JOURNAL OF APPLIED POLYMER SCIENCE VOL. 10, PP. 1111–1119 (1966)

Nonlinear Least Squares: A Method for Simultaneous Thermal Property Determination in Ablating Polymeric Materials

ROBERT C. PFAHL, JR., *Avco Research and Development Division, Wilmington, Massachusetts*

Synopsis

A method of data interpretation known as nonlinear least squares has recently been applied by several authors to the study of polymeric materials. Nagler has used a modified method proposed by Blizzard and Jirka and has concluded that the method is impractical because it requires excessive computer time. It is shown that the difficulties Nagler encountered are inherent in Blizzard and Jirka's method, but not in the basic method. Three steps are outlined to minimize computer time, and a summary of successful applications is presented.

Introduction

In a recent article,[1] Nagler has applied a nonlinear least-squares technique to the determination of temperature-variable thermal conductivities. Unfortunately, new techniques proposed by Blizzard and Jirka[2] in an appendix to Nagler's article have led Nagler to believe that the least-squares technique is impractical for a two-parameter problem because of the excessive amount of computer time required. The present author, through the correct application of nonlinear least squares, has solved successfully a seven parameter problem describing internal ablation mechanisms in a polymeric material. The purpose of this note is to summarize what the author believes to be the correct techniques for applying nonlinear least squares and to indicate the difficulties in the method presented by Blizzard and Jirka.[2]

Theory

It is useful to present first the classical manner in which the method of least squares has been applied to nonlinear problems. This derivation is attributed to Gauss. The notation is similar to that of Blizzard and Jirka,[2] but a more general problem is considered. We consider a problem in which experimental values of temperature, τ, have been measured during a transient experiment by n_x temperature sensors at n_t discrete times. Thus the dependent variable τ has been measured at $n = n_x \times n_t$ pairs of values of the two independent variables, x (distance) and t (time); symbolically

$$\tau_i = \tau(x_i,t_i) \qquad i = 1, 2, \ldots, n \tag{1}$$

The purpose of the experiment is to determine the magnitude of q parameters, $p_1, p_2, \ldots, p_q$. The parameters are quantities such as thermal conductivities, specific heats, heats of decomposition, and decomposition rate constants.

A theoretical model has been hypothesized to describe the experiment. This model, which may be a differential equation as in reference 2, expresses the functional dependence of the dependent variable, v (temperature), upon the independent variables, x and t, and the q parameters, $p_1, p_2, \ldots, p_q$, that appear in the model; symbolically, the solution to this model may be expressed as

$$v = v(x, t; p_1, p_2, \ldots, p_q) \tag{2}$$

and

$$v_i = v(x_i, t_i; p_1, p_2, \ldots, p_q) \tag{2'}$$

It is assumed throughout this communication that eqs. (2) and (2′) represent solutions obtained by numerical methods on a high-speed digital computer.

Nonlinear least squares determines the set of the parameters, $p_1, p_2, \ldots, p_q$ (which may be represented by a vector, $\mathbf{P}$), which minimizes in the least-squares sense the difference between experimental and theoretical temperatures. Mathematically it is desired to minimize

$$F = \sum_{i=1}^{n} (\tau_i - v_i)^2 \tag{3}$$

The value of any variable at this minimum is denoted by a bar ($\bar{F}$, $\bar{\mathbf{P}}$, $\bar{v}$). The least-squares function is related directly to the root-mean-square (rms) temperature difference between experimental and theoretical temperatures.

$$v_{\text{rms}} = (F/n)^{1/2} \tag{4}$$

If a minimum of F exists, then

$$\left.\frac{\partial F}{\partial p_1}\right|_{\mathbf{P}=\bar{\mathbf{P}}} = \left.\frac{\partial F}{\partial p_2}\right|_{\mathbf{P}=\bar{\mathbf{P}}} = \cdots \left.\frac{\partial F}{\partial p_q}\right|_{\mathbf{P}=\bar{\mathbf{P}}} = 0 \tag{5}$$

or

$$\sum_{i=1}^{n} \left[(\tau_i - \bar{v}_i) \left.\frac{\partial v_i}{\partial p_k}\right|_{\mathbf{P}=\bar{\mathbf{P}}} \right] = 0 \qquad k = 1, 2, \ldots, q \tag{6}$$

The usual iterative method, attributed to Gauss, for solving eq. (6), is to linearize the equation by expanding v_i in a first-order Taylor series with the parameters as the independent variables in the expansion. v_i is expanded about the point v_i^m (the value of the v_i at the mth iteration) to obtain an improved estimation of $\bar{v}_i$, namely, v_i^{m+1}.

$$\bar{v}_i \approx v_i^{m+1} \approx v_i^m + \sum_{j=1}^{q} (p_j^{m+1} - p_j^m) \left.\frac{\partial v_i}{\partial p_j}\right|_{\mathbf{P}=\mathbf{P}^m} \tag{7}$$

In this expansion $(p_j^{m+1} - p_j^m)$ (the change in parameter j at the mth iteration) is an iteration parameter for which an optimum value is sought, and p_j^m (the value of parameter j at the mth iteration) may be regarded as a fixed constant. The property derivatives at $\mathbf{P}$ in eq. (6) are approximated by their value at the mth iteration.

$$\left.\frac{\partial v_i}{\partial p_k}\right|_{\mathbf{P}=\mathbf{P}} \approx \left.\frac{\partial v_i}{\partial p_k}\right|_{\mathbf{P}=\mathbf{P}^m} \equiv \left.\frac{\partial v}{\partial p_k}\right|_{(i;\,m)} \tag{8}$$

The so-called "normal equations" are derived from eqs. (6), (7), and (8);

$$\sum_{i=1}^{n} (\tau_i - v_i^m) \left.\frac{\partial v}{\partial p_k}\right|_{(i;\,m)} = \sum_{j=1}^{q} \left[(p_j^{m+1} - p_j^m) \times \sum_{i=1}^{n} \left.\frac{\partial v}{\partial p_j}\right|_{(i;\,m)} \left.\frac{\partial v}{\partial p_k}\right|_{(i;\,m)} \right] k = 1, 2, \ldots, q \tag{9}$$

Equation (9) is identical in form to eq. (A-9) of reference 2 except for minor changes in notation to make the equation more general. The only essential difference in the present derivation from that of Blizzard and Jirka[2] is the point in the derivation at which $\bar{v}_i$ is expanded in a Taylor series. The linear form of eq. (9) may be more clearly exhibited through the use of matrix notation; letting

$$b_k^m = \sum_{i=1}^{n} (\tau_i - v_i^m) \left.\frac{\partial v}{\partial p_k}\right|_{(i;\,m)} \tag{10}$$

$$a_{kj}^m = a_{jk}^m = \sum_{i=1}^{n} \left.\frac{\partial v}{\partial p_j}\right|_{(i;\,m)} \left.\frac{\partial v}{\partial p_k}\right|_{(i;\,m)} \tag{11}$$

and defining the three matrices

$$\mathbf{B}^m = \begin{bmatrix} b_1^m \\ \cdot \\ \cdot \\ \cdot \\ b_q^m \end{bmatrix}$$

$$\mathbf{A}^m = \begin{bmatrix} a_{11}^m \cdots a_{1q}^m \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ \cdot \quad\quad \cdot \\ a_{q1}^m \cdots a_{qq}^m \end{bmatrix}$$

$$\mathbf{P}^m = \begin{bmatrix} p_1^m \\ \cdot \\ \cdot \\ \cdot \\ p_q \end{bmatrix} \tag{12}$$

eq. (9) becomes

$$\mathbf{A}^m(\mathbf{P}^{m+1} - \mathbf{P}^m) = \mathbf{B}^m \tag{13}$$

or

$$\mathbf{P}^{m+1} = \mathbf{P}^m + (\mathbf{A}^m)^{-1}\mathbf{B}^m \tag{14}$$

Equation (14) is a linear equation for $\mathbf{P}^{m+1}$ which is readily solved by any of several methods once the elements of $\mathbf{A}^m$ and $\mathbf{B}^m$ have been computed.

The computation of these elements requires the determination of the parameter derivatives $\partial v/\partial p_k|_{(i;\, m)}$. These derivatives cannot be computed directly since $v(x, t, p_1, p_2, \ldots, p_q)$ represents the numerical solution to a set of differential equations. The customary method of computing the parameter derivatives (as opposed to the new method proposed by Blizzard and Jirka[2]) is to approximate the derivatives by finite differences.

$$\left.\frac{\partial v}{\partial p_k}\right|_{(i;\, m)} \approx \frac{v(x_i, t_i; p_1^m, p_2^m, \ldots, (1+\epsilon)p_k^m, \ldots, p_q^m) - v_i^m}{\epsilon p_k^m} \tag{15}$$

where ϵ is a small number. Therefore, to solve for the elements of the matrices $\mathbf{A}^m$ and $\mathbf{B}^m$ of eq. (14), it is necessary to solve eq. (2) $q + 1$ times: first at $\mathbf{P}^m$ and then varying each parameter a small amount in succession.

The iterative procedure represented by eq. (14) is normally continued until $|\mathbf{P}^{m+1} - \mathbf{P}^m| \leq \delta$, where δ is an arbitrary small number.

Methods of Reducing the Number of Calculations

Since the solution of the mathematical model represented by eq. (2) requires the use of time-consuming numerical methods, if steps are not taken to insure rapid convergence, the method may become impractical. Nagler[1] was discouraged as to the future for nonlinear least squares because of the inherently slow convergence of the computational method proposed by Blizzard and Jirka.[2] There are three steps that should be taken to speed convergence to $\bar{\mathbf{P}}$ and to minimize computer time. (Although space does not permit the discussion of these steps in detail, references to detailed discussions are indicated.)

(*1*) Calculations may be reduced by careful selection of the initial estimate of the parameter vector $\mathbf{P}$.[3]

(*2*) Calculations may be reduced by using modified forms of the Gauss method of nonlinear least squares to speed convergence. These modified forms include an interpolative method,[4] an hybrid Gauss-steepest descent method proposed by Marquardt,[5] and a class of methods based upon the assumption that the $\mathbf{A}^m$ matrix in eq. (14) does not vary greatly during succeeding iterations.[6]

(*3*) Calculations may be reduced by careful design of the experiment. Not only is careful design necessary to reduce calculations and to improve accuracy, but also without careful design it is, in many cases, completely impossible to determine simultaneously all of the desired parameters.

A carefully designed experiment is one in which there is a minimum of correlation between the parameters. Box and Lucas presented one of the first discussions of nonlinear design.[7] Beck has performed extensive studies on the optimum experimental design for the simultaneous determination of thermal conductivity and specific heat.[8–10] One point to be gained from these investigations for our immediate use is that an optimum experiment is one in which the temperatures are measured at "points at which the [parameter] derivatives are large in absolute value, but also, so far as possible, uncorrelated."[7]

Applications

Nonlinear least squares has been applied successfully for property determination in a variety of problems. Marquardt et al.[11] have used the method for an electron paramagnetic resonance spectra problem. Kittrell, Mezaki, and Watson[3] have applied nonlinear least squares to determining adsorption rate constants. They have determined up to six parameters simultaneously. Booth and Peterson[4] present an example involving two chemical reactions in which they determine two reaction rate constants.

Beck[8–10] has demonstrated in numerous problems the ability of nonlinear least squares to determine two parameters from one experiment. His work has been concerned with the simultaneous determination of thermal conductivity and specific heat and with the determination of two parameters describing a linearly temperature dependent conductivity (the same problem treated by Nagler).

The present author has utilized nonlinear least squares to attack the same problem as Nagler, that of determining the internal behavior of a charring ablator.[12] A model of ablation was hypothesized in which a virgin material with temperature-independent properties underwent an endothermic reaction at a constant temperature to form a char matrix and a transpiring gas, both with temperature-independent properties. This thermal model involved seven thermal parameters; the conductivity of the virgin material, the specific heat of the virgin material, the temperature of decomposition, the enthalpy of decomposition, the conductivity of the char layer, the specific heat of the char layer, and the specific heat of the gas phase. An hypothetical experiment using four thermocouples was designed following criterion established by Beck;[8] in reference 12, a sample calculation demonstrates that from this one transient experiment all seven parameters can be determined. The calculations were started approximately 10% from the correct parameter values, and the method converged within 0.01% of the true values in six iterations. Experiments were conducted on a cork-phenolic material to determine the seven parameters. The least-squares analysis revealed that the hypothesized model was not adequate for describing the behavior of charring cork.

The author currently is extending this earlier work to polymeric materials described more accurately by the hypothesized model. In addition, stud-

ies are being conducted to determine the feasibility of using the nonlinear least-squares method in a more general model involving 16 parameters nd including surface as well as internal ablation mechanisms.

Discussion of the Method Proposed by Blizzard and Jirka

Blizzard and Jirka in their appendix have attempted to derive a new technique for determining the parameter derivatives $\partial v/\partial p_k|_{(i;\,m)}$ of eq. (9), but unfortunately they have neglected several terms. They consider one-dimensional heat conduction with temperature-variable properties. The temperature-variable thermal conductivity is

$$k(v) = k_0 + bv \tag{16}$$

Thus, for their problem, the parameter vector, $\mathbf{P} = (k_0, b)$. The one-dimensional heat conduction equation is

$$\frac{\partial v}{\partial t} = \frac{1}{\rho c_p(v)} \frac{\partial}{\partial x}\left(k(v) \frac{\partial v}{\partial x}\right) = \frac{1}{\rho c_p(v)} \frac{\partial}{\partial x}\left((k_0 + bv) \frac{\partial v}{\partial x}\right) \tag{17}$$

where $\rho c_p(v)$ is the temperature-dependent volumetric specific heat.

Blizzard and Jirka attempt to compute the parameter derivatives $\partial v/\partial k_0|_{(i;m)}$ and $\partial v/\partial b|_{(i;m)}$ by computing

$$\left.\frac{\partial^2 v}{\partial t \partial k_0}\right|_{(i;\,m)} \equiv \left.\frac{\partial}{\partial t}\right|_t \left(\left.\frac{\partial v}{\partial k_0}\right|_m\right) = \left.\frac{\partial}{\partial k_0}\right|_m \left(\left.\frac{\partial v}{\partial t}\right|_t\right) \equiv \left.\frac{\partial^2 v}{\partial k_0 \partial t}\right|_{(i;\,m)} \tag{18a}$$

and

$$\left.\frac{\partial^2 v}{\partial t \partial b}\right|_{(i;\,m)} \equiv \left.\frac{\partial}{\partial t}\right|_t \left(\left.\frac{\partial v}{\partial b}\right|_m\right) = \left.\frac{\partial}{\partial b}\right|_m \left(\left.\frac{\partial v}{\partial t}\right|_t\right) \equiv \left.\frac{\partial^2 v}{\partial b \partial t}\right|_{(i;\,m)} \tag{18b}$$

These two equations require that $v(x, t; k_0, b)$ and its derivatives are continuous at $(i; m)$. Substitution of eq. (17) into eqs. (18a) and (18b) yields eqs. (19a) and (19b), respectively, in which the terms in brackets are neglected by Blizzard and Jirka.

$$\left.\frac{\partial^2 v}{\partial t \partial k_0}\right|_{(i;\,m)} = \frac{1}{(\rho c_p)_i}\left\{\left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} + \left[2b^m \left.\frac{\partial v}{\partial x}\right|_{(i;\,m)} \left.\frac{\partial^2 v}{\partial k_0 \partial x}\right|_{(i;\,m)} + (k_0{}^m + b^m v_i{}^m) \left.\frac{\partial^3 v}{\partial k_0 \partial x^2}\right|_{(i;\,m)} + b^m \left.\frac{\partial v}{\partial k_0}\right|_{(i;\,m)} \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)}\right]\right\} \tag{19a}$$

$$\left.\frac{\partial^2 v}{\partial t \partial b}\right|_{(i;\,m)} = \frac{1}{(\rho c_p)_i}\left\{\left(\left.\frac{\partial v}{\partial x}\right|_{(i;\,m)}\right)^2 + v_i{}^m \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} + \left[2b^m \frac{\partial v}{\partial x}_{(i;\,m)} \left.\frac{\partial^2 v}{\partial b \partial x}\right|_{(i;\,m)} + (k_0{}^m + b^m v_i{}^m) \left.\frac{\partial^3 v}{\partial b \partial x^2}\right|_{(i;\,m)} + b^m \left.\frac{\partial v}{\partial b}\right|_{(i;\,m)} \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)}\right]\right\} \tag{19b}$$

The additional terms occur because v and its partial derivatives are functions of k_0 and b, as well as of x and t.

If the terms in brackets are neglected, eqs. (19a) and (19b) may be integrated with respect to time by finite differences to obtain the parameter derivatives $\partial v/\partial k_0|_{(i;\,m)}$ and $\partial v/\partial b|_{(i;\,m)}$. However, if the terms cannot be neglected, Blizzard and Jirka's procedure has not served to calculate the derivatives with respect to the parameters, but rather to introduce additional derivatives which must be calculated. The terms in brackets can be neglected if the parameter derivatives and mixed parameter derivatives are small. The experiment can be designed to make these derivatives small, but such a design leads to a paradox because the design contradicts Box's criterion that the parameter derivatives be large for an optimum experiment.

Since Nagler[1] did not present his temperature data, it is impossible to determine the importance of the neglected terms in his computations. Regardless of the magnitude of the terms, Nagler's calculations will converge slowly, if at all. If the terms are small, the experiment is designed poorly for convergence, while if the terms are large, they cannot be neglected without causing errors in the computations.

The present author has analyzed, by the conventional least-squares method, the data from two experiments similar to Nagler's. These two experiments do not represent optimum experimental designs. For these two experiments the importance of the neglected terms was estimated by forming the ratio of one of the neglected terms to one of the included terms in both eqs. (19a) and (19b).

$$R_1 = \left(b^m \left.\frac{\partial v}{\partial k_0}\right|_{(i;\,m)} \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} \right) \Big/ \left(\left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} \right) = b^m \left.\frac{\partial v}{\partial k_0}\right|_{(i;\,m)} \tag{20a}$$

$$R_2 = \left(b^m \left.\frac{\partial v}{\partial b}\right|_{(i;\,m)} \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} \right) \Big/ \left(v_i{}^m \left.\frac{\partial^2 v}{\partial x^2}\right|_{(i;\,m)} \right) = \frac{b^m}{v_i{}^m} \left.\frac{\partial v}{\partial b}\right|_{(i;\,m)} \tag{20b}$$

These particular ratios were selected because they involve only the parameter values, the temperatures, and the simple parameter derivatives. All of this information is available from the conventional least-squares calculations. R_1 and R_2 both depend on i and m. For the author's two experiments the ratios were found to change strongly from one iteration to the next, increasing as the iterative procedure approached the solution. In one experiment both $|R_1(i;\ 1)|$ and $|R_2(i;\ 1)| < 0.04$, while at the second iteration $|R_1(i;\ 2)|_{\max} = |-0.49|$ and $|R_2(i;\ 2)|_{\max} = |-0.65|$. For the second experiment at one point $R_2 = -0.78$. Thus, for these two experiments, the magnitudes of some of the individual terms neglected by Blizzard and Jirka are of the same order as the included terms. (However, it is still conceivable, but unlikely, that the sum of all of the neglected terms could be fortuitously zero.) Furthermore, these neglected terms become more significant as the solution is approached.

The present author's experiments also revealed that $\partial v/\partial k_0|_{(i;\, m)}$ and $\partial v/\partial b|_{(i;\, m)}$ were highly correlated. Beck,[10] unaware of the neglected terms in Blizzard and Jirka's procedure, concluded that high correlation caused by a nonoptimum least-squares design was probably responsible for the slow convergence in reference 1. One method of eliminating correlation is to transform the parameters. Beck[10] has proposed an extremely valuable redefinition of eq. (13).

$$k(v) = k_1 + (k_2 - k_1)\frac{(v - v_1)}{(v_2 - v_1)} \tag{16'}$$

and

$$\mathbf{P} = (k_1, k_2)$$

k_1 is the conductivity at v_1, and k_2 is the conductivity at v_2. v_1 and v_2 may be chosen to aid in the experimental design. Beck has suggested v_1 be the lowest temperature and v_2 the highest temperature in the model.

The present author found that when this transformation of parameters was applied to his two experiments, it dramatically reduced the correlation and improved the convergence of the method. By using the conventional method of solving nonlinear least-squares problems, convergence was obtained in only three iterations when eq. (16′) was used instead of eq. (16). Modifying the calculation procedure by the method outlined in reference 6 further reduced the computations by approximately 30%. Nagler, using Blizzard and Jirka's method, was unable to obtain convergence in ten iterations.

Summary

The nonlinear least-squares procedure proposed by Blizzard and Jirka is inherently unsuitable because any attempt to design the experiment to minimize the neglected parameter derivatives contradicts the basic criterion for an optimum experiment. The conventional nonlinear least-squares procedure has been presented and three steps outlined for optimizing the effectiveness of this method. A summary of successful applications of nonlinear least squares has been presented. One application was the simultaneous determination, from one transient experiment, of seven thermal properties describing the internal ablation mechanisms of a polymeric material. These successful applications serve to indicate the broad scope of possible uses of nonlinear least squares.

The author wishes to acknowledge the support of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force, under Contract AF 33(615)-1937.

References

1. R. G. Nagler, *J. Appl. Polymer Sci.*, **9**, 801 (1965).
2. E. M. Blizzard and R. J. Jirka, *J. Appl. Polymer Sci.*, **9**, 816 (1965).
3. R. R. Kittrell, R. Mezaki, and C. C. Watson, *Ind. Eng. Chem.*, **57**, No. 12, 18 (1965).

4. G. W. Booth and T. I. Peterson, *Non-Linear Estimation (IBM-Princeton): IBM 7094 Program WL NLI*, IBM Data Systems Division, Mathematics and Applications Department, 1960.

5. D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).

6. C. G. Broyden, *Math. Computation*, **19**, 577 (1965).

7. G. E. P. Box and H. L. Lucas, *Biometrika*, **46**, 77 (1959).

8. J. V. Beck, Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1964.

9. J. V. Beck and A. M. Dhanak, ASME Paper No. 65-HT-14, August 1965.

10. J. V. Beck, paper submitted for presentation at the International Heat Transfer Conference and Exhibit, Chicago, Illinois, August 8–12, 1966.

11. D. W. Marquardt, R. G. Bennett, and E. J. Burrell, *J. Mol. Spectry.*, **7**, 269 (1961).

12. R. C. Pfahl, Jr., Ph.D. Thesis, Cornell University, Ithaca, N. Y., September 1965.

Résumé

Une méthode d'interprétation de résultats connue comme méthode nonlinéaire aux moindres carrés a récemment été appliquée par de nombreux auteurs, a l'étude des matériaux polymériques. Nagler a étudié une méthode modifiée proposée par Blizzard et Jirka et a conclu que la méthode n'est pas utilisable par suite du temps excessif nécéssaire au computer. On a montré que les difficultés rencontrées par Nagler sont inhérentes à la méthode de Blizzard et Jirka, mais non pas à la méthode de base elle-même. Trois étapes sont soulignées qui permettent de minimiser le temps nécéssaire au computer et un résumé d'applications favorables est donné.

Zusammenfassung

Eine als nichtlineares Verfahren der kleinsten Quadrate bekannte Auswertmethode wurde neuerdings von mehreren Autoren auf die Untersuchung polymerer Stoffe angewendet. Nagler benützte eine modifizierte, von Blizzard und Jirka vorgeschlagene Methode und kam zu dem Schluss, dass die Methode wegen der erforderlichen exzessiven Computerzeit praktisch nicht verwendbar ist. Es wird gezeigt, dass die von Nagler festgestellten Schwierigkeiten zwar für die Methode von Blizzard und Jirka, nicht aber für die ihr zugrunde liegende Methode spezifisch sind. Drei Schritte werden aufgezeigt, um die Computerzeit klein zu halten, und eine Zusammenstellung erfolgreicher Anwendungen wird gegeben.

Received March 8, 1966
Prod. No. 1367