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To cite this version:
P. Korpiun, R. Tilgner, D. Schmidt. MODEL OF OSCILLATING INTERFACE AT FIRST ORDER PHASE TRANSITION AND AT GLASS TRANSITION - NONVANISHING AMPLITUDE APPROXIMATION. Journal de Physique Colloques, 1983, 44 (C6), pp.C6-43-C6-53. 10.1051/jphyscol:1983607. jpa-00223166

HAL Id: jpa-00223166
https://hal.archives-ouvertes.fr/jpa-00223166
Submitted on 1 Jan 1983

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MODEL OF OSCILLATING INTERFACE AT FIRST ORDER PHASE TRANSITION AND AT GLASS TRANSITION - NONVANISHING AMPLITUDE APPROXIMATION

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Abstract - A theoretical model for PA amplitude and phase angle at first order phase transition is generalized to arbitrary thermal thickness of the sample. It can be applied to second order phase transitions, too. Results of measurements at the melting point of indium and in the glass transition region of polystyrene confirm the model.

I - INTRODUCTION

Amplitude of pressure $\delta p$ and phase angle $\phi$ measured in a gas-microphone cell depend on
1. The optical absorption coefficient of the sample and the conversion process for heat;
2. The thermal properties of the sample determining the transport of the heat to the surrounding gas: density $\rho$, thermal conductivity $\lambda$, specific heat capacity $c_p$ and latent heat $L$.

Therefore, the photoacoustic effect (PAE) should be sensitive to phase transitions. First measurements were performed by Pelzl and coworkers /1/, other followed /2-8/.

II - THE PAE AT FIRST ORDER PHASE TRANSITIONS - MODEL OF OSCILLATING INTERFACE

The model /7/ is sketched in fig. 1 for a solid liquid transition. The sample is illuminated by modulated light. The power per unit surface area converted to heat in an opaque absorber is assumed to be

$$Q(t) = Q_0 (1 + e^{j\omega t}) . \quad (1)$$

It causes a steady state linear temperature distribution in the cell expressed by a temperature gradient $e_{2k}$ (fig.1). It is superposed by a temperature oscillation. In that region of the sample where the transition temperature $T_m$ is reached the boundary between solid and liquid phase oscillates with amplitude $\xi(x,t)$ around a mean value $\eta_0$ /7/.

The position of the interface between two phases is

$$\eta(T_0,t) = \eta_0(T_0) + \xi(T_0,t) , \quad (2)$$

$$\xi(T_0,t) = \epsilon(T_0) e^{j\omega t} . \quad (3)$$
Increasing in an experiment the ambient temperature $T_0$, the oscillating interface and thus $n_0$ is shifted more to the inside of the sample, and vice versa. Vanishing amplitude approximation means that the amplitude $\varepsilon$ of the interface oscillation is small compared to the length of the sample or

$$|\varepsilon|/l_1 << 1 \quad ;$$

(4)

nonvanishing amplitude approximation means

$$2|\varepsilon|/l_1 \geq 1 \quad ,$$

(5)

see also sect. II.2

Experiments to investigate phase transitions are performed in that way, that amplitude and phase angle of the PA signal are measured as function of ambient temperature using a microphone. This PA signal is proportional to the pressure variation $\delta P$ of the gas surrounding the sample. Using the model of Rosencwaig and Gershko $\delta P$ again is proportional to the average temperature variation $<\delta T>$ in the gas /9,10/. $<\delta T>$ is the spatial average over the temperature distribution in the gas, that is obtained as a solution of the equation of heat conduction. The position $n$ of the phase boundary and the latent heat $L$ enter some boundary condition for temperature and heat flux.

II.1 - Temperature distribution

The problem is described by one dimensional differential equation of conduction of heat for region $k$
\[
\frac{\partial^2 \Phi_k}{\partial x^2} - \frac{\rho_k c_{pk}}{\lambda_k} \frac{\partial \Phi_k}{\partial t} = 0
\]

where

\[
\Phi_k(x,t) = T_k(x,t) - T_0
\]

with the ambient temperature \(T_0\) and \(k = 0: \text{backing}, k = 1: \text{sample (solid)}, k = 2: \text{sample (liquid)}, k = 3: \text{gas}\).

The most general form for the temperature distribution according to Rosencwaig and Gersho /9/ is

\[
\Phi_k(x,t) = e_{1k} + e_{2k} x + (U_k e^{\sigma_k k x} + V_k e^{-\sigma_k k x}) e^{i\omega t}
\]

with

\[
\sigma_k = (1+j) a_k,
\]

\[
\alpha_k^{-1} = (2\lambda_k / c_{pk} \rho_k \omega)^{1/2} : \text{thermal diffusion length of medium } k.
\]

The real constants \(e_{1k}\) and complex constants \(U_k, V_k\) are determined from the boundary conditions: continuity of temperature and heat flux. The latent heat \(L\) comes in by the boundary condition for the heat flux at the oscillating boundary between the two thermodynamic phases /7/: \(d \xi / dt = \text{velocity of the oscillating interface}\). We find solutions of eq. (6) for the temperature distribution with boundary condition (10) for samples with arbitrary thermal length \(a_{11}\) if the amplitude \(|\xi|\) of the interface is small compared to the thermal diffusion length, \(|\xi| a_{11} << 1\).

II.2 - Pressure Variation, Complex Temperature and Characteristic Quantities

As mentioned above, the pressure variation in the gas /9,10/ is connected by

\[
\delta P \propto \langle \delta > = V_3 e^{i\omega t}
\]

to the complex temperature amplitude in the periodic part of the solution (8)

\[
V_3 = |V_3| \exp[i(\varphi_3 - \pi/4)]
\]

at the sample to gas boundary. The real valued quantities amplitude \(|V_3|\) and the phase angle \(\varphi_3\) are functions of all thermal properties \(\rho_k, \lambda_k, c_{pk}\), the latent heat of the sample \(L\), the geometry of the sample cell assembly, e.g. lengths \(l_k\), the heat \(Q_0\), the ambient temperature \(T_0\), and the difference \(\delta\) between the temperature in the sample and the melting temperature

\[
\delta = T - T_m.
\]

The explicit expression for \(|V_3|\) is given elsewhere /7,8/ and in a paper that will be published.

The amplitude of the interface oscillation in the vicinity of \(x = 0\) is

\[
\varepsilon = -\lambda_1 V_3(\tau_0 = 0)/ \lambda_2 e^{21}
\]
with the temperature gradient

\[ e_{21} = \frac{\lambda_2 \left[ Q_0 R_3 + \epsilon (\lambda_1 / \lambda_2 - 1) \right]}{\lambda_1^2 (R_0 + R_1 + R_3 \lambda_2 / \lambda_1)} , \]  

(16)

in the low temperature state \((k = 1)\) of the sample. The condition (4) for vanishing interface approximation becomes now

\[ |\epsilon|/l_1 << 1 \Rightarrow Q_0/a_1 l_1 << a_1 \lambda_2 L/c p_1 . \]  

(17)

This condition can be fulfilled experimentally for thermally thick samples \( a_1 l_1 \approx 1 \). Nonvanishing amplitude approximation (5) means now

\[ 2|\epsilon|/l_1 \approx 1 \Rightarrow Q_0/a_1 l_1 \approx 2L(\lambda_2 a_2 + \lambda_3 a_3)/r c p_1 (1+s) \]  

(18)

with

\[ r = a_2 / a_1, s = (1-\lambda_0 a_0 / \lambda_1 a_1 )/(1+\lambda_0 a_0 / \lambda_1 a_1) . \]

Care should be taken to the inequality with respect to the light intensity performing measurements on thermally very thin samples, \( a_1 l_1 \approx 1 \).

Some quantities should be introduced that are used in the further formal description of amplitude and phase angle of the temperature oscillation.

The difference between ambient temperature \( T_0 \) and temperature at the sample surface \( x = 0 \) is

\[ \delta = \frac{R_k (R_0 + R_1)}{R_0 + R_1 + R_3} Q_0 \]  

(19)

if the average position of the boundary \( n_0 = 0 \). Here

\[ R_k = 1 / \lambda_k \]  

(20)

is the thermal resistance of medium \( k \). The results will be expressed as functions of a reduced temperature defined as

\[ \theta = 1 - \delta / \delta_0 . \]  

(21)

\( \theta = 0 \) means \( n_0 = 0 \).

II.3 - Variation of Ambient Temperature

Experiments on samples that undergo a phase transition are performed by varying the ambient temperature \( T_0 \). The expression (13) for \( V_3 \) only describes the temperature amplitude in that temperature region where an interface and therefore two different phases of the sample exist. On the scale of the reduced temperature (21) it is the range \( \theta_2 \leq \theta \leq \theta_3 \) where at the top side of the sample, \( x = 0 \), the temperature never is lower, or at the bottom of the sample, \( x = -l_1 \), never is higher than the transition temperature \( T_m \) respectively. For temperatures sufficiently far below and above the transition temperature \( T_m \) there exists no interface. The whole volume of the sample is in state \( k = 1 \) or \( 2 \) respectively. The temperature distribution is a solution of eq. (6) without the presence of a phase transition:

\[ V_3^{(k)} = |V_3^{(k)}| \exp[j (\phi_3^{(k)} - \pi/4)] \]  

(22)

with \( k = 1,2 \) respectively. \( V_3^{(1)} \) describes amplitude and phase angle in the
temperature range $\theta \leq \theta_3$ where the temperature at $x = 0$ never is higher than $T_m$. The high temperature phase described by $V_3^{(2)}$ exists for $\theta \geq \theta_5$ if the temperature at $x = -l_1$ is never lower than $T_m$. One obtains

$$\theta_1 = -|V_3^{(1)}|/\delta_0$$

and

$$\theta_5 = \theta_4 + |V_3^{(2)}| \exp(-a_2 l_1)/\delta_0 .$$

There are two more characteristic temperatures essential for the model. At $\theta=0$ the average position of the interface is at the top side of the sample, $n_0 = 0$. The interface is at the bottom of the sample, $n_0 = -l_1$, at the reduced temperature

$$\theta_4 = 1/[1+\lambda_2 R_0 (R_0 + R_1 + R_3)/\lambda_1 R_1 (R_0 + R_1 + \lambda_2 R_3/\lambda_1)].$$

Varying continuously the ambient temperature there are the regions $\theta_1 \leq \theta \leq \theta_2$ and $\theta_3 \leq \theta \leq \theta_5$ where exists an interface only for a fractional part $\omega t_m/\pi$ of a heating cycle. For a first approach we suppose the temperature variation in time to be composed of the solutions $V_3$, eq. (13), and $V_3^{(k)}$, eq. (22) as sketched in fig.2. Measurements are performed using the lock-in technique. A lock-in detector measures the first harmonic of a function. The complex Fourier coefficient of the first harmonic of the function shown in figure 2 has the form

$$V_3^t = \frac{1}{\pi} (V_3^{(k)}(\pi-\omega t_m)+V_3^{(k)}(\omega t_m)+(V_3^{(k)}-V_3)\sin(2\omega t_m)/2] = |V_3^t| \exp[j(\psi_3^t-\pi/4)].$$

Both, amplitude $|V_3^t|$ and phase angle $\psi_3^t$ can be evaluated with the explicit expressions / 7 / for $V_3$, eq. (13) and $V_3^{(k)}$, eq. (22) in the temperature range $\theta_1 \leq \theta \leq \theta_2$ for $k = 1$ and within $\theta_3 \leq \theta \leq \theta_5$ for $k = 2$. The characteristic temperatures $\theta_2$ and $\theta_3$ are

$$\theta_2 = V_3(n_0=0) (R_0 + R_1 + R_3 \lambda_2/\lambda_1)/Q_0 R_3 (R_0 + R_1)$$

and

$$\theta_3 = \theta_4 - \theta_2 \exp(-a_2 l_1) .$$
The expression (26) for $V_3^+$ is a first approach to describe the amplitude and phase angle of the periodic temperature and pressure variation in the gas of a PA cell for samples of arbitrary thermal thickness $a_1l_1$ as long as the oscillation of the interface does not exceed the sample thickness, eq. (5).

The results obtained agree with experimental data. This is shown in sec.III for the melting of indium and in sec.IV for a glass transition of atactic polystyrene.

III - MELTING OF INDIUM

The photoacoustic signal has been measured on indium samples in the vicinity of the melting temperature $T_m = 156.6$ °C for samples with thermal lengths $a_1l_1 = 1.7$, 0.3 and 0.02 on a backing of copper. The measurements were performed with a gas microphone cell. The samples were illuminated by white light of a 250 Watt halogen lamp. Its intensity was modulated by a mechanical chopper (PAR 192). A condensor microphone (Brüel & Kjaer, Type 4166) was used. Amplitude and phase were detected using a lock-in amplifier (Ithaco, Dynatrac 393). The experimental results are shown in the figs. 3, 5 and 7. Amplitude $\Phi_3^{\text{ex}}$ and phase angle $\varphi_3^{\text{ex}}$ are plotted versus temperature. The corresponding theoretical quantities are shown in the figs. 4, 6 and 8. The normalized amplitude $\Phi_3 = |V_3|^t/|V_3^{(1)}|$ and phase angle $\varphi_3^t$ are plotted versus the reduced temperature $\theta$, eq. (21). The thermal data of indium used for the calculations are listed in table 1.

From the figs. 3 to 8 it becomes obvious that the characteristic behaviour of amplitude and phase angle with temperature is described satisfactorily by the model of oscillating interface. Comparing the experimental results with calculated data one has to take into account a temperature gradient in the sample perpendicular to the x-direction. It is very difficult to realize in a photoacoustic cell isothermes parallel to the y-z-plane. The temperature gradient will smear out the signal on the temperature scale. It is obvious that with decreasing thermal length of the sample the temperature oscillation $V_3^t$ should become more sensitive to the light intensity expressed by $Q_0$ or $\delta_0^t$, eq. (19), respectively. At a thermally very thin sample a variation of $\delta_0^t$ may change essentially the characteristic behaviour of the phase angle with temperature, Fig. 8b.

### Table 1 - Thermal Properties of In

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_m$</td>
<td>429.76 K = 156.6 °C</td>
</tr>
<tr>
<td>$L$</td>
<td>28.62 J g$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_1$</td>
<td>0.729 Watt cm$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\lambda_2$</td>
<td>0.360 Watt cm$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$c_{p1}$</td>
<td>0.2657 J g$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$c_{p2}$</td>
<td>0.2669 J g$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>7.31 g cm$^{-3}$</td>
</tr>
<tr>
<td>$\rho_2$</td>
<td>7.13 g cm$^{-3}$</td>
</tr>
</tbody>
</table>

Figs. 3, 5, 7 - a) PA amplitude $\Phi_3^{\text{ex}}$ and b) phase angle $\varphi_3^{\text{ex}}$ measured on indium samples versus ambient temperature $T$. $l_1$: sample thickness, $\nu$: modulation frequency, $a_1l_1$: thermal thickness. Backing: copper.

Figs. 4, 6, 8 - a) Normalized amplitude $\Phi_3$ and b) phase angle $\varphi_3^t$ calculated for indium samples with thermal thickness $a_1l_1$ on copper versus reduced temperature $\theta$; $\delta_0 = 5K$. 
IV - PAE AT THE GLASS TRANSITION OF ATACTIC POLYSTYRENE

The PAE has been measured on an amorphous polymer in the glass transition region. The sample was atactic polystyrene (168 N, BASF). The sample was thermally well annealed. Its glass transition region is between 100 and 110 °C. The sample geometry was 12 x 5 x 3 mm³, its thermal thickness $a_1 \approx 10 > \tau_\nu = 29$ Hz. The PA-cell, illumination and detection were the same as for the measurements on indium. Ambient temperature increased at a rate of 5 K min⁻¹. PA-amplitude and phase angle measured as a function of the mean temperature $T$ of the sample are plotted in Fig. 9.

Arriving at the temperature of $\approx 120$ °C the sample was cooled at a rate of 8 K min⁻¹ down to 60 °C. Measuring again the PA-signal at increasing temperature along the glass transition region no effect could be observed.

IV.1 - Interpretation of Experimental Results

Experiments show that amplitude and phase shift $\Delta \varphi$ of the PA-signal have a minimum in the glass transition region. The experimental results can be interpreted with the model of oscillating interface, Fig. 10, if

1. in eq. (10) $\rho L \frac{d \xi}{dt} = 0$,

2. $(\lambda c_p \rho)_{\text{liquid}} > (\lambda c_p \rho)_{\text{glass}}$.

Condition 2 holds generally for amorphous polymers /11/. $\rho L \frac{d \xi}{dt} = 0$ means

1.1 $L = 0, \frac{d \xi}{dt} \neq 0$: Second order phase transition or any kinetic transition: $\alpha = \frac{\lambda}{c_p} \rho$ changes.

1.2 $L \neq 0, \frac{d \xi}{dt} = 0$: Phase boundary does not oscillate; phase transition is irreversible within the time $2\pi/\omega$.

1.3 $L = 0, \frac{d \xi}{dt} = 0$: Irreversible second order or kinetic transition.

The experimental result that no effect is observed if the measurement is repeated (sample not annealed) is consistent with measurements of the specific heat $c_p$. 

![Fig. 9 - a) PA amplitude and b) phase angle measured on polystyrene in glass transition region 100 - 110 °C. Solid line: first measurement; dashed line: second measurement. $T = \text{ambient temperature}$](image)
Fig. 10 - a) Normalized amplitude and b) phase angle versus reduced temperature for various values of \( \gamma = \frac{\lambda c_p \rho}{\lambda c_p \rho_{\text{glass}}} \).

IV.2 - Temperature Range of Kinetic Transition

The transition can be observed with PAE only if it occurs in the sample within a region \( \ll \alpha^{-1} \). Since the temperature gradient in the sample can be determined, \( \sim 5 \times 10^{-3} \text{ K } \mu \text{m}^{-1} \), the temperature (transition) region \( \Delta T \) where \( \alpha \) or \( \rho \), \( c_p \) and \( \lambda \) respectively vary essentially can be estimated to be \( \Delta T < 10^{-2} \text{ K} \).

V - CONCLUSION

The PAE is sensitive not only to first order phase transitions but also to higher order and kinetic transitions. Those transitions can be observed if the thermal properties vary considerably in the temperature gradient along a distance that is small compared to the wavelength of the temperature wave. From the quantities that are measured it is especially the behaviour of the phase angle with temperature that depends in a characteristic manner on the thermal thickness of the sample, the spatial variation of the thermal properties and a moving or not moving interface. Though the description of the temperature signal in the intermediate temperature region is relatively rough, it describes fairly well the mean features of amplitude and phase angle along the transition region.

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/10/ KORPIUN P., and BOCHNER B., Appl.Phys. B30 (1983); Journ.de Physique (this issue)