1.3 Diffusing-Wave Spectroscopy

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This section focuses on recent work on *temporal* fluctuations of the intensity of multiply scattered light which are caused by motion of the scatterers. While parts of the underlying physics had already been discussed in 1983/84 [85, 86], dynamic multiple scattering of light was introduced by the work on calibrated colloidal latex particles in aqueous suspensions [29, 30, 87], and has since rapidly evolved into a powerful technique called "diffusing-wave spectroscopy" (DWS).

1.3.1 Basic Physics

The principle and mathematical treatment of DWS can be found in various reviews (e.g. [74, 88]). We therefore just briefly summarize the physics. Coherent light waves (of, say, an incident monomode laser beam) travel inside the sample along various random scattering paths described by a photon random walk, and set up at the detector a highly irregular intensity pattern called "speckle" as a result of interference between many waves from many paths of various lengths. As in conventional dynamic single scattering, the intensity in a given speckle spot fluctuates when the scatterers move with respect to each other. Since the transit time of photons along a typical multiple-scattering path is much shorter than the time τ_0 it takes a colloidal particle to move a distance of order of the optical wavelength $\lambda_0 = 2\pi/k_0$ ($\tau_0 = 1/Dk_0^2$ for Brownian motion with diffusion coefficient D), the problem is treated in a quasi-stationary approximation. The time-dependent phase shifts $\varphi(t)$ of the scattered optical fields due to motion of the scatterers accumulate along the paths, giving rise to speckle fluctuations on a path-length-dependent timescale. Consequently, under conditions of strong multiple scattering, this timescale is much faster than τ_0. Unlike single scattering, the timescale does not depend on the angle of observation, but rather on the geometry of the scattering cell, which controls the typical path length and its distribution. The seemingly complicated calculation of measurable quantities such as the frequency spectrum or the time autocorrelation function of the scattered intensity becomes, in fact, rather straightforward in the photon diffusion picture. This is seen in the important autocorrelation function of the scattered field [29], $G_1(\mathbf{r}, t) = \langle E(\mathbf{r}, t_0) E^*(\mathbf{r}, t_0 + t) \rangle$, which can be put into a normalized form $g_1(t)$:

$$g_1(t) = \int_{\ell^*}^{\infty} P(s)\, \mathrm{e}^{-(s/\ell^*)\langle \delta\varphi^2(t)\rangle} \mathrm{d}s \,/ \int_{\ell^*}^{\infty} P(s)\, \mathrm{d}s\,, \tag{1.15}$$

where $\langle \delta\varphi^2(t) \rangle$ is the mean square phase shift per scattering event and $P(s)$ is a quantity – the path-length distribution – depending on sample geometry,

size and transport mean free path ℓ^*, describing how much light intensity is scattered on average into paths of length s. For independent Brownian motion of the scatterers with mean square displacement $\langle \delta r^2(t) \rangle$, we infer that $\langle \delta \varphi^2(t) \rangle = k_o^2 \langle \delta r^2(t) \rangle \approx D k_o^2 t$. Explicit formulas for $P(s)$ and hence $g_1(t)$ have been worked out for various geometries, such as backscattering and transmission from slabs, pairs of optical fibers dipping into a turbid sample, and others, and (1.15) has successfully been tested experimentally on well-characterized colloidal suspensions (e.g. [74, 88]).

Another useful description of the correlation function $G_1(t)$ is related to the solution of the steady-state diffusion equation [89]. In the case of negligible absorption, this equation can be written as

$$\left[-\nabla^2 + k^2(t)\right] G_1(\mathbf{r}, t) = \frac{S(\mathbf{r})}{D_p}, \tag{1.16}$$

where $k^2(t)$ describes the attenuation of temporal fluctuations with time, $D_p = v_E \ell^*/3$ is the photon diffusion constant and $S(\mathbf{r})$ is the light-source distribution. In the case of pure Brownian motion, as described previously, $k^2(t) = 3t/(2\tau_o \ell^{*2})$. This type of analysis can be generalized to the situation of a Poiseuille flow of scatterers, which is simply changing the t dependence of $k^2(t)$.

1.3.2 Specificity of Diffusing-Wave Spectroscopy

DWS has tremendously stimulated the use of light scattering in many fields, in particular in the physics and chemistry of colloids and other complex fluids. *First*, it provides – without the need for index matching – quantitative information about particle displacements $\langle \delta r^2(t) \rangle$ up to concentrations well into the regime of high-order multiple scattering. It works best when single and low-order scattering are negligible and therefore ideally complements other recent techniques such as two-color cross-correlation spectroscopy [90] and single-mode fiber-optic dynamic light scattering [91–93], which essentially suppress the multiple scattered light but still require measurable amounts of single-scattering intensity. DWS is therefore well suited to study interparticle correlations in colloidal suspensions at very high volume fractions and the dynamics of densely packed systems such as concentrated emulsions, foams etc. The *second* important feature of DWS is its extraordinary sensitivity to small displacements of scatterers. In contrast to single scattering of light, which probes fluctuations on length scales larger than $\lambda/2$, displacements as small as $\lambda/1000$ (or even less, in principle) can be monitored with DWS. The probed length scale is easily controlled experimentally by means of the typical path length, i.e. the maximum of $P(s)$, which is set by the sample size and shape and the distance between the injection and detection points of the light. The examples below highlight fluctuations measurable at length scales down to about 0.1 nm, which puts DWS in competition with X-ray and neutron scattering, but covering timescales from tens of nanoseconds to hundreds of

seconds. *Third*, DWS experiments on other types of motion, such as shear or oscillatory flow, demonstrate the possibility to characterize flow fields and measure velocity gradients over the experimentally adjustable length scale ℓ^*. *Fourth*, because of the high sensitivity to motion of the scatterers, DWS can detect very small numbers of particles undergoing motion with respect to their surroundings, making it possible to image or localize them even well below the surface of the sample, and to detect sporadic, rare dynamic events. *Last* but not least, DWS is easier to implement experimentally than dynamic single scattering of light because of the intrinsically high scattered intensities and the rather weak sensitivity to misalignment and definition of scattering angle, beam size and polarization.

DWS experiments [94–96] on the short-time crossover from ballistic to Brownian motion of colloidal spheres have clearly revealed a long-time tail in the velocity autocorrelation function and a scaling of its characteristic timescale with the high-frequency shear viscosity of the solution up to high volume fractions, due to hydrodynamic interactions.

DWS is sensitive to relative motions of scatterers other than Brownian motion, as first illustrated by $g_1(t)$ measurements on latex suspensions under Poiseuille flow [97]. If the particle's displacements $\delta\mathbf{r}_i$ are completely correlated because of a deterministic motion as in convective flow, the relevant phase shift $\delta\varphi$ due to two successive scattering events (i) and $(i+1)$ in the expression (1.15) for $g_1(t)$ is $\mathbf{k}_i \cdot (\delta\mathbf{r}_i - \delta\mathbf{r}_{i+1})$. Since $\delta\mathbf{r}_i = \mathbf{v}_i \times t$, it immediately follows that a homogeneous velocity field $\mathbf{v}_i = \text{const.}$ does not generate any temporal speckle fluctuations. Inhomogeneous velocities, however, cause phase fluctuations, thereby generating a decay of $g_1(t)$. The phase fluctuations are given by the velocity difference over the length ℓ^*, since consecutive random scattering events have on average a separation ℓ^*. For homogeneous shear at a rate Γ one again finds the familiar expression (1.15) for $g_1(t)$, the mean square phase shift per scattering event now being $\langle\delta\varphi^2\rangle \approx (\Gamma\ell^* k_0 t)^2$. The t^2 dependence of $\langle\delta\varphi^2\rangle$ – as opposed to the linear t dependence for Brownian motion – is the signature of the deterministic nature of the shear motion. For inhomogeneous shear gradients, such as in Poiseuille flow or plug flow, the decay of $g_1(t)$ becomes somewhat different since the cloud of diffusing photons does not scan the different regions of the flow field with equal weight [98]. Experiments comparing planar flow, Poiseuille flow and Couette flow [99] clearly demonstrate this and are in quantitative agreement with theory. It is thus possible to distinguish between different types of flow and to determine shear gradients in totally turbid liquids by dynamic multiple scattering of light. The Couette flow experiments have been extended to higher shear gradients well into the regime of hydrodynamic instabilities [99]. Beyond a critical shear rate, a characteristic convective roll pattern ("Taylor rolls") appears. The associated additional shear is clearly seen in $g_1(t)$, and scanning the position of a tightly focused incident beam allows one to visualize the otherwise invisible rolls through the position dependence of the characteristic

relaxation rate $\Gamma \ell^* k_o$. These experiments are readily extended to turbulent flow, opening the possibility of scale-dependent measurements of $\langle \Gamma^2 \rangle$ [100].

Small longitudinal relative displacements of the particles can also be detected with the help of DWS. This is illustrated by DWS measurements of the variance of the AC electrophoretic mobility in electrorheological fluids [101], and of ultrasound-generated sinusoidal modulation of particle positions, from which the ultrasound amplitude could be estimated optically in solid or liquid multiple-scattering media [102].

1.3.3 Foams and Liquid Crystals

Foams belong to a class of materials with structural features and optical properties very different from those of dense colloidal suspensions, despite their overall "white" appearance in many cases. Dense collections of (air) bubbles are separated by more or less organized soap films and hence the multiple scattering of light cannot be described by scattering from large spheres, but rather should be modeled by multiple reflections from more or less random surfaces. The coarsening and aging of foams have been studied experimentally since 1991 [103, 104], describing the overall slow dynamics as a stochastic sequence of bubble rearrangement events, which are easily detected by the large extension of the diffuse photon cloud, despite the rare occurrence of rearrangements.

Single scattering of light from macroscopically oriented nematic liquid crystals is well understood and is treated in many textbooks. It arises from collective orientation fluctuations of molecules with anisotropic optical polarizability $\delta\epsilon/\epsilon \neq 0$. The statics and dynamics of these fluctuations are described in a continuum-elastic model involving several elastic constants (K) and viscosities (η). In the one-elastic-constant approximation, the amplitude of the light scattered at wave vector q is proportional to $(\delta\epsilon/\epsilon)^2 k_o^4 kT/(Kq^2)$, where kT has the usual meaning. The corresponding relaxation time is $(Kq^2/\eta)^{-1}$, very similar to that of Brownian motion, $(Dq^2)^{-1}$, with a "rotational diffusion constant" $K/\eta \equiv D$. Both scattering amplitude and relaxation time diverge for long wavelengths ($q \to 0$), as it does not cost elastic energy to perform a rotation at $q = 0$. In practice this divergence is avoided by a large-scale cutoff given by the sample size or by a finite electric or magnetic field.

Samples of macroscopically oriented nematic liquid crystals look turbid, although much less so than non-oriented samples. The multiple scattering from unoriented samples has not been studied in detail so far, and thus we focus on dynamic multiple scattering of light studied in [79–84]. In the above model, the low-q divergence of the static structure factor results in a *vanishing* scattering mean free path ℓ, while the transport mean free path ℓ^* stays finite. The photon diffusion constant becomes anisotropic and the orientationally averaged value of ℓ^* is of order $(\delta\epsilon/\epsilon)^2\ K/(kTk_o^2)$ [79–84]. On scales beyond ℓ^* we therefore recover an anisotropic photon diffusion

picture (see Sect. 1.4.3), and for not too large an anisotropy $\delta\epsilon/\epsilon$ the dynamic correlation function $g_1(t)$ can be written in a form very similar to (1.15).

1.3.4 Imaging with Diffusing-Wave Spectroscopy

Recent years have seen substantial progress in optical imaging "beyond the transport mean free path" (see e.g. [105] and references therein). Various techniques, such as interferometric detection of the weak unscattered coherent beam, time-resolved selection of early-arriving almost-unscattered photons, and measurements of photon density waves and diffuse photon intensities, have been applied in order to locate and eventually image objects which are buried several optical transport mean free paths deep inside the medium. In these techniques the optical contrast of the object with respect to the turbid medium is due to enhanced transparency or enhanced absorption, both of which modify the spatial distribution of the diffuse light intensity. The object basically acts as a source or a sink for diffusing photons, and therefore generates a glow or shadow respectively on the sample surface. The glow or shadow is less in amplitude but larger in size for deeply buried objects than for objects near the surface, because of the diffusive spread of photons from the object to the surface. This allows one to localize the object. The spatial resolution degrades roughly linearly with the distance of the object from the surface [106].

The DWS principle can also be used to image or locate objects which have *dynamic* contrast because of some motion with respect to the surrounding medium. While in this case the average scattered intensity does not necessarily depend on the position at the sample surface, the temporal fluctuations of it – as seen in $g_1(t)$ – do. This idea was suggested by work on speckle tomography [107], which pointed out the fact that if scatterers are moved even a small distance, the corresponding changes of the speckle pattern are most pronounced in the surface region closest to these scatterers. Boas et al. [89, 108] have reported images of a spherical cavity containing a colloidal suspension in Brownian motion (with $\ell^* = 1.5$ mm), located 0.75 diameters below the surface of a solid multiple-scattering medium (with $\ell^* = 2.2$ mm). In this case, there was contrast both in the scattering and in the dynamics. Heckmeier et al. [109–112] have performed experiments on objects having different types of purely dynamic contrast (i.e. identical ℓ^* values inside and outside the object). Position-dependent $g_1(t)$ measurements [109] from a capillary containing a flowing colloidal suspension embedded in the same suspension undergoing Brownian motion revealed that the flow rate, depth and in-plane location of the object can be obtained and $g_1(t)$ is in excellent agreement with simple photon diffusion theory [110]. The dynamic contrast has a maximum for a well-defined correlation time t. This is because $g_1(t)$ at very short times is dominated by Brownian motion (which is of course identical inside and outside the object) as compared to flow, while at very long times only scattering paths too short to sense the embedded object contribute to $g_1(t)$.

It is also possible to obtain dynamic contrast between Brownian particles having different sizes [110]. In the particularly sensitive situation in which the $g_1(t)$ measurement was made on a dark spot of the static speckle of a solid background medium containing a dynamic inclusion undergoing Brownian motion or flow, objects could be located as deep as five diameters and more than $30\ell^*$ inside the medium [111]. Finally, the probability distribution of the scattered intensity sampled at long times, rather than the full time dependence of $g_1(t)$, can be used for imaging purposes [112].

1.3.5 Perspectives

The above principles are expected to turn out useful in many applications, in particular in biomedical sciences. This may be illustrated by a recent experiment [208] on superficial burns of animal tissues, where indications about the depth of burn could be obtained from the analysis of the temporal decay of $g_1(t)$; the superficially burned layer of tissue behaves like a solid, while the nonburned tissue below generates time-dependent speckle fluctuations due to blood flow.

Diffusing-wave spectroscopy has become a very useful tool to probe dynamical properties of multiple-scattering media of various kinds. Studies on calibrated colloidal suspensions have borne out its potential to investigate fundamental problems in the physics of fluids, as illustrated for instance by the observation [94–96] of the short-time motion of spherical particles governed by hydrodynamic interactions. Many novel contributions of DWS to diverse problems in statistical physics are expected, primarily because of the wide range of time and distance scales covered. The quantitative understanding of DWS allows one to tackle more complex systems now. Foams, sand, liquid crystals, emulsions and polymer gels doped with scattering particles have been mentioned briefly, and many more applications are foreseen, particularly important perhaps for the quality control of food, cosmetics and paints. Multiple-scattering imaging and remote sensing of buried objects in motion may evolve into a versatile tool of particular interest in medical applications, given the relatively low optical extinction of biological tissue in the near infrared and the possibility to select particular objects spectroscopically. Examples include blood vessels, coagulates and dye-stained tumors. Such applications will be complementary to and, with the availability of low-cost sources and detectors of light, substantially cheaper than current NMR or X-ray imaging techniques.

1.4 Coherent Beam, Diffuse Beam and Speckles: A New View

Studies in the last 10 years have substantially modified the old picture of multiple scattering of light. The most dramatic revolution was undoubtedly

in 1985 when the first experimental reports of coherent backscattering came in. This phenomenon is now successfully explained in terms of constructive interference between two waves propagating in opposite directions. New phenomena have also been found for the coherent beam and the speckles.

1.4.1 Diffuse Beam: Coherent Backscattering and Localization

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On the basis of reciprocity, interference between two opposite paths can be argued to be constructive in the backscattering direction of, for instance, a slab geometry, and *exactly* as large as the conventional diffuse background calculated from (1.8). At backscattering, the equation of radiative transfer is thus 100 % wrong! As always, the width of an interference effect is roughly given by the wavelength divided by the typical distance between two typical points of scattering, in this case the mean free path, giving $\Delta\theta \approx 1/k\ell$ [113]. One can still argue as to what mean free path should be used here: the transport or the scattering mean free path. Although a physical argument favors the first (recall Fig. 1.2), a rigorous confirmation for anisotropic scatterers (for which both mean free paths differ) has only been given recently [114, 115]. Thus

$$\Delta\theta \approx \frac{1}{k\ell^*} . \tag{1.17}$$

The smallness of $1/k\ell^*$ in typical experiments probably explains why the serendipitous discovery of coherent backscattering was unlikely (Fig. 1.4).

Coherent backscattering has been investigated in a variety of circumstances. The general reciprocity relation that can be written down between the transition matrix (relating the incoming and outgoing electric fields of the light) of any event, D, and that for the same event in the opposite sequence, R, placed in a magnetic field $\mathbf{B}_0$, is [22]

$$D(\sigma, \mathbf{k} \to \sigma', \mathbf{k}' \,|\, \mathbf{B}_0) = R(\sigma', \mathbf{k}' \to \sigma, \mathbf{k} \,|\, -\mathbf{B}_0) , \tag{1.18}$$

where σ ($= \pm$) indicates the two possible states of circular polarization. In the absence of a magnetic field one can verify that $D(\sigma, \mathbf{k} \to \sigma, -\mathbf{k}) = R(\sigma', \mathbf{k} \to \sigma, -\mathbf{k})$. This means that for the diagonal channel $\sigma = \sigma'$ the inverse scattering sequence has the same scattering amplitude as, and therefore interferes constructively with, its opposite partner. More precisely,

$$|R + D|^2 = |R|^2 + |D|^2 + 2 \text{ Re } RD^* = 2(|R|^2 + |D|^2)$$

at backscattering. This argument leads to the famous and apparently universal factor of two for the diagonal polarization channel. Absorption is allowed and therefore does not change this conclusion. Reciprocity does not inform us about the off-diagonal helicity channel. Experiments [116] and calculations [117–119] give a value of only 1.12 for this channel.