DERIVATION OF TEMPERATURE-MODULATED DSC THERMAL CONDUCTIVITY EQUATIONS

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Abstract

One of the benefits of temperature-modulated DSC (TMDSC) is its ability to measure thermal conductivity and thermal diffusivity without DSC cell modifications or additional accessories. Thermal conductivity of solid materials from 0.1 to about 1 $W \, m^{-1} \, K^{-1}$ may be measured. Applications of this approach have been discussed in the literature but no description is yet available concerning the derivation of the working equations. This presentation provides a detailed derivation of the working equations used to obtain thermal conductivity and thermal diffusivity from TMDSC data.

Keywords: DSC, TMDSC, thermal conductivity, thermal diffusivity

Introduction

TMDSC is a high performance version of traditional differential scanning calorimetry in which an oscillatory temperature program (modulation) is superimposed on the traditional linear heating program. In the TA Instruments embodiment of TMDSC, the resultant oscillatory heat flow signal is deconvoluted using discrete Fourier transformation into its reversing (heat capacity) and nonreversing (kinetic) components. The reversing and nonreversing heat flow signals provide sensitivity and interpretation benefits unavailable in traditional DSC.

In TMDSC, the ratio of the oscillatory heat flow amplitude to the oscillatory temperature amplitude yields heat capacity information. Users have found that the best heat capacity results are obtained when experimental conditions are selected to obtain maximum temperature uniformity across the test specimen. Small, thin specimens, long oscillation periods and complete encapsulation of the test specimen in sample pans of high conductivity (aluminum has a conductivity of about 235 $W \, m^{-1} \, K^{-1}$) [1] produce the best results. When test conditions lie outside of these guidelines, the accuracy of the measured heat capacity de

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clines. This is due to the thermal conductivity of the material preventing uniform temperature conditions across the test specimen.

Alternativity, maximization of this non-uniform temperature condition (through the use of thick test specimens and the application of the temperature oscillation to only one side of the test specimen) may be used to measure the thermal conductivity of a solid specimen.

Thermal conductivity information, derived from TMDSC use, is described in a number of publications [2–5]. The approach has been applied to neat polymers, glasses and to filled thermoset composites [2, 3, 6]. The approach has gained sufficient attention that it has been approved as an ASTM standard test method [7].

These publications start with a series of relevant working equations with little information as to their source. These working equations include:

$$K_o = \frac{8LC^2}{C_p M d^2 P} \tag{1}$$

for the observed thermal conductivity, and for the true thermal conductivity:

$$K_t = \frac{K_o - 2R + (K_o^2 - 4RK_o)^{1/2}}{2} \tag{2}$$

obtained by correcting for the heat flow shunting of the test specimen by the correction factor R, where

$$R = (K_o K_t)^{1/2} - K_t \tag{3}$$

Of course, the relationship between thermal diffusivity and thermal conductivity is well known:

$$\alpha = \frac{K}{C_p \rho} \tag{4}$$

In these equations: α=thermal diffusivity; C=apparent heat capacity; C_p=specific heat capacity; d=diameter; K=thermal conductivity; K_o=observed thermal conductivity; K_t=true thermal conductivity; L=length; M=mass; R=correction factor; P=temperature oscillation period; ρ=density.

It is purpose of this offering to describe the detailed derivation of these working equations.

Derivation of the equations is a two step process. The first is based upon the one dimensional periodic diffusivity equation which assumes all heat flow is through the sample. The second takes into account the shunting heat flow of the purge gas in contact with the sample when the measurement is performed.

One dimensional thermal conductive model

In a typical measurement, a sinusoidal temperature program, with amplitude of about $\pm 0.5°C$ and a period of 80 s, is applied to one end of the test specimen in the form of a right circular cylinder or rod, 0.63 mm is diameter and 3.5 mm in length. The temperature distribution $T(x,t)$ along a rod in response to a periodic temperature variation applied to one end of the rod is given, in complex form, by [8]:

$$T(x,t) = T(x)e^{i\omega t} \equiv T(x)\exp(i\omega t) \tag{5}$$

where

$$T(x) = A\exp[-x(i\omega/\alpha)^{1/2}] + B\exp[x(i\omega/\alpha)^{1/2}] \tag{6}$$

where T is temperature, x is the distance along the rod, t is time, i is $(-1)^{1/2}$, ω is the angular frequency of the periodic temperature variation, α is the thermal diffusivity of the rod, and A and B are constants determined by the boundary conditions.

The first term in Eq. (6) is associated with the propagation of the damped temperature wave down the rod while the second term is due to the reflection of the wave back from the opposite end.

Substituting the identity $i^{1/2}=(1+i)/2^{1/2}$ into Eq. (6) yields:

$$T(x) = A\exp[-x(1 + i)(\omega/2\alpha)^{1/2}] + B\exp[x(1 + i)(\omega/2\alpha)^{1/2}] \tag{7}$$

Defining a new term

$$Z = (\omega/2\alpha)^{1/2} \tag{8}$$

and substituting it into Eq. (7) leads to:

$$T(x) = A\exp[-xZ(1 + i)] + B\exp[xZ(1 + i)] \tag{9}$$

The temperature gradient along the sample is obtained by taking the derivative of Eq. (9).

$$\frac{dT}{dx} = -AZ(1 +i)\exp[-xZ(1 + i)] + BZ(1 + i)\exp[xZ(1 + i)] =$$

$$- Z(1 + i)\{-A\exp[-xZ(1 + i)] + B\exp[xZ(1 + i)]\} \tag{10}$$

The values for constants A and B are determined by the boundary conditions at $x=0$ and $x=L$, the length of the test specimen; specifically, 1) the amplitude of

the temperature oscillation at the base of the rod (i.e., $x=0$) is given by T_0 and
2) there is no heat flow through the opposite end of the rod (i.e., $dQ/dt)_{x=L}=0$.

Using the first boundary condition, if the amplitude of the applied tempera-
ture at $x=0$ is defined as T_0 then Eq. (9) reduces to:

$$T(0) = T_0 = A + B \qquad (11)$$

To make use of the second boundary condition, the steady state thermal con-
ductivity equation is used.

$$\frac{dQ}{dt} = -Ka\frac{dT}{dx} \qquad (12)$$

where dT/dx is the steady state temperature gradient through the cross sectional
area a produced by the heat flow dQ/dt.

Setting the heat flow through the opposite end of the rod (i.e., $x=L$) equal to
zero and substituting this boundary condition into Eq. (12) along with Eq. (10)
yields:

$$\left(\frac{dQ}{dt}\right)_{x=L} = 0 = -KaZ(1 + i)\{-A\exp[-LZ(1 + i)] + B\exp[LZ(1 + i)]\} \qquad (13)$$

Solving Eq. (13) for B yields:

$$B = A\exp[-2ZL(1 + i)] \qquad (14)$$

The values for A and B may be derived by substituting Eq. (14) into Eq. (11).

$$A = \frac{T_0}{1 + \exp[-2ZL(1 + i)]} \qquad (15)$$

$$B = \frac{T_0\exp[-2ZL(1 + i)]}{1 + \exp[-2ZL(1 + i)]} \qquad (16)$$

Substituting these values for A and B into Eq. (10) yields:

$$\frac{dT}{dx} = ZT_0(1 + i)\frac{-\exp[-xZ(1 + i)] + \exp[xZ(1 + i)]\exp[-2ZL(1 + i)]}{1 + \exp[-2ZL(1 + i)]} \qquad (17)$$

Substitution Eq. (17) into Eq. (12):

$$\frac{dQ}{dt} = -KaZT_0(1 + i)\frac{-\exp[-xZ(1 + i)] + \exp[xZ(1 + i)]\exp[-2ZL(1 + i)]}{1 + \exp[-2ZL(1 + i)]} \qquad (18)$$

Evaluating Eq. (18) at $x=0$:

$$\left(\frac{dQ}{dt}\right)_{x=0} = -KaZT_0(1+i)\frac{-1+\exp[-2ZL(1+i)]}{1+\exp[-2ZL(1+i)]} \qquad (19)$$

The square of the amplitude of heat flow is obtained by multiplying Eq. (19) by its complex conjugate:

$$\left|\frac{dQ}{dt}\right|^2_{x=0} = -KaZT_0(1+i)\frac{-1+\exp[-2ZL(1+i)]}{1+\exp[-2ZL(1+i)]}$$

$$\cdot(-KaZT_0)(1-i)\frac{-1+\exp[-2ZL(1-i)]}{1+\exp[-2ZL(1-i)]} = \qquad (20)$$

$$= (-KaZT_0)^2(1+i)(1-i)\frac{\{-1+\exp[-2ZL(1+i)]\}\{-1+\exp[-2ZL(1-i)]\}}{\{1+\exp[-2ZL(1+i)]\}\{1+\exp[-2ZL(1-i)]\}}$$

The multiplication steps for Eq. (20) include:

$$(1+i)(1-i) = 2 \qquad (21)$$

while the exponential numerator ($\equiv G$) is given by:

$$G = \{ -1 + \exp[-2ZL(1+i)]\}\{-1 + \exp[-2ZL(1-i)]\} = \qquad (22)$$

$$= 1 - \exp[-2ZL(1-i)] - \exp[-2ZL(1+i)] + \exp[-2ZL(1+i)]\exp[-2ZL(1-i)] =$$

$$= 1 - \exp[-2ZL]\exp[-2ZLi] - \exp[-2ZL]\exp[2ZLi] + \exp[-2ZL\{(1+i)+(1-i)\}] =$$

$$= 1 - \exp[-2ZL](\exp[2ZLi] + \exp[-2ZLi]) + \exp[-4ZL]$$

From Euler's formula [9, 10]:

$$\exp[2ZLi] = \cos(2ZL) + i\sin(2ZL) \qquad (23)$$

and

$$\exp[-2ZLi] = \cos(2ZL) - i\sin(2ZL) \qquad (24)$$

Substituting these identities into Eq. (22):

$$G = 1 - \exp[-2ZL]\{\cos(2ZL) + i\sin(2ZL) + \cos(2ZL) - i\sin(2ZL)\} + \exp[-4ZL] =$$

$$= 1 - 2\cos(2ZL)\exp[-2ZL] + \exp[-4ZL] \qquad (25)$$

By a similar process the denominator ($\equiv D$) of Eq. (20) is:

$$D \equiv \{1 + \exp[-2ZL(1+i)]\}\{1 + \exp[-2ZL(1-i)]\} =$$

$$= 1 + 2\cos(2ZL)\exp[-2ZL] + \exp[-4ZL] \tag{26}$$

Recasting Eq. (20) using Eqs (21), (25) and (26):

$$\left|\frac{dQ}{dt}\right|^2_{x=0} = 2(KaZT_o)^2 \frac{1 - 2\cos(2ZL)\,\exp[-2ZL] + \exp[-4ZL]}{1 + 2\cos(2ZL)\,\exp[-2ZL] + \exp[-4ZL]} \tag{27}$$

Multiplying the numerator and the denominator by exp[4ZL], Eq. (27) becomes:

$$\left|\frac{dQ}{dt}\right|^2_{x=0} = 2(KaZT_o)^2 \frac{1 - 2\cos(2ZL)\,\exp[2ZL] + \exp[4ZL]}{1 + 2\cos(2ZL)\,\exp[2ZL] + \exp[4ZL]} \tag{28}$$

If exp[4ZL] is very much greater than 1. which is the case if thermal conductivity is low, then Eq. (28) reduces to:

$$\left|\frac{dQ}{dt}\right|^2_{x=0} = 2(KaZT_o)^2 \tag{29}$$

Actual values of exp[4ZL] range between 3000 and 40 for materials with thermal conductivities ranging between $K=0.15$ and 1.1 W m^{-1} K^{-1}, the approximate range of the application.

The relationship between thermal diffusivity (α) and thermal conductivity (K) is given by Eq. (4). Substituting this relationship into Eq. (8):

$$Z = \left(\frac{\omega C_p \rho}{2K}\right)^{1/2} \tag{30}$$

and Eq. (30) into Eq. (29):

$$\left|\frac{dQ}{dt}\right|^2_{x=0} = 2K^2 a^2 T_o^2 \frac{\omega C_p \rho}{2K} = Ka^2 T_o^2 \omega C_p \rho \tag{31}$$

Solving for K:

$$K = \frac{\left|\dfrac{dQ}{dt}\right|^2_{x=0}}{a^2 T_o^2 \omega C_p \rho} \tag{32}$$

From traditional MDSC [11], the apparent heat capacity (C) is given by:

$$C = \frac{\left|\frac{dQ}{dt}\right|}{\omega T_o} \qquad (33)$$

Substituting Eq. (33) into Eq. (32),

$$K = \frac{\omega^2 T_o^2 C^2}{T_o^2 a^2 \omega C_p \rho} = \frac{\omega C^2}{C_p \rho a^2} \qquad (34)$$

The density value in Eq. (34) is equal to the specimen mass (M) divided by the specimen volume ($V=aL$). In addition, the angular frequency (ω) is related to the experimental period (P) by $\omega=2\pi/P$. Substituting these values into Eq. (34) yields:

$$K = \frac{2\,\pi C^2 V}{C_p a^2 M P} \qquad (35)$$

This equation is applicable to any appropriate cross sectional area. For the case of a rod (i.e., cylinder), however, the area $a=\pi d^2/4$, where d is the diameter of the rod. Substituting this value into Eq. (24) yields:

$$K = \frac{8 L C^2}{C_p M d^2 P} \qquad (1)$$

This is the working equation used in earlier publications. Sample length (L), diameter (d) and mass (M) are easily measured physical parameters. The specimen's specific heat capacity (C_p) may be measured using the MDSC under the optimum conditions described previously [11]. The period (P) is an experimental parameter. And the apparent heat capacity (C) is the measured parameter from the thermal conductivity optimized experimental conditions.

Determination of shunting conductivity

The one-dimensional calculation above does not take into account heat flow shunting of the test specimen. The following calculations provide a first approximation method for accounting for this heat flow. The method uses the measurement of a material having known thermal conductivity to obtain a correction factor, which is observed to vary with experimental conditions [5]. This correction factor, however, may be applied to the thermal conductivity measurement of materials having similar dimensions, measured under similar experimental conditions.

For the calculation of the shunting heat flow, it is assumed that the heat flow into the gas surrounding the specimen is proportional to the temperature gradient

at the base of the specimen. The temperature near the base of the rod may be approximated by the first term in Eq. (9).

$$T(x) = A\exp[-xZ(1 + i)]$$ (36)

By the same assumption, Eq. (11) reduces to $A=T_o$, so

$$T(x) = T_o\exp[-xZ(1 + i)]$$ (37)

Taking the derivative of Eq. (37):

$$\frac{dT}{dx} = -ZT_o(1 + i)\exp[-xZ(1 + i)]$$ (38)

As x approaches zero, the exponential term in Eq. (38) goes to unity.

$$\left(\frac{dT}{dx}\right)_{x=0} = -ZT_o(1 + i)$$ (39)

And as the heat flow into the gas surrounding the rod is proportional to the temperature gradient on the sample surface at the sample base, by analogy to Eq. (12) along with Eq. (39):

$$\left(\frac{dQ}{dt}\right)_s = -Ra\left(\frac{dT}{dx}\right)_{x=0} - RaZT_o(1 + i)$$ (40)

where R is a scale factor that is dependent on the gas surrounding the sample, the dimension of the sample and the experimental conditions.

With the assumption of $\exp[-2ZL] \ll 1$, Eq. (19) becomes:

$$\left(\frac{dQ}{dt}\right)_t = K_t aZT_o(1 + i)$$ (41)

The assumption of $\exp[-2ZL] \ll 1$ is more restrictive than the previous condition of $\exp[4ZL] \gg 1$ with $\exp[-2ZL]$ ranging between 0.018 and 0.16 for the thermal conductivity range of this application.

The total observed heat flow $[(dQ/dt)_o]$, consisting of the sum of the heat flow through the sample $[(dQ/dt)_t]$ and the heat flow shunted around the sample through the gas $[(dQ/dt)_s]$, is used to calculate the measured 'true' thermal conductivity K_t.

$$\frac{K_t}{K_o} = \frac{\left|\dfrac{dQ}{dt}\right|_t^2}{\left|\dfrac{dQ}{dt}\right|_o^2} = \frac{\left|\dfrac{dQ}{dt}\right|_t^2}{\left|\left(\dfrac{dQ}{dt}\right)_t + \left(\dfrac{dQ}{dt}\right)_s\right|^2}$$ (42)

where K_o is the measured effective thermal conductivity at $x=0$. Substituting Eqs (29), (10) and (11), along with their complex conjugates, into Eq. (42) we have:

$$\frac{K_t}{K_o} = \frac{2K_t^2 a^2 Z^2 T_o^2}{[K_t aZT_o(1-i) + RaZT_o(1-i)]} =$$

$$= \frac{2K_t^2 a^2 Z^2 T_o^2}{(aZT_o)(K_t+R)(1+i) \cdot aZT_o(K_t+R)(1-i)} = \frac{2K_t^2 a^2 Z^2 T_o^2}{a^2 Z^2 T_o^2 (K_t+R)^2 (1+i)(1-i)} \quad (43)$$

The squared term in the denominator is obtained by multiplying the bracketed quantity by its complex conjugate:

$$\frac{K_t}{K_o} = \frac{K_t^2}{(K_t+R)^2} \quad (44)$$

Solving for R:

$$K_o = \frac{(K_t+R)^2}{K_t}$$

$$R = (K_o K_t)^{1/2} - K_t \quad (3)$$

Thus R can be computed from the values of K and K_t. If a sample of known thermal conductivity (K_t) is measured, thereby determining its observed thermal conductivity (K_o), the correction factor R can be calculated. The calculated value of the correction factor can be applied to subsequent measurements, to compute the true thermal conductivity from the measured effective thermal conductivity.

Eq. (3) may be recast in the quadric form:

$$K_o K_t = (K_t+R)^2 = K_t^2 + 2 K_t R + R^2$$

$$0 = K_t^2 + (2R - K_o)K_t + R^2 \quad (45)$$

and solving for K_t using the positive root of the quadratic formula:

$$K_t = \frac{K_o - 2R + (K_o^2 - 4 RK_o)^{1/2}}{2} \quad (2)$$

where R is the previously calculated correction factor and K_o is the measured effective thermal conductivity of the sample.

Equations (2) and (3) represent the remaining working equations for obtaining thermal conductivity information by MDSC.

As an item of practical experimental consideration, to obtain the maximum accuracy in the determination of R, the thermal conductivity of the material chosen to serve as the reference material should be as small as possible, close (but several times larger than) that of the purge gas. The thermal conductivity of nitrogen purge gas is about 0.026 W m^{-1} K^{-1} [12]. Polymer materials are a convenient source of such a material. Polystyrene, with its low thermal conductivity of about 0.15 W m^{-1} K^{-1} [13] and its amorphous form (one does not need to be terribly concerned about its thermal history), is the reference material of choice.

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