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Universal Nature of Particle Displacements close to Glass and Jamming Transitions

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We examine the structure of the distribution of single particle displacements (van Hove function) in a broad class of materials close to glass and jamming transitions. In a wide time window comprising structural relaxation, van Hove functions reflect the coexistence of slow and fast particles (dynamic heterogeneity). The tails of the distributions exhibit exponential, rather than Gaussian, decay. We argue that this behavior is universal in glassy materials and should be considered the analog, in space, of the stretched exponential decay of time correlation functions. We introduce a dynamical model that describes quantitatively numerical and experimental data in supercooled liquids, colloidal hard spheres, and granular materials. The tails of the distributions directly explain the decoupling between translational diffusion and structural relaxation observed in glassy materials.

The slow dynamics of disordered materials close to glass and jamming transitions is characterized by just a few universal features [1]: dramatic dynamical changes upon mild changes of control parameters (temperature, density), broad distribution of relaxation times leading to stretched exponential decay of time correlation functions, and spatially heterogeneous dynamics [2]. Here we argue that the detailed structure of the distribution of particle displacements (van Hove function [3]) constitutes an additional universal signature of glassy dynamics. We show that, for time scales corresponding to structural relaxation, the self-part of the van Hove function has broad tails that are well described by an exponential, rather than a Gaussian, decay. We provide a broad range of numerical and experimental data, physical arguments, and a dynamical model to support this claim.

The non-Fickian character of single particle displacements in materials with glassy dynamics is well known [4–12]: time correlation functions decay nonexponentially, mean-squared displacements exhibit at intermediate time scales a subdiffusive plateau, van Hove distributions are non-Gaussian. This affects transport properties since translational diffusion is decoupled from structural relaxation [13], leading to an anomalous relation between time scales and length scales [14]. Virtually all glass theories address the stretched decay of correlation functions, but comparatively much less attention has been paid to the detailed shape of the self-part of the van Hove function [11,12,15–18], although new techniques now directly access this quantity in different materials [4–7]. Its non-Gaussian, "heterogeneous" character is often discussed in qualitative terms [16,17], and quantitative measures focus on the distribution kurtosis (non-Gaussian parameter [9]) which contains, however, very indirect information about its shape. Deviations from Gaussian behavior are usually ascribed to dynamic heterogeneity [2], i.e., to the presence of particles that are substantially faster or slower than the

average. We argue that van Hove functions contain quantitatively relevant information about the relaxation of glassy materials, and that its functional form is simple and universal, just as the stretched exponential decay of time correlation functions. Glass theories should therefore treat both phenomena on an equal footing.

We present our central observations in Figs. 1 and 2, which show the self-part of the van Hove functions for a silica melt [19], a binary Lennard-Jones (LJ) mixture [20],
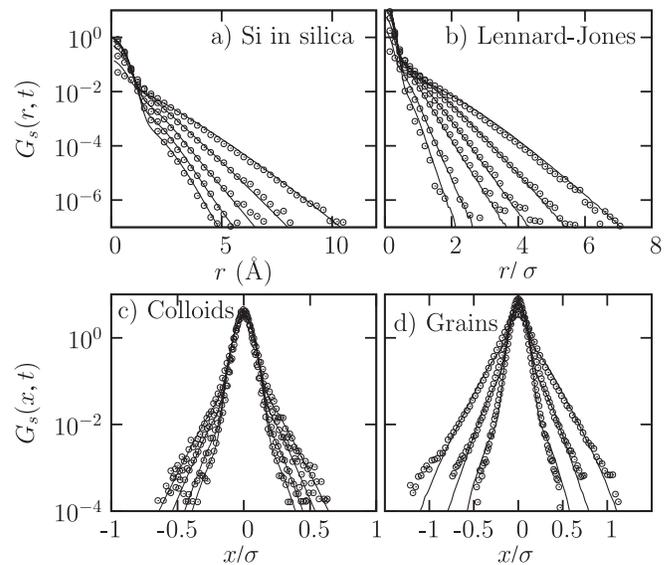
FIG. 1. Time evolution of the self-part of van Hove functions for silicon atoms in silica, Lennard-Jones particles, hard-sphere colloids, and grains (open circles), fitted with the model in Eq. (2) (full lines). They exhibit a Gaussian central part and a broad, exponential tail. (a) $T = 3000$ K and $t \in [27, 1650]$ ps. (b) $T = 0.435$ and $t \in [75 \times 10^3, 41 \times 10^6]$. (c) $\varphi = 0.517$ and $t \in [90, 1008]$ s. (d) $\varphi = 0.84$ and $t \in [10, 1000]$ cycles. (a) and (b) show the distributions of $|\mathbf{r}(t) - \mathbf{r}(0)|$, (c) and (d) the distributions of $x(t) - x(0)$.
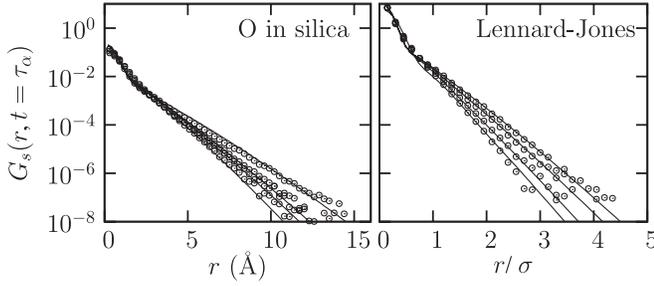
FIG. 2.   Temperature evolution of the self-part of the van Hove function for $t = \tau_\alpha$ for oxygen atoms in silica at $T = 3580$, 3200, 3000, and 2715 K (from left to right) and Lennard-Jones particles at $T = 0.5, 0.47, 0.45$, and 0.435 (from left to right). The exponential tail gets more pronounced at low temperatures. This trend is smaller in silica than for Lennard-Jones, as is the translational decoupling.

a dense suspension of colloidal hard spheres [4], and a slowly driven dense granular assembly [5]. It reads [3]

$$G_s(r, t) = \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle, \qquad (1)$$

where $\mathbf{r}_i(t)$ denotes the position of a particle i (molecule, colloid, grain) at time t, the brackets indicate an ensemble average. For technical reasons, experiments sometimes record the one-dimensional version of (1), $G_s(x, t) = \langle \delta[x - |x_i(t) - x_i(0)|] \rangle$, where $x_i(t)$ is the projection of $\mathbf{r}_i(t)$ on a given unit vector. For our purposes, the difference between the two functions is irrelevant. For all systems we find that $G_s(r, t)$ has the same structure over a broad time window comprising the structural relaxation. Most of its statistical weight is carried by particles that have barely moved, $r < \sigma$, but a "broad" tail extends to much larger distances, $r > \sigma$, where σ is the particle diameter. The small r behavior is not far from a Gaussian distribution, corresponding to quasiharmonic vibrations, but the large distance decay appears linear in Fig. 1, i.e., $G_s \propto \exp[-r/\lambda(t)]$. For a Fickian particle, one expects instead a Gaussian decay, $G_s \propto \exp[-r^2/(4D_s t)]$, where D_s is the self-diffusion constant. Although the existence of a broad tail in $G_s(r, t)$ was recognized before [4–8,12,15–17,21], its nontrivial functional form and universality went largely unnoticed.

The exponential tail extends to larger distances when t increases, but $\lambda(t)$ grows very slowly with t. Eventually, at very large times, a crossover to Fickian behavior is observed, see the latest time in Fig. 1(b). For the LJ system the crossover takes place for $t \approx 30\tau_\alpha$ [21], where $\tau_\alpha(T)$ is defined from the time decay of the self-intermediate scattering function, $F_s(q, t)$, the Fourier transform of $G_s(r, t)$. Our observations correspond to times that are shorter than this crossover. In Fig. 2, we present the evolution of $G_s(r, t)$ when the glass transition is approached, keeping t fixed to $\tau_\alpha(T)$. Clearly the shape of $G_s(r, t)$ remains unchanged, but the tail becomes more pronounced closer to the glass transition.

These observations confirm that van Hove functions can be qualitatively described as the superposition of two families of particles: localized particles contributing to the Gaussian central part and mobile particles contributing to the exponential tail. Evidence has recently been given that the distinction between mobile and immobile particles cannot be explained on a structural basis [22]. We therefore seek a purely dynamical explanation. In Fig. 3 we present representative trajectories of duration τ_α for mobile and immobile particles in the LJ system. Similar pictures have been presented before [4,5]. A large fraction of the particles perform localized, vibrational motion around their initial positions, as in a disordered solid. These "slow" particles are "caged" by their neighbors and contribute to the quasi-Gaussian central part of $G_s(r, t)$.

More interesting is the behavior of the particles contributing to the tail. On top of the localized vibrations, these particles perform a (distributed) number of quasi-instantaneous "jumps." This suggests that particles perform a form of continuous time random walk (CTRW [23]) [11,15,18,24,25]. From direct inspection of the trajectories we note that the size of the jumps is distributed, and represents on average only a small fraction of the particle size, implying that jumps probably result from cooperative events involving a large number of particles moving by a small amount [26]. Regarding time scales, trajectories also reveal that the time of the first jump after $t = 0$ is distributed. This observation directly implies that van Hove functions can be described, for $t > 0$, as a superposition between particles that have jumped, and those that have not [15]. We insist [10,22] that this coexistence is dynamically generated and we will avoid the assumption of a material being composed of two dynamically distinct families of particles [18,27].

The final empirical observation from Fig. 3 is that once a particle has managed to make a jump, it very likely makes one or several additional jumps during the rest of our observation time. We believe that this results from dynamic heterogeneity. Spatial clustering of particles with correlated dynamics implies indeed that it takes a very long time
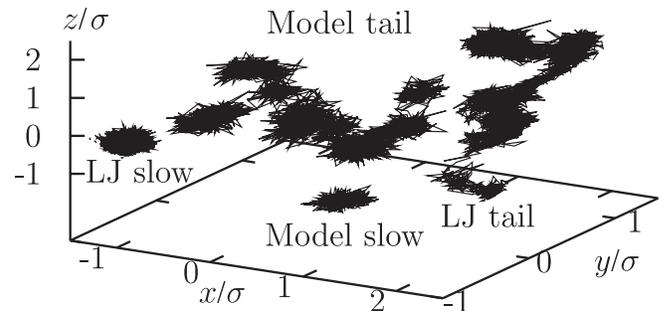
FIG. 3.   Four trajectories of duration τ_α for particles contributing to the center of the distribution (slow) and to the tail ("tail") taken from simulations of the LJ liquid at $T = 0.435$ ("LJ") and for random walkers described by (2).

for a particle belonging to a slow region to become mobile. But when this happens, the particle then likely belongs to a mobile region, which enhances considerably its probability to move further. Widely different time scales for initial and subsequent moves naturally arise, for the reason mentioned above, in kinetically constrained models [15,28], and originate from the existence of a broad distribution of waiting times between the moves [28,29]. This is likely a generic consequence of spatially heterogeneous dynamics.

We now introduce a model, inspired by Refs. [15,28], which incorporates these observations with as few free parameters as possible. The system is viewed as an assembly of dynamically indistinguishable particles, compatible with structural homogeneity. We assume solid behavior at short times. In between jumps, particles perform on a microscopic time scale a Gaussian exploration of their environment with the distribution $f_{\rm vib}(r) = (2\pi\ell^2)^{-3/2} \times \exp(-r^2/2\ell^2)$. We assume that particles perform jumps with a size sampled from $f_{\rm jump}(r) = (2\pi d^2)^{-3/2} \times \exp(-r^2/2d^2)$. We similarly assume simple forms for time distributions. The time of the first jump is drawn from $\phi_1(t) = \tau_1^{-1} \exp(-t/\tau_1)$. We then assume that subsequent jumps arise with higher frequency, using the distribution $\phi_2(t) = \tau_2^{-1} \exp(-t/\tau_2)$, with $\tau_2 < \tau_1$. It is now a simple task [23] to express the van Hove function, $G_s(r, t) = \sum_{n=0}^{\infty} p(n, t) f(n, r)$, where $p(n, t)$ is the probability to make n jumps in a time t, and $f(n, r)$ the probability to move a distance r in n jumps. These probabilities involve convolutions and are more easily expressed in the Fourier-Laplace domain, $(r, t) \rightarrow (q, s)$. We obtain

$$G_s(q, s) = f_{\rm vib}(q)\Phi_1(s) + f(q)f_{\rm vib}(q)\frac{\phi_1(s)\Phi_2(s)}{1 - \phi_2(s)f(q)},$$
(2)

where $\phi_{1,2}(s) \equiv 1 - s\Phi_{1,2}(s)$ and $f(q) \equiv f_{\rm vib}(q)f_{\rm jump}(q)$. The Montroll-Weiss equation [23] is recovered when $\phi_1 = \phi_2$ and vibrations are not considered, $f_{\rm vib}(q) = 1$. The result in Eq. (2) is valid for any choice of distributions ($f_{\rm vib}, f_{\rm jump}, \phi_1, \phi_2$). Here, we restrict to simple choices (Gaussian and exponential distributions) to emphasize the universality and physical origin of our results and to introduce as few free fitting parameters as possible: (ℓ, d, τ_1, τ_2). Equation (2) makes very transparent the fact that G_s is the superposition of localized particles, and mobile particles. We show below that the second term produces a tail that is close to exponential and arises from particles which have performed one or several jumps.

For the four systems considered in Fig. 1 we have used Eq. (2) to fit the self-part of the van Hove functions, as shown with full lines. The fits evidently match the data very well. In practice, we sought the set of parameters that allows for data fitting on the largest time window comprising structural relaxation. We find that fitting several times fixes the set of parameters with little ambiguity, while multiple choices remain possible when fitting data for a

single t. In Fig. 3 we present numerically generated trajectories of the generalized CTRW model of (2) using the parameters used to fit the LJ data, leaving us with no doubt that such a model captures the main qualitative aspects of the real trajectories. As expected, we find that both cage and jump sizes represent only a fraction of the particle size, and are very weakly dependent on the control parameters. As a rule of thumb we find $d \approx 2\ell$. For instance ($d/\sigma, \ell/\sigma$) is (0.1, 0.051) in colloids, (0.15, 0.06) in grains, and (0.35, 0.15) in the Lennard-Jones. Moreover, our results for d^2 agree well with plateau values directly measured in mean-squared displacements for all systems.

These results imply that the changes observed in Fig. 2 are mostly due to a change in the balance between τ_1 and τ_2. We naturally find that, in a first approximation, both times track the structural relaxation of the system. More interesting is the evolution of their ratio $\alpha = \tau_1/\tau_2$, reported in Fig. 4. Unfortunately, we had not enough data for grains and colloids to report accurate estimates of α in these systems and thus we concentrate on the two numerical models. In order to account for the increasingly broad tails reported in Fig. 2, α has to grow significantly when temperature decreases, as expected from the above discussion. The growth of α directly impacts on transport properties [15,28]. Within the model (2) the time decay of $F_s(q, t)$ at large q (small distance) is governed by $\phi_1(t)$, so that $\tau_\alpha \sim \tau_1$. Fickian diffusion is recovered when the average number of jumps becomes large. It is easy to show from the $q, s \rightarrow 0$ limit of (2) that $D_s \sim (\ell^2 + d^2)/\tau_2$, so that the product between self-diffusion constant and structural relaxation time scales as $D_s\tau_\alpha \sim \alpha$. Our model therefore makes a direct prediction about translational decoupling [15,28]. We have measured the normalized product, $R_{\rm dec}(T) = D_s(T)\tau_\alpha(T)/D_s(T_0)\tau_\alpha(T_0)$ (where T_0 is a high temperature) for Lennard-Jones, silicon, and oxygen atoms directly in numerical simulations; see Fig. 4. This ratio is $R_{\rm dec} = 1$ at high temperatures, and becomes
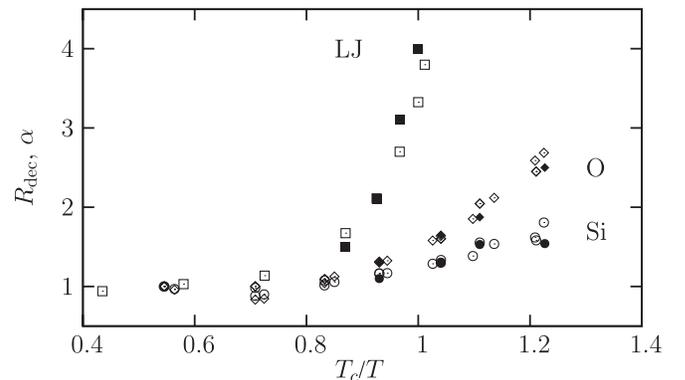
FIG. 4. Comparison of the amount of translational decoupling in silica and LJ systems measured in molecular dynamics simulations through $R_{\rm dec}$ (open symbols), and of the ratio $\alpha = t_1/t_2$ (filled symbols) employed to fit the data with the model (2). The agreement is excellent.

$R_{dec} > 1$ whenever translational decoupling occurs [14]. For three types of particles with different degrees of decoupling, we find quantitative agreement between α obtained from fits of the self-part of the van Hove function and the decoupling R_{dec} directly measured in the simulations. Thus, Fig. 4 provides a quantitative link between dynamic heterogeneity and decoupling, and supports the present modeling of self-diffusion close to a glass transition [15,28].

Why are the tails of the distributions described by an exponential decay? Non-Gaussian decay is in fact present in the original CTRW model when distances outside the realm of the central limit theorem are considered. These tails are enhanced, and hence more easily detectable, when $\alpha > 1$ and decoupling occurs. Consider the case $\alpha = 1$, $\ell = 0$ in Eq. (2). Inverting the Laplace transform yields

$$G_s(r, t) = G_0 + \frac{4\pi e^{-\bar{t}}}{r} \int_0^\infty dq [e^{\bar{t}f(q)} - 1] q \sin(qr), \quad (3)$$

where $G_0(r, t) \equiv \delta(r)\Phi_1(t)$ and $\bar{t} \equiv t/\tau_1$. We then expand the exponential in (3), integrate each term, and convert the sum into an integral to get

$$G_s(r, t) = G_0(r, t) + \frac{\pi e^{-\bar{t}}}{4d^3} \int_1^\infty dn \frac{e^{-f(n)}}{n^2}, \qquad (4)$$

with $f(n) = n \ln n - n \ln \bar{t} - n + r^2/(8d^2 n)$. The large distance limit of (4) is evaluated using a saddle point approximation,

$$G_s(r, t) \sim \frac{(\pi Y)^{3/2} e^{-\bar{t}}}{(rd)^{3/2}\sqrt{1 + Y^2}} e^{-r[Y - 1/Y]/2d}, \qquad (5)$$

where Y satisfies $Y^2 \exp Y^2 = r^2/(2d\bar{t})^2$; $Y^2 \sim 2 \log(\frac{r}{2d\bar{t}})$ for large r. Thus, we find that $G_s(r, t)$ decays exponentially (with logarithmic corrections) at large r. Interestingly, this expansion can be obtained independently of the actual shape of the distributions, establishing its universality. Considering that the tail of G_s stems from particles that have performed a number of jumps larger than average, one finds $p(n, t) \sim (\bar{t}/n)^n$ and $f(n, r) \sim e^{-r^2/(8d^2 n)}$, yielding an expression similar to (5).

We have reported the existence of a new universal feature characterizing the dynamics of materials close to glass and jamming transitions, seen in the structure of the distribution of single particle displacements which exhibits exponential decay at large distances. We argued it is a generic consequence of the existence of spatially heterogeneous dynamics, which has profound consequences on transport properties. Our results apply to a wide variety of materials from atomic liquids [1] to biophysical materials [6] and grains [5]. We strongly encourage more systematic experimental exploration of particle displacements in amorphous materials with slow dynamics.

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