

Absorption length for photon propagation in highly dense colloidal dispersions

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The absorption length for photon propagation in highly concentrated colloidal dispersions calculated from temporal intensity profiles of 100 femto-second pulses is much longer than the absorption length obtained from the measurements of static light transmission in the pure continuous phase fluid. The difference between these two values is explained on the basis of small interparticle spacing at high particle concentration and hence shorter paths traveled by photons through the absorbing medium relative to the total diffusive path in the dispersion. The two values are in good agreement when the absorption length is rescaled with the interparticle separation.

I. INTRODUCTION

Light propagation in highly scattering and absorbing media is a problem of great technological importance and scientific interest for diverse fields such as colloidal dynamics, materials processing,¹ biomedical diagnostics,² and remote sensing.³ Our interest in this phenomenon arises from stereolithography (SL),⁴ a novel technique for processing complex shaped materials from colloidal suspensions. SL is a sequential layering process, converting a virtual object into a real, solid structure. It begins with a 3-dimensional, computer-aided design (CAD) model of an object of interest. The virtual object is computationally sliced into 2-dimensional, thin patterns. Each 2D pattern is then transmitted in turn to another computer which controls a patterning laser, each section is solidified by scanning the ultraviolet laser onto the surface of a photocurable polymer resin. A layer is built upon another by lowering the platform supporting the 3D object into the resin bath. Fresh, uncured resin flows over and covers the cured layer, and the next section is patterned on top of the preceding layer. The process is continued until the entire structure has been replicated in solid form. A precise manipulation of light penetration and the profile of the cured region in the colloidal suspension is of utmost importance for the success of this process.

The "diffusion approximation" is now well established for modeling the light propagation in highly scattering and absorbing media.⁵ The essential approximation underlying the diffusion approach is that after going through a large number of scattering events, the phases of the scattered waves are randomized so that any

interference effects in the medium can be neglected. As a result, only the light intensity needs to be considered in the description of light propagation.

The two essential parameters to describe the photon propagation in the diffusive process are the transport length, l_{tr} , and the absorption length, l_a . The transport length represents the average distance traveled by the photon before being completely randomized in direction. For dilute dispersions, the transport length is given by $l_{tr} = (n\sigma_{tr})^{-1}$ and has been verified by many researchers.⁶ Here σ_{tr} represents the transport cross section of the particle which is calculated from the Mie theory and n is the particle number density which is related to the volume fraction ϕ by $n = \phi/V$, and V is the volume of a single particle. For concentrated dispersions, the interparticle correlations modify the transport cross section by the interparticle structure factor.⁷ We have recently observed an increase in the transport length as the concentration of dense media increased.⁸

The second characteristic parameter for the diffusion theory is the absorption length, the average distance traveled by the photons before being absorbed. The absorption length in the nonscattering case, i.e., when no particles are present in the medium, can be calculated from steady state transmission in the medium in a conventional spectrophotometer. In the scattering case, the pico-second, time-resolved spectroscopy is a powerful technique which allows the determination of both the transport length and the absorption length from a single experiment. The quantitative determination of absorption length in a highly scattering medium is of particular interest for a number of biomedical applications.⁹ For

example, the physiological information on the oxygenation state in tissue can be obtained by absorption measurement. In ceramic processing by stereolithography, the quantitative measurement of absorption length is required to predict the penetration depth of the laser in the ceramic colloidal dispersions. The absorption in the process of stereolithography arises mainly due to the photocuring polymers that are added in the colloidal dispersions. In this study, absorbing dye was added to the colloidal dispersions to mimic the absorption due to the photocuring polymer.

In this paper, we present the absorption length measurements in highly concentrated alumina and silica dispersions from the temporal profile of 100 femto-second ultrafast laser pulses for a wide range of absorption. The absorption lengths were controlled by the concentration of the absorbing dye in the medium. The lowest absorption length was three orders of magnitude larger than the transport length so the diffusion approximation is valid. Proskurin *et al.*¹⁰ found that for small absorption, the absorption values from time-resolved measurements were in agreement with the absorption values measured without titania particles. Tsunazawa *et al.*¹¹ demonstrated the same for latex particles. In highly concentrated dispersions, we find that the absorption lengths calculated from the time-resolved experiments were much longer than those calculated from steady state light transmission in the medium alone. We explain this by rescaling the absorption length measured using steady-state spectrophotometry on the interparticle separation. Since at high concentrations the distance between the particles is small, the distance traveled by the photon in the absorbing medium is small compared to the total diffusive path, and hence the absorption length measured by the diffusion approach is longer. Rigorously speaking, the absorption in the medium is inhomogeneous. We find that the absorption length values in the dispersions estimated from the time-resolved measurement are in good agreement with those estimated in the medium when we rescale the absorption length with respect to the interparticle separation.

II. EXPERIMENTAL

A. Setup

The experimental system used to measure the temporal intensity profiles of transmitted light pulses is schematically shown in Fig. 1. Ultrashort laser pulses of 100 fs duration at a wavelength of 625 nm and 82 MHz repetition rate were generated by a colliding-pulse-mode (CPM)-locked laser. Part of the laser beam was split by a glass slide to be used as a reference pulse which marks the zero time of the signal beam and monitors the intensity of laser pulses. The main part of the beam was coupled into an optical fiber (core

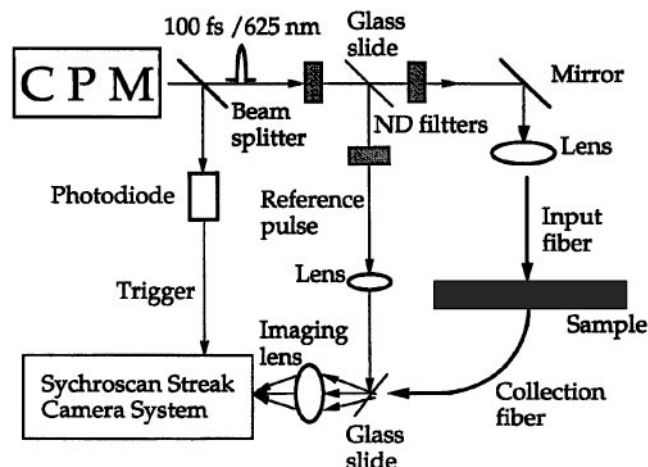


FIG. 1. Schematic of the experimental setup.

diameter 200 μm) which was positioned near the front face of the sample cell. The sample cell consisted of two glass windows (50 \times 50 mm) with 0.5 to 5 mm spacers. The sample thickness is much larger than l_{tr} so that diffusion approximation is valid. The transmitted light was collected by another optical fiber (core diameter 200 μm) and was imaged into a streak camera detection system (10 ps time resolution). The scattered light was time resolved by the streak camera and recorded on a CCD camera. Neutral density filters were used to adjust the incident light level for intensity comparison between scattered pulse profiles obtained from different samples.

B. Materials

The scattering samples were alumina and silica dispersions. The alumina dispersions were prepared by adding the powder (0.5 μm diameter, Sumitomo Chemical) to water using a 15,000 Mw ammonium salt of polymethacrylic acid (R. T. Vanderbilt Company, Inc.) as the dispersant. The dispersions were then ultrasonicated for a few minutes to homogenize. The silica dispersions (0.3 μm diameter, Nissan Chemicals) were centrifuged to obtain a dispersion of desired volume fraction. The absorbing dye Napthol (Sigma Chem.) was used to control the absorption length in the medium. The concentration of the absorbing dye was changed from 5×10^{-3} to 5×10^{-5} M/L which corresponds to an absorption length ranging from 0.18 to 18 mm.

III. CALCULATION OF l_a FROM TRANSMITTED PULSE PROFILE

A narrow beam of ultrashort laser pulses was incident normally onto a scattering slab. The transmitted pulses at the point on the opposite side of the slab were measured. The transmitted pulse can be described by the solution of diffusion equation for the slab geometry.

The solution is given by¹²

$$I_z(t, l_{tr}, l_a) = \frac{1}{4d^2t} \sum_{m=1}^{\infty} m \sin\left(\frac{m\pi z}{d}\right) \times \exp\left[-Dt\left(\frac{m\pi}{d}\right)^2\right] \exp\left(\frac{-\nu_m t}{l_a}\right), \quad (1)$$

where ν_m is the velocity of light in the medium, $d = z + 2z_0$, $z_0 = 0.71l_{tr}$ is the extrapolation length, and z is the thickness of the slab. In obtaining the above solution, perfectly absorbing boundary conditions at the extrapolated surfaces are used. The transport length and the absorption length can be calculated by numerically fitting the experimental temporal profiles to Eq. (1). The absorption length is also calculated from the experimental temporal profiles as follows.¹¹ The natural logarithm of the ratio of the transmitted intensity of the pulse at time t for a sample with absorption length l_a and transport length l_{tr} to a reference sample with the same l_{tr} but absorption length l_{ref} is obtained from Eq. (1) as

$$\ln\left[\frac{I(t, l_{tr}, l_a)}{I(t, l_{tr}, l_{ref})}\right] = \left(\frac{1}{l_{ref}} - \frac{1}{l_a}\right)\nu_m t. \quad (2)$$

Thus, from the knowledge of the absorption length in the reference sample, the absorption length of the desired sample can be calculated from the gradient of the plot of natural logarithm of the ratio of the transmitted intensity of the sample to that of a reference sample versus time. The reference sample is taken as the dispersion at the same particle concentration (thus keeping the scattering characteristics and hence transport length identical in two cases) without any absorbing dye in the medium.

IV. RESULTS

Figure 2 shows the semilog plot of the ratio of the transmitted intensity for the silica dispersions (at a particle volume fraction of 0.2 and at various absorption lengths in the medium) to a reference sample as a function of time. The reference sample was the silica dispersion at $\phi = 0.2$ with no absorbing dye. At long times, for large absorption (or smaller absorption length) the exponential decay is not seen because the intensity decays below the sensitivity of the instrument. A similar plot for the alumina dispersion at 0.4 volume fraction of particles is shown in Fig. 3. The reference sample was an alumina dispersion at $\phi = 0.4$ with no absorbing dye. The transport length and the absorption length of the reference sample were determined by numerical fitting of the temporal transmitted profile to Eq. (1). The transport length for the alumina dispersion is $3 \mu\text{m}$ and the absorption length is found to be 61 mm . The transport length calculated for the alumina dispersion in an uncorrelated case is $2 \mu\text{m}$; whereas, on incorporating the correlation, the calculated value is same as the

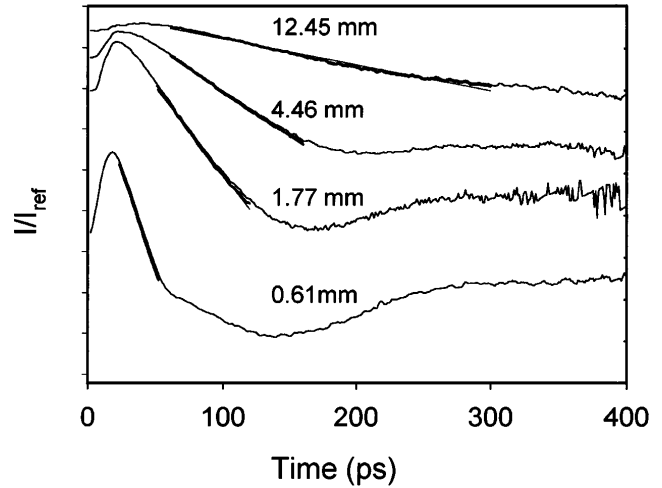


FIG. 2. The semilog plot of the intensity temporal profiles of the silica dispersions at various values of the absorption length in the medium with reference to the nonabsorbing case. The absorption length (l_a) in the dispersion is calculated from the slope of the linear fit.

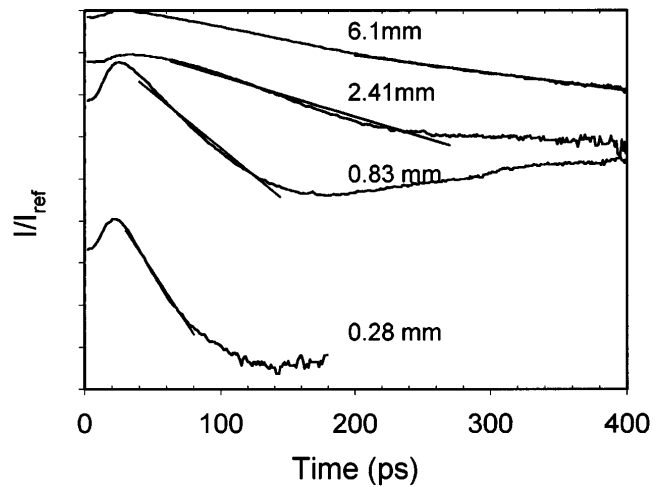


FIG. 3. The semilog plots of the intensity temporal profiles of the alumina dispersions at various values of the absorption length in the medium (l_m) with reference to the nonabsorbing case. The straight-line fit gives the absorption length (l_a).

experimental value. For the silica dispersion the transport length is $60 \mu\text{m}$ and the absorption length is on the order of a few meters. The transport length calculated for the silica dispersion in the uncorrelated case is $48 \mu\text{m}$; whereas, on incorporating the correlation, the calculated value is the same as the experimental value.

The absorption length in the dispersion with added absorbing dye is then calculated from the slope of the straight line of the plot as described in Sec. III as well as by numerical fitting of the temporal profile to Eq. (1). The absorption length calculated using the slopes method and the numerical fitting are similar. The absorption length of the medium (i.e., without any particles and same dye concentration as in the dispersion)

at a wavelength of 625 nm was measured using a spectrophotometer (UV-Visible 9430 Spectrophotometer, IBM Instruments, Inc.). The absorption length of the medium was much larger than the transport length so that the diffusion approximation is valid.

Figures 4 and 5 compare the absorption lengths measured in the medium to the absorption lengths obtained from the gradient of the plot for the silica and alumina dispersions, respectively. Also shown are the absorption lengths calculated from numerical fitting of the temporal profile to Eq. (1). The absorption lengths obtained in the alumina and silica dispersions are much longer compared to those in the medium.

The difference in the two sets of values can be understood by looking at the photon propagation path in the colloidal dispersion using a model schematically shown in Fig. 6. As the photon propagates, it encounters an absorption of length scale l_m only in the medium. Here l_m is defined as the length scale where the light intensity decays by a factor e^{-1} on traversing through the medium for a length of l_m . For a given diffusive path of the photon, the path traveled through the medium is relatively shorter compared to the total diffusive path at high particle concentrations. Thus, the effective absorption length l_a measured by the temporal transmission experiments is larger. Alternatively, the absorption in the sample is inhomogeneous and what is calculated from the diffusion experiments is an effective homogeneous absorption length of the sample where the sample is considered a single phase continuum. We account for the actual inhomogeneity in the dispersion by considering the actual length traveled by the photon through the medium relative to the total length traveled by the photon in the dispersion and using that to rescale the absorption length l_m as discussed in the next section.

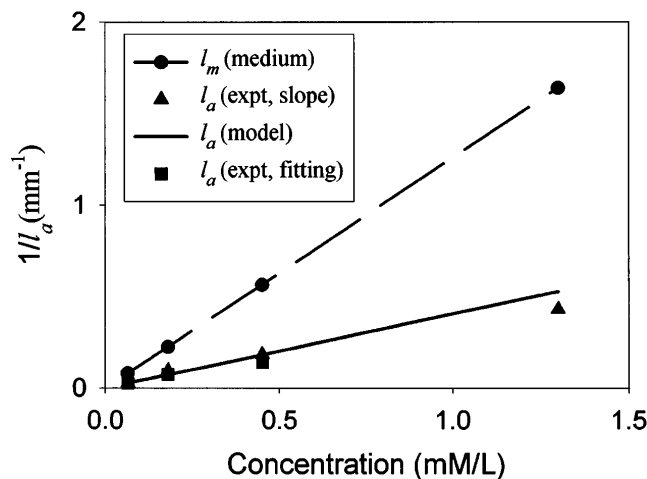


FIG. 4. The inverse absorption length versus absorbing dye concentration for silica dispersion. The absorption length, l_a , calculated from the experimental intensity temporal profiles [fitting (■), slope (▲)] is compared to the model (—) and the l_m (•) calculated in the medium.

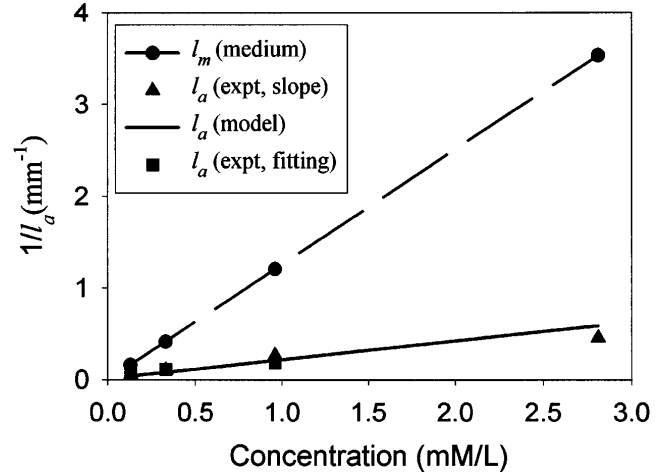


FIG. 5. The inverse absorption length versus dye concentration for the alumina dispersion. The absorption length, l_a , calculated from the experimental intensity temporal profiles [fitting (■), slope (▲)] is compared to the model (—) and the absorption length in the medium l_m (•).

V. MODEL FOR l_a IN HIGHLY CONCENTRATED DISPERSIONS

Consider a diffusive path followed by the photon between two successive scattering events (Fig. 6). In Eq. (2), it is assumed that the photon experiences an absorption length l_a along the entire path L . In highly concentrated dispersions, the particles occupy most of the space, and thus in path L the photon experiences the absorption length of the medium l_m for length L_m and no absorption or the absorption length of the particle l_p for length a , where a is the particle diameter. Here l_p is defined as the length scale where the light intensity decays by a factor e^{-1} on traversing through the particle for a length of l_p . Thus,

$$L = \nu_m t = L_m + a. \quad (3)$$

The transmitted intensity depends on the absorption as

$$I \propto \exp \left[- \left(\frac{L_m}{l_m} + \frac{a}{l_p} \right) \right]. \quad (4)$$

L is the average interparticle separation and is given by

$$L = a \left(\frac{\phi_m}{\phi} \right)^{1/3} = a c \phi^{-1/3}, \quad (5)$$

where ϕ_m is the maximum packing fraction for the dispersion and $c = (\phi_m)^{1/3}$. From Eqs. (3) and (5) we get

$$L_m = a(c\phi^{-1/3} - 1). \quad (6)$$

With Eqs. (3), (5), and (6), the exponential factor in Eq. (4) becomes

$$\frac{L_m}{l_m} + \frac{a}{l_p} = \frac{\nu_m t}{(c\phi^{-1/3})} \left(\frac{c\phi^{-1/3} - 1}{l_m} + \frac{1}{l_p} \right). \quad (7)$$

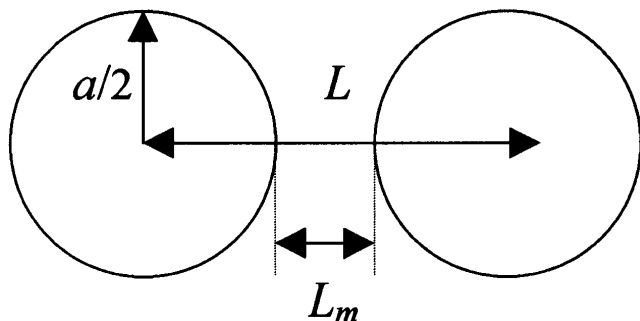


FIG. 6. A typical diffusive path of length L in the medium at high particle concentration. The photon experiences the absorption due to the medium only over length L_m and absorption due to the particle over the rest of the path.

By comparing the exponential factor in Eq. (1) with the exponential factor in Eq. (4) and using Eq. (7), we obtain

$$\frac{1}{l_a} = \frac{1}{(c\phi^{-1/3})} \left(\frac{c\phi^{-1/3} - 1}{l_m} + \frac{1}{l_p} \right). \quad (8)$$

If the particles are nonabsorbing as is the case for the silica dispersion, then Eq. (8) indicates that the absorption length in the medium (l_m) is modified by a factor of $(c\phi^{-1/3} - 1)/(c\phi^{-1/3})$ due to the addition of the volume fraction ϕ of the particles in the medium.

Figures 4 and 5 compare the absorption lengths in the dispersion calculated using Eq. (8), where l_m is the absorption length measured in the medium, with the experimental data. For silica dispersions, the value for ϕ_m used in the calculation was 0.64, which is the random close-packing limit for spherical particles. The silica particles used are highly spherical and fairly monodisperse. The alumina particles are highly polydisperse so they can pack much more efficiently. Thus, for alumina dispersions the value for ϕ_m used in the calculation was 0.68. As can be seen the absorption length values measured in the medium without any particles, when rescaled based on the particle volume fraction, are in close agreement with the absorption length obtained from the temporal profiles.

VI. CONCLUSIONS

In conclusion, the absorption lengths were measured in highly concentrated colloidal ceramic dispersions over a wide range of absorption in the continuous phase. The absorption lengths in the dispersions measured using time-resolved transmission measurement of ultrafast laser pulses are found to be much longer than those

measured in the medium (without any particles). This is explained on the basis of the shorter path traveled by the photon through the medium in highly concentrated dispersions as compared to the total diffusive path length in the dispersion. A simple model has been presented to rescale the absorption length based on the volume fraction of the particles. For stereolithographic processing of ceramics, this implies that to use the diffusion model in the design algorithms, the appropriate absorption length to be used is the absorption length in the medium scaled on the interparticle separation.

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