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LINEAR SYSTEM THEORY OF A HEAT CONDUCTION CALORIMETER. PART 1. SOME PROPERTIES OF A LINEAR SYSTEM WITH ZERO INITIAL CONDITIONS

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ABSTRACT

The calorimeter is treated in terms of the input–output relation of a linear time-invariant system described by a differential equation with constant coefficients. The transfer function of the system is derived under some initial conditions. The initial conditions are that the values of the input and output signals are zero when time t is negative ($t < 0$), but they are not necessarily zero when time t approaches zero from the right, $t \to 0+$. The procedure of the derivation of the transfer function involves a clear definition of the function which is zero for the negative value of time t using the double-sided Laplace transform.

Initial values of the unit step response of the system and its derivatives are calculated in some cases. Some characteristic properties of the unit step response and its derivatives are obtained in connection with the transfer function of the system. Proportionality—the relationship between the time integral of the input signal and that of the output signal—is obtained.

INTRODUCTION

Some workers [1–3] have treated the calorimetric system as a linear time-invariant system which is described by the differential equation

$$\frac{d^n y}{dt^n} + a_1 \frac{d^{n-1} y}{dt^{n-1}} + \dots + a_{n-1} \frac{dy}{dt} + a_n y$$
$$= b_0 \frac{d^m x}{dt^m} + b_1 \frac{d^{m-1} x}{dt^{m-1}} + \dots + b_{m-1} \frac{dx}{dt} + b_m x \qquad b_0 \neq 0 \tag{1}$$

where $x = x(t)$ is the input variable, $y = y(t)$ is the output variable and t is the time. In the calorimetric system, the input variable $x(t)$ refers to the thermogenesis, i.e. the rate of internal energy or enthalpy change caused by the reaction or transition under investigation, or to the applied electric power to the calorimeter; the output variable $y(t)$ usually refers to the temperature change or the temperature deviation from the convergence (steady state) temperature which is observed in the calorimeter experiment. Coefficients a_0, $a_1, \dots, a_n$ and b_0, $b_1, \dots, b_m$ are time-invariant constants.

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Using the formula of the Laplace transform of derivatives [4]

$$L[f^{(n)}(t)] = s^n\bar{f}(s) - s^{n-1}f(0+) - s^{n-2}f^{(1)}(0+) - \ldots - sf^{(n-2)}(0+) - f^{(n-1)}(0+) \tag{2}$$

assuming all zero initial conditions

$$\begin{aligned} y(0+) &= y^{(1)}(0+) = \ldots = y^{(n-1)}(0+) = 0 \\ x(0+) &= x^{(1)}(0+) = \ldots = x^{(m-1)}(0+) = 0 \end{aligned} \tag{3}$$

and taking the Laplace transform on both sides of eqn. (1), we have

$$\left(s^n + a_1 s^{n-1} + \ldots + a_{n-1}s + a_n\right)\bar{y}(s) = \left(b_0 s^m + b_1 s^{m-1} + \ldots + b_{m-1}s + b_m\right)\bar{x}(s) \tag{4}$$

where $\bar{f}(s)$, $\bar{y}(s)$ and $\bar{x}(s)$ are the Laplace transforms of functions $f(t)$, $y(t)$ and $x(t)$ respectively, and s is the parameter in the Laplace transform. The transfer function $G(s)$ of the linear system (1) is defined as the ratio of $\bar{y}(s)$ to $\bar{x}(s)$; therefore,

$$G(s) = \frac{\bar{y}(s)}{\bar{x}(s)} = \frac{b_0 s^m + b_1 s^{m-1} + \ldots + b_{m-1}s + b_m}{s^n + a_1 s^{n-1} + \ldots + a_{n-1}s + a_n} \tag{5}$$

Some workers have added a condition [3,5]

$$n > m + 2 \tag{6}$$

or another slightly different condition [6,7]

$$n \geqq m + 2 \tag{7}$$

to the above equations. Equation (5) which is derived under all zero initial conditions (eqn. (3)) is used as one of the fundamental equations for the deconvolution methods in thermokinetics [2,8–10]. Margas and Zielenkiewicz have also derived the rational form of the transfer function from their multibody model of a calorimeter [11,12].

However, it can be shown by simple examples that eqn. (5) applies in a linear system when conditions (3), (6) and (7) are not valid. The most simple equation of heat conduction calorimeters is the Tian equation [13]

$$C\frac{\mathrm{d}y}{\mathrm{d}t} + hy = x(t) \tag{8}$$

where C is the heat capacity of the reaction vessel and its contents and h is the cooling constant. Assuming a zero initial condition

$$y(0+) = 0 \tag{9}$$

and applying the Laplace transform of eqn. (8), we obtain

$$G(s) = \frac{\bar{y}(s)}{\bar{x}(s)} = \frac{1}{Cs + 1} \tag{10}$$

Textbooks [14,15] usually give the formula of the Laplace transform of the impulse signal $\delta(t)$ as

$$\mathrm{L}[\delta(t)] = 1 \tag{11}$$

We can obtain the output response $y(t)$ for the impulse input $x(t) = \delta(t)$ using eqns. (10) and (11) and the inverse Laplace transform

$$y(t) = \mathrm{L}^{-1}\left(\frac{1}{Cs + h}\right) = \frac{1}{C} \exp\left(-\frac{h}{C}t\right) \tag{12}$$

Thus, we have

$$y(0+) = \frac{1}{C} \neq 0 \tag{13}$$

Equation (13) is inconsistent with the zero initial condition (9). Comparing eqns. (5) and (10), we can identify

$$n = 1 \text{ and } m = 0 \tag{14}$$

for the Tian equation. Relation (14) also conflicts with conditions (6) and (7).

Other examples can be found of the treatment of a two-body model of a calorimeter by Margas and coworkers [16,17]. They applied the Laplace transform to the differential equations of the two-body calorimeter system under zero initial conditions (3) and derived the transfer functions of the system. When the thermometer and heat source are located in the same body, the transfer functions ($H_{11}(s)$ and $H_{22}(s)$, ref. 18, Tables I and II) show identifications $n = 2$ and $m = 1$, which are also in conflict with eqns. (6) and (7). Impulse responses of the system are calculated from relation (5) and the transfer functions are calculated for cases where the thermometer and heat source are located in the same body. The results ($h_{11}(t)$ and $h_{22}(t)$, ref. 18, Fig. 3) show that the initial values of the responses are not zero at $t = 0+$ in spite of the derivation of relation (5) and the transfer functions under the assumptions of zero initial values at $t = 0+$.

The above examples show that relation (5) can be applied to a linear system when initial conditions (3) are not valid, and that conditions (6) and (7), proposed by some workers, fail in some cases.

Kailath [18] points out an error in the formula of the Laplace transform of $\delta(t)$ described in many textbooks and states that eqn. (11) should be replaced by

$$\mathrm{L}[\delta(t)] = 0 \tag{15}$$

and

$$\mathrm{L}_{-}[\delta(t)] = 1 \tag{16}$$

In the above equations, the L_{-} transform is defined as

$$\mathrm{L}_{-}[f(t)] = \int_{0-}^{\infty} f(t)\, \mathrm{e}^{-st}\, \mathrm{d}t \tag{17}$$

while the usual Laplace transform L is defined as

$$L[f(t)] = \int_{0+}^{\infty} f(t)\, e^{-st}\, dt \tag{18}$$

Kailath's statement suggests an alternative method for the derivation of relation (5) from the linear differential (eqn. (1)) which allows non-zero values at $t = 0+$. The L_- transform of the derivatives gives

$$L_-\left[f^{(n)}(t)\right]$$
$$= s^n \bar{f}_-(s) - s^{n-1} f(0-) - s^{n-2} f^{(1)}(0-) \ldots - s f^{(n-2)}(0-) - f^{(n-1)}(0-) \tag{19}$$

where $\bar{f}_-(s)$ is the L_- transform of $f(t)$. Assuming the initial conditions

$$\begin{aligned} x(0-) &= x^{(1)}(0-) = \ldots = x^{(m-1)}(0-) = 0 \\ y(0-) &= y^{(1)}(0-) = \ldots = y^{(n-1)}(0-) = 0 \end{aligned} \tag{20}$$

and applying the L_- transform of eqn. (1), we obtain relation (5) which allows non-zero values of $x(t)$, $y(t)$ and their derivatives at $t = 0+$.

However, eqn. (20) does not express the correct initial conditions in our problem. For example, function $x(t) = t^m$ and its derivatives satisfy eqn. (20), but they are not zero for $t < 0$. The correct initial conditions in our problem are that the functions and derivatives are all zero for $t < 0$ as follows

$$\left.\begin{aligned} x(t) &= x^{(1)}(t) = \ldots = x^{(m)}(t) = \ldots = 0 \\ y(t) &= y^{(1)}(t) = \ldots = y^{(n)}(t) = \ldots = 0 \end{aligned}\right\} \text{ for } t < 0 \tag{21}$$

Equation (20) gives zero values only at $t = 0-$ and does not provide the correct zero initial conditions for $t < 0$. Moreover, the method suggested by Kailath does not provide clear insights into the behaviour of the functions at $t = 0$. The function $\delta(t)$ plays an important role in our problems, and the general theory of the delta function $\delta(t)$ is almost in the domain $-\infty < t < \infty$ [19]. It is desirable to start our discussion from the argument in the domain $-\infty < t < \infty$. The double-sided Laplace transform L_b is defined in the domain $(-\infty, \infty)$ (see next section), and so the L_b transform is preferred to the L_- transform which is defined in the domain $(0-, \infty)$.

EXPRESSION OF FUNCTION WHICH IS ZERO FOR $t < 0$ AND THE DOUBLE-SIDED LAPLACE TRANSFORM

The zero initial state function $F(t)$ which is zero for $t < 0$ is defined by

$$F(t) = f(t)u(t) \tag{22}$$

In eqn. (22), the function $f(t)$ and its derivatives $f^{(n)}(t)$ are continuous for $-\infty < t < \infty$, and $u(t)$ is the unit step function

$$\begin{aligned} u(t) &= 0, \qquad \text{for } t < 0, \\ u(t) &= 1/2, \qquad \text{for } t = 0 \\ u(t) &= 1, \qquad \text{for } t > 0. \end{aligned} \tag{23}$$

The value of $u(t)$ at $t = 0$ is defined in accordance with the theorem of the inverse Laplace transform at discontinuity [20]. The double-sided Laplace transform L_b is defined as

$$L_b[F(t)] = \int_{-\infty}^{\infty} F(t)\, e^{-st}\, dt \tag{24}$$

The following properties of function $F(t)$ and the L_b transform are easily obtained.

Property A1, when $t > 0$

$$F(t) = f(t) \tag{25}$$

$$F^{(n)}(t) = f^{(n)}(t) \tag{26}$$

Property A2, when $t < 0$

$$F(t) = F^{(n)}(t) = 0 \tag{27}$$

Property A3, when $-\infty < t < \infty$

$$\begin{aligned} F(t) &= f(t)u(t) \\ F^{(1)}(t) &= f^{(1)}(t)u(t) + f(t)\delta(t) \\ F^{(2)}(t) &= f^{(2)}(t)u(t) + 2f^{(1)}\delta(t) + f(t)\delta^{(1)}(t) \\ &\cdots\cdots \\ F^{(n)}(t) &= \sum_{r=0}^{n} {}_nC_r f^{(n-r)}(t)u^{(r)}(t) \end{aligned} \tag{28}$$

Property A4

$$\int_{-\infty}^{\infty} f^{(n)}(t)u(t)\, dt = f^{(n-1)}(\infty) - f^{(n-1)}(0) \tag{29}$$

$$\begin{aligned} \int_{-\infty}^{\infty} f^{(n-r)}(t)u^{(r)}(t)\, dt &= \int_{-\infty}^{\infty} f^{(n-r)}(t)\delta^{(r-1)}(t)\, dt \\ &= (-1)^{r-1} f^{(n-1)}(0) \qquad r \geqq 1 \end{aligned} \tag{30}$$

The integration of the left-hand side of eqn. (29) is carried out as follows

$$\begin{aligned} \int_{-\infty}^{\infty} f^{(n)}(t)u(t)\, dt &= [f^{(n-1)}(t)u(t)]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} f^{(n-1)}(t)u^{(1)}(t)\, dt \\ &= f^{(n-1)}(\infty) - \int_{-\infty}^{\infty} f^{(n-1)}(t)\delta(t)\, dt \\ &= f^{(n-1)}(\infty) - f^{(n-1)}(0). \end{aligned}$$

Equation (30) is proven by induction to be as follows. When $r=1$, we have

$$\int_{-\infty}^{\infty} f^{(n-1)}(t)u^{(1)}(t)\,\mathrm{d}t=\int_{-\infty}^{\infty} f^{(n-1)}(t)\delta(t)\,\mathrm{d}t=f^{(n-1)}(0)$$

If we suppose the validity of eqn. (30) for r, then we have

$$\begin{aligned}
&\int_{-\infty}^{\infty} f^{(n-r-1)}(t)u^{(r+1)}(t)\,\mathrm{d}t\\
&\quad=\int_{-\infty}^{\infty} f^{(n-r-1)}(t)\delta^{(r)}(t)\,\mathrm{d}t\\
&\quad=\left[f^{(n-r-1)}(t)\delta^{(r-1)}(t)\right]_{-\infty}^{\infty}-\int_{-\infty}^{\infty} f^{(n-r)}(t)\delta^{(r-1)}(t)\,\mathrm{d}t\\
&\quad=-\int_{-\infty}^{\infty} f^{(n-r)}(t)\delta^{(r-1)}(t)\,\mathrm{d}t\\
&\quad=-(-1)^{r-1}f^{(n-1)}(0)\\
&\quad=(-1)^{r}f^{(n-1)}(0)
\end{aligned}$$

Property A5

$$\int_{-\infty}^{\infty} F(t)\,\mathrm{d}t=\int_{0}^{\infty} f(t)\,\mathrm{d}t \tag{31}$$

$$\int_{-\infty}^{\infty} F^{(n)}(t)\,\mathrm{d}t=f^{(n-1)}(\infty) \tag{32}$$

Proof of eqn. (32) is as follows. From eqns. (28), (29) and (30), we have

$$\begin{aligned}
\int_{-\infty}^{\infty} F^{(n)}(t)\,\mathrm{d}t&=\sum_{r=0}^{n}{}_{n}\mathrm{C}_{r}\int_{-\infty}^{\infty} f^{(n-r)}u^{(r)}\,\mathrm{d}t\\
&={}_{n}C_{0}\{f^{(n-1)}(\infty)-f^{(n-1)}(0)\}+\sum_{r=1}^{n}{}_{n}\mathrm{C}_{r}(-1)^{r-1}f^{(n-1)}(0)\\
&=f^{(n-1)}(\infty)-\left\{\sum_{r=0}^{n}{}_{n}\mathrm{C}_{r}(-1)^{r}\right\}f^{(n-1)}(0)\\
&=f^{(n-1)}(\infty)-(1-1)^{n}f^{(n-1)}(0)=f^{(n-1)}(\infty)
\end{aligned}$$

Property A6

$$\mathrm{L_b}[F(t)]=\mathrm{L}[F(t)]=\mathrm{L}[f(t)]=\bar{f}(s) \tag{33}$$

Property A7

$$\mathrm{L_b}\left[F^{(n)}(t)\right]=s^{n}\mathrm{L}[F(t)]=s^{n}\mathrm{L}[f(t)]=s^{n}\bar{f}(s) \tag{34}$$

The last property A7 is a remarkable property of $F(t)$ and $\mathrm{L_b}$, and is proven by induction. When $n=1$, we have

$$\begin{aligned}
\mathrm{L_b}\left[F^{(1)}(t)\right]&=\mathrm{L_b}\left[f^{(1)}(t)u(t)\right]+\mathrm{L_b}[f(t)\delta(t)]\\
&=\mathrm{L}\left[f^{(1)}(t)\right]+\int_{-\infty}^{\infty} f(t)\delta(t)\,\mathrm{e}^{-st}\,\mathrm{d}t\\
&=\{s\mathrm{L}[f(t)]-f(0+)\}+f(0)\\
&=s\mathrm{L}[f(t)]=s\bar{f}(s)
\end{aligned}$$

Supposing the validity of eqn. (34) for n and using a formal integration by parts, we take the L_b transform of $F^{(n+1)}(t)$

$$L_b[F^{(n+1)}(t)] = \int_{-\infty}^{\infty} F^{(n+1)}(t)\,e^{-st}\,dt$$
$$= [F^{(n)}(t)\,e^{-st}]_{-\infty}^{\infty} + s\int_{-\infty}^{\infty} F^{(n)}(t)\,e^{-st}\,dt$$
$$= sL_b[F^{(n)}(t)] = s^{n+1}L[F(t)]$$

DERIVATION OF TRANSFER FUNCTION ALLOWING NON-ZERO VALUES OF INPUT AND OUTPUT SIGNALS AT $t = 0+$

Let us define the input and output signal functions $X(t)$ and $Y(t)$ respectively, as follows

$$\begin{aligned} X(t) &= x(t)u(t) \\ Y(t) &= y(t)u(t) \end{aligned} \tag{35}$$

In eqn. (35), $x(t)$ and $y(t)$ are continuous and differentiable functions of t in the domain $-\infty < t < \infty$ and $u(t)$ is the unit step function previously defined in eqn. (23).

It is easily seen that the signal functions satisfy the following initial conditions

$$\left.\begin{aligned} X(t) = X^{(1)}(t) = \ldots = X^{(m)}(t) = \ldots = 0 \\ Y(t) = Y^{(1)}(t) = \ldots = Y^{(n)}(t) = \ldots = 0 \end{aligned}\right\} t < 0 \tag{36}$$

It is supposed that our calorimetric system is described by the following differential equation

$$\frac{d^nY}{dt^n} + a_1\frac{d^{n-1}Y}{dt^{n-1}} + \ldots + a_{n-1}\frac{dY}{dt} + a_nY$$
$$= b_0\frac{d^mX}{dt^m} + b_1\frac{d^{m-1}X}{dt^{m-1}} + \ldots + b_{m-1}\frac{dX}{dt} + b_mX \tag{37}$$

The coefficients $a_1, a_2, \ldots, a_n$ and $b_0, b_1, \ldots, b_m$ are time-invariant constants. In an actual calorimeter, the coefficients are determined by the thermal physical properties of the calorimeter system and change slowly with temperature. Therefore, the temperature is restricted for real calorimetry and treatments of a calorimeter as a time-invariant linear system are effectively applied during quasi-isothermal operation [21].

Taking the double-sided Laplace transform L_b of eqn. (37), and using the properties A6 and A7 described in the previous section, we obtain eqn. (4) and the transfer function $G(s)$ described by eqn (5). It is important that no restriction is made on the values of $x(t)$ and $y(t)$ at $t = 0+$.

THE TRANSFER FUNCTION OF THE HEAT CONDUCTION CALORIMETER AND INITIAL VALUES OF THE UNIT STEP RESPONSE

The heat conduction calorimeter used in the quasi-isothermal mode [21] can be treated by the present theory. The typical response of the heat conduction calorimeter to the unit step power input (the unit step response) is illustrated in Fig. 1 [22]. In some cases, a time delay d is observed in the response. The response reaches the final temperature $h(\infty)$ as $t \to \infty$. It should be noted that the temperature change caused by the power input is always positive. The unit step response is measured in most experiments and the behaviour of the response shows the characteristics of the calorimeter system. The response with time delay $Y_D(t)$ is written in the form

$$Y_D(t) = Y(t-d) = y(t-d)u(t-d) = y_D(t)u(t-d) \tag{38}$$

In eqn. (38), $Y(t)$ is the response with no time delay and is zero for $t < 0$; $y(t)$ is a differentiable function in the domain $-\infty < t < \infty$. Subscript D denotes the response of the system with time delay d. Taking the Laplace transform of eqn. (38), we obtain [4]

$$\bar{Y}_D(s) = \bar{y}(s)\,e^{-sd} = \bar{y}_D(s) \tag{39}$$

The transfer function of a system with time delay d, $G_D(s)$, is therefore

$$G_D(s) = \frac{\bar{y}_D(s)}{\bar{x}(s)} = \frac{\bar{y}(s)\,e^{-sd}}{\bar{x}(s)} = G(s)\,e^{-sd} \tag{40}$$

where $G(s)$ is the transfer function of the system with no time delay.

Output reponses $H(t)$ and $H_D(t)$ to the unit step power input (the unit step responses) are written in a similar form

$$H(t) = h(t)u(t) \tag{41}$$

and

$$H_D(t) = H(t-d) = h(t-d)u(t-d) = h_D(t)u(t-d) \tag{42}$$

where $h(t)$ is a differentiable function of t in the domain $-\infty < t < \infty$ and

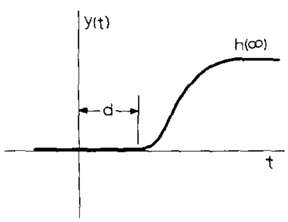

Fig. 1. The typical response of the heat conduction calorimeter to the unit step power input (the unit step response). In some cases, it has a time delay d. It reaches a final temperature $h(\infty)$ as $t \to \infty$.

subscript D denotes the response with time delay d. They can be written in the form of the Laplace transform as follows

$$\bar{H}(s) = \bar{h}(s) \tag{43}$$

$$\bar{H}_D(s) = \bar{h}_D(s) = \bar{h}(s)\, e^{-sd}$$

Using eqns. (40) and (43), we can write

$$\bar{h}_D(s) = G_D(s)L[u(t)] = G(s)\, e^{-sd}(1/s) \tag{44}$$

and

$$G(s) = s\bar{h}(s) \tag{45}$$

Significant features which are contained in the unit step response in Fig. 1 determine the properties of the transfer function of the heat conduction calorimeter. Figure 1 shows that

$$H_D(d+) = h_D(d+) = h(0+) = 0 \tag{46}$$

Now, we can calculate the initial value of the unit step response of the calorimeter system when the transfer function of the system is given by eqn. (5). From the initial value theorem of the Laplace transform [4], we obtain

$$\begin{aligned} h_D(d+) &= h(0+) = \lim_{s\to\infty} s\bar{h}(s) = \lim_{s\to\infty} G(s) \\ &= \lim_{s\to\infty} \frac{b_0 s^m + b_1 s^{m-1} + \ldots + b_{m-1}s + b_m}{s^n + a_1 s^{n-1} + \ldots + a_{n-1}s + a_n} \\ &= \lim_{s\to\infty} s^{m-n} \frac{b_0 + b_1 s^{-1} + \ldots + b_{m-1}s^{m-1} + b_m s^{-m}}{1 + a_1 s^{-1} + \ldots + a_{n-1}s^{n-1} + a_n s^{-n}} \end{aligned} \tag{47}$$

Case 1. When $m < n$, we obtain

$$h_D(d+) = h(0+) = 0 \tag{48}$$

Case 2. When $m = n$, we obtain

$$h_D(d+) = h(0+) = b_0 \tag{49}$$

Case 3. When $m > n$, we obtain

$$h_D(d+) = h(0+) = \infty \tag{50}$$

The heat conduction calorimeter is the system in case 1. The system in case 2 has one of the necessary functions available for the study of thermokinetics because it shows an instantaneous finite response to the step input. The system can follow immediately the energy change caused by the reaction under investigation. The system in case 3 shows an infinite response to the unit step input, and therefore is not available for usual calorimeter experiments.

Textbooks usually state that the linear system described by eqn. (1) should be accompanied by condition $m < n$. However, they do not state clearly why condition $m < n$ should be added to eqn. (1) Our result (eqn. (48)) shows that the linear system (eqn. (1)) should not be accompanied by the condition $m > n$, otherwise the system will give an infinite response to the unit step input.

Next, we can calculate the first derived function, $h_D^{(1)}(d+)$ and $h^{(1)}(0+)$. When $m < n$, from eqn. (48) we obtain

$$h_D^{(1)}(d+) = h^{(1)}(0+) = \lim_{s\to\infty} s\mathrm{L}[h^{(1)}(t)] = \lim_{s\to\infty} s\{s\bar{h}(s) - h(0)\}$$

$$= \lim_{s\to\infty} sG(s) = \lim_{s\to\infty} s^{m+1-n}\frac{b_0 + b_1 s^{-1} + \ldots + b_m s^{-m}}{1 + a_1 s^{-1} + \ldots + a_n s^{-n}} \tag{51}$$

When $m + 1 < n$, we obtain

$$h_D^{(1)}(d+) = h^{(1)}(0+) = 0 \tag{52}$$

When $m + 1 = n$, we obtain

$$h_D^{(1)}(d+) = h^{(1)}(0+) = b_0 \tag{53}$$

Case $m + 1 > n$ is not possible since there is no integer n which satisfies $m + 1 > n > m$.

When $m = n$, we already have $h_D(d+) = h(0+) = b_0$, and we obtain

$$h_D^{(1)}(d+) = h^{(1)}(0+) = \lim_{s\to\infty} s\{s\bar{h}(s) - b_0\}$$

$$= \lim_{s\to\infty} \frac{(b_1 - a_1 b_0) + (b_2 - a_2 b_0)s^{-1} + \ldots + (b_m - a_m b_0)s^{-m+1}}{1 + a_1 s^{-1} + \ldots + a_m s^{-m}}$$

$$= b_1 - a_1 b_0 \tag{54}$$

Furthermore, we can calculate the second derived functions, $h_D^{(2)}(d+)$ and $h^{(2)}(0+)$. When $m + 1 < n$, we obtain

$$h_D^{(2)}(d+) = h^{(2)}(0+) = \lim_{s\to\infty} s\mathrm{L}[h^{(2)}(t)]$$

$$= \lim_{s\to\infty} s\{s^2\bar{h}(s) - sh(0+) - h^{(1)}(0+)\}$$

$$= \lim_{s\to\infty} s^3\bar{h}(s) = \lim_{s\to\infty} s^2 G(s)$$

$$= \lim_{s\to\infty} s^{m+2-n}\frac{b_0 + b_1 s^{-1} + \ldots + b_m s^{-m}}{1 + a_1 s^{-1} + \ldots + a_n s^{-n}} \tag{55}$$

When $m + 2 < n$, we obtain

$$h_D^{(2)}(d+) = h^{(2)}(0+) = 0 \tag{56}$$

When $m + 2 = n$, we obtain

$$h_D^{(2)}(d+) = h^{(2)}(0+) = b_0 \tag{57}$$

The $m + 2 > n$ case is not possible since there is no integer n which satisfies $m + 2 > n > m + 1$.

When $m + 1 = n$, we already have $h(0+) = 0$ and $h^{(1)}(0+) = b_0$, and so we obtain

$$h_D^{(2)}(d+)$$
$$= h^{(2)}(0+) = \lim_{s \to \infty} s\{s^2\bar{h}(s) - b_0\}$$
$$= \lim_{s \to \infty} \frac{(b_1 - a_1 b_0) + (b_2 - a_2 b_0)s^{-1} + \ldots (b_m - a_m b_0)s^{-m+1} - b_0 s^{-m}}{1 + a_1 s^{-1} + \ldots + a_{m+1} s^{-m-1}}$$
$$= b_1 - a_1 b_0 \tag{58}$$

When $m = n$, we already have $h(0+) = b_0$ and $h^{(1)}\ (0+) = b_1 - a_1 b_0$, and so we obtain

$$h_D^{(2)}(d+) = h^{(2)}(0+) = \lim_{s \to \infty} s\{s^2\bar{h}(s) - sh(0+) - h^{(1)}(0+)\}$$
$$= b_2 - a_2 h(0+) - a_1 h^{(1)}(0+)$$
$$= b_2 - a_2 b_0 - a_1(b_1 - a_1 b_0) \tag{59}$$

Similarly, we obtain

$$h_D^{(p)}(d+) = h^{(p)}(0+)$$
$$= b_p - a_p h(0+) - a_{p-1} h^{(1)}(0+) - \ldots - a_2 h^{(p-2)}(0+)$$
$$- a_1 h^{(p-1)}(0+) \tag{60}$$

By similar successive calculations, we obtain the following properties of the unit step response and the transfer function of the system.

Property B1. When the transfer function of the system is given by

$$G_D(s) = G(s)\,e^{-sd}$$
$$= \frac{b_0 s^m + b_1 s^{m-1} + \ldots + b_{m-1}s + b_m}{s^n + a_1 s^{n-1} + \ldots + a_{n-1}s + a_n}\,e^{-sd} \qquad b_0 \neq 0$$

the initial values of the unit step response $H_D(t) = h_D(t)u(t-d) = h(t-d)u(t-d)$ are given as follows: when $m < n$, $h_D(d+) = h(0+) = 0$; when $m = n$, $h_D(d+) = h(0+) = b_0$; when $m > n$, $h_D(d+) = h(0+) = \infty$.

Property B2. When the transfer function of the system is the same as that described previously, then the initial values of the unit step response and its derivatives are given as follows: when $m + r < n$, $h(0+) = h^{(1)}(0+) = \ldots = h^{(r)}(0+) = 0$; when $m + r = n$, $h^{(r)}(0+) = b_0$, $h^{(r+1)}(0+) = b_1 - a_1 h^{(r)}(0+), \ldots, h^{(r+p)}(0+) = b_p - a_p h^{(r)}(0+) - a_{p-1} h^{(r+1)}(0+) - \ldots - a_1 h^{(p+r-1)}(0+)$; when $m > n$, $h(0+) = h^{(1)}(0+) = h^{(2)}(0+) = \ldots = \infty : r = 0, 1, 2, \ldots$

The final value of the unit step response $h(\infty)$ is given by the final-value theorem of the Laplace transform [4] as follows

$$h_D(\infty) = h(\infty) = \lim_{s \to 0} s\mathrm{L}[h(t)] = \lim_{s \to 0} G(s) = b_m/a_n \tag{61}$$

Here, it is assumed that $G(s)$ does not contain any poles whose real part is zero or positive, because the unit step response of the calorimeter does not usually show any periodic or infinite behaviour as $t \to \infty$ [23,24].

Property B3. The final value of the unit step response of the system whose transfer function is given by eqn. (5) is b_m/a_n.

TIME INTEGRALS OF INPUT AND OUTPUT SIGNALS

When the integrals $\int_0^\infty x(t)\,dt$ and $\int_0^\infty y(t)\,dt$ have finite values, we can obtain the following equation by integrating both sides of eqn. (37) from $-\infty$ to ∞ and using eqns. (31) and (32)

$$y^{(n-1)}(\infty) + a_1 y^{(n-2)}(\infty) + \ldots + a_{n-1} y(\infty) + a_n \int_0^\infty y(t)\,dt$$
$$= b_0 x^{(m-1)}(\infty) + b_1 x^{(m-2)}(\infty) + \ldots + b_{m-1} x(\infty) + b_m \int_0^\infty x(t)\,dt \quad (62)$$

When

$$\begin{aligned} x(\infty) &= x^{(1)}(\infty) = x^{(2)}(\infty) = \ldots = x^{(m-1)}(\infty) = 0 \\ y(\infty) &= y^{(1)}(\infty) = y^{(2)}(\infty) = \ldots = y^{(n-1)}(\infty) = 0 \end{aligned} \quad (63)$$

are valid, then eqn. (62) becomes

$$a_n \int_0^\infty y(t)\,dt = b_m \int_0^\infty x(t)\,dt \quad (64)$$

Equation (64) is identical with the proportionality relation between the total change in the energy evolved in a calorimeter and the peak area observed in the time–temperature curve in the heat conduction calorimeter experiments [21,25].

Property B4. When integrals $\int_0^\infty x(t)\,dt$ and $\int_0^\infty y(t)\,dt$ have finite values and the values of $x(t)$, $y(t)$ and their derivatives become zero as $t \to \infty$, the following relation is valid

$$\int_0^\infty y(t)\,dt = \frac{b_m}{a_n} \int_0^\infty x(t)\,dt = h(\infty) \int_0^\infty x(t)\,dt \quad (65)$$

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