An empirical correction for moderate multiple scattering in super-heterodyne light scattering

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Frequency domain super-heterodyne laser light scattering is utilized in a low angle integral measurement configuration to determine flow and diffusion in charged sphere suspensions showing moderate to strong multiple scattering. We introduce an empirical correction to subtract the multiple scattering background and isolate the singly scattered light. We demonstrate the excellent feasibility of this simple approach for turbid suspensions of transmittance $T \geq 0.4$. We study the particle concentration dependence of the electro-kinetic mobility in low salt aqueous suspension over an extended concentration regime and observe a maximum at intermediate concentrations. We further use our scheme for measurements of the self-diffusion coefficients in the fluid samples in the absence or presence of shear, as well as in polycrystalline samples during crystallization and coarsening. We discuss the scope and limits of our approach as well as possible future applications. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983688>]

INTRODUCTION

Multiple scattering (MS) strongly affects the studies of turbid colloidal suspensions using laser light scattering. Depending on the degree of MS, several different sophisticated approaches have been taken to use, correct for, or suppress MS in studies on suspension dynamics. At very large turbidities and small optical path lengths, suspension dynamics can be determined using diffusive wave spectroscopy (DWS).^{1,2} In the regime of low to moderate multiple scattering, index matching is regularly employed,^{3–5} but it is not easily applicable in water based systems. Further, optical path lengths may be shortened by utilizing fibre optics.⁶ In addition, cross correlation schemes⁷ were pioneered by Phillies in the early 1980s⁸ and further developed to two-color or 2D cross correlation schemes.^{9,10} This way the methods and theory developed for (single) dynamic light scattering in the time domain¹¹ could be used also in turbid samples. Alternatively, in frequency domain, special mode selective heterodyne instrumentation was developed and applied to Brillouin scattering.^{12–14} Both cross correlation and mode selection, however, afford complex instrumentation and data evaluation schemes. A much simpler instrumentation is needed for the statistical analysis of heterodyne speckle fields taken at different times providing information about the velocity field in the fluid in a given plane perpendicular to the optical axis.¹⁵ This information can be extracted, either by measuring their cross correlation function or by recovering the power spectrum corresponding to the difference between the two speckle fields. Multiple scattering in this approach is minimized by using confocal geometry.¹⁶ Yet another simple approach is path length resolved low coherence

interferometry, which also is a static heterodyne technique.^{17,18}

There a certain small path length can be selected which corresponds to a single back-scattering event. Then only singly scattered light is recorded and can be analyzed for sample dynamics. For larger path lengths and weakly forward scattering samples, however, the scattering vector becomes ill defined due to the detection of additional multiply scattered photons. In the present paper, we are concerned with the Laser Doppler Velocimetry (LDV), a far field heterodyne frequency domain technique to study the suspension flow. This technique will be used in a standard super-heterodyne low angle version¹⁹ with spatially restricted detection volume for electro-kinetic studies over an extended range of volume fractions. We study samples of very different scattering contrast and turbidity. To prepare the ground for future systematic studies, we have been particularly interested in minimizing any extra instrumental complexity.

Doppler velocimetry is a well-established frequency domain technique used to study the flow properties of colloidal dispersions.¹¹ A typical application is the determination of the electro-phoretic mobility, μ_{ep} , from the particle drift velocity, $\mathbf{v}_{ep} = \mu_{ep} \cdot \mathbf{E}$, of a particle in the applied electric field $\mathbf{E}$. The mobility can be interpreted in terms of the particle zeta potential and effective charge.^{20,21} Previous research has revealed two differing types of particle concentration dependence for this central electro-kinetic quantity. In studies on isolated particles in either aqueous²² or organic solvent,²³ very small mobilities were observed. In studies starting from very low concentrations, the mobility was found to first increase, but then it was found to saturate with increasing particle number density, n (related to the volume fraction, Φ , as $n = \Phi/V_p = 3\Phi/4\pi a^3$, where a is the particle radius).^{24–26} There, the transition to a concentration independent mobility seems to correlate with the onset of inter-particle ordering, i.e., with

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conditions of strongly overlapping electric double layers. Moreover, increase and saturation have been observed in systems of quite different salt concentrations, $10^{-6} \text{ mol l}^{-1} \leq c_s \leq 10^{-2} \text{ mol l}^{-1}$.²⁷ The observed behavior stays theoretically unexplained. However, in other studies, we observed the mobility to start with a plateau, but then to decrease.^{28,29} In the latter case, the onset of the decrease coincides with the onset of counterion dominance, i.e., when the counterions of the charged particles start to dominate the small ion population.³⁰ This is reproduced in computer simulations²⁹ and theoretically understood in terms of the electrolyte concentration dependence of the zeta potential.³¹ Together, the experimental observations seem to suggest the existence of a broad maximum in the density dependent mobility.³⁰ However, so far, no single study has reported all the three different dependencies for a given particle species, which would resolve the apparent contrast between different observations.

The reason for this lack of data is mainly technical. Practically all data showing the ascent were measured on particles in aqueous suspension with large scattering cross section, i.e., particles with large radii, a , and/or refractive index contrast. This yields a good signal-to-noise-ratio even at low particle number density, n , but leads to problems with MS contributions at large n , where the descent occurs. Conversely, small particles are causing less MS and can be investigated up to large n and even in the crystalline region of the phase diagram.³² However, at low n the signal becomes vanishingly small, and the ascent is not accessible.

In the present paper, we therefore suggest a facile empirical correction applicable to moderate multiple scattering, which considerably extends the accessible range of particle number densities in the presently used LDV-setup. It is based on the use of a low angle scattering configuration, which restricts the detection volume as well as the direction and magnitude of detected MS-scattering vectors. In our geometry, the remaining MS signal is well approximated in the frequency space by a single Lorentzian. We exploit the observed pronounced difference in the relaxation time scales for multiply and singly scattered light. This allows subtracting the MS contribution to the Doppler spectra after a simple fit procedure and thus isolating the singly scattered spectral contribution. The isolated MS contribution shows a number of interesting features. It is a well-defined Lorentzian of finite width, which increases linearly with particle concentration over the range of n studied. These observations may in future studies help to develop a heterodyne MS theory for light scattering in transmission geometry, which is presently lacking.

We demonstrate the scope and limits of our correction scheme by three examples. First, we utilize our approach in measurements of Doppler spectra in low salt suspensions of low to moderate turbidity under a Poiseuille-type electrokinetic flow. The sample investigated consists of weakly ordering optically homogeneous but polydisperse latex spheres yielding a dominance of incoherent scattering and thus an independence of the signal from the sample structure.¹⁹ Using our empirical MS-correction scheme, we evaluate the isolated single scattering spectra for electrokinetic velocities. We observe a broad maximum for μ_e at moderate particle number

densities. Albeit still preliminary, our study thus indicates the possibility for a reconciliation of previously divergent interpretations of the concentration dependence of the electro-phoretic mobility in future systematic studies.

For this sample, we also obtain the effective diffusion coefficient, D_{eff} , with and without the presence of shearing flow. In the absence of shear, D_{eff} stays close to the standard Stokes-Einstein-Sutherland diffusion coefficient, D_0 . This is in accordance with the expectation for low salt charged sphere suspensions with dominant incoherent scattering and the very small volume fraction dependence of the there-measured self-diffusion coefficient, D_s .³³ In the electro-kinetic experiments, D_{eff} increases linearly with increasing field strength and increasing concentration of particles, but D_0 is recovered in the limit of zero shear and infinite dilution.

In a second set of experiments, we study suspensions of optically inhomogeneous co-polymer colloids of low polydispersity under conditions of strong mutual interaction. We demonstrate the possibility to follow the decrease of D_s during solidification and annealing of grain boundaries in two crystallizing samples with different n .

Our measurements demonstrate the suitability of the empirical correction scheme for measurements of electrokinetic and self-diffusive properties of multiply scattering suspensions without much extra effort as compared to standard low angle integral LDV. We anticipate that this approach may also turn out useful for other configurations used in dynamic light scattering.

In what follows, we first outline the experimental procedure, sketch the integral low angle super-heterodyne LDV setup and the corresponding single scattering theory, introduce the samples, show typical spectra, and explain the novel correction scheme. The results section reports on the characterization of the MS signal contribution and presents the MS corrected results of electro-kinetic and diffusion experiments. In the discussion section, we address the limits and scope of our approach, anticipate future applications, and discuss the results obtained from MS-corrected data. We end with some short conclusions.

EXPERIMENTAL METHODS AND EVALUATION SCHEME

Integral, low-angle, super-heterodyne LDV

Our home-built Laser Doppler Velocimetry (LDV) instrument combines the reference beam integral measurement of Ref. 34 (allowing to measure the complete flow-profile in a single measurement) with super-heterodyning^{35–37} (allowing to separate the heterodyne part of the power spectrum from the homodyne part, electronic and low frequency noises) and a significant restriction of the detection volume^{15,16} (to reduce detection of MS photons by approaching confocal detection conditions). The present machine is a modification of a previously described setup,¹⁹ now also allowing a continuous variation of the scattering angle. For additional technical details, see the [supplementary material](#). An essential part of this instrument is the detection geometry sketched in Fig. 1. Additional details are given in the [supplementary material](#) (Fig. S1 and S3).

FIG. 1. Sketch of the detection geometry. Shown is a cut in the scattering plane (x - z). In the cell (C) containing the suspension, the frequency shifted illumination beam (thick red line) is crossed by the reference beam (thin red line) under an angle Θ_S . (Note that for simplicity we here only show light paths in air with $\Theta = 8^\circ$.) The illumination beam is stopped by a beam stopper. Light leaving the cell parallel to the reference beam is focused by the lens (L, $f = 50$ mm) into the focal plane, where a circular aperture (CA) is placed. The position and the width of CA define the direction of the scattering vector $\mathbf{q}$ and the q -resolution Δq , respectively. The minimum opening is chosen to about 1 mm in order let a sufficient amount of reference beam light pass. A grin lens (GL, diameter 4 mm) mounted on an optical fiber (OF) is aligned collinear with the reference beam and guides the collected light to the detector. The distance between CA and GL defines the diameter of the detection volume (light grey). It is chosen as to contain the complete illuminating beam crossing the cell. Light originating outside the detection volume as well as light leaving the cell in directions not sufficiently parallel to the reference beam (e.g., dashed red lines) is blocked. Light scattered out of the x - z plane is optionally rejected by a horizontally mounted slit aperture (HA). A polarizer (P) assures V/V detection. If L and CA are removed, the q -resolution is defined solely by the acceptance angle of the grin lens and the maximum detection volume by the acceptance angle and the GL diameter. It typically is larger than with CA and L and is slightly conical.

The (single) scattering vector $\mathbf{q}_1 = \mathbf{k}_i - \mathbf{k}_1$ (where $\mathbf{k}_i$ and $\mathbf{k}_1$ are the wave vectors of the illuminating and one-time scattered beams) is parallel to the applied field direction (cf. Fig. S1 of the [supplementary material](#)). In the present sign convention, $\mathbf{q}$ is proportional to the momentum transfer from the photon to the scattering particle. Its modulus is given by $q = (4\pi v_S/\lambda_0) \sin(\Theta_S/2) = (4\pi/\lambda) \sin(\Theta/2)$, where v_S is the index of refraction of the solvent and $\Theta_S = 6^\circ$ is the beam crossing angle in suspension. The electric field points downward in the negative z -direction (Fig. S1). We note that light scattered by a particle j moving with a velocity $\mathbf{v}_j$ in the z -direction is Doppler-shifted by the circular frequency $\omega_D = -\mathbf{q} \cdot \mathbf{v}(x, y)$, where the velocity can be a function of the position. The frequency shift, ω_D , is positive, if the particle velocity shares an obtuse angle with the scattering vector, $\mathbf{q} = q\hat{\mathbf{z}}$, where $\hat{\mathbf{z}}$ is the unit vector in the z -direction. Hence, a positive Doppler shift corresponds to particles moving towards the detector with a negative velocity with respect to the field direction.

The reference beam is also directed into the fiber and is superimposed with the scattered light. It therefore acts as a local oscillator and gives rise to beats in the intensity observed at the detector. These are analyzed by a fast Fourier transform analyzer (Ono Sokki DS2000, Compumess, Germany) to yield the power spectrum as a function of frequency, $f = \omega/2\pi$. To obtain a good signal to noise ratio, typically some 200-2000 subsequent spectra are averaged. The power spectra are transferred to a computer, where the MS correction is applied and the corrected spectra are further evaluated for the electro-kinetic mobilities.

Single scattering super-heterodyne Doppler spectra

Some progress has been made in the treatment of double scattering in homodyne experiments.^{13,38,39} Still, the

complexity of theory for triple and higher-order scattering means that the theoretical approach has found little application in practice. Multiple scattering has been treated for heterodyne low coherence backscattering experiments,^{17,18} but a general theory of MS scattering for (super-)heterodyne techniques is not known to us. We therefore correct our experimental signals for noise background and MS contributions (see below) and apply single scattering theory for their evaluation. (Super-)heterodyning is based on the detection of Doppler shifts imposed on the scattered photons at the instant of scattering and therefore does not suffer from de-coherence of scattered beams due to changes of the relative distance between scatterers. Our theoretical frame for single scattering is based on earlier work on homo- and heterodyning techniques in dynamic light scattering.^{11,40} A theory of conventional heterodyne LDV using an integral reference beam setup was outlined in Ref. 40. Super heterodyne theory for integral measurements at low angles has been detailed in Ref. 19. Further extensions to include de-correlation effects such as Taylor-dispersion arising in sheared solvents⁴¹ and a rigorous treatment of electro-phoretic mobility polydispersity will be presented in a forthcoming paper.⁴² Here, we only summarize the main theoretical expressions for the single scattering.¹⁹ Some additional details are given in the [supplementary material](#).

The power or Doppler spectrum $C_{shet}(\mathbf{q}, \omega)$ is the time Fourier transformation of the mixed-field intensity autocorrelation function, $C_{shet}(\mathbf{q}, \tau)$,

$$C_{shet}(\mathbf{q}, \omega) = \frac{1}{\pi} \int_{-\infty}^{\infty} d\tau \cos(\omega\tau) C_{shet}(\mathbf{q}, \tau), \quad (1)$$

with circular frequency ω and correlation time τ . For a scattered light field of Gaussian statistics, the latter quantity is given as

$$C_{shet}(\mathbf{q}, \tau) = (I_r + \langle I_1(\mathbf{q}) \rangle)^2 + 2I_r \langle I_1(\mathbf{q}) \rangle \text{Re}[\hat{g}_E(\mathbf{q}, \tau) \times \exp(-i\omega_B\tau)] + \langle I_1(\mathbf{q}) \rangle^2 |\hat{g}_E(\mathbf{q}, \tau)|^2, \quad (2)$$

where I_r is the reference beam intensity, $\langle I_1(\mathbf{q}) \rangle$ is the time-averaged singly scattered intensity, and $\hat{g}_E(\mathbf{q}, \tau) = g_E(\mathbf{q}, \tau)/\langle I_1(\mathbf{q}) \rangle$ is the normalized field autocorrelation function. For homogeneous suspensions of interaction monodisperse, optically homogeneous, mono-sized particles, $\langle I_1(\mathbf{q}) \rangle$ is given by

$$\langle I_1(\mathbf{q}) \rangle = I_0 n b^2(0) P(q) S(q). \quad (3)$$

Here, I_0 is a constant comprising experimental boundary conditions like illuminating intensity, distance from the sample to the detector, and polarization details. $b^2(0)$ is the single particle forward scattering cross section, n is the particle number density, $P(q)$ denotes the particle form factor, and $S(q)$ the static structure factor.³⁹

We assume the particles to undergo Brownian motion with an effective diffusion coefficient D_{eff} and directed motion with a constant and homogenous drift with velocity $\mathbf{v}_0$. For this simple case, indicated by the index 0, the power spectrum reads

$$\begin{aligned}
C_{shet}^0(\mathbf{q}, \omega) = & [I_r + \langle I_1(\mathbf{q}) \rangle]^2 \delta(\omega) \\
& + \frac{I_r \langle I_1(\mathbf{q}) \rangle}{\pi} \left[\frac{q^2 D_{eff}}{(\omega + [\omega_B - \omega_D])^2 + (q^2 D_{eff})^2} \right. \\
& + \left. \frac{q^2 D_{eff}}{(\omega - [\omega_B - \omega_D])^2 + (q^2 D_{eff})^2} \right] \\
& + \frac{\langle I_1^0(\mathbf{q}) \rangle^2}{\pi} \frac{2q^2 D_{eff}}{\omega^2 + (2q^2 D_{eff})^2}. \quad (4)
\end{aligned}$$

D_{eff} is the effective diffusion coefficient and $\omega_D = \mathbf{q} \cdot \mathbf{v}_0$ is the frequency of the resulting Doppler shift. We note that D_{eff} may depend on q , in case collective diffusion is measured. Further, due to the presence of different relaxation times in $C_{shet}(\mathbf{q}, \tau)$, we have to replace the expression in square brackets in the second term by a summation over individual terms for each individual relaxation time τ_i , e.g., τ_S and τ_L for short and long time collective diffusions. As discussed later, there may be limits for their discrimination. In the here investigated case, we restrict ourselves to the measurements of D_S for which we assume a single relaxation time.

The spectrum contains three contributions: a trivial constant term centered at zero frequency, two super-heterodyne Lorentzians of spectral width $q^2 D_{eff}$ shifted away from the origin by both the Bragg frequency and the Doppler frequency, and the homodyne Lorentzian of double width which is independent of the particle drift motion and is again centered at the origin. The homodyne term is known to be seriously affected by shear⁴³ and multiple scattering resulting in the loss of coherence of the scattered light, which renders it ill defined. From Eq. (4), we note that the desired information about the electrophoretic and diffusive particle motion is fully contained in each of the super-heterodyne Lorentzians which are symmetric about the origin. In Fig. 4, and also the following, we therefore display the measured data only for positive frequencies centered about the positive Bragg shift frequency. Interestingly, this is already sufficient to infer the sign of the electro-kinetic velocities. (The complete positive part of a complete Doppler spectrum is displayed in Fig. S2 of the [supplementary material](#)). According to our sign convention, a positive shift of the center of mass frequency with respect to the Bragg frequency ($\omega > \omega_B$) corresponds to a negative electro-phoretic velocity $\mathbf{v}_{ep}$ and hence a negative electro-phoretic mobility μ_{ep} and a negative particle charge. A maximum at the high frequency side corresponds to a positive wall velocity $\mathbf{u}_{eo}$ and hence to a negatively charged wall.

Under inhomogeneous flow, particles show a normalized velocity distribution, $p(\mathbf{v})$. The Doppler spectra then display a corresponding normalized distribution of Doppler frequencies, $p(\omega_D)$. This can be accounted for by a convolution integral,

$$C_{shet}(\mathbf{q}, \omega) = \int d\omega_D p(\omega_D) C_{shet}^0(\mathbf{q}, \omega). \quad (5)$$

Most notably, the structure may couple to flow properties resulting in inhomogeneous shear thinning or shear banding,^{44,45} alteration of the particle flow profile due to local

crystal cohesion,^{46,47} and even time-dependent effects.³² In such cases, where $p(\omega_D)$ is not known, only the electrophoretic velocity can be obtained as the y -average of the x -averaged particle velocities $\mathbf{v}_{ep} = \langle \langle \mathbf{v}_P \rangle_x \rangle_y$.³² A suitable expression of $p(\mathbf{v})$ for Poiseuille-type electro-osmotic electrophoretic flow is given in Eq. (S1) and displayed in Fig. S3 in the [supplementary material](#).

In previous studies, it was further observed that flow may couple to the diffusivity, and a dependence of fitted D_{eff} on the field strength has frequently been observed and in most cases was found to be linear.³⁴ Underlying reasons could be Taylor dispersion⁴¹ accounting for effects of shear, field induced velocity fluctuations,¹² or a polydispersity of the electro-phoretic mobility.⁴⁹ In the present study, we fit measured spectra using an effective diffusion coefficient $D_{eff}(E)$, but only in the field free case or for the values obtained by extrapolation to $E = 0$, an interpretation in terms of a diffusion coefficient is attempted.

For truly mono-sized, optically homogeneous particles, only collective diffusion is measured, with $D_{eff} = D_C(q)$ depending on the scattering vector through hydrodynamic and direct particle interactions. The presently used samples in addition show a significant amount of depolarized scattering due to MS and incoherent scattering from individual particles differing in size or being optically inhomogeneous. The presence of these contributions can be noted already from visual inspection (cf. Fig. S4 in the [supplementary material](#)) and influence on the power spectrum. For optically homogeneous particles with a finite size polydispersity of standard deviation s , the field autocorrelation function can be written using the decoupling approximation as¹⁹

$$\begin{aligned}
g_E(\mathbf{q}, \tau) = & I_0 n f^2(q) S_M(\mathbf{q}, \tau) \\
& \approx I_0 n f^2(q) [9s^2 G(q, \tau) + S(\mathbf{q}, \tau)]. \quad (6)
\end{aligned}$$

The corresponding normalized field autocorrelation function $\hat{g}_E(\mathbf{q}, \tau) = g_E(\mathbf{q}, \tau) / I_0 n f^2(q) S_M(\mathbf{q})$ is then used in Eq. (2). Here, $f^2(q)$ is the average scattering cross section of the particles. $S_M(\mathbf{q}, \tau)$ is the so-called measurable dynamic structure factor, $S(\mathbf{q}, \tau)$ is the dynamic structure factor or intermediate scattering function arising from coherent scattering, and $G(q, \tau)$ is the self-intermediate scattering function. The amplitude of the latter for $\tau = 0$ is independent of the suspension structure and the chosen $\mathbf{q}$.⁵¹ Note that Eq. (6) describes a limiting case of size-polydispersity. Any additional optical polydispersity, e.g., due to internal inhomogeneity of the particles further increases the weight of $G(q, \tau)$.

With the evolving structure, coherently scattered and incoherently scattered contributions to the spectra will differ. The difference is most pronounced at small q , where $S(q)$ becomes very small due to the decreased isothermal compressibility of the suspension.^{50,51} For charged particles with large optical polydispersity under low salt conditions, this may even lead to a dominance of the incoherent scattering contribution at small angles which was previously utilized to measure electro-kinetic properties of ordered colloidal fluids and crystals showing negligible MS.³² It is here used to study self-diffusion using $D_{eff} = D_S$. The field free self-diffusion coefficient is expected to scale with the volume fraction Φ as

$D_S = D_0 (1 - a_s \Phi^{4/3})$ with a_s decreasing with increasing interaction strength.³³ The opposite limit of a vanishing incoherent contribution in which collective properties are measurable would be obtained for suspensions of optically homogeneous particles of low polydispersity, but it was not investigated here.

Samples and optical characterization

Sample PnBAPS118 was employed for measurements of self-diffusion in crystallizing and coarsening colloidal solids. These particles are a 35:65 W/W copolymer of Poly-n-Butylacrylamide (PnBA) and Polystyrene (PS), kindly provided by BASF, Ludwigshafen (Lab code PnBAPS118 manufacturer Batch No. 1234/2762/6379). Their nominal diameter of (117.6 ± 0.65) nm and nominal polydispersity index of $PI = 0.011$ were determined by the manufacturer utilizing dynamic light scattering. TEM analysis and form factor measurements using SAXS yield $PI \approx 0.06$. The effective charge for PnBAPS118 is $Z_{\text{eff}} = 647 \pm 18$. Due to the combined effect of optical inhomogeneity and moderate polydispersity, these particles show strong incoherent scattering.

Sample PS310 was used for measurements of electrokinetic properties and self-diffusion with and without shearing flow. It comprises commercial polystyrene latexes stabilized by carboxylate surface groups (lab code PS310, manufacturer batch #1421, IDC, Portland, USA). Their nominal diameter is 310 nm as given by the manufacturer. Their hydrodynamic radius $a_H = 167$ nm and polydispersity index $PI = s/\langle a \rangle = 0.08$ were determined by dynamic light scattering measurements on dilute samples.⁵² Their effective charge is $Z_{\text{eff}} = 5260 \pm 100$. Also these particles show a considerable amount of incoherent scattering due to size polydispersity. Typical distributions of singly scattered light in dependence on scattering angle are shown for the two investigated suspensions in Figs. S5(a) and S5(b) of the [supplementary material](#).

Suspensions of different n were first conditioned as described in the [supplementary material](#). Small amounts of the PS310 suspension were then pipetted to rectangular quartz cells of $2d = 1$ mm and $2d = 2$ mm optical path length (Hellma, Germany) and transferred to a home-built turbidity measurement working at 633 nm. The transmittance or relative transmitted intensity, $T = I/I_0$, was recorded as a function of n , where I_0 refers to the cells filled with filtered Milli-Q grade water. Fig. 2 shows the result in terms of attenuation, A , per millimeter with $A = 10 \cdot \lg \left(\frac{I_0}{I} \right)$ (dB). We note that conductivity measurements are not feasible in this setup. Therefore, samples were exposed to ambient air to obtain CO_2 -saturation. Here, the residual ion concentration was estimated to be $c_S \leq 5 \times 10^{-6} \text{ mol l}^{-1}$.

The transmitted intensity for deionized or low salt suspensions is known to obey the Lambert-Beer law in both the fluid and crystalline state,⁵³

$$2dn\sigma_{633} = -\ln \left(\frac{I}{I_0} \right). \quad (7)$$

From fits of Eq. (7) to the data, we obtained an attenuation cross section of $\sigma_{633} = 0.013 \pm 0.1 \mu\text{m}^2$.

It is paramount to ensure identical optical properties in both turbidity experiments and LDV. PS310 were therefore

FIG. 2. Attenuation of transmitted intensity normalized to the cell thickness $2d$ as a function of the number density n . Results of the two measurements coincide. A fit of Eq. (7) returns an attenuation cross section of $\sigma_{633} = 0.013 \pm 0.1 \mu\text{m}^2$.

conditioned in the same way in both experiments. The background salinity in addition is advantageous for the goals of the present LDV study. At the volume fractions utilized, the suspensions will develop only a weak fluid order and a pronounced forward scattering will still be present. This is ideally suited to demonstrate the scope of the here introduced MS-correction scheme.

For each concentration, a second amount of sample was therefore filled into the electrophoresis cell (Standard EL10 by Rank Bros., Bottisham, Cambridge, UK or replica by Lightpath Optical Ltd., Milton Keynes, UK) used in the SH-LDV experiment. The u-shaped electro-phoretic cell has its electrode chambers separated from the actual optical section of rectangular cross section of (10×1) or $(10 \times 2) \text{ mm}^2$ and width $l = 40$ mm. The effective platinized platinum electrode distance is $L \approx 80$ mm. It was determined precisely before each measurement series from calibration with an electrolyte dilution series. We further checked by measurements of the conductance in dependence on conductivity that electrode polarization effects by particles or salt are negligible small as long as the conductivity stays below $20 \mu\text{S cm}^{-1}$. During the electrokinetic measurements, the electrode chambers are sealed. An alternating square-wave field of strength up to $E_{\text{MAX}} = U/L = 15 \text{ V cm}^{-1}$ was applied. To avoid accumulation of particles at the electrodes and to further ensure fully developed stationary flows,³⁵ field switching frequencies $f_{AC} = (0.02-0.1) \text{ Hz}$ were used. Measurement intervals were restricted to one field direction. Each was starting after the full development of electro-osmotic flow profile and ending shortly before the field reversal. For each field strength, we recorded and averaged 250-400 full time-frame power spectra. For diffusion measurements in PnBAPS118, no field was applied. We here typically averaged over 1000-2000 time frames. For rapidly crystallizing samples of that species, many repeated shear-melting-recrystallization cycles were needed to obtain the temporal evolution of the diffusive properties.

Typical spectra and fitting procedure

Typical examples of averaged power spectra for PS310 and $E = 0$ at $n = 1.64 \times 10^{16} \text{ m}^{-3}$ as well as for $E = 4.3 \text{ V cm}^{-1}$ and increasing n are shown in Figs. 3 and 4, respectively.

FIG. 3. Power spectrum of PS310 at $n = 1.64 \times 10^{16} \text{ m}^{-3}$ and $2d = 2 \text{ mm}$, recorded in the multiple scattering regime without applied electric field. A single broad spectral feature is visible which is centered at the Bragg shift frequency, $f_B = 2000 \text{ Hz}$.

Fig. 3 shows that without applied field, only a single broad spectral feature centered at 2 kHz is present. Raw spectra for PnBAPS118 appear to be similar at smaller overall spectral power. The singular feature varies in strength and broadness for changing n .

This is different in Fig. 4 for the case of an applied field, where we can clearly discriminate different types of spectral

FIG. 4. Examples of power spectra obtained at a field strength of $E = 4.3 \text{ V cm}^{-1}$ for CO_2 -saturated suspensions of PS310 at different particle number densities as indicated. Background noise, electro-phoretic spectrum, and the broad MS peak each show distinct spectral shapes. The ratio of these contributions changes with increasing n . For PS310, the actual Doppler-spectra emerge from the background noise for $n > 5 \times 10^{14} \text{ m}^{-3}$ and vanish in the broad feature for $n > 1 \times 10^{17} \text{ m}^{-3}$. Both contributions are centered close to the Bragg shift frequency, $f_B = 2000 \text{ Hz}$. In the limiting case of optically dense samples, transparency is lost and the signal disappears completely leaving only the contributions of electronic noise. Note that the characteristic Doppler spectrum is clearly visible for concentrations covering more than two orders of magnitude in n .

contributions due to their different spectral shapes. At very low n , the characteristic shape of the electro-phoretic signal²¹ is barely visible in the background noise. With extensive further averaging, an acceptable signal may be obtained for $n \geq 6 \times 10^{14} \text{ m}^{-3}$. Excellent low noise signals are obtained for $9 \times 10^{14} \text{ m}^{-3} \leq n \leq 8 \times 10^{15} \text{ m}^{-3}$. A broad additional signal component becomes clearly discernible for $n \geq 1 \times 10^{16} \text{ m}^{-3}$. It increases with increasing n until it dominates the power spectrum for $n > 10^{17} \text{ m}^{-3}$. It appears to be symmetric with a maximum close to the Bragg frequency, $f_{MS} \approx f_B = 2000 \text{ Hz}$. As will be shown below, it can be demonstrated to originate from multiple scattering. At $n = 1 \times 10^{17} \text{ m}^{-3}$, the sample transmission $T < 0.1$ and also the reference beam are strongly attenuated. The spectrum becomes noisier and the signal to background ratio decreases significantly. Finally, all super-heterodyne signal contributions disappear, and the spectrum becomes finally dominated by electric power grid harmonics.

For evaluation of spectra taken at low densities which are free of the extra signal contribution, we average the noise background at frequencies far off the other spectral features and subtract it from the data. We then perform a least square fit of the single scattering (SS) theoretical expression for $C_{shet}(q, \omega)$ derived from a combination of Eqs. (1)–(5) and Eq. (S1) of the [supplementary material](#) with the cell geometry, the field strength, and the particle number density as inputs. For spectra in the range of $8 \times 10^{14} \text{ m}^{-3} \leq n \leq 5 \times 10^{15} \text{ m}^{-3}$, we obtained excellent fits with u_{eo} , v and D_{eff} as independent fit parameters. However, attempts to fit the spectrum at larger n lead to unsatisfactory results due to the contribution by multiple scattering (MS). This is illustrated in Fig. 6(a) for a spectrum recorded on PS310 at deionized conditions, $E = 5.3 \text{ V cm}^{-1}$, $n = 1.64 \times 10^{16} \text{ m}^{-3}$, and $2d = 2 \text{ mm}$.

Empirical correction procedure

We devised a simple empirical scheme that can be applied for the correction of MS contaminated data. We first address the field free case (cf. Fig. 5). We assume a superposition of different, statistically independent spectral contributions as

FIG. 5. Power spectrum of PS310 at $n = 1.64 \times 10^{16} \text{ m}^{-3}$ and $2d = 2 \text{ mm}$, recorded in the multiple scattering regime at $T = 0.4$ without applied electric field (black circles). Also shown is the fit of Eq. (8) (solid green line) which is the superposition of a constant background noise (solid black line), the Lorentzian single scattering super-heterodyne power spectrum (solid blue line) and a second Lorentzian describing the multiple scattering contribution (solid orange line). Inset: magnification of the central region of the signal.

FIG. 6. Fitting of data recorded with applied field. (a) Uncorrected low angle integral super-heterodyne spectrum of PS310 recorded at $E = 5.3 \text{ V cm}^{-1}$ with $n = 1.64 \times 10^{16} \text{ m}^{-3}$, cell depth $2d = 2 \text{ mm}$, and cell height $2h = 10 \text{ mm}$. Data are normalized to unity at the maximum. The red solid line shows the best least square fit obtainable using Eqs. (1)–(5) and (S1) of the [supplementary material](#). (b) Experimental data of (a) after subtraction of the small constant noise background term. The MS Lorentzian (orange solid line) is fitted to the wings of the spectral feature. (c) Isolated single scattering power spectrum obtained by subtraction the fitted MS contribution from the data in (b). The single scattering data are fitted with the theoretical expression for the single scattering integral super-heterodyne power spectrum based on Eqs. (1)–(5) and (S1). The fit returns $v_{\text{ep}} = 37.4 \mu\text{m s}^{-1}$, $u_{\text{eo}} = 64.1 \mu\text{m s}^{-1}$, $D_{\text{eff}} = 4.49 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. (d) Isolated single scattering power spectrum of poly-crystalline PnBAPS118 at $n = 4.47 \times 10^{18} \text{ m}^{-3}$ obtained after noise and MS correction. Note the low signal intensity as compared to Fig. 6. This spectrum was recorded 44 min after the stop of the shear over a time interval of 5 min. A minute plug-flow was applied to separate the spectral contributions (for details see text). Data are fitted with the theoretical expression for the single scattering integral super-heterodyne power spectrum based on Eqs. (1)–(5) plus an additional Lorentzian for the 2 kHz peak. The fit returns $D_S = 1.43 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

described by

$$C_{\text{shet}}(\mathbf{q}, \omega) = A_1 + A_2 \int d\omega p(\omega) C_{\text{shet}}^0(\mathbf{q}, \omega, v, D_{\text{eff}}) + \frac{A_3}{2\pi} \frac{w_{\text{MS}}}{(\omega - \omega_0)^2 + w_{\text{MS}}^2}. \quad (8)$$

Here, A_1 is a constant describing the frequency independent noise background, A_2 is the integrated spectral power of the Doppler spectrum depending on $I_r \langle I_1(\mathbf{q}) \rangle$, and A_3 is integrated spectral power of the MS contribution depending on $I_r \langle I_N(\mathbf{q}) \rangle$, where N denotes the number of scattering events. The MS term is modelled as Lorentzian centered at ω_0 and of full width at half height, w_{MS} .^{18,54} For $E = 0$, $v = 0$ and only Eqs. (1)–(4) are necessary to calculate the single scattering super-heterodyne spectrum. An example fit to data obtained in the field free case is shown in Fig. 5, with the inset magnifying the central region of the spectrum. An excellent fit is obtained, showing the applicability of our empirical correction scheme.

Next, we applied the correction scheme to data obtained at finite field strengths. In Fig. 6(b) we show the background noise corrected spectrum with a Lorentzian fitted (orange solid curve) to the wings of the remaining MS spectral feature. After subtraction of the MS contribution, the remaining experimental data are fitted in Fig. 6(c) by a theoretical expression based on Eqs. (1)–(5) and (S1) (blue curve) of the [supplementary material](#). An excellent fit is obtained for the fit

parameters: $v_{\text{ep}} = 37.4 \mu\text{m s}^{-1}$, $u_{\text{eo}} = 64.1 \mu\text{m s}^{-1}$, $D_{\text{eff}} = 4.49 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

For PnBAPS118, MS contribution, background noise, and SS signal appeared to be much weaker than for PS310 even at large number densities. Still, MS correction was both necessary and unproblematic. In some cases, however, the single scattering spectrum was so weak that it became comparable to a residual 2 kHz feature. The latter originates from the interference of the reference with parasitic reflections from the illumination beam and is not considered in Eq. (4). We therefore applied a minute plug flow ($v \approx 1 \mu\text{m s}^{-1}$) to shift the centre of the heterodyne Lorentz by a few Hz and separate the signal from the artefact. This is shown in Fig. 6(d). We then fitted the spectrum by our expression for the single scattering integral super-heterodyne power spectrum based on Eqs. (1)–(5) plus an additional narrow Lorentzian for the 2 kHz-peak (blue curve). An excellent fit is obtained returning $D_S = 1.43 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$.

RESULTS

The multiple scattering contribution

We performed several tests of the origin and behavior of the different signal contributions. These are shown in the [supplementary material](#) (Figs. S7–S9) and discussed in detail below. From these, we attribute the broad-peaked spectral contribution appearing at elevated particle concentrations to

FIG. 7. MS and SS characteristics obtained from fits of a Lorentz function to the MS (up triangles) and fits of Eqs. (1)–(5) to the SS (down triangles) contributions as measured in field free samples of PS310 at different number densities n . (a) Spectral width, w_{MS} and $w_{SS} = D_{eff} q^2$. (b) Noise normalized integrated spectral power. In order to minimize effects of altered reference beam detection conditions after sample exchange, we show the data in terms of the noise normalized integrated spectral power $A_i^* = A_i/A_1$.

multiple scattering. The super-heterodyne spectra taken in the frequency range close to f_B are thus composed of a background resulting from noise, a Doppler spectrum, and a symmetric MS background (Fig. S7(a)).

The MS contribution can be excellently fitted by a single Lorentzian and characterized by its width, w_{MS} , integrated spectral power, A_3 , and the position of its center of mass, ω_0 . The statistical errors are small for w_{MS} and A_3 , but somewhat larger for ω_0 due to the restriction of the fit range to spectral regions outside the SS-signal. A_3 is reliably characterized for $n \geq 10^{16} \text{ m}^{-3}$. A_3 , A_2 , and A_1 are related linearly to the reference beam intensity (Fig. S7(b) of the [supplementary material](#)). Further, in plots of the dependence of the integrated spectral

powers versus number density, the scatter in the absolute values of A_3 and A_2 is highly correlated with the scatter in A_1 (see Figs. S8, S9(a), and S9(b)). This highly non-reproducible but a systematic scatter is attributed to inevitable slight differences in cell alignment after each change of sample leading to slightly different reference beam intensities at the detector. Therefore, we show these data in terms of the noise normalized integrated spectral power $A_i^* = A_i/A_1$.

Fig. 7(a) shows that w_{MS} increases linearly starting from a finite value. By contrast, $w_{SS} = D_{eff} q^2$ used in fits of Eqs. (1)–(5) for the SS contribution stays constant at a low value. Fig. 7(b) compares the zero field integrated spectral power of the SS contribution to that of the MS contribution. The

FIG. 8. (a) Width of the MS contribution as a function of the applied field strength for different number densities as indicated. We observe a roughly linear increase from an n -dependent offset at $E = 0 \text{ V cm}^{-1}$. (b) Central frequencies of the MS Lorentzian as a function of the applied field strength for different number densities as indicated.

FIG. 9. (a) Isolated single scattering Doppler spectra for PS310 at $n = 3.3 \times 10^{16} \text{ m}^{-3}$ and various field strengths as indicated. Solid lines are fits based on Eqs. (1)–(5). (b) Field strength dependence of the electro-osmotic velocity at the cell walls, u_{eo} , and the negative of the electro-phoretic particle velocity, $-v_{ep}$, as obtained from the fits in (a). The field dependence of both velocities is strictly linear. From the slope, we obtain the electro-phoretic and electro-osmotic mobilities: $\mu_{ep} = -5.4 \pm 0.1 \cdot 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu_{eo} = 1.2 \pm 0.2 \cdot 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$.

single scattering A_2^* increases monotonously with decreasing slope. The multiple scattering A_3^* increases with a constant slope.

Upon the application of an electric field, the MS-Lorentzian broadens approximately linearly with the increasing field strength. Measured widths start from a small n -dependent offset of a few tens of Hz and increase approximately linearly up to values between 200 and 300 Hz at $E = 7.5 \text{ V cm}^{-1}$. This is shown in Fig. 8(a). The MS contribution is shifted towards larger frequencies with increasing field. Fig. 8(b) shows data for the central frequency for six n -series. For each n , data assemble on approximately straight lines with lesser slopes for the larger n .

Spectra of PnBAPS118 were in general found to be much less affected by MS. However, when the turbidity was adjusted to large values by using $(10^3\text{--}10^4)$ -fold larger number densities, the behavior of the MS contribution for PnBAPS118 was qualitatively similar to that of PS310. An example obtained at $n = 2 \times 10^{20} \text{ m}^{-3}$ is shown in Fig. S10 of the [supplementary material](#). The MS contribution characteristics therefore appear to be independent of particle size and structure. The samples, of course, differ in their physical quantities due to different electro-kinetic properties, sample structure, diffusivity, and interaction strength. This is revealed in the SS contributions and is discussed next. However, little of that information is retained in the MS signal.

Evaluation of the isolated single scattering power spectrum

Electro-kinetics

The main goal of this study was to find and apply a suitable MS-correction scheme in order to measure electro-kinetic velocities over an extended range of particle concentrations. In our measurements on deionized but approximately CO_2 -saturated conditions, we measured five different field strengths per number density. For each parameter set, 250 spectra were averaged. An example of the obtained high quality MS free single scattering super-heterodyne power spectra is displayed in Fig. 9(a). For this sample at $n = 3.3 \times 10^{16} \text{ m}^{-3}$, the transmittance was merely 0.4. As the field strength was increased, the spectra stretched and their centers of mass shifted to larger frequencies. This is excellently described by the

FIG. 10. Reduced electro-phoretic mobilities μ_{ep}^{red} for PS310, measured under deionized conditions as a function of the particle number density n over roughly two orders of magnitude in n . Data for $n > 5 \times 10^{15} \text{ m}^{-3}$ were obtained performing both a correction for noise and for the MS scattering contribution. Note that the mobilities are negative for the negatively charged particle species. With increasing particle concentration, the electro-phoretic mobility shows an increase followed by a broad maximum and a steep decrease. The arrow marks the range for which MS-correction was necessary to obtain reliable fits of the electro-kinetic spectra.

corresponding fits, which were performed using a combination of Eqs. (1)–(5). They return the electro-phoretic velocity of the particles, v_{ep} , the electro-osmotic solvent velocity at the cell walls, u_{eo} , and an effective diffusion coefficient, D_{eff} . The obtained field-dependent velocities are displayed in Fig. 9(b). They are on the order of several tens of $\mu\text{m s}^{-1}$ and show a strictly linear dependence on the applied field strength.

Under this condition of linear electro-kinetic response, the respective slopes equal the electro-phoretic particle mobility, μ_{ep} , and the electro-osmotic mobility along the cell wall, μ_{eo} . Following the IUPAC convention, both mobilities are converted to reduced units to eliminate the dependencies on solvent viscosity, η , and solvent dielectric permittivity $\epsilon_0\epsilon_r$ as well as on temperature, T ,²⁰

$$\mu^{\text{red}} = \mu \frac{3\eta e}{2\epsilon_0\epsilon_r k_B T}, \quad (9)$$

where e is the elementary charge and $k_B T$ denotes the thermal energy. The results for μ_{ep}^{red} are plotted in Fig. 10 as a function of particle number density. The reduced mobility first increases, then displays a plateau at a value of about 5.8, and then decreases again. The corresponding reduced

FIG. 11. Diffusive properties of PS310 with and without applied field. (a) Field dependence of the effective diffusion coefficients obtained from fits to noise and MS corrected Doppler spectra at number densities indicated. (b) Comparison of the field free self-diffusion coefficient (diamonds) to the zero field extrapolated effective diffusion coefficients (circles). At any finite concentration, the extrapolated zero field effective diffusion coefficients are appreciably larger than the self-diffusion coefficients obtained in the field free case.

electro-osmotic mobilities are systematically larger, and show a somewhat larger scatter due to wall coating effects and a much less pronounced density dependence.

Diffusion

While our experiment was not (yet) optimized for diffusion measurements, we nevertheless took the chance to check the performance of our correction scheme for such investigations. At low salt conditions, PS310 shows weak ordering at elevated n . The SS-signal is dominated by incoherent scattering relating to the self-intermediate scattering function $G(q, \tau)$ and the effective self-diffusion coefficient, $D_S(q)$.

We fitted the noise and MS corrected spectra of PS310 by Eqs. (1)–(5) and (S1) of the [supplementary material](#). $D_{\text{eff}}(E)$ obtained at different concentrations are displayed in Fig. 11(a) as a function of applied field strength. For each n , D_{eff} depends linearly on E . This has been observed before,^{12,19,34,49} but currently still lacks a clear explanation. Following Ref. 34, we performed least square linear fits to the data which return a slope that decreases with increasing n and zero field extrapolated values of $D_{\text{eff}}(E \rightarrow 0)$ that increase with increasing E . This is shown in Fig. 11(b). The offset increases approximately linearly with increasing n starting from a value of $D_{\text{eff}}(n = 0) = (1.23 \pm 0.4) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

We further performed field free experiments and fitted the data using $v_{\text{ep}} = u_{\text{eo}} = 0 \text{ m s}^{-1}$. Fig. 11(b) shows that within experimental uncertainty, $D_{\text{eff}} = D_S$ is independent of n at a value of $D_S = (1.25 \pm 0.3) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$. For comparison, the Stokes-Einstein-Sutherland self-diffusion coefficient for PS310 is $D_0 = k_B T / 6\pi\eta a_H = (1.47 \pm 0.12) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, where we used a viscosity of water of 0.89 mPas, $T = 298.15 \text{ K}$ and $a_H = 167 \text{ nm}$ as determined by standard dynamic light scattering.⁵²

PnBAPS118 crystallizes for $n > 0.2 \times 10^{18} \text{ m}^{-3}$ under deionized conditions. Application of shearing flow generates an isotropic meta-stable melt of fluid order, from which the samples readily re-crystallize after cessation of the shear flow. MS correction becomes necessary for $n > 5 \times 10^{19} \text{ m}^{-3}$. Incoherent scattering dominates over coherent scattering at low angles. The forward scattering characteristic is less pronounced and additional Bragg reflections are present at larger angles (cf. Fig. S5 of the [supplementary material](#)). This allows studying the zero field self-diffusion coefficient during and

shortly after the crystallization. In general, D_S decreases with increasing n and with time. For the early measurements, we averaged over many repeated shear-melting–re-crystallization cycles. This ensured an acceptable quality of the spectra for each time window. In Fig. 12, we display the observed trends obtained for two series of crystallization/coarsening experiments at $n = 0.5 \times 10^{18} \text{ m}^{-3}$ and $n = 2.5 \times 10^{18} \text{ m}^{-3}$. At all times, diffusion is way below D_0 and notably slower in the case of the more concentrated and hence more strongly interacting sample. With increasing coarsening time, the data approach plateau values. This occurs faster for the less concentrated sample.

DISCUSSION

We performed super-heterodyne Doppler velocimetry on turbid suspensions of charged particles in the presence and absence of electric fields. Standard super-heterodyne theory outlined above could be used to evaluate the electro-kinetic spectra of PS310 in the range of $8 \times 10^{14} \text{ m}^{-3} \leq n \leq 5 \times 10^{15} \text{ m}^{-3}$. For larger concentrations, an additional spectral feature appeared, not considered in SS theory. We introduced and successfully tested an empirical isolation and correction scheme for this spectral component. The isolated contribution was found to be present only in the case of sample illumination by two mutually frequency shifted beams. This identifies it as genuinely super-heterodyne. Further it has a spectral shape clearly distinct from the SS super-heterodyne signal in the presence of electro-kinetic flows (as described by Eqs. (1)–(5) and (S1) of the [supplementary material](#)). This requires it to arise from multiple scattering events of light originating from the illumination beam.

The MS contribution observed in our super-heterodyne experiment with restricted detection volume displays some remarkable characteristic features: Most importantly, it can be excellently modelled by a simple Lorentzian of well-defined finite width w_{MS} . For both increasing particle number density and increasing shear, this simple line shape is retained. Its width increases linearly with both n and applied field strength. But even at the largest number densities, it appears to be only two orders of magnitude wider than that the SS spectral component. The MS integrated spectral power increases with increasing n and depends linearly on the reference beam intensity. Under flow, the center of mass of the MS Lorentzian appears to be shifted, but no electro-kinetic information can be obtained in a reliable way. Most of these observations were not expected from our experience with MS in standard homodyne dynamic light scattering. They may, however, be partially rationalized from recalling the conceptual differences in homodyne and super-heterodyne techniques.

Homodyning detects mutual phase shifts between photons scattered under in-phase illumination. Any MS event with its ill-defined phase due to the arbitrary location of the intermediate scatterer destroys this phase coherence. It thus leads to a fast decorrelation of $C_{\text{sher}}(\mathbf{q}, \tau)$ translating into a broad (and ill-defined) homodyne peak at $\omega \approx 0$ (cf. Eq. (4)). By contrast, super-heterodyning signals are independent of the mutual distance of the scatterers and the phase

FIG. 12. Temporal development of the zero field self-diffusion coefficient for two series of crystallization/coarsening experiments at $n = 0.5 \times 10^{18} \text{ m}^{-3}$ (circles) and $n = 2.5 \times 10^{18} \text{ m}^{-3}$ (diamonds).

difference of light simultaneously scattered from different particles. They only depend on the instantaneous motion of these particles during the scattering event. Taking this motion to be composed of a drift velocity and diffusion, one obtains a frequency shifted Lorentzian in the case of SS. Its amplitude is limited by the attenuation of the reference beam and attenuation of the SS light by additional scattering events. In the case of N_{MS} scattering events, one observes a convolution of N_{MS} Lorentzians (corresponding to the multiplication of N_{MS} $C_{shet}(\mathbf{q}, \tau)$ in time domain). This again yields a Lorentzian with width,¹⁷

$$w_{MS} = N_{MS} D_{eff} q_{MS}^2, \quad (10)$$

where q_{MS} is the average scattering vector for multiple scattering. The signal strength of the MS contribution scales with $I_r \langle I_N \rangle$ and thus is limited by reference beam attenuation. It is further limited by attenuation of the scattered light on its path through the sample. Most importantly, however, it is restricted by the requirements that any detectable scattering event has to be located inside the detection volume and the direction of the photon after the last scattering event has to be parallel to the reference beam direction. In fact, most of the MS light goes undetected. This can be rationalized in a qualitative way by considering a typical scattering event at moderate turbidity (cf. Fig. S11 in the [supplementary material](#)). Example photon paths and corresponding $\mathbf{q}$ are shown in Fig. S12).

Eq. (10) can be used to estimate the average number of MS events if further assumptions about q_{MS} are made. For isotropic or weakly ordered suspensions, there is only little restriction to the scattering directions from $S(\mathbf{q})$, but for large particles there is a strong bias for forward scattering due to their form factor $P(\mathbf{q})$. For PS310, we assume the average scattering vectors for double and multiple scattering to be mainly determined by $P(\mathbf{q})$ and the detection volume restriction. For PnBAPS118 they will

be determined by the product $P(\mathbf{q}) S(\mathbf{q})$ and the same geometrical restriction. For simplicity, the average scattering vector, q_{MS} , is further assumed to be independent of number density. In the limit of vanishing n the number of scattering events responsible for the MS-contribution is $N_{MS} = 2$, i.e., only double scattering (DS) is observed. We extrapolated the w_{MS} data for PS310 shown in Fig. 7(a) to $n = 0$ to obtain the limiting width for DS and an average double-scattering vector $q_{DS} = (w/2D)^{1/2} = 4.2 \mu\text{m}^{-1}$. This corresponds to an average scattering angle of 18.2° which is much larger than the SS-angle but smaller than the angle at half width of $P(\Theta)$ (cf. Fig. S5(a) of the [supplementary material](#)). We finally assume that on average that the same geometric restrictions apply to every scattering event, irrespective of the scatterer location. Setting $q_{DS} = q_{MS}$, we calculate the average number of scattering events as $N_{MS}(n) = w_{MS}(n)/q_{MS}^2$ and plot the result in Fig. 13(a). N_{MS} increases roughly linearly with increasing n and reaches a value of about 5 at $n = 4 \times 10^{16} \text{ m}^{-3}$.

The field strength dependence of the MS central frequency is approximately linear at each n . At low n where double scattering prevails, it is weaker than but still close to that of the SS central frequency corresponding to the particle velocity $\mathbf{v}$ in the mid-cell x-z-plane. Dependence appears to become weaker for increased n , where N_{MS} gets large. This is shown in Fig. 13(b) for four selected number densities. We attribute this effect to an averaging of $\mathbf{q} \cdot \mathbf{v}$ over all successive scattering events. Here, $\mathbf{v}$ follows from the applied field direction and the average velocity, i.e., v_{ep} , and $\mathbf{q}$ follows from the direction of the incoming photon and $P(\mathbf{q})S(\mathbf{q})$, as well as from the geometric restrictions. For $n = 6.5 \times 10^{15} \text{ m}^{-3}$ DS prevails and the most probable $\mathbf{q}$ are those resulting from forward scattering as discussed in Fig. S12 of the [supplementary material](#). Thus two small angle scattering events add up to yield a total scattering angle Θ_S . In turn, the total $\mathbf{q}_2$ stays close to $\mathbf{q}$. For larger n , however, $\mathbf{q}$ is successively averaged out to zero, and $\mathbf{q} \cdot \mathbf{v}$ drops.

FIG. 13. (a) Average number of scattering events contributing to the MS signal. (b) Central frequencies of the MS Lorentzian plotted versus the centre of mass frequencies of the SS contribution for different particle densities as indicated. In each data set the strength of the applied field was increased in steps from left to right. The dotted line is a guide to the eye denoting $f_{0,MS} = f_{0,SS}$. (c) Log-log plot of the data in Fig. 8(b) showing the noise normalized integrated spectral powers $A_i^* = A_i/A_1$ for SS and MS. Blue line: least square fit to the SS data returning $A_2^* \propto n^\alpha$ with $\alpha = 0.337$; dashed line: guide to the eye with $A_3^* \propto n$.

Another interesting feature is the dependence of the integrated spectral power on number density. In Fig. 13(c) we plot the data of Fig. 8(a) in a log-log fashion to check for power law behavior. Compared to the expectations arising from the pre-factor of heterodyne scattering in Eq. (4), both the SS and the MS contributions show a less pronounced dependence than that expected. Instead of a direct proportionality, the fit of the A_2^* data over more than a decade in n returns a power law of exponent $\alpha = 0.337$. The MS data appear compatible with $\alpha = 1$. This differs from the expectations given for SS in Eqs. (3) and (4) from which a linear scaling of A_2 with n is expected. Such a scaling indeed has been observed previously in well-ordered, single scattering systems of small particles (diameter 70 nm) where their coherent scattering cross section was very small and the dominant incoherent scattering was not prone to attenuation.¹⁹ Our observation also deviates from the simple expectation for attenuation-free MS for which $A_3^* \propto I_r \langle I_{MS}(q) \rangle = I_r \langle I_1(q) \rangle \langle I_2(q) \rangle \langle I_3(q) \rangle \dots \propto n^{N_{MS}} P(q)S(q)$.

Several possibilities for a sub-linear increase of A_2^* and a liner increase in A_3^* may in principle be considered. In the present case going from non-interacting to weakly structured suspensions, we cannot exclude some influence of structure formation. Even under the present conditions of strong incoherent scattering, this may result in a decrease of $S(q)$ at small angles and enter into A_2^* and A_3^* . Further, we may expect the influence of attenuation of the reference beam entering through the pre-factors in Eq. (4) for every successive scattering event. However, at the same time one should also account for attenuation of the illumination beam on its way through the sample, the loss of detectable scattered light by additional scattering events, and the generation of detectable light by scattering from paths not parallel to the reference beam direction. A full theoretical description explicitly including all these gain and loss terms for single scattering and every following generation of scattering events is clearly beyond the scope of this paper. At present, we therefore cannot explain this behavior and regard it as an interesting observation occurring in the case of attenuation by multiple scattering as well as a constraint for theoretical descriptions to be developed in future.

The next point to discuss is the usefulness of the here proposed and tested scheme in other turbid systems and for other physical properties. Standard dynamic light scattering can be applied for samples of transmittance $T \approx 0.9$ -0.95.^{7,55} Our experiments were performed on particles showing dominant incoherent scattering with more or less pronounced forward scattering characteristics. This allowed neglecting the influences of structure formation on electro-kinetic and diffusion spectra. MS became discernible for $T \approx 0.9$ and our scheme was successfully tested to $T \geq 0.4$ but may in principle be applied up to limit of the Beer-Lambert law, which for PS310 is at $n = 1 \times 10^{17}$. Applications may include rheological measurements or measurements of active particles, both up to high particle concentrations and strong mutual interaction strengths.

We profited from super-heterodyning and a strong restriction of the detection volume, such that we were not concerned with homodyne phase decorrelation and most of the MS light produced went undetected. Our method appears to be very

flexible and our correction scheme should be readily applicable also many other cases without the need for instrumentally demanding cross correlation or mode selection schemes. We measured particle velocities and self-diffusion in ergodic and non-ergodic samples. For the latter, standard homodyne experiments require additional efforts to obtain a correct averaging in order to apply the Siegert relation and calculate $g_E(q,t)$ from $g_I(q,t)$.⁵⁶ For the presently studied poly-crystalline samples, ensemble averaging is provided by the large illumination volume which exceeds that observed in a typical dynamic light scattering experiment by about two orders of magnitude. Moreover, super-heterodyning directly accesses $g_E(q,t)$ instead of $g_I(q,t)$. This makes it very interesting to test our approach also in other samples and at larger angles. The present experiments were performed only at a single angle without yet exploiting the possibility of q -dependent measurements. Preliminary experiments show that we can use the correction scheme also for angles up to some 15° . It remains, however to be tested, whether it can still be applied in a standard light scattering goniometer when illumination beam and reference beam are crossed at 90° .

In principle, we do not see any principle objection to applying our correction scheme also to samples with dominant coherent scattering. However, a few issues may arise. One is discrimination of SS and MS contributions. Since super-heterodyning does not record phase de-coherence, but successive Doppler broadening events, no strong separation of time scales is observed. With $w_{MS} = N_{MS} D q_{MS}^2$ and D being the same for MS and SS, signal discrimination may become difficult where $q \approx q_{MS}$. For diffusion measurements close to the maximum of $S(q)$, it may be useful to employ minute plug-flows, which do not interfere with structure (cf. Fig. 7(c)) and perform discrimination via the location of the spectral maxima. Alternatively, one may increase the particle scattering cross section (e.g. by refractive index mismatching) to increase N_{MS} . A second issue may be the discrimination of relaxation processes occurring on different time scales.⁵⁷ For glassy samples with well separated short and long-time dynamics, a superposition of Lorentzians is expected for both SS and MS. A convolution of a Lorentzian with a distribution of line widths can be expected. It remains to be tested how these can be discriminated. In general, however, measurements of stretched exponentials or power-law decays or other complex temporal behavior, which are easily feasible in standard dynamic light scattering,⁵⁸ appear to be difficult in frequency domain due to the *a priori* unknown spectral shape. A workaround may possibly be provided by Fourier-back-transformation.

In the present study, our correction scheme was applied to obtain different physical properties from the isolated SS-spectra. It was utilized (i) to investigate the spectral broadening under electro-kinetically driven solvent flow and particle drift, (ii) to quantify Brownian motion in the field free case in differently ordered samples, and (iii) to study the drift motion in an electric field. Concerning diffusion measurements with applied electric field, our data support earlier findings of a linear dependence of $D_{eff}(E)$ on field strength, respectively, the average shear rate $\gamma = dv/dx$. This demonstrates the possibility to apply our approach also to sheared systems, not

easily studied by standard dynamic light scattering. Moreover, we could for the first time observe a pronounced n dependence of the field dependent broadening. This seems to favor field induced velocity fluctuations¹² or a polydispersity of the electro-phoretic mobility⁴⁹ over Taylor dispersion⁴¹ accounting for effects of shear. The mobility polydispersity scales directly with the size polydispersity²⁷ and therefore should follow the n -dependent mobility. Velocity fluctuations are expected to be most pronounced when the structural correlation length is on the order of the interparticle distance, i.e., at intermediate n , where the structure is still weak. By contrast, shear in our experiments depends on the electro-osmotic velocity (cf. Eq. (S1) of the [supplementary material](#)), which shows only very little dependence on n .

For solidifying PnBAPS118, the field free self-diffusion coefficient was observed to decrease to a limiting value. The more dilute sample showed the slower temporal evolution. This is in line with previous experiments using Forced Rayleigh scattering or microscopy.^{59,60} We therefore believe, that such experiments contain interesting information about grain boundary dynamics. Future experiments will complement existing structural studies on coarsening samples.^{61–64}

For the electro-kinetic measurements on PS310 our approach facilitated an extension of the accessible volume fraction range by nearly one order of magnitude (cf. Fig. 12). We found that under low salt conditions, the electro-phoretic mobility, μ_e first increases, then displays a plateau and finally decreases again. The initial ascent is in line with earlier observations on extremely low mobilities for isolated particles and on particles observed at low number densities.^{24–27} The plateau and final descent are compatible with previous observations made on particles at large number density under conditions of counterion dominance.^{27–30} The previous data were gathered for particles of different surface chemistry and size, at fully deionized conditions and in the presence of salt. In view of the present findings we propose that each has been covering different parts of a universal curve.

A rigorous quantitative test, however, would in addition require a precise control of the salt concentration. In the present study, we worked under CO₂-saturation without conductometric control in both transmission and electro-kinetic experiments to test the correction scheme at known turbidities. Any residual uncertainty of the electrolyte content, however, can have large effects on mobility. Measurements with precise adjustment of different low salt concentrations are under way.

CONCLUSION

We have introduced a simple yet powerful empirical MS-correction scheme for super-heterodyne light scattering in frequency domain. We demonstrated its scope and limits by systematic LDV measurements on different charged particle suspensions. We discussed its versatility and limits and indicated a variety of possible applications beyond electro-kinetics. We anticipate that this approach will allow for a number of interesting investigations on the dynamic properties of turbid suspensions at moderate to a very low

transmittance. A full theoretical description of the MS contribution to describe its interesting characteristics is highly desired.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for additional details concerning the experimental setup, particle flow profile, and multiple scattering contribution.

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