Observation of Resonant Behavior in the Energy Velocity of Diffused Light

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In this Letter we demonstrate Mie resonances mediated transport of light in randomly arranged, monodisperse dielectric spheres packed at high filling fractions. By means of both static and dynamic optical experiments we show resonant behavior in the key transport parameters and, in particular, we find that the energy transport velocity, which is lower than the group velocity, also displays a resonant behavior.

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Disordered optical media, like random collections of microspheres, are opaque and usually white. That is, they are usually only mildly dispersive and their optical properties do not depend strongly on wavelength [1]. A single dielectric microsphere can support, however, electromagnetic resonances, called Mie modes [2], and thereby act as a microresonator, with both long dwell times, and high Q values (up to 10^{10} [3]). This can have an enormous impact on the velocity of light in random systems. Transport of light in random dielectric systems is described correctly neither by the group velocity nor by the phase velocity. It has recently been shown that the correct velocity in that case is a so-called energy velocity (v_E) [4,5], given by the ratio of the energy flux to the energy density, which takes into account possibly very strong delay by resonant scattering.

The energy velocity can be drastically reduced in the presence of scattering resonances in cold atom clouds, where the atomic level structure can exhibit such a strong resonance that the energy velocity can be as low as few thousands of meters per second ($v_E/c \sim 10^{-5}$) [6]. Mie resonances are strongly morphology dependent [7] and can be smeared out by a size or shape distribution of the spheres. Initial single scattering experiments on Mie resonances have been performed in ZnS sphere suspensions, pointing out a variation of the optical constants with frequency, the finer structure not being fully resolved because of the polydispersity (~10%–20%) [8]. Recent investigations on the transport velocity have also sought indications of resonant behavior in solid samples of TiO_2 particles; however, the polydispersity (~20%) and irregular particles shape did not allow for conclusive results [9].

Theoretical predictions on the expected effect in realistic samples have been contradictory. While the original theory was developed for modest particle densities [10], successive models based on a mean field approach predicted the effect to disappear at high packing fractions as encountered in solid samples [11]. Therefore, both approaches are developed in different scattering regimes and cannot be expected to give exact results for intermediate filling fractions. This led to discussion in the literature over the existence of the resonances [12,13]. Furthermore, two experiments have been performed with different results: at microwave frequencies [14,15] weak resonances were found at low densities that disappeared at packing fractions (ϕ) approaching $\phi \simeq 60\%$, whereas in the acoustic domain [16] resonant behavior was found at $\phi \simeq 63\%$, albeit for an inverse geometry (analogous to low dielectric scatterers in a high dielectric background).

In this Letter we report on the observation of resonances in all the key transport parameters in random systems of highly monodisperse spheres. We have performed both static and dynamic measurements and can determine from these the wavelength dependence of the energy velocity of light with high accuracy. We find clear proof of resonances in the transport velocity. These resonances are observed even at high packing fractions. We also find that the typical polydispersity of solid TiO_2 samples does not allow to observe the resonances.

Our samples consist of a collection of highly monodisperse (2% diameter dispersion) spheres that are arranged in a random way to form a solid sample. To that end, a deposition method was developed that avoids the natural arrangement of such spheres in a periodic photonic crystal type structure [17]. We have dubbed this material *photonic glass*. This material is random, and the spheres composing it are optically connected, yet it exhibits strongly resonant behavior as we will see below. Slabs were grown of about 1 cm in width and with varying thickness between 50 μm to 1.6 mm, as presented in Fig. 1. The great advantage of these samples is that they are made of polystyrene (PS) spheres in air, and therefore the refractive index contrast is much higher than in a colloidal suspension. Complete randomness is ensured by ballistic transmission and reflection measurements, which present no trace of photonic band gaps, and by autocorrelation analysis of the SEM pictures, which show no long-range positional correlations [17].

Light transport in a photonic glass is diffusive, $k\ell_t \simeq$ 20–25, where k is the light wave vector and ℓ_t the transport

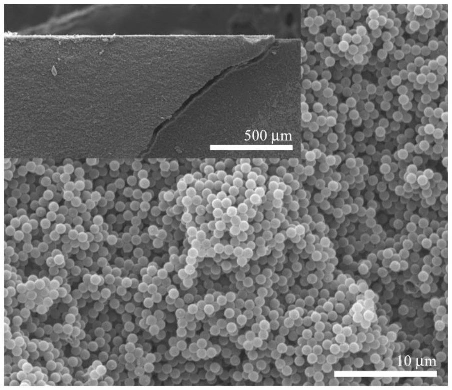

FIG. 1. SEM images of a photonic glass made of PS spheres embedded in air, whose refractive index n is 1.58. The diameter of the spheres is 1220 nm with a polydispersity of 2%, as measured from transmission electronic microscopy. The diameter value has been independently confirmed via an optical measurement of the spectral features of an opal made from these spheres.

mean free path, the average distance after which light propagation is fully randomized. Therefore, here we use a diffusive model to analyze static and dynamic measurements. ℓ_t is the length that enters in the diffusion constant, together with v_E [4]:

$$\mathcal{D} = \tfrac{1}{3} v_E \ell_t. \tag{1}$$

The total transmission of a photonic glass, as a function of wavelength, $T(\lambda)$, can be measured via an integrating sphere technique. Figure 2 shows the result of the measurements, for different sphere diameters (d). This is a simple and direct evidence of collective Mie resonances in the static transport of light. Many resonances are visible, and the peak separation is clearly related to the ratio of the sphere optical diameter (dn) to the light wavelength. As a reference, we show the same measurement on a polydisperse TiO_2 particles sample (polydispersity ~36%) with an average particle size of 850 nm, which does not show any resonant features because of a combination of random particle shape and polydispersity. We have also tested a photonic glass made of spheres of 200 nm diameter (see inset of Fig. 2) that are too small to sustain resonances in the visible range, and that indeed show a featureless transmission.

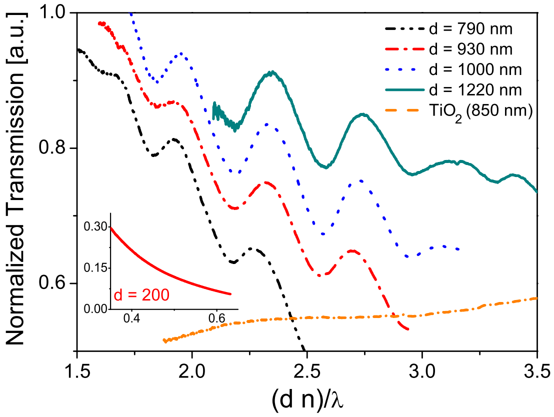

FIG. 2 (color online). Normalized total transmission as a function of the reduced parameter $(dn)/\lambda$ for four different PS sphere diameters and for one reference sample of polydisperse TiO_2 of average $d = 850$ nm. In the inset, the total transmission for $d = 200$ nm, which does not show any resonance. All samples have thickness of around 100 μm.

By solving the diffusion equation, the transport time and space light distribution can be calculated. The total *static* transmission from a slab of random scattering material as a function of the sample thickness L can be expressed by the so-called *photonic* Ohm's law [14]:

$$\begin{aligned} T(L, \lambda) &= \frac{1}{\alpha z_e} \frac{\sinh[\alpha(z_p + z_e)]\sinh(\alpha z_e)}{\sinh[\alpha(L + 2z_e)]} \\ z_e &= \frac{1}{2\alpha} \ln\left[\frac{1 + \alpha z_0}{1 - \alpha z_0}\right] \qquad z_0 = \frac{2}{3}\ell_t(\lambda)\left(\frac{1 + R}{1 - R}\right), \end{aligned} \tag{2}$$

where $\alpha = 1/\ell_i$ is the inverse absorption length, z_e the extrapolation length, which is the position where the diffusive mode is zero, and z_p the penetration length, the position of the effective source for the diffusion equation. These two latter lengths are typically set to be identical ($z_p = z_e$), and for no absorption they are equal to z_0. Care is taken to include the proper reflectivity (R) in the boundary conditions ($R \simeq 0.39$ for $\langle n \rangle / n_{\rm air} = 1.29$, $n = 1.58$, and $\phi = 55\%$) [18].

In the absence of absorption, resonances in the total transmission are directly resonances in ℓ_t. We have measured the transmission spectra of 25 photonic glasses, of different thicknesses (50 μm $< L <$ 1.6 mm), and sphere diameter of 1220 nm. For each λ, a fit of the transmission curve $T(L)$ from Eq. (2) gives $\ell_t(\lambda)$ and $\ell_a(\lambda)$, the scattering and absorption lengths, respectively. These two lengths are not independent as $\ell_a = \sqrt{\ell_t \ell_i / 3}$, where ℓ_i is the ballistic (or inelastic) absorption length. In our samples the effect of absorption is negligible as $\ell_a \sim 1.8$ mm and $\ell_i \sim 10$ m, apart from a small absorption peak that we attribute to water, around 876 nm, for which $\ell_a \sim 0.36$ mm and $\ell_i \sim 0.42$ m. In Fig. 3, we compare the experimental and theoretical (based on Mie theory) resonances of $\ell_t(\lambda)$. The accordance with the theory is qualitative, both in shape and magnitude due to the neighbor coupling of the modes in different spheres, which is neglected in the independent-scattering approximation of the model [10]. Because of the high confinement of the field inside the sphere, this interaction is weak, resulting in a mode shift of around 5%–10%.

The diffusion constant $\mathcal{D}(\lambda)$ is a *dynamical* quantity and therefore can be probed directly with a measurement of the spread in time, $T(t)$, of a short pulse crossing the sample. The time profile of the transmitted light is measured with a streak camera, while the pulses are provided by a Ti:Al_2O_3 laser (2 ps pulse duration), tunable within 700–920 nm.

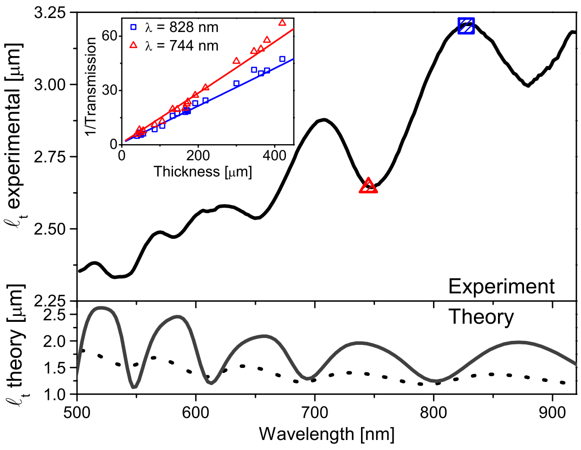

FIG. 3 (color online). Comparison of experimental and theoretical transport mean free path in a photonic glass made of 1220 nm spheres of polystyrene. The dotted line in the lower panel is Mie theory, while the full line includes the structure factor for close-packed hard spheres [23]. In the inset $T^{-1}(L)$ and its best fit for 828 and 744 nm, corresponding to a minimum [$\ell_t(744) = 2.64\ \mu$m] and a maximum of the transport mean free path [$\ell_t(828) = 3.22\ \mu$m], are shown.

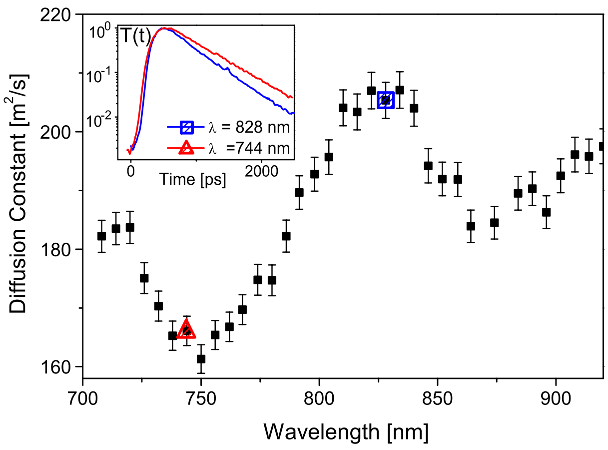

FIG. 4 (color online). Diffusion constant for different laser frequencies. The error bars are obtained from the statistics of repeated fits, while the frequency precision is smaller than the symbol size. In the inset a profile of $T(t)$ is shown for two wavelengths, 744 and 828 nm, in the position of a minimum [$\mathcal{D}(744) = 166$ m^2/s] and a maximum of the diffusion constant [$\mathcal{D}(828) = 205$ m^2/s].

For long times, the pulse spread is exponential with a time constant given by $\tau(\lambda) = (L + 2z_e)^2/\pi^2\mathcal{D}(\lambda)$ (in the absence of absorption), while the full solution at all times (for δ-function light source) is [19]:

$$T(t,\lambda) = \frac{I_0 \exp(-t/\tau_i)}{4t[4\pi t\mathcal{D}(\lambda)]^{3/2}}\left\{\sum_{j=-\infty}^{+\infty} A\exp[-A^2/4\mathcal{D}(\lambda)t] - \sum_{j=-\infty}^{+\infty} B\exp[-B^2/4\mathcal{D}(\lambda)t]\right\}, \qquad (3)$$

where $A = (1 - 2j)(L + 2z_e) - 2(z_p + \ell_t)$ and $B = (2j + 1)(L + 2z_e)$. The absorption length turns into an absorption time (τ_i), which is $\tau_i = \ell_a^2/\mathcal{D} \simeq 10$–$12$ ns [20] everywhere except on the absorption peak at 876 nm, where it is $\simeq 1.5$ ns. The independent measurement of ℓ_a, obtained from the Ohm's law, is essential to compensate for this absorption peak and extract correct values of $\mathcal{D}$ in the wavelength range 700–920 nm. We have fitted the time profile $T(t)$ with Eq. (3) including both the proper boundary conditions [18], the convolution with the response of the detection system (of 20 ps), and the value of $\ell_a(\lambda)$ calculated from the fit to Ohm's law. Figure 4 shows the obtained diffusion constant whose resonances are precisely at the same position as in the independent measurement of ℓ_t.

From Eq. (1), the value of v_E can be computed from the simple relation $v_E = 3\mathcal{D}/\ell_t$. The result is plotted in Fig. 5. The energy velocity is below the average value of the group velocity obtained from the sample average refractive index $v_g = c/\langle n\rangle \simeq 0.77c$, and it shows clear resonances. Here, v_g is used only for comparison, as in a disordered system there is no translational symmetry, the k vector is not well defined, and, hence, neither is the phase nor group velocity. Qualitatively, the minima of $\ell_t(\lambda)$, for which the scattering strength is maximum, correspond to wavelengths that excite a Mie mode, and therefore experience a longer dwell time. This turns into a minimum transport velocity (Fig. 5). For comparison, we show at the bottom of the top panel of Fig. 5 the lack of velocity dispersion of a TiO$_2$ powder sample measured in the same experimental conditions. For ideal micrometer spheres, the single-particle resonances are 10%–20% wide in wavelength, and therefore they are expected to be washed out for polydispersity

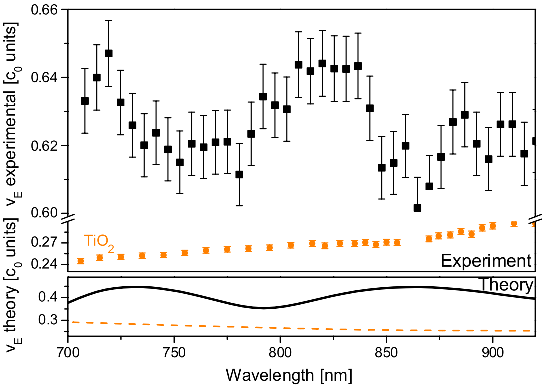

FIG. 5 (color online). The energy velocity is plotted as a function of the wavelength, for a photonic glass of sphere diameter $d = 1220$ nm. A full oscillation of around 5% amplitude is visible. The average medium group velocity is $0.77c$. At the bottom of the top panel the flat velocity dispersion of a TiO$_2$ powder is shown, obtained with the same procedure. The lower panel shows the prediction [10] for ideal spheres (full line) and 15% polydisperse TiO$_2$ spheres (dashed line).

$>5\%$–10% (see the lower dashed curve in the bottom panel of Fig. 5). Recently, Storzer *et al.* [9] have reported a wavelength dependent diffusion constant in 15%–20% polydisperse, irregularly shaped titania powders, which in the light of our findings is unlikely to be the result of Mie resonances. The importance of the morphology of the sphere is evident, as a considerable size distribution or a random shape of the dielectric resonator is, no doubt, expected to wash out the resonant properties [7,21].

Mie theory is a single scattering theory that assumes independent scatterers. This implies, in particular, that dielectric spheres are not optically connected [22]; therefore, we used it only as a qualitative test. We believe that the deviation from the single-particle theory is mainly related to the coupling of the modes of connected spheres (dependent scattering) and the consequential collective optical excitations. Additionally and lastly, since the spheres are touching, a minor short-range correlation is induced as at least one other sphere is always one diameter away [17], but this is minor and has been taken into account including the structure factor for close-packed hard spheres (see Fig. 3) [23]. It is interesting to see that at a packing fraction of as much as 55%, one is still able to resolve the effect of Mie resonances in the transport mean free path and transport velocity. It can be an enticing challenge to look further into the physics behind the resonant behavior of light transport in disordered media, especially at high packing density and closer to the Anderson localization regime.

In conclusion, with independent dynamical and static measurements, we have observed resonant transport of light through solid, random, and resonant media. We find an energy velocity that is lower than the group velocity and shows clear resonances. We find the existence of resonances as predicted by low density theory [4,5], but with different fine details, which reveal the need for an improved theoretical description, able to account for high filling fractions. Photonic glasses are disordered, opaque, but also dispersive. This latter property is relevant for a spectral control of light diffusion. Resonant amorphous dielectrics could be exploited for a mode selection mechanism in random lasing, as well as for more practical coloring applications, based on interference rather than on pigmentation.

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