Active Nonlinear Microrheology in a Glass-Forming Yukawa Fluid

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A molecular dynamics computer simulation of a glass-forming Yukawa mixture is used to study the anisotropic dynamics of a single particle pulled by a constant force. Beyond linear response, a scaling regime is found where a force-temperature superposition principle of a Peclet number holds. In the latter regime, the diffusion dynamics perpendicular to the force can be mapped on the equilibrium dynamics in terms of an effective temperature, whereas parallel to the force a superdiffusive behavior is seen in the long-time limit. This behavior is associated with a hopping motion from cage to cage and can be qualitatively understood by a simple trap model.

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Introduction.—In active microrheology [1–4], the response of a tagged particle to an external force f is investigated. The steady-state motion of the tagged particle is characterized by an average constant velocity v that is related to f by a friction coefficient ξ via $\xi = f/v$ [5]. When the force f is sufficiently weak, the steady-state motion of the particle follows linear response theory which predicts a simple relationship between the equilibrium diffusion constant D of the tagged particle and the friction coefficient, $D\xi = k_B T$ (with k_B the Boltzmann constant and T the temperature). In glass-forming liquids [6,7] relatively small forces f suffice to observe a nonlinear response of the pulled particle. This has been shown in recent microrheological experimental studies of colloidal systems [8–10] as well as simulation and mode-coupling theory [11–15]. However, it remains unclear how the diffusion dynamics of the pulled particle changes with respect to the linear response behavior.

In this Letter, we address this issue using a molecular dynamics simulation of a glass-forming soft-sphere mixture. Deviations from linear response of the pulled particle can be quantified by a Peclet number Pe^* that compares the diffusive time scale at equilibrium with the time scale due to the external force. At intermediate values of Pe^* (beyond linear response) a scaling regime is found where a force-temperature superposition principle holds. The diffusion dynamics in the latter scaling regime exhibits strong anisotropies: In the direction perpendicular to the force, the long-time motion of the pulled particle is diffusive and the diffusion coefficient can be mapped onto the equilibrium diffusion coefficient in terms of an effective temperature. In contrast, in the direction parallel to the force a superdiffusive behavior is found at long times and the diffusion coefficient does not exist. This finding challenges the relation between active microrheology and macrorheology [3,16,17] as far as the nonlinear response in glass-forming liquids is concerned. In macrorheological experiments of glass-forming liquids under shear, only weak anisotropies are found in the (diffusion) dynamics [18,19] and there is no problem with the nonexistence of transport coefficients.

The anisotropic diffusion dynamics of the pulled particle in the nonlinear scaling regime is associated with a hopping motion from cage to cage: the particle is localized for some time in a cage formed by the surrounding particles before it quickly moves to the next cage. Whereas in the cage the motion of the particle exhibits only small anisotropies, it becomes strongly anisotropic with respect to the motion out of the cages. An essential feature for the motion of the particle in the direction of force is a broad waiting time distribution. We argue below that the dynamics of the pulled particle can be qualitatively understood in terms of an asymmetric hopping model [20,21].

Details of the simulation.—We consider a glass-forming Yukawa fluid which consists of an equimolar mixture of A and B particles. Thus, interactions between the particles are given by the pair potential $V_{\alpha\beta}(r) = \varepsilon_{\alpha\beta} d_{\alpha\beta} \exp[-\kappa(r - d_{\alpha\beta})]/r$, with r the distance between a particle of type α and one of type β ($\alpha, \beta = A, B$). The functions $V_{\alpha\beta}(r)$ are truncated at a cutoff distance $r_c^{\alpha\beta}$ defined by $V_{\alpha\beta}(r = r_c^{\alpha\beta}) = 10^{-7}\varepsilon_{AA}$. The parameters of the potential are chosen as follows: $d \equiv d_{AA} = 1.0$, $d_{BB} = 1.2d$, and $d_{AB} = 1.1d$ for the particle diameters, $\varepsilon \equiv \varepsilon_{AA} = 1.0$, $\varepsilon_{BB} = 2.0\varepsilon$, and $\varepsilon_{AB} = 1.4\varepsilon$ for the energy parameters, and $\kappa_{AA} = \kappa_{AB} = \kappa_{BB} = 6/d$ for the screening parameters. With these parameters, neither crystallization nor phase separation can occur on the time scale of our simulations. The critical temperature T_c of a mode-coupling analysis at the number density $\rho = 0.68$ (considered in this work) is $T_c \approx 0.14$.

Two different system geometries with periodic boundary conditions are used. The smaller system has cubic shape with linear size $L = 13.3d$ and 1600 particles (i.e., 800 of each type). The second system geometry is elongated by the factor of 8 in force direction, $L_x = 8L$, $L_y = L_z = L$,

which allows longer simulation runs for large forces (in the latter case longer runs are required to avoid finite size effects due to the periodic boundary conditions). All simulation runs start with fully equilibrated configurations in the temperature range $0.34 \geq T \geq 0.14$. During the production runs a constant force f with $0.5 \leq f \leq 20$ (in units of k_BT/d) was applied to one of the particles in the system. These simulations were done for 100 000 to 3×10^6 time steps and were repeated for around 1000 different particles. A dissipative particle dynamics thermostat [22] was applied to keep the temperature constant (for details see Refs. [19,23]).

Results.—In the steady state, a particle pulled by a constant force f in x direction moves with a constant velocity v such that $f = \xi v$. The friction coefficient ξ as a function of f is displayed in Fig. 1(a) for A particles and different temperatures T. Here and in the following, we show only the results for pulled A particles, because the behavior of the B particles is similar. Three different force regimes can be inferred from the figure: Toward small f, the linear response regime is approached and ξ is constant. The nonlinear regime at intermediate f is characterized by a decrease of ξ with increasing f, while for very large forces the friction coefficient becomes constant and independent of temperature. A detailed discussion of the latter "force-dominated" regime can be found in Refs. [14,15] and shall not be further considered here.

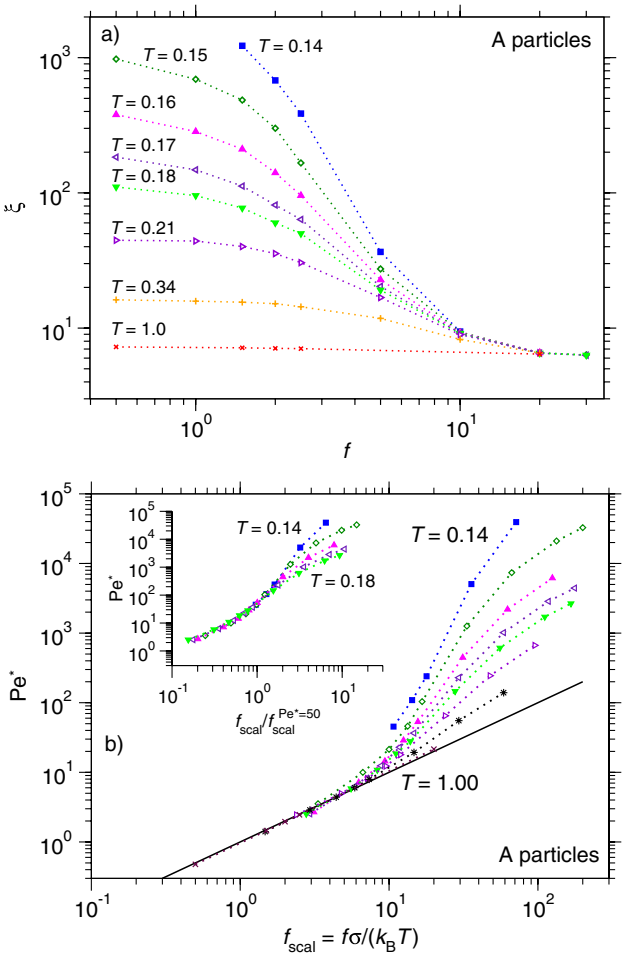

FIG. 1 (color online). (a) Friction coefficient ξ for A particles and different temperatures T as function of force f. (b) Modified Peclet number Pe^* for A particles as function of the scaled force f_{scal} for different temperatures T. The solid line indicates the linear response regime where $\mathrm{Pe}^* = f_{\mathrm{scal}}$ holds. The inset shows Pe^* as function of $f_{\mathrm{scal}}/f_{\mathrm{scal}}^{\mathrm{Pe}^*=50}$ (see text).

In order to quantify the effect of the external force f in terms of a dimensionless number, we define a Peclet number [8,13] by $\mathrm{Pe}^* = \frac{\tau_D}{\tau_f}$, with τ_D the time scale of the equilibrium diffusion (i.e., for $f = 0$) and τ_f that is set by the external force f. τ_D can be expressed as the time for which a particle diffuses a distance equal to its diameter σ, $\tau_D = \sigma^2/D_{\mathrm{eq}}$, with $D_{\mathrm{eq}}^{(\alpha)}$ the self-diffusion constant in equilibrium. τ_f is the time the particle drifts with velocity v over the distance σ, $\tau_f = \sigma/v = \sigma\xi/f$. With the scaled force $f_{\mathrm{scal}} = f\sigma/(k_BT)$ and the "Einstein" friction $\xi_0 = k_BT/D_{\mathrm{eq}}$ the Peclet number can be written as $\mathrm{Pe}^* = \xi_0 f_{\mathrm{scal}}/\xi$. In the linear response regime, $\xi = \xi_0$ holds and thus, in this case, Pe^* is equal to f_{scal}.

Figure 1(b) shows Pe^* for A particles and different temperatures as a function of f_{scal}. At the highest temperature, $T = 1.0$, almost no deviations from linear response are seen up to the high force regime (where $\mathrm{Pe}^* \approx 20$). With decreasing temperature, the linear response regime shifts to smaller values of f. For low temperature $T = 0.14$, the aforementioned nonlinear regime of intermediate forces corresponds to Pe^* numbers in the range from about 10 to 1000. In the intermediate regime of Peclet numbers a force-temperature superposition principle holds, as demonstrated in the inset of Fig. 1(b). Here, we have plotted Pe^* as a function of $f_{\mathrm{scal}}/f_{\mathrm{scal}}^{\mathrm{Pe}^*=50}$ with $f_{\mathrm{scal}}^{\mathrm{Pe}^*=50}$ the value of f_{scal} at $\mathrm{Pe}^* = 50$ for a given temperature. Obviously, the data for the different temperature fall onto a master curve at intermediate Pe^* numbers.

The latter scaling regime marks the values of Pe^* numbers where, at given temperature and force, the motion of the pulled particle is strongly affected by the specific properties of the cages formed by the surrounding particles. In contrast, at very high values of f the nonlinear response of the pulled particle is independent of temperature and force and thus of the details of the cages. In the following, we focus on the force-temperature superposition principle regime at the temperature $T = 0.14$. We shall see that the dynamics of the tagged particle is strongly anisotropic in the long-time limit whereas at intermediate times the motion of the particle in the cage is similar in the directions parallel and perpendicular to f.

A simple quantity to analyze the diffusive transport of a tagged particle is the mean-squared displacement (MSD). For the directions perpendicular to the force (y and z direction), the MSD is defined by

$\langle \Delta y^2(t) + \Delta z^2(t) \rangle \equiv \langle [y(t) - y(0)]^2 + [z(t) - z(0)]^2 \rangle$. In Fig. 2(a), these MSDs are displayed in a double-logarithmic plot for different forces at the temperature $T = 0.14$. Note that we have multiplied the MSDs by $3/2$ to allow for a direct comparison to the equilibrium MSD ($f = 0.0$). As Fig. 2(a) indicates, the external drive leads to a faster diffusive motion of the particle in the orthogonal direction.

At long times, the MSDs are linear in time as can be inferred from the inset of Fig. 2(a) where these functions are divided by t. In the long-time limit this is directly related to the self-diffusion constant $D_{\text{orth}} = \lim_{t\to\infty} \langle \Delta y^2(t) + \Delta z^2(t) \rangle / (4t)$. The logarithm of D_{orth} for different forces in comparison to equilibrium ($f = 0$) is shown in Fig. 2(b) as a function of an inverse effective temperature, $1/T_{\text{eff}}$. Here, T_{eff} is obtained by force-dependent rescaling of temperature T via $T_{\text{eff}} = C(f)T$. The function $C(f)$ was determined such that at least at low temperatures all the data for the different forces superimpose onto D_{eq}. The force dependence of $T_{\text{eff}}/T - 1$ is shown in the inset of Fig. 2(b). It can be well described by a quadratic function of f, $T_{\text{eff}}/T - 1 = C(f) - 1 = 0.0322 \times f^2$, as predicted recently by a mean-field theory for Brownian particles in the presence of a strong external force [24].

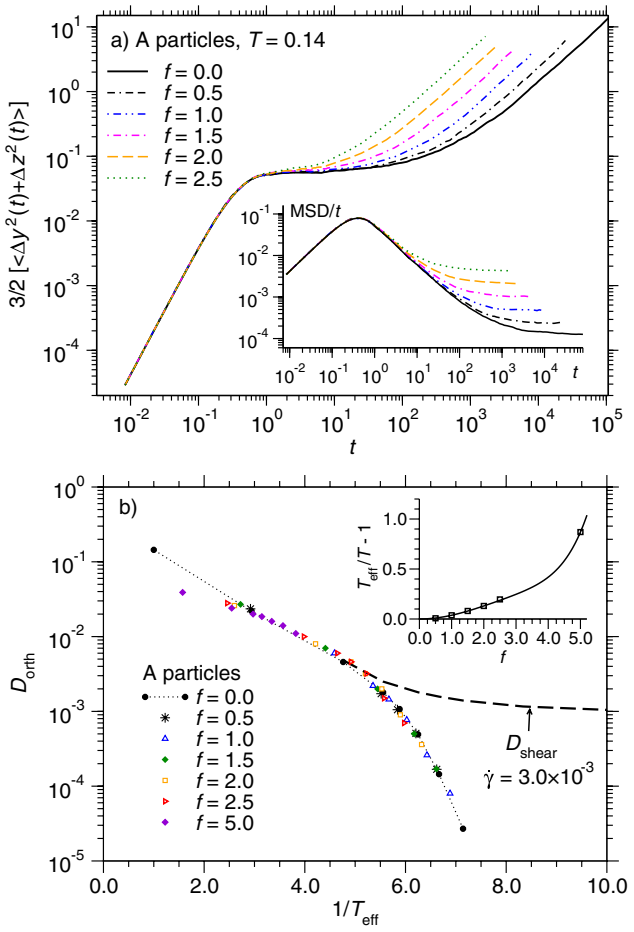

FIG. 2 (color online). (a) Mean-squared displacement of A particles for the directions perpendicular to the force for different values of f, as indicated. The temperature is $T = 0.14$. The inset shows the same mean-squared displacements divided by t. (b) Self-diffusion constant D_{orth} as function of the inverse effective temperature $1/T_{\text{eff}}$ (see text). The bold dashed line shows D_{shear} for the corresponding sheared system, applying a shear rate of $\dot{\gamma} = 3.0 \times 10^{-3}$ (from Ref. [19]). The inset shows $T_{\text{eff}}/T - 1$ as function of f (here, the solid line is a fit with $C(f) - 1 = 0.0322 \times f^2$).

Also shown in Fig. 2(b) is the self-diffusion coefficient D_{shear} for the sheared Yukawa system applying the constant shear rate $\dot{\gamma} = 3.0 \times 10^{-3}$ (from our previous simulation study [19], where also a direct comparison to experiment was performed, showing that we access the relevant regime of Pe numbers). Here, only the self-diffusion coefficient in shear direction is shown since D_{shear} in shear and vorticity direction exhibits a similar temperature dependence and differs only by a small amount. Obviously, at low temperature D_{shear} depends very weakly on temperature, as opposed to the behavior of the microrheological counterpart, D_{orth}.

The mean-squared displacement in force direction, $\langle \Delta x^2(t) \rangle - \langle \Delta x(t) \rangle^2$, exhibits a different behavior from that in the orthogonal direction. Note that the term $\langle \Delta x(t) \rangle^2 \equiv \langle [x(t) - x(0)] \rangle^2$ has to be subtracted in the latter formula in order to correct for the drift of the particle due to the external force. Also $\langle \Delta x^2(t) \rangle$ indicates an acceleration of the dynamics with increasing f, but now the MSD exhibits a superlinear behavior in the long-time regime (Fig. 3), $\langle \Delta x^2(t) \rangle \propto t^{\alpha}$ with α varying between about 1.3 and 1.45, as indicated by the solid lines. Thus, the diffusion is anomalous in x direction and the self-diffusion coefficient does not exist in this case [note that all the considered values of f at $T = 0.14$ are beyond the linear response regime, cf. Fig. 1(b)].

The inset of Fig. 3 shows a comparison between the MSD in parallel and in the orthogonal direction for the force $f = 1.5$. Both MSDs exhibit a ballistic regime at short times ($\propto t^2$) and a plateau region at intermediate times due to the caging of the particles. In the long-time regime, the MSD for the orthogonal direction crosses over to diffusive behavior ($\propto t$) while that for the parallel direction shows a superlinear behavior at long times ($\propto 1.35$). It is remarkable that the two MSDs almost coincide with each other in the plateau region which indicates that the motion in the cages exhibits only weak anisotropies. However, the motion of the pulled particle becomes strongly anisotropic when it jumps out of the cage. Whereas in the orthogonal direction the diffusive motion is qualitatively similar to the behavior in equilibrium (if one replaces temperature T by an effective, force-dependent temperature T_{eff}), in parallel direction the diffusion constant does not exist.

Now, we relate the anomalous diffusion in force direction to the distribution of waiting times. At the low temperature $T = 0.14$, the pulled particle performs a hopping

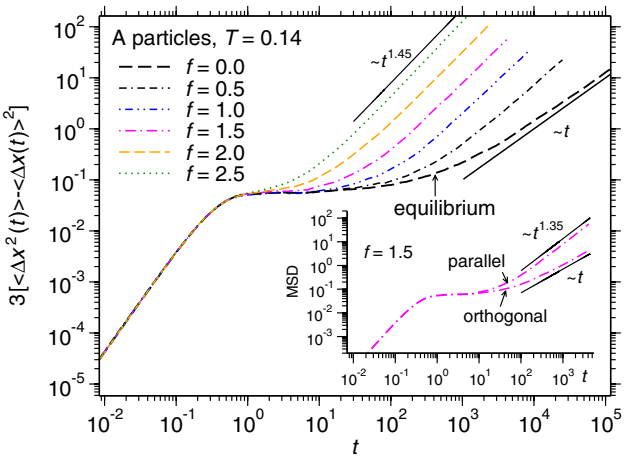

FIG. 3 (color online). Mean-squared displacement of A particles in the direction of force for different values of f, as indicated. The temperature is $T = 0.14$. The inset shows a comparison between the MSD's for the parallel and orthogonal direction for $f = 1.5$.

motion from cage to cage. This is indicated by the trajectory $x(t)$ in the inset of Fig. 4. After being localized in a cage for a time τ, the particle moves quickly to the next cage which is a distance Δx apart. Figure 4 shows the waiting time distribution $P(\tau)$ for different values of f, again at $T = 0.14$. The decay of $P(\tau)$ can be well described by a stretched exponential function $F(\tau) \propto \exp(-C\tau^{\beta})$ with $\beta = 0.5$ (solid lines in the figure). Thus, $P(\tau)$ can be described by a broad distribution associated with the superlinear behavior of the MSD in force direction.

The scenario that we find here is reminiscent of a certain class of trap models, introduced by Bouchaud *et al.* [20,21]. The directed walk among traps with a broad release time distribution is given by a master equation for

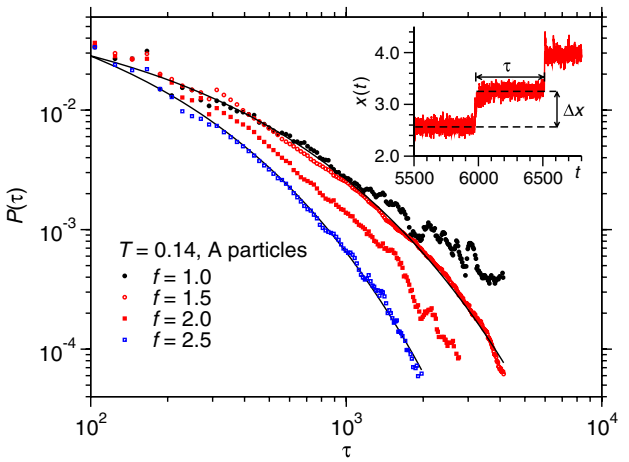

FIG. 4 (color online). Waiting time distribution $P(\tau)$ for different values of f. The solid lines are fits with stretched exponentials with $\beta = 0.5$. The inset shows an example for a trajectory $x(t)$ to illustrate the definition of waiting time τ.

a one-dimensional lattice model with a random distribution of asymmetric transition rates at each lattice site (caused in our case by the force on a tagged particle in $+x$ direction and considering the surrounding particles as a random energy landscape). This model yields superdiffusive behavior if the ratio between the mean bias and fluctuating part of the random potential seen by the random walker is between 1 and 2 (the latter ratio is quantified by a parameter μ [20]). In our case, the fluctuating part of the random potential corresponds to the rattling motion of the tagged particle in the cage and the mean bias to the directed hopping from cage to cage. Note that for very high forces (see above), the motion of the pulled particle becomes diffusive again; in fact, this is predicted by the trap model for $\mu > 2$.

Summary and conclusions.—We have presented an extensive molecular dynamics simulation to reveal active nonlinear microrheology in a binary Yukawa mixture. Beyond linear response, we find a regime of intermediate Peclet numbers Pe^* where Pe^* follows a force-temperature superposition principle. In this regime, the motion of the pulled particle exhibits strong anisotropies in the long-time limit; in particular, superdiffusion in parallel force direction is found. We have shown that the diffusion dynamics is completely different from that of glass-forming liquids under shear, and so we challenge a possible relationship between microrheology and macrorheology.

The superdiffusive regime is only seen in the strongly supercooled regime, characterized by a broad waiting time distribution and a hopping motion of the pulled particle through a quasifrozen environment. Thus, the latter regime has not been observed in recent microrheological studies, focussing on the diffusion dynamics of "nonglassy" fluids [17,25]. We have indicated that superdiffusion at intermediate Pe^* can be understood in terms of a simple trap model. However, this model does not take into account the concept of an effective temperature T_{eff} for the transverse diffusion. As indicated above, T_{eff} has a quadratic dependence on the external force f and can be understood in terms of a mean-field theory [24]. Via this route, the transverse diffusion can be incorporated into a three-dimensional trap model. This is an issue for forthcoming studies.

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