Speed of Propagation of Classical Waves in Strongly Scattering Media

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We present results of optical experiments which demonstrate that in a strongly scattering medium containing resonant scatterers the velocity for electromagnetic energy may differ by an order of magnitude from the phase velocity. We derive a microscopic theory that yields an expression for this velocity. Discrepancies are removed, and excellent agreement is found between experiment and theory.

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The interest in multiple scattering of waves has undergone a tremendous revival.[1] New investigations of multiple scattering of classical waves were undertaken in both the visible and microwave[2] regions of the electromagnetic spectrum and in acoustic[3,4] systems, under conditions where multiple scattering is dominant and where diffusion theory may be used as a starting point. Crucial parameters are the diffusion coefficient D and the mean free path l. In steady-state transport measurements the outcome is determined by the transport mean free path, whereas the diffusion coefficient is obtained from dynamic experiments. The two parameters are related according to $D=\frac{1}{3}v_E l$, with v_E a transport velocity. It is our aim to point out that the velocity that appears in the diffusion constant is neither the phase velocity nor the group velocity but instead a transport velocity. The phase velocity, either found from volume-fraction arguments, or obtained from more sophisticated coherent potential approximations,[5,6] has frequently been used as the velocity entering in the diffusion constant.

The group velocity, $v_g \equiv dE(p)/dp$, on the other hand, describes the propagation of the coherent beam. In transparent dispersive media multiple scattering is absent, and energy is transported by the coherent wave. In the presence of multiple scattering the scattered waves also carry energy and their propagation is not contained in the group velocity. Especially near resonance, where the scattering contribution becomes large, the group velocity fails to describe transport of energy.[7,8] Indeed the group velocity can become much larger than the vacuum speed of light. We will show, both experimentally and theoretically, that the actual velocity, which we shall refer to as transport velocity v_E, can be very much lower than the phase velocity in the case of resonant scattering.

Studying optical transport in strongly scattering media, we came across a persistent discrepancy between l as found from steady-state measurements (e.g., total transmission) and D as found from dynamic experiments (e.g., time-resolved transmission of a pulse). For the two measured quantities to agree, a very low value had to be assumed for the transport velocity. An independent measurement of the transport mean free time was then undertaken, and showed that the transport velocity was indeed very low. The discrepancy was thus removed.

Our findings seem to have important consequences: The outcome of theories in which diffusion constants are calculated on the basis of the phase velocity should be reconsidered. Likewise, they show that great care is needed in inferring a mean free path from dynamic measurements. Previously reported exceptionally small diffusion constants can be attributed to small transport velocities rather than to small mean free paths.[9] When no resonance scattering is occurring the difference between the two velocities will become unimportant.

Samples of finely divided TiO_2 in air were prepared on the basis of commercial rutile pigment with size distribution centered around $d=220$ nm.

The transport mean free path for visible light in the samples was determined by two different static techniques: Cones of enhanced backscattering were recorded using previously described[10] methods and the total transmission was monitored. The transport mean free path l was calculated from the full width at half maximum[10] and from the apex angle of the triangular cusp[11] at the top of the cones of enhanced backscattering, yielding 0.66 ± 0.03 and 0.58 ± 0.04 μm, respectively, at wavelength $\lambda=633$ nm. Alternatively, the transport mean free path was determined from transmission experiments. For slabs of thickness L, with $l \ll L \ll l_{\rm abs}$, where $l_{\rm abs}\equiv(l_{\rm in}l/3)^{1/2}$ is the absorption length, the total transmission is given by $T=\gamma l/(L+2z_0 l)$. We estimated $\gamma\simeq 2z_0\simeq 2.1$ on the basis of computer simulations, differing somewhat from the values for scalar isotropic scattering. The total transmission T was measured as a function of the slab thickness at $\lambda=633$ nm: Samples, mounted in the entrance port of an integrating sphere, were illuminated from the outside and the resulting intensities inside the sphere were compared to the intensity in the absence of a sample. The results are plotted in Fig. 1. From the slope of this plot we find $l=0.57\pm0.05$ μm, in agreement with the enhanced-backscattering data. The absorption length in our samples was

determined to be about 80 μm at $\lambda=633$ nm and does not need to be taken into account. The diffusion constant D and the transport mean free time τ were obtained from dynamical speckle measurements: Using a dye laser as a source, we studied the intensity correlation function $\langle \delta I_\omega \delta I_{\omega+\Delta\omega}\rangle$ within a single coherence area (speckle spot) in the scattered intensity pattern over the wavelength range between 585 and 630 nm. This object measures the distribution of photon flight times in the sample.[12] In a backscattering geometry and at some constant value of $l \ll L$, the distribution of path lengths is fixed, and hence the decay of the correlation as a function of $\Delta\omega$ will depend on the mean free time τ only. In a transmission geometry, on the other hand, the path-length distribution depends on the proportion L/l and the decay will be determined by D and L.

Following the method by which Genack and Drake[13] calculated the correlation in transmission speckle, we obtained for the normalized correlation in reflection and transmission speckle

$$\langle \delta I_\omega \delta I_{\omega+\Delta\omega}\rangle_R = \left(\frac{B}{B-1-z_0}\right)^2 \frac{\cosh[(B-1-z_0)y]-\cos[(B-1-z_0)y]}{\cosh(By)-\cos(By)}, \quad (1)$$

and

$$\langle \delta I_\omega I_{\omega+\Delta\omega}\rangle_T = B^2 y^2/[\cosh(By)-\cos(By)], \quad (2)$$

respectively, with $B=2z_0+L/l$ and $y=\sqrt{6\Delta\omega\tau}$. From Eq. (1) we expect that for large $\Delta\omega$ the correlation in the backscattered intensity will decay as $\exp[-(1+z_0)\times\sqrt{6\Delta\omega\tau}]$. Figure 2 is a test for this behavior for an $L=78$ μm sample. The constant slope of the plot confirms the expected type of decay. From a series of determinations using samples with L values ranging from 8 to 200 μm we found τ to be 12.3 ± 2.1 fs.

In transmission, the correlation is a function of $By \simeq (2\Delta\omega L^2/D)^{1/2}$. In Fig. 3 the experimental width[14] at half maximum of the correlation function is plotted versus L. From Fig. 3 we find $D=11.7\pm1$ m^{2}s^{-1}. Combining τ and D as found from the dynamical experiments, it follows from $l=\sqrt{3\tau D}$ that 0.57 μm $\leq l \leq 0.74$ μm, in agreement with the value of $l\simeq0.60$ μm found from the static experiments.

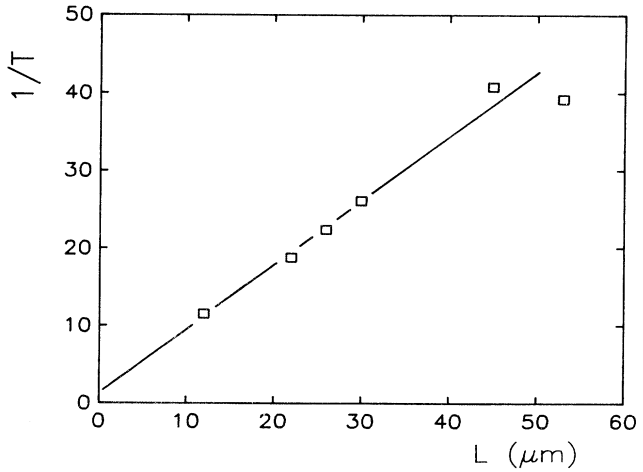

FIG. 1. Reciprocal of the total transmission through slabs of 36 vol% TiO_2 in air, as a function of slab thickness L. The straight line is a fit with diffusion theory and yields $l=0.57\pm0.05$ μm.

Now that we know our set of experimentally found parameters is consistent, we may use it to calculate the transport velocity for electromagnetic waves v_E. We find $l/\tau=v_E=(5\pm1)\times10^7$ m s^{-1}.

We will now present an outline of a derivation of the expression for the transport velocity in terms of microscopic properties of the scatterers. We start with the scalar wave equation

$$\left[\varepsilon(\mathbf{x})\frac{\partial^2}{\partial t^2}-\nabla\right]\Psi(\mathbf{x},t)=0, \quad (3)$$

in which $\varepsilon=1/c^2$ is the dielectric constant. The scalar correlation function $\langle\Psi(\mathbf{x}_1,t_1)\Psi^*(\mathbf{x}_2,t_2)\rangle$, averaged over disorder, can be shown to satisfy the following generalized Boltzmann equation:[3]

$$\left[\frac{-2E\omega}{c_0^2}+2\mathbf{q}\cdot\mathbf{p}+\Sigma(E^+,\mathbf{p}^+)-\Sigma(E^-,\mathbf{p}^-)\right]\Phi_{\mathbf{p}}(\mathbf{q},\omega|E)=\Delta G(\mathbf{q},\omega|E,\mathbf{p})\left[1+\sum_{\mathbf{p}'}U_{\mathbf{pp}'}(\mathbf{q},\omega|E)\Phi_{\mathbf{p}'}(\mathbf{q},\omega|E)\right]. \quad (4)$$

Here $\Phi_{\mathbf{p}}$ represents $\langle\Psi(\mathbf{x}_1,t_1)\Psi^*(\mathbf{x}_2,t_2)\rangle$ Laplace transformed with respect to time and Fourier transformed with respect to position; E and $\mathbf{p}$ are the internal oscillations of the wave packet. Furthermore Σ is the mass operator, U the irreducible vertex, ΔG the difference between retarded and advanced Green functions $G(E^+,\mathbf{p}^+)-G(E^-,\mathbf{p}^-)$, and $E^\pm\equiv E\pm i\varepsilon\pm\frac{1}{2}\omega$, $\mathbf{p}^\pm\equiv\mathbf{p}\pm\frac{1}{2}\mathbf{q}$. The empty-space speed of light is c_0.

In order to calculate the diffusion coefficient we require the solution in the Kubo limit: $\mathbf{q},\omega\rightarrow0$. We will solve Eq. (4) to lowest order of the density ("Boltzmann limit"): ΔG is taken completely "on shell," and Σ and U are approximated by

$$\Sigma(E^\pm,\mathbf{p})=nt_{\mathbf{pp}}(E^\pm), \quad (5)$$

$$U_{\mathbf{pp}'}(\mathbf{q},\omega|E)=nt_{\mathbf{p}+\mathbf{p}'^+}(E^+)t_{\mathbf{p}'-\mathbf{p}^-}(E^-), \quad (6)$$

with n the density, and t the T matrix of one scatterer. Next a careful expansion for Σ and U in terms of ω and $\mathbf{q}$ is employed. With c_p the phase velocity, we let

$$\Phi_{\mathbf{p}}(\mathbf{q},\omega|E)\equiv\delta(E^2/c_p^2-p^2)\tilde{\Phi}_{\hat{\mathbf{p}}}(\mathbf{q},\omega|E). \quad (7)$$

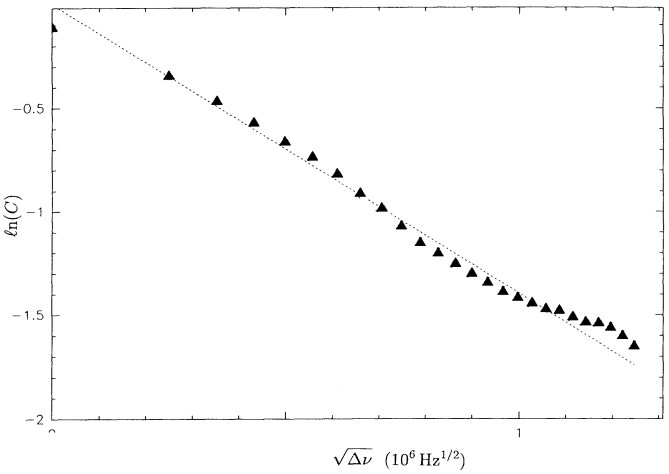

FIG. 2. Frequency-dependent intensity-intensity correlation in light backscattered from a sample of 36 vol% TiO_2 in air. Experimental points are averages over sixteen scans, probing different areas of the same sample. (Except for a slight flattening at small $\Delta\nu$ that is due to the nonzero spectral linewidth of the source, no systematics is found in the "structure" of curves, obtained by probing different samples. This structure is therefore due to insufficient statistics.) The slope of the plot yields a value for the mean free time τ. Determinations on a series of samples of different thicknesses yield an average value of $\tau = 12.3 \pm 2.1$ fs.

We identify energy density and energy current according to

$$\Xi(\mathbf{q},\omega) \equiv \int \frac{d\hat{\mathbf{p}}}{4\pi} \tilde{\Phi}_{\hat{\mathbf{p}}}(\mathbf{q},\omega|E)\,, \tag{8}$$

$$\mathbf{J}(\mathbf{q},\omega) \equiv v_E \int \frac{d\hat{\mathbf{p}}}{4\pi} \hat{\mathbf{p}} \tilde{\Phi}_{\hat{\mathbf{p}}}(\mathbf{q},\omega|E)\,. \tag{9}$$

The yet unknown velocity v_E is the speed at which energy transport takes place, and is fixed once we require Ξ and J to obey an equation of continuity. After summing Eq. (4) over angles $\hat{\mathbf{p}}$, we obtain

$$i\omega\Xi(\mathbf{q},\omega) - i\mathbf{q}\cdot\mathbf{J}(\mathbf{q},\omega) = \text{const}\,, \tag{10}$$

provided

$$v_E = \frac{c_0^2}{c_p}\left[1 - n\frac{d}{dp^2}\mathrm{Re}\,t_{pp}(p) + n\left\langle I(\Omega)\frac{d\phi(\Omega)}{dp}\right\rangle_\Omega\right]^{-1}. \tag{11}$$

$I(\Omega)$ and $\phi(\Omega)$ denote the scattered intensity and the phase shift in the direction Ω. It is very important to note that the second and third terms in Eq. (11) cancel in the case of electrons, due to a Ward-Takahashi identity,[15] but *not* for classical waves. We will not pursue this point any further here, but mention that the wave equation is *second order* in time, in sharp contrast with the Schrödinger wave equation. The third term in Eq. (11), containing $I(\Omega)$, comes from the ladder diagrams and

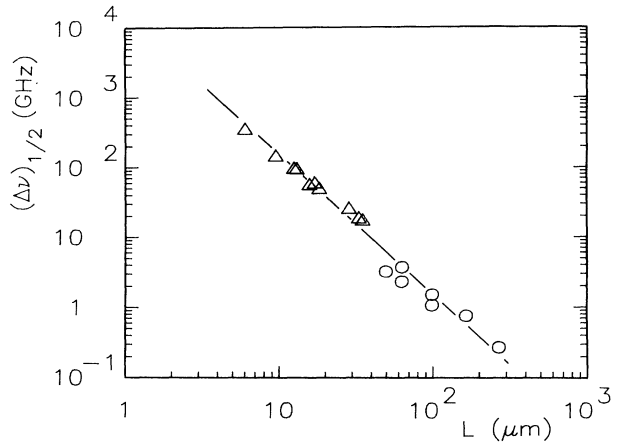

FIG. 3. Width at half maximum of the frequency-dependent intensity-intensity correlation in light transmitted through a sample of 36 vol% TiO_2 in air. From the figure we infer a diffusion coefficient $D = 11.7 \pm 1$ m^{2}s^{-1}.

represents the contribution of the scattered intensity in all directions. Without this term the transport velocity becomes equal to the group velocity, which is the analog of effective mass in electron-transport theory. The group velocity is known to be anomalous near a resonance, which in fact is largely compensated for by the third term in the right-hand side of Eq. (11). Application of this general expression to a semiclassical scattering model gives the same result as obtained by Loudon.[8] Insertion of the on-shell T matrix of a Mie scatterer[16] and application of the orthogonality property of the different partial waves yields

$$\frac{v_E}{c_0} = \frac{c_0^2}{c_p^2}\left[1 + \frac{3}{4}\frac{f}{x^2}\sum_{n=1}^{\infty}(2n+1)\left(\frac{d\alpha_n}{dx} + \frac{d\beta_n}{dx}\right)\right]^{-1}, \tag{12}$$

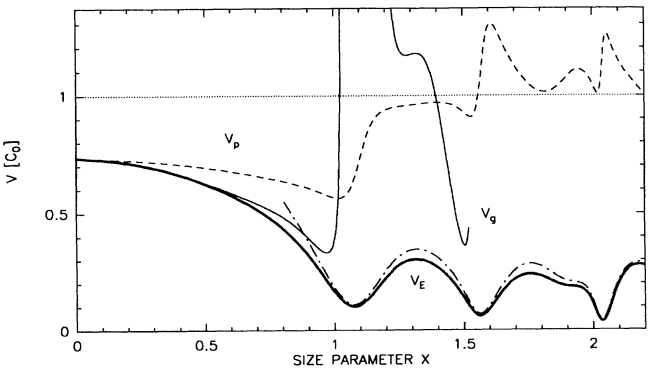

FIG. 4. Transport velocity for 36 vol% TiO_2 spheres in air ($n = 2.73$) as a function of the size parameter $2\pi a/\lambda$, calculated from our microscopic theory (bold solid line) and inferred from energy-density arguments (dash-dotted line). Dashed line: phase velocity. Solid line: part of the strongly anomalous group velocity.

where f is the volume fraction of the Mie spheres, $x = aE/c_0$ is the size parameter, and α_n and β_n represent the (Van de Hulst) phase shifts of the individual partial waves. It is easily shown that the Boltzmann diffusion constant becomes $D = \frac{1}{3} v_E l$, with $l = l_{sc}/(1 - \langle \cos\theta \rangle_\Omega)$, where l_{sc} represents the scattering mean free path. In Fig. 4 we have plotted for a volume fraction $f = 0.36$ the values for v_E as a function of the size parameter x, as well as the outcome of a heuristic model based on the difference between energy density inside and outside a scatterer. This simple model turns out to reproduce the results of Eq. (12) very well. In this model one estimates $v_E = c_0/[f(W-1)+1]$. Here W is the energy density within the scattering particles relative to the surrounding air and is much larger than unity on a resonance.[17]

The size parameters of our samples lie within $x = 0.8$ and 2.5. Averaging over this range of size parameters leads to $v_E/c_0 \simeq 0.18$, in good agreement with the experimental value: $v_E/c_0 = 0.16 \pm 0.03$.

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[1]For reviews see, for instance, *Scattering and Localization of Classical Waves in Random Media,* edited by Ping Sheng (World Scientific, Singapore, 1990); *Analogies in Optics and Micro Electronics,* edited by W. van Haeringen and D. Lenstra (Kluwer, Dordrecht, 1990); S. John, Commun. Condens. Matter Phys. **14**, 1193 (1990); M. Kaveh, Philos. Mag. B **56**, 693 (1987).

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