Counting particles by means of optoacoustics: Potential limits in real solutions

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The irradiation of an inhomogeneous liquid sample with a long train of short laser pulses and subsequent recording of a histogram of the magnitudes of the acoustic responses can serve as a diagnostic tool for various applications. The absorption of an incident light by a suspended particle may cause a cavitation event. Exploitation of the random cavitation events which, in turn act as effective acoustic radiators, may provide a useful measurement tool rather than an inconvenience.
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I. INTRODUCTION

The examination of turbid media by optoacoustic methods provides important diagnostic tools in a wide range of research applications spanning from the study of biological tissue to the characterization of high molecular weight polymer solutions.[1] Recently we used pulsed optoacoustic methods to detect low concentrations of particles in liquids.[2] While similar in nature, these examples are distinguishable. The optoacoustic conversion in a medium composed of well-defined separate particles, such as occurs in a fog or in a suspension is the focus of the current work.

Linear photothermal contributions due to absorption of pulsed irradiation by inhomogeneities suspended in a liquid have previously been described.[3] However, even at relatively low laser fluence (<1 mJ/cm^2), nonlinear cavitation events in liquid samples can distort the ''classical'' pattern of an acoustic response. Both the magnitude and the profile of the combined cavitation and photothermal signal appear to be random in nature. The principal statistical features of the acoustic response of various suspensions were described by Alimpiev *et al.*[4] The low-fluence laser-driven cavitation should not be confused with a well-known laser breakdown, which yields a stable response.

The subject of the present study is a further development of the low-fluence optoacoustic diagnostics of diluted suspensions.[5] The essential principle of the method is represented by cavitation events of well characterized particles under dilute conditions. It is necessary to understand the parameters that lead to cavitation of a fluid solution heated by a particle that has absorbed pulsed ultraviolet light.

In the study, laser fluence is limited to avoid the breakdown phenomenon. Cavitation, i.e., vapor bubble formation, is instead observed as a set of individual events, and the possibility of detection of the parameters of the suspension is thus provided. We also present results from Monte Carlo simulations created to model and predict acoustic responses as a function of fluence. Experimental optoacoustic data collected using sphere and peanut shaped polystyrene particles are also presented.

II. THEORETICAL MODELING

A. Acoustic response and histograms

The interaction of a laser beam with weakly absorbing inhomogeneous particles suspended in solution can lead to optoacoustic conversion within the pencil-shape irradiated volume [Fig. 1(a)]. At low fluence the optoacoustic signal consists of the thermoacoustic response of the host liquid and an occasional strong heating of particles. If a definite fluence threshold condition is satisfied, the temperature of the particles can exceed the boiling temperature of the host liquid. A vapor layer appears adjacent to the particle [Fig. 1(b)], which experiences rapid expansion thus giving rise to a effective acoustic signal. In turn, the observed signal is marked by a random magnitude and waveform since the overall signal is composed of the pulses coming from different points and having other random parameters. However, the in-phase pickup of these random signals is possible if a relatively low frequency (for example, up to 200 kHz) transducer positioned out of the irradiated ''pencil-shape'' volume. The first peak detection of the acoustic signal is obtained by an appropriate gating of the incoming response. After recording the acoustic responses generated by many subsequent laser shots, one can build a histogram of acoustic magnitudes and use it as a diagnostic tool.

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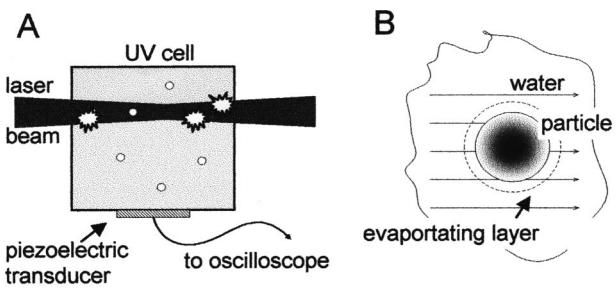

FIG. 1. Concept: (A) the geometry, asterisks mark the particles which meet the threshold condition and give rise to the bubble growth, while the circles mark the particles which are underheated or not illuminated at all. (B) describes what happens around the overheated particle.

B. Thresholds for the particles of various types

The evaporation threshold depends greatly on the material of the particle. This fact presents the possibility to investigate suspension by means of optoacoustics. Particles of low absorption and low effusivity such as polystyrene particles are of special interest for our study and are considered here in more detail.

In order to simplify estimates within the assumption of independent and single scattering in the medium, we deal with the dilute solutions[6] and we consider the host liquid as a nonabsorbing medium. If ϵ is the laser fluence at the arbitrary point of the beam cross section, then $\epsilon\sigma$ is the energy absorbed by a particle which occasionally finds itself at this very point $\sigma = Q\pi d^3\beta/4$; here σ is the absorption cross section of a particle, d is the diameter of the particle, β is light absorption coefficient where $d \ll \beta^{-1}$, and Q is a coefficient, depending on the refraction index of a particle as well as on the ratio d/λ, where λ is an optical wavelength.[6] The absorbed energy causes heating of a particle with subsequent heating and evaporating of the adjacent water layer. Since the effusivity of polystyrene is about 5 times less than that of water, it is natural that water effectively extracts heat from the particle. Hence, a major fraction of the energy absorbed is spent maintaining the evaporation of water resulting in a rapidly expanding bubble. This energy is equal to $E = VL$, where $V = \pi d^2 l$ is the volume of evaporating water layer, L is evaporation heat, and l is the thickness of the evaporating layer. Hence, the energy conservation equation is $\epsilon_{\text{th}}\ \sigma = \rho VL$, where ρ is the density of water. As a result we get threshold fluence for this type of the particles $\epsilon_{\text{th}} = 4\rho lL/Q\beta d$.

Similar considerations yield the estimates for threshold fluence in the case of other types of particles. For example, almost all energy absorbed by a high effusivity opaque particle is spent to bring the particle to the water boiling temperature that yields $\epsilon_{\text{th}} \sim d$ (see Table I).

C. Calculations and results

To analyze the peak pressure response of the near-focal point volume as a function of laser energy, we will use a simple model assuming the spherical symmetry of expanding vapor bubbles and taking into account their collective response. The expanding vapor cavity is an effective radiator of a spherical sound wave. During the early stages of the bubble growth, the temperatures and pressures inside the bubble become very high, and the conversion from laser to acoustic energy takes place with the highest efficiency. Usually, the methods used for determining the acoustic pulse emitted due to the acceleration of the bubble wall are based on the Kirkwood–Bethe model.[7,8] From the model, it follows that the peak pressure of an individual response is proportional to the difference between the energy absorbed by a given type particle and the threshold energy (Table I).

TABLE I. Comparison of threshold energy fluence and magnitude of acoustical response for various particles of low and high effusivity, size, and absorptivity.

Types of particles	Example particles	How the threshold fluence ϵ_{th} depends upon the diameter of particle	How the magnitude of an individual acoustical response depends upon various parameters
Opaque particles of high effusivity	metal	$\sim d$	$\sim d^2(\epsilon\text{-}\epsilon_{\text{th}})$
Opaque particles with low effusivity	carbon	independent of diameter	$\sim d^2(\epsilon\text{-}\epsilon_{\text{th}})$
Low absorption particles of high effusivity	quartz	independent of diameter	$\sim d^3(\epsilon\text{-}\epsilon_{\text{th}})$
Low absorption particles of low effusivity	polystyrene	$\sim 1/d$	$\sim d^3(\epsilon\text{-}\epsilon_{\text{th}})$

We performed Monte Carlo simulations to create an ensemble of microparticles of arbitrary radii and of arbitrary threshold energy demands in order to calculate their joint response in point of reception. The method predicts random cavitation configuration while the focused laser beam was assumed to illuminate the virtual diluted suspension. Four hundred particles were assumed to be randomly positioned within the virtual cylindrical volume having a 100 μm diameter and 10 000 μm length. This cylindrical volume, in turn, was coaxial with the laser beam having Gaussian fluence distribution in the cross section. The effective focal length was 140 μm and the crossover diameter was 4 μm.

The random heating of the particles was due to their stochastic coordinates within the laser beam of nonuniform intensity. Due to cylindrical nature of the simulation, two random vectors were introduced, defining the position of each particle with respect to the laser beam axis. The simulation involved 50 000 trials each of them yielding an in-phase sum of several random responses from a random number of overheated particles. While, the usual thermoacoustical response of the host liquid could be taken into consideration, it was not principal for the present study and the host liquid was assumed to be absolutely transparent.

After 50 000 virtual laser shots, histograms were generated and the mean response magnitude, the most probable magnitude, and the mean number of the ''overthreshold'' particles were calculated. Some of the simulation results are shown in Figs. 2 and 3.

In Fig. 2, curves for the average number of the overthreshold particles versus laser fluence are plotted. The two monodisperse suspension samples of low absorption low effusivity spherical particles are considered. The first set, with

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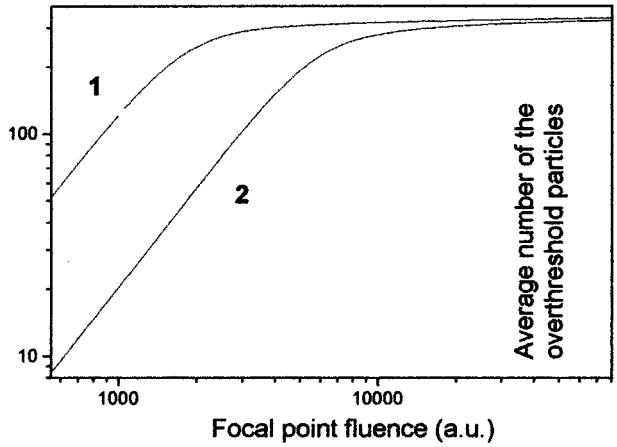

FIG. 2. Average number of overheated particles vs focal point fluence from Monte Carlo simulation for large particles (1) and small particles (2) sets.

large particles, having diameter $D=6\ \mu$m (1) and second set, small particles, $d=1.75\ \mu$m (2). The average number of overheated particles in the first sample is sufficiently larger than that of the second sample at relatively low fluence values. Both curves tend to the upper limit of about 400 particles at large fluence values.

If the samples composed of opaque high effusivity particles are considered (the case not shown), the simulation gives an opposite result, i.e., the number of the overthreshold events for smaller particles is larger.

Mean peak pressure ratios versus laser fluence from Monte Carlo simulation are plotted in Fig. 3. We consider four monodisperse suspension samples. They are: low absorption low effusivity $D=6\ \mu$m and $d=1.75\ \mu$m spheres and opaque high effusivity $D=6\ \mu$m and $d=1.75$ spheres. The two ratios versus laser fluence are calculated; first, the mean peak pressure ratio between responses obtained in low absorption large and small particles sets (curve 1) and, second, mean peak pressure ratio between responses obtained in opaque large and small particles sets (curve 2). It can be seen that ratios exhibit opposite tendencies with limits $(D/d)^3$ and $(D/d)^2$ correspondingly at high fluence values.

It follows from Fig. 3 that the response parameters in the

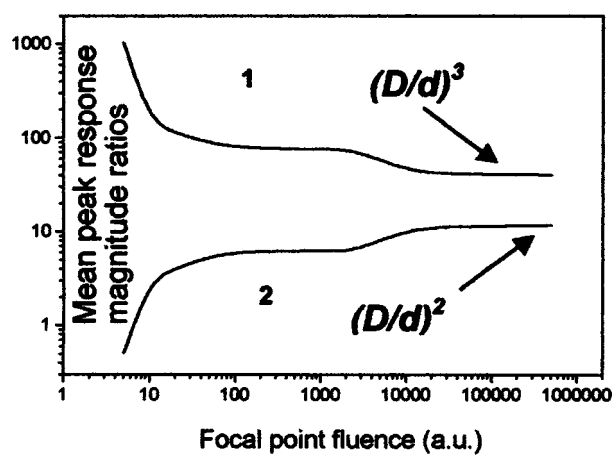

FIG. 3. Mean peak pressure ratios of the acoustic response from Monte Carlo simulation for low absorption particles (1) and opaque particles (2) sets.

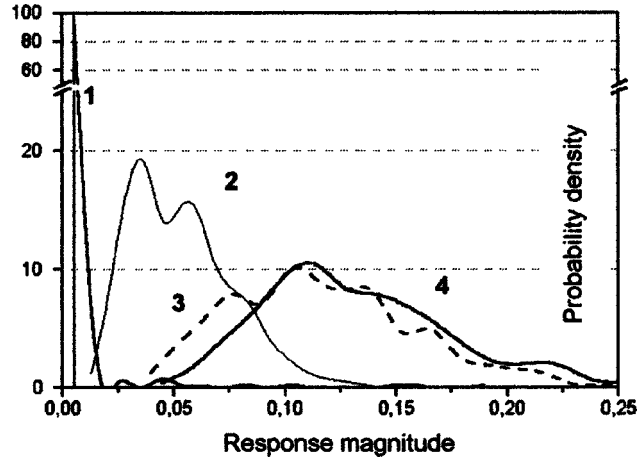

FIG. 4. Experimental histograms for latex particles of different shapes. Here (1) pure water (the histogram added for reference); (2) spheres 1.75 μm; (3) peanuts $1.75\times 2\ \mu$m; (4) peanuts $1.75\times 3.3\ \mu$m.

case of low absorption low effusivity suspensions are much more sensitive to the diameter of particles. This sensitivity is especially large at relatively low fluence. The second case (opaque high effusivity particles) shows less sensitivity with respect to diameters. Moreover, one may not extract any information concerning the size of such particles at low fluence.

III. EXPERIMENTAL AND DISCUSSION

In this section, we present the results of experiments on diluted Latex polystyrene suspensions of various size, shape, and concentration of particles with UV light from an excimer XeCl laser having wavelength 308 nm and energy 3.6 mJ/pulse.

The liquid sample was magnetically stirred to keep the particles in suspension in a spectrophotometric FUV cuvette (cell pathlength 3 cm$\times$1 cm wide). Polystyrene particles of spherical and peanut shapes (Magsphere, Pasadena, CA, 1.75 μm spheres, 6 μm spheres, $1.75\times 2.0\ \mu$m peanuts, $1.75\times 3.3\ \mu$m peanuts) were used. The excimer laser beam was focused to the center of the cell by means of 7.5 cm lens. The laser energy was measured using of a joule meter (Ophir RT-30P). The numerical concentration of suspended particles was about 1000 per microliter, which equals 2×10^{-6} in the illuminated region. A piezoelectric transducer (PAC R15) having the responsivity 7 μV/Pa and the frequency band up to 200 kHz was acoustically coupled to the side of the cell so its face was parallel to the laser beam. The output signal of the transducer passed through the preamplifier with the gain 25 (SRS 240 DC-300 MHz). After additional amplification by the final stage amplifier, the peak to peak signal amplitude was recorded by a digitizing oscilloscope (Lecroy 534) and transferred to a PC computer for data analysis. Histograms of acoustic signal magnitude were collected from a series of 1000 shots per sample and analyzed using a MATLAB-based software program. The number of events was normalized over the width of a bin, so the area under histogram remained constant. Analysis of the shape of the histograms, as well as the calculation of mean and modal acoustic magnitude, is used to reveal the properties of the suspensions.

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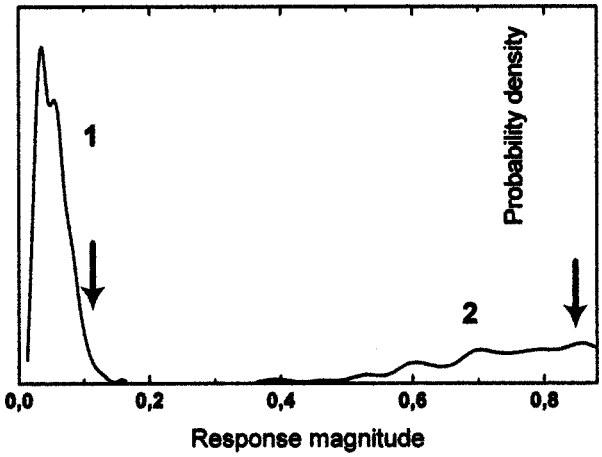

FIG. 5. Experimental histograms for Latex spheres of different size. Here (1) a histogram for a suspension of spheres 1.75 μm diameter; (2) a histogram for a suspension of spheres 6 μm diameter. The arrows mark mean peak response magnitudes.

Following Fig. 4, the technique is very sensitive with respect to content of the suspension. The histogram for pure water (distilled, deionized water, purified using a Barnstead Nanopure Diamond Ultrapure Water System resulting in 18.2 MΩ water) was used as the reference. The acoustic signal in pure water represents some mixture of the bulk thermoacoustical response and signals from ultrasmall natural impurities. The signals from pure water show relatively good repetition (i.e., the ''water'' histogram width is narrow). The response histograms of test suspensions are well separated from the response histograms of the host liquid even if the suspensions are diluted to a great extent. The technique described appears to be less influenced by the host liquid response as opposite to the traditional thermal optoacoustic spectroscopy, which has potential limits determined by the background signal from the solvent.

Figure 4 shows that histograms from elongated (peanut) particles is shifted to the right (higher response) as compared to spherical particles. The histograms are also broader (in width) for the peanut shaped than the spherical shaped particles. This is probably due to the fact that elongated particles have approximately twice the larger volume and also interact with the incident light in a variety of angles.

Figure 5 shows that the ratio of mean peak magnitudes recorded in the two suspensions, the first containing spheres of $d=1.75$ μm and second containing spheres of $D=6$ μm is about 20 which is near $(D/d)^3$. This observation is consistent with the model of low absorption low effusivity particles.

IV. CONCLUSIONS

These results form the basis for which useful parameters of the low-fluence optoacoustic diagnostics of diluted suspensions can be evaluated. For example, we can roughly estimate the potential detection limits of the technique assuming that the limiting factor is a half width of the response histogram from the host liquid. The estimation of the limiting volume concentration for polystyrene 1.75 μm spheres appears to be 10^{-8}–10^{-7}. After optimizing the technique described, the effect may find application in detection of individual microparticles in high purity liquids. Analysis of the acoustic signal statistics can be used to estimate the content of the liquid sample. Moreover, the additional information on the optical properties and size distribution of microparticles can be obtained by analyzing the laser fluence dependence of the averaged acoustic response magnitude.

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[1] (a) J. A. Viator, G. Au, G. Paltauf, S. L. Jacques, S. A. Prahl, H. W. Ren, Z. P. Chen, and J. S. Nelson, Lasers Surg. Med. **30**, 141 (2002); (b) T. Sekine, S. Naito, Y. Kino, and H. Kudo, Radiochim. Acta **82**, 135 (1998).
[2] S. V. Egerev, O. M. Zozulya, and O. V. Puchenkov, in *Photoacousic and Photothermal Phenomena III* (Springer, Berlin, 1992), pp. 50–52.
[3] M. I. Khan and G. J. Diebold, Ultrasonics **33**, 265 (1995).
[4] S. S. Alimpiev, Ya. O. Simanovskii, S. V. Egerev, and A. E. Pashin, Laser Chem. **16**, 63 (1995).
[5] S. V. Egerev and A. V. Fokin, Proc. SPIE **3916**, 210 (2000).
[6] H. C. Van De Hulst, *Light Scattering by Small Particles* (Wiley, New York, 1957).
[7] K. A. Naugol'nykh and N. A. Roi, *Electric Discharges in Water* (Nauka, Moscow, 1971).
[8] R. M. Roberts, J. A. Cook, and T. A. Griffy, J. Acoust. Soc. Am. **99**, 3465 (1996).

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