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Distributed τ_2 effect in relaxation calorimetry

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Abstract

The so-called “distributed τ_2 effect” distorts the time evolution of temperature in the relaxation calorimetry of samples of poor thermal conductance. Very often a problem with non-metallic and powder samples at temperatures below 1 K, the effect appears as a fast initial relaxation of temperature that is non-exponential. Conventionally, calorimetry data suffering from this effect have been analyzed by the methods that are only appropriate for data affected by a contact resistance between the sample and the calorimeter. We show that a systematic error introduced by these methods in the heat capacity can be eliminated by a thermodynamically rigorous data-analysis method.

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

$$C_{\text{total}} = \kappa\tau, \quad (1)$$

where τ is the time constant of the exponential temperature relaxation of the sample platform and κ is the thermal conductance of the weak link between the platform and a thermal reservoir. In actual experiments, an exponential temperature relaxation with a single time constant occurs only if resistances other than that of the weak link are negligible. This condition is violated at millikelvin temperatures, where the contact resistance between the sample and the sample platform of the calorimeter is significant. The problem becomes even more serious, if the sample is non-metallic or composed of compressed powder, a situation where the internal resistance of the sample comes into play.

As is well known, the temperature relaxation takes a double-exponential form, when the parasitic resistance is mainly due to poor contact between the sample and the calorimeter [2,3]. The sample heat capacity C in this case is correctly obtained [2] (For example see Ref. [4]) from the time constant and weight 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. An obvious but cumbersome alternative is to fit the data to a sum of two exponentials, from which the sample heat capacity is extracted [3].

When the parasitic resistance is internal to the sample itself, then the temperature relaxation exhibits a rapid initial drop that is non-exponential in shape, followed by a single, slow exponential. This is often called the distributed τ_2 effect.

When both the internal resistance of the sample and the contact resistance between the sample and the calorimeter are significant, the model shown in Fig. 1 describes the heat flow in the calorimeter. Here κ_s is the conductance of the sample, and κ' that of the sample-to-platform contact. $T(x)$ is the temperature profile within the sample, T_p the uniform temperature of the sample platform, and T_r that of the reservoir. This model can be solved analytically [5]. In particular, the expression

$$\frac{T_p(t) - T_r}{T_p(0) - T_r} = \sum_{n=1}^{\infty} a_n \exp(-t/\tau_n) \quad (2)$$

gives the time evolution of T_p after the platform heater is turned off at $t = 0$, where thermal equilibrium has been established between the sample and the platform. Here the time constant τ_n and weight a_n of each exponential term are given by

$$\tau_n = C/(k_n^2 \kappa_s) \quad (3)$$

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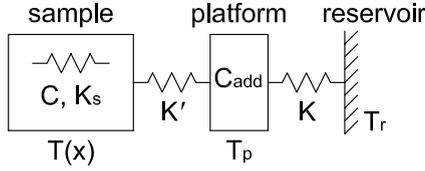


Fig. 1. Heat-flow model for a relaxation calorimeter, with the thermal conductance of the sample and the contact between the sample and the sample platform explicitly included. See the text for an explanation of all the elements of the model.

and

$$a_n = 2\alpha\alpha'^2 \{ \alpha^2 \beta^2 k_n^6 + \beta [\alpha' \beta (\alpha' + \alpha) - 2\alpha^2 (\alpha' + 1)] k_n^4 + [\alpha^2 (\alpha' + 1)^2 + \alpha' \beta (\alpha\alpha' - 2\alpha' - 2\alpha)] k_n^2 + \alpha' (\alpha\alpha' + \alpha' + \alpha) \}^{-1}. \quad (4)$$

In these equations, k_n are the roots of the eigenvalue equation

$$\frac{\alpha}{\alpha'} (\alpha' + 1 - \beta k_n^2) k_n \sin k_n = (1 - \beta k_n^2) \cos k_n, \quad (5)$$

which must be solved numerically, $\alpha \equiv \kappa_s/\kappa$ and $\alpha' \equiv \kappa'/\kappa$ are conductance ratios, and $\beta \equiv C_{\text{add}}\kappa_s/(C\kappa)$.

The heat capacity C_{add} of the addenda and the thermal conductance κ of the weak link are separately determined either during or prior to the experiment. This still leaves Eq. (2) with three parameters κ_s , κ' , and C , which make the determination of the sample heat capacity C from the temperature-relaxation data extremely difficult, if not totally impossible.

On the other hand, there is no justification for fitting the data to a sum of only two exponentials or extracting the sample heat capacity C from the time constant and weight of the slow relaxation alone, unless the internal thermal resistance of the sample is negligible. As it turns out, the conservation of energy dictates that the total heat capacity $C_{\text{total}} = C + C_{\text{add}}$ is simply the area under the temperature-relaxation curve in proper units, regardless of the origin of the parasitic resistance [5]:

$$C_{\text{total}} = \kappa \int_0^\infty \frac{T_p(t) - T_r}{T_p(0) - T_r} dt. \quad (6)$$

Fig. 2 shows data of a magnetic insulator taken with a novel calorimeter [6] at 0.65 K in a 6 T magnetic field, exhibiting a distributed τ_2 effect [7]. 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, the relaxation time and weight of the single exponential gives 1.01 $\mu\text{J}/\text{K}$, the double exponential fit gives 1.11 $\mu\text{J}/\text{K}$, and Eq. (6) yields 1.24 $\mu\text{J}/\text{K}$. Clearly, the first two methods, which are most commonly used,

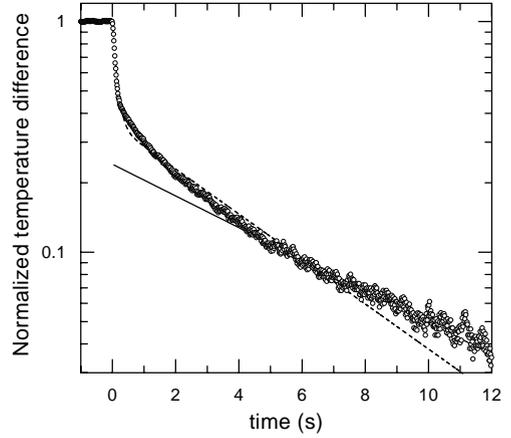


Fig. 2. Temperature relaxation data of a 5.47 mg sample of deuterated $\text{Ni}(\text{C}_5\text{D}_{14}\text{N}_2)_2\text{N}_3(\text{PF}_6)$, taken at 0.65 K in a 6 T magnetic field [7]. For clarity, only one out of every 10 points is shown. The lines are fits discussed in the text.

underestimate the heat capacity. To minimize random errors in the method of Eq. (6), the integral should be evaluated by fitting a late part of the data to a single exponential and by applying numerical integration to only the residual of the early part.

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