A FRACTIONAL DIFFUSION EQUATION FOR CALCULATING THERMAL PROPERTIES OF THIN FILMS FROM SURFACE TRANSIENT THERMOREFLECTANCE MEASUREMENTS

Vladimir V. Kulish - mvvkulish@ntu.edu.sg
School of Mechanical & Production Engineering
Nanyang Technological University
50 Nanyang Ave., Singapore 639798
José L. Lage - JLL@SEAS.SMU.EDU
Mechanical Engineering Department
Southern Methodist University
Dallas, Texas, 75275-0337
Pavel L. Komarov - pavel@seas.smu.edu
Mechanical Engineering Department
Southern Methodist University
Dallas, Texas, 75275-0337
Peter E. Raad - praad@seas.smu.edu
Mechanical Engineering Department
Southern Methodist University
Dallas, Texas, 75275-0337

Abstract: *The thermoreflectance method, suitable for determining the thermal properties of thin films, consists of measuring changes in the reflectivity of a thin film under pulsed laser heating, and relating these changes to corresponding temperature variations. Analytical or numerical solutions of the diffusion problem are then used to determine the thermal property of the material following an iterative matching process between the analytical and the experimental results. The existing analytical or numerical solutions, valid when the laser energy is absorbed at the surface or when it is absorbed volumetrically by the thin film, allow for the determination of only one thermal property (thermal conductivity or diffusivity), with the other one assumed to be equal to the bulk material property. A complete solution to the non-homogeneous diffusion equation with surface and volumetric heating, found using fractional calculus and presented in a semi-derivative form, provides the means to determine the two thermal properties of thin films (thermal conductivity and diffusivity) concomitantly. This can be achieved by utilising a secondary laser for heating the material. The solution component for surface heating is validated by comparison with experimental data for a GaAs bulk sample using the classical thermoreflectance method.*

Keywords: *thermoreflectance, thin films, fractional calculus*

1. INTRODUCTION

Obtaining analytical solutions for transient heat diffusion problems within a certain domain is complicated because of the mathematical intricacies involved in solving the differential equation governing the phenomenon (Özisik, 1980, Kakaç and Yener, 1985, Poulikakos, 1994). Numerical simulations are often the only choice for solving the problem.

When seeking a relationship between temperature and heat flux at a particular location, say at the boundary (surface) of the domain, the diffusion equation must be solved within the entire domain first.

There are practical situations in thermal engineering in which a relationship between surface (local) temperature and heat flux would suffice. Consider for instance the experimental transient thermoreflectance method (TTR) used to determine the thermal conductivity of different materials including thin films (Xu et al., 1995, Chen et al., 1994, Goodson and Flik, 1994). The TTR method consists of heating the surface of the material with a laser-pulse and then tracking the time-decay of the surface temperature (by measuring the surface reflectivity). Therefore, the time evolutions of the surface temperature and of the heat flux are known. A solution of the transient diffusion equation that models the phenomenon has to be found within the entire domain. Then, the results of surface temperature values obtained with an initial (guessed) conductivity value (specific heat is assumed known) are compared with the experimental results. The thermal conductivity is then modified until the results match the experimental results. Although the comparison between numerical and experimental results is limited to the surface temperature values, a solution to the diffusion equation for the *entire domain* is necessary before the TTR method can be useful.

An analytical solution exists only for the laser radiation absorbed at the surface of the film (opaque material). When the laser radiation penetrates through the material, a numerical simulation approach is followed (semi-transparent material). Either way, only one thermophysical property can be determined, i.e., thermal conductivity or diffusivity.

A relatively simple methodology for deriving an analytical equation involving surface temperature, surface heat flux, volumetric heating and thermal properties is presented here. This methodology is based on *fractional calculus*. Lage and Kulish (2000) demonstrated the applicability and limitations of fractional calculus to solving transient diffusion problems. In the following sections, the derivation of a general fractional equation for the surface temperature as function of the surface heat flux is presented. This fractional equation is then validated using experimental thermoreflectance measurements of a GaAs thin-film.

2. EXTRAORDINARY DIFFUSION EQUATION

Consider a one-dimensional time-dependent diffusion problem in a semi-infinite medium, with a space and time dependent volumetric heat source or sink. The diffusion equation, assuming constant and uniform properties, is

$$\frac{\partial T(x,t)}{\partial t} - \alpha \frac{\partial^2 T(x,t)}{\partial x^2} - \frac{\dot{q}'''(x,t)}{\rho c} = 0 \tag{1}$$

where $T(x,t)$ is the scalar temperature field, t is the time, α is the thermal diffusivity (equal to $k/\rho c$), k is the thermal conductivity, ρ is the density, c is the specific heat of the material being heated, and $\dot{q}'''$ is the volumetric heat sink or source (power per unit volume).

The system is initially at equilibrium, so $T(x,t) = T_0$ for $t \le 0$, where T_0 is a constant and uniform temperature everywhere in the domain. Implementing the change of variables $\xi = \alpha^{-1/2}x$, and $T^* = T - T_0$, Eq. (1) becomes

$$\frac{\partial T^*(\xi,t)}{\partial t} - \frac{\partial^2 T^*(\xi,t)}{\partial \xi^2} - \frac{\dot{q}'''(\xi,t)}{\rho c} = 0 \tag{2}$$

and the initial condition is now written as $T^*(\xi, 0) = 0$. Taking the Laplace transform of Eq.

(2), and using the initial condition $T^*(\xi, 0) = 0$,

$$\frac{d^2\Theta}{d\xi^2} - s\Theta + Q(\xi,s) = 0 \tag{3}$$

where $\Theta(\xi,s)$ is the Laplace transform of $T^*(\xi,t)$, and $Q(\xi,s)$ is the Laplace transform of $\dot{q}'''(\xi,t)/(\rho c)$.

Equation (3) is an ordinary differential equation, which is known as the *forced oscillations equation*, commonly found in the field of dynamics (see Kamke, 1959). The solution to this nonhomogeneous equation can be written as

$$\Theta(\xi,s) = C_1(s)exp\left[\xi s^{1/2}\right] + C_2(s)exp\left[-\xi s^{1/2}\right] + P(\xi,s) \tag{4}$$

where the two first terms in the right side of the equal sign form the general solution of the associated homogeneous equation, when $Q(\xi,s) = 0$, and $P(\xi,s)$ is a particular solution.

For the solution Eq. (4) to be bounded as $\xi \to \infty$, the constant $C_1(s)$ must be zero, so

$$\Theta(\xi,s) = C(s)exp\left[-\xi s^{1/2}\right] + P(\xi,s) \tag{5}$$

Hence, the constant $C(s)$ can be written as

$$C(s) = [\Theta(\xi,s) - P(\xi,s)]exp\left[\xi s^{1/2}\right] \tag{6}$$

On differentiating Eq. (5) with respect to ξ,

$$\frac{\partial\Theta(\xi,s)}{\partial\xi} = -C(s)s^{1/2}\,exp\left[-\xi s^{1/2}\right] + \frac{\partial P(\xi,s)}{\partial\xi} \tag{7}$$

Eliminating C in Eq. (7) using Eq. (6), one obtains

$$\frac{\partial\Theta(\xi,s)}{\partial\xi} = -s^{1/2}\Theta(\xi,s) + s^{1/2}P(\xi,s) + \frac{\partial P(\xi,s)}{\partial\xi} \tag{8}$$

Applying the inverse Laplace transform and restoring the original variables, then

$$\frac{\partial T(x,t)}{\partial x} = \frac{1}{\alpha^{1/2}}\left[\frac{T_0}{(\pi t)^{1/2}} - \frac{\partial^{1/2}T(x,t)}{\partial t^{1/2}} + \frac{\partial^{1/2}p(x,t)}{\partial t^{1/2}} - \frac{p(x,0)}{(\pi t)^{1/2}}\right] + \frac{\partial p(x,t)}{\partial x} \tag{9}$$

where $p(x,t)$ is the inverse Laplace transform of the function $P(x,s)$.

Invoking the Fourier Law together with Eq. (9), a relationship between the heat flux $\dot{q}''$ and the temperature T in any location inside the domain, including the boundary, is obtained

$$\dot{q}''(x,t) = \frac{k}{\alpha^{1/2}}\left[\frac{\partial^{1/2}T(x,t)}{\partial t^{1/2}} - \frac{T_0}{(\pi t)^{1/2}} - \frac{\partial^{1/2}p(x,t)}{\partial t^{1/2}} + \frac{p(x,0)}{(\pi t)^{1/2}}\right] - k\frac{\partial p(x,t)}{\partial x} \tag{10}$$

An expression for the local temperature $T(x,t)$ can be derived from Eq. (10) by the use of the fractional operator $\partial^{-1/2}()/\partial t^{-1/2}$ and the fractional calculus properties

$$\frac{d^h}{dt^h}\left(\frac{d^f g(t)}{dt^f}\right)=\frac{d^{h+f} g(t)}{dt^{h+f}}\ ;\ \frac{\partial^f\left[t^n\right]}{\partial t^f}=\frac{\Gamma(n+1)}{\Gamma(n+1-f)}t^{n-f}\ ;\ \frac{\partial^{-1/2}[C]}{\partial t^{-1/2}}=2C\left(\frac{t}{\pi}\right)^{1/2} \tag{11}$$

The result is

$$T(x,t)=T_0-p(x,0)+p(x,t)+\frac{\alpha^{1/2}}{k}\frac{\partial^{-1/2}\left[\dot{q}''(x,t)+k\frac{\partial p}{\partial x}\right]}{\partial t^{-1/2}} \tag{12}$$

Equations (10) and (12) depend on two distinct groups of thermal properties, namely, $(k\rho c)^{1/2}$ and k. Results particular to the zero volumetric heat source/sink case and to the uniform volumetric heat source/sink case can be obtained from Eq. (10) and (12) by setting $p(x,t) = 0$ and assuming $p(x,t) = p(t)$, respectively. The resulting equations are peculiar for depending on one group of thermal properties, $(k\rho c)^{-1/2}$. This aspect can be highlighted by re-writing the last term of Eq. (12) as

$$T(x,t)=T_0+T_f(x,t)+T_v(x,t) \tag{13}$$

where the last two terms are the individual contributions from the local heat flux and the local volumetric heat source, respectively,

$$T_f(x,t)=\frac{1}{\left(k\rho c_p\right)^{1/2}}\frac{\partial^{-1/2}[\dot{q}''(x,t)]}{\partial t^{-1/2}} \tag{14a}$$

$$T_v(x,t)=-p(x,0)+p(x,t)+\left(\frac{k}{\rho c_p}\right)^{1/2}\frac{\partial^{-1/2}\left[\frac{\partial p(x,t)}{\partial x}\right]}{\partial t^{-1/2}} \tag{14b}$$

3. TRANSIENT THERMOREFLECTANCE METHOD

The TTR method comprises heating the surface of the material under test with a short laser pulse. Part of the radiation energy from the laser is reflected by the surface of the material. The remaining radiation energy is absorbed within the material during the heating process. The surface reflectivity of the material is continuously measured as it changes during the heating process. Relating the relative surface reflectivity variation to the relative surface temperature variation allows one to infer the time variation of the surface temperature from the reflectivity data.

If the heating area is much bigger than the probing area and the properties of the material are considered uniform and constant, the energy balance equation can be considered unidirectional.

The radiation power flux distribution at the surface is Gaussian in time, i.e., $I''(0,t) = I''_0 \exp\{-[(t-b)/\sigma]^2\}$, where I''_0 — the incidence radiation flux intensity at $t = b$ — equals $F/(2A\sigma\pi^{1/2})$, with F being the fluence of the laser irradiation, A the heated surface area, and b and σ the mean and variance of the normal distribution, respectively.

Two alternatives exist for modeling the laser heating process. The first and most common alternative is to assume the material as opaque, in which case the material absorbs all the radiation at the surface. In this case, the volumetric (internal) heat source $\dot{q}'''$ of Eq. (1) is set equal to zero, consequently $T_v(0,t) = 0$ and the surface temperature, from Eq. (13) and (14), becomes

$$T_s(t) = T_0 + \frac{1}{(k\rho c_p)^{1/2}} \frac{\partial^{-1/2} \dot{q}''_s(t)}{\partial t^{-1/2}} \tag{15}$$

where the surface heat flux (the boundary condition at the surface of the layer) is

$$\dot{q}''_s(t) = \frac{F(1-r)}{2A\sigma\pi^{1/2}} exp\left[-\left(\frac{t-b}{\sigma}\right)^2\right] \tag{16}$$

where r is the surface reflectivity. Notice that Eq. (15) can be shown to be identical to the solution provided by Özisik (1989), p.77, Eq. (2-138), supporting the validity of the fractional solution with no source/sink term.

The second alternative, normally pursued via numerical simulations, is to consider the material semi-transparent. Hence, the boundary heat flux is set as equal to zero and the laser energy is absorbed volumetrically within the material. The energy balance is then identical to Eq. (1) with $\dot{q}'''$, the absorbed laser radiation per unit of volume, expressed as

$$\dot{q}'''(x,t) = I''_0(1-r)\kappa\, exp(-\kappa x) exp\left[-\left(\frac{t-b}{\sigma}\right)^2\right] \tag{17}$$

where κ is the extinction or attenuation coefficient of the material. The Laplace transform of Eq. (17), after dividing it by ρc, and using $\xi = \alpha^{-1/2} x$, is

$$Q(\xi;s) = \frac{I''_0}{2\rho c}(1-r)\kappa\sigma\pi^{1/2} e^{\left(-\kappa\alpha^{1/2}\xi\right)} e^{\left(\frac{\sigma^2}{4}s^2 - bs\right)} erfc\left[\frac{\sigma}{2}\left(s - \frac{2b}{\sigma^2}\right)\right] \tag{18}$$

It follows that

$$P(\xi;s) = \frac{\tilde{Q}(s)}{s-\kappa^2\alpha} exp\left(-\kappa\alpha^{1/2}\xi\right) \tag{19}$$

where $\tilde{Q}(s) = Q(\xi;s) exp\left(\kappa\alpha^{1/2}\xi\right)$. By applying the convolution theorem and taking into account that the inverse Laplace transform of $\tilde{Q}(s)$ is $I_0\kappa \exp\{-[(t-b)/\sigma]^2\}$ and the inverse Laplace transform of $1/(s-\kappa^2\alpha)$ is $\exp(\kappa^2\alpha t)$, we obtain

$$p(x,t) = \frac{I''_0(1-r)\kappa e^{-\kappa x}}{\rho c_p} e^{\kappa^2\alpha t} \frac{\sigma\pi^{1/2}}{2} e^{\left[\frac{-b^2}{\sigma^2}+K^2\right]} \left[erf\left(\frac{t}{\sigma}+K\right) - erf(K)\right] \tag{20}$$

where,

$$K = \frac{\kappa^2 \alpha \sigma^2 - 2b}{2\sigma} \tag{21}$$

Noticing from Eq. (20) that $\partial p(x,t)/\partial x = -\kappa p(x,t)$, and

$$p(0,t) = \frac{I_0 \alpha \kappa \sigma}{2\pi^{1/2}} \left[erf\left(\frac{b}{\sigma}\right) exp\left(\kappa^2 \alpha t\right) - erf\left(\frac{b-t}{\sigma}\right) \right] \tag{22}$$

$$\frac{\partial p(0,t)}{\partial z} = \frac{I_0 \alpha \kappa^2 \sigma}{2\pi^{1/2}} \left[erf\left(\frac{b-t}{\sigma}\right) - erf\left(\frac{b}{\sigma}\right) exp\left(\kappa^2 \alpha t\right) \right] \tag{23}$$

then, from Eq. (14b) with $p(0,0) = 0$, we have

$$T_V(0,t) = A^* \left(-B^* + \kappa \sqrt{\alpha} \frac{\partial^{-1/2} B^*}{\partial t^{-1/2}} \right) \tag{24}$$

where $A^* = I_0 \alpha \kappa \sigma / (2\pi^{1/2})$, $B^* = erf(t^*) - erf(b/\sigma) exp(\kappa^2 \alpha t)$, and $t^* = (b-t)/\sigma$.

Equations (15) and (24) can be combined into a single equation (Eq. (13)) if two lasers are used to heat the sample material, and one laser has wavelength tuned such that the laser radiation is absorbed preferentially at the surface and the other has the wavelength tuned such that the laser radiation is absorbed volumetrically. The advantage of this combination, not yet explored, is that the temperature solution becomes dependent on two independent groups of thermal properties, extending the applicability of the TTR method.

4. EXPERIMENTAL RESULTS

The model verification is accomplished by utilizing an experimental set-up for the TTR measurements, shown in Fig. 1, consisting of a pulsed Nd:YAG laser radiating at 532 nm wavelength used as a heating source, with a fluence F that can be set from 0 to 1.0 mJ.

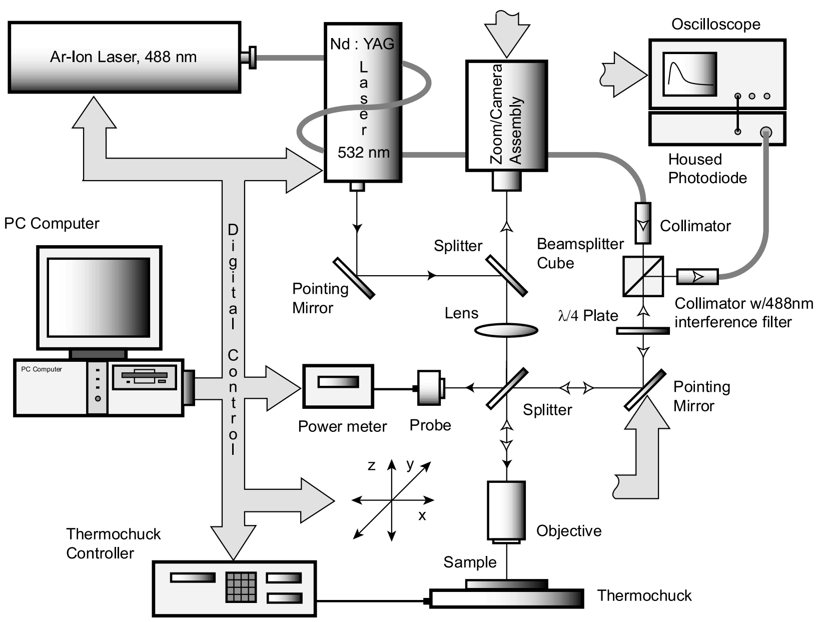

Figure 1 - Schematic of the experimental set-up (http://ww.seas.smu.edu/setsl).