Diffusion-Coefficient Power Laws and Defect-Driven Glassy Dynamics in Swap Acceleration

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Particle swaps can drastically accelerate dynamics in glass. The mechanism is expected to be vital for a fundamental understanding of glassy dynamics. To extract defining features, we propose a partial swap model with a fraction ϕ_s of swap-initiating particles, which can only swap locally with each other or with regular particles. We focus on the swap-dominating regime. At all temperatures studied, particle diffusion coefficients scale with ϕ_s in unexpected power laws with temperature-dependent exponents, consistent with the kinetic picture of glassy dynamics. At small ϕ_s, swap initiators, becoming defect particles, induce remarkably typical glassy dynamics of regular particles. This supports defect models of glass.

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Under rapid cooling, most liquids experience a considerable dynamic slowdown accompanied by an increase in viscosity [1,2]. Despite decades of research and significant progress, an encompassing theoretical description of this dynamic arrest has proven elusive. Even the most fundamental questions, such as whether the arrest is of thermodynamic or kinetic origin, are still under heated debate [3]. Complementary to experimental approaches, molecular dynamics (MD) simulations play a pivotal role because they enable one to examine the microscopic dynamics directly. For a long time, preparation of equilibrium MD systems in the deeply supercooled regime was challenging due to the slow dynamics. Recently, lots of attention has been focused on a swap Monte Carlo algorithm [4–7], which speeds up the equilibration of polydisperse fluids by over 10 orders of magnitude [8]. A further ingenious observation by Wyart and Cates [9] is that the extraordinary speedup is not only useful technically, but has strong theoretical implications on the underlying mechanism of glassy dynamics. They argue that the success of swap evidences the kinetic school against the thermodynamic picture. This has initiated an interesting debate [10]. The advancements on swap acceleration have spurred a flurry of theoretical works on possible explanations based on a variety of approaches [11–14]. Existing simulation results, aiming predominantly at computational efficiency, lack hallmark features that can conclusively discriminate the theories and settle the debate.

In this Letter, we study generalizations of the swap algorithm that are not necessarily the most efficient, aiming rather at a better understanding of both swap and glassy dynamics. We consider polydisperse soft repulsive particles in two dimensions. Hybrid dynamics of MD evolution with periodic Monte Carlo swap attempts is applied. We adopt particle swap following Refs. [4,5], rather than radius swap [8] so that all particle attributes including positions are swapped. Swaps thus contribute to particle movements directly. In addition, we consider local, i.e., nearest neighboring, swaps by restricting the swaps to particle pairs within a short distance of the order of particle diameters. Local and nonlocal swaps have been found to generate similar results [8]. This local particle swapping scheme, without long jumps, leads to realisticlike particle dynamics in which standard measures such as the diffusion coefficient are well defined.

Partial swap.—A key feature of our model is that only certain particle pairs enjoy swap attempts. Before a simulation starts, we randomly select a fraction ϕ_s of particles in the system, referred to as *swap initiators*. Only these particles can perform swaps with themselves or with other regular particles. Regular particles cannot swap directly among themselves. Previous studies are thus akin to $\phi_s = 1$ [4–8]. By varying ϕ_s, an expanded parameter space is explored. At small ϕ_s, one gets a system of regular particles with a small density of swap initiators as defects. In our study, we focus on a swap-dominating regime by applying a sufficiently high swap attempt frequency, so that the diffusion coefficient of the regular particles must be enhanced by swaps by at least 10 times. MD steps then only lead to negligible direct motions but are essential to position the particles for effective swaps.

We use dimensionless units in which the average particle diameter, the particle mass, and the Boltzmann constant are all set to 1. Particle diameters follow a uniform distribution with a standard deviation of 0.18 to ensure disordered arrangements. Two particles separated by a distance r

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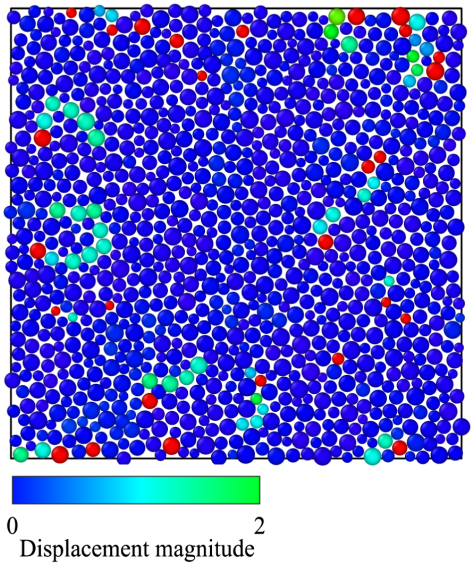

FIG. 1. A system with a fraction $\phi_s = 0.026$ of swap-initiating particles (red circles), only which can exchange positions with regular particles or with each other. The regular particles are color coded according to their displacements over a duration 0.015 at $T = 0.16$. Stringlike motions can be observed.

interact with a repulsive pair potential $\sim r^{-12}$. Unit particle density is considered. Our local swaps can only exchange the positions of particles within a cutoff distance of 1.5, the first minimum in the particle pair distribution function. Swaps are conducted using standard Monte Carlo algorithms following detailed balance so that the system thermodynamics is exactly preserved, while dynamics is dramatically accelerated. Further details can be found in the Supplemental Material [15], which includes Refs. [16–25].

Results.—Figure 1 shows an example of the overall system, consisting of a small density of swap initiators (red) in a background of regular particles (blue to green). It is seen that regular particles with larger displacements (light blue to green) are those close to the swap initiators, as the latter induce these motions. We measure the diffusion coefficient of the regular particles defined as $D_r = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle / 4t$ measured at long time t, where $\mathbf{r}_i(t)$ is the position of regular particle i. Figure 2(a) shows D_r as a function of ϕ_s. The remarkably straight lines in the log-log plot show the power law

$$D_r \sim \phi_s^{\alpha} \tag{1}$$

for small ϕ_s. Similarly, Fig. 2(b) plots the diffusion coefficient D_s of the swap initiators analogously defined. We observe a related power law,

$$D_s \sim \phi_s^{\alpha-1}. \tag{2}$$

It appears that these power laws cannot be inferred from existing theories of swap dynamics [11–13].

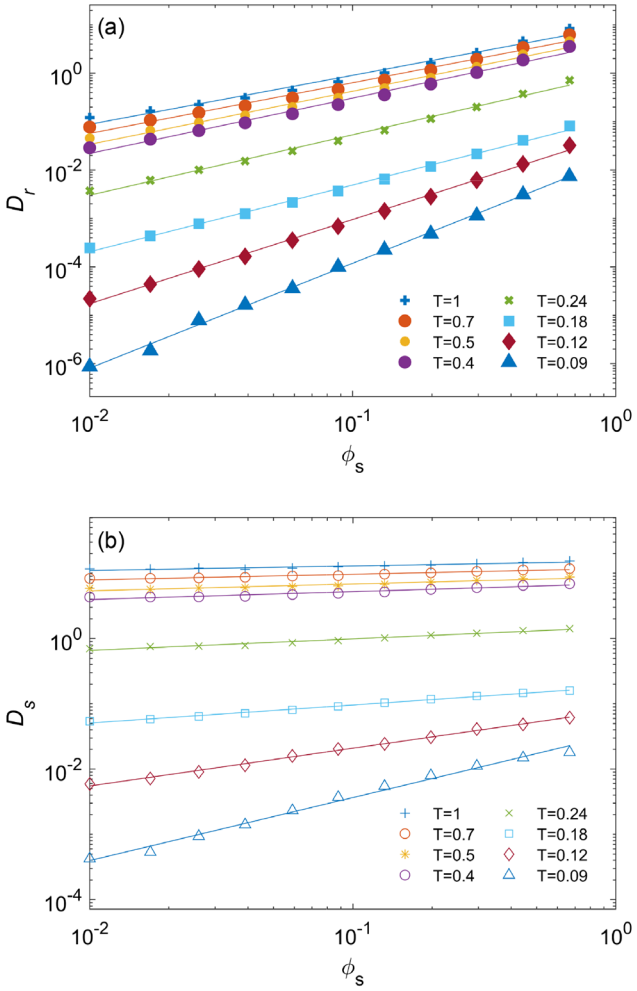

FIG. 2. Diffusion coefficients (a) D_r of regular particles and (b) D_s of swap initiators against the fraction ϕ_s of swap initiators.

We first explain the relationship between the two power laws. For small ϕ_s, swap initiators are sparse so that they typically swap with regular particles. An equal number of swaps is thus shared between the entire population of the two species. The ratio of the swapping rates for regular particles against swap initiators is hence inversely proportional to their population ratio $(1 - \phi_s)/\phi_s \simeq \phi_s^{-1}$. This implies $D_r/D_s \propto \phi_s$. The exponents in Eqs. (1) and (2) thus differ by 1 and can be denoted by α and $\alpha - 1$, respectively. Figure 3 plots α against T from fitting D_r and D_s to Eqs. (1) and (2), respectively. The reasonable consistency between values of α obtained from the two power laws supports our arguments.

The exponent α approaches 1 at high T, as observable from Fig. 3. In that case, D_s is independent of ϕ_s and the swap initiators are simply independent random walkers, indicating that thermal motions readily overcome random particle interactions in the disordered system. More interestingly, α rises as T decreases and exceeds two at $T \lesssim 0.09$. Consider for example $\alpha = 2$ at $T \simeq 0.09$. Based on elementary chemical kinetics, we suggest that

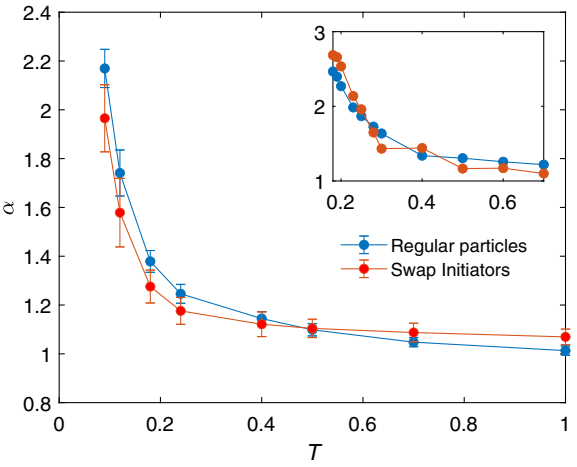

FIG. 3. Scaling exponent α measured from regular particles (blue) and swap initiators (red) against temperature T. Inset: exponent α against T from distinguishable particle lattice model simulations.

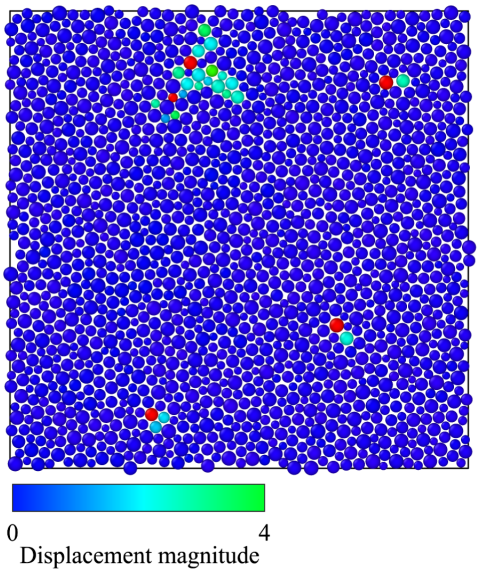

FIG. 4. A 1600 particle system with $\phi_s = 0.003$ at $T = 0.08$ showing facilitation. Regular particles (colored according to their displacements during a time interval of 0.32) are more mobile when they are close to a pair of swap initiators (red).

pairs of nearby swap initiators dominate the dynamics. These pairs have a density $\sim\phi_s^2$ so that the total swapping rate in the system is proportional to ϕ_s^2. Distributing these swaps to individual initiators of population $\sim\phi_s$, we get $D_s \sim \phi_s$. We expect that nonintegral values of α are associated with crossover situations due to fluctuations in the dominant mobile group size. As α can exceed two, our arguments may be applied to α equal to 3 or beyond corresponding to larger group of initiators that dominate the dynamics.

The above picture of dynamics-dominating groups of defects, akin to the facilitation picture of glassy dynamics, was pioneered by the Fredrickson-Andersen model [26] and further developed in numerous works [27–30]. The facilitation in our model is probabilistic, unlike the rigid rules in typical kinetically constrained models [26,27]. Its relevance can be illustrated from real-space displacement profiles. Figure 4 shows the displacement of a system at $T = 0.08$ corresponding to $\alpha \simeq 2.1$. We have also taken a small ϕ_s so that individual groups of swap initiators can be examined. As a typical trend at such a low T, we can observe that regular particles close to a pair of swap initiators are, in general, much more mobile than those next to isolated initiators. We corroborate this quantitatively in the Supplemental Material [15] by comparing systems in which swap initiators are isolated, in pairs, or in triplets.

Figure 5 compares the position-time graphs of swap initiators at high and low T. It is clear that, at high T, all swap initiators are mobile with motions consistent with random walks. In contrast, there are much stronger fluctuations at low T. Some swap initiators are trapped for long duration within small regions. Importantly, they do not only vibrate as one may naively expect for caged particles. Instead, they swap frequently, albeit only back and forth, leading to little net movements. They are thus essentially caged, but in a more general sense with back-and-forth swaps and vibrations. We also observe two other swap initiators that are much more mobile. We have checked in this and other examples that the mobile initiators are mainly those in groups of two or more. Some of these coupled groups are completely mobile and move over long distances. When they reach trapped swap initiators, partners may be exchanged, and thus no initiator is permanently trapped in a sufficiently large system.

Another intriguing feature of our model is that the regular particles exhibit remarkably glasslike dynamics at small ϕ_s. In this regime, dynamics is predominantly induced by only a small population of frequently swapping initiators. Yet, the regular particles demonstrate typical glassy behaviors. These include a mean-squared displacement exhibiting a plateau, a two-step decay of the self-intermediate scattering function with a stretching exponent decreasing with T, a Stokes-Einstein violation, and a peak in a time-dependent four-point susceptibility with a height increasing as T decreases (see Supplemental Material [15]).

More directly, real-space features typical of glass formers can also be observed and intuitively understood. Specifically, Fig. 4 shows dynamic heterogeneity revealed as a cluster of regular particles with a much higher mobility than the others. This high mobility results simply from the proximity to a facilitated pair of swap initiators. Another important real-space feature is stringlike motions, involving strings of particles displacing their preceding neighbors [31]. These are revealed as strings of mobile regular particles in Figs. 1 and 4. Some mobile regular particles in Fig. 4 seem to form compact geometries, which indeed can be broken down into strings at shorter

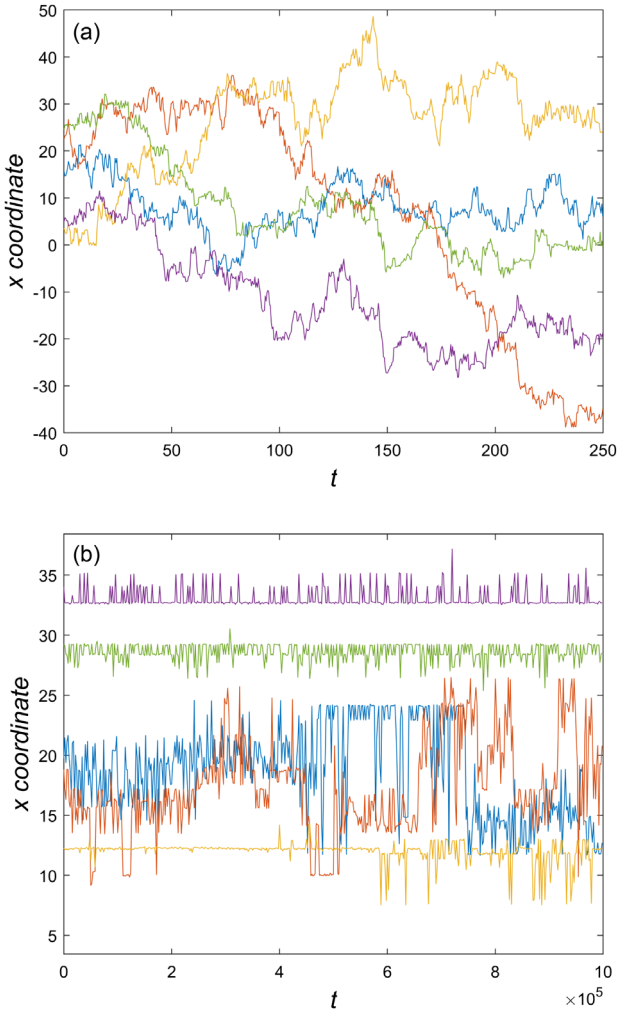

FIG. 5. Plots of x coordinates of all five swap initiators (randomly colored) in a system with 1600 particles for $\phi_s = 0.003$ against time t at (a) $T = 0.5$ and (b) $T = 0.08$. The coordinates are unwrapped with respect to the periodic boundary conditions for clarity. In (a), motions are consistent with simple random walks. In (b), some swap initiators are strongly trapped, but two initiators close to each other are more mobile.

time intervals. A more informative illustration is provided by particle trajectories, where individual trajectories of groups of particles nicely connect to form strings (see Supplemental Material [15]). We observe a striking resemblance of these strings to those in, for example, experimental glassy colloidal systems [32]. Unlike in realistic glass, stringlike motions in our model can be trivially understood. Each is simply caused by a few consecutive local swaps of a swap initiator, leaving behind a linear trail of displaced particles. Their trajectories thus align to form a string.

Many important properties of glass are captured by lattice models [27]. We have recently proposed a distinguishable particle lattice model (DPLM) [30], which exhibits a wide range of glassy phenomena (see, e.g., [33,34]). Generalizing the DPLM to incorporate swap, we have reproduced both power laws with exponents showing similar T dependence (see inset in Fig. 3 and Supplemental Material [15]).

Discussion.—We have shown that introducing a density ϕ_s of swap initiators and implementing local particle swaps, simple power-law relations between diffusion coefficients, the most fundamental dynamic measures, and ϕ_s are established. The scaling exponents depend nontrivially on temperature. These are highly specific hallmark features fundamental to swap dynamics in glass formers. Power laws play key roles in theoretical descriptions of many physical systems and techniques to tackle them are abundant [35]. Incorporating them into existing [11–13] and future theories of swap dynamics should be important in scrutinizing and perfecting them. In addition, we have shown that the power laws can be reproduced using the DPLM. A theoretical description of swap with the power laws appears readily achievable, as lattice models are, in general, much more tractable analytically than MD systems [27,36].

We have found that glassy dynamics is exhibited by regular particles at small ϕ_s. This is a highly nontrivial finding because, in contrast to realistic glass formers in which all particles, in principle, can move spontaneously, particle motions here are mainly induced by a sparse population of swap initiators. In our opinion, the regular particles constitute the simplest molecular model of glass, as motions are clearly known to be caused by and localized around swap initiators. It is so simple that dynamic heterogeneity and stringlike motions are trivially understandable as explained above. A theory for swap dynamics at small ϕ_s should be highly inspiring, if not directly applicable, for a quantitative description of glassy dynamics.

We have argued that the power laws in the nontrivial regime with $\alpha > 1$ result from elementary chemical kinetics and relate to facilitation [27]. It can further be explained intuitively as follows. Consider, e.g., $\alpha \simeq 2$. Although a swap initiator can, in principle, swap with all its nearest neighbors associated with various energy costs, only some of them can be energetically favorable at such a low T. If these neighbors do not percolate throughout the whole system, the initiator will be trapped to move back and forth only within a few sites defined by the rugged energy landscape. Isolated initiators thus tend to have a low mobility at a sufficiently low T. Importantly, in addition to being affected by the energy landscape, motions of swap initiators indeed also perturb the landscape as particle arrangements along their pathways are altered. Therefore, if a swap initiator happens to move close to another one, the landscape experienced by the latter will be perturbed and this may unlock previously unfavorable swaps. More generally, both initiators perturb the energy landscape of each other and provide additional swapping possibilities. This mutual facilitation can enable both to move far away in a dynamically coupled way. Analogous facilitation based on void-induced dynamics has been explained in detail previously [36–38].

The swap initiators at small ϕ_s are mobile point defects in the system of regular particles. Our results thus show that many features of glassy dynamics can well be realized by defect-induced motions. An important question is whether there are analogous dynamics-dominating defects in realistic glasses. In close association with the free-volume theory, a major candidate is a void or, more generally, a fragmented version called a quasivoid, which has been recently identified in colloid experiments via a reversible transformation into a vacancy at a glass-crystal interface [32]. In this picture of void-induced dynamics, a particle hopping into a nearest-neighboring void, leaving another void behind, can be equivalently described as a local swap between a particle and a void. This is fully analogous to a local swap between a regular particle and a swap initiator. The two formalisms are thus intimately related. We have recently proposed a description of such void-induced glassy dynamics [36,38], which will be applied in the future in an attempt to account for the present results quantitatively.

Conclusion.—We have introduced a partially swapping system and found simple power laws relating diffusion coefficients to the density ϕ_s of swap-initiating particles. The exponents of the power laws depend nontrivially on temperature. These observations have not been predicted by existing theories of swap, but can be explained by facilitation and are reproduced with a lattice model. In addition, the system exhibits remarkably typical glassy dynamics at small ϕ_s, implying that main characteristics of glass formers can be defect induced.

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