Distributed τ_2 effect in relaxation calorimetry

H. Tsujii, B. Andraka, K. A. Muttalib, Y. Takano [1]

Department of Physics, University of Florida, PO Box 118440, Gainesville, Florida 32611-8440, USA

Abstract

The so-called "distributed τ_2 effect" influences the time evolution of temperature in relaxation calorimetry of samples of poor thermal conductance. Very often a problem for non-metallic and powder samples at temperatures below 1 K, this effect appears as a fast initial relaxation of temperature that is non-exponential. If calorimetry data displaying such a feature are analyzed by conventional methods that are appropriate for data affected by a "lumped τ_2 effect" due to a contact resistance between the sample and the calorimeter, a systematic error is introduced in the measured heat capacity. We show how this error can be eliminated by a data-analysis method recently proposed by Takano and Muttalib, drawing an example from our experimental data of a magnetic insulator sample in a high magnetic field.

Key words: relaxation calorimetry; specific heat; τ_2 effect

The relaxation calorimetry [1] measures the heat capacity C_{total} of the sample and addenda using the simple relation

$$C_{\text{total}} = \kappa\tau, \tag{1}$$

where τ is the time constant of the exponential temperature relaxation and κ is the thermal conductance of the weak link. However, resistances other than that of the weak link cause the temperature relaxation to deviate from a single-exponential behavior, complicating the extraction of the heat capacity from the data. This is particularly a problem at millikelvin temperatures, where the contact resistance between the sample and the sample platform of the calorimeter becomes non-negligible. If the sample is non-metallic or made of compressed powder, its internal resistance often presents even more serious complications.

When the additional resistance is mainly due to poor thermal contact between the sample and the calorimeter, the temperature relaxation takes up a double-exponential form [2,3]. The sample heat capacity C in this case can be correctly obtained [2,4] from the time constant τ_1 and weight a_1 of the slow relaxation alone, if the data are taken after the platform heater is turned on or off starting from thermal equilibrium between the sample and the platform. A convenient expression [5] to use for this purpose is

$$C = \kappa a_1 \tau_1 \left(1 - \frac{C_{\text{add}}/\kappa}{\tau_1}\right)^2 \bigg/ \left(1 - \frac{a_1 C_{\text{add}}/\kappa}{\tau_1}\right), \tag{2}$$

where the addenda heat capacity C_{add} comes from the sample platform including the heater, thermometer, and 1/3 of the weak link [1,5]. An obvious but cumbersome alternative is to fit the data to two exponentials, from which the sample heat capacity is extracted [3,5].

If the additional resistance primarily comes from the sample itself, then the temperature decay exhibits a rapid initial relaxation that is non-exponential in shape, followed by a single, slow exponential. This is often called the distributed τ_2 effect, a misleading term inherited from the ac calorimetry [6], where it made perfect sense. This effect has been discussed by Bachmann *et al.*[1], who pioneered the relaxation calorimetry.

Recently, Takano and Muttalib [5] have given detailed analysis of this effect. In the most general case,

[1] Corresponding author. E-mail: takano@phys.ufl.edu

where both the internal resistance of the sample and the contact resistance between the sample and the calorimeter are significant, they have considered the heat-flow model given in Fig. 1. Here $\kappa_{\rm s}$ is the thermal conductances of the sample, and $\kappa'$the conductance of the contact between the sample and the calorimeter. The non-uniform temperature $T(x)$ is that within the sample, $T_{\rm p}$ the uniform temperature of the sample platform, and $T_{\rm r}$ the temperature of the reservoir.

Starting from a thermal equilibrium between the sample and the platform, the time evolution of $T_{\rm p}$ after the platform heater is turned off is given by [5]

$$\frac{T_{\rm p}(t)-T_{\rm r}}{T_{\rm p}(0)-T_{\rm r}}=\sum_{n=1}^{\infty}a_n\exp(-t/\tau_n), \qquad (3)$$

where the time constant τ_n and weight a_n of each exponential term are given by

$$\tau_n=C/({k_n}^2\kappa_{\rm s}) \qquad (4)$$

and

$$\begin{aligned}a_n = {} & 2\alpha\alpha'^2\{\alpha^2\beta^2k_n^6 \\ & +\beta\left[\alpha'\beta(\alpha'+\alpha)-2\alpha^2(\alpha'+1)\right]k_n^4 \\ & +\left[\alpha^2(\alpha'+1)^2+\alpha'\beta(\alpha\alpha'-2\alpha'-2\alpha)\right]k_n^2 \\ & +\alpha'(\alpha\alpha'+\alpha'+\alpha)\}^{-1}.\end{aligned} \qquad (5)$$

Here k_n are the roots of the eigenvalue equation

$$\frac{\alpha}{\alpha'}(\alpha'+1-\beta k_n^2)k_n\sin k_n=(1-\beta k_n^2)\cos k_n, \qquad (6)$$

which must be solved numerically, $\alpha\equiv\kappa_{\rm s}/\kappa$ and $\alpha'\equiv\kappa'/\kappa$ are conductance ratios, and $\beta\equiv C_{\rm add}\kappa_{\rm s}/(C\kappa)$. Takano and Muttalib have further shown [5] that an underestimate by up to $1-8/\pi^2\simeq19\%$ can occur in the sample heat capacity, if Eq. 2 or equivalent formulae [2,4] are used for data affected by a sample resistance. Based on conservation of energy alone and independent of any heat-flow model, they have proposed that the heat capacity should be extracted by combining a fit of the slow late-time relaxation to an exponential with a numerical integration of the residuals at the early time.

Figure 2 shows data of a magnetic insulator taken with a novel calorimeter [7] at 0.65 K in a 6 T magnetic field, exhibiting a distributed τ_2 effect [8]. The solid line is a fit of a late part of the data to a single exponential, and the broken line is a best fit of the entire data to a double exponential. For the heat capacity of the sample, Eq. 2 gives 1.01 μJ/K, the double exponential fit 1.11 μJ/K, and the method proposed by Takano and Muttalib 1.24 μJ/K. The difference between the first and the third, correct value is exactly 19%, the maximum error predicted by Takano and Muttalib.

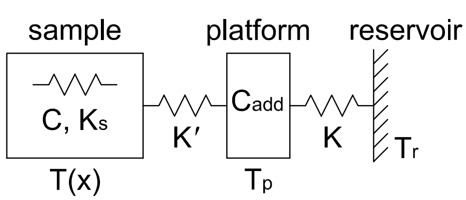

Fig. 1. Heat-flow model for a relaxation calorimeter, with the thermal conductance of the sample and the contact between the sample and the sample platform explicitly included. See the text for an explanation of the various elements of the model.

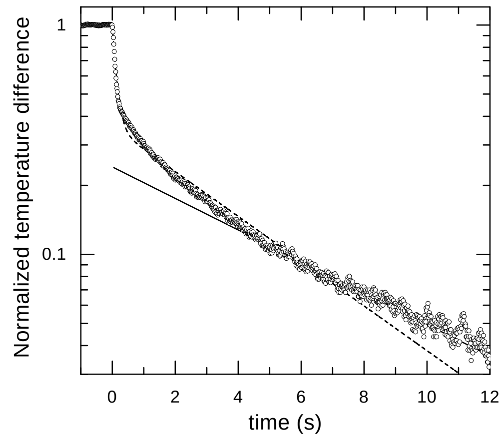

Fig. 2. Temperature relaxation data of a 5.47 mg sample of deuterated $Ni(C_5D_{14}N_2)_2N_3(PF_6)$, taken at 0.65 K in a 6 T magnetic field [8]. For clarity, only one out of every ten points is shown. The lines are fits discussed in the text.

A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084173 and by the State of Florida. We thank E. C. Palm and T. P. Murphy for assistance. This work was supported by the NSF through DMR-9802050 and the DOE under Grant No. DE-FG02-99ER45748.

References

[1] R. Bachmann, F. J. DiSalvo, T. H. Geballe, R. L. Greene, R. E. Howard, C. N. King, H. C. Kirsch, K. N. Lee, R. E. Schwall, H.-U. Thomas, R. B. Zubeck, Rev. Sci. Instr. **43** (1972) 205.

[2] R. E. Schwall, R. E. Howard, G. R. Stewart, Rev. Sci. Instr. **46** (1975) 1054.

[3] J. P. Shepherd, Rev. Sci. Instr. **56** (1985) 273.

[4] For example, see M. Regelsberger, R. Wernhardt, M. Rosenberg, J. Phys. E: Sci. Instrum. **19** (1986) 525.

[5] Y. Takano, K. A. Muttalib, to be published.

[6] P. F. Sullivan, G. Seidel, Phys. Rev. **173** (1968) 679.

[7] H. Tsujii, B. Andraka, E. C. Palm, T. P. Murphy, Y. Takano, in these Proceedings.

[8] H. Tsujii, Z. Honda, B. Andraka, K. Katsumata, Y. Takano, in these Proceedings.