Universal wave phenomena in multiple scattering media

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In this chapter, we introduce a new approach for measuring both the transport and the effective medium properties of light propagation in inhomogeneous media. These properties include the diffusion constant, the path length distribution, and the derivative of the effective index of refraction with respect to the changes in the density of the host medium. This method utilizes the equivalence of frequency variation to a change in the index of refraction, which was derived in chapter 2. Experimentally, we measure the correlations in the speckle via spectrally resolved refractive index tuning (RIT), controlling the latter via changes in the ambient pressure. This new generic measurement technique can be used to characterize a wide variety of materials, including photonic crystals, random photonic media, photonic meta-materials, and certain porous biological samples like bone and wood. In this chapter, we report some proof-of-principle measurements on well-characterized samples to show the precision of the RIT method [44].

Optical properties of quenched random samples are dominated by speckle, a highly irregular intensity pattern dependent upon spatial (or angular) or time (or frequency) coordinates caused by interference. Correlations, which are inherent properties of speckle despite the apparent irregularity, provide important information about transport parameters. In fact, the description of intensity correlations is at the heart of understanding transport theory [49]. In the past, correlations have been measured in time [24] and frequency [55] as a means of, for example, determining the diffusion constant of light.

What is often overlooked is the degree to which effective medium properties are essential for determining correlation functions, and thereby transport properties. Indeed, the importance of the effective medium, in some sense, exceeds that of the transport properties as the latter only becomes important when the material is turbid. Furthermore, as we have seen in developing a theory of transport in chapter 2, the effective medium is used as a building block. That is to say, the diffusion constant of light depends on the average index of refraction but not the other way around.

In this chapter, we make use of the symmetry between changes in refractive index
and frequency variation that was explained in section 2.2. This symmetry allows us to perform “dynamic” measurements without using sophisticated time-resolved experiments or a pulsed light source, which is often much more costly than a monochromatic CW laser. By tuning the effective index and measuring intensity-intensity correlations, we show that a variety of transport properties of the sample can be measured in an entirely new way. Furthermore, by combining measurements of refractive index correlations with frequency correlations, the applicability of effective medium assumption is directly tested. This type of effective medium measurement is unprecedented, in that it is not affected by surface irregularities, does not require a coherently transmitted beam, and can be measured for any irregular sample shape. This new technique allows for transport properties to be determined without resorting to gross approximations for the effective medium. Given the importance of understanding disorder in a wide variety of fields including biology [57], advanced materials [120], solar cells [100], and in general modern photonics, we expect from our approach to find broad and cross-disciplinary applications.

Our method is based on controlled change of the optical path length distribution by refractive index tuning (RIT). It is the optical analogue of a class of experiments in condensed matter physics that control the elongation of electron trajectories by using a magnetic field. Those electronic experiments resulted in the observation of electronic weak localization and universal conductance fluctuations [18]. Due to its simplicity and high precision, RIT measurements can be applied to a diverse set of rigid samples, which cannot be analyzed by other dynamic methods due to the limitation of time (or frequency) resolution. The concept of changing the optical path length distribution has also been exploited for diffusing wave spectroscopy [85, 104], and for other types of waves in evolving media [77, 80, 121].

6.1 Theoretical principles

We assume a multiple scattering medium with quenched disorder. Previously, we have seen that in the diffusion approximation, the amplitude Green function, the amplitude correlator, and the intensity propagator only depend on the product $n_e \omega$. That is to say changing the frequency by $\Delta \omega$ is equivalent to changing $n_e$ by $\Delta n_e$ if $n_e \Delta \omega = \omega \Delta n_e$. This symmetry relation sets the basis for all the experiments in this chapter. It holds in a regime where

$$\frac{\Delta \text{Im} K}{\Delta \text{Re} K} \sim \frac{1}{4\pi} \left( \frac{\lambda_e}{\ell_s} \right)^2 \left| \frac{\Delta \ell_s}{\Delta \lambda_e} \right| \ll 1,$$

(6.1)

where $K$ is the effective wavenumber for the average amplitude Green function, introduced in section 2.1.3.

By using this symmetry, we can generalize the results for the frequency correlation function, $\Delta n_e = 0$, to our case of variable refractive index. In this chapter, we will use this correlation for the slab geometry [55].

To take one example, relevant to our measurements, consider a slab of porous material, for which the host refractive index, $n_h$, may be tuned. The correlation is then measured as a function of $n_h$ instead of $n_e$. In this case, $C^{(1)}_{\omega,\omega}(n_h, n_h + \Delta n_h)$ is given by:

$$C^{(1)}_{\omega,\omega}(n_h, n_h + \Delta n_h) = \frac{\tau_\delta \Delta n_h}{\cosh \sqrt{\tau_\delta \Delta n_h} - \cos \sqrt{\tau_\delta \Delta n_h}},$$

(6.2)

with RIT decay coefficient (generalized analogue of diffuse decay time)

$$\tau_\delta \equiv \frac{2\omega \delta L^2}{D}.$$

(6.3)
6.2 Samples

For proving the principles of RIT technique, we have chosen samples that can be characterized by both RIT and conventional time-resolved measurements, allowing us to validate the accuracy of this technique. We consider a composite porous system with open channels consisting of a solid backbone and a gaseous host. The refractive indices of the solid backbone and the gaseous host medium are $n_s$ and $n_h$ respectively. In our measurements the index of the host, $n_h$, is tuned by increasing the pressure of the gas.

**Porous polystyrene filters**

The first measurements are performed on slabs of commercially available porous plastic air-filters (XS-7744, Porex Corp.) with various thicknesses. They are composed of sintered polyethylene spheres with a broad size distribution of 7 to 12 $\mu$m. The refractive index of the polyethylene is $n_s = 1.49$. This material has a porosity of $\phi = 0.46 \pm 0.02$ and a mean free path of $\ell_s = 20.6 \pm 0.2 \mu$m in the frequency range of interest. The porosity was determined by weighing a larger sample of the same material. The mean free path was determined from total transmission measurements. The result for the transport mean free path is $\ell_s = 20.6 \pm 0.2 \mu$m in the frequency range of interest. The reported values are measured with an accuracy of $\pm 0.2 \mu$m.

Here, we have introduced the tuning response $\delta$, as

$$\delta \equiv \frac{1}{n_e} \frac{\partial n_e}{\partial n_h}. \quad (6.4)$$

The tuning response relates the change of $n_e$, a more or less theoretical concept, to the changes in $n_h$ which can be easily experimentally controlled. We have accurately measured $\delta$ as will be shown later in this section. Knowing the accurate value of $\delta$ enables us to extract the diffusion constant by measuring the RIT correlation function $C_{\omega,\omega}^{(1)}(n_h, n_h + \Delta n_h)$. The tuning response $\delta$ is an important effective medium parameter, since it can be measured even for opaque samples with large optical thicknesses and unconventional geometries. Such samples pose a formidable and often insurmountable challenge for the more conventional measurements of effective refractive index.

Figure 6.1: The mean free path as a function of light frequency measured for a 1-mm thick layer of porous polystyrene filter using a total transmission setup. The reported values are measured with an accuracy of $\pm 0.2 \mu$m.
Refractive index tuning

Figure 6.2: Optical characterization of opal photonic crystals. The dots show the scattering parameter \( k \ell \) as a function of frequency. The dashed line is the specular reflection at normal incidence and the dotted line is the total transmission of light impinging at normal incidence, which is measured by using an integrating sphere. The gray shaded area indicates the stop band.

path is shown in Fig. 6.1. These measurements reveal a negligible (max 2%) variation of \( \ell \) in the frequency span, justifying the assumption in Eq. (6.1).

Self-assembled photonic crystals

We have also performed RIT measurements on a set of photonic crystal samples. These crystals are made of polystyrene colloidal spheres of 300 nm diameter (Duke Scientific) using the method of vertical controlled drying [61]. The grown crystal shows a stop-band in transmission of the visible frequencies, which puts restriction on the use of effective medium description for the average index of refraction. By using these measurements we can quantify the validity of an effective medium model experimentally determine the tuning response dispersion for such a resonant photonic environment.

The optical behavior of these crystals is characterized by reflection and transmission measurements. A thickness of 10 µm was measured using an optical microscope. The scattering strength is measured for this sample by using a white-light enhanced backscattering setup [99]. The summary of these results is shown in Fig. 6.2. The stop-band is clearly visible in the reflection measurements. This stop-band occurs around the incident wavelength of 667 nm. Interpretation of the fluctuation in scattering parameter at the band edges is a very interesting topic on its own but it is beyond the scope of this chapter. The refractive index of bulk polystyrene is \( n_s = 1.59 \pm 0.02 \) in visible and near infrared frequencies.

6.3 Setup and measurements

The sample was kept in a pressurized chamber and illuminate by a HeNe laser at 632.8 nm. Part of the transmitted speckle pattern was filtered by a linear polarizer and recorded on a 16-bit CCD-camera with \( 10^6 \) pixels. This setup is schematically drawn in Fig. 6.3(a) The recorded image consisted of roughly \( 10^4 \) independent coherence areas. Gradually tuning the air pressure in the chamber changes \( n_h \), causing the speckle pattern to evolve. By monitoring the sequence of images, we can directly measure the autocorrelation coefficient of the evolving intensity pattern.
Figure 6.3: (a) The experimental setup. The sample is placed in a pressurized chamber and illuminated by a HeNe laser. A single polarization of the transmitted speckle is recorded by a CCD-camera. (b) RIT autocorrelation coefficient as a function of $\Delta n_h$. Data points show measurement results for 3 slabs of polyethylene filters ($L = 1, 1.5, \text{and } 2 \text{ mm for black squares, red circles, and blue triangles, consequently}$). The lines show the fit to theory (Eq. (6.2)).

The first experiment was performed on three samples. The extracted correlation coefficients are plotted in Fig. 6.3(b) versus $\Delta n_h$. Each data series is fitted to the correlation function of Eq. (6.2) with a separate single fitting parameter, $\tau_\delta$. We see an excellent agreement between the theory and the experimental results. The optical path length distribution can be extracted from these measurements by applying a Fourier transform [56]. Remarkably, the sensitivity to the change of refractive index, demonstrated in Fig. 6.3(b), is close to some of the state-of-art refractive index sensors [144].

6.4 Results and discussion

6.4.1 Diffusion constant of porous plastic

Having measured the RIT decay coefficient $\tau_\delta$ it is possible to extract the diffusion constant. This requires the value of tuning response $\delta$. We present a precise method of measuring $\delta$, which also makes use of the symmetry relation in the Green’s function discussed earlier in this chapter. This symmetry implies that $C_{\omega, \omega+\Delta \omega}(n_e, n_e + \Delta n_e)$ has a peak equal to one for a nonzero shift $\Delta \omega$ given by

$$\frac{\Delta \omega}{\omega} = \frac{\Delta n_e}{n_e}.$$  

In other words, $\delta$ can be extracted from the spectral shift of every individual speckle spot while the host index of refraction $n_h$ is varied.

To monitor this spectral shift the experimental setup was slightly altered. The light source was replaced by a white-light super-continuum laser (Fianium). The CCD-camera was replaced by a spectrometer, which was run in the imaging mode. The entrance slit of the spectrometer selects a transmission direction in form of a narrow rectangle, which contains roughly 10 independent coherence areas along the slit. The beam is spectrally resolved perpendicular to the slit direction by a grating. This configuration allows us to simultaneously monitor the spectral evolution of several speckle spots while $n_h$ is changed.
Refractive index tuning

Figure 6.4: Measured relative change of $n_e$ as a function of $\Delta n_h$. The value of $\Delta n_e/n_e$ is extracted by measuring this spectral shift. The refractive index of air is calculated based on the Edlen formula \[39\]. Inset: The shifted cross-correlation coefficient $C$ versus the spectral shift $\Delta \nu$ for certain pressures (From right to left: $\Delta P = 0.0, 0.075, 0.18, 0.28, 0.37, \text{ and } 0.46$ bar). The peak position of each curve denotes the spectral shift, which is proportional to the relative change in the effective refractive index. The spiky feature at zero position is an artifact of the slight inhomogeneity over the detection efficiency of CCD pixels.

The measurement was performed on a 100-$\mu$m-thick slice of the polyethylene filter. The selected thickness was optimized for the resolution of our monochromator. The intensity spectrum between 649 and 651 nm was measured while changing the pressure in the chamber from 1 to 1.5 bar in steps of 10 mbar.

RIT correlation functions at different frequencies are calculated from the measurements and plotted as a function of $\Delta \omega$ for each pressure. A collection of these plots is shown for six different pressures in the inset of Fig. 6.4 as typical representatives. As predicted, the peak value is shifted and equals unity within the experimental error. The peak position, measured by fitting a parabola to the top of each curve, denotes the overall spectral shift. Using our symmetry relation (6.5), the relative change of effective refractive index is calculated and plotted as a function of $\Delta n_h$ in Fig. 6.4. We get a value of $\delta = 0.212 \pm 0.003$ from the slope of a linear fit to the data, for these set of samples, with a remarkably high precision.

In principle, it is possible to extract the diffusion constant from each separate RIT measurement. To improve the accuracy, we plot the auxiliary parameter $a \equiv 4\pi\nu\delta/\tau_3$ versus $L^{-2}$ from the three measurements presented in Fig. 6.3. This plot is shown in Fig. 6.6. The slope gives the diffusion constant $D = 2.2 \pm 0.1$ m$^2$/ms using Eq. (6.3).

6.4.2 Comparison with the time-resolved method

To prove the quantitative exactness of our method, we compare our result for the diffusion constant with the result of conventional time-resolved measurements. The diffuse transmission through the same samples was recorded using a time-correlated photon counting setup and a subpicosecond pulsed laser at 600 nm wavelength. The resulting temporal decay curves are presented in Fig. 6.5. Following the guidelines of Ref. [67] and considering the response function of the detector, the diffuse decay time $\tau_d \equiv L^2/\pi^2D$ is extracted from a fit to these measurements. The diffusion constant is calculated from the slope of a linear fit of the parameter $b \equiv 1/\pi\tau_d$, vs. $L^{-2}$, shown in Fig. 6.6, resulting in $D = 2.1 \pm 0.1$ m$^2$/ms, This result is in excellent agreement with the value obtained from the index tuning experi-
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Figure 6.5: Time resolved intensity decay curve for slabs of polyethylene filters. Different datasets correspond to different sample thicknesses ($L = 1, 1.5$, and $2$ mm for black squares, red circles, and blue triangles, respectively). The lines show the fit to the diffusion model after considering the absorption and the response of the detector.

ment. The high precision of this agreement is an important confirmation of the concept of effective wavenumber in random media. This concept has never been examined so directly in strongly scattering media, simply because it was a very difficult parameter to access experimentally.

Figure 6.6: The measurement parameters $a \equiv \frac{4 \pi \nu \delta}{\tau \delta}$ and $b \equiv \frac{1}{\pi \tau \delta}$ are plotted versus the inverse of the thickness squared. Black squares and red dots correspond to the index tuning and time-resolved measurements respectively. The slope of each data set is equal to the diffusion constant $D$ measured by each specific method. The fact that the two slopes are equal proves the consistency of our index tuning method with the time resolved measurements.

6.4.3 Tuning response of a photonic crystal

RIT enables us to monitor the behavior of tuning response as a function of frequency. This measurement is especially interesting if there medium has a resonance behavior like a photonic crystal. For this measurement we divide the frequency spectrum to narrow bands of 5 nm wide. For a finer frequency resolution, thicker samples must be used.

By recording the spectrum of a narrow transmission angle and monitoring its shift while changing the pressure inside the chamber, we can measure the tuning response. Measuring
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Figure 6.7: (a) The tuning response of the opal photonic crystal as a function of wavelength. The dashed line is the specular reflection at normal incidence and shows the position of the stop band. (b) The (average) diffusion constant as calculated from the frequency correlation in the spectrum of a narrow transmission channel.

does not consider the dispersion in a photonic crystal fail in describing its effective refractive index. The RIT method for measuring $\delta$ is applicable to a variety of samples, and assumes no specific effective medium model. Such a property can be a perfect check for the accuracy of numerical simulations when applied to complex photonic structures such as metamaterials or photonic crystals. The parameter $\delta$ can also be predicted using theories of the effective medium [22, 23, 117] which are all based on long-wavelength limits. This comparison is further discussed in the following section.

6.5 A test for effective-medium theories

In this section results from different effective medium theories are reviewed. The tuning parameter $\delta$ is calculated for the same sample that was investigated earlier in this chapter using three of the models. The predictions are compared the result of the RIT measurement. Before showing this comparison, we briefly mention the idea behind these models.

Geometric ray picture

In this model the refractive indices are linearly averaged, weighted by the volume filling fraction of each component. This method is used in most of the hand-waving estimated [61]. In specific, it was used by Zhang and Sheng [117] for describing scalar-wave localization.

$$n_e = \phi n_s + (1 - \phi)n_h,$$  \hspace{1cm} (6.6)

$$\delta = 1 - \phi.$$ \hspace{1cm} (6.7)

Scalar long-wavelength limit

This model is similar to the geometric picture except for averaging permittivities in place of refractive indices. It was used by Vos et al. for describing photonic crystals and derived
by Busch and Soukoulis from coherent potential approximation. To derive refractive index
derivatives from dielectric constant derivatives one should note:

\[ n_e = \sqrt{\varepsilon_e}, \quad n_h = \sqrt{\varepsilon_h}, \quad n_s = \sqrt{\varepsilon_s}, \quad (6.8) \]

\[ \delta \equiv \frac{\partial n_e}{\partial n_h} = \frac{n_h}{n_e} \frac{\partial \varepsilon_e}{\partial \varepsilon_h}, \quad (6.9) \]

This model averages the dielectric constants according to the volume fraction.

\[ \varepsilon_e = \phi \varepsilon_s + (1 - \phi) \varepsilon_h, \quad (6.10) \]

\[ \delta = \frac{n_h}{n_e} (1 - \phi). \quad (6.11) \]

**Maxwell-Garnett dielectric function**

The Maxwell-Garnett formula is perhaps the most widely used estimate for the effective
refractive index in colloidal suspensions. It is given by

\[ \varepsilon_e = \varepsilon_h \left[ 1 + \frac{\phi \beta (\varepsilon_s - \varepsilon_h)}{1 - \phi + \phi \beta} \right], \quad (6.12) \]

Where \( \beta \) is a function of the shape and orientation distribution of the scatterers. This
theory assumes low volume fraction of the solid part. Therefore, we calculate \( \delta \) only up to
the first order in \( \phi \).

\[ \delta = \frac{n_h}{n_e} \left( 1 + \left[ (n_s^2 - 2 n_h^2) \beta + \frac{n_h}{2} (n_s^2 - n_h^2) \frac{\partial \beta}{\partial n_h} \right] \phi \right). \quad (6.13) \]

**Bruggeman dielectric function**

This model was suggested by Bruggeman to correct for the asymmetry of the Maxwell-
Garnett formula with respect interchanging the host medium and the inclusion. However,
it is still a phenomenological model, and is not fully justified apart from the Rayleigh
scattering regime. It suggests

\[ \phi \frac{\varepsilon_s - \varepsilon_e}{\varepsilon_s + 2\varepsilon_e} + (1 - \phi) \frac{\varepsilon_h - \varepsilon_e}{\varepsilon_h + 2\varepsilon_e} = 0. \quad (6.14) \]

The explicit formulae for the tuning response in this model is rather lengthy, but it can be
easily estimated for a specific choice of refractive indices and filling fractions. An extensive
discussion on the applicability of conventional models can be found in the book by Bohren
and Huffman [22].

For illustrative purposes, we present the predicted value for \( n_e \) and \( \delta \) by three of the
more popular effective medium theories: (i) the average permittivity, (ii) the Maxwell-
Garnett and (iii) the Bruggeman models. The predictions for our porous plastic samples
are \( n_e = 1.29 \pm 0.02, \quad 1.25 \pm 0.02, \quad \) and \( 1.22 \pm 0.02 \) and \( \delta = 0.28 \pm 0.02, \quad 0.45 \pm 0.03, \quad \) and
\( 0.52 \pm 0.03 \) respectively. These predictions for \( \delta \) differ from each other and from our ex-
perimental result by as much as a factor of two. It is also worth noting that the predicted
value of \( \delta \) is more model-dependent than \( n_e \) itself. The main reason for this discrepancy
is perhaps the assumption of the long wavelength limit, which does not hold in our exper-
imental conditions. Our unambiguous measurement of \( \delta \) highlights the necessity of more
sophisticated models of the effective medium [23]. For such models, which are usually based
on numerical simulations, the tuning response parameter serves as a very sensitive test.
6.6 Further applications

Apart from the fundamental insight, the concept of RIT is also useful for gas sensing or other daily life applications. Correlation function (6.2) decays exponentially with $\Delta n_h$ and can also serve as a very sensitive probe of the refractive index changes in the ambient medium.

**Refractive index sensor**

For the 2-mm sample, a change of $10^{-6}$ in the refractive index of air results in 3% reduction in the autocorrelation coefficient, which is easily detectable. Most of refractive index sensing methods are based on resonances and their shifts (see [144] for a recent review). The sensitivity demonstrated in this paper is already close to the state-of-art surface-plasmon-resonance sensors while the instrumentation for our method is much simpler. However, the present work is by no means showing a limit for the sensitivity of our method, since it can be easily enhanced using thicker slabs (the sensitivity increases quadratically with the sample thickness). For higher sensitivities, technical details such as the stability of the light source and thermal isolation of the sample must be considered. These details were not optimized for the current proof-of-principle experiments. Another downside of our method is the rather large detection volume needed for a reasonable sensitivity. This disadvantage can be overcome by using larger index contrasts and shorter wavelengths, which is readily available in plasmonic sensors.

**Evolution detection in turbid media**

Measuring correlations of multiple-scattered waves in evolving media has shown a wide range of application in different branches such as rheology, geophysics and medicine [77, 80, 85, 104, 121]. Adding RIT to the arsenal of optical characterization techniques for turbid media, broadens the choice of samples that can be investigated. As a low-cost and portable measurement, RIT can perhaps reduce the cost of analysis in comparison with the existing spectroscopic methods in diffuse media.

6.7 Conclusions

In conclusion, we have presented a new effective medium quantity and a new transport correlation function and shown how to precisely measure both of them by using refractive index tuning. Our measurements directly test and approve the validity of assuming an effective wavenumber for an inhomogeneous medium, which is very important for describing all sorts of photonic metamaterials. Using these two quantities one can measure several dynamic transport properties with high precision, as we have demonstrated for the lowest order $C^{(1)}$-correlations and the diffusion constant. Measuring higher order correlations and studying Anderson localization is a natural follow-up to our research.