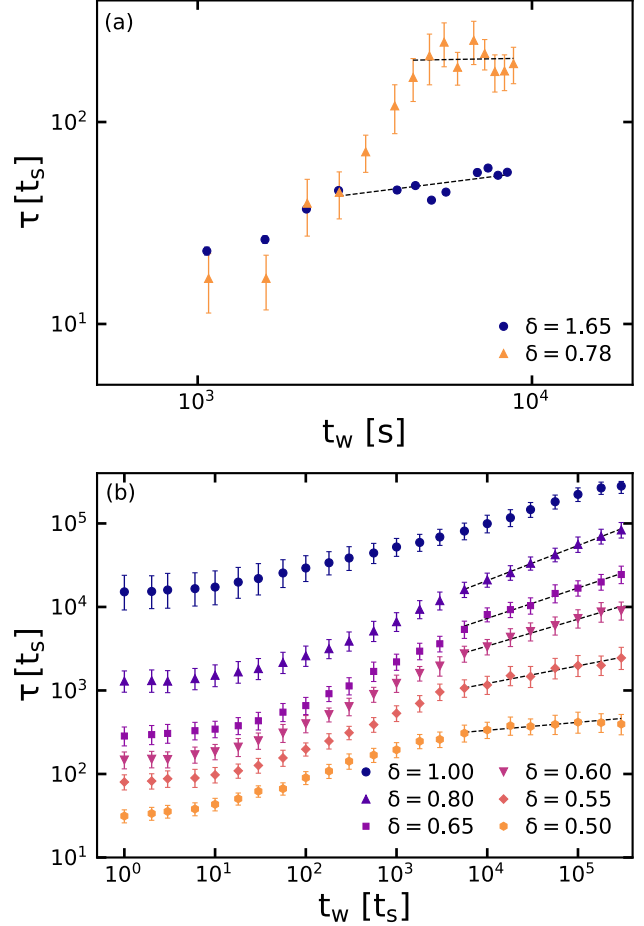


Figure 2. Relaxation time τ at a wavevector $q\sigma = 3.5$ as a function of waiting time t_w for tracers of different size as measured (a) in experiments and (b) with simulations. Dashed lines are guides to the eye to indicate power-law behaviors.

tic modulus of the matrix,^{72,73} the localization length should scale with tracer size as $L_l \sim (\delta - \delta_0)^{-1/2}$ (Supporting Information). The derived scaling behavior cleanly captures the trend in the data with $\delta_0 = 0.38 \pm 0.01$ (inset to Fig. 4). This value of δ_0 is in good agreement with the size ratio at which tracers become delocalized, $\delta \approx 0.35 \pm 0.05$, reported in previous studies on anomalous tracer dynamics in glassy matrices.^{16,20} Although electrostatic interactions are present in experiments, the hard-sphere mapping leads to quantitative agreement between simulation and experiment independent of relative sample age t_w/τ .

The agreement between the predicted scaling behavior and the measured localization length provides insights into the physics governing tracer transport through glassy matrices. First, delocalization depends not only on the structure of the surrounding matrix but also on the competition between tracer and matrix relaxations.^{16,20} Within the resolution of experiments and simulations, L_l does not vary with t_w across the range of time scales investigated here (Supporting Information). The lack of a significant aging effect on L_l suggests that the matrix structure, which does not change appreciably with age, may play a larger role in localizing tracer motion than the competition between matrix and tracer relaxations, which both slow with age (Fig. 2). Near delocalization with $\delta \approx \delta_0$, however, the mobility of the matrix is essential for tracers to fully relax out of the

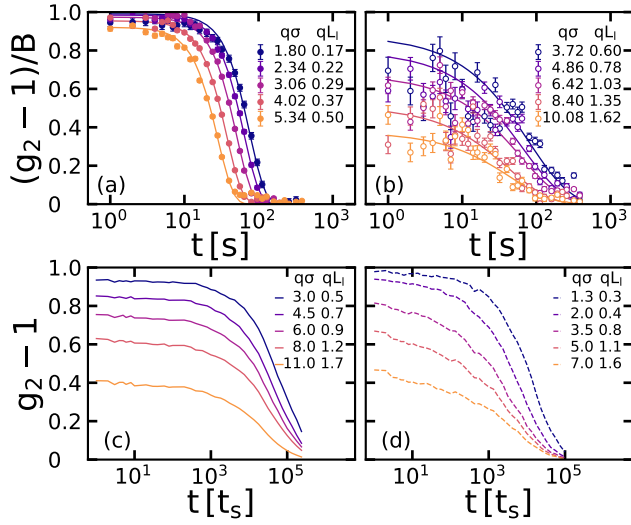


Figure 3. Normalized intensity correlation function $(g_2 - 1)/B$ as a function of time t for different values of normalized wavevector $q\sigma$. (a,b) Experimental data for tracers of size (a) $\delta = 1.65$ and $t_w = 8400$ s and (b) $\delta = 0.78$ and $t_w = 8800$ s. (c,d) Simulation data at $t_w = 10^5$ for tracers of size (c) $\delta = 1$ and (d) $\delta = 0.65$. Curves in (a,b) are best fits to stretched exponential functions.

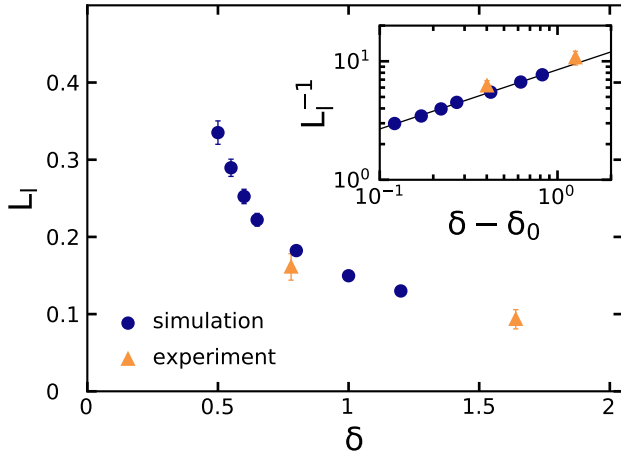


Figure 4. Localization length L_l in units of σ as a function of tracer size δ . *Inset:* Inverse of localization length as a function of $\delta - \delta_0$, where δ_0 is a critical tracer size at which dynamics become delocalized. Solid curve shows scaling $L_l^{-1} \sim (\delta - \delta_0)^{1/2}$.

transient localization plateau.¹⁶ Second, the agreement between the scaling prediction and observed localization indicates that the relaxations of tracers with $\delta > \delta_0$ are coupled to those of the matrix and thus probe the bulk viscoelasticity of the dense colloidal suspension. This coupling explains the qualitatively similar evolution of tracer and matrix relaxations with t_w (Fig. 2).

Our experiments and simulations address how the relative size of tracer particles affect their transport and localization in a glassy matrix. Tracer relaxations are coupled to those of the matrix as the system ages. The tracers become less localized with decreasing size, eventually approaching a delocalization transition at a critical relative size of $\delta_0 \approx 0.38$. The physical picture developed in this work provides direct insight into how particles move and transport through crowded environments with heterogeneous structure and slowly relaxing dynamics, present in materials from cells and tissues to polymer composites to membranes. These findings thus provide a base for predicting particle trans-

port in a wide range of scientifically and industrially relevant processes. Our work addresses localization to matrix structure and dynamics in the simplest case, in which particles interact as pseudo-hard spheres at a single volume fraction. Understanding how this localization transition depends on volume fraction, particle anisotropy, or interparticle interaction strength and range remains poorly understood and should be explored in future studies.

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Supporting information available: Static scattering patterns, hard-sphere mapping, fitting parameters τ and β , relaxations of small tracers, simulated tracer mean-squared displacements, derivation of L_l scaling, and L_l vs t_w .

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