Photoacoustic determination of heat capacity per unit volume at room temperature of thin metallic foils

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A photoacoustic method for the determination of the heat capacity per unit volume ($\rho C_p$), at room temperature, for thin metallic foils is presented. The method is based on the use of a variant of a conventional photoacoustic cell. © 2003 American Institute of Physics.

[I. INTRODUCTION]

Heat capacity plays a crucial role in physics, chemistry, and biology. Diverse experimental methods have been developed to measure it. These methods can be grouped in two classes, those based on thermal relaxation methods and those based on semiadiabatic techniques.1,2

In photothermal techniques, the thermal parameter most frequently measured is the thermal diffusivity, this is because the photothermal effects are strongly dependent on the heat diffusion in the sample. However, depending on the configuration of the experiment, heat capacity can also be determined. For example, in photopyroelectric techniques the simultaneous measurement of specific heat and thermal conductivity through the amplitude and phase of the signal is performed.3

Recently, making use of the fact that, in photoacoustic (PA) techniques, the semiadiabatic conditions are reached due to the low effusivity of the air ($e = 5.47 \text{ W s}^{-1/2} \text{ m}^{-2} \text{ K}^{-1}$), the thermal effusivity in materials which have a good thermal contact with a reference material was measured.4 In these cases, the reference material was a metallic or semimetallic thin plate, and their thermal properties should be known in order to obtain the thermal effusivity of the materials under study. In this method, the procedure of measuring can be inverted, i.e., if the thermal effusivity of the material, with good thermal contact, is known the thermal properties of the reference material can be measured.

In this article the potentialities of the photoacoustic technique for the determination of the heat capacity per unit volume are explored, based on a method that involves a modification of the conventional PA cell and a calibration of the system using a standard liquid.

[II. EXPERIMENT]

In Fig. 1 a schematic representation of the PA cell used in this work is shown. The PA cell is closed, at the bottom end, by a glass window and, at the top end, by the metallic sample. The diameter of the PA cell is 6 ± 0.5 mm. An electret microphone, coupled to the cavity wall, is used to sense the pressure fluctuations in the PA chamber, produced by the periodic heating of the sample due to the pumping beam. A liquid deposited on the external surface of the sample is used as a reference material. The samples studied were foils of copper, aluminum, and brass with 8 ± 1 mm of diameter. The reference liquid used was distilled water ($e_b = 1601 ± 20 \text{ W s}^{1/2} \text{ m}^{-2} \text{ K}^{-1}$).

[FIG. 1. Cross section of the conventional photoacoustic cell used.]

[III. THEORY]

The geometry shown in Fig. 2 represents schematically the physical configuration of our experiments. A modulated laser beam, $I(t) = I_0 \left[ 1 + \cos(\omega t) \right]/2$, impinges the internal surface of the sample ($s$), of thickness $l$, which is in contact with the air ($g$) of the PA chamber. The backing material ($b$), of thickness $l_b$, is now the reference. Here, $I_0$ is the intensity of the laser beam and $\omega$ is angular modulation frequency.

In this kind of experiment two PA signals are measured, the first one is obtained when the backing is air ($\theta_b = 0$), and the other one is obtained when the backing is the liquid reference ($\theta_b \neq 0$). Solving the thermal diffusion equations for the configuration shown in Fig. 2, with a modulated radiation source, and taking into account that, for the metallic samples, the radiation is absorbed at their surface and, in the frequency range used in our experiments, the samples are in the

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thermally thin regimen, the ratio between the PA amplitudes, \( q = |\theta|/|\theta_0| \), in the Rosencwaig–Gersho model, can be reduced to

\[
q = \frac{1}{\sqrt{1 + \frac{p^2}{1 + \frac{f^2}{2}}}}\left(1 + \frac{p^2}{1 + \frac{f^2}{2}}\right),
\]

with \( P \) given by

\[
P = \varepsilon_b \sqrt{\pi \rho C_p}.
\]

Here \( f \) is the modulation frequency, \( \rho C_p \) is heat capacity per unit volume of the metallic sample, and \( \varepsilon_b \) is the thermal effusivity of the backing.

The value of \( \rho C_p \) is obtained by fitting the experimental data to Eq. (1), taking \( P \) as a fitting parameter.

**IV. RESULTS**

Figure 3 shows the PA amplitude for a copper foil of (8 ± 1) mm of diameter and (90 ± 5) \( \mu \)m of thickness. Squares represent the experimental data of the signal amplitude with the PA cell without liquid and circles are the data of the signal amplitude when the sample supports the liquid.

The continuous line, for the case without liquid, represents the best fit of the experimental data to an equation of the form \( a f^b \), with \( a \) and \( b \) as the fitting parameters. The value obtained for \( b = -1.45 \) is in agreement with the literature.\(^4\)

In Fig. 4 the ratio of the experimental data with liquid divided by the experimental data without liquid is shown. The continuous line is the best fit of the normalized data to Eq. (1). For this sample, we find a \( \rho C_p = 3.17 \pm 0.24 \times 10^6 \) J/m\(^3\) K. We can see that, our results are in complete agreement with the values specified by provider of the copper (Goodfellow), which is 3.5 \( \times 10^6 \) J/m\(^3\) K.

In Table I, the values obtained for different metallic samples are shown. We can see that these values are very close to the values reported by the company. However, the accuracy of these values is affected mainly by the thermal expansion effects. The value of the commercial brass is not reported.

The complete characterization of a sample would require a heat transmission configuration. Given that this method provides a direct measurement of heat capacity its possibilities for the study of phase transitions are worth to be explored. It is clear that in each case a proper choice of the reference liquid and a characterization of the system would be required.

**V. CONCLUSION**

The potentialities of a simple and accurate photoacoustic method for the determination of heat capacity per unit volume (\( \rho C_p \)) at room temperature of metallic foils have been presented. This method in combination with heat transmission configuration as the open photoacoustic cell, could be useful for the whole thermal characterization of materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (( \mu )m)</th>
<th>( \rho C_p )(( \times 10^6 ) J/m(^3) K)</th>
<th>Measured</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>90 ± 2</td>
<td>3.17 ± 0.24</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>125 ± 2</td>
<td>2.02 ± 0.21</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>45 ± 2</td>
<td>2.04 ± 0.40</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Commercial brass</td>
<td>50 ± 2</td>
<td>1.27 ± 0.40</td>
<td>⋯</td>
<td></td>
</tr>
</tbody>
</table>
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