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Transition from diffuse to subdiffusive motion in colloidal liquids

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In this work we report experimental and theoretical results for the motion of single colloidal particles embedded in complex fluids with different interparticle interactions. The motion of particles is found to follow a similar behavior for the different systems. In particular, the transition from the short-time diffusive motion to the subdiffusive intermediate-time motion, is found to occur when the square root of its mean squared displacement is in the order of 1 tenth of the neighbors interparticle distance, thus following a quantitative criterion similar to the Lindemann's criterion for melting.

The motion of single colloidal particles in complex fluids is widely use to probe physical properties of the hosting media. The description of such properties in terms of microscopical quantities makes the study of such phenomenon also quite interesting form a fundamental point of view. Single particle motion is described in terms of the particle's mean squared displacement (MSD) $\langle \Delta \mathbf{r}^2(t) \rangle$, where $\Delta \mathbf{r}(t)$ is the particles displacement at time t, with the angular parenthesis representing an equilibrium ensemble average. The general behavior of this quantity can be summarized as follows. At short-times the MSD is a linear function of time, i.e., $\langle \Delta \mathbf{r}^2(t) \rangle = 2dD_S t$ where d is the systems's dimensionality, and D_S is the short-time diffusion coefficient which, for hard-sphere interparticle interaction, depends essentially on the particles concentration via the indirect hydrodynamic interactions[1]. The span of this initial linear regime of the MSD defines the short-time scale. At much larger times, when the particle probes the structure of the media, the motion is also diffusive with a different diffusion constant which depends on the interparticle interactions. The time between those limits, is simply referred to as the intermediate-times regime and it is characterized by a subdiffusive motion of the particles.

The transitions from the short- to the intermediate-time and from the intermediate- to the long-time regime are not abrupt, i.e., the change in the slope of the MSD is smooth from the initial linear regime to the asymptotic one at long times. Nev-

ertheless, the former transition, as we show here, exhibits a regular behavior independent of the interparticle interactions, i.e., the onset of such transition of dynamics follows a simple criterion, namely, that the square root of the MSD is in the order of the 10% of the mean distance between neighboring particles. As one can note here, such criterion resembles the Lindeman's criterion for melting of solids as temperature increases[2]. Here, however, we are concern with a transition of dynamics in fluid systems and not with a phase transition. Thus, the mentioned transition is not locate at an exact value but within a narrow range. Then, here we focus on the particle's motion at short-time which is visualized as occurring within the instantaneous cage formed by the neighboring particles[3]. In such time scale, the system's structure does not change appreciably, and the individual particles move randomly inside the cage probing the interstitial spaces between the neighboring particles. As time increases, the average displacement increases and the cage "melts" allowing the particle to move through.

In this work, we investigate the motion of colloidal particles in fluid media under two quite dissimilar experimental conditions. In one case, we study quasi-two-dimensional (Q2D) systems, consisting of aqueous suspensions of monodisperse polystyrene particles confined between two plates, in such a way that the particles motion is practically only along the plane parallel to the plates. Here, the tracer particles are solid and belong to the same species as the other particles in the system. In this case, the initial motion is hindered by the interparticle hydrodynamic interactions (HI) and from the hydrodynamic coupling to the walls. In the other case studied here, the systems consist of solid particles, at a very low concentration, embedded in aqueous solutions of polymer of high molecular weight with a radius of gyration similar to the radius of the solid particles. Thus, in this second case, the tracers are embedded in a sea of particles of about the same size but of different nature. The former are solid and the latter are not, they can interpenetrate each other. Thus, here the HI should be vanishing small, but the short-time dynamics is hindered by the direct contact with polymer particles . It is found in those systems, that the onset of the intermediate-times, i.e., the "melting" of the cage and the passage of the

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particles throughout the layer of first neighbors, occurs following the Lindemann-like criterion mentioned above. This criterion appears to be satisfied in other systems, with different interactions from those studied here. van Megen *et al.*[4], reported measurements by dynamic light scattering (DLS) of the incoherent scattering function of hard spheres at various concentrations of the colloidal particles. In those references, the authors reported the MSD normalized with the particles diameter. However, when we re-plot the same data but using the mean interparticle distance ℓ as the normalization length, it was shown that the MSD behaves as describe above, i.e., there is an initial linear regime and then the motion becomes subdiffusive when $[\langle\Delta\mathbf{r}^2(t)\rangle]^{1/2} \sim 0.1\ell$, where $\ell \equiv [\pi/6\phi]^{1/3}\sigma$, with ϕ and σ being the particles volume fraction and diameter, respectively. The same observation was made when we re-plotted the measurements of the lateral motion in mixtures of superparamagnetic particles at the interface water-air reported by König et. al.[5].

The Q2D systems studied here were prepared as follows[6]. Monodisperse water suspensions of polystyrene spheres carrying negative charged sulfate end groups on the surface are extensively dialyzed against nanopure water to eliminate the surfactant added by the manufacturer (Invitrogen). In a clean atmosphere of nitrogen gas, the suspension of particles of diameter $\sigma = 1.9 \pm 0.05$ μm is mixed with a small amount of larger particles of diameter $h = 2.92 \pm 0.08$ μm. A small volume of the mixture (≈ 1 μl), is confined between two clean glass plates (a slide and a cover slip), which are uniformly pressed one against the other until the separation between the plates is h. Thus, the larger particles scattered across the sample serve as spacers with an average distance of ~ 100 μm between them. The system is then sealed with epoxy resin, and the species of mobile particles allowed to equilibrate in this confined geometry at room temperature (23.6 ± 0.5 $^\circ C$). The samples are observed from a top view (perpendicular to the walls plane), using an optical microscope and the motion of the particles is recorded using standard video equipment. The particles positions in each frame are determined using the algorithm devised by Crocker and Grier[7], which allows to locate a particle's position with a precision of 1/5 pixel. In our setup, a Zeiss microscope with a 40$\times$ objective, we measure 1μm =10 pixels. Thus, the spatial accuracy is 20 nm. From the analysis of the images, the 2D trajectories $\mathbf{r}_j(t)$ of the particles are determined in runs of 2 hours with a time resolution Δt =1/30 s.

In the second case, the MSD of the solid colloidal particles in the bulk of the polymer solutions is measured by light scattering. At the concentrations of polymer studied here, the polymer solutions scatter light by themselves. Thus, in order to avoid the contribution from the polymer matrix itself, the solid particles we use here are optically anisotropic particles and the intermediate scattering functions are mea-

sured by depolarized dynamic light scattering (DDLS). The solid particles are made of liquid crystal (LC) with radius 200 nm and size polydispersity of about 5%. The particles are dispersed in aqueous solutions of Polyethyleneoxide (PEO) which is a no-adsorbing polymer. The preparation of particles and polymer solutions is done as described in references[8–10]. We studied solutions of PEO of three different values of the molecular weight M_W, 900 kDa, 4000 kDa and 8000 kDa, at concentrations above the overlapping concentration $C^* = M_W/(4\pi N_A R_G^3/3)$, where R_G is the polymer radius of gyration and N_A is the Avogadro's number. For PEO $R_G = 0.215M_W^{0.583\pm0.031}$ Å. Thus, for the polymers studied here, $R_G = 64$, 152 and 228 nm, for $M_W = 900$, 4000 and 8000 KDa, respectively. Let us note here that the size of the liquid crystal particles is close to that of the polymers of higher M_W. In order to avoid interactions between LC particles, the volume fraction used in the experiments was $\phi_{LC} \approx 10^{-5}$. All experiments were performed at a constant temperature of 25 $^\circ$C.

The use of DDLS is described in more detail elsewhere[8,9]. Briefly, in a DDLS experiment a polarized laser beam of wavelength $\lambda = 488$ nm is focused onto the sample, the scattered light passes throughout a second polarizer and detected at an angle θ with respect to the direction of the incident beam. The scattered light is split and directed toward two photomultipliers whose output is used in the pseudo cross correlation mode. Due to its optically anisotropy, LC particles depolarize light, thus the intermediate scattering time correlation function can be measured in two different geometries of the polarizers: both vertical (VV) and one vertical and the second horizontal (VH). These correlation functions describe the particles dynamics, and for no-interacting particles they can be written as $g_{VV}^{(1)}(k,t) = \left[A + Bf_R(t)\right]f(k,t)$ and $g_{VH}^{(1)}(k,t) = f_R(t)f(k,t)$, where $f_R(t)$ and $f(k,t)$ are the dynamic correlation functions describing single particle rotational and translational motion in the host matrix, respectively. A and B are constants depending only on the components of the particle's polarizability tensor, which are intrinsic particle properties, and can be measured in a known host fluid (water in this work), $k = (2\pi n/\lambda)sin(\theta/2)$ with n being the sample's index of refraction. The results shown below correspond to measurements at $\theta = 30^\circ$. The mean squared displacements, rotational and translational, can be obtained from the dynamic correlation functions by using the Gaussian approximation, i.e., by assuming $f(k,t) = \exp(-k^2\langle\Delta\mathbf{r}^2(t)\rangle/6)$ and $f_R(t) = \exp(-6\Omega(t))$ with $\Omega(t)$ being the angular mean squared displacement. Here we report only the translational MSD.

Figure 1 shows the MSD of colloidal particles measured in the Q2D systems for various values of the area fraction ϕ_a and for a wide range of time, spanning from the short-
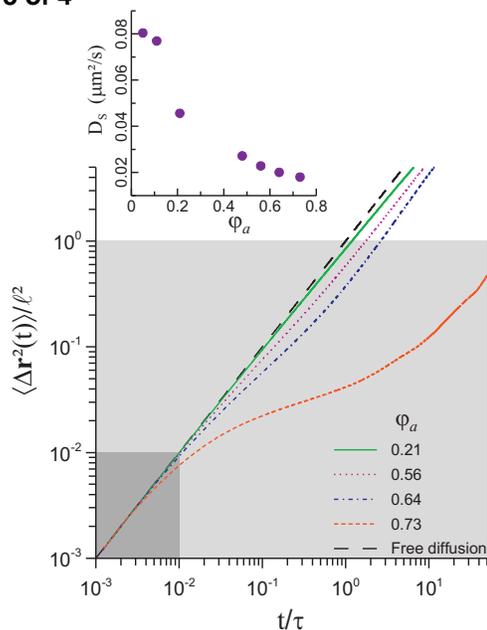
Fig. 1 Scaled mean squared displacement of colloidal particles in monodisperse suspensions, confined in a quasi-two-dimensional geometry, for various values of the particle area fraction. The inset shows the measured short-time diffusion coefficient.

to the long-time regimes. The MSD is normalized here with the square of the mean interparticle distance $\ell \equiv [\pi/4\phi_a]^{1/2}\sigma$. The time t is normalized with the inverse of the initial slope of the normalized MSD, i.e., with $\tau \equiv \ell^2/4D_S$, which is the time it takes a particle with a diffusion coefficient D_S to diffuse a distance equal to the interparticle distance. Thus, at short-times, $\langle\Delta\mathbf{r}^2(t)\rangle/\ell^2 = t/\tau$. For low particle concentrations, ϕ_a in the order of 10^{-2} or lower, the measured MSD is a linear function of time during the experimental time window reported here (data not shown), i.e., no cage effect is produced due to the large interparticle separation. As shown in previous works[6,11], in these Q2D systems the interparticle interaction is essentially that of hard sphere. As the concentration of particles increases, the MSD is linear only within some time interval, which is by definition the short-time regime. At larger times the MSD deviates from linearity (for comparison a straight line of slope 1 is drawn as a dashed line) and at even larger times it is linear again but the slope is less than unity. The time span for the transition from the short- to the long-time regime depends on the particle concentration and can be as long as several decades of time. As we anticipated above, the interesting feature to note here, is that the onset of the intermediate-time scale, i.e., the transition form diffusive to subdiffusive motion, occurs for all systems at times when the amplitude of the particle displacements is about 10% of the interparticle distance, i.e., when $[\langle\Delta\mathbf{r}^2(t)\rangle]^{1/2} \sim 0.1\ell$. This fea-

ture is highlighted in figure 1 by the dark-shadow area within which the MSD for all systems is practically linear. Thus, one can see that for the Q2D systems studied here, particle escaping from the cage occurs also following the Lindemann-like criterion. The inset of figure 1 shows the measured D_S whose value depends essentially on the particles concentration via the indirect hydrodynamic interactions which increase the effective friction on the particles as the concentration increases. The light-shadow area highlights the intermediate-time zone. Let us note here that, for the sake of clarity, in this figure we use lines instead of symbols and no error bars are presented. In any case, errors bars would be within the symbol size.

Figure 2 shows the translational MSD of LC colloidal particles of radius 200 nm, measured in PEO solutions of $M_W = 8000$ kDa at polymer concentrations $c = 0.051, 0.1, 0.25$ % (W/W), which are above the overlapping concentration $c^* = 0.03$ % (W/W). The MSD is normalized with the square of the interpolymer mean distance $\ell_p \equiv (M_W/c)^{1/3} = 298, 237, 175$ nm, corresponding to the lower, intermediate and higher concentration, respectively. The time is normalized with $\tau \equiv \ell_p^2/6D_S$. In this case, we measure the motion of solid particles embedded in a sea of overlapping particles of roughly the same size. Thus, the particles do not move in a continuum nor they probe the details of the mesh. The interparticle interaction in this system can be assumed to be, in a first approximation, that of the Asakura-Oosawa (AO) model, i.e., the polymers are non-interacting particles whereas the particle-polymer and particle-particle interaction is considered to be that of hard spheres. Since the solid particles are highly diluted, the interparticle interactions do not play a significant role in their dynamics. As one can see here, the MSD of the solid particles exhibits a behavior similar to that observed in monodispersed suspensions of solid particles i.e., there is a short-and a long-time diffusive regime, separated by a subdiffusive intermediate-time regime. Thus, the short-time motion of a solid particle can also be pictured as occurring inside a cage of polymers from which it escapes when its MSD satisfies the same quantitative criterion observed in the Q2D system of hard-spheres. The results for the intermediate value of M_W (data no shown) shows similar behavior as that in fig. 2, whereas for the lower M_W the MSD is practicaly a linear function of time in the range of polymer concentration considered in this work.

In order to see whether the behavior of the MSD in the second case is amenable to theoretical modelling, we calculate the dynamic properties of an AO colloid-polymer mixture within the scheme of the multicomponent self-consistent generalized Langevin equation (SCGLE) theory[12–15]. The required inputs in this theory are the partial static structure factors $S_{\alpha\beta}(k)$, the concentrations of both species, the ratio $D^* = D_0^p/D_0^c$ of the polymer/colloidal particle free diffusion coefficients D_0^p and D_0^c, respectively, and their size ratio $q = \sigma_p/\sigma_c$,
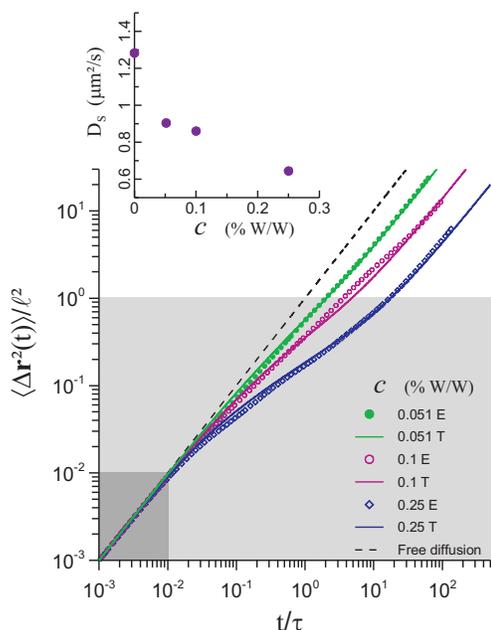
Fig. 2 Scaled mean squared displacement of solid particles moving in solutions of polymers of high molecular weight at concentrations above the overlapping concentration. Symbols represent experimental results and lines represent theoretical results. The inset shows the measured short-time diffusion coefficient.

where σ_p and σ_c are the polymer and the colloidal particles diameters, respectively. Here, the partial static structure factors are calculated using the density functional approximate theory of Ref. [16]. The colloids volume fraction is kept constant at the same value of that in the experimental systems, i.e., $\phi_c = 10^{-5}$. The free diffusion coefficients ratio is determined experimentally to be $D^* = 1.7$, and the size ratio is taken as $q = 0.68$. For the mean interpolymer distance we were required to use smaller values than the experimental values. Thus, in this way, we have an approximate theoretical determination of the dynamic properties of the mixture including, of course, the MSD of the colloidal particles, which can then be compared with the experimental measurements. The solid lines in figure 2 are the results from the SCGLE theory using values of ℓ_p reduced from the experimental ones by a factor of 1.65, 1.49 and 1.28 for the lower, intermediate and higher polymer concentrations, respectively. As one can appreciate from this figure, most of the important qualitative features and tendencies of the experimental data are also observed in the theoretical predictions. In this sense, theories such as the SCGLE theory (or the analogous mode coupling theory) can help us glimpse the dynamic behavior in the system, even if it is only in a qualitative manner. Although we still made use of an adjustable physical quantity, this figure illustrates that the current status of this comparison constitutes a good starting point for further

developments in this system.

In summary, here we have reported a study of the motion of colloidal particles embedded in two different complex fluid media. Although the environment probed by the particles is quite dissimilar in both systems, the MSD exhibits in general a qualitative coincident behavior in both cases and also with those reported by other groups in other kinds of systems. As we show here, coincidences are also quantitative. In particular, the transition from the short-time diffusive dynamics to subdiffusive motion, although it is not abrupt, exhibits the same behavior for a variety of systems with different interparticle interactions which can be cast in a form of a Lindemann's-like criterion. We consider here systems with short ranged interparticle potential, but we expect the scaling to be valid for repulsive potentials, as it is the case for the one in ref. 5 where the effective interaction is repulsive of long range. The colloid-polymer mixture is also considered from a theoretical perspective. This system is actually quite complex. However, it appears to be well described by the SCGLE theory, using the simple Asakura-Oosawa model interaction, but we need to use one of the physical quantities as a fitting parameter. The fact that we can achieve an excellent agreement with the experimental data motivates further investigation along this direction.

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