Photoacoustic Point Source

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We investigate the photoacoustic effect generated by heat deposition at a point in space in an inviscid fluid. Delta-function and long Gaussian optical pulses are used as sources in the wave equation for the displacement potential to determine the fluid motion. The linear sound-generation mechanism gives bipolar photoacoustic waves, whereas the nonlinear mechanism produces asymmetric tripolar waves. The salient features of the photoacoustic point source are that rapid heat deposition and nonlinear thermal expansion dominate the production of ultrasound.

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The production of ultrasonic waves from absorption of electromagnetic radiation, known as the photoacoustic effect [1], is generally described as arising from a linear thermal expansion mechanism. The optical deposition of energy causes a heating and thermal expansion of the absorber, the motion from expansion acting as a source for the production of sound waves. Since acoustic radiation is emitted wherever heat is deposited, the spatial and temporal character of emitted acoustic wave necessarily carries information about the geometry and optical properties of the absorber [1–3], which principle has recently been used as the basis for a photoacoustic imaging method [4–6]. It is not surprising that the spatial and temporal profile of a photoacoustic wave can be used analogously to give information on the mechanism of sound generation in cases where the linear thermal expansion is not operative. In this Letter we describe photoacoustic waves generated by thermal diffusion from a point source for delta function and long pulse deposition of heat. The waves are shown to possess features highly characteristic of both the thermal nonlinearity of the fluid and the point character of the source.

For a fluid whose heat capacity ratio can be approximated as unity, the coupled differential equations [7] for the pressure and temperature uncouple, giving a heat diffusion equation and a wave equation for pressure. The former, for a problem with spherical symmetry, is given by

$$\kappa\nabla^2 T(r,t) + H(r,t) = \rho c_P \frac{\partial T(r,t)}{\partial t}, \qquad (1)$$

where T is the temperature, H is the optical energy deposited per volume and time, κ is the thermal conductivity, ρ is the density, c_P is the specific heat capacity, r is the radial coordinate, and t is the time. Rather than working with the wave equation for pressure, it is often more convenient to work with the equivalent wave equation for the displacement potential Φ

$$\left(\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\Phi(r,t) = T(r,t)[\beta_1 + \beta_2 T(r,t)], \qquad (2)$$

where c is the sound speed. The parameters β_1 and β_2 are the first two coefficients in a power series expansion of the thermal expansion coefficient [1]. The two parameter approximation provides some latitude in describing the expansion coefficient of a number of fluids, notably H_2O, but, at the same time, restricts on the range of applicability of the results given here. The acoustic pressure p and displacement $\boldsymbol{u}$ are found from the potential as

$$p = -\rho\frac{\partial^2\Phi(r,t)}{\partial t^2} \quad \text{and} \quad \boldsymbol{u} = \nabla\Phi(r,t). \qquad (3)$$

The substitution of $\Phi^\dagger = r\Phi$ converts the three-dimensional wave equation (2) into a one-dimensional equation of the form

$$\left(\frac{\partial^2}{\partial t^2} - c^2\frac{\partial^2}{\partial r^2}\right)\Phi^\dagger = rQ(r,t), \qquad (4)$$

where $Q(r,t)$ is a radial source function odd in r, the d'Alembert solution to which can be written [8]

$$\Phi^\dagger(r,t) = \frac{1}{2c}\int_0^t ds \int_{r-c(t-s)}^{r+c(t-s)} Q(u,s)u\,du. \qquad (5)$$

For the present problem, $\Phi^\dagger$ can be decomposed into two components, $\Phi^\dagger = \Phi_1^\dagger + \Phi_2^\dagger$, where $\Phi_1^\dagger$ is a solution to Eq. (5) with $\beta_2 = 0$ and $\Phi_2^\dagger$ is the corresponding solution with $\beta_1 = 0$.

Consider the solution of Eq. (2) with only the source term linear in T with a delta function optical heating pulse. The temperature distribution found from the heat equation for such a source for $t \geq 0$ is given by [9]

$$T(r,t) = \frac{E_0\sigma}{8\rho c_P}\frac{e^{-r^2/4\chi t}}{(\pi\chi t)^{3/2}}, \qquad (6)$$

where E_0 is the fluence in the laser beam, σ is the optical cross section of the particle, and χ is the thermal diffusivity given by $\chi = \kappa/\rho c_P$. Substitution of Eq. (6) into Eq. (2) gives an equation for $\Phi_1^\dagger$ whose solution according to Eq. (5) is

$$\Phi_1^\dagger(r,t) = -\frac{E_0\sigma\beta_1 c}{16\rho c_P(\pi\chi)^{3/2}} \times \int_0^t \frac{ds}{s^{3/2}}\int_{r-c(t-s)}^{r+c(t-s)} ue^{-u^2/4\chi s}\,du. \qquad (7)$$

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The integrand is a perfect differential in u so that the integration is immediate. Substitution of $\xi = (c^2 s/\chi)^{1/2}$ into the resulting integral over s gives

$$\Phi_1^\dagger(r,t) = \frac{E_0 \sigma \beta_1}{4\rho c_P \pi^{3/2}} \int_0^{(c^2 t/\chi)^{1/2}} [e^{-(\hat{r}^+ - \xi^2)^2/4\xi^2} - e^{-(\hat{r}^- + \xi^2)^2/4\xi^2}]\, d\xi\,, \tag{8}$$

where the dimensionless distance parameters $\hat{r}^+$ and $\hat{r}^-$ have been defined as $\hat{r}^- = \frac{c}{\chi}(r - ct)$ and $\hat{r}^+ = \frac{c}{\chi}(r + ct)$. The integrals in Eq. (8) can be evaluated [10] for large values of $(c^2 t/\chi)^{1/2}$ to give

$$\Phi_1(r,t) = \frac{E_0 \sigma \beta_1}{4\pi \rho c_P r}[1 - e^{\hat{t}^-}][1 - \mathsf{u}(\hat{t}^-)], \tag{9}$$

where u is the Heaviside function, Φ_1 is the displacement potential corresponding to $\Phi_1^\dagger$, and $\hat{t}^-$ is the dimensionless retarded time from the origin. The dimensionless times corresponding to $\hat{r}^-$ and $\hat{r}^+$ are defined as $\hat{t}^- = \frac{c^2}{\chi}(t - \frac{r}{c})$ and $\hat{t}^+ = \frac{c^2}{\chi}(t + \frac{r}{c})$. The photoacoustic pressure according to Eq. (3) is thus given as

$$p_1 = \frac{E_0 \sigma \beta_1 c^4}{4\pi c_P \chi^2 r}[e^{\hat{t}^-}[1 - \mathsf{u}(\hat{t}^-)] - \delta(\hat{t}^-)], \tag{10}$$

which is a compressive, rising, exponential wave followed by a delta function rarefaction, as shown in Fig. 1.

Values of rise time of the waveform predicted by Eq. (10) for common fluids are so short, e.g., 60 fs for H_2O, that recording of the waveform would present serious experimental difficulties for this reason alone. It is more useful to determine the limiting form of the wave when the laser pulse is long compared with χ/c^2. For long optical pulses, the photoacoustic pressure is given by convolution of the pressure response from a delta function heating pulse from Eq. (10) with the intensity profile of the exciting optical beam. For an optical pulse with an intensity of the form $I(t) = \frac{E_0}{\theta} f(t/\theta)$, the pressure is thus given as

$$p = \frac{E_0 \sigma \beta_1 c^4}{4\pi \theta c_P \chi^2 r}[e^{\hat{t}^-}\mathsf{u}(-\hat{t}^-) - \delta(\hat{t}^-)] * f(t/\theta), \tag{11}$$

where $*$ indicates a convolution over t, and θ is a pulse width parameter. The convolution integral can be expressed as a frequency domain integral over the product of the Fourier transforms of both factors in Eq. (11), which, after appropriate grouping, can be expressed as

$$p = \frac{E_0 \sigma \beta_1 c^4}{4\pi \theta c_P \chi^2 r}\left\{\left[\frac{e^{-c^2\theta/\chi|t/\theta|}}{2} - \frac{\delta(\frac{t}{\theta})}{c^2\theta/\chi}\right] * f(\hat{\tau}) + \left[\frac{e^{-c^2\theta|t/\theta|}}{2c^2\theta/\chi}\right] * f'(\hat{\tau})\right\}, \tag{12}$$

where $\hat{\tau}$ is given by $\hat{\tau} = (t - r/c)/\theta$. The quantity $c^2\theta/\chi$ is generally large for common fluids even with a laser pulse width parameter as small as 10^{-8} s; thus, the exponential functions in Eq. (12) can be considered as highly peaked around the zero of the argument of the exponential, $t \cong 0$.

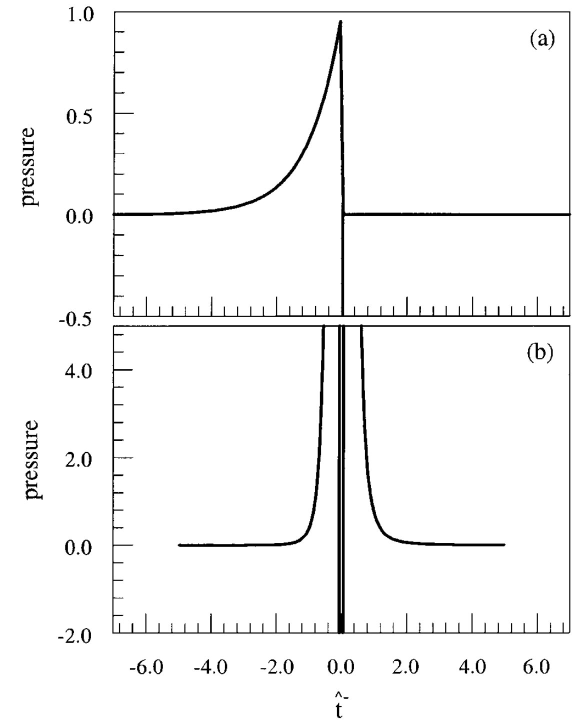

FIG. 1. Photoacoustic pressure in arbitrary units versus retarded time from the origin from (a) the linear temperature contribution, and (b) from the nonlinear temperature contribution, to the wave equation for a delta function heating pulse.

Now Laplace's method of approximation is based on the limiting form of the argument of an exponential function as λ becomes large,

$$e^{-\lambda \hat{f}(t)} \cong \delta(t - t_0) \int_{-\infty}^{\infty} e^{-\lambda \hat{f}(x)}\, dx\,, \tag{13}$$

where t_0 is the unique zero of function $\hat{f}(t)$, and where it is sufficient that $\hat{f}(t)$ be non-negative for all t. For the present problem $c^2\theta/\chi$ corresponds to λ which is large, but finite, and the point t_0 corresponds to 0. Since the required integral in Laplace's method is simply $\int_{-\infty}^{\infty} \exp(-\frac{c^2\theta}{\chi}|x|)\, dx$, it follows that $\exp(-\frac{c^2\theta}{\chi}|\frac{t}{\theta}|) \cong (2\chi/c^2\theta)\delta(\frac{t}{\theta})$. Thus, the term in Eq. (12) with the convolution over $f(\hat{\tau})$ vanishes, leaving only the term with the derivative of $f(\hat{\tau})$, and the long pulse photoacoustic response is given by

$$p = \frac{E_0 \sigma \beta_1}{4\pi \theta^2 c_P r}\frac{d}{d\hat{\tau}} f(\hat{\tau})\,. \tag{14}$$

A plot of the acoustic pressure produced by a Gaussian heating pulse is shown in Fig. 2.

For delta function heating, the d'Alembert solution to the wave equation with the nonlinear source is

$$\Phi_2^\dagger(r,t) = -\frac{1}{128}\left(\frac{E_0\sigma}{\rho c_P}\right)^2 \frac{\beta_2 c}{(\pi\chi)^3} \times \int_0^t \frac{ds}{s^2}\int_{r-c(t-s)}^{r+c(t-s)} u e^{-u^2/2\chi s}\, du\,. \tag{15}$$

Following integration over u, and substitution of $\zeta = \chi/c^2 s$, Eq. (15) can be written as

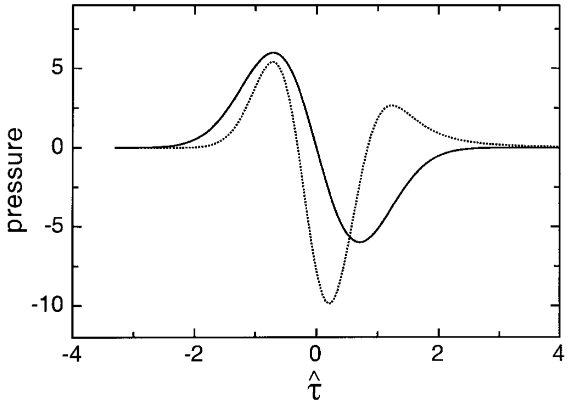

FIG. 2. Photoacoustic pressure versus retarded time $\hat{\tau}$ from the origin for long, Gaussian heating pulses from (–) the linear source, and $(\cdots)$ the nonlinear source given by Eq. (25). The latter is found by numerical differentiation of the displacement potential. The pressure minimum is found numerically to be at $\hat{\tau} = 0.291$.

$$\Phi_2^{\dagger}(r,t) = -\frac{\beta_2}{128}\left(\frac{E_0\sigma}{\rho c_P}\right)^2\left(\frac{c}{\pi\chi}\right)^3 \times \int_{(\chi/c^2 t)}^{\infty}\left[e^{-(\hat{r}^+\zeta-1)^2/2\zeta} - e^{(\hat{r}^-\zeta+1)^2/2\zeta}\right]d\zeta\,. \tag{16}$$

To determine the far field acoustic pressure where $c^2t/\chi \gg 0$, the range of integration can be taken as 0 to ∞, giving the displacement potential corresponding to $\Phi_2^{\dagger}$ as

$$\Phi_2(r,t) = \left(\frac{\beta_2}{64r}\right)\left(\frac{E_0\sigma}{\rho c_P}\right)^2\left(\frac{c}{\pi\chi}\right)^3 \times \left[e^{\hat{t}^+}\,\frac{K_1(\hat{t}^+)}{\hat{t}^+} - e^{\hat{t}^-}\,\frac{K_1(|\hat{t}^-|)}{|\hat{t}^-|}\right], \tag{17}$$

where K_1 is a modified Bessel function. The photoacoustic pressure is found from Eq. (3), which for small values of $\hat{t}^-$, can be approximated as

$$p_1 = \frac{3E_0^2\sigma^2\beta_2 c^7}{64c_P^2\pi^3\rho\chi^5 r}\left[\frac{1}{|\hat{t}^-|^4} - \frac{2}{3}\,\frac{\delta(\hat{t}^-)}{|\hat{t}^-|^3}\right]. \tag{18}$$

As shown in Fig. 1 the photoacoustic pressure is a sharply rising wave with a discontinuity at $\hat{t}^- = 0$.

Consider the solution to the wave equation with the nonlinear source term for long laser pulses. Here, since the temperature distribution must be given explicitly before it is squared and used as a source in the wave equation, the functional form of the heating pulse must be specified from the outset. For a Gaussian laser pulse where $f(t/\theta) = \pi^{-1/2}\exp[-(t/\theta)^2]$, the temperature distribution is given by the convolution integral,

$$T(r,t) = \frac{E_0\sigma}{8\pi^2\rho c_P\chi^{3/2}\theta}\int_0^{\infty}\left[\frac{e^{-r^2/2\chi\xi}}{\xi^{3/2}}\right]e^{-(t-\xi/\theta)^2}\,d\xi\,. \tag{19}$$

The d'Alembert solution to the wave equation is thus

$$\Phi_2^{\dagger}(r,t) = -\frac{\beta_2 c}{128\chi^3}\left(\frac{E_0\sigma}{\pi^2\rho c_P\theta}\right)^2 \times \int_{-\infty}^{t}ds\int_{r-c(t-s)}^{r+c(t-s)}dw\int_{-\infty}^{s}ds_1\int_{-\infty}^{s}ds_2 \times w\left[\frac{e^{-w^2/2\chi s_1 - w^2/2\chi s_2}}{s_1^{3/2}\,s_2^{3/2}}\right]e^{-[(s-s_1)/\theta]^2-[(s-s_2)/\theta]^2}, \tag{20}$$

which, after integration over w, elimination of the term containing $\hat{t}^+$, and division of the remaining integration variables by θ, gives

$$\Phi_2^{\dagger}(r,t) = -\frac{c\beta_2}{128\theta}\left(\frac{E_0\sigma}{\pi^2\chi\rho c_P}\right)^2\int_{-\infty}^{t/\theta}du\int_0^{\infty}du_1\int_0^{\infty}du_2\left[\frac{e^{-(u-u_1)^2-(u-u_2)^2}}{(u_1+u_2)\sqrt{u_1u_2}}\right]e^{-[(u_1+u_2)/u_1u_2][(u-\hat{\tau})^2/(2\chi/c^2\theta)]}. \tag{21}$$

Now, for a typical fluid, the quantity $\chi/c^2\theta$ is small even for a laser pulse with a duration as short as 1 ns. For a 1 ns pulse irradiating water, for example, this parameter has a value of 6.3×10^{-5}, which means that the last exponential function in Eq. (21) is highly peaked around the zero of its argument. Laplace's approximation method can be used in the integration over u. The zero of the function is found at $u = \hat{\tau}$, and the required integral in Laplace's method is $\int_{-\infty}^{\infty}\exp-(\frac{u_1+u_2}{u_1u_2})\frac{(u-\hat{\tau})^2}{2\chi/c^2\theta}\,du = (2\pi\chi/c^2\theta)^{1/2}[u_1u_2/(u_1+u_2)]^{1/2}$. After integration over the delta function, Eq. (21) becomes

$$\Phi_2^{\dagger}(r,t) = -\frac{\sqrt{2}\,\beta_2}{128(\pi\theta\chi)^{3/2}}\left(\frac{E_0\sigma}{\pi\rho c_P}\right)^2 \times \int_0^{\infty}du_1\int_0^{\infty}du_2\,\frac{e^{-(\hat{\tau}-u_1)^2-(\hat{\tau}-u_2)^2}}{(u_1+u_2)^{3/2}}\,. \tag{22}$$

Transformation of the integration variables by the rotation $v_1 = \frac{1}{\sqrt{2}}(u_1+u_2)$ and $v_2 = \frac{1}{\sqrt{2}}(u_1-u_2)$ reduces $\Phi_2^{\dagger}$ to

$$\Phi_2^{\dagger}(r,t) = -\frac{\sqrt{2}\,\beta_2}{128(\pi\theta\chi)^{3/2}}\left(\frac{E_0\sigma}{\pi\rho c_P}\right)^2\int_0^{\infty}dv_1\int_{v_1}^{-v_1}dv_2 \times\left[\frac{e^{(1/2)[\sqrt{2}\,\hat{\tau}-(v_1-v_2)]^2-(1/2)[\sqrt{2}\,\hat{\tau}-(v_1+v_2)]^2}}{(\sqrt{2}\,v_1)^{3/2}}\right], \tag{23}$$

which can then be written as

$$\Phi_2(r,t) = -\frac{\beta_2}{128\pi^3(\chi\theta)^{3/2}r}\left(\frac{E_0\sigma}{\rho c_P}\right)^2 e^{-2\hat{\tau}^2} \times\int_0^{\infty}\left[\frac{\mathrm{erf}(\xi/\sqrt{2})}{\xi^{3/2}}\right]e^{-(\xi^2/2-2\xi\hat{\tau})}\,d\xi\,. \tag{24}$$

The acoustic pressure for long laser pulses is thus

$$p = \left(\frac{\beta_2E_0^2\sigma^2}{128\pi^3c_P^2\chi^{3/2}\theta^{7/2}\rho r}\right)\frac{\partial^2}{\partial\hat{\tau}^2}\,e^{-2\hat{\tau}^2} \times\int_0^{\infty}\left[\frac{\mathrm{erf}(\xi/\sqrt{2})}{\xi^{3/2}}\right]e^{-(\xi^2/2-2\xi\hat{\tau})}\,d\xi\,, \tag{25}$$

which, as is shown in Fig. 2, is an asymmetric tripolar wave.

The waveforms given here necessarily reflect characteristics of the heat diffusion equation, most notably, a rapid temperature rise that extends throughout space immediately after $t = 0$, which manifests itself in the acoustic wave as a failure to obey causality. As shown by Eq. (14), the photoacoustic pressure generated a long light pulse for the linear problem and is proportional to the first time derivative of the optical intensity [2], which according to Ref. [11], is identical to that for a uniformly irradiated sphere. Thus, no change in the functional form of the photoacoustic wave for a uniformly irradiated particle as its diameter is reduced to zero is predicted—even the θ^{-2} dependence of the amplitude on pulse width is preserved. For the nonlinear sound generation mechanism, there is an asymmetry of wave with respect to the retarded time. The initial deposition of heat at the beginning of the heating pulse acts to increase the thermal expansion coefficient. Generation of sound by the subsequent addition of heat takes place with higher efficiency causing a shift in the center of the waveform to positive values of the retarded time. In a qualitative way, the tripolar shapes of either the short or long pulse response from the $T^2(r,t)$ source can be pictured as the effect of two thermal pulses, the first giving a compression followed by a rarefaction as the result of a heating pulse, added together with a rarefaction followed by a compression caused by a "cooling" pulse a short time later. The cooling pulse represents the effect of rapid heat diffusion from an already compressed region of fluid around the point source that reduces the magnitude of the temperature squared term to zero launching a wave that is initially a rarefaction. The reason that the linear and quadratic temperature terms act so differently is that the space integral of $T(r,t)$ is a time independent quantity, whereas the same integral of $T^2(r,t)$ vanishes for a long time. Unlike the linear photoacoustic effect where heat diffusion is of no consequence, the nonlinear photoacoustic effect is highly sensitive to the volume in which heat is deposited and to the rate at which it diffuses.

The absorption of 100 fJ by room temperature water, an estimated based on what a carbon particle with a radius of 100 nm irradiated by the unfocused, 1 cm^2 output of an 16 ns, 1 J Q-switched laser with would absorb, gives a photoacoustic wave where the nonlinear contribution is 1500 times as large as the linear contribution. The fact that the thermal nonlinearity dominates the production of sound from a small source suggests the thermal nonlinearity as playing a role in generation of the remarkably intense photoacoustic pulses reported by Egerev and co-workers [12] in microparticulate suspensions. In the case of transient grating experiments where both the thermal and acoustic modes of wave motion determine the time dependence of the diffracted light signal, the T^2 source term discussed here gives an acoustic wave and a vanishing thermal mode wave. The disappearance of the latter in time provides a mechanism for production of the "frequency doubled" signal which heretofore has been attributed only to chemical reaction [13,14]. Although the role of the thermal nonlinearity in the expansion coefficient of water has been identified in the anomalous dependence of the photoacoustic effect on temperature in water [15–17] at 4 °C, it is clear from the present investigation that the thermal nonlinearity is paramount in determining the character of the photoacoustic effect in multiphase solutions such as colloids, micelles, and solid suspensions where a high concentration of heat results from the absorption of radiation.

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