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Electronic Supplementary Information (ESI): Structure and dynamics of concentration fluctuations in a non-equilibrium dense colloidal suspension

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Abstract

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I. THEORY OF NON-EQUILIBRIUM FLUCTUATIONS IN A COLLOIDAL SUSPENSION

In the first part of this section we will briefly review the main theoretical results presented by R. Schmitz in Ref. [1], where the dynamic structure factor $S(\mathbf{q},\omega)$ of concentration fluctuations is calculated with fluctuating hydrodynamics [2] for both a suspension in equilibrium conditions and a buoyancy matched suspension in the presence of a steady concentration gradient maintained by continuous pumping of the solvent through semi-permeable walls. We will then derive a more general expression for $S(\mathbf{q},\omega)$ that holds for a non-buoyancy matched suspension in non-equilibrium conditions. This expression will be provided by using the variables originally chosen by Schmitz and also in terms of the variables that are more commonly employed in standard literature of hydrodynamic fluctuations in binary mixtures (see, for example [3]), which are also the variables used in the main text. This choice was made to express our results in a form that is easier to compare with the relevant literature on molecular binary mixtures, while at the same time maintaining a strong link with Ref. [1].

In Ref. [1] the colloidal suspension is described in terms of the set of basic variables ($n(\mathbf{r}$,t),$\rho(\mathbf{r}$,t),$\mathbf{G}(\mathbf{r}$,t)), where $n(\mathbf{r}$,t) is the number density of the colloidal particles, $\rho(\mathbf{r}$,t) the total mass density of the suspension and $\mathbf{G}(\mathbf{r}$,t) its the momentum density. Also, to get rid of the contributions to the dynamics of the fast, propagating sound modes, the alternative set ($c(\mathbf{r}$,t),$p(\mathbf{r}$,t),$\mathbf{G}(\mathbf{r}$,t)) is also used in Ref. [1], where $c(\mathbf{r}$,t) $= n(\mathbf{r}$,t)$/\rho(\mathbf{r}$,t) is specific number density (the number of particles per unit mass) and $p(\mathbf{r}$,t) is the pressure.

The derivation of an analytical expression for $S(\mathbf{q},\omega)$ in non-equilibrium conditions requires linearizing around the steady state solution (n, ρ, $\mathbf{G}$) the nonlinear conservation equations, as well as the constitutive equations, and adding random terms to the dissipative currents. This series of operations leads to a system of stochastic Langevin equations in the fluctuations ($\delta n(\mathbf{r}$,t),$\delta\rho(\mathbf{r}$,t),$\delta\mathbf{G}(\mathbf{r}$,t)) around the steady state. The equations take their simplest form in the Fourier domain when written in terms of the normalized variables $\delta c'(\mathbf{q},\omega)$ and $\delta v'(\mathbf{q},\omega)$. Here $\delta c'(\mathbf{q},\omega)$ is the normalized fluctuating part of the specific number density, defined as $\delta c'(\mathbf{q},\omega) = \sqrt{\mu_c(q)\rho}\delta c(\mathbf{q},\omega)$ and $\delta v'(\mathbf{q},\omega) = \hat{\mathbf{z}} \cdot (1 - \hat{\mathbf{q}}\hat{\mathbf{q}}) \cdot \frac{1}{\sqrt{\rho}}\delta\mathbf{G}(\mathbf{q},\omega)$ is a projection along the z axis, oriented in the opposite direction of the acceleration of gravity $\mathbf{g}$, of the normalized fluctuating momentum density. Also, $1/\mu_c(q)$ is the osmotic compressibility of the suspension, where $\mu_c(q)$ is defined as the Fourier transform of the functional derivative of $\mu(\mathbf{r})$ with respect to $c(\mathbf{r})$ at constant pressure: $\mu_c(q) = \int d\mathbf{r}\mu_c(\mathbf{r})e^{-i(\mathbf{q}\cdot\mathbf{r})}$, where $\mu_c(\mathbf{r}-\mathbf{r}') = \mu_c(\mathbf{r}, \mathbf{r}'|[p, c]) = \frac{\delta\mu(\mathbf{r})}{\delta c(\mathbf{r}')}$. Here, $\mu(\mathbf{r}) = m\left[\mu^1(\mathbf{r}) - \mu^0(\mathbf{r})\right]$ is the relative chemical potential of the colloidal phase with respect to the solvent i.e. the difference in chemical potentials per unit mass between the colloidal phase ($\mu^1(r) = \frac{\delta F^{Th}}{\delta\rho^1(\mathbf{r})}$) and the solvent ($\mu^0(r) = \frac{\delta F^{Th}}{\delta\rho^0(\mathbf{r})}$) multiplied by the mass m of a particle. In addition, $F^{Th}[\rho^0, \rho^1]$ is the thermal free energy, expressed as a functional of the mass density $\rho^0(\mathbf{r}, t)$ of the solvent and the mass density $\rho^1(\mathbf{r}, t)$ of the colloidal phase.

In the case where the macroscopic concentration gradient is parallel or antiparallel to the acceleration of gravity $\mathbf{g} = -g\hat{\mathbf{z}}$, the stochastic Langevin equations describing the suspension read:

$$\begin{pmatrix} j\omega + D(q,\omega)q^2 & -\nabla c\sqrt{\mu_c(q)} \\ \frac{\rho_c(q)g}{\rho\sqrt{\mu_c(q)}} & j\omega + \nu_T(q,\omega)q^2 \end{pmatrix} \begin{pmatrix} \delta c'(\mathbf{q},\omega) \\ \delta v'(\mathbf{q},\omega) \end{pmatrix} = \begin{pmatrix} \tilde{\xi}(\mathbf{q},\omega) \\ \tilde{\eta}(\mathbf{q},\omega) \end{pmatrix} \tag{1}$$

where j is the imaginary unit, $D(q,\omega)$ the mass diffusion coefficient, $\nu_T(q,\omega)$ the transverse kinematic viscosity, ∇c is the concentration gradient, and $\rho_c(q)/\rho$ is the solutal expansion coefficient of the suspension, whose dependence on q results from the possible interactions between the colloidal particles. Explicitly, $\rho_c(q)$ is the Fourier transform of the functional derivative of $\rho(\mathbf{r})$ with respect to $c(\mathbf{r})$ at constant pressure: $\rho_c(q) = \int d\mathbf{r}\rho_c(\mathbf{r})e^{-i(\mathbf{q}\cdot\mathbf{r})}$, where $\rho_c(\mathbf{r}-\mathbf{r}') = \rho_c(\mathbf{r}, \mathbf{r}'|[p, c]) = \frac{\delta\rho(\mathbf{r})}{\delta c(\mathbf{r}')}$.

In Ref. [1] the concentration gradient ∇c is explicitly given as the sum of two terms $\nabla c = \left(\frac{\rho_c}{\rho\mu_c}g + \frac{c}{\rho D}j_0\right)$. The first term coincides with the concentration gradient ∇c_{sed} that would be present at equilibrium due to sedimentation, while the second one is an externally imposed concentration gradient ∇c_{ext}, which, in the case explicitly discussed by Schmitz, is maintained across the sample by pumping the solvent at a fixed rate j_0. The symbols (ρ_c, μ_c, D), written without explicit indication of the arguments, indicates the macroscopic, q-independent, values of the corresponding microscopic quantities. The random forces $\tilde{\xi}(\mathbf{q},\omega)$ and $\tilde{\eta}(\mathbf{q},\omega)$ have a zero average and their covariance is given by Eqs. 6.13 in Ref. [1] *i.e.*

$$\begin{aligned}
\left\langle \tilde{\xi}(\mathbf{q},\omega)\tilde{\xi}^{*}(\mathbf{q}',\omega')\right\rangle &= 2k_BT\Re[D(q,\omega)]q^2(2\pi)^4\delta(\mathbf{q}-\mathbf{q}')\delta(\omega-\omega') \\
\left\langle \tilde{\xi}(\mathbf{q},\omega)\tilde{\eta}^{*}(\mathbf{q}',\omega')\right\rangle &= 0 \\
\left\langle \tilde{\eta}(\mathbf{q},\omega)\tilde{\eta}^{*}(\mathbf{q}',\omega')\right\rangle &= 2k_BT\Re[\nu_T(q,\omega)]q^2(2\pi)^4\delta(\mathbf{q}-\mathbf{q}')\delta(\omega-\omega')
\end{aligned} \tag{2}$$

where $\Re[...]$ indicates the real part operation. The explicit solution of Eqs. 1 in the general case was not calculated in Ref. [1] where the assumption $\bar{\rho}_c = 0$ was made. After some manipulation we obtain the following general expression for the normalized specific fluctuating number density

$$\delta c'(\mathbf{q},\omega) = \frac{\left[\nu_T(q,\omega)q^2\tilde{\xi}(\mathbf{q},\omega) + \nabla c\sqrt{\mu_c(q)}\tilde{\eta}(\mathbf{q},\omega)\right]}{[j\omega+\nu_T(q,\omega)q^2][j\omega+D(q,\omega)q^2] + \frac{\rho_c(q)}{\rho}\nabla c\cdot\mathbf{g}} \tag{3}$$

and using Eqs. 2 we finally obtain the expression

$$\left\langle|\delta c'(\mathbf{q},\omega)|^2\right\rangle = k_BT\frac{\left[2\Re(D(q,\omega))q^2|j\omega+\nu_T(q,\omega)q^2|^2 + 2\Re(\nu_T(q,\omega))q^2\left(\nabla c\right)^2\mu_c(q)\right]}{|[j\omega+\nu_T(q,\omega)q^2][j\omega+D(q,\omega)q^2] + \frac{\rho_c(q)}{\rho}\nabla c\cdot\mathbf{g}|^2} \tag{4}$$

for the Fourier power spectrum of the fluctuating reduced specific number density. In order to make easier the comparison with previous work on binary mixtures in is worth recasting the last equation in terms of the mass fraction

$$w(\mathbf{r},t) = \frac{\rho^1(\mathbf{r},t)}{\rho(\mathbf{r},t)} = mc(\mathbf{r},t) \tag{5}$$

and the corresponding susceptibilities. In particular we introduce the osmotic compressibility $\chi(q)$ as $\chi^{-1}(q) = \mathcal{F}\left\{\frac{\delta\mu^{mix}(\mathbf{r})}{\delta w(\mathbf{r}')}|_{p,T}\right\}$, where $\mu^{mix}(\mathbf{r})$ is as the difference in chemical potentials per unit mass between the solute (the colloidal phase, in the present case) and the solvent: $\mu^{mix}(\mathbf{r}) = \mu^1(\mathbf{r}) - \mu^0(\mathbf{r})$ [3]. This notation follows standard practice in the literature [2]. Taking in to account the above reported definition of $\mu_c(q)$, we obtain the following identity:

$$\chi(q) = \frac{m^2}{\mu_c(q)}. \tag{6}$$

In a similar fashion, if we define a q-dependent solutes expansion coefficient $\beta(q)$ at constant pressure and temperature as $\beta(q) = \frac{1}{\rho_0}\mathcal{F}\left\{\frac{\delta\rho(\mathbf{r})}{\delta w(\mathbf{r}')}|_{p,T}\right\}$, from the definition of $\rho_c(q)$ and of Eq. 5 we get

$$\beta(q) = \frac{1}{m}\frac{\rho_c(q)}{\rho}. \tag{7}$$

It is now straightforward to obtain the following expression for the structure factor $S(\mathbf{q},\omega) = \langle|\delta w(\mathbf{q},\omega)|^2\rangle$ of the concentration fluctuations:

$$S(\mathbf{q},\omega) = \frac{k_B T}{\rho}\chi(q)\frac{\left[2\Re(D(q,\omega))q^2|j\omega + \nu_T(q,\omega)q^2|^2 + 2\Re(\nu_T(q,\omega))q^2\left(\nabla w\right)^2\chi^{-1}(q)\right]}{|[j\omega + \nu_T(q,\omega)q^2][j\omega + D(q,\omega)q^2] + \beta(q)\nabla w \cdot \mathbf{g}|^2}, \tag{8}$$

The dynamic structure factor in Eq. 8 is the most general expression that describes the structure (in the q- space) and the dynamics (in the ω-space) of the concentration fluctuations in a dense colloidal suspension.

In a colloidal suspension the relaxation of density fluctuations by diffusion is much slower than the relaxation of viscous modes. It is thus possible to focus on the dynamics at the Smoluchowski timescale by imposing $|j\omega + \nu_T q^2| \simeq |\nu_T q^2|$. This assumption leads to the simplified expression

$$S(\mathbf{q},\omega) = \frac{k_B T}{\rho}\chi(q)\left[1 + \frac{1}{\chi(q)\left|\nu_T(q,\omega)\right|^2}\frac{\Re\left[\nu_T(q,\omega)\right]}{\Re\left[D(q,\omega)\right]}\frac{\left(\nabla w\right)^2}{q^4}\right]\frac{2\Re\left[D(q,\omega)\right]q^2}{\left|[j\omega + D(q,\omega)q^2] + \beta(q)\nabla w\cdot\mathbf{g}\right|^2}, \tag{9}$$

which corresponds to Eqs. 3 and 4 in the main text.

II. DETERMINATION OF THE MICROSCOPE TRANSFER FUNCTION

As discussed in the main text, the amplitude $A(q)$ associated with the image structure function obtained with DDM (Eq. 22) is given by the product of two contributions $A(q) = T(q)I(q)$, namely the intensity $I(q)$ of the light scattered by the sample and the transfer function $T(q)$, accounting for the response of the optical system. In order to extract an information on $I(q)$ from the amplitude $A(q)$ the knowledge of the microscope transfer function is thus required. $T(q)$ can be determined via a calibration procedure with a dilute suspension of non-interacting colloidal particles for which one has $I(q) \simeq const$ in the accessible wave-vector range so that for the calibration sample $A(q) \simeq const\, T(q)$. With such procedure, it is possible to determine $T(q)$ up to a constant [4]. To this aim, we used an aqueous suspension of polystyrene particles with nominal diameter 100 *nm* at a volume fraction of approximately 10^{-3}. The cell was assembled as described in the subsection of the main text, by placing in contact two identical drops of the calibration colloidal suspension. A few movies of 8000 images each were then acquired at different times during diffusion at 100 frames per second and analyzed with DDM. Care was taken to ensure that the position of the image plane with respect to the confining plates, as well as all the relevant microscope and camera setting were the same used in the free diffusion experiment. The calibration sample exhibits an almost ideal diffusive behavior, with $f(q, \Delta t) = e^{-D_{cal} q^2 \Delta t}$ and $D_{cal} = 4.62 \pm 0.2$ $\mu m^2/s$. This diffusion coefficient corresponds to a particle radius $R_{cal} = 48 \pm 2$ nm, in excellent agreement with the nominal value. In this way, by using Eq. 17 in the main text, we could determine unambiguously $T(q)$ (up to a multiplicative constant) over the wave-vector range: $[5 \times 10^{-2}$, $2.6]$ μm^{-1}. Results obtained for movies acquired at different times (from few minutes to about one hour after the creation of the gradient) show no significant differences, indicating that the sample attains almost immediately an equilibrium state.

The obtained $T(q)$ is shown in Figure 1a as black crosses. In the same panel the amplitudes $A(q)a_s(q) = I_s(q)T(q)$ corresponding to the slow decay and the amplitude $A(q)a_f(q) = I_f(q)T(q)$ corresponding to the fast decay in the image structure functions measured at various times t_d from the beginning of diffusion are also shown. After division with $T(q)$ (Figure 1 b)), while the scattering intensity $I_f(q)$ clearly shows the expected excess of scattering at the smallest wave-vectors, which is the signature of NEF, $I_s(q)$ is substantially flat in the accessible q-range and its mean value is substantially t_d-independent. As discussed in more detail in the next section, the results for $I_s(q)$ can be attributed to the presence of colloidal aggregates of LUDOX particles.

III. CHARACTERIZATION OF LUDOX COLLOIDAL AGGREGATES

We interpret the slow relaxation process observed in our experiments as due to the presence of aggregates of LUDOX particles. In fact, the associated correlation rate shows a diffusive scaling $\Gamma_s(q) = D_{agg} q^2$ (Figure 2a), leading to an estimated hydrodynamic radius $R_{agg} = 66 nm$. This value is comparable to the value found in Ref .[5] for the same dense colloidal suspension. However, in our case the majority of the particles present in the sample is represented by non-aggregated silica particles, since the ratio between the number N of non-aggregated particles and the number N_{agg} of aggregates is estimated to be

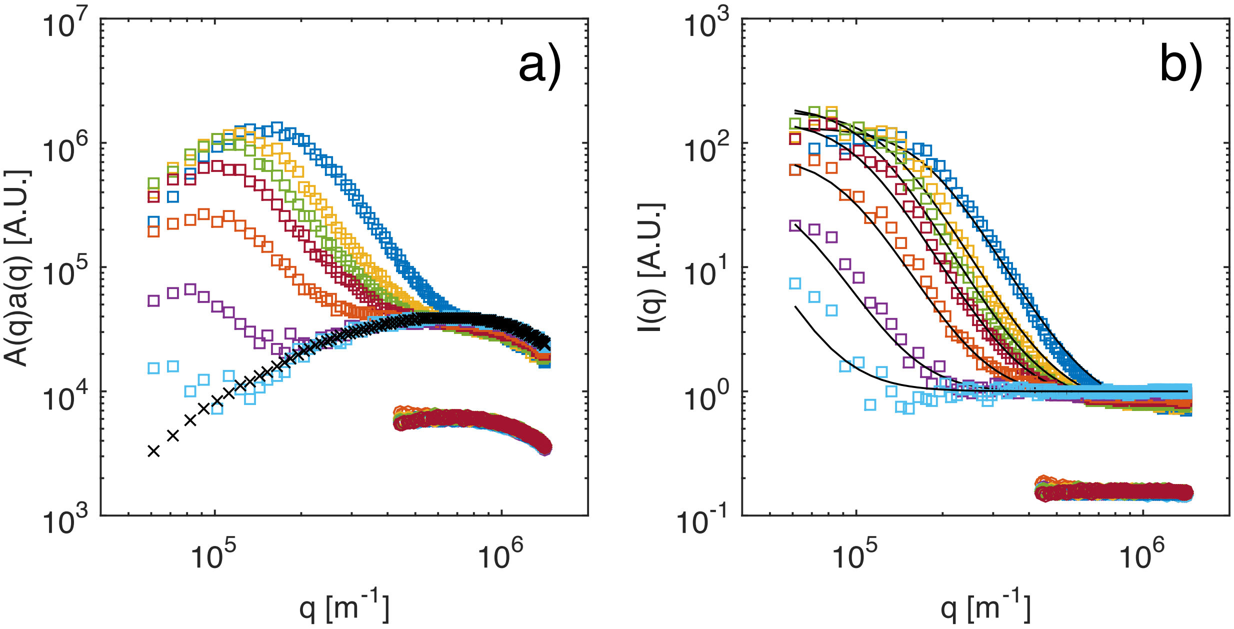

Figure 1. a) (squares) Amplitude $A(q)a_f(q)$ of the fast process, as determined from fitting the experimental image structure functions measured at various times t_d from the beginning of diffusion: $t_d = 180$, 690, 1230, 2010, 3390, 6540, 10000 s (from top to bottom); (circles) With the same color code, amplitude $A(q)a_s(q)$ of the slow process divided by a factor of 10 for clarity; (black crosses) amplitude measured for the calibration sample i.e., up to a multiplicative constant, transfer function $T(q)$ of the microscope. b) Scattering intensity $I_s(q)$ (circles) and $I_f(q)$ (squares) of the slow and fast processes obtained at various times t_d by dividing the amplitudes shown in a) with the experimentally determined transfer function $T(q)$. Continuous lines are best fits to Eq. 9 in the main text.

$\frac{N}{N_{agg}} = \frac{I_f}{I_s}\frac{R_{agg}^6}{R^6} \simeq 1\times 10^4$. As pointed out in the previous section, the scattering intensity $I_s(q)$ associated to this slow process is substantially q-independent and constant in time (Figure 1 b)), indicating that the number of aggregates within the depth of field of the microscope is approximately conserved during the whole duration of the experiment. On the other hand, as shown in Fig. 2, the diffusion coefficient D_{agg} of the aggregates decreases with time.

This result can be at least qualitatively explained as follows. Initially all the aggregates are confined in the lower half of the cell and they diffuse in a dispersing medium made by water and by the non-aggregated particles at a concentration equal to the initial concentration

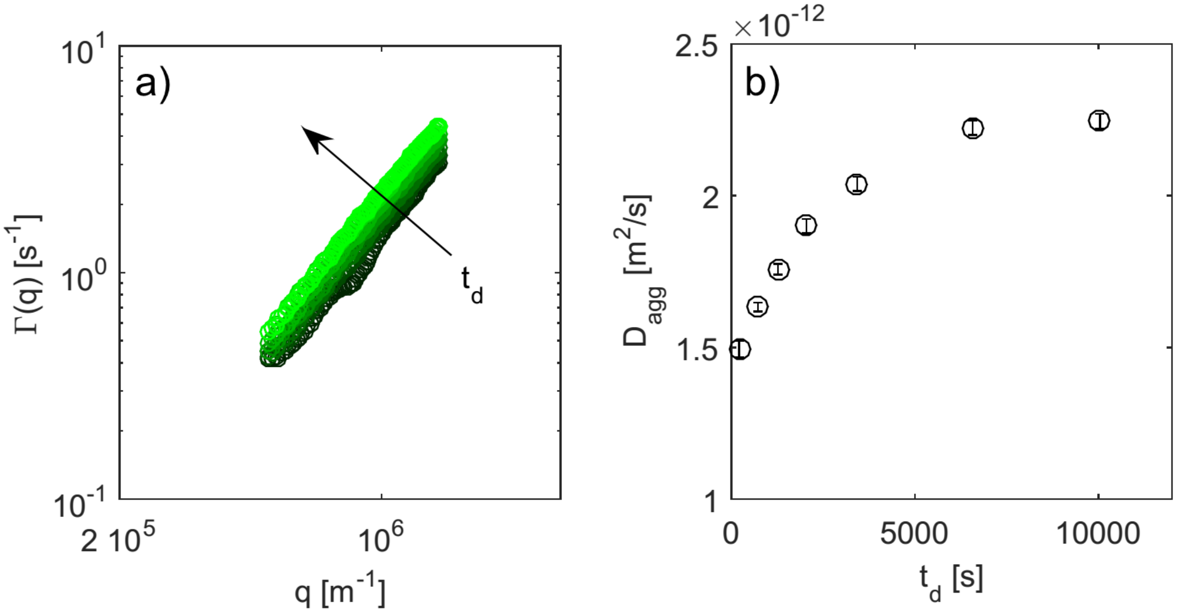

Figure 2. a) Correlation rates of the slow relaxation processes as a function of the scattering wave-vector q at various times t_d from the beginning of diffusion: $t_d = 180, 690, 1230, 2010, 3390, 6540, 10000\ s$ (from bottom to top) . b) D_{agg} at different t_d, extracted from fitting of the data in panel a)

w_0. During diffusion the concentration of the small particles progressively decreases until it attains its equilibrium value $\frac{w_0}{2}$. Correspondingly, the aggregates diffuse in a dispersing medium whose effective viscosity decreases with time. This picture, while surely oversimplified due to the small mismatch between the single particles and the aggregates, is roughly valid, as confirmed by independent measurements of the viscosity of the suspension at w_0 and $\frac{w_0}{2}$ with a capillary viscometer, which provide the values $\nu = (2.52 \pm 0.03)\, 10^{-6}\ m^2 \cdot s^{-1}$, $\nu = (1.34 \pm 0.04)\, 10^{-6}\ m^2 \cdot s^{-1}$, respectively. Finally, the value of the stretching exponent $\gamma = 0.55$ obtained from the fit of the slower decay of the intermediate scattering functions (Eq. 18 in the main text) points to a large polydispersity of the aggregates. Fitting of the slower process with a third order cumulant expansion $\tilde{a}_s(q)e^{-\tilde{\Gamma}_s(q)\Delta t}\left(1 + \frac{\mu_2(q)}{2}\Delta t^2 - \frac{\mu_2(q)}{6}\Delta t^3\right)$ gives a decay rate that is fully consistent with the one obtained with the stretched exponential model ($\tilde{\Gamma}_s \simeq \Gamma_s$) and allows estimating a polydispersity index $\sigma \simeq \frac{\mu_2}{\Gamma_s^2} = 0.4 \pm 0.1$.

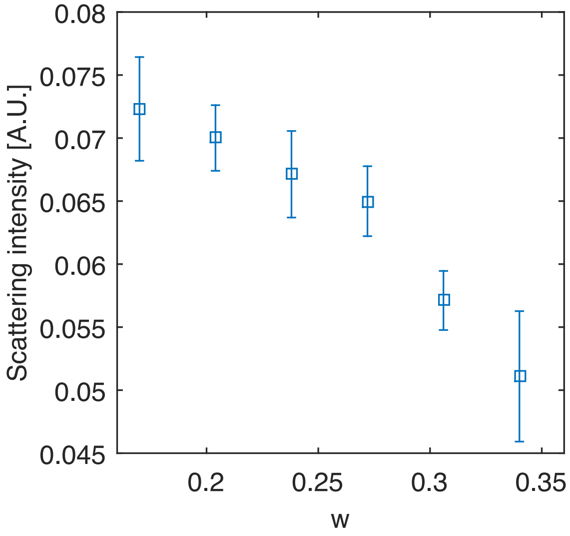

Figure 3. Scattering intensity obtained from DDM analysis of aqueous suspensions of LUDOX particles at uniform concentration. Mass fractions are $w = 0.17$, 0.2, 0.22, 0.26, 0.31, 0.34.

IV. DDM MEASUREMENTS WITH COLLOIDAL SAMPLES OF VARYING CONCENTRATION AT EQUILIBRIUM

We have performed a set of reference DDM measurements aimed at characterizing the static and dynamic scattering properties of aqueous suspensions of LUDOX particles prepared at uniform concentration. Measurements were repeated at mass fractions $w = 0.17$, 0.2, 0.22, 0.26, 0.31, 0.34. Cell assembly, image acquisition and image processing are performed as described in section II. Like in the non-equilibrium experiment described in the main text, the obtained image structure functions displays two distinct relaxation processes. The faster decay is purely exponential and it is associated with the diffusion of non-aggregated LUDOX particles, while the slower relaxation is due to the presence of large aggregates as described in the previous section.

At variance with the non-equilibrium case we find no deviation from a purely quadratic dependence of the fast relaxation rate on the scattering wave-vector $q : \Gamma_s(q) = Dq^2$. Plots of the scattering intensity associated to the faster decay of (obtained as an integral of $I_f(q)$ over all wave-vectors q) and the diffusion coefficient D as a function of the volume fraction

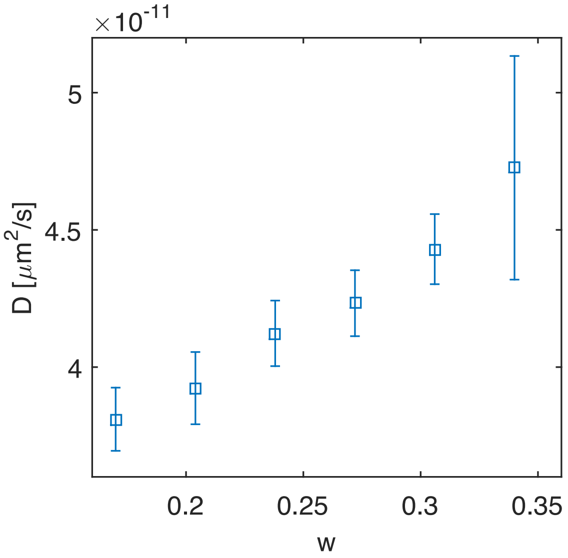

Figure 4. Diffusion coefficient obtained from DDM analysis of aqueous suspensions of LUDOX particles at uniform concentration. Mass fractions are $w = 0.17, 0.2, 0.22, 0.26, 0.31, 0.34$.

of the suspension are reported in Figures 3 and 4, respectively.

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