Single-File Diffusion of Colloids in One-Dimensional Channels

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Single-file diffusion, prevalent in many processes, refers to the restricted motion of interacting particles in narrow micropores with the mutual passage excluded. A single-filing system was developed by confining colloidal spheres in one-dimensional circular channels of micrometer scale. Optical video microscopy study shows evidence that the particle self-diffusion is non-Fickian for long periods of time. In particular, the distribution of particle displacement is a Gaussian function.

where \( F \) is the SF mobility and \( t \) is time. Accordingly, SFD processes, in contrast to 2D and 3D self-diffusion seen in colloidal systems (12), cannot be described by a diffusion coefficient; that is, the SFD does not obey Fick’s laws.

Experimental evidence confirming non-Fickian behavior was unavailable for a long time because of the lack of ideal experimentally accessible SF systems. Recently, measurements of SFD became feasible in artificial crystalline zeolites. Adsorbate molecules, like methane or \( \text{CF}_2 \) with diameters of 3.8 and 4.7 Å, respectively, confined in \( \text{AlPO}_4-5 \) zeolite with a pore size of 7.3 Å, are considered to be good realizations of SF systems. Although some experimental evidence for the occurrence of SFD was found by pulsed field gradient nuclear magnetic resonance study (13, 14), some results from different groups and experimental methods are still in contradiction, even for the same system (15, 16), as indicated by Hahn and Kärger (17), who suggest and explore several possible reasons. Other effects, such as attractive particle interaction (18), the possible existence of correlations between particles of neighboring pores (19), have also been shown to play a vital role in the mechanism and rates of intracrystalline diffusion. Because of the shortage of structural information on the atomic level, the mechanism of molecular diffusion in zeolites, however, is still under debate.

We created a well-defined SFD model system by confining paramagnetic colloidal spheres of several micrometers in a set of circular trenches fabricated by photolithography. The channels are well-characterized, and the particle-particle interaction can be precisely adjusted by an external magnetic field. Moreover, because the time and length scales in such a colloidal system are easily accessed

References and Notes


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with video microscopy, the trajectories of individual particles can be followed over long periods of time. We unambiguously observed the non-Fickian behavior of SFD and confirm the theoretically predicted Gaussian distribution of particle displacements.

The sample cell was composed of two optical flats separated by an O ring of 0.5-mm thickness. The bottom plate was first coated with a thin layer of poly(methyl methacrylate) to prevent colloidal particles from sticking to the glass surface. On top of this film, a 5-μm-thick layer of a transparent photoresist was deposited. Afterward, a set of concentric circular channels (7 μm in width and 33 to 1608 μm in diameter) was etched into the photoresist by means of photolithography (Fig. 1A). The distance between adjacent channels, 63 μm, is much larger than the mean particle separation (11 μm), which rules out correlation between particles in neighboring channels.

We used an aqueous suspension of paramagnetic poly styrene colloids with a diameter of 3.6 μm (M-350 Dyno AS, Lillestøløm, Norway). The particles were doped with Fe₃O₅ clusters and are paramagnetic. Thus, when an external magnetic field is applied perpendicular to the sample plane, a magnetic dipole moment \( M \) is induced in the colloids (which is proportional to the weak field strengths \( B \) that we used) that gives rise to a repulsive pair interaction potential of the form \( V(\mathbf{r}) = (\mu_0/4\pi)M^2/B^2r^3 \), where \( r \) is the particle distance and \( \mu_0 \) is the vacuum permeability. In order to characterize the interaction strength between particles, we introduce the quantity \( \Gamma = \beta(\mu_0/4\pi)M^2_Br^3 \), which is the mean interaction energy normalized by the thermal energy \( 1/\beta = k_B T \), where \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Here, \( R \) is the mean particle distance, and \( \chi_{eff} \) is the magnetic susceptibility of the particles, which was determined to be \( 2.2 \times 10^{-12} \) A² m⁻¹ T⁻¹ (20). The particle-wall interaction can be considered as a hard sphere-wall interaction to a good approximation.

A typical real-space configuration of the particles at \( \Gamma = 4 \) is shown in Fig. 1B. Each channel appears as two closely spaced concentric rings because of the diffraction of the light at its walls into the photoresist. The particles are the dark objects within the channels. Most of the particles are trapped in the channels, whereas only a few reside on the elevated areas and do not influence the diffusion behavior of particles in the channels. The channels are narrow enough to meet the SF condition and prohibit the mutual passage of particles.

In Fig. 2A, we plotted typical trajectories of eight neighboring particles obtained at \( \Gamma = 4 \) from the largest channel in Fig. 1B. The particle position \( x \) corresponds to their angular coordinate multiplied by the channel radius. As can be seen, the trajectories never cross during the measuring time, which indicates that the SF condition is satisfied. The correlation of particle positions for long periods of time, as a characteristic of SFD, can also be seen from Fig. 2A.

The results of MSD in a log-log plot for five different magnetic field strengths (\( \Gamma = 0.66, 1.10, 2.34, 4.03, \) and 7.42) are shown in Fig. 2B. For the calculation of MSD, we averaged over both the time \( t \) and all of the particles in the channel, or \( (\Delta x^2) = \sum_i (x_i(t) + t' - x_i(t'))^2/N \), where \( N \) is the total number of particles and \( t \) is the particle index. The solid lines in Fig. 2B correspond to the best fits according to Eq. 1 with the mobility \( F \) as the only adjustable parameter. The predicted \( t^{1/3} \) behavior was seen over more than two decades of time. The small deviations from the solid lines at small time scales correspond to the crossover between the long-time and short-time diffusion of the particles. The crossover time \( t_c \) (arrows in Fig. 2B) is significantly shifted to larger values when the magnetic dipole repulsion between the particles decreases.

We also calculated the distribution function of displacements \( p(x, t) \), which is defined...
as the conditional probability of finding a particle at position \( x \) after time \( t \) with the particle located for \( t = 0 \) at \( x = 0 \). In Fig. 3A, we show the result of \( p(x, t) \) for \( \Gamma = 4 \) at four different times, which are all greater than \( t_c \). Self-diffusion of particles causes \( p(x, t) \) to broaden with time.

Despite the simplicity of the physical situation describing SF conditions, theoretical treatment remains a highly sophisticated task. Analytical results are only obtained for long time limits for hard rods hopping in an infinite 1D lattice (called a 1D exclusion model). Analytical results are only obtained for long time limits for hard rods hopping in an infinite 1D lattice (called a 1D exclusion model).

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p(x, t) = \frac{1}{\sqrt{4\pi Ft^{3/2}}} \exp(-x^2/4Ft^{1/2})
\]

This form, however, is suggested to remain valid under more general conditions whenever the SF effect is important.

To compare our data with Eq. 2, we replotted the data of Fig. 3A in Fig. 3B; all of the data points collapse to a master curve plotted the data of Fig. 3A in Fig. 3B; all of the data points collapse to a master curve.

However, unlike the hard-rod interaction in the theoretical exclusion model, we have a long-range pair interaction, and the hydrodynamic interactions caused by the particles moving in the surrounding fluid also play an important role. Therefore, detailed comparison with theory should take these two aspects into account.

References and Notes
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Three-Dimensional Direct Imaging of Structural Relaxation Near the Colloidal Glass Transition

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Confocal microscopy was used to directly observe three-dimensional dynamics of particles in colloidal supercooled fluids and colloidal glasses. The fastest particles moved cooperatively; connected clusters of these mobile particles could be identified; and the cluster size distribution, structure, and dynamics were investigated. The characteristic cluster size grew markedly in the supercooled fluid as the glass transition was approached, in agreement with computer simulations; at the glass transition, however, there was a sudden drop in their size. The clusters of fast-moving particles were largest near the \( \alpha \)-relaxation time scale for supercooled colloidal fluids, but were also present, albeit with a markedly different nature, at shorter \( \beta \)-relaxation time scales, in both supercooled fluid and glass colloidal phases.

As a glass-forming liquid is cooled, its viscosity smoothly but rapidly increases by many orders of magnitude (\( \Gamma \)). This mac-

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mroscopic viscosity divergence is related to the divergence of the microscopic structural relaxation time (\( \alpha \)-relaxation time). Microscopically, a glass still has liquid-like structure; no structural change has been found which would explain the glass transition (\( \beta \)-relaxation). Instead, theories for the glass transition focus on microscopic dynamical mechanisms (\( \Gamma \)). The underlying concept of many of these theories is the Adam and Gibbs hypothesis (\( \sigma \)), which states that flow in a supercooled fluid involves cooperative motion of