Anomalous Diffusion of Driven Particles in Supercooled Liquids

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We perform nonequilibrium dynamics simulations of a binary Lennard-Jones mixture in which an external force is applied on a single tagged particle. For the diffusive properties of this particle parallel to the force, superdiffusive behavior at intermediate times as well as giant long-time diffusivity is observed. A quantitative description of this nontrivial behavior is given by a continuous time random walk analysis of the system in configuration space. We further demonstrate that the same physical properties which are responsible for the superdiffusivity in nonequilibrium systems also determine the non-Gaussian parameter in equilibrium systems.

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Introduction.—Because of the distinct multiparticle dynamics of glass-forming systems, several interesting properties can be observed, such as the occurrence of dynamical heterogeneities [1] or the violation of the Stokes-Einstein relation [2,3]. In the nonequilibrium situation, the observed phenomena can become even more complex. Recently, Winter *et al.* have performed computer simulations of a tracer particle which is driven by a constant external field through a binary Yukawa fluid [4]. It was shown that for this microrheological simulation the diffusive properties of the particle become highly anisotropic: While the mean squared displacement (MSD) of the tracer particle perpendicular to the force direction $\langle x_\perp^2 \rangle(t)$ increases with increasing force but still displays a diffusive behavior, the centered MSD parallel to the force direction,

$$\sigma^2(t) = \langle x_\parallel^2(t) \rangle - \langle x_\parallel(t) \rangle^2, \tag{1}$$

displays a superdiffusive behavior at the observed time range. This result has been rationalized in terms of a special type of biased trap model [5] in which a superdiffusive behavior is predicted due to rising fluctuations. Therefore, it was stated that the diffusion constant for the parallel direction of the tracer particle does not exist [4]. However, this model has to be regarded with care because the rising fluctuations would lead to a permanently increasing energy barrier. This scenario is difficult to reconcile with the observed stationary behavior.

A different approach is used by Jack *et al.* [6]. Motivated by the analysis of a one-dimensional spin facilitated model, they have performed an analytical calculation for a biased continuous time random walk (CTRW). For this ansatz, a diffusive regime is predicted for long times. This diffusive regime is characterized by a strong dependence on the width of the used waiting-time distribution. Broader waiting time distributions lead to a dramatic increase of spatial fluctuations, denoted as "giant diffusivity" [7]. Furthermore, in simulations of similar systems, superdiffusivity can be observed at intermediate time scales before approaching the long-time diffusive state [8,9].

The key goal of this Letter is to elucidate the properties of the superdiffusivity in the driven particle dynamics. First, we present a formal expression which relates the superdiffusivity to dynamic heterogeneities in the CTRW framework. Second, for the trajectories of a glass-forming model system, we can extract the relevant observables from an appropriate CTRW analysis and predict the superdiffusive behavior in a quantitative way. For the long-time limit our expression reduces to the giant diffusivity as calculated in Ref. [6]. Third, we are able to show that the superdiffusivity has a deep physical connection to the non-Gaussian parameter (NGP) in equilibrium, thereby establishing a strong connection between the nonequilibrium and the equilibrium dynamics of glass-forming systems. This result is discussed with respect to recent results from mode-coupling theory [10–13].

Simulations.—We have performed computer simulations of a binary mixture of Lennard-Jones particles (BMLJ) [14] which we have extended by applying a constant force on one randomly selected particle. The system has been equilibrated under continuous application of the force, thereby reaching the steady-state regime. Constant temperature conditions are ensured by using a Nosé-Hoover thermostat [15].

By applying a suitable minimization procedure, it is possible to track the minima of the potential energy landscape, called inherent structures, which the system has explored during its time evolution. Combining the inherent structures between which one observes reversible transitions to mesoscopic entities, called metabasin (MB), enables one to describe the dynamics of small systems (consisting of 65 particles, denoted as BMLJ65) as discrete transitions in terms of a CTRW [16–18]. Recently, we have demonstrated that this concept can also be transferred to stationary nonequilibrium systems [19] as used throughout this Letter.

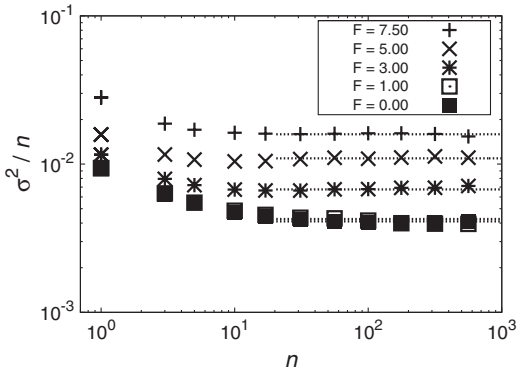

FIG. 1. Centered MSD $\sigma^2(n)$ divided by the number of transitions n of BMLJ65 at a temperature $T = 0.475$. The dashed lines indicate the diffusive lengths $a_\parallel^2$ [Eq. (2)] parallel to the force direction.

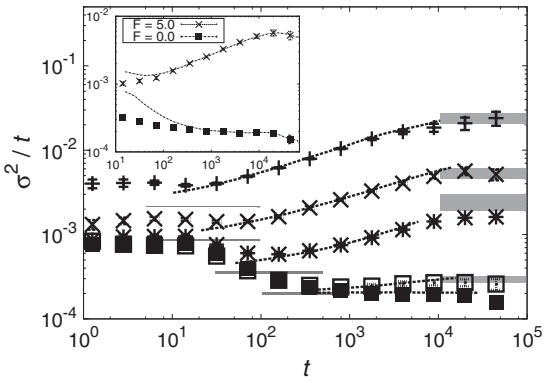

FIG. 2. Centered MSD $\sigma^2(t)$ divided by time t of BMLJ65 at a temperature $T = 0.475$. The dashed lines correspond to the theoretical prediction by Eq. (5). The gray bars at intermediate times indicate the equilibriumlike diffusion [Eq. (6)], and at long times the long-time diffusion [Eq. (10)] under consideration of the numerical error. Inset: $\sigma^2(t)/t$ of BMLJ65 at $T = 0.475$, evaluated from both MB transitions (points) and real space (lines).

MB transitions are dynamical events which are characterized by the distribution of particle displacements during one transition and the distribution of the corresponding waiting times. In the case of equilibrium [16] as well as nonequilibrium [19] systems, the waiting time distribution expands over several orders of magnitude and decays close to a power law. As shown in Ref. [19] the linear and nonlinear response only shows very small finite size effects. Here we will also show that the results of this work can be transferred to the properties of large systems as well.

Results.—Focusing on the diffusive behavior of the tracer particle parallel to the force direction, our approach offers two different routes to define the centered MSD: On the one hand, one can consider the centered MSD after a certain number of MB transitions n, on the other hand it can be evaluated after a certain time t. In the following we will distinguish between these quantities by writing $\sigma^2(n)$ and $\sigma^2(t)$, respectively. Similar to the equilibrium dynamics [16], $\sigma^2(n)$ grows linearly after more than ~ 20 transitions (see Fig. 1). In marked contrast, $\sigma^2(t)$ displays a superdiffusive behavior (see Fig. 2) as it was reported for the binary Yukawa fluid [4]. From $\sigma^2(n)$ one can define for large n the diffusive length scale $a_\parallel^2$ via

$$a_\parallel^2 = \lim_{n\to\infty} \frac{\sigma^2(n)}{n}; \tag{2}$$

see also Ref. [19]. To achieve a more quantitative understanding and to unravel the surprising qualitative differences between $\sigma^2(n)$ and $\sigma^2(t)$, we have performed an analytical calculation of $\sigma^2(t)$ within the CTRW framework. We start with a one-dimensional CTRW with an elementary step $x_{i,\parallel} = a_{i,\parallel} + \Delta x_\parallel$. $\Delta x_\parallel$ denotes the average translation the particle performs along the force direction during one MB transition. As shown in Ref. [19], $\Delta x_\parallel$ is basically proportional to F in the whole force interval considered in this work. $a_{i,\parallel}$ is considered to be the remaining translational length with $\langle a_\parallel \rangle = 0$. Successive steps are regarded as uncorrelated so that $\langle a_{i,\parallel} a_{j,\parallel} \rangle = \delta_{i,j} \langle a_\parallel^2 \rangle$. The quantity $\langle a_\parallel^2 \rangle$ can be identified with the apparent diffusive length $a_\parallel^2$ in Eq. (2) and Ref. [19], respectively. For reasons of consistency we will further denote it as the average value. Then, the MSD of the particle is given by the sum over all steps n which were performed up to a time t:

$$\langle x_\parallel^2(t) \rangle = \left\langle \left[\sum_{i=0}^{n(t)} (a_{i,\parallel} + \Delta x_\parallel) \right]^2 \right\rangle. \tag{3}$$

This yields for the time evolution of the MSD

$$\langle x_\parallel^2(t) \rangle = \langle n(t) \rangle \langle a_\parallel^2 \rangle + \langle n^2(t) \rangle \Delta x_\parallel^2. \tag{4}$$

In Eq. (4) $\langle n(t) \rangle$ denotes the average number of jumps the particle performs in a certain time t and $\langle n^2(t) \rangle$ the fluctuation of these, respectively. Considering $\sigma^2(t)$ instead of the MSD, one has to subtract the squared first moment of the particle displacement, which is given by $\langle x_\parallel(t) \rangle^2 = \langle n(t) \rangle^2 \Delta x_\parallel^2$.

After subtracting this expression from Eq. (4), one finally obtains

$$\sigma^2(t) = \langle n(t) \rangle \langle a_\parallel^2 \rangle + [\langle n^2(t) \rangle - \langle n(t) \rangle^2] \Delta x_\parallel^2. \tag{5}$$

The first term of Eq. (5) can be identified with the one-dimensional equilibrium diffusive process

$$2 D_\parallel t = \langle a_\parallel^2 \rangle \frac{t}{\langle \tau \rangle}. \tag{6}$$

However, due to the fact that our numerical data suggest a force dependence of both $\langle a_\parallel^2 \rangle$ (see Fig. 1) and $\langle \tau \rangle$ (see Ref. [19]), the magnitude of $D_\parallel$ also depends on the applied force. Because the origin is the same as in equilibrium, we will denote $D_\parallel$ as "equilibriumlike" diffusion constant, rather than equilibrium diffusion constant. The superdiffusivity of $\sigma^2(t)$ can be related to the latter term

which is only visible in driven systems. The expression $[\langle n^2(t)\rangle - \langle n(t)\rangle^2]$ describes the heterogeneity of the number of occurring jumps in a certain time interval and can be directly obtained from our trajectories.

For BMLJ65 one is able to perform a complete CTRW analysis so that each observable in Eq. (5) is directly accessible. As can be seen in Fig. 2, this ansatz allows us to quantitatively reproduce the behavior of $\sigma^2(t)$.

The time evolution can be divided into four regimes: At very short times ($t < \langle\tau\rangle$) one observes a plateau value which corresponds to the first escape process of the tracer particle out of its local cage. At $\langle\tau\rangle < t < 20\langle\tau\rangle$, $\sigma^2(t)/t$ decays to a second short diffusive regime. This behavior corresponds to the slight forward-backward correlation of the particles displacement during subsequent MB transitions (see Fig. 1 and Ref. [16] for further details). The second diffusive regime is characterized by the equilibriumlike diffusion constant $D_\parallel$. It is important to note that only in the case of small forces ($F \leq 1$) this minimum of $\sigma^2(t)/t$ indicates the true value of $D_\parallel$, while at higher forces it is already superimposed by superdiffusive contributions. We would like to emphasize that the data which are shown in Fig. 2 are calculated from a MB trajectory and therefore exhibit a different behavior at short times as compared to real space data (see also the inset of Fig. 2). Indeed, as can be seen in the inset of Fig. 2, the properties at intermediate and long times are exactly the same. A more detailed discussion about the different short-time behavior of the MB trajectories can be found in the Supplemental Material [20].

At intermediate times ($t > 20\langle\tau\rangle$), one observes a superdiffusive behavior which is caused by the nonlinear evolution of $[\langle n^2(t)\rangle - \langle n(t)\rangle^2]$. At long times, indeed, there is an indication that the MSD becomes diffusive again but with a significantly larger diffusion constant. For this particular long-time behavior one is able to yield an analytical prediction by the present CTRW ansatz.

The waiting time distribution $\varphi(\tau)$ of a single transition can be characterized by its average value $\langle\tau\rangle$ and its variance $V = \langle\tau^2\rangle - \langle\tau\rangle^2$. Because of the central limit theorem, the distribution of the cumulated waiting time τ_n of a large number of jumps n, $P_n(\tau_n)$, is given by

$$\lim_{n\to\infty} P_n(\tau_n) \propto \exp\left[-\frac{(\tau_n - n\langle\tau\rangle)^2}{2Vn}\right]. \tag{7}$$

The corresponding probability to find n jumps in a large time interval t, $P_t(n)$, is directly related to $P_n(\tau_n)$. With the substitution $n = t/\langle\tau\rangle$ in the denominator and identifying $\tau_n = t$, we obtain from Eq. (7) the expression

$$\lim_{t\to\infty} P_t(n) \propto \exp\left[-\frac{(n - \frac{t}{\langle\tau\rangle})^2}{2V\frac{t}{\langle\tau\rangle^3}}\right]. \tag{8}$$

Determination of the second moment of $P_t(n)$ yields

$$\lim_{t\to\infty}[\langle n^2(t)\rangle - \langle n(t)\rangle^2]\frac{1}{t} = \frac{V}{\langle\tau\rangle^3} = \left[\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} - 1\right]\frac{1}{\langle\tau\rangle}, \tag{9}$$

and hence, by combining Eqs. (9) and (5), for the long-time behavior of $\sigma^2(t)$

$$\lim_{t\to\infty}\frac{\sigma^2}{t} = D_\parallel f = D_\parallel\left[1 + \frac{\Delta x_\parallel^2}{\langle a_\parallel^2\rangle}\left(\frac{\langle\tau^2\rangle}{\langle\tau\rangle^2} - 1\right)\right]. \tag{10}$$

In this equation, f describes the factor which relates the equilibriumlike and the long-time diffusion constants. Independent from our derivation, Jack *et al.* analytically obtained a similar result for the giant diffusivity by considering the Montroll-Weiss equation of a biased CTRW [6]. The long-time diffusion constant $D_\parallel f$ was already indicated in Fig. 2. For BMLJ65, it is possible to explicitly compute the long-time diffusivity because of the direct access to the CTRW observables in Eq. (10). Importantly, it is also possible to estimate the long-time behavior for larger system sizes. As shown in the Supplemental Material [20], the numerically observed degree of superdiffusivity is fully compatible with the theoretical expectation. Therefore, the present approach suggests that one always obtains a diffusive behavior for long times.

The presented ansatz allows one to give an explicit criterion of how long a particle requires to reach the diffusive regime. It is related to the applicability of the central limit theorem and thus to the width of the waiting time distribution: The narrower the waiting time distribution, the earlier the particle becomes diffusive. Since the application of a strong microrheological perturbation causes a narrowing of the waiting time distribution [19], one expects an earlier advent of the long-time diffusivity at high forces. This behavior can be qualitatively observed in Fig. 2 as well.

Besides the MSD of a driven particle, the heterogeneity of MB transitions can also be observed in equilibrium systems by analyzing the NGP $\alpha_2(t)$ of the one-dimensional particle displacement which is defined as

$$\alpha_2(t) = \frac{\langle x^4(t)\rangle - 3\langle x^2(t)\rangle^2}{3\langle x^2(t)\rangle^2}. \tag{11}$$

Using the ansatz of an unbiased CTRW, one obtains for the NGP

$$\alpha_2(t) = \frac{[\langle n^2(t)\rangle - \langle n(t)\rangle^2]}{\langle n(t)\rangle^2} + \int dn P_t(n) A(n). \tag{12}$$

The latter term describes the non-Gaussianity of the cumulated displacements a_n after n transitions

$$A(n) = \frac{[\langle a_n^4\rangle - 3\langle a_n^2\rangle^2]}{3\langle a_n^2\rangle^2} \tag{13}$$

weighted by the probability to find exactly n transitions at a time t. In what follows we use the approximation that $\int dn P_t(n) A(n) \approx A(\langle n(t)\rangle)$.

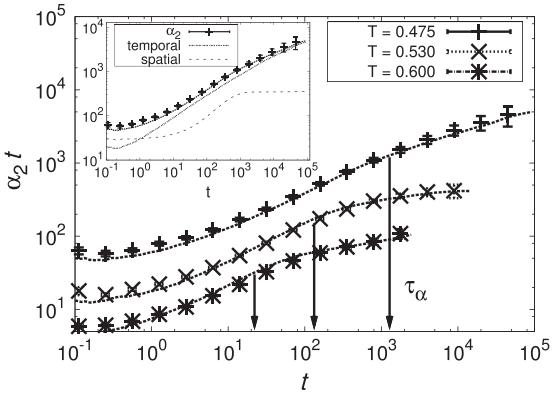

FIG. 3. One-dimensional NGP $\alpha_2(t)$ multiplied by time t as a function of t. The dashed lines correspond to the theoretical prediction in Eq. (12), the arrows indicate the structural relaxation time τ_α for the different temperatures. Inset: $\alpha_2(t)t$ at a temperature $T = 0.475$ together with its temporal and spatial contributions (see text).

Equation (12) contains two contributions: The first term includes the heterogeneity of the performed jumps n in a certain time interval. It is the same quantity that was observed to be responsible for the superdiffusive behavior in the nonequilibrium system. Because this term is independent of any length scales, one can regard it as a measure for the temporal heterogeneities of the system dynamics. The latter term reflects spatial heterogeneities of the elementary MB transition which become less important at a larger number of transitions because the distribution of the cumulated lengths approaches a Gaussian shape. In Fig. 3, $\alpha_2(t)t$ is shown at different temperatures together with the theoretical prediction by Eq. (12). Note that, as it was also shown by Liao and Chen [21], in the case of transitions between adjacent MB, $\alpha_2(t)$ displays a monotonic decay. This behavior can be understood by considering that the initial growth of $\alpha_2(t)$ is caused by vibrational parts (short times) and the β-relaxation process (at intermediate times) [14,22] while, by construction, MB trajectories only resolve the α-relaxation process [23]. As one can see, the theoretical prediction allows one to fully describe the NGP at each temperature. One further observes that for long times $\alpha_2(t)t$ approaches a constant that corresponds to a decay of $\alpha_2(t) \propto 1/t$, which is exactly the expectation for $[\langle n^2(t)\rangle - \langle n(t)\rangle^2]/\langle n(t)\rangle^2$ when the central limit theorem becomes valid [see Eq. (9)].

In the inset of Fig. 3 the different temporal and spatial contributions to $\alpha_2(t)t$ are shown. At very short times, the behavior of $\alpha_2(t)t$ is mainly determined by $A(\langle n(t)\rangle)$, while above $t \approx 10^0$, the temporal part of Eq. (12) is found to be the major contribution. At $t \approx 10^3$, one observes $A(\langle n(t)\rangle) \propto 1/t$, which indicates that the central limit theorem starts to hold for the distribution of the spatial displacement. Indeed, for the waiting time distribution the central limit theorem is only fulfilled on a larger time scale, so that there is still a growth of $\alpha_2(t)t$.

It is known from a comparison between mode-coupling theory and Brownian dynamics simulations of BMLJ [24] that mode-coupling theory tends to strongly underestimate the magnitude of $\alpha_2(t)$ in the diffusive regime. This difference between theory and simulation is also known for the hard-sphere system [25,26]. More recent results of mode-coupling theory could show that it is very successful to predict, e.g., the nonlinear dependence of the mobility on the applied force in microrheological simulations [10–13]. However, simplified models were not able to reproduce the superdiffusive behavior of a driven particle along its force direction [13]. Therefore, it is quite remarkable that the CTRW approach enables us to relate both the non-Gaussianity of the equilibrium system and the superdiffusive behavior of the stationary nonequilibrium system to have the same origin, reflecting the presence of the dynamic heterogeneities. One thus might argue whether mode-coupling theory, possibly due to its dependence on average quantities [25], is not able to fully describe these fluctuations. As a consequence, *both* effects cannot be qualitatively reproduced.

Summary.—In the this Letter we have demonstrated that a model of a biased CTRW allows us to fully predict the anomalous diffusion of a driven particle in a supercooled medium which is characterized by equilibriumlike diffusion, superdiffusivity, and long-time diffusivity. It was further shown that the origin of the superdiffusivity results from temporal fluctuations of the system dynamics which become visible due the applied bias. Indeed, also in equilibrium the same fluctuations are present and determine the evolution of the NGP $\alpha_2(t)$. Therefore, the connection between superdiffusive behavior and non-Gaussianity is a remarkable example of how nonequilibrium dynamics also enables a deeper physical understanding of the equilibrium system by uncovering essential underlying physical properties.

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