Appendix: An Outline of the Least-Squares Technique Used in Matching Time–Temperature Curves with Linear Thermal Conductivities

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The form of the one-dimensional heat equation is assumed to be

$$\frac{\partial v}{\partial t} = \frac{1}{\rho C_p(v)} \frac{\partial}{\partial x}\left((k(v) \frac{\partial v}{\partial x}\right) \tag{A-1}$$

where v is relative temperature, t is time, and

$$k(v) = k_0 + bv$$

Given a temperature profile,$\tau_i(t_i)$ vs. t_i $(i = 1, ..., n)$, at some point, x_l, k (v) is to be determined in the least-squares sense (n = number of observations).

With the above definition of $k(v)$, eq. (A-1) becomes

$$\frac{\partial v}{\partial t} = \frac{1}{\rho C_p}\left[b\left(\frac{\partial v}{\partial x}\right)^2 + (k_0 + bv)\frac{\partial^2 v}{\partial x^2}\right] \tag{A-2}$$

The solution of eq. (A-2) is of the form

$$v = f(x,t,k_0,b) \tag{A-3}$$

At the point $x = x_l$, and at specific times t_i,

$$v_i = f(x_l,t_i,k_0,b) \tag{A-4}$$

In the least-squares sense the following function must then be minimized:

$$\sum_{i=1}^{n} [v_i - \tau_i]^2 = E \tag{A-5}$$

Expanding f in Taylors series about (k'_0,b'), using initial guesses for (k_0, b), and dropping the high order terms yields

$$f(x_l,t_i,k_0,b) = f(x_l,t_i,k_0', b') + \frac{\partial f}{\partial k_0}\bigg|_{k'_0b'}(k_0 - k'_0) + \frac{\partial f}{\partial b}\bigg|_{k'_0b'}(b - b') \tag{A-6}$$

Letting $\Delta k_0 = k_0 - k'_0$, $\Delta b = b - b'$ and substituting eq. (A-6) into eq. (A-5) yields:

$$\sum_{i=1}^{n}\left[\tau_i - f(x_l,t_i,k'_0,b') - \frac{\partial f}{\partial k_0}\Delta k_0 - \frac{\partial f}{\partial b}\Delta b\right]^2 = E \tag{A-7}$$

For minimization, k_0 and b must be formed to satisfy eqs. (A-8), where letting $f_i = f(x_i,t_i,k'_0,b')$:

$$\left.\begin{aligned} \frac{\partial E}{\partial \Delta k_0} &= \sum_{i=1}^{n} 2\left[\tau_i - f_i - \frac{\partial f_i}{\partial k_0}\Delta k_0 - \frac{\partial f_i}{\partial b}\Delta b\right]\left(-\frac{\partial f_i}{\partial k_0}\right) = 0 \\ \frac{\partial E}{\partial \Delta b} &= \sum_{i=1}^{n} 2\left[\tau_i - f_i - \frac{\partial f_i}{\partial k_0}\Delta k_0 - \frac{\partial f_i}{\partial b}\Delta b\right]\left(-\frac{\partial f_i}{\partial b}\right) = 0 \end{aligned}\right\} \qquad \text{(A-8)}$$

Rearranging terms,

$$\left.\begin{aligned} \sum_{i=1}^{n}\left[(\tau_i - f_i)\frac{\partial f_i}{\partial k_0}\right] &= \Delta k_0 \sum_{i=1}^{n}\left(\frac{\partial f_i}{\partial k_0}\right)^2 + \Delta b \sum_{i=1}^{n}\left(\frac{\partial f_i}{\partial k_0}\right)\left(\frac{\partial f_i}{\partial b}\right) \\ \sum_{i=1}^{n}\left[(\tau_i - f_i)\frac{\partial f_i}{\partial b}\right] &= \Delta a \sum_{i=1}^{n}\left(\frac{\partial f_i}{\partial k_0}\right)\left(\frac{\partial f_i}{\partial b}\right) + \Delta b \sum_{i=1}^{n}\left(\frac{\partial f_i}{\partial b}\right)^2 \end{aligned}\right\} \qquad \text{(A-9)}$$

Setting $\psi_i = \partial f_i/\partial k_0$ and $\psi'_i = \partial f_i/\partial b$,

Then

$$\begin{aligned} \frac{\partial \psi_i}{\partial t_i} &= \frac{\partial}{\partial t}\left(\frac{\partial f_i}{\partial k_0}\right) = \frac{\partial}{\partial k_0}\left(\frac{\partial f_i}{\partial t_i}\right) = \frac{\partial}{\partial k_0}\left(\frac{\partial v_i}{\partial t}\right) \\ &= \frac{1}{(\rho C_p)_i}\frac{\partial^2 v_i}{\partial x^2} \end{aligned} \qquad \text{(A-10)}$$

where

$$\psi_1(k_0,0) = 0$$

In like manner,

$$\frac{\partial \psi'_i}{\partial t_i} = \frac{1}{(\rho C_p)_i}\left[\left(\frac{\partial v'}{\partial x}\right)^2 + v_i \frac{\partial^2 v_i}{\partial x^2}\right] \qquad \text{(A-11)}$$

where

$$\psi'_i(b,0) = 0$$

The computational sequence is as follows.

1. Select initial guesses: $k = k_0$, $b = b_0$.
2. Solve to $t = t_i$, $i = 1,2,\ldots n$:

a. $$\frac{\partial v}{\partial t} = \frac{1}{\rho C_p}\left[b\left(\frac{\partial v}{\partial x}\right)^2 + (k_0 + bv)\frac{\partial^2 v}{\partial x^2}\right]$$ Solve by use of C–N heat equation solver

b. $$\frac{\partial \psi}{\partial t} = \frac{1}{\rho C_p}\frac{\partial^2 v}{\partial x^2}$$

c. $$\frac{\partial \psi'}{\partial t} = \frac{1}{\rho C_p}\left[\left(\frac{\partial v}{\partial x}\right)^2 + v\frac{\partial^2 v}{\partial x^2}\right]$$

Solve by finite differences

3. At the point $x = x_i$ form:

$$\sum_{i=1}^{n} (\tau_i - v_i)\psi_i, \sum_{i=1}^{n} \psi_i \cdot \psi'_i, \sum_{i=1}^{n} (\tau_i - v_o)\psi'_i \cdot \sum \psi_i^2, \sum (\psi'_i)^2$$

4. Solve eq. (A-9) for Δk_0 and Δb.
5. Set $k_{0_i} = k_{0_{i-1}} + \Delta k_0$

   $b_i = b_{i-1} + \Delta b$
6. $|\Delta k_0| < \epsilon_1, |\Delta b| < \epsilon_2$
7. Yes → Stop; No → Go to Step 2.

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Résumé

On a obtenu des relations linéaires pour la conductivité thermique au-dessus de la température de chambre à partir des résultats de la température de transition en fonction du temps pour le polyéthylène, le polytétrafluoroéthylène et le polyméthylate de méthyle. Les relations sont en bon accord avec les données de la littérature pour le même domaine de température, mais la durée du calcul et les frais pour obtenir ces résultats sont plus grands si on compare cette méthode à d'autres techniques de mesure qui possèdent une précision équivalente.

Zusammenfassung

Die linearen Beziehungen der Wärmeleitfähigkeit oberhalb Raumtemperatur wurden aus übergang temperatur-Zeitabhängigkeitsergebnissen für Polyäthylen, Polytetrafluoräthylen und Polymethylmethacrylat bestimmt. Die Beziehungen stimmen mit den Literaturdaten für denselben Temperaturbereich gut überein, die Rechenzeit und -kosten sind für die einzelnen Ergenispunkte jedoch viel grösser, verglichen mit anderen Messmethoden mit äquivalenter Genauigkeit.

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