Anisotropic hindered motion close to an interface studied by resonance-enhanced dynamic light scattering

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Abstract. The influence of a solid–liquid interface on the diffusion of dispersed spherical particles has been studied using resonance enhanced dynamic light scattering. Particle radii ranging from 11 to 204 nm have been investigated at a fixed penetration depth of the evanescent wave of 200 nm. For particles with radii smaller than 40 nm, the correlation function measured near the interface is similar in shape to the one measured in bulk solution. For particles with radii higher than 40 nm the correlation function loses the distinct single exponential shape. To study particles with radii higher than 40 nm, we had to solve the problem of an unwanted contribution to the correlation function. This problem is generic with dynamic light scattering using single-mode fibre detection and is thus of general interest. This contribution has been identified as stemming from temporal fluctuations in the fibre used. Furthermore, we give an estimation of the effect of rotation on translation for spherical particle mobility near an interface.

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1. Introduction

Dynamic light scattering (DLS) extracting information via autocorrelation functions is a powerful method to measure the dynamics of polymers or particles in bulk solution [1]. Compared to free diffusion in bulk solution, the dynamics or movement close to an interface is influenced by several factors, e.g. hydrodynamic or electrostatic forces. Many evanescent wave dynamic light scattering (EWDLS) experiments report the anisotropic diffusion (parallel versus perpendicular) of particles close to interfaces [2]–[7]. In these publications, only polystyrene (PS) latex particles larger than 27 nm in hydrodynamic radius \( R_h \) could be used because of the resolution limit of this technique [6]. The form of the correlation functions was different compared to the measurements performed in bulk solution.

Hydrodynamic theory attributes this (as the main source of difference) to an increase of the drag force near the interface [8]. As a contribution and extension of evanescent light scattering methods resonance-enhanced dynamic light scattering (REDLS) has been recently developed to study the dynamics close to a metal surface with a currently unrivalled resolution and the possibility of monitoring surface modifications (e.g. adsorption processes) [9, 10]. In these studies, PS latex particles with \( R_h \) ranging from 11 to 40 nm were considered. Even though the surface-induced diffusion anisotropy could be shown, the form of the correlation function of the small particle was very similar to the one measured in bulk, in particular at the magnitude of the scattering vector \( q \geq 0.019 \text{ nm}^{-1} \). This forms a contrast to the bigger particles which were already examined by EWDLS.

The questions we want to answer are: do we also get a large difference for larger particles between the shape of the correlation function measured in bulk solution and close to the interface at a penetration depth of 200 nm? If so, can we identify the onset of these changes by changing the particle size relative to the penetration depth? For this purpose, we have investigated PS latex spheres with \( R_h \) up to 204 nm, i.e. up to the range of penetration depths of the surface plasmon, and down to 11 nm. To close the gap between small-sized objects already studied by
REDLS, and larger objects studied in EWDLS, we had to solve a problem concerning the DLS part of our technique: in most modern DLS setups, single-mode fibre detection [1, 11] is used. Here, a correlated noise signal appears with a contrast \( g_{\text{add}}(q, 0) \) of the order of \( 10^{-4} \), which can be neglected in the so-called homodyne [1] case, where the contrast of the intensity autocorrelation function \( g_2(q, t) \) is usually close to one. The contrast of the field autocorrelation function \( g_1(q, t) \) measured by REDLS in the heterodyne [1] case is of the order of \( 10^{-3} \). In this case, \( g_{\text{add}} \) is not negligible. In section 5, we describe in detail the origin of this spurious contribution and how to reduce it to below the noise level.

2. Theory: influence of hydrodynamic effects on the dynamics near interfaces

Interfaces have an important influence on the dynamics of colloidal suspensions in their vicinity. A hard sphere with hydrodynamic radius \( R_h \), moving at a drift velocity \( \vec{v} \) in a bulk solution of viscosity \( \eta \), experiences a hydrodynamic drag force \( \vec{F} \) opposite to the drift velocity. Using the Stokes–Einstein relation, this equation can be expressed by the diffusion coefficient \( D_0 \), the Boltzmann constant \( k_B \) and the temperature \( T \) of the system:

\[
\vec{F} = -6\pi \eta R_h \vec{v} = -\frac{D_0}{k_B T} \vec{v}.
\]

When the sphere approaches a solid surface, the drag force increases and the diffusion of the sphere is hindered. This can be taken into account by a correction factor. From here on, we neglect non-hydrodynamic effects such as chemical, electrostatic and electro-osmotic forces. Assuming a ’non-slip’ boundary condition and low Reynolds numbers, this correction factor can be obtained using Stokes’ law, equation (1) [12]. Because of the linearity of Stokes’ law, the drag force as well as the diffusion coefficient can be separated into independent components for motions parallel and normal to the wall.

The diffusion coefficient close to a wall in the normal direction \( D_\perp \) has been derived by Happel and Brenner [8]:

\[
\frac{D_0}{D_\perp} = \lambda_\perp = \frac{4}{3} \sinh(A) \sum_{n=1}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \left\{ \frac{2 \sinh[(2n+1) A] + (2n+1) \sinh(2A)}{(2 \sinh[(n+0.5) A])^2 - (2n+1)^2 \sinh^2(A)} - 1 \right\},
\]

with \( A = \text{arccosh}(z/R_h) \) with \( z \) representing the distance from the centre of the particle to the solid surface.

The solution for the motion of a sphere parallel to a wall is more complicated, because one has to take into account the torque acting on the sphere. The shear on the side facing the wall is stronger than the shear on the opposite side. The consequence is a torque, resulting in rotation of the sphere [12]. The magnitudes of the force \( F \) and the torque \( M \) acting on a sphere moving parallel to a planar wall with velocity \( v_\parallel \) and rotating with an angular frequency \( \omega \) can be described by [12, 13]

\[
F = 6\pi \eta R_h (v_\parallel F_t + \omega R_h F_r)
\]

and

\[
M = 8\pi \eta R_h^2 (v_\parallel M_t + \omega R_h M_r).
\]

\( F_t, F_r, M_t \) and \( M_r \) are dimensionless functions depending on the normalized distance \( z/R_h \). The indices ‘\( t \)’ and ‘\( r \)’ represent translation and rotation, respectively. If the sphere is free
Figure 1. Normalized diffusion coefficients of \( R_h = 31 \) and 204 nm particles for motion parallel to the surface. Circles: full numerical solution of O’Neill (6); solid lines: Faxen’s approximation (7).

To rotate, the torque \( M \) is zero and the angular frequency of the sphere can be calculated using

\[
\omega = -\frac{M_t}{RM_t} \cdot \nu_\parallel. \tag{5}
\]

Therefore, the correction factor for the motion of a sphere parallel to a wall is given by

\[
\frac{D_0}{D_\parallel} = \lambda_\parallel = F_t - \frac{M_t}{M_r} F_r. \tag{6}
\]

Based on the numerical calculations of O’Neill [12]–[14], figure 1 shows the solution of \( \lambda_\parallel \) depending on the distance from the surface \( h = z - R_h \) (sketch in figure 2) of particles with \( R_h = 31 \) and 204 nm. Neglecting rotation \( (F_r = 0) \) a deviation of less than 2.5% for \( z/R_h > 1.00067 \) was found. Thus, particle rotation is induced close to the surface, but the influence of rotation on the translation can be ignored as an approximation.

An analytical approximation of (6) has been derived by Faxen and has been reported in the literature [8, 12]:

\[
\frac{D_0}{D_\parallel} = \lambda_\parallel \approx \left( 1 - \frac{9 R_h}{16 z} + \frac{1 R_h^3}{8 z^3} - \frac{45 R_h^4}{256 z^4} + \frac{1 R_h^5}{16 z^5} \right)^{-1}. \tag{7}
\]

It is only valid for large distances \( z/R_h > 1.4 \). Comparing Faxen’s result with O’Neill’s exact numerical calculations, a deviation of less than 10% for \( z/R_h > 1.04 \) was found [6] that is illustrated in figure 1.

Close to a wall, the values of \( \lambda_\perp \) and \( \lambda_\parallel \) are not lower than unity. As a result, the diffusion of an isolated sphere slows down and becomes anisotropic in the direction perpendicular versus parallel to the surface. The influence of these effects on the particle size is depicted in figure 2. For the calculation of \( \lambda_\perp = D_0/D_\perp \), the first hundred terms of the sum in (2) were used.

This theory was adopted for DLS using evanescent wave geometry. It is possible to extract information from the correlation functions measured with EWDLS or REDLS by using the

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Figure 2. Normalized diffusion coefficients for motion parallel and perpendicular to the wall of particles with $R_h = 31$ nm (dot line and dash line) and $R_h = 204$ nm (solid line and dash-dot-dot line). Calculations have been performed with the help of (2) and (7). The sketch illustrates the distances $h$ and $z$ of the particle from the surface.

cumulant analysis (also called initial slope analysis) [6, 9]:

$$\ln(C(q,t)) = -\Gamma_c \cdot t + \frac{\mu}{2!} \cdot t^2 - \cdots.$$  

(8)

$C(q,t)$ represents the normalized field autocorrelation function $g_1(q,t)$, $\Gamma_c$ is the initial decay rate and $\mu$ is the variance of the distribution. Note that in bulk solution, $\Gamma_c = D_0 q^2$ [1]. We will use this cumulant analysis in the following to compare our results with other published works, where this analysis was used as well. However, one has to treat the results with caution in case the width of the distribution of relaxation times exceeds certain limits (see e.g. [10] and references therein).

Taking into account the hydrodynamic interactions between the spherical particle and the surface as well as the evanescent geometry, the initial decay rate $\langle \Gamma_c \rangle$ describing the short-time behaviour of the normalized field autocorrelation function $C(q,t)$ can be rewritten [6] as

$$\langle \Gamma_c \rangle = q^2_{||} \cdot \langle D_{||} \rangle + \left( q^2_{\perp} + \frac{1}{\xi^2} \right) \cdot \langle D_{\perp} \rangle,$$

(9)

where $q_{||,\perp}$ are the magnitudes of the components parallel and perpendicular to the surface of $\vec{q}$. Thus, the ‘mean diffusivities’ are given by

$$\langle D_{||,\perp} \rangle = \frac{2D_0}{\xi} \int_R^\infty dz \cdot \exp\left[-\frac{2(z - R_h)}{\xi}\right] \cdot \lambda_{1,\perp}^{-1}.$$  

(10)

Note that with the help of DLS using evanescent wave geometry, it is not possible to measure the diffusivity of a particle at a well-defined distance from the interface [6]. The ‘mean decay rates’ $\langle \Gamma_c \rangle$ and ‘mean diffusivities’ $\langle D_{||,\perp} \rangle$ obtained from the cumulant analysis are averaged over the entire depth illuminated by the evanescent wave.
Figure 3. The REDLS-setup is a standard Kretschmann–Raether configuration combined with elements for DLS detection.

3. Experimental

The basic idea of REDLS is to combine the spatial resolution of surface plasmon resonance (SPR) spectroscopy [15] with the spatiotemporal resolution of DLS. The REDLS setup is described in detail elsewhere [10]. A surface plasmon is excited in a standard Kretschmann–Raether configuration [15]–[17] and is used as the illumination beam in a DLS experiment (figure 3). The monochromatic light from a helium–neon laser ($\lambda = 632.8$ nm) passes through a polarizer (p-polarization) before being reflected at the metal-coated base of a prism attached to a quartz cell. The reflected light is detected with a photodiode. To find the incidence angle for SP excitation $\psi_P$, angular reflectivity scans are performed. Probes like particles in solution interact with the electromagnetic field of the surface plasmon and scatter light. The scattered light is recorded on the opposite side of the cell by a DLS detector system, consisting of the following: a single-mode fibre with a fibre coupler, a Static and Dynamic Enhancer (ALV GmbH, Langen, Germany), a fibre–beam splitter, two avalanche photodiodes and an ALV7004/fast multiple tau digital correlator. The Static and Dynamic Enhancer is necessary for minimizing the contribution from thermal fluctuations of the single-mode fibre. A detailed treatment of this problem is given in section 5.

The DLS detector system can be rotated to measure correlation functions at different scattering angles $\Theta$ defining the scattering vector $\vec{q} = \vec{k}_s - \vec{k}_i$ with $\vec{k}_i$ and $\vec{k}_s$ being the wave vectors of the incident and the scattered wave.

The radiative part of the decay of the surface plasmon leads to surface plasmon radiation [16]. This radiation forms a local oscillator; thus one works in REDLS in the heterodyne detection mode and measures the field-autocorrelation function $g_1(q, t)$ [9], with

$$q = \frac{4\pi n}{\lambda} \cdot \sin(\Theta/2)$$

being the magnitude of the scattering vector $q$ and $t$ being time (a detailed discussion on the value of $q$ is given in [10]). In this equation, the scattering angle $\Theta$ is obtained from the angle...
Note that the following notation is used: $C(q,t)$ is the converted field auto-correlation function measured by DLS ($\alpha \equiv 1$ in our experiment) and $C_s(q,t)$ is the field auto-correlation function measured by REDLS. The contrast of $C_s(q,t)$ is normalized to one.

Figure 4 compares $C(q,t)$ recorded in bulk solution with $C_s(q,t)$ measured by REDLS at a fixed scattering angle of $\Theta = 90^\circ$ (the magnitude of the scattering wave vector $q = 0.019$ nm$^{-1}$). For this purpose, PS latex particles with $R_h = 31$ and 204 nm suspended in pure water have been used.

For the smaller particles the shape of $C_s(q,t)$ is similar to the shape of $C(q,t)$. For the bigger particles $C_s(q,t)$ loses the distinct single exponential shape and the decay rate slows down. This slowing down is expressed as an apparent hydrodynamic radius $R'_h$ (used here, instead of the more physical diffusion coefficient, to relate to previous works in this field). The deviations of $C_s(q,t)$ from $C(q,t)$ may be due to several reasons.

Hydrodynamic theory predicts anisotropic diffusion behaviour of the particle close to the wall (parallel versus perpendicular to it). Since $D_\parallel > D_\perp$ near a wall Lan et al [19] expected two decays of the correlation function. The first decay represents the time it takes for a particle to diffuse in a plane parallel to the wall on a length scale $q_\parallel^{-1}$ [19]. The second decay involves $\xi$
Figure 4. Correlation functions of PS latex particles at a scattering angle of \( \Theta = 90^\circ \) \((q = 0.019 \text{ nm}^{-1})\) and a penetration depth of the evanescent wave of \( \xi = 200 \text{ nm} \). Solid lines represent DLS in bulk solution and symbols the measurements performed with REDLS. Inset: initial decay of \( C_s(q, t) \) for particles with \( R_h = 204 \text{ nm} \) (symbols) and a simulated function with \( t^{-1/2} \) behaviour (solid line).

and \( q_{\perp}^{-1} \) \cite{19} and therefore movement perpendicular to the wall. In addition, the presence of an interface leads to broken translation symmetry and therefore to the so-called mirror effect \cite{2}. Last but not least \( R_h \) is not negligible compared to the penetration depth of the evanescent wave. The evanescent wave may illuminate only parts of the particle, which may also cause deviations of \( C_s(q, t) \) from \( C(q, t) \).

Furthermore, due to the decaying nature of the evanescent wave, a long-time tail of \( C_s(q, t) \) with a \( t^{-1/2} \) behaviour was predicted in \cite{2, 7}. This we do not find in our REDLS measurements. The shape or functional form of a simulated correlation function with \( t^{-1/2} \) behaviour is not in accordance with the long-time tail of \( C_s(q, t) \) measured with particles of \( R_h = 204 \text{ nm} \) (the inset of figure 4).

To see the onset of visibility of the interfacial effects described in the section above, correlation functions have been measured at \( q = 0.019 \text{ nm}^{-1} \) using different particle sizes. Figure 5 is a plot of the calculated and apparent hydrodynamic radii of particles close to the surface

\[
R_h^* = \frac{k_B T q^2}{6 \pi \eta \langle \Gamma_c \rangle},
\]

measured by REDLS, versus the hydrodynamic radius \( R_h \) received from conventional DLS. For particles with \( R_h > 90 \text{ nm} \), the hydrodynamic radius calculated from a correlation function measured by REDLS is much higher than to the one obtained in bulk. In addition, \( C_s(q, t) \) loses the distinct single exponential shape for particles with \( R_h > 40 \text{ nm} \).

To compare our results with the hydrodynamic theory, the normalized initial decay rates \( \langle \Gamma_c \rangle / \Gamma_0 \) are plotted versus the normalized penetration depth of the evanescent field \( \xi / R_h \) for all particle (the inset of figure 5). Since the penetration depth of the surface plasmon is constant in our experiment \((\xi \approx 200 \text{ nm})\), the normalized averaged diffusion coefficient depends on the
Figure 5. Hydrodynamic radii $R_h^s$ of PS latex particles measured by REDLS as a function of the hydrodynamic radii $R_h = 11, 16, 20, 31, 42, 51, 61, 76, 95, 97, 114, 153, 179$ and $204$ nm obtained by DLS at a scattering angle of $\Theta = 90^\circ (q = 0.019 \text{nm}^{-1})$. Open symbols are the values measured by REDLS and the solid line represents the result of the DLS measurement. Inset: the ratio between the initial decay rate $\langle \Gamma_c \rangle$ obtained by REDLS and the bulk decay rate $\Gamma_0$ measured with DLS as a function of the normalized penetration depth $\xi/R_h$. The dashed line represents the theory given by (9) using the values in figure 4 of [6].

particle size, as predicted by hydrodynamic theory [6]. Deviations from theory may be explained by non-hydrodynamic effects such as electrostatic double-layer forces [20]. We observed a slowing down of the decay rate for particles of $R_h > 40$ nm.

Detailed information on Brownian motion can be extracted from the dependence of $C(q, t)$ on the scattering angle, also known as $q$-dependence. For this purpose, correlation functions for particles with $R_h = 204$ nm are measured at different scattering angles $\Theta$ or scattering vectors $\vec{q}$, respectively. For comparison, the $q$-dependence of particles with $R_h = 31$ nm is shown [9].

In bulk solution using conventional DLS, one receives a linear dependence between the decay rate and the square of the scattering vector ($\Gamma = D_0 q^2$, solid lines in figure 6). In this case, the diffusion behaviour is isotropic. The trend of $\Gamma_c(q)$ measured by REDLS deviates from the linear $q^2$ dependence in bulk solution because of the hindered anisotropic diffusion and the evanescent geometry for both particle sizes.

When only the hydrodynamic effects are considered, the confined Brownian motion (dotted lines in figure 6) can be modelled by (9). We used $\langle D_\parallel \rangle = 0.80D_0$ and $\langle D_\perp \rangle = 0.60D_0$ for $R_h = 31$ nm and $\langle D_\parallel \rangle = 0.56D_0$ and $\langle D_\perp \rangle = 0.26D_0$ for $R_h = 204$ nm (cf figure 4 of [6]). We have not been able to find a reasonable set of adjusting parameters to fit the dependence we have found experimentally.

First we focus on $q \approx 0.019 \text{nm}^{-1}$. In the case of $R_h = 31$ nm, our result for $\langle \Gamma_c \rangle$ falls close to the free diffusion. Fittingly, in this range, $R_h^s$ of the small particles compare well (figure 5) with the hydrodynamic radii of the particles measured with conventional DLS. In contrast, for the bigger particles we observe a slowing down of the decay rate. The measured result for these is close to the theoretical predictions (the inset of figure 5).
Figure 6. Particle diffusion at a water/gold interface. The solid lines indicate the results of conventional DLS performed with particles of radius \( R_h = 31 \) and 204 nm, whereas the expected confined Brownian motion (9) is represented by the dotted lines. The closed (small particle) and open (big particle) symbols show the results obtained by REDLS at a penetration depth of 200 nm.

Finally, we focus on the \( q \)-dependence, in REDLS, of the particles of \( R_h = 204 \) nm. In this case, the theoretical predictions for the confined Brownian motion describe the results qualitatively. Deviations are found at \( q < 0.019 \) nm\(^{-1} \), where the measured \( \langle \Gamma_c \rangle \) are slightly above, and at \( q > 0.019 \) nm\(^{-1} \), where the measured \( \langle \Gamma_c \rangle \) are slightly below that predicted by theory.

Michailidou et al [21] found, for the diffusion coefficient of latex particles of polymethylmethacrylate in a dilute solution, a linear dependence that, in terms of figure 6, is equivalent to a linear \( q^2 \) dependence of \( \langle \Gamma_c \rangle \). They found, as in our case, a deviation from the results for the bulk solution case: a slowing down was observed.

5. Thermal fluctuations in single-mode fibre transmission

5.1. Spurious contribution

Problems caused by slow fluctuations of throughput often occur in fibre optic systems. An additional correlation signal \( g_{\text{add}}(q, t) \) can be found at correlation times in the range of seconds, typically between 1 and 100 s (figure 7). The contrast \( g_{\text{add}}(q, 0) \) is of the order of \( 10^{-4} \) and can be neglected in the homodyne case, where the contrast is usually of the order of one. The contrast of the heterodyne correlation functions \( g_1(q, 0) \) measured by REDLS is typically \( 10^{-4} \)–\( 10^{-2} \) [10] and, thus, of the magnitude of \( g_{\text{add}}(q, t) \). Here, we estimate quantitatively the origin of this spurious signal.

5.2. Single-mode fibre as an interferometer

Because of multiple reflections at the fibre ends, a single-mode fibre acts as a Fabry–Perot interferometer. As with any interferometer, transmission through the fibre is sensitive to the
Figure 7. Correlation functions $g_1(q,t)$ measured by directly aligning the laser beam onto the DLS detector system. A correlation function of the fluctuations from the Fabry–Perot effect can be seen using a single-mode fibre (filled symbols). After introducing the Static and Dynamic Enhancer (open symbols), this contribution from the experimental conditions is removed and only a baseline can be detected.

changes of the optical path length, which in turn lead to variations of the fibre throughput. The theory of the Fabry–Perot interferometer can be found in any optics textbook (e.g. [22]), but for convenience to the reader we will briefly recapitulate the basics. To simplify the analysis of a possible effect of path length fluctuations, we assume that the fibre is polarization-maintaining and consider only one state of polarization. We also neglect attenuation, which is indeed small in a fibre of a few metres length. Summing up the infinite series of reflected and transmitted contributions yields the amplitude transmission function $t_f(\nu; \Omega)$ of the fibre as

$$ t_f(\nu; \Omega) = \frac{t_1 t_2 \exp(ik_0 \Omega)}{1 - r_1 r_2 \exp(2ik_0 \Omega)}, $$

where $t_1$, $t_2$ and $r_1$, $r_2$ are the Fresnel amplitude transmission and reflection coefficients at the fibre ends and $k_0 = 2\pi/\lambda_0 = 2\pi \nu/c_0$ is the wave number, expressed in terms of the considered frequency $\nu$ or the wavelength $\lambda_0$ in vacuum; $c_0$ represents the speed of light in vacuum. The optical path length $\Omega$ is defined as the integral of the refractive index over the geometrical length of the fibre:

$$ \Omega = \int_0^L ds \cdot n(s). $$

Assuming that $n(s) = \text{const} \approx n_q$ (where $q$ stands for quartz), one obviously gets $\Omega = n_q L$. The refractive index depends on the frequency $\nu$, but we shall neglect dispersion here, since we are only interested in a narrow frequency range. The spectral power transmittance of the fibre $T_f = I_{\text{out}}/I_{\text{in}} = |t_f|^2$, where $I_{\text{in}}$ and $I_{\text{out}}$ are the incident and transmitted intensities, is obtained by taking a complex square of (14):

$$ T_f(\nu; \Omega) = \frac{T_r^2}{(1 - R)^2} \cdot \frac{1}{1 + F \sin(k_0 \Omega)^2}. $$
Figure 8. Example of a transmission curve $T_f(\nu; \Omega)$ of a Fabry–Perot interferometer with a low finesse coefficient $F = 0.15$. The vertical line indicates a laser line and the horizontal double arrow shows the motion of the transmission maxima in response to changes of optical path length $\Omega$.

$T_r = \sqrt{T_1 T_2}$ is the total transmission, and $T_1 = t_1^2$ and $T_2 = t_2^2$ are the power transmission coefficients of the two reflecting surfaces. Correspondingly, $R = \sqrt{R_1 R_2}$ is the reflection coefficient of the surfaces, $R_1 = r_1^2$ and $R_2 = r_2^2$. (Note that if $r_1 = r_2$, then $T_r = 1 - R$.) Finally, $F$ is the so-called coefficient of finesse:

$$F = \frac{4 R}{(1 - R)^2}.$$  \hfill (17)

Equation (16) represents a periodic frequency filter. The modulation depth of the periodic filter function is given by the coefficient of finesse $F$. Note that unless precautions are taken to minimize the reflections at fibre ends, the filter modulation is quite large. For a perpendicular reflection at the quartz–air interface, one obtains $R \approx 0.035$ and thus $F \approx 0.15!$ This case is illustrated in figure 8. Transmission maxima are found at frequencies where $\sin(k_0 \Omega) = 0$, i.e. $k_0 \Omega \text{ MOD } \pi = 0$. In other words, transmission maxima are at frequencies $\nu_m$ such that

$$2 \nu_m \frac{\Omega}{c_0} = 2 \frac{\Omega}{\lambda_m} = m,$$

where $m$ is an integral number. Correspondingly, the spacing of the maxima is given by $\Delta \nu = c_0/2\Omega$. For example, a fibre of about 2 m length would have a $\Delta \nu$ of $0.5 \times 10^8$ Hz. (For comparison, this is approximately the linewidth of a single-frequency green diode-pumped solid state laser. On the other hand, a single line Ar-ion laser (equipped with a Fabry–Perot etalon) exhibits a linewidth of only $3 \times 10^6$ Hz.)

5.3. From path length fluctuations to fluctuations of transmitted signal

Consider a light source with a certain frequency spectrum $S(\nu)$. The power transmitted through the fibre $J$ is given by the overlap integral of the source spectrum $S(\nu)$ and the filter function $T_f(\nu; \Omega)$:

$$J \propto \int \, d\nu S(\nu) T_f(\nu; \Omega).$$ \hfill (19)
It is obvious that whenever $\Omega$ fluctuates, these fluctuations are transferred to the transmitted signal $J$. However, the transfer of the fluctuation from $\Omega(t)$ to $J(t)$ is rather complicated, since it depends not only on $\Omega(t)$ and $T_f(v; \Omega)$, but also on the width and form of $S(v)$. The resulting fluctuations will decrease with the source bandwidth $\delta v$ and may become negligible when $\delta v$ is much larger than the spacing $\Delta v$ of filter maxima. We only consider the worst case, such that $S(v) \approx \delta(v - \nu_L)$ (narrow linewidth single-frequency laser operating at $\nu_L$), so that $J(t) \propto T_f[\nu_L; \Omega(t)]$. Taking the input wavelength $\lambda_L$ as a convenient unit to measure the optical path, we introduce the dimensionless path length $\Lambda(t) = \Omega(t)/\lambda_L$ and write the transmitted signal as

$$J(t) \propto \frac{1}{1 + F \sin[2\pi \Omega(t)]^2} = \frac{1}{1 + F \sin[2\pi \Omega_0 + 2\pi \delta \Omega(t)]^2}.$$  

On the right-hand side, we introduced the decomposition $\Lambda(t) = \Lambda_0 + \delta \Lambda(t)$, where $\Lambda_0$ is an undisturbed reference value and $\delta \Lambda(t)$ represents the fluctuations.

Fluctuations $\delta \Lambda(t)$ may be of mechanical or thermal origin. We neglect the mechanical effects (i.e. changes of refractive index due to stresses caused by bending or vibrations of the fibre) and concentrate on thermal effects. We can then identify two different cases. The first case is a fibre in an imperfect thermal environment, so that its temperature $T(t)$ drifts or fluctuates with time. We also allow for distributed temperature fluctuations $T(s, t)$ along the length of the fibre. The second case is more fundamental: every material exhibits thermal fluctuations, even if the bath temperature is kept perfectly constant. Brownian motion measured by DLS is of this kind. Spontaneous thermal fluctuations in quartz are much less pronounced, but still these thermal fluctuations pose the fundamental limit to the performance of a fibre interferometer.

### 5.4. Drift and fluctuations of fibre temperature

Changes of temperature affect the optical path length $\Omega = n_\Omega L$ in two ways: both the refractive index $n_\Omega$ and the geometrical length $L$ depend on temperature. Assuming small temperature variations with respect to a reference temperature $T_0$, one may write $\delta \Omega$ in (20) as

$$\delta \Omega(t) = \Lambda_0 \beta T(t),$$  

where $\beta = \alpha_T/n_\Omega + \alpha_L$ is the thermo-optic coefficient and $\alpha_L$ is the linear thermal expansion coefficient of the fibre. In the literature, the values $\alpha_T \approx 1 \times 10^{-5} \text{K}^{-1}$ and $\alpha_L \approx 0.5 \times 10^{-6} \text{K}^{-1}$ are found (see e.g. [23, 24] and references therein).

#### 5.4.1. Temperature drift

As the first illustration of the effect of temperature, we consider the following situation: the temperature profile is uniform over the length of the fibre, but there is a linear temperature drift in time, such that $\delta T(t) = \gamma t$. Inserting this $\delta T(t)$ into (21) and the result in turn into (20), one finds the time variation of the transmitted signal to be

$$J(t) \propto \frac{1}{1 + F \sin(2\pi \Lambda_0 + 2\pi \nu_D t)^2},$$  

where $\nu_D = \nu_L \Omega_0 \beta \gamma/\nu_0$. This result can be interpreted as follows: when changing the optical path length continuously, the transmission maxima keep shifting across the laser frequency $\nu_L$ (recall figure 8). Thus, the transmitted signal oscillates (an example of such data is shown in [24]). The amplitude of the oscillations spans the full modulation depth, according to the
finesse coefficient $F$. The period $T_D$ of the oscillation is

$$T_D = \frac{1}{2\nu_D} = \frac{c_0}{2\nu_\lambda \Omega_0 \beta \gamma}.$$  \hfill (23)

With plausible numbers: laser frequency $\nu_\lambda = 4.74 \times 10^{14}$ Hz corresponding to HeNe, $\lambda_\lambda = 633$ nm, optical path length $\Omega_0 = n_\lambda L = 2.9$ m ($n_\lambda = 1.45$, fibre length 2 m), $\beta = 10^{-5}$ K$^{-1}$ and a moderate temperature drift $\gamma = 0.4$ K, a signal oscillation period of approximately 100 s is calculated. Note that such slow oscillations are likely to remain undetected when analysing the signal fluctuations with a correlator, especially when employing symmetric normalization!

5.4.2. Small fluctuations. The assumption of a uniform temperature profile along the fibre is not very realistic. In the second example, we allow for space–time temperature fluctuations along the length of the fibre. However, we assume that these fluctuations are small, such that $\delta \Lambda \ll 1$ (namely (20)). Then, it is sufficient to expand $J(t)$ up to the first order in $\delta \Lambda$, which yields the normalized signal fluctuations as

$$\frac{\delta J(t)}{J_0} = F 2\pi \delta \Lambda(t) f,$$  \hfill (24)

where

$$f = \frac{2 \sin(2\pi \Lambda_0) \cos(2\pi \Lambda_0)}{1 + F \sin(2\pi \Lambda_0)^2}.$$  \hfill (25)

Note that through the factor $f$ the magnitude of signal fluctuations depends on the position of the laser frequency $\nu_\lambda$ with respect to the extrema of the transmission curve. At a maximum or minimum, the first-order fluctuations are negligible. Within the small fluctuation approximation, the signal correlation function is proportional to the correlation function of the optical path length:

$$\frac{\langle \delta J(t) \delta J(t + \tau) \rangle}{J_0^2} = g_\delta(\tau) = (f F 2\pi)^2 \langle \delta \Lambda(t) \delta \Lambda(t + \tau) \rangle.$$  \hfill (26)

For simplicity, we neglect thermal expansion of the fibre length and consider only the fluctuations of the refractive index. Recalling (15) we write $\delta \Lambda(t)$ as

$$\delta \Lambda(t) = \frac{1}{\lambda_\lambda} \int \limits_0^L ds \delta n(s, t).$$  \hfill (27)

Thus, we obtain

$$\langle \delta \Lambda(t) \delta \Lambda(t + \tau) \rangle = \frac{1}{\lambda_\lambda^2} \int \limits_0^{L'} ds' \int \limits_0^L ds \langle \delta n(s, t) \delta n(s', t + \tau) \rangle.$$  \hfill (28)

The fluctuations $\delta n(s, t)$ of the refractive index reflect the distributed temperature fluctuations $\delta T(s, 0)$, i.e. $\delta n(s, t) = \alpha T \delta T(s, t)$ (recall (21)). Thus, we write

$$\langle \delta \Lambda(t) \delta \Lambda(t + \tau) \rangle = \frac{\alpha^2}{\lambda_\lambda^2} \int \limits_0^{L'} ds' \int \limits_0^L ds \langle \delta T(s, t) \delta T(s', t + \tau) \rangle.$$  \hfill (29)

As usual, we assume statistical homogeneity so that the correlation function depends only on $|\sigma|$ (where $\sigma = s' - s$) and $|\tau|$. Assuming further that the correlation length $\sigma_C$ is much
shorter than the length of the fibre, we obtain
\[ \int_0^{L'} ds' \int_0^L ds \left\langle \delta T(s, t) \delta T(s', t + \tau) \right\rangle = L \int_{-\infty}^{+\infty} d\sigma \left\langle \delta T(0, 0) \delta T(\sigma, \tau) \right\rangle. \quad (30) \]

Rigorous modelling of the space–time correlation function would be rather difficult, but a good insight can be obtained by simple physical plausibility arguments. Like any correlation function, \( \left\langle \delta T(0, 0) \delta T(\sigma, \tau) \right\rangle \) can be expressed in the following form:
\[ \left\langle \delta T(0, 0) \delta T(\sigma, \tau) \right\rangle = \left\langle \delta T^2 \right\rangle g(\tau, \sigma, \tau_c, \sigma_c). \quad (31) \]

Here \( \langle \delta T^2 \rangle \) is the temperature variance and \( g \) is a normalized space–time correlation profile such that \( g(0, 0) = 1 \). The most important parameters of \( g \) are the correlation length \( \sigma_C \) and the correlation time \( \tau_C \). A plausible definition of \( \sigma_C \) is
\[ \int_{-\infty}^{+\infty} d\sigma g(\tau, \sigma) = 2\sigma_C g'(\tau; \tau_c), \quad (32) \]
where \( g'(0) = 1 \). With this definition, the correlation function of the signal reads as
\[ g_\delta(\tau) = (f F 2\pi)^2 2\alpha_T^2 \frac{L\sigma_C}{\lambda L} \langle \delta T^2 \rangle g'(\tau; \tau_c). \quad (33) \]

This result is quite plausible: the shorter the correlation length \( \sigma_C \), the better the averaging of the local temperature fluctuations and therefore the smaller the resulting signal variance. We cannot provide a model for the time course of the temperature correlation function \( g'(\tau; \tau_c) \), but the correlation time \( \tau_c \) is easily accessible in an experiment. This correlation time is the result of the complex dynamics of thermal energy transfer between the fibre and its surroundings and within the fibre, along its length. Since the fibre core is more or less insulated by various protecting layers, the exchange of energy with the surroundings can be expected to be relatively slow. The dominant effect is the diffusion of temperature along the fibre. The correlation time \( \tau_c \) is the time the thermal disturbance takes to diffuse over a certain characteristic length. The only characteristic length along the fibre is the correlation length \( \sigma_C \). Thus, we write
\[ \sigma_C^2 = 2\tau_C D_T, \quad (34) \]
where \( D_T = \kappa / \rho c_p \) is the thermal diffusivity (\( \kappa \) is the thermal conductivity of the material, \( \rho \) the mass density and \( c_p \) the specific heat capacity). Inserting the observed correlation time \( \tau_C \approx 2 \) s and the material properties of fused silica (\( \kappa = 1.38 \text{ W m}^{-1} \text{ K}^{-1} \), \( c_p = 703 \text{ J kg}^{-1} \text{ K}^{-1} \) and \( \rho = 2200 \text{ kg m}^{-3} \)) one obtains a correlation length \( \rho C \approx 0.002 \) m.

We are now in a position to estimate the temperature fluctuations required for explaining the observed root mean square (rms) signal fluctuations of about 2%. Inserting our typical values (\( \lambda_L = 633 \text{ nm} \), \( L = 2 \) m and \( \alpha_T = 10^{-5} \), finesse coefficient \( F = 0.15 \)) and the worst case \( f \approx 1 \), one finds that local rms temperature fluctuations as small as 0.01 K are sufficient to induce signal fluctuations of about 2%. Therefore, this seems to be the most likely origin of our experimentally observed spurious correlation function.

5.5. Fundamental thermodynamic fluctuations

Last but not least, we have to check for the role of fundamental thermodynamic fluctuations in generating the spurious correlation function.

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As was already pointed out, thermal fluctuations are present even when the temperature of a thermostating bath is kept perfectly constant. Such fluctuations are certainly small and therefore we can use the first-order expansion. According to statistical thermodynamics [25], the variance of the fundamental temperature fluctuations in a volume of interest $V$ is given by

$$\langle \delta T^2 \rangle = \frac{k_B T^2}{\rho c_p V}. \quad (35)$$

Here $\rho$ is the mass density and $c_p$ the specific heat capacity of the material. In this case, the ‘volume of interest’ is a tiny cylinder whose radius corresponds roughly to the fibre mode-field radius $\varpi_0$ (this is where light propagates and thus where the fluctuations matter) and whose length is $2\sigma_C$ (outside $\sigma_C$ the fluctuations are uncorrelated): $V = 2\pi \varpi_0^2 \sigma_C$. Inserting this $V$ into (35) and then $\langle \delta T^2 \rangle$ into (33), we obtain the normalized correlation function of signal fluctuations due to fundamental thermal fluctuations as

$$g_s(\tau) = f^2 F^2 \cdot 4\pi \frac{Lk_B T^2 \varpi_0^2}{\lambda_1^2 \sigma_0^2 \rho c_p} g'(\tau; \tau_C) \quad (36)$$

(note that $\sigma_C$ cancels out). A more rigorous expression, including the time correlation $g'(\tau)$, can be deduced from [26] by Wanser (see also [27]). The signal variance $g_s(0)$ turns out to be practically identical to our plausibility result. However, inserting our typical values, one finds that at a given fibre length the fundamental temperature fluctuations would be much too small when compared with the effect of thermal disturbances discussed in section 5.4.

5.6. Removal of spurious contributions

Most likely, the noise correlation signal results from a combination of temperature fluctuations and drifts on various time and length scales, from which the correlator processing selects a certain time range. A rigorous analysis would require more experimental data obtained in a well-controlled thermal environment. For avoiding vibrations mechanical insulation has been used in our experiment (TS300, TableStable Company, Switzerland), but thorough control of the polarization state would also be needed for reliable data.

For minimizing the signal fluctuations, the first measure would be to minimize the reflections on the fibre ends. Further, one could use some kind of mode scrambling to average the fluctuations.

Since reducing the reflections at the fibre ends by introducing fibre ends cut by $8^\circ$ together with appropriate coupling optics is not sufficient for suppressing this spurious contribution, we used a commercial solution from ALV Company, Langen, Germany, as the mode scrambler—the so-called Static and Dynamic Enhancer. This mode scrambler consists of a combination of single- and multi-mode fibres. After splitting the signal with a single-mode fibre splitter, two multimode fibres are attached with an index matching fluid to suppress reflections from the end of the single-mode fibre and thus lower the Fabry–Perot effect considerably. The modes of the light from the direct signal and those from the spurious signal are scrambled in the multimode fibre, further diminishing the Fabry–Perot effect. We succeeded in minimizing the above effects to below the observation threshold (figure 7), i.e. from a contrast of $10^{-4}$ to below $10^{-5}$. 

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6. Conclusions

The influence of a solid interface on the dynamics of colloidal suspensions has been shown for particle radius ranging from $R_{bh} = 11 \text{ nm}$ to $R_{bh} = 204 \text{ nm}$ using REDLS at a penetration depth of 200 nm.

In the case of the smaller particles, the correlation function measured near the interface is similar in shape to the one measured in bulk. For particles with $R_{bh} > 40 \text{ nm}$, the correlation function loses the distinct single exponential shape and the decay rate slows down additionally. The surface-induced hindered and anisotropic motion of particles with $R_{bh} = 204 \text{ nm}$ has been recorded by scattering angle-dependent measurement and compared to the measurement for $R_{bh} = 31 \text{ nm}$. In contrast to the smaller particles the bigger ones match hydrodynamic theory qualitatively.

Since the penetration depth of the evanescent wave can only be adjusted by changing the wavelength of the laser, measurements were carried out at a penetration depth of 200 nm. It should be mentioned that it is possible to tune the range of the evanescent field that probes the dynamics of the interface by using the optical field of two coupled SP modes propagating along a very thin metal layer in contact with the dielectric media of (nearly) identical refractive index. The long-range SP mode can extend the range of the probing electromagnetic field to micrometers, while the short-range SP can be utilized to reduce the exponential decay of the evanescent wave to a range of a few tens of nanometres. Measurements are in progress.

In DLS using single-mode fibre detection, an additional signal appears that is particularly disturbing in the heterodyne detection mode. This signal can be suppressed to below the noise level with the Static and Dynamic Enhancer. It has been deduced that the signal originates from temperature fluctuations.

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