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Direct visualization of free-volume-mediated diffusion in colloidal glass

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The relationship between particle diffusion and free volume of colloidal glass was studied in real space by laser scanning confocal microscopy. By quantifying the particle diffusion distance and the free volume size, we found a strong spatial correlation between these two quantities. Large free-volume regions were observed to possess low elastic modulus and thus results in a low energy cost of diffusion-induced strain, indicating that a large free-volume region presents a low energy barrier to structural rearrangement, thereby benefiting particle diffusion.

Keywords: Amorphous materials; Diffusion; Point defects; Kinetics

The nature of atomic diffusion in disordered media has been the subject of extensive theoretical and experimental studies over the past decade [1–5], since it is central to our understanding of many processes in amorphous solids, such as crystallization, structural relaxation and phase separation [6–8]. However, our understanding of this kind of diffusion is still rather incomplete. The approach most commonly used to account for the atomic transport in amorphous systems is the free-volume model, which was originally applied to liquids [9,10] and later extended to amorphous solids [11–14]. According to this hypothesis, diffusion of atoms in condensed amorphous materials is mediated by a kind of empty space surrounding atoms, the so-called "free volume", which is frozen in upon cooling the alloy melt through the glass transition. In analogy with vacancy defects in crystals, vacancy-like defects in dense randomly packed structures resulting from the redistribution of free volumes through thermal fluctuation are considered to be the vehicle for atomic transport in amorphous solids [15–17]. Some indirect evidence for this hypothesis was found in radiation experiments with metallic glasses, which showed that atomic diffusion was enhanced by the increase in the number of vacancy-like defects produced by irradiation [18,19]. Unfortunately, however, there has been no direct experimental proof of this free-volume-mediated diffusion. Moreover, it is extremely difficult to directly observe it within atomic and molecular solids due to the small length and time scales that characterize the atomic diffusion and free volume distribution.

By contrast, colloidal glass comprising of micrometer-sized spherical particles can serve as a good model for free-volume-assisted diffusion studies as the larger size and concomitant slower time scale of colloidal particles make them much more experimentally accessible. The colloidal particles can be directly observed in real time and their positions in three dimensions can be determined accurately by high-speed confocal microscopy. Subsequent image analysis enables us to track the trajectories and calculate the free volume of individual particles, providing an accurate picture of the interrelationship between particle diffusion ability and free volume distribution.

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In this paper, we experimentally investigate free-volume-mediated diffusion directly in three dimensions and real time by visualizing the spatial distribution of particle diffusion distance and free volume. A large diffusion distance is observed to occur preferentially at the low packing fraction and large free volume regions. We determine the elastic modulus relating to the elastic energy cost of diffusion-induced strain and illustrate the free-volume-mediated diffusion based on energy barrier considerations. Our results thus highlight the role of free volume in the particle diffusion.

We used 1.55 μm diameter colloidal silica particles with a polydispersity <3.5% to prepare an 80 μm thick colloidal glass with a volume fraction of ~0.60, well into the colloidal glassy state. A schematic of the experimental setup is shown in Figure 1a. The silica particles were suspended in a mixture of deionized water and dimethyl sulfoxide. To make the particles appear as dark spots on a bright background under fluorescence microscopy, we dyed them with fluorescein–NaOH solution. We used a fast laser scanning confocal microscope to image a 70 μm × 70 μm × 27 μm volume (Fig. 1b) and identified particle positions in three dimensions with a horizontal accuracy of 0.03 μm and a vertical accuracy of 0.05 μm [20]. We tracked the motion of individual particles over a period of 33 min by acquiring image stacks every 200 s.

To quantify the particle diffusion in quiescent colloidal glass, we followed the particle trajectories and determined the diffusion distance of each particle by $\Delta r = (\Delta x_i^2 + \Delta y_i^2 + \Delta z_i^2)^{1/2}$. The x-, y- and z-axes are along the edges of the chosen volume shown in Figure 1b. We show reconstructions of the Δr distribution for two subsequent 200 s intervals in 5 mm thick x–y sections centered at z = 10 μm as shown in Figure 2a and b. The Δr distributes heterogeneously within the colloidal glass. There are some localized regions of large Δr extending over many particles (red regions). Moreover, we find that the localized large Δr regions presented in Figure 2a disappear in the subsequent image of Figure 2b. This fluctuation of Δr can be interpreted as the particle diffusion being activated by thermal fluctuation [21,22]. The heterogeneous spatial distribution and thermally induced evolution of particle diffusion may have structural reasons. To rationalize this hypothesis, we plot the distribution of Δr between t = 200 s and t = 400 s in Figure 2c, which also shows the mean volume fraction as a function of Δr during the same time interval. The mean volume fraction is calculated by averaging the volume fractions of particles with the same Δr between t = 200 s and t = 400 s. We notice a negative correlation between the Δr and the volume fraction, i.e. longer distance diffusion tends to occur at positions with lower volume fractions, revealing that particles can diffuse more easily in loosely packed regions, where the large free volume may be enriched.

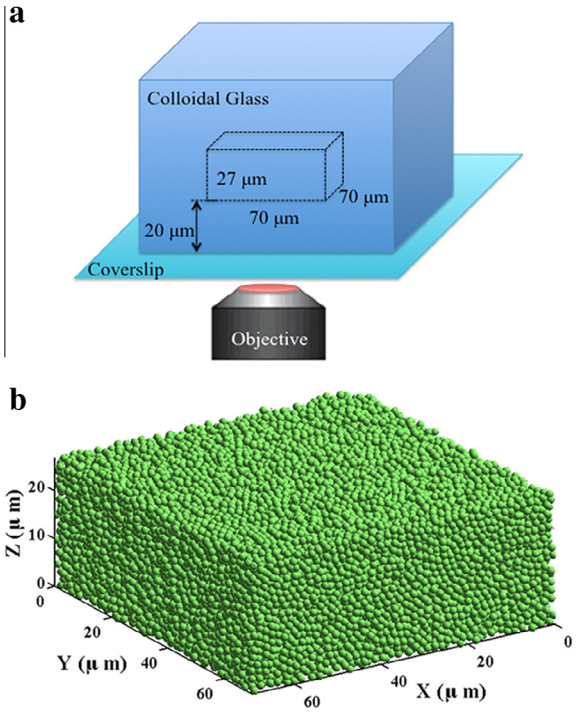

Figure 1. (a) Schematic showing the experimental setup with colloidal glass. (b) Reconstruction of a 70 μm × 70 μm × 27 μm volume depicted by a rectangle in (a).

To further explore the link between the spatial heterogeneity in Δr and the inhomogeneous glass structure, we determined the free volume of the particles. A schematic of the free volume is shown in Figure 3a. The free volume is defined as the volume over which the center of a given particle can move without moving its neighbors [23]. To calculate the free volume, we construct Voronoi cells including all points closer to the given particle than to any other particles by using the particle positions. We then move the Voronoi faces inside a distance equal to the given particle diameter. The remaining small volume gives an estimation of the free volume. We show the colored contour plots of free volume of a 3 μm thick x–y glass section centered at z = 10 μm at t = 1400 s in Figure 3b. The free volume is inhomogeneously distributed across the glass, reflecting the strong heterogeneity of the glass structure. This free volume distribution corresponds to the glass configuration just before the subsequent particle diffusion process. In addition, the white circles plotted overlaid on this figure indicate particles that experienced significant diffusion distance, i.e. $\Delta r > 0.1$ μm, during the time interval between t = 1400 s and t = 1600 s. An apparent good correlation between the spatial distribution of free volume and Δr is observed. Large diffusion distances have a strong tendency to occur in large free volume domains. We further quantify the correlation between the V_f of a given time step and the Δr during the following 200 s interval by calculating the normalized correlation coefficient $C_{\Delta r, V_f}$:

$$C_{\Delta r, V_f} = \frac{\sum_i (\Delta r_i - \langle \Delta r \rangle)(V_{f,i} - \langle V_f \rangle)}{\sqrt{\sum_i (\Delta r_i - \langle \Delta r \rangle)^2 \cdot \sum_i (V_{f,i} - \langle V_f \rangle)^2}}, \quad (1)$$

where Δr_i and $V_{f,i}$ are the diffusion distances and free volume of the ith particle, and $\langle \Delta r \rangle$ and $\langle V_f \rangle$ are the mean diffusion distance and mean free volume of all particles. Figure 3c shows the normalized correlation coefficient as a function of time. The correlation coefficients for all particles indicated by blue bars fluctuate between 0.3 and 0.4, showing a positive correlation on average.