

Universal Scaling Law for Colloidal Diffusion in Complex Media

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Using video microscopy and simulations, we study the diffusion of probe particles in a wide range of complex backgrounds, both crystalline and disordered, in quasi-2D colloidal systems. The dimensionless diffusion coefficients D^* from different systems collapse to a single master curve when plotted as a function of the structural entropy of the backgrounds, confirming the universal relation between diffusion dynamics and the structure of the medium. A new scaling equation is proposed with consideration for the viscous friction from the solvent, which is absent in previous theoretical models. This new universal law quantitatively predicts the diffusion coefficients from different systems over several orders of magnitude of D^* , with a single common fitting parameter.

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Diffusion is a fundamental process ubiquitous in physics, chemistry, biology, and material sciences. The diffusion coefficient for the simplest case—the Brownian motion of a mesoscopic spherical particle in a Newtonian fluid—is well described by the Stokes-Einstein equation [1]. In most practices, however, diffusion occurs in complex environments with dynamical structures and interactions. Examples include the diffusions of dopants in semiconductors [2–4], colloids in polymer matrices [5–7], biological molecules in cells [8–10], and defects in crystals [11,12]. A universal model that can quantitatively predict the diffusion coefficients of atoms or macromolecules in complex environments therefore will be of fundamental importance to some of the most challenging problems in condensed matter physics and biological sciences.

For dense fluids, Dzugutov [13] and Rosenfeld [14] discovered that the transport coefficient of a tagged molecule can be quantitatively obtained using the structural entropy of the fluids with the simple form of

$$D^* = Ae^{\alpha S_2}. \quad (1)$$

Here, D^* is the dimensionless diffusion coefficient normalized by Γd^2 with d being the particle diameter, Γ is the Enskog collision frequency, S_2 is the two-body structural entropy of the system, and A and α are the scaling factors. This universal scaling law has been verified by simulations in simple liquids [15–18], binary mixtures [19–23], liquid metals [24–27], and Lennard-Jones chain systems [28]. However, at low densities, it is found that the diffusion coefficients deviate significantly from this relation with

much higher values [15,17,29–31]. In 2004, Samanta *et al.* [23] proposed a refined universal scaling law with

$$D^* = \frac{k_B T}{\Gamma d^2 \xi_B} \frac{1}{A(1 - S_2)}. \quad (2)$$

Here, $k_B T$ is the thermal energy, ξ_B is the binary collision friction in the Enskog gas theory, and A is a free parameter. This new relation has been tested in simulations to work at both high and low densities.

Despite many existing simulation studies, experimental testings of the scaling laws for diffusion are rare [32], since it is difficult to simultaneously track the diffusing particles and measure the structural entropy of medium in molecular (or ionic) liquids. Recently, Ma *et al.* [33] experimentally studied the diffusion of colloidal particles at different interfaces and recovered a Dzugutov-like scaling relation using the diffusion coefficient D_0 obtained at the low-density limit as the normalization parameter for $D_M^* = D/D_0$. However, this result cannot confirm a truly *universal* scaling law, as different α is obtained for different samples. Similar nonuniversal scaling of the diffusion coefficient to the excess entropy is also reported in experiments of n alkanes [31]. Wang *et al.* [34] studied the relation between D and S_2 in dissipative granular systems and found that the results cannot be fitted to existing scaling laws at low densities. Therefore, it is highly desirable to establish a general scaling formula that quantitatively relates the diffusion coefficients to media structures. Moreover, it is important to note that, in previous simulations and experiments, the media are disordered fluids

consisting of the diffusing particles themselves. A more general and often-encountered scenario is the diffusion of probe particles in a background with qualitatively different structures and interactions.

In this Letter, we study the diffusion of small probe particles in ordered and disordered backgrounds that consist of a monolayer of large interacting particles in both colloidal experiments and simulations. Colloids have obvious advantages over atomic or molecular systems, as the trajectories of micron-sized colloids can be continuously tracked with high precision using digital video microscopy [35]. They have been widely employed as a model system to study diffusion related phenomena [5,7,33,36–43]. In our experiments and simulations, the normalized diffusion coefficients D^* collapse to a single master curve as a function of structural entropy S_2 for both ordered and disordered backgrounds, confirming the universality between diffusion coefficients and media structures. The obtained master curve, however, does not quantitatively agree with any existing theories. We propose a new universal law by considering the frictional forces exerted on the colloidal particles by the solvent, which is absent in previous models. Our new formula can be well fitted to the experimental and simulation data over several orders of magnitude of D^* .

The samples consist of an aqueous solution of binary mixture of polystyrene (PS) spheres with diameters $d_l = 1.0 \mu\text{m}$ for large particles and $d_s = 0.2 \mu\text{m}$ for small particles, confined between two cover slides, forming a quasi-2D system. The large particles are negatively charged by sulfonation in sulfuric acid [44]. The screening length of the large particles is tuned by varying the sulfonation time and the quantity of the sulfuric acid used. These charged PS particles constitute a monolayer background in which small fluorescent probe particles diffuse. In our experiments, we employ five differently charged particles with different charge densities and screening lengths to obtain crystalline backgrounds with the lattice constant from 1.43 to $2.42 \mu\text{m}$. The disordered backgrounds are formed by the same particles forming the crystal backgrounds with lattice constant of $1.49 \mu\text{m}$. The particles forming the liquid backgrounds are diffusive, while those forming the crystal backgrounds fluctuate *randomly* around their lattice positions. The number of large particles in the field of view ranges from 200 to 2000, and the number of the small probe particles is kept below 5% of the background particles to minimize correlations between the motion of the probe particles. The images of the samples are recorded by video microscopy in a combined bright field and fluorescent mode at 110 frames/s. The large particles are slightly out of focus to enhance the contrast for small probe particles. Snapshots of probe particles diffusing in a crystal lattice and a disordered liquid background are shown in Fig. 1. The trajectories $\mathbf{r}(t)$ of all the particles are extracted using particle tracking software.

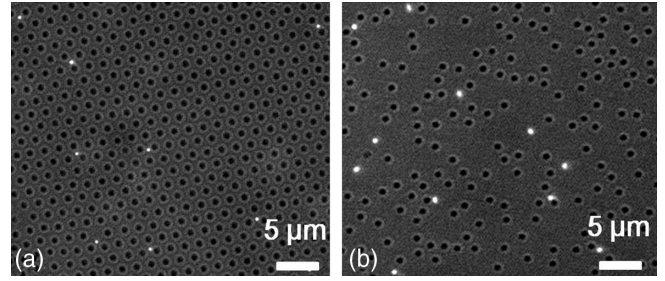


FIG. 1. Snapshots of probe particles diffusing in a crystal lattice (a) and a disordered liquid background (b) formed by large sulfonated PS particles. The bright particles are small fluorescent probe particles and the dark particles with a bright edge are the large background particles.

Figure 2 plots two representative mean square displacements (MSDs) of the probe particles in ordered and disordered backgrounds. The longtime diffusion coefficient D is obtained by linearly fitting the MSD curves at long times with $\langle \Delta \mathbf{r}^2(t) \rangle = 4Dt$. The structure of the background is quantified by the two-body structural entropy S_2

$$S_2 = -\pi\rho \int_0^\infty \{g(r) \ln[g(r)] - [g(r) - 1]\} r dr, \quad (3)$$

where ρ is the mean number density, and $g(r)$ is the radial distribution function of the large background particles with respect to the small probe particles. The radial distribution function $g(r)$ is the relative probability of finding another particle at the distance r from a reference particle. The structural entropy, which is also known as the excess entropy, is the entropy difference between a many-body system and the ideal gas under equivalent conditions (temperature and density), due to positional correlations.

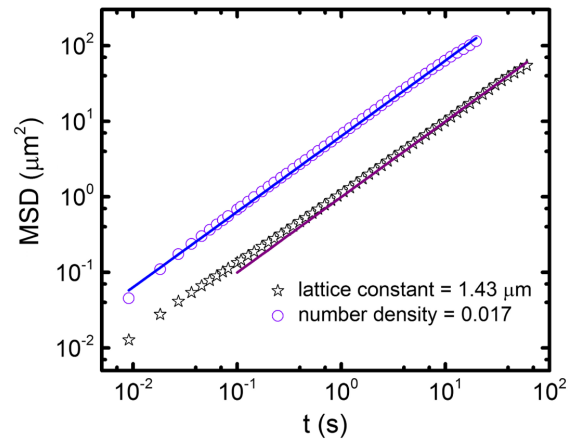


FIG. 2. The mean square displacement of the small probe particles from two representative backgrounds. Symbols are experimental data [crystalline background with lattice constant of $1.43 \mu\text{m}$ (stars) and disordered background with number density of the large particles at 0.017 (circles)]. The solid lines represent the best fit using $\langle \Delta \mathbf{r}^2(t) \rangle = 4Dt$ at long times.

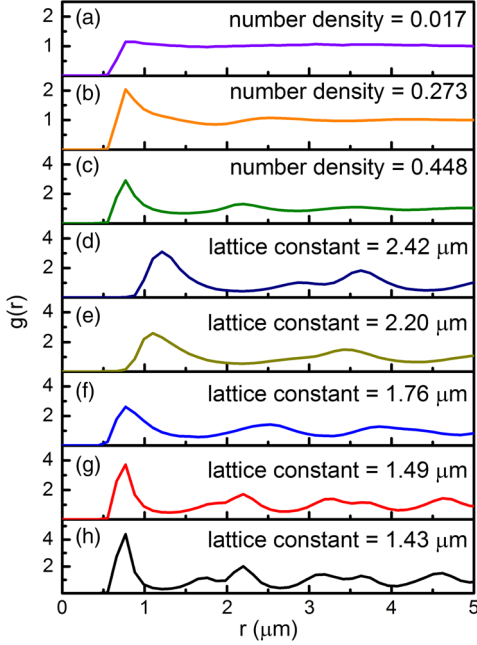


FIG. 3. The measured radial distribution functions of the large background particles with respect to the probe particles. (a)–(c) Corresponds to three disordered backgrounds with number density from 0.017 to 0.448, and (d)–(h) are from five crystalline backgrounds with the lattice constant from 2.42 to 1.43 μm .

S_2 is used as an approximation of the total structural entropy, as the two-body structural entropy contributes more than 85% of the total structural entropy in a wide range of densities [45]. Figure 3 shows the measured radial distribution function for various backgrounds. For soft particles, including the charged particles employed in our experiments, the measured $g(r)$ depends on the particles' size, number density, and the softness of both the large and small particles. Features of the disordered [Figs. 3(a)–3(c)] and crystalline backgrounds [Figs. 3(d)–3(h)] can be clearly seen in the $g(r)$ curves. In experiments, the S_2 of the background varies from sample to sample. For disordered backgrounds, the S_2 decreases with the packing fraction, and for crystalline backgrounds, the S_2 varies with the lattice quality for a given lattice constant (see Supplemental Material [46]). At high packing fractions, S_2 from disordered backgrounds, which are formed with the same particles in the crystalline background with lattice constant of 1.49 μm , can overlap with the S_2 from the crystalline backgrounds with larger lattice constants, due to higher number densities.

In Fig. 4, we plot the normalized diffusion coefficients D/D_0 as a function of S_2 in different systems, where D_0 is the free diffusion coefficient of the probe particles measured in dilute samples without any large particles. Results from individual background groups (liquid or crystalline backgrounds with the same lattice constants) can be well fitted by an exponential function

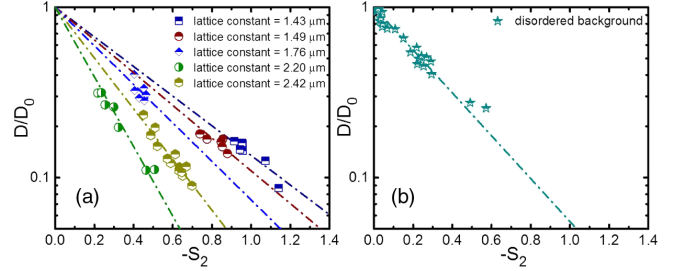


FIG. 4. The normalized diffusion coefficient of the probe particles D/D_0 as a function of the two-body structural entropy S_2 , in crystal lattices (a) and the disordered fluid backgrounds (b), shown in semilog plots. Different symbols in (a) correspond to crystal backgrounds with different lattice constants. The dashed-dotted lines are the fits to the experimental data using Eq. (4).

$$D/D_0 = e^{\alpha S_2}. \quad (4)$$

The value of α , however, varies from system to system, similar to the results in the previous study of monodisperse colloidal fluids [33,36], which suggests that D/D_0 is not uniquely determined by S_2 , and Eq. (4) is not universal. The slopes for the crystalline backgrounds decreases monotonically with the lattice constant except for the lattice group with lattice constant of 2.20 μm , which has lower particle number density than the group with lattice constant of 2.42 μm , due to poorer lattice qualities [36,46].

In the following, we normalize the diffusion coefficient by $D^* = D\Gamma^{-1}d_s^{-2}$, as in the work of Dzугutov [13]. Here, the d_s is the probe particle diameter and the particle collision frequency of the two-dimensional system Γ is calculated using [34]

$$\Gamma = 2\sigma\rho g(\sigma)\sqrt{\pi k_B T/m}, \quad (5)$$

with σ being the position of the first peak of $g(r)$, and m is the effective mass of the probe particle. Figure 5(a) shows the dimensionless diffusion coefficients D^* , as a function of S_2 for all the samples measured in our experiments, from both ordered and disordered backgrounds. All the data collapse onto a single master curve, suggesting a universal relation between the diffusion of the probe particles and the structure of the environments. At low S_2 values, which correspond to crystalline or high-density amorphous backgrounds, the results can be well fitted by the Dzугutov equation (1) [13], as shown by the solid purple line. The experimental data deviate significantly from the Dzугutov equation (underestimation) for low-density disordered backgrounds. The scaling relation by Samanta *et al.* [Eq. (2)] [23] agrees with the experimental data qualitatively at both high and low S_2 regimes, as shown by the dashed-dotted line in Fig. 5(a). Quantitatively, however, the Samanta equation still misses the experimental results by about one order of magnitude (overestimation) for high S_2 backgrounds. These deviations indicate that neither Eq. (1)

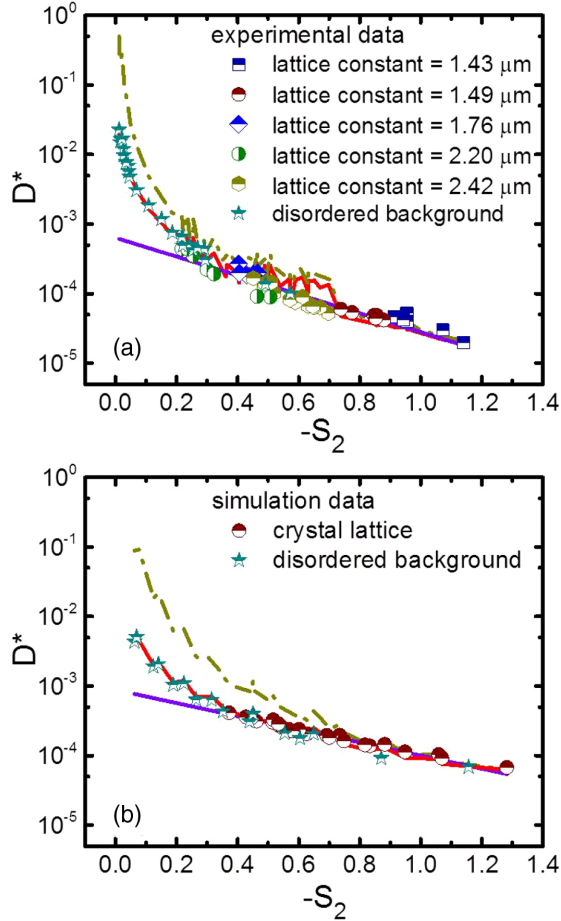


FIG. 5. The dimensionless longtime diffusion coefficient D^* of the probe particles as a function of the two-body structural entropy S_2 in both the ordered and disordered backgrounds. (a), (b) Symbols are the experimental and simulation results, respectively. The purple (solid), yellow (dashed-dotted), and red (solid) lines represent the fits to the data using Eq. (1) by Dzugutov, Eq. (2) by Samanta *et al.*, and our formula (8), respectively.

nor Eq. (2) is complete for the present systems and some extra contributions to the D need to be taken into account.

In the derivation of Eq. (2), the friction experienced by a tagged molecule is attributed to the binary collision term ξ_B and the structural relaxation term $\xi_{\rho\rho}$ [23]. The binary collision rate is sensitive to the particle size and density, but not directly to the symmetry of the underlying structures. The structural relaxation term measures the relaxation of confinements to the probe particles by the background structure. In two-dimensional systems, the frictional coefficient from the binary collision among particles can be expressed by the Enskog gas theory [49–51] as

$$\xi_B = 2\sigma\rho g(\sigma)\sqrt{\pi k_B T m}. \quad (6)$$

The $\xi_{\rho\rho}$ can be related to S_2 using mode coupling theory [23]. In addition to these two sources of friction, colloidal

particles also experience friction from the solvent, which can be determined by the Einstein relation $\xi_S = k_B T / D_0$, where D_0 is the free diffusion coefficient. Hence, the total frictional coefficient of the probe colloidal particle reads $\xi = \xi_B + \xi_{\rho\rho} + \xi_S$. The corresponding diffusion constant is thus $D = k_B T / (\xi_B + \xi_{\rho\rho} + \xi_S)$. Following similar procedures in the work by Samanta *et al.* [23], the diffusion coefficient can be expressed as

$$D = \frac{k_B T}{\xi_B} \frac{1}{A(1 - S_2) + \xi_S / \xi_B}, \quad (7)$$

with A being the only free parameter. This equation constitutes an important extension of the Einstein relation to complex environments. In the absence of the background particles, the binary collision contribution ξ_B vanishes and Eq. (7) reduces to $D = k_B T / \xi_S$, namely, the Einstein relation widely used in dilute solutions. From Eq. (7), we obtain a new scaling law for the dimensionless diffusion coefficients of colloidal particles in solutions,

$$D^* = \frac{k_B T}{\Gamma d_s^2 \xi_B} \frac{1}{A(1 - S_2) + \xi_S / \xi_B}. \quad (8)$$

All the parameters in Eq. (8) can be quantitatively evaluated in experiments except A . This new scaling relation between D^* and the structural entropy S_2 can be satisfactorily fitted to the experimental data in both ordered and disordered backgrounds, in the wide range of S_2 available to the experiment, as shown by the red solid line in Fig. 5(a). In particular, D^* evolves smoothly with S_2 when the background changes qualitatively from diffusive liquids to arrested crystals, which highlights the universality of our model.

To further test the new universal law for colloidal diffusion in complex media, we perform 2D Brownian dynamics simulations of small particles diffusing in both crystalline and disordered backgrounds, without hydrodynamic interactions (see Supplemental Material [46]). The background consists of 1600 large particles interacting with the repulsive Lennard-Jones (LJ) type of potentials. The area fraction is changed to create backgrounds from disordered liquid to ordered crystals. The small probe particle is 1/4 the size of the large particles, interacting with the background particles also via the repulsive LJ potentials. Similar to the experiments, the diffusion coefficient of the probe particle is extracted from the measured MSD, and the structural entropy S_2 is calculated from the $g(r)$. Figure 5(b) plots the dimensionless diffusion coefficient D^* as a function of S_2 from simulations. The results can be quite well fitted by Eq. (8) in the range of S_2 explored, while the scaling laws proposed by Dzugutov and Samanta *et al.* both deviate from simulation results at the dilute regime.

We note that Eq. (8) does not consider the hydrodynamic interactions between particles mediated by the solvent. The good agreement between Eq. (8) and the experimental data suggests that the hydrodynamic interactions may not be important to the diffusion of colloidal particles in our systems. We speculate that the hydrodynamic interactions are probably suppressed by the quasi-2D confinements of the systems [52]. Or alternatively, the hydrodynamic effects on the longtime diffusion of colloidal particles are somehow effectively absent [36].

To summarize, we study the general scenario of small probe particles diffusing in complex environments consisting of large colloidal particles. The normalized diffusion coefficient D^* can be uniquely determined by the structural entropy S_2 of the background, thus establishing a universal dynamics-structure relation for both disordered and ordered backgrounds. We obtain a new universal scaling law that can quantitatively predict the longtime diffusion coefficient of the probe particles in a wide range of backgrounds. Based on the new scaling relation, there exist many interesting open questions that deserve further investigation in the future, e.g., testing the validity of the relation during the colloidal glass transition when the system is driven out of equilibrium or investigating the effect of hydrodynamic interactions on the law in bulk solutions.

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