Chapter 6
Thermal Characterization

The development of new materials is a research intensive area, which is fueled by ever-increasing technological demands. With relevant applications, both in engineering and medicine, there is an obvious need for using adequate techniques for the characterization of new materials to verify if they meet the physical and chemical properties specified in the design phase, such as viscosity, elasticity, density, etc. In this context, the meaning of characterization differs from the meaning we have established in Chapters 1 and 2. Here *characterization* means determination of the properties of the material, which we call inverse identification problem, and requires, most commonly, the conduction of laboratory tests. We recognize the ambiguity with our previous use of the word “characterization”, but since in the area of materials the word characterization is used in the sense of identification we prefer to maintain it and be able to have the chosen chapter title.

During the development and operation of an experimental device, it is common to control different degrees of freedom to correctly estimate the properties under scrutiny. Frequently, with such a procedure, practical limitations are imposed that restrict the full use of the possibilities of the experiment.

Using a blend of theoretical and experimental approaches, determining unknown quantities by coupling the experiment with the solution of inverse problems, a greater number of degrees of freedom can be manipulated, involving even the simultaneous determination of new unknowns, included in the problem due to more elaborate physical, mathematical and computational models [18].

The *hot wire method*, for example, has been used successfully to determine the thermal conductivity of ceramic materials, even becoming the worldwide standard technique for values of up to 25 W/(m K). For polymers, the parallel hot wire technique is replaced by the cross-wire technique, where a junction of a *thermocouple*—a temperature sensor—is welded to the hot wire, which works as a thermal source at the core of the sample whose thermal properties are to be determined [17].

In this chapter we consider the determination of thermal properties of new polymeric materials by means of the solution of a heat transfer inverse problem, using experimental data obtained by the hot wire method. This consists of an identification inverse problem, being classified as a Type III *inverse problem* (see Section 2.8).

6.1 Experimental Device: Hot Wire Method

In this section we briefly describe the experimental device used to determine the thermal conductivity of new materials.

The hot wire method is a *transient technique*, i.e., it is based on the measurement of the time variation of temperature due to a linear heat source embedded in the material to be tested. The heat generated by the source is considered to be constant and uniform between both ends of the test body. The basic elements of the experimental device are sketched in Fig. 6.1. From the temperature variation, measured by the slope in Fig. 6.2a, in a known time interval, the thermal conductivity of the sample is computed. In practice, the linear thermal source is approximated by a thin electric resistor and the infinite solid is replaced by a finite size sample.

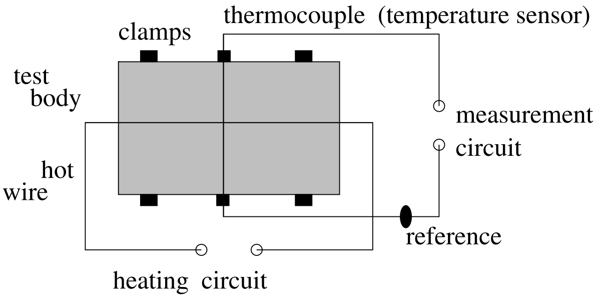

Fig. 6.1 Experimental apparatus for the standard hot wire technique

The experimental apparatus is made up of two test bodies. In the upper face of the first test body, two orthogonal incisions are *carved* to receive the measuring cross. The depth of these incisions corresponds to the diameter of the wires to be inserted within.

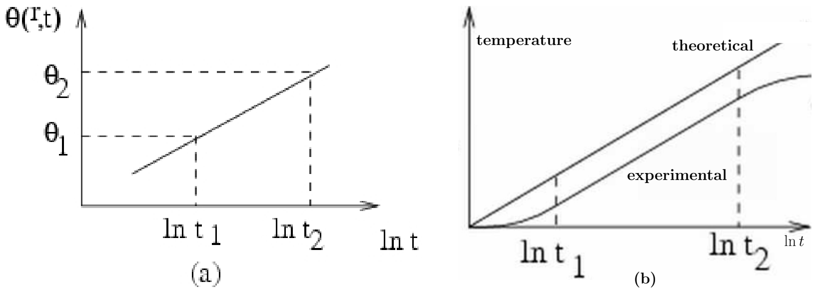

Fig. 6.2 Hot wire method. (a) Increase in temperature $\theta(r,t)$ as a function of time; (b) Theoretical (infinite sample size) and presumed experimental (finite sample size) graphs.

The measuring cross is formed by the hot wire (a resistor) and the thermocouple, whose junctions are welded perpendicular to the wire. After placing the measuring cross in the incisions, the second test body is placed upon it, wrapping the measuring cross. The contact surfaces of the two test bodies must be sufficiently flat to ensure good thermal contact. Clamps are used to fulfill this goal, pressing the two bodies together.

Some care should be taken when working with the hot wire method to ensure the reliability of the results: (i) a resistor must be used as similar as possible to the theoretical linear heat source; (ii) ensure the best possible contact between the sample and the hot wire; (iii) the initial part of the *temperature* × *time* graph should not be used for the computations —use only times in the range $t > t_1$, in Fig. 6.2b,— thus eliminating the effect of the thermal contact resistance between the electric resistor (the wire) and the sample material; (iv) limit the test time to ensure that the finite size of the sample does not affect the linearity of the measured temperatures ($t < t_2$ in Fig. 6.2b).

6.2 Traditional Experimental Approach

Consider a linear thermal source that starts releasing heat due to Joule's effect—a resistor, for example— at time $t = 0$, inside an infinite medium that is initially at temperature $T = T_0$. Let the linear thermal source be infinite in extension and located in the z axis. Due to the symmetry of the problem in the z direction, we have a solution that does not depend on z and this situation can be modeled as an initial value problem for the heat equation in two-dimensions,

$$\frac{\partial T}{\partial t} = k \triangle T + s(\mathbf{x},t)\,, \quad \mathbf{x} = (x,y) \in \mathbb{R}^2\,,\; t > 0\,, \tag{6.1a}$$

$$T(\mathbf{x},0) = T_0(\mathbf{x})\,, \quad \mathbf{x} \in \mathbb{R}^2\,. \tag{6.1b}$$

Here $T = T(\mathbf{x},t)$ is the temperature, $\triangle T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2}$ is the laplacian of T with respect to the spatial variables, k is the medium's thermal conductivity, s is the thermal source term, and T_0 is the initial temperature. Under the previous hypothesis, T_0 is a constant, and s is a singular thermal source corresponding to a multiple of a *Dirac's delta* (generalized) function centered at the origin,

$$s(\mathbf{x},t) = q'\delta(\mathbf{x})\,, \tag{6.2}$$

where q' is the linear power density.

The solution of Eq. (6.1) can be written as the sum of a general solution of a homogeneous initial value problem, T^1, and a particular solution of a non-homogeneous initial value problem, T^2, that is, $T = T^1 + T^2$, where T^1 satisfies

$$\frac{\partial T^1}{\partial t} = k \triangle T^1\,, \quad \mathbf{x} \in \mathbb{R}^2, t > 0\,, \tag{6.3a}$$

$$T^1(\mathbf{x},0) = T_0\,, \quad \mathbf{x} \in \mathbb{R}^2\,. \tag{6.3b}$$

and T^2 satisfies

$$\frac{\partial T^2}{\partial t} = k \triangle T^2 + s(\mathbf{x},t)\,, \quad \mathbf{x} \in \mathbb{R}^2, t > 0\,, \tag{6.4a}$$

$$T^2(\mathbf{x},0) = 0\,, \quad \mathbf{x} \in \mathbb{R}^2\,. \tag{6.4b}$$

The solution of Eq. (6.3) relies on the fundamental solution of the heat equation [39], through a convolution with the initial condition,

$$T^1(\mathbf{x},t) = \frac{1}{4k\pi t} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{|\mathbf{x}-\mathbf{y}|^2}{4kt}} T_0(\mathbf{y})\, dy_1\, dy_2 \,. \tag{6.5}$$

The solution of Eq. (6.4) is attained by *Duhamel's principle* [39, 61]. One looks for a solution in the form of *variation of parameters*,

$$T^2(\mathbf{x},t) = \int_0^t U(\mathbf{x},t,\tau)\, d\tau \,, \tag{6.6}$$

where, for each τ, $U(\cdot\,,\,\cdot\,,\tau)$ satisfies a homogeneous initial value problem, with initial time $t = \tau$,

$$\frac{\partial U}{\partial t} = k \triangle U \,, \quad \mathbf{x} \in \mathbb{R}^2, t > \tau \,, \tag{6.7a}$$

$$U(\mathbf{x},\tau,\tau) = s(\mathbf{x},\tau) \,, \quad \mathbf{x} \in \mathbb{R}^2 \,. \tag{6.7b}$$

Since Eq. (6.7) is, in fact, a family of homogeneous problems, parametrized by τ, its solution is obtained by convolution with the fundamental solution of the heat equation,

$$U(\mathbf{x},t,\tau) = \frac{1}{4k\pi(t-\tau)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{|\mathbf{x}-\mathbf{y}|^2}{4k(t-\tau)}} s(\mathbf{y},\tau)\, dy_1\, dy_2 \,,$$

and then, substituting this result in Eq. (6.6),

$$T^2(\mathbf{x},t) = \int_0^t \frac{1}{4k\pi(t-\tau)} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{|\mathbf{x}-\mathbf{y}|^2}{4k(t-\tau)}} s(\mathbf{y},\tau)\, dy_1\, dy_2\, d\tau \,.$$

Since

$$\frac{1}{4k\pi t} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-\frac{|\mathbf{x}-\mathbf{y}|^2}{4kt}}\, dy_1\, dy_2 = 1 \,, \tag{6.8}$$

T_0 is a constant, and s is given by Eq. (6.2), we have

$$\begin{aligned} T(\mathbf{x},t) &= T_0 + \frac{q'}{4k\pi} \int_0^t \frac{1}{t-\tau} e^{-\frac{|\mathbf{x}-\mathbf{y}|^2}{4k(t-\tau)}}\, d\tau \,, \\ &= T_0 + \frac{q'}{4k\pi} \int_{|x|^2/4kt}^{+\infty} \frac{e^{-u}}{u}\, du \,, \end{aligned} \tag{6.9}$$

where we have made the change of variables $u = |\mathbf{x}|^2/4k(t-\tau)$.

For times sufficiently greater than $t = 0$, and for radial distances, r, near the linear source, more precisely, when $|\mathbf{x}|^2/4kt \to 0$, the temperature increases in the following way, [12],

$$T(\mathbf{x},t) = T_0 + \frac{q'}{4\pi k}(\ln t - 2\ln|\mathbf{x}|) + \mathcal{O}(1), \quad \text{as } |\mathbf{x}|^2/4kt \to 0 \,, \tag{6.10}$$

as can be seen from Eq. (6.9), and the following result,

$$\int \frac{e^{-u}}{u}\,du = \ln u\, e^{-u} + (u\ln u - u)\, e^{-u} + \int (u\ln u - u)\, e^{-u}\,du\,. \tag{6.11}$$

This dependence is represented in Fig. 6.2a.

Now, from Eq. (6.10) and Fig. 6.2, letting $\mathbf{x}_0 \neq 0$ be a certain fixed point of the medium, and denoting $\theta_1 = T(\mathbf{x}_0,t_1)$, and $\theta_2 = T(\mathbf{x}_0,t_2)$, we get

$$\text{'slope'} \approx \frac{\theta_2 - \theta_1}{\ln t_2 - \ln t_1} = \frac{q'}{4\pi k}\,,$$

$$\text{and then} \quad k = \frac{q'}{4\pi}\,\frac{\ln\left(\frac{t_2}{t_1}\right)}{(\theta_2 - \theta_1)}\,. \tag{6.12}$$

In the traditional experimental approach, temperatures are measured for different times, (t_l, T_l), for $l = 1,2,\ldots,L$, where L is the total number of experimental measurements, and, from the fitting of a line to the points

$$(\ln t_l, \theta_l)\,,\ \text{with}\ \theta_l = T_l - T_0\,,\ l = 1,2,\ldots,L\,,$$

by means of the least squares method, the slope of the line is obtained, and from it the thermal conductivity of the material by means of Eq. (6.12). A few more details can be found in Exercise 6.4.

This method was used to determine the thermal conductivity of a phenolic foam, with 25 % of its mass being of lignin.[1] The lignin used was obtained from sugarcane bagasse. This is an important by-product of the sugar and ethanol industry, and different applications are being sought for it, besides energy generation. The thermal conductivity was found as

$$k = (0.072 \pm 0.002)\ \mathrm{W/(m\,K)}\,. \tag{6.13}$$

The theoretical curve for an infinite medium and the expected curve, presumably obtainable in an experiment with a finite sample are presented in Fig. 6.2b. Observe that for time values relatively small ($t < t_1$) and relatively large ($t > t_2$), deviations from linearity occur. Therefore, experimental measurements in these situations are to be avoided. The deviation for $t < t_1$ is due to the thermal resistance between the hot wire and the sample. The deviation from linearity for $t > t_2$ occurs when heat reaches the sample's surface, thus starting the process of heat transfer by convection to the environment.

In a real experiment the sample's dimensions are finite. Moreover, for materials with high thermal diffusivity, $\alpha = k/\rho c_p$, where ρ is the specific mass and c_p is the specific heat at constant pressure per unit mass, the interval where linearity occurs can be very small. This feature renders experimentation unfeasible, within the required precision.

[1] The experimental data used here was obtained by Professor Gil de Carvalho from Rio de Janeiro State University [18].

6.3 Inverse Problem Approach

In this section, we present a more general approach to identifying the relevant parameters in the physical model, based on solving an inverse problem. First we present the model, next we set up an optimization problem to identify the model, present an algorithm to solve the minimization problem, and present the results on the determination of the thermal conductivity and specific heat of a phenolic foam.

6.3.1 Heat Equation

We shall consider the determination of the thermal conductivity of the medium using the point of view of applied inverse problems methodology. That is, we select a mathematical model of the phenomenon —heat transfer by conduction,— then formulate a least squares problem and set up an algorithm to solve it.

To deal with the inverse problem of heat transfer by conduction used here, consider a sample of cylindrical shape with radius R, with a linear heat source along its centerline, exchanging heat with the surrounding environment (ambient), and set initially at room temperature, T_{amb}. To keep the description as simple as possible, it will be considered that the cylinder is long enough, making the heat transfer depend only on the radial direction. The mathematical formulation of this problem is given by the *heat equation* and Robin's boundary conditions [12, 61],

$$\frac{1}{r}\frac{\partial}{\partial r}\left(k\,r\,\frac{\partial T}{\partial r}\right) + g(r,t)\,\delta(r) = \rho\, c_p\,\frac{\partial T(r,t)}{\partial t} \tag{6.14a}$$

in $0 \le r \le R$, for $t > 0$, and

$$-k\frac{\partial T}{\partial r}\,(R,t) = h\,(T(R,t) - T_{\mathrm{amb}})\,, \qquad \text{for } t > 0 \tag{6.14b}$$

$$T(r,0) = T_{\mathrm{amb}} \qquad \text{in } 0 \le r \le R\,, \tag{6.14c}$$

where $g(r,t)$ is the volumetric power density, h is the convection heat transfer coefficient, and the remaining symbols have already been defined.

When the geometry, material properties, boundary conditions, initial condition and source term are known, Eq. (6.14) can be solved, thus determining the medium's transient temperature distribution. This is a direct problem.

If some of these magnitudes, or a combination of them, are not known, but experimental measurements of the temperature inside or at the boundary of the medium are available, we deal with an inverse problem, which allows us to determine the unknown magnitudes, granted that the data holds enough information.

Most of the techniques developed to solve inverse problems rely on solving the direct problem with arbitrary values for the magnitudes that are to be determined. Usually, the procedures involved are iterative, so the direct problem has to be solved several times. It is thus desirable to have a method of solution of the direct problem capable of attaining a high precision. At the same time, it should not consume much computational time. In the example considered in Section 6.3.5, the finite difference method was used to solve the problem of heat transfer through the sample.

6.3.2 Parameter Estimation

Here we consider the formulation of the problem of simultaneously estimating the thermal conductivity and the specific heat of a material. These parameters are represented by

$$\mathbf{Z} = \left(k, c_p\right)^T .$$

Notice that other parameters could be estimated simultaneously with the thermal conductivity and the specific heat, such as the coefficient of heat transfer by convection from the sample to the environment, h. In this case, we should also perform measurements at times $t > t_2$.

Let $T_c(r_m,t_l)$ be computed temperatures, and $T_e(r_m,t_l)$ experimentally measured temperatures, at positions r_m, with $m = 1, 2, \ldots, M$, where M is the number of temperature sensors employed, at times t_l, with $l = 1, 2, \ldots, L$, and L denoting the number of measurements performed by each sensor. Consider the norm given by half the sum of the squares of the residues between computed and measured temperatures,

$$Q(\mathbf{Z}) = \frac{1}{2} \sum_{m=1}^{M} \sum_{l=1}^{L} \left[T_c(r_m, t_l) - T_e(r_m, t_l)\right]^2 , \tag{6.15}$$

or, simply,

$$Q = \frac{1}{2} \sum_{i=1}^{I} (T_i - W_i)^2 = \frac{1}{2} \mathbf{R}^T \mathbf{R} .$$

Here, T_i and W_i, are compact notations, respectively for the calculated and measured temperature, referred to the same sensor and at the same time. Also, $R_i = T_i - W_i$ and $I = M \times L$.

The inverse problem considered here is solved as a finite dimension optimization problem, where the norm Q is to be minimized, and the parameters correspond to the minimum point of Q.

6.3.3 Levenberg-Marquardt

We describe here the *Levenberg-Marquardt method* [54], presented in section 5.3, to estimate the parameters.

The minimum point of Q, Eq. (6.15), is pursued by solving the critical point equation

$$\partial Q / \partial Z_j = 0 , \; j = 1, 2 .$$

Analogously to Section 5.3, an iterative procedure is built. Let n be the iteration counter. New estimates of parameters, $\mathbf{Z}^{n+1}$, of residuals, $\mathbf{R}^n$, and corrections, $\Delta\mathbf{Z}^n$, are computed sequentially,

$$\mathbf{R}^n = \mathbf{T}^n - \mathbf{W} \quad (6.16a)$$

$$\Delta\mathbf{Z}^n = -\left[(J^n)^T J^n + \lambda^n \mathcal{I}\right]^{-1} (J^n)^T \mathbf{R}^n \,, \quad (6.16b)$$

$$\mathbf{Z}^{n+1} = \mathbf{Z}^n + \Delta\mathbf{Z}^n \quad (6.16c)$$

for $n = 0, 1, 2, \ldots$, until the convergence criterion

$$\left|\Delta Z_j^n / Z_j^n\right| < \varepsilon \,, \; j = 1, 2$$

is satisfied. Here, ε is a small number, for example, 10^{-5}.

The elements of the $I \times 2$ Jacobian matrix,

$$J_{ij} = \partial T_i / \partial Z_j \,, \text{ for } i = 1, \ldots, I \,, \text{ and } j = 1, 2 \,,$$

as well as the residuals, $\mathbf{R}^n$, are computed at every iteration, by the solution of the direct problem given by Eq. (6.14), using the estimates for the unknowns obtained in the previous iteration.

6.3.4 Confidence Intervals

As presented in Section 5.4, Walds's *confidence intervals* of the estimates $\mathbf{Z} = (k,c_p)^T$ are computed by [59], page 87, [34]. In this case, the square of the *standard deviation* is given by [38]

$$\sigma_Z^2 = \begin{pmatrix} \sigma_k^2 \\ \sigma_{c_p}^2 \end{pmatrix} = \sigma^2 \left\{ \text{diag} \left[(\nabla\mathbf{T})^T \, \nabla\mathbf{T} \right]^{-1} \right\} . \quad (6.17)$$

where $\mathbf{T} = (T_1, \ldots, T_I)^T$, $\mathbf{T} = \mathbf{T}(\mathbf{Z}) = \mathbf{T}(k, c_p)$, and σ is the *standard deviation* of the experimental errors.

Assuming a normal distribution for the experimental errors and 99 % of confidence, the confidence intervals of the estimates of k and c_p are [33],

$$]k - 2.576\, \sigma_k \;,\; k + 2.576\, \sigma_k[\;,$$

and

$$\left]c_p - 2.576\, \sigma_{c_p} \;,\; c_p + 2.576\, \sigma_{c_p}\right[\;.$$

6.3.5 Application to the Characterization of a Phenolic Foam with Lignin

This section presents the results obtained in the estimation of thermal conductivity and specific heat of a phenolic foam, with 25 % of its mass being of lignin. As mentioned at the beginning of this chapter, in materials's literature the word 'characterization' is used to mean what we call model identification, therefore we give credit to this usage by employing it in this section's title.

Recall that the traditional experimental approach, described in Section 6.1, was only able to determine the thermal conductivity. With the approach based on the inverse heat transfer problem, described in Section 6.3.2, we were able to obtain, from the same set of experimental data, not only the thermal conductivity, but also the sample's specific heat. The thermal conductivity was estimated as being

$$k = 0.07319\,\mathrm{W/(mK)}\,,$$

with the following 99 % confidence interval:

$$]0.07313, 0.07325[\,\mathrm{W/(m\,K)}\,.$$

This value excellently agrees with the one obtained by the traditional approach, Eq. (6.13).

For the specific heat, determined simultaneously with the thermal conductivity, the estimate obtained was $c_p = 1563.0\,\mathrm{J/(kg\,K)}$ and the following 99 % confidence interval was obtained

$$]1559.6, 1566.4[\,\mathrm{J/(kg\,K)}\,.$$

Vega [91] presents an expected value of 1590 J/(kg K) for the specific heat of phenolic resins, and this agrees very well with the value obtained by the solution of the inverse problem considered here. The traditional approach provides no means of estimating this property.

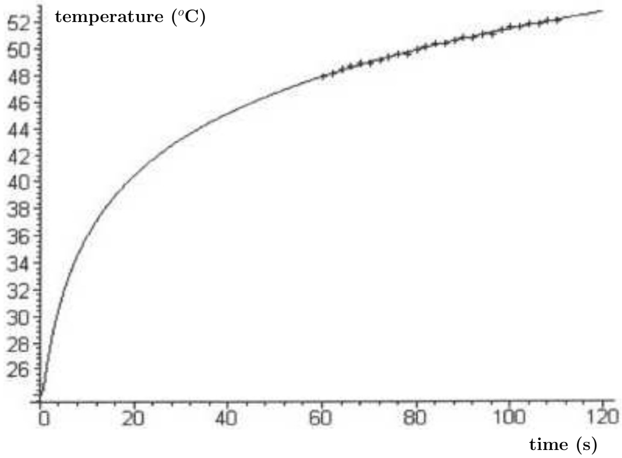

Fig. 6.3 Temperature profiles (– theoretical +++ experimental)

Figure 6.3 presents the *temperature*×*time* plot, which exhibits the computed temperatures with the estimated properties k and c_p. The values of the measured temperatures W_i, $i = 1,2,\ldots,I$, which were used in the solution of the inverse problem, are exhibited in the same graph. Notice the excellent agreement between experimental data and temperature determined by the computational simulation.

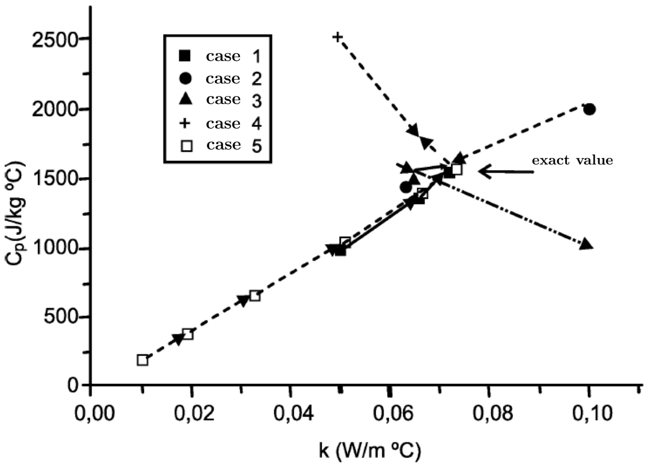

Fig. 6.4 Results of the simulations considering different initial estimates

Figure 6.4 shows that the minimization iterative process converges to the same solution, no matter which one of several initial estimates of the unknown magnitudes is used. This suggests that the global minimum of Q is reached.

6.4 Experiment Design

Using the mathematical model and the computational simulation presented here, it is possible to design experiments to obtain, precise and economically, physical parameters, determining *a priori* the best localization for the temperature sensors, as well as the best time intervals in which the experimental measurements are to be performed.

The concepts of "best" or "optimum" are necessarily bound to a judgment criterion that, in the situation described here, may, for example, consist in the minimization of the region contained in the confidence intervals that, as previously described in this chapter, and in Chapter 5, is related to larger values of the sensitivity coefficients.

Further details on inverse problems and experiment design for applications related to heat and mass transfer phenomena may be found in [50, 71, 45, 51, 89, 52, 49].

Exercises

6.1. Show that T^2 defined in Eq. (6.6) satisfies Eq. (6.4).
Hint. Use Bernoulli's formula

$$\frac{d}{dt}\int_a^t f(s,t)\,ds = f(t,t) + \int_a^t \frac{\partial f}{\partial t}(s,t)\,ds\,.$$

6.2. Show validity of Eq. (6.8).
Hint. Use polar coordinates in $\mathbb{R}^2$.

6.3. Use integration by parts to show Eq. (6.11).

6.4. From Eq. (6.10), $\theta = \alpha \ln t$, for $\alpha = q'/4\pi k$. (a) Given measurements (t_i,θ_i), obtain the least squares formulation to determine α; (b) obtain an expression for α in terms of the experimental data; (c) write an expression for k.

6.5. Let

$$\mathcal{D} = \sum_{l=1}^{L}\left(\frac{\partial T_l}{\partial k}\right)^2 \sum_{l=1}^{L}\left(\frac{\partial T_l}{\partial c_p}\right)^2 - \left(\sum_{l=1}^{L}\frac{\partial T_l}{\partial k}\frac{\partial T_l}{\partial c_p}\right)^2 .$$

Show that

$$\sigma_k^2 = \frac{\sigma^2}{\mathcal{D}}\sum_{l=1}^{L}\left(\frac{\partial T_l}{\partial c_p}\right)^2 \text{, and}$$

$$\sigma_{c_p}^2 = \frac{\sigma^2}{\mathcal{D}}\sum_{l=1}^{L}\left(\frac{\partial T_l}{\partial k}\right)^2$$

6.6. Write the matrix $J^T J$, to be used in Eq. (6.16b), for the vector of unknowns $Z = (k,c_p,h)^T$, where k is the thermal conductivity, c_p is the specific heat, and h is the convection heat transfer coefficient, for the inverse heat conduction problem in which these three parameters are to be estimated simultaneously.

6.7. Why, for $t < t_2$, is the approximation of infinite medium, in the situation represented in Fig. (6.2), a good one?

6.8. The sensitivity coefficients, [11], are defined by

$$X_{z_j} = \frac{\partial T}{\partial Z_j}$$

where T represents the observable variable, that may be measured experimentally, and z_j one unknown to be determined with the solution of the inverse problem. Considering the situation represented in Fig. (6.2), is it possible to estimate the convection heat transfer coefficient, i.e. $Z_j = h$ considering the experimental data acquired at $t < t_2$? What is the link between this exercise and Exercise 6.7?