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Metrological aspects of thermal relaxation technique by radiation loss for volumetric heat capacity measurements

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Abstract. One of the best-known methods to measure the heat capacity of solids consists in the illumination of the sample and the analysis of the thermal relaxation when the illumination is stopped. In this work, the energy balance equation with heat losses due to radiation is solved exactly. This is used to establish the limits of the usual approximations used to obtain the heat capacity from the experimental data. It is shown that large temperature changes, induced by the heat source during the experiment can generate errors in the calculation of heat capacity when the traditional approach is used.

1 Introduction

In the thermal relaxation method, a thin sample is attached to a holder and isolated from the surrounding environment inside a Dewar chamber in which a vacuum of around 1 mtorr is present. The sample previously blackened with a very thin layer of black paint, is illuminated by a continuous light source. The time that the sample takes to heat or to cool when the illumination is interrupted is used to determine the heat capacity [1–3]. In this configuration the losses due to convection and conduction can be minimized. The theoretical approach that is used is based on the energy balance equation with heat losses due only to radiation and it is considered that the changes of temperature are much lower than the bath temperature.

In this paper it is shown that, the energy balance equation with losses by radiation for plate shape solid, can be solved exactly. We get the temperature evolution as a function of time, and these results can be used to determine the heat capacity with higher accuracy than the traditional methods. It is also shown that the theoretical predictions of previous works can be obtained and that the limits and applicability of the usual approach can be explored.

2 Theory

Let the intensity of the heat flux be given by a continuous light beam of power P_0. When the light is turned on, the temperature of the sample is increased from the bath temperature to a maximum temperature. On the other hand, when the light is turned off, the temperature decreases, from the maximum temperature to the bath temperature. The energy balance equation can be written as

$$\frac{\partial Q}{\partial t} = P_0 - P_R, \tag{1}$$

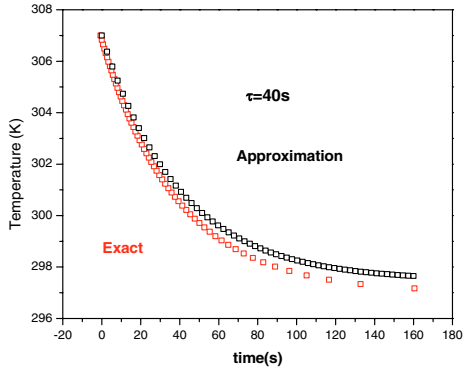

Fig. 1. Mathematical simulation on equations (3) and (4).

where, $Q(t) = \rho c_p V \Delta T$ is the heat given (transferred) to the sample when it increases (decreases) its temperature by ΔT. Here, ρ is the density, c_p is the specific heat at constant pressure, V is the volume of the sample, P_0 is the power of the incident light, and P_R is the heat lost by radiation, which is given by the Stefan-Boltzmann law, $P_R = A\,\varepsilon\sigma\,(T^4 - T_b^4)$. A is the total area of the sample, ε is the emissivity, σ is the Stefan-Boltzmann constant ($5.670 \times 10^{-8}\ \mathrm{J\,K^{-4}\,m^{-2}\ s^{-1}}$), T_b is the bath temperature and $T(t)$ is the temperature at any time.

The differential equation to be solved in case of the cooling and heating of the sample is

$$\frac{d\Delta T}{dt} = \frac{A\sigma\varepsilon}{\rho C V}[T_\infty^4 - T^4(t)]. \tag{2}$$

Here, $T(t) = T_0 + \Delta T(t)$, T_0 is the initial temperature and T_∞ is the temperature when the sample has reached the equilibrium. The initial condition to be fulfilled is $\Delta T(0) = 0$. Solving the Eq. (2) we find

$$\exp\left(-\frac{t}{\tau}\right) = \left(\frac{T_\infty + T_0}{T_\infty - T_0}\right)\left(\frac{T_\infty - T}{T_\infty + T}\right)\exp\left\{-2\left[\tan^{-1}\left(\frac{T}{T_\infty}\right) - \tan^{-1}\left(\frac{T_0}{T_\infty}\right)\right]\right\}, \tag{3}$$

with $\tau = \rho c_p\ l/8\sigma\, T_\infty^3$ the thermal relaxation time that provides the heat capacity per unit volume and l is the sample thickness. On the other hand, in the conventional approach, the approximation, it is considered that the changes during the measurement are not large, i.e. $\Delta T \ll T_0$, and therefore: $T^4 = (T_0 + \Delta T)^4 \approx T_0^4 + 4T_0^3\Delta T$, and therefore the simpler equation is obtained:

$$\Delta T = T^* - T_0 = \left(\frac{T_\infty^4 - T_0^4}{4T_0^3}\right)\left[1 - \exp\left(-\frac{t}{\tau^*}\right)\right] \tag{4}$$

with $\tau^* = (\rho c_p) * l/8\sigma\ \mathrm{T}_0^3$ [2,3].

3 Results and discussion

For the case when the light beam is obstructed, T_∞ corresponds to the environmental temperature and T_0 to the maximum temperature reached by the illumination. As can be easily observed, the difference in the relaxation times, τ and τ^* leads to different values of the heat capacity. In fact, using the expressions for such quantities the following relation is obtained:

$$\frac{(\rho c_p)}{(\rho c_p)^*} = \left(\frac{T_\infty}{T_0}\right)^3 \frac{\tau}{\tau^*}. \tag{5}$$

The error introduced in the measurement will be larger when the initial and final temperatures differ appreciably. Using mathematical simulation on equations (3) and (4), it can also be

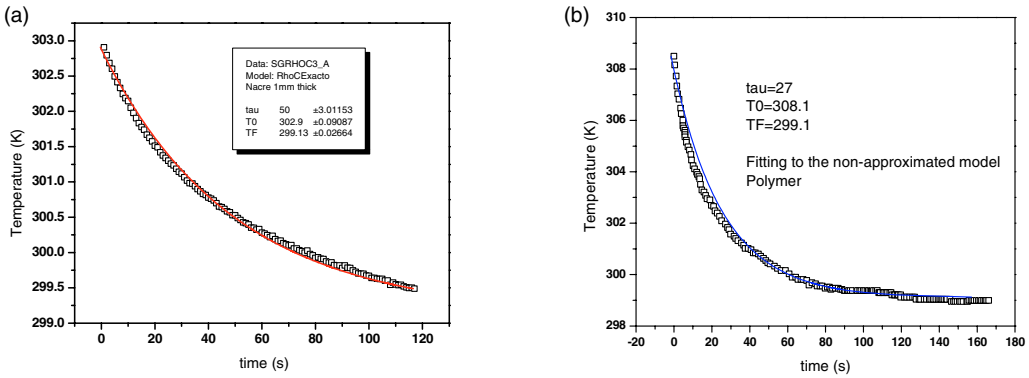

Fig. 2. The results of the fitting of the experimental data for nacre (a) and polyethylene terephtelate (b) samples using equation 3.

observed that the results provided near T_0 are very close, however at the end of the experiment the difference has grown (Figure 1).

In Figure 2(a) and 2(b) the results of the fitting of the experimental data for nacre and a polyethylene terephtelate samples using equation 3, can be observed. The fitting of the experimental data provide the results for the heat capacities per unit volume: $\rho c_p = 0.61 \times 10^6\,\mathrm{J\,K^{-1}\,m^{-3}}$ for the nacre, and $\rho c_p = 3.28 \times 10^6\,\mathrm{J\,K^{-1}\,m^{-3}}$ for the polymer.

It is important to mention that if equation 4 is used, and the first factor in this equation is taken only as a fitting constant, the values provided for the relaxation time are smaller in the approximate case than using the complete expression (Equation 4), given than $T_\infty < T_0$. This compensates the error in the measurement making the quotient close to 1. This can explain the success of this technique in obtaining experimental data based in Equation 4, and also indicates that the results for the heat capacity would be better when the process is studied when the sample is cooling after obstructing the light beam.

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References

1. I. Hata, Rev. Sci. Instrum. **50**, 292 (1979)
2. G. Gutiérrez-Juárez, O. Zelaya-Angel, J.J. Alvarado-Gil, H. Vargas, H. de O. Pastore, J.S. Barone, M. Hernández-Velez, L. Baños, J. Chem. Soc. Faraday Trans. **92**, 2651 (1996)
3. H. Valiente, E. Marin, J. Phys. IV (France) **125**, 305 (2005)