

## Research Article

## Photoacoustic transients generated by laser irradiation of thin films



Lian Xiong, Jennifer M. Ruddock, Gerald J. Diebold

Brown University, Department of Chemistry, Providence, RI, 02912, USA

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## ABSTRACT

Irradiation of an optically thin layer immersed in a transparent fluid with pulsed laser radiation can generate photoacoustic waves through two mechanisms. The first of these is the conventional optical heating of the layer followed by thermal expansion, in which the mechanical motion of the expansion launches a pair of oppositely directed sound waves. A second, recently reported mechanism, is operative when heat is conducted to the transparent medium raising its temperature, while at the same time reducing the temperature in the absorbing body. The latter mechanism has been shown to result in compressive transients at the leading edges of the photoacoustic waveforms. Here the photoacoustic effect produced by irradiating thin metal films which undergo negligible thermal expansion under optical irradiation, but which generate sound solely by the heat transfer mechanism is investigated. Solution to the wave equation for the photoacoustic effect from the heat transfer mechanism is given and compared with the results of experiments using nanosecond laser pulses to irradiate thin metal films. © 2015 The Authors. Published by Elsevier GmbH. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

The photoacoustic effect is governed a pair of coupled [1–3] differential equations for the temperature  $\tau$  and the pressure  $p$  given by

$$\begin{aligned} (\nabla^2 - \frac{\gamma}{c^2} \frac{\partial^2}{\partial t^2}) p &= -\rho\beta \frac{\partial^2 \tau}{\partial t^2} \\ \frac{\partial}{\partial t} (\tau - \frac{\gamma-1}{\gamma\alpha} p) &= \frac{K}{\rho C_p} \nabla^2 \tau + \frac{H}{\rho C_p}, \end{aligned} \quad (1)$$

where  $c$  is the sound speed,  $\gamma$  is the heat capacity ratio,  $\rho$  is the density,  $\beta$  is the thermal expansion coefficient,  $C_p$  is the specific heat capacity,  $K$  is the thermal conductivity, and  $H$  is the energy deposited per unit volume and time by radiation source. Except for extremely small bodies, the time scale for heat diffusion is much longer than that for sound generation, hence, the properties of the photoacoustic pressure are commonly determined by assuming the thermal conductivity to be zero, in which case the coupled equations reduce [4] to a single wave equation

$$(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) p = -\frac{\beta}{C_p} \frac{\partial H}{\partial t}, \quad (2)$$

obviating solution to the fourth order equation [1,5] that corresponds to Eqs. 1.

It has recently been shown in the case of optically thin fluid bodies immersed in transparent fluids that large amplitude compressive transients are found on the leading edges of the photoacoustic waveforms that are not accounted for by Eq. 2. Despite the fact that production of the photoacoustic effect

with pulsed lasers has been intensely investigated [6–8] since the 1970's, the existence of the compressive transients has only been reported recently. It is likely that such transients had not been previously reported owing to the fact that slight misalignment of a plane transducer with respect to a plane absorbing object results in integration of the transient in time, reducing its amplitude so it is not evident from examination of the photoacoustic waveform. In fact, it was shown [9–11] that misalignment of a plane polyvinylidene fluoride (PVDF) transducer by as little as one degree resulted in the complete disappearance of the transient on the wave recorded from a weakly absorbing glass flat. As the disappearance of the transient is caused by its integration over the plane surface of the transducer, recording the wave with a small diameter transducer can be expected to alleviate this difficulty. With spherically or cylindrically symmetric objects, observation of the transients would require the geometry of the transducer to be matched to that of the irradiated object.

In so far as determining the origin of the transients, it was shown in Refs. [12,11,10] that their presence could be accounted for by taking into account heat conduction in the region of the irradiated object nearest the interface between the absorbing object and the transparent fluid. By keeping the heat conduction term in Eqs. 1 and approximating the heat capacity ratio as unity, it was shown that the coupled equations reduce to the wave equation

$$(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) p = -\rho\beta\chi \frac{\partial}{\partial t} \nabla^2 \tau - \frac{\beta}{C_p} \frac{\partial H}{\partial t}, \quad (3)$$

which contains two source terms, the one found in Eq. 2 and a new term dependent on both the space and time derivatives of the temperature as well as the thermal diffusivity  $\chi$ . The work reported in Refs. [12,11,10] was restricted to determining the character of the transients when, following short pulse irradiation of an optically thin target, the temperature at the surface of the irradiated object decreased, while that of the liquid in contact with its surface increased. Here we investigate the solution of Eq. 3 for the case of delta function deposition of heat in space and time where only a temperature increase in the fluid surrounding target is considered.

The deposition of heat as a delta function in space can be described by considering a layer whose absorption coefficient tends to infinity while its thickness approaches zero, with the product of the two remaining finite. This product gives a dimensionless quantity denoted  $\hat{\alpha}$ . The heating function for a laser pulse with a fluence  $E_0$  irradiating a delta function layer can be written

$$H(x, t) = \hat{\alpha} E_0 \delta(x) \delta(t). \quad (4)$$

The heat diffusion equation, which determines  $\tau$  in Eq. 3, is given by

$$\frac{\partial}{\partial t} \tau = \chi \nabla^2 \tau + \frac{H}{\rho C_p}, \quad (5)$$

which, for the heating function given by Eq. 4, gives the well-known solution [13]

$$\tau(x, t) = \frac{\hat{\alpha} E_0}{2 \rho C_p \sqrt{\pi \chi t}} e^{-x^2/4\chi t}. \quad (6)$$

In determining the photoacoustic effect from short pulse excitation, it is convenient to work with the velocity potential  $\varphi$ , which is governed by the wave equation

$$(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2}) \varphi = \frac{\beta}{\rho C_p} H + \beta \chi \nabla^2 \tau, \quad (7)$$

where the acoustic pressure [14] is determined from  $\varphi$  through

$$p = -\rho \frac{\partial \varphi}{\partial t}. \quad (8)$$

The solution for the conventional photoacoustic effect, which arises from the first term on the right of Eq. 7, can be found by integrating this term over the Green's function for the one-dimensional wave equation [15], giving the velocity potential as

$$\varphi = -\frac{\hat{\alpha} \beta E_0 c}{2 \rho C_p} \int dx' \int dt' \delta(x') \delta(t') \times \quad (9)$$

$$[1 - u(\frac{x-x'}{c} - (t-t'))], \quad (10)$$

where the factor in brackets containing the Heaviside function  $u$  is the Green's function (divided by  $2\pi c$ ) for the one-dimensional wave equation. By differentiating  $\varphi$  with respect  $t$ , the factor in brackets becomes  $\delta[t' - t - (x - x')/c]$ . The integration in Eq. 9 can then be carried out immediately to give

$$p = \frac{\hat{\alpha} \beta E_0 c}{2 C_p} \delta(t - x/c), \quad (11)$$

which describes the right-going photoacoustic wave.

The contribution of the second source term on the right hand side of Eq. 7 can be found by Laplace transformation. The Laplace transform of the time variable in  $t$  given in Eq. 6 can be found in mathematical tables [16]. The wave equation for the velocity

potential in Laplace space  $\varphi$  is thus given by the Helmholtz equation

$$(\frac{\partial^2}{\partial x^2} - k^2) \varphi = \frac{\hat{\alpha} \beta \chi E_0}{\rho C_p} \frac{\partial^2}{\partial x^2} e^{-\sqrt{s\chi}/x}, \quad (12)$$

where  $k = s/c$ , and  $s$  is the Laplace variable. The velocity potentials  $\varphi^R$  and  $\varphi^L$ , which denote potentials to the right and left of the origin, are both governed by Eq. 12 and must obey the acoustic boundary conditions

$$\begin{aligned} \varphi^R|_{x=0} &= \varphi^L|_{x=0} \\ \frac{\partial}{\partial x} \varphi^R|_{x=0} &= \frac{\partial}{\partial x} \varphi^L|_{x=0}. \end{aligned} \quad (13)$$

To simplify solution of the wave equation further, it is convenient to introduce two potentials  $\tilde{\Phi}^R$  and  $\tilde{\Phi}^L$  defined through  $\partial^2 \Phi / \partial x^2 = \varphi$ , which, on substitution into Eq. 12, gives the Helmholtz equation for both potentials as

$$(\nabla^2 - k^2) \tilde{\Phi} = \frac{\hat{\alpha} \beta \chi E_0}{\rho C_p} e^{-\sqrt{s\chi}/x}. \quad (14)$$

Solutions for the two potentials are found to be

$$\tilde{\Phi}^R = \frac{\hat{\alpha} \beta E_0 c^2 \chi^{3/2} e^{-x\sqrt{s/\chi}}}{2s^{3/2}(c^2 - s\chi)\rho C_p} + C_R e^{-sx/c} \quad (15)$$

$$\tilde{\Phi}^L = \frac{\hat{\alpha} \beta E_0 c^2 \chi^{3/2} e^{x\sqrt{s/\chi}}}{2s^{3/2}(c^2 - s\chi)\rho C_p} + C_L e^{sx/c},$$

where  $C_R$  and  $C_L$  are constants. The boundary conditions for  $\Phi$  can be found from Eqs. 13 as

$$\begin{aligned} \frac{\partial^2}{\partial x^2} \tilde{\Phi}^R|_{x=0} &= \frac{\partial^2}{\partial x^2} \tilde{\Phi}^L|_{x=0} \\ \frac{\partial^3}{\partial x^3} \tilde{\Phi}^R|_{x=0} &= \frac{\partial^3}{\partial x^3} \tilde{\Phi}^L|_{x=0}. \end{aligned} \quad (16)$$

Since only the terms in Eqs. 15 containing exponential factors of the form  $\exp(\pm sx/c)$  result in travelling waves when transformed back to the time domain, the other terms in Eq. 15 are not carried forward, as they correspond to thermal mode [1] waves that do not propagate. After applying the boundary conditions to determine the constants in Eqs. 15, the velocity potential for the right-going acoustic wave is found to be

$$\begin{aligned} \tilde{\varphi}^R &= -\frac{\hat{\alpha} \beta E_0 c}{2s\rho C_p} e^{-sx/c} - \frac{\hat{\alpha} \beta E_0 \chi}{2c\rho C_p} e^{-sx/c} \\ &+ \frac{\hat{\alpha} \beta E_0 \chi^3 s^2}{2c^3 \rho C_p (s\chi - c^2)} e^{-sx/c}. \end{aligned} \quad (17)$$

The time domain velocity potential is found using the following two inverse Laplace transforms [16] calculated with  $x > 0$ ,

$$\begin{aligned} \mathcal{L}^{-1}[-\frac{\hat{\alpha} \beta E_0 c}{2s\rho C_p} e^{-sx/c}] &= -\frac{\hat{\alpha} \beta E_0 c}{2\rho C_p} u(t - x/c) \\ \mathcal{L}^{-1}[-\frac{\hat{\alpha} \beta E_0 \chi}{2c\rho C_p} e^{-sx/c}] &= -\frac{\hat{\alpha} \beta E_0 \chi}{2c\rho C_p} \delta(t - x/c). \end{aligned}$$

The pole in complex integration [17] used to determine the inverse Laplace transform of the last term in Eq. 17 lies in the right hand complex plane; hence the value of the integral is taken to be zero. The velocity potential  $\varphi^R$  is thus found to be

$$\varphi^R = \frac{\hat{\alpha} \beta E_0 \sqrt{\chi}}{2\rho C_p} [\sqrt{\frac{c^2}{\chi}} u(t - x/c) + \sqrt{\frac{\chi}{c^2}} \delta(t - x/c)]. \quad (18)$$

The right-going photoacoustic wave, which includes contributions from Eq. 11 and Eq. 18, determined according to Eq. 8, is thus found to be

$$p = \frac{\alpha \beta E_0 c}{2C_p} [2\delta(t - x/c) - \frac{\chi}{c^2} \delta'(t - x/c)], \quad (19)$$

the factor of two in the delta function term arising from contributions from the conventional photoacoustic effect and the photoacoustic effect from heat diffusion.

When comparing the calculated time dependence of the photoacoustic pressure with experimental waveforms, it is convenient to consider the exciting laser pulse as a Gaussian function of time. Convolution of the result given by Eq. 19 with a Gaussian function the form  $(1/\sqrt{\pi})\exp(-t^2/\theta^2)$ , where  $\theta$  is the pulse width parameter, gives for the wave travelling along the positive  $x$  direction

$$p = \frac{\alpha \beta E_0 c}{\sqrt{\pi} \theta C_p} \left[ e^{-\frac{(t-x/c)^2}{\theta^2}} - \frac{\chi}{c^2 \theta^2} (t - x/c) e^{-\frac{(t-x/c)^2}{\theta^2}} \right]. \quad (20)$$

Equation 20 indicates that the photoacoustic pressure emanating from a film irradiated by a laser pulse with a Gaussian time profile consists of a travelling compressive wave with a Gaussian time profile and a second wave proportional to the time derivative of the compressive wave.

The propagation of a fast acoustic pulse through a fluid results in broadening of the pulse as a result of viscous and heat conduction effects. The effect of these loss mechanisms on a Gaussian pulse can be found by Fourier transforming the Gaussian pulse and multiplying it by the frequency domain attenuation [18] given by

$$e^{-\chi \frac{\omega^2}{2\rho c^3} (\frac{4}{3}\mu + \eta + K \frac{V_p - 1}{c_p})}$$

and then carrying out the inverse Fourier transform to give the profile of the pulse in the time domain. This procedure gives the photoacoustic pressure after traveling a distance  $x$  as

$$P(x, t) = \frac{\alpha \beta E_0 c}{\sqrt{\pi} C_p \Theta} e^{-\frac{(t-x/c)^2}{\Theta^2}}, \quad (21)$$

where the effective pulse width is now given by

$$\Theta = \sqrt{\theta^2 + \frac{2x}{\rho c^3} (\frac{4}{3}\mu + \eta)},$$

where  $\mu$  and  $\eta$  are the shear and bulk viscosities, respectively. The effects of heat conduction, which are of negligible magnitude here, have been omitted. It can be seen that viscous effects act to broaden and reduce the amplitude of the Gaussian pulse as it propagates.

Experiments were carried out by irradiating metallized plastic foils attached to a flat plate. Two foils were studied, the first was a 17  $\mu\text{m}$  thick, fluorinated ethylene propylene plastic film with an 8  $\mu\text{m}$  thick Al coating; the second was a gold target made by pressing 0.5  $\mu\text{m}$  thick gold foil against transparent, 10  $\mu\text{m}$  thick, polyvinyl chloride film. The targets were suspended on precision rotation stages so that they could be accurately aligned with a plane PVDF transducer that was located approximately 4 cm from the target. The transducer was made from a poled 50  $\mu\text{m}$  thick PVDF film glued to a cylindrical block of PVDF, which was encased in a stainless steel housing. The transducer output was attached directly to a 200 MHz bandwidth, 1 M $\Omega$  input impedance amplifier (Femto, Inc. Model HVA 200M-40F) with a gain of 20 db. As shown in Fig. 1, the 532 nm frequency doubled output from a Q-switched Nd:YAG laser was directed through a lens with a focal length of 25 cm placed

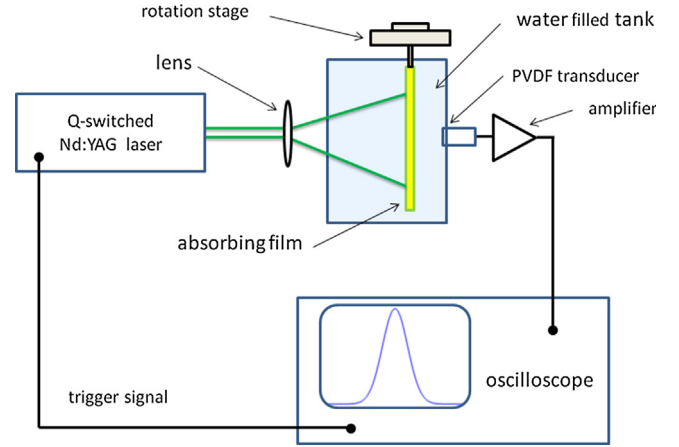


Fig. 1. Diagram of the apparatus for generating the photoacoustic effect from a thin absorbing layer.

roughly 1.2 m from the target to expand the beam on the film so as to approximate a one-dimensional geometry. The spatial beam profile of the laser, as specified by the laser manufacturer, is a “top hat”. Fig. 2 shows the results of an experiment with the Al coated foil showing a single compressive photoacoustic pulse. The additional slow rise in the signal after the acoustic pulse arises from a slight heating of the PVDF transducer from imperfections in the target which allows a small amount of light to strike the transducer producing a photothermal signal that underlies the baseline beginning at the time of firing of the laser. The results from the gold foil are virtually identical to those from the Al coated foil.

As can be seen from Eq. 21, the pulse width parameter  $\Theta$  gives the 1/e point for the pulse amplitude. For  $\theta$  equal to 10 ns, and  $\mu$  and  $\eta$   $2.47 \times 10^{-3}$  and  $8.88 \times 10^{-4} \text{ Pa} \cdot \text{s}$ , respectively, for water at room temperature (taken from Ref. [19]), the parameter  $\Theta$  is 14 ns. The 29 ns 1/e point for the ultrasonic pulse shown in Fig. 2 is considerably larger than the figure calculated from viscous damping. However, given that the sound speed in PVDF is 2300 m/s, the transit time broadening caused by the finite thickness of the transducer, 21 ns, is almost surely what accounts for the pulse width of the recorded photoacoustic wave. The experimental results given here are thus only a qualitative confirmation of the predictions of Eq. 19.

The problem chosen here considers a one-dimensional fluid possessing an infinitesimally thin absorbing region having the same acoustic properties as the surrounding transparent fluid, which generates a photoacoustic effect through two mechanisms. The first is the conventional photoacoustic genera-

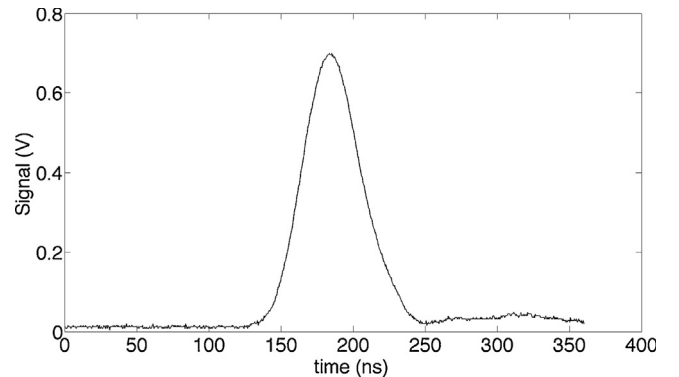


Fig. 2. Transducer output voltage (after amplification by 20 db) versus time for an Al film irradiated by a 532 nm laser pulse. The laser fluence on the target was 12 J/m<sup>2</sup>.

tion mechanism of heating of the absorbing region, creating immediate temperature and pressure increases, followed by the launching of sound through the mechanical motion of the expansion. It can be seen from Eq. 11 that a delta function heating pulse generates a compressive, delta function acoustic pulse. The second mechanism of sound production is caused by heat diffusion outwardly from the irradiated layer to create a thermal expansion in the surrounding transparent fluid, which, according to Eq. 18 gives both a compressive delta function pressure pulse, qualitatively identical to that from conventional photoacoustic effect, and a second pulse proportional to the derivative of a delta function containing both compressions and rarefactions – both pulses arising from heat conduction to the surrounding fluid following optical deposition of energy rather than thermal expansion of the absorbing body itself, as in the conventional photoacoustic effect. Note that the factor of  $\chi/c^2\theta$ , which multiplies the dimensionless retarded time in Eq. 20, for a 10 ns laser pulse generating a photoacoustic effect in water is on the order of  $6 \times 10^{-6}$ , making the second wave virtually undetectable without employment of significantly shorter light pulses than those used here.

Previously [20], it was shown for short pulse excitation that the time profile of conventional photoacoustic effect, which is described by the first forcing term in Eq. 3, can be found as a mapping of the spatial deposition of heat in the absorbing fluid. In the present case, the mapping shows that the delta function light pulse generates a traveling delta function acoustic pulse. The conventional mechanism of sound generation using pulsed optical excitation is based on thermal expansion of the irradiated object, which, as a result of the mechanical motion of the target itself launches a sound wave. For the mechanism arising from heat conduction considered here, the target acts only as a passive absorber, transmitting energy through rapid heat conduction to the surrounding fluid where a photoacoustic effect is generated. In so far as sound generation from the thermal conduction mechanism is concerned, the results of the above calculations indicate that for thin fluid targets excited by nanosecond long optical pulses, the same delta function compressive pulse as expected from the conventional photoacoustic effect will be seen in experiments, as only the factor of two in amplitude given in Eq. 19 is the consequence of the heat conduction. In general, however, for bodies that cannot be taken as vanishingly thin, the heat conduction mechanism, as shown in Refs. [12,11,10] results in pressure transients on the leading edge of the photoacoustic waveform having an entirely different character than that calculated from the conventional wave equation for pressure.

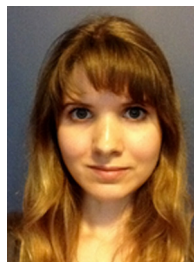
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**Lian Xiong** was born in Hubei, China. He attended the University of Science and Technology in Hefei and was awarded a B.S. degree in physics. He is currently a graduate student in the Chemistry Department at Brown University working for his Ph.D.



**Jennifer Ruddock**, a native of Massachusetts, attended Vanderbilt University in Tennessee and graduated with a B.S. degree in chemistry. She is currently a graduate student at Brown University working on her Ph.D. in physical chemistry.



**Gerald Diebold** graduated from the University of Notre Dame and obtained his Ph.D. in physics from Boston College. After holding postdoctoral positions at Boston College, Columbia University, and Stanford Universities, he joined the faculty at Brown, where he is currently Professor of Chemistry. Professor Diebold was granted Fellowship in the American Physical Society and has been awarded the Smith Prize for his work in photoacoustics.