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► **To cite this version:**

B. Bein, J. Pelzl. THEORY OF SIGNAL GENERATION IN A PHOTOACOUSTIC CELL. Journal de Physique Colloques, 1983, 44 (C6), pp.C6-27-C6-34. 10.1051/jphyscol:1983604 . jpa-00223163

HAL Id: jpa-00223163

<https://hal.science/jpa-00223163v1>

Submitted on 4 Feb 2008

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THEORY OF SIGNAL GENERATION IN A PHOTOACOUSTIC CELL

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RESUME - La pression dans une cellule photoacoustique est déduite des équations fondamentales décrivant la dynamique des gaz.

ABSTRACT - Based on the fundamental physical equations governing the dynamical behaviour of a gas, the pressure signal is derived for a gas-filled photoacoustic cell in contact with a radiation-heated solid sample.

1. INTRODUCTION

The photoacoustic effect (PAE) associated with solids is known since a century. Only during the last decade, however, it has found considerable application in connection with Photoacoustic Spectroscopy (PAS) and Photoacoustic Calorimetry (PAC) for the surface and subsurface analysis of solids.

The understanding of this effect has been obscure and controversial for a long time, and only in recent years a theoretical description of the sound generation in the gas volume has been achieved, thereby giving the possibility of relating the thermal or optical properties of the solid to the pressure signals in the PA cell. Generally accepted for the interpretation of PA measurements is the intuitive piston model /1/ which considers two distinct regions in the gas volume: A thin isobaric thermal boundary layer expanding and contracting at the solid gas interface, thus acting as a piston on the major part of the gas volume which is characterized by the adiabatic gas law. Another limit of the general equation of state of the ideal gas, the isochoric limit, has recently been used for the interpretation of the pressure signals in a PA cell of rather short gas length /2/. Alternatively, various other theories for the interpretation of PA measurements have been based on the formalism of linearized acoustics /3,4,5,6/.

In the present work, the signal generation in a gas-filled PA cell is treated

- without such restrictive a-priori assumptions about the equation of state of the gas,
- with one formalism valid for the entire gas volume,
- and avoiding an a-priori linearization.

Starting point of this analysis are the basic equations of fluid dynamics, then a generalized equation for the acoustic signal generation is derived, special solutions are given, and various solution limits (piston model, PA cell of short gas length, etc.) are discussed subsequently.

2. THE PHYSICAL MODEL - BASIC FLUID DYNAMIC EQUATIONS

The basic four laws of fluid dynamics valid for the entire gas region are

$$p = R \rho T, \quad (1)$$

$$\frac{D\rho}{Dt} + \rho \operatorname{div} \vec{v} = 0 \quad , \quad (2)$$

$$\rho \frac{D\vec{v}}{Dt} = \vec{G} - \operatorname{grad} p + \mu \Delta \vec{v} + \frac{\mu}{3} \operatorname{grad} \operatorname{div} \vec{v} \quad , \quad (3)$$

$$\rho c_v \frac{DT}{Dt} = - \operatorname{div} \vec{F} - p \operatorname{div} \vec{v} + \mu \Phi \quad . \quad (4)$$

The above equations apply to a compressible Newtonian fluid in laminar motion. Constant shear viscosity μ is assumed whereas the bulk viscosity can be neglected for the ideal gas. In what follows, the general equation of state (1) of the perfect gas is considered, without any special assumption about the thermodynamic processes involved, neither isobaric-adiabatic nor isochoric. The derivatives with respect to time

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + (\vec{v} \operatorname{grad})$$

in the continuity equation (2), the momentum (3) and internal energy balance (4) are the substantial ones which include local and convective changes due to nonzero fluid velocities. In the momentum balance, external body forces \vec{G} , such as buoyancy forces may appear. The energy balance relates the temperature field to the heat fluxes in the gas volume,

$$\vec{F} = -k \operatorname{grad} T \quad ,$$

and to the rate of work,

$$- p \operatorname{div} \vec{v} + \mu \Phi \quad ,$$

where $\mu \Phi$ describes the energy dissipation rate due to viscosity. The specific heat at constant volume c_v is assumed to be constant, independent of time or frequency. Thus, the relaxation processes in diatomic or polyatomic molecules are excluded from treatment. Furthermore, it is assumed that there are no mass or heat sources or sinks in the gas volume.

3. GENERALIZED EQUATION FOR THE PRESSURE SIGNAL

By incomplete elimination between the fundamental equations (1) - (4), a single first order partial differential equation for the pressure distribution $p(\vec{r}, t)$ is now derived, given by

$$\begin{aligned} \frac{\partial p}{\partial t} + \gamma \operatorname{div} (p \vec{v}) = (\gamma-1) [& - \operatorname{div} \vec{F} + \vec{v} \vec{G} - \rho \vec{v} \frac{\partial \vec{v}}{\partial t} + \\ & + \mu (\Phi + \vec{v} \Delta \vec{v} + \frac{1}{3} \vec{v} \operatorname{grad} \operatorname{div} \vec{v}) \\ & - \rho \vec{v} (\vec{v} \operatorname{grad}) \vec{v}] \quad . \quad (5) \end{aligned}$$

Here, γ is the adiabatic constant. On the right hand side of this equation and based on order-of-magnitude assumptions, we can neglect

- the cubic terms of the convective or acoustic velocities \vec{v} or their local derivatives $\partial \vec{v} / \partial \vec{r}$,
- and the terms containing products of the shear viscosity μ with squares of the velocities or their local derivatives.

Then we have

$$\frac{\partial p}{\partial t} + \gamma \operatorname{div} (p \vec{v}) = (\gamma-1) [- \operatorname{div} \vec{F} + \vec{v} \vec{G} - \rho \vec{v} \frac{\partial \vec{v}}{\partial t}] \quad . \quad (6)$$

This differential equation can be simplified by using further physical restrictions, namely,

- body forces acting directly on the gas are ignored,
- and there may be no mean (time averaged) convective motion in the gas volume.

Under this assumption, the last term of equation (6) is of higher order as compared with the heat flux divergence and can be neglected. Thus we have the simple differential equation

$$\frac{\partial p}{\partial t} + \gamma \operatorname{div} (p \vec{v}) = - (\gamma - 1) \operatorname{div} \vec{F} \quad (7)$$

which can be integrated over the gas volume V to give an integro-differential equation

$$\int_V dV \frac{\partial p(\vec{r}, t)}{\partial t} + \gamma \int_S p(\vec{r}_s, t) v_s(\vec{r}_s, t) dS = - (\gamma - 1) \int_S F_s(\vec{r}_s, t) dS \quad (8)$$

This equation relates the time and space dependent pressure distribution $p(\vec{r}, t)$ in the gas volume to the heat fluxes $F_s(\vec{r}_s, t)$ and to the gas velocities $v_s(\vec{r}_s, t)$ at the sample-gas interface and at the cell boundaries S (Fig. 1).

The gas velocities at the solid-gas interface can be caused by gas oscillations across the surface of a porous solid sample or by thermoelastically induced surface vibrations of the sample. For the frequency range used in gas-microphone detected photoacoustics,

$$10 \text{ Hz} \leq \nu \leq 10^4 \text{ Hz} ,$$

a measurable effect of the latter can be detected with thin solid disks in the quasi-static limit of thermoelastic oscillations /7,8/.

The integro-differential equation (8) applies to the usual PA cell where the gas length l_g is limited from below by the thermal boundary layer thickness l_{th} , and where l_g is small as compared to the wave length of the acoustic signals,

$$l_{th} < l_g \ll \lambda_s .$$

As the general equation (8) has been derived without any geometrical restriction, it should also apply to extended gas volumes used in PA experiments at low temperatures /9/ as well as to PA cells of short gas length /2/. In this case the modulated heat fluxes to the walls of the cell have to be taken into account and it has to be provided that the gas still can be treated as a continuum.

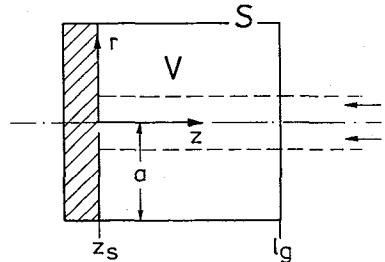


Fig.1. Schematic PA cell

4. SIGNAL GENERATION - SPECIAL SOLUTIONS

Now we will write down and discuss some special solutions obtained from the general equation of signal generation (8) under the following geometrical and physical restrictions:

- A PA cell of cylindrical symmetry is considered, appropriate to describe focussed radiation heating. The ends of the cylinder are closed by the solid disk and an optical window, respectively.
- The gas length may be small as compared to the acoustic wave length,

$$l_g \ll \lambda_s .$$

Due to this assumption, the pressure evolution in the cell may be independent of the spatial coordinates, $p(\vec{r}, t) = p(t)$.

- At the solid-gas interface an oscillating gas velocity is prescribed due to thermoelastic oscillations of the solid surface. The surface may be represented by a rigid oscillating disk.

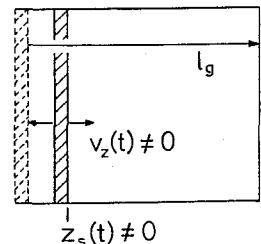


Fig.2. Thermoelastic contributions

The position of this disk $z_s(t)$ and the oscillating gas velocity are then related by

$$v_z(r, z_s, t) = d z_s(t)/dt .$$

Observing these restrictions, equation (8) can be integrated over the gas volume. Subsequently, the result can be integrated over the time to give the pressure evolution $p = p(t)$. Now, the heat fluxes at the boundaries of the gas volume may be separated in a stationary or quasi-stationary part which is constant or only slowly varying on the time scale of the heating modulation and a part rapidly changing on this time scale, viz.

$$F_z(r, z_s, t) = \bar{F}_z(r, z_s, t) + \delta F_z(r, z_s, t) .$$

Furthermore, it is assumed that there are no rapidly changing heat fluxes to the window or the walls,

$$\delta F_z(r, l_g, t) = \delta F_r(a, z, t) = 0 .$$

These conditions are fulfilled if the gas length exceeds the thickness of the thermal boundary layer and if an appropriate cell radius a is chosen. Then the pressure evolution can be written as

$$\begin{aligned} p(t) = & p(t_0) / \left[1 - z_s(t) / l_g \right]^\gamma + \\ & + \frac{2(\gamma-1)}{a^2 l_g} \int_{t_0}^t d\tau \left[\frac{1-z_s(\tau)/l_g}{1-z_s(t)/l_g} \right]^{\gamma-1} \int_0^a r dr \delta F_z(r, z_s, \tau) + \\ & + \frac{2(\gamma-1)}{a^2 l_g} \int_{t_0}^t d\tau \left[\frac{1-z_s(\tau)/l_g}{1-z_s(t)/l_g} \right]^{\gamma-1} \left\{ \int_0^a r dr \left[\bar{F}_z(r, z_s, t) - \right. \right. \\ & \left. \left. - \bar{F}_z(r, l_g, t) \right] + \right. \\ & \left. - a \int_{z_s}^{l_g} dz \bar{F}_r(a, z, t) \right\} \quad (9) \end{aligned}$$

- The first term of this result is the main term of the thermoelastic contributions to the pressure signal.
- The second term contains the usual surface heat flux contribution (Rosencwaig and Gersho's piston model) coupled here with a "thermoelastic factor".
- The third term normally should cancel out when the time averaged heat balance for the gas volume is closed; perhaps it could give contributions to the pressure signal when transient imbalances occur. This third term is coupled to thermoelastic contributions, and if these are absent, it cannot contribute to the acoustic signal but only to a continuous pressure increase.

A more general solution of the integro-differential equation (8) can be obtained if we additionally admit porosity of the solid sample. In this case, the oscillatory gas velocities at the solid-gas interface are decoupled from the position of the sample surface,

$$\begin{aligned} v_z(r, z_s, t) & \neq d z_s(t)/dt , & v_z(r, z_s, t) & = v_s(t) \neq 0 , \\ z_s(t) & \neq 0 \end{aligned}$$

If we assume 1D geometry and fulfill the other conditions as observed for solution (9), we have

$$p(t) = p(t_0) \exp \left[\frac{\gamma}{l_g} \int_{t_0}^t \frac{d\tau v_s(\tau)}{[1-z_s(\tau)/l_g]} \right] +$$

$$\begin{aligned}
 & + \frac{(\gamma-1)}{\ell_g} \int^t \frac{d\tau}{[1-z_s(\tau)/\ell_g]} \exp\left[\frac{\gamma}{\ell_g} \int_{\tau}^t \frac{d\sigma v_s(\sigma)}{[1-z_s(\sigma)/\ell_g]}\right] \delta F_z(z_s, \tau) + \\
 & + \frac{(\gamma-1)}{\ell_g} \int^t \frac{d\tau}{[1-z_s(\tau)/\ell_g]} \exp\left[\frac{\gamma}{\ell_g} \int_{\tau}^t \frac{d\sigma v_s(\sigma)}{[1-z_s(\sigma)/\ell_g]}\right] \left[\bar{F}_z(z_s, t) - \right. \\
 & \qquad \qquad \qquad \left. - \bar{F}_z(\ell_g, t) \right] \quad (10)
 \end{aligned}$$

- The first term is the main contribution due to porosity and surface vibrations of the solid sample.
- The second term contains the usual modulated surface heat flux coupled here with effects due to porosity and surface vibrations.
- The third term again exists due to imbalances of the time averaged heat balance for the gas volume.

In what follows now, we assume:

- Vibrations of the solid surface can be neglected, $z_s(t)/\ell_g \rightarrow 0$.
- The time averaged heat balance for the gas volume is closed.
- The gas velocities at the solid surface due to porosity are small,

$$v_s(t) = \delta v_s(t)$$

so that nonlinear contributions and non-linear coupling between the modulated surface heat flux and surface gas oscillations can be neglected.

Then, equation (10) is simplified to give the pressure signal in a gas-filled PA cell with a porous solid sample at rest:

$$\begin{aligned}
 (11) \quad \delta p(t) = & p(t_0) \frac{\gamma}{\ell_g} \int^t d\tau \delta v_s(\tau) + \\
 & + \frac{(\gamma-1)}{\ell_g} \int^t d\tau \delta F_z(z_s, \tau)
 \end{aligned}$$

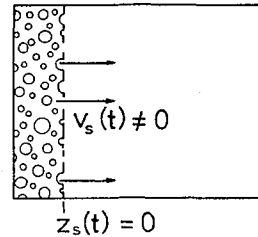


Fig.3. PA cell with a porous solid sample

5. REPRODUCTION OF THE PISTON MODEL AND OF OTHER SOLUTIONS

Starting from our solution (9), we will reproduce some known solutions (piston model, PA cell of short gas length, etc.) in the following. To this finality, we assume that

- surface oscillations may be negligible, $z_s(t)/\ell_g \rightarrow 0$,
- the time averaged heat balance is closed,
- and that 1 D geometry may be considered,

$$\int_0^a dr r = a^2/2$$

Then we obtain from equation (9)

$$\delta p(t) = \frac{(\gamma-1)}{\ell_g} \int^t d\tau \delta F_z(z_s, \tau) \quad (12)$$

When we here insert the thermal wave solution for the semi-infinite space,

$$\delta T(z, t) = \Theta \exp(-z/\mu_g) \exp[i(\omega t - z/\mu_g)] \quad , \quad \mu_g = (2\alpha/\omega)^{1/2}$$

and use

$$\delta F_z(z_s, t) = -k \left[\frac{\partial \delta T(z, t)}{\partial z} \right]_{z \rightarrow z_s}$$

we have

$$\delta p(t) = \frac{(\gamma-1)}{\ell_g} \frac{2k}{\omega \mu_g} \frac{\Theta}{\sqrt{2}} \exp\left[i\left(\omega t - \frac{\pi}{4}\right)\right] \quad (13)$$

where the thermal diffusion length in the gas μ_g is related to the thickness of the thermal boundary layer by

$$\ell_{th} = 2 \pi \mu_g .$$

We now use the specific heat capacity at constant pressure to define the thermal diffusivity in the isobaric thermal boundary layer,

$$(14) \quad \alpha = k / (c_p \rho_o) .$$

Furthermore, we use the equation of state applied to the time averaged quantities at the solid-gas interface,

$$(15) \quad (c_p - c_v) \rho_o = p_o / T_o ,$$

and then we can transform equation (13) to coincide with the pressure signal as given by Rosencwaig and Gersho /1/,

$$\begin{aligned} \delta p(t) &= \frac{(\gamma-1)}{\ell_g} c_p \rho_o \frac{2k / (c_p \rho_o \omega)}{\mu_g} \frac{\Theta}{\sqrt{2}} \exp\left[i\left(\omega t - \frac{\pi}{4}\right)\right] \\ &= \frac{c_p}{c_v} \frac{p_o}{T_o} \frac{\mu_g}{\ell_g} \frac{\Theta}{\sqrt{2}} \exp\left[i\left(\omega t - \frac{\pi}{4}\right)\right] . \end{aligned}$$

The equivalence between our pressure signal (12) and the piston model also can be shown without the restriction to the thermal wave solution. We use an integral relation between the arbitrarily prescribed surface heat flux and the corresponding temperature distribution in the semi-infinite space,

$$\int_0^t d\tau \delta F_z(z_s, \tau) = \frac{k}{\alpha} \int_0^{\ell_{th}} dz \delta T(z, t) = \frac{k}{\alpha} \ell_{th} \langle \delta T(z, t) \rangle ,$$

as an approximation for the thermal boundary layer of finite thickness to transform equation (12). We then have

$$\delta p(t) = \frac{(\gamma-1)}{\ell_g} \frac{k}{\alpha} \ell_{th} \langle \delta T(z, t) \rangle \quad (16)$$

Using once more the equations (14) and (15), we can transform our equation (16) to coincide with a more general formulation of Rosencwaig and Gersho's piston model,

$$\begin{aligned} \delta p(t) &= (\gamma-1) c_p \rho_o \frac{\ell_{th}}{\ell_g} \langle \delta T(z, t) \rangle \\ &= \frac{c_p}{c_v} \frac{p_o}{T_o} \frac{\ell_{th}}{\ell_g} \langle \delta T(z, t) \rangle . \end{aligned} \quad (17)$$

Korpiun and Büchner recently proposed the isochoric limit of the gas law for the interpretation of PA measurements.

In fact, the isochoric limit should apply for PA cells with a rather thin gas layer where the gas length is comparable with or shorter than the thermal boundary layer thickness or the thermal diffusion length (Fig.5.),

$$\ell_g < \mu_g, \ell_{th} .$$

In such a case, the thermal diffusivity has to be defined with the specific heat capacity at constant volume

$$\alpha = k / (c_v \rho_o) .$$

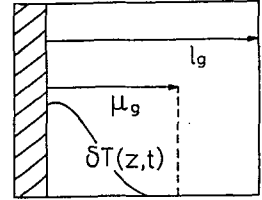


Fig.4. Piston model

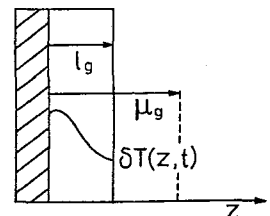


Fig.5. Thin gas layer

When we use this last definition and equation (15) to transform our pressure signal (16), the final form should be independent of the adiabatic constant as Korpiun and Büchner proved experimentally /2/.

$$\begin{aligned} \delta p(t) &= (\gamma-1) c_v \rho_0 \frac{l_{th}}{l_g} \langle \delta T(z,t) \rangle \\ &= \frac{P_0}{T_0} \frac{l_{th}}{l_g} \langle \delta T(z,t) \rangle \end{aligned} \quad (18)$$

Naturally for thin gas layers the time dependent heat transfer to the opposite window has to be taken into account for a correct derivation of the pressure signal.

A further solution can be obtained from our integral (9): For small relative displacements,

$$z_s(t)/l_g < 1$$

integral (9) can be expanded to coincide with the usual composite piston model,

$$\delta p(t) = \frac{(\gamma-1)}{l_g} \int_0^t d\tau \delta F_z(z_s, \tau) + \gamma p(t_0) \delta z_s(t)/l_g \quad (19)$$

Based on integral (9), higher order terms in the relative displacements and nonlinear coupling of the surface displacements with the oscillating heat flux effect at the solid-gas interface (Fig.6.) could be possible.

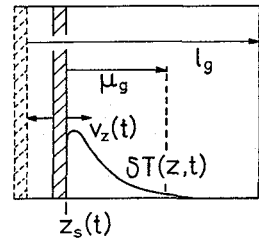
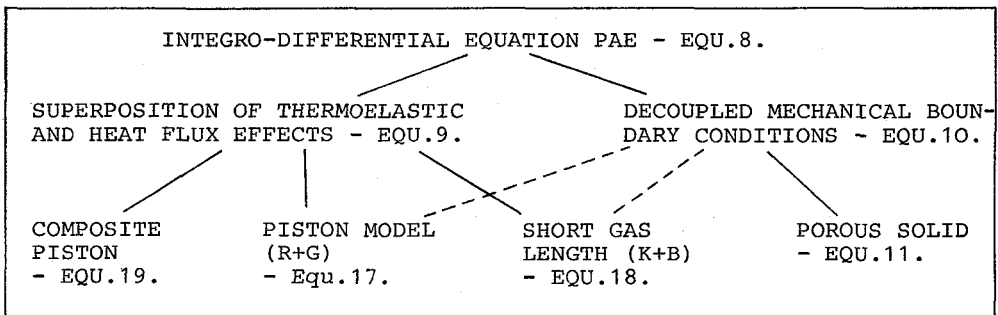


Fig.6. Composite piston model

6. CONCLUSION

Based on the general equation of state of the ideal gas and on the fundamental equations of fluid dynamics (the equation of continuity, the momentum and energy balance), a general integro-differential equation is derived for the acoustic signal associated with the Photoacoustic Effect on solids. Under the assumption of spatially constant pressure evolution in the surrounding gas volume, two principal solutions of this equation are given which differ by the mechanical boundary conditions considered at the solid-gas interface. Starting from these two solutions and with the help of further assumptions simpler solutions can be derived and reproduced (pressure signal in a gas volume in contact with a porous solid, piston model, PA cell of short gas length, and composite-piston model). The lines of descent and the relations between the various solutions are presented in the scheme below.



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