Improved diffusing wave spectroscopy based on the automatized determination of the optical transport and absorption mean free path

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Diffusing wave spectroscopy (DWS) can be employed as an optical rheology tool with numerous applications for studying the structure, dynamics and linear viscoelastic properties of complex fluids, foams, glasses and gels. To carry out DWS measurements, one first needs to quantify the static optical properties of the sample under investigation, i.e. the transport mean free path $l$ and the absorption length $l_a$. In the absence of absorption this can be done by comparing the diffuse optical transmission to a calibration sample whose $l$ is known. Performing this comparison however is cumbersome, time consuming, and prone to mistakes by the operator. Moreover, already weak absorption can lead to significant errors. In this paper, we demonstrate the implementation of an automatized approach, based on which the DWS measurement procedure can be simplified significantly. By comparison with a comprehensive set of calibration measurements we cover the entire parameter space relating measured count rates $(CR_i, CR_o)$ to $(l, l_a)$. Based on this approach we can determine $l$ and $l_a$ of an unknown sample accurately thus making the additional measurement of a calibration sample obsolete. We illustrate the use of this approach by monitoring the coarsening of a commercially available shaving foam with DWS.

Keywords: diffusing wave spectroscopy, microrheology, linear viscoelasticity, light scattering

1. Introduction

Diffusing wave spectroscopy (DWS) is a modern optical technique derived from dynamic light scattering (DLS), allowing the measurements of thermally driven dynamics in strongly scattering media (Maret and Wolf, 1987; Pine et al., 1988; Pine et al., 1990). One of the most significant advantages of this technique is that it allows the measurement of the dynamics over a large range of time scales (10^{-7} to 10 s) and at much shorter length scales (down to \sim 1 nm) than traditional single light scattering experiments (Scheffold and Schurtenberger, 2003; Weitz and Pine, 1993; Zhu et al., 1992). Moreover, DWS can be used to perform non-invasive microrheology, extracting rheological properties on the micron scale without making actual contact to the sample (Furst and Squires, 2017; Mason and Weitz, 1995; Waigh, 2016). Since it was developed in the late 1980’s, DWS has been widely used in the study of soft matter, such as colloidal suspensions, microgels, emulsions, foams, and biological media (Lee et al., 2013; Li et al., 2005; Palmer et al., 1999; Scheffold, 2002; Scheffold et al., 2010).

Since the samples studied with DWS are turbid, one needs to calculate the intensity autocorrelation function of the multiple scattered light. This can be done by considering the diffuse propagation of photons along paths of different lengths $s$. Each path length $s$ contributes to the intensity correlation function in a defined way and its weight is determined by the path length distribution. It has been shown that, for a given cuvette size and geometry, the path length distribution only depends on the transport mean free path $l$ of the sample and the absorption length $l_a$ (Pine et al., 1988). Using the diffusion equation to model the transport of light in an opaque medium, analytic expressions for the DWS intensity correlation function in dependence of $(l, l_a)$ and of the thermally driven colloidal dynamics can be obtained. For the case of bead motion in a viscous or viscoelastic matrix the internal dynamics is given by the particle mean square displacement (MSD) $\langle \Delta \vec{X}^2(t) \rangle$ (Weitz and Pine, 1993). Therefore, to extract the dynamic properties of the sample, one first needs to quantify the static, ensemble averaged optical properties $(l, l_a)$ of the sample. Since the dynamics of the target sample is not known, this is normally done by comparing the optical properties of the sample with another sample whose $l$ is either known, can be calculated or most often can be measured. For example, with the commercial DWS-RheoLab instrument (LS Instruments, Switzerland), an extra sample denoted the ‘calibration standard’ has to be measured prior to the actual measurement of interest. This calibration standard must have similar turbidity (i.e. similar $l$) as the target sample and its dynamics must be known. Typically,
for monodisperse particles with known diameter $2R$ dispersed in water $\langle \Delta F(t) \rangle = 6D_{g}$ where $D_{g}$ is the known Brownian diffusion coefficient of the particles. Currently, the instrument first measures $I'$ of the calibration standard by fitting the correlation function. Then comparing the transmission count rate of the two samples, the instrument then can determine $I'$ for the target sample, with an accuracy of approximately 5-10\% [Technical note, LS Instruments].

However, in some cases, the target sample could be absorbing at the incident laser wavelength. For this case, additional knowledge about the sample absorption length $l_{a}$ is required to extract e.g. the MSD. Until now it was not possible to determine the absorption length $l_{a}$ with the commercial instrument and therefore the rheological properties of absorbing, or colored, samples could not be accurately characterized.

In this paper, we implement an automatized calibration of the DWS measurement procedure. With this approach, we can determine not only the transport mean free path $l'$ directly but also the absorption length $l_{a}$ of the sample, by simply measuring the photon count rate of both the light scattered in transmission and backscattering geometry. In this way, the calibration step as well as the preparation of the calibration standard will be no longer needed. This allows us to perform DWS experiments more conveniently and extend the range of application of quantitative DWS and DWS microrheology to absorbing samples, as long as $l_{a} >> l'$.

2. Methods

The photon count rate of light in the transmission $C_{t}$ and backscattering geometry $C_{b}$ are easily measurable. Here we denote with $C_{t} = C_{t} \ast VH + C_{t} \ast VH$ the sum of the count rates measured independently for the polarization preserving ($VH$) and the cross polarized ($VH$) detection channel. Therefore, if we can derive an unambiguous mathematical relation between ($C_{t}$, $C_{b}$) and ($l'$, $l_{a}$), we will be able to quantify $l'$ and $l_{a}$ by simply measuring the photon count rates. Numerically we expect this approach to work even if this relationship is very complicated for a specific experimental configuration (finite cuvette width, residual surface reflectivity and so on).

We begin by summarizing again the most important concepts governing light transport and intensity fluctuations and correlations in the frame of DWS which can be obtained by summing over the contribution from all photons arriving at the detector via different optical paths. Denoting $P(s)$ as the probability that the photon follows the path $s$ in the absence of absorption, we can write the field correlation function with absorption as (Weitz and Pine, 1993)

$$g_{s}(t) = \frac{1}{C} \int_{0}^{\infty} P(s) e^{-\frac{s}{\tau}} e^{-2\sigma/\nu_{0} \nu_{s} i} \, ds$$

(1)

where $\tau = 1/k_{0}^{2}D_{g}$ is the characteristic decay time and $C$ is the normalizing constant. For simplicity, we consider Brownian motion but the same equations apply more generally to other dynamic processes such as bubble rearrangements in foams or tracer bead motion in a viscoelastic medium, for the latter $\tau/t$ is simply replaced by $k_{0}^{2} \langle \Delta F(t) \rangle / 6$, where $k_{0} = 2\pi n/\lambda$ (laser wavelength $\lambda$) denotes the wavenumber in the scattering medium with a refractive index $n$.

The field correlation function $g_{t}(t)$ is obtained from the measured intensity correlation function $g_{a}(t)$ in the common way using the Siegert relation $g_{a}(t) = 1 + \beta g_{t}(t)$. The instrument specific coherence factor $\beta \sim 0.9$ is obtained experimentally by extrapolation $t \rightarrow 0$.

The first exponential term in Eq. (1) describes the photon loss due to possible absorption, and the second exponential sums up the decay of correlation due to multiple interactions with scattering particles. Both terms are weighted by the probability that the light follows a path of length $s$. It has been shown that if the incident laser beam is expanded to fill the full surface of the sample (flat cell geometry, thickness $L$), we can write the correlation function in transmission as (Weitz and Pine, 1993)

$$g_{t}(t) = \frac{1}{C_{t}} \left( \frac{L/l'}{1 + 4/3 \sinh (L/l')} + \frac{2/3 \cosh (2z_{0}/l')}{} \right)$$

(2)

and for the backscattering direction as

$$g_{b}(t) = \frac{1}{C_{b}} \left( \frac{\sinh (L/l')}{1 + 4/3 \sinh (L/l')} + \frac{2/3 \cosh (2z_{0}/l')}{} \right)$$

(3)

where $C_{t}$, $C_{b}$ are the normalizing constants which ensure $g_{t}(t = 0) = 1$, and $z_{0}$ describes the distance inside the sample where the light propagation can be considered as diffusive. The latter can be roughly estimated as $z_{0} \approx l'$. In these equations, $\Delta = (6\tau/\tau + 3\tau/l_{a})^{1/2}$ denotes the sum of the particle displacements and the absorption contribution. The normalizing constants $C_{t}$, $C_{b}$ are related to the transmission and backscattering count rate as discussed later in the text. For an ideal, non-absorbing sample, i.e. $l_{a} \rightarrow \infty$, always $C_{t}$, $C_{b} = 1$.

Next, we treat the transmission case explicitly. The backscattering case can be derived in the same way. Since DWS only can be applied in the diffusive limit $L > l'$, the measured transmission count rate recorded at some scattering angle, not too far from the normal, is proportional to the total transmission $T$ (total transmitted flux). We denote the transmission rate of an ideal non-absorbing sample as $T_{ideal}$ ($l'$). When some absorption is present (quantified by the absorption length $l_{a}$), the transmission coefficient of this sample then can be written as