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Barothermal Theory of Two Devices for Measuring Absorption Coefficients

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Two devices are proposed for measuring absorption coefficients in weakly absorbing materials. The first device measures cylindrical samples and the second device measures flat plate or disk samples. This paper reports on the derivations for the steady-state and transient solutions to the heat diffusion equations which describe the barothermal behavior of the two proposed devices. In addition, Green's function techniques are used to describe the cyclic heating and cooling of the cylinders and plates.

Key words: Absorption coefficients; barothermal behavior; Green's function; heat diffusion; weakly absorbing materials.

1. Introduction

Optical communications, integrated optics, and high power lasers are developing technologies which depend in part upon highly transparent solids. For example, optical communication systems use optical fibers with absorption coefficients which are less than 10⁻⁴ cm⁻¹ at operating wavelengths [1].¹ Continuing further advances in these technologies and determining the absorption mechanisms in highly transparent materials require improved methods for measuring very small absorption coefficients.

Four general techniques for measuring absorption coefficients exist. These techniques involve respectively calorimetry, spectrophotometry, emissivity, and gas pressure measurements.

In the calorimetric technique, one measures the temperature rise of the solid which occurs when a fraction of the energy in a beam of radiation is absorbed. When the temperature rise, reflectivity, and laser power are known to within an accuracy of 1 percent, this method is capable of giving absorption coefficients on the order of 10^{-4} cm⁻¹ within an accuracy of a few percent. This method then has reasonably high sensitivity, and requires laser beam powers of the order of tens of mW for absorption coefficients of the order of 10⁻³ cm⁻¹. It also is insensitive to those scattering centers which do not absorb any of the radiation. However, the sample must be contacted with thermocouples to measure its temperature and the absorption coefficient can be determined only at those wavelengths for which sufficiently powerful lasers are available.

The second technique involves measuring the transmission loss of a beam of radiation passing through the solid. Variations of this technique include either a single beam or double beam spectrophotometer and may use samples of two different lengths. Double beam methods using samples of different lengths give products of the absorption coefficients α with the sample thickness d as small as $\alpha d \sim 0.002$ with an accuracy of ± 0.0002 . The photometric technique has the advantage of using light sources with continuous values of wavelengths present; but it has the disadvantages that sample preparation is important to avoid surface scratches and dust and that the samples should nothave scattering centers such as inclusions.

In the third technique one measures the emission of the sample at a given temperature and compares it directly to a blackbody at the same temperature. When the product αd is very small, the emittance E (the ratio of thermal radiation per unit area emitted by the sample to that emitted by a blackbody at the same temperature) becomes $E \sim \alpha d$. For values of αd less than 0.001, the emittance measurements can be more sensitive for determining α than the photometric measurements. In addition, by this technique, one can obtain values of absorption coefficients over a continuous range of wavelengths. But exceptional temperature control is essential to achieve such sensitivity.

In the fourth technique, the energy absorbed from a beam of radiation passing through the sample produces heat. The heat then diffuses from the solid to a nonabsorbing, confined gas which is adjacent to the sample. The heat transfer process leads to a pressure rise in the gas. Because this technique tends to average over any absorption inhomogeneities in the sample, we also expect that localized absorbing or scattering

¹ Figures in brackets indicate the literature references at the end of this paper.

centers could be less of a problem for this technique than for the calorimetric techniques in which the placement of thermocouples may be important.

To develop further this last technique, Bennett and Forman recently proposed alternative ways to measure very small absorption coefficients. They considered in a series of papers [2–6] both barothermal and photoacoustic modes of operation for devices to characterize weakly absorbing materials. In these papers, they cited only the results for the solutions to the heat diffusion equations which describe the behavior of the proposed devices. They did not derive the solutions because they wanted to stress in those papers the major conclusions for designing absorption devices with optimum performance.

Figures 1 and 2, respectively, show schematics of their proposed devices for measuring absorption coefficients of long cylindrical samples and of thin disk or plate-shaped samples. Each of these devices has a characteristic frequency which is related to the inverse of the time required for transferring a heat pulse from the solid to the gas. The barothermal mode of operation occurs whenever the modulation frequency of the beam of radiation is less than the characteristic frequency of the device; and the photoacoustic mode of operation occurs whenever the modulation frequency of the beam of radiation is greater than the characteristic frequency of the device [7].

In this paper, the author gives derivations for the steady-state and transient solutions to the heat diffusion equations which describe the barothermal behavior of the two proposed devices. The equations which describe the photoacoustic behavior of the devices are derived in (separate papers [4, 6]).

The steady-state and transient solutions for cylindrical samples are derived here, respectively, in section 2 and section 3; and the steady-state and transient solutions for disk or plate-shaped samples are derived, respectively, in section 4 and section 5. The Green's functions which describe the cyclic heating and cooling of the cylinders and plates are constructed in section 6. And finally, frequently occurring integrals involving the eigenfunctions for the equations are given in appendix A for cylinders and in appendix B for disks or plates.

2. Steady-State Solution-Cylinder

From [3], the steady-state temperature v(r) satisfies the following heat diffusion equations for the proposed device in figure 1: When $0 \le r \le r_{s_1}$

$$k_{s} \frac{d^{2} v_{s}(r)}{dr^{2}} + \frac{k_{s}}{r} \frac{dv_{s}(r)}{dr} + \frac{Q_{s}(r)}{\rho_{s} C_{s}} = 0;$$
(1)

and when $r_s \leq r \leq r_i$,

$$k_g \frac{d^2 v_g(r)}{dr^2} + \frac{k_g}{r} \frac{d v_g(r)}{dr} = 0.$$
 (2)

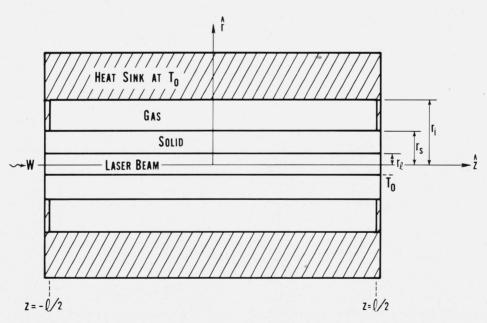


FIGURE 1. Schematic of an absorption measuring device (barothermal) for long cylindrical samples.

Insulating annuli support coaxially the long cylindrical transparent sample of radius r_s inside a larger cylinder of radius r_i . A confined nonabsorbing gas at ambient pressure p_0 fills the space between the two cylinders. The walls of the outer cylinder are at a constant temperature T_0 . A collimated beam of radiation, such as a laser beam, propagates coaxially through the cylindrical sample. The beam of radiation has a power W_i and an effective radius r_i . A pressure transducer, which is not shown, monitors the pressure at the heat sink – gas interface.

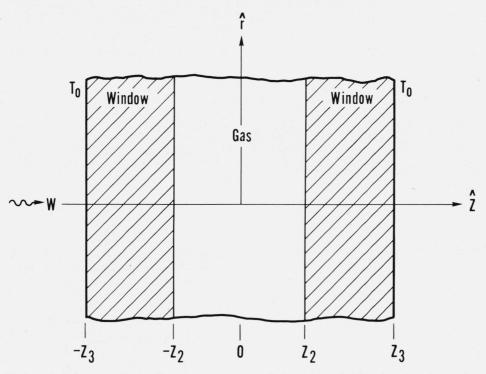


FIGURE 2. Schematic of an absorption measuring cell (barothermal) for plate-shaped samples.

A confined, nonabsorbing gas at ambient pressure p_0 fills the space inside the cell between two windows. The walls of the cell may have a polygonal or circular cross section. The windows which enclose the gas at each end of the cell are made from the weakly absorbing material under investigation. The external faces of the two windows are at a constant temperature T_0 . A collimated beam of radiation, such as a laser heam, with power W_i and effective radius r_i propagates along the z direction through the pressure cell and its windows. A pressure transducer, which is not shown, measures the pressure in the gas at $|z| \leq z_2$.

The temperature in the solid is $v_s(r)$ and the temperature in the gas is $v_g(r)$. The power absorbed per unit volume in the solid is

$$Q_s(r) = \begin{cases} Q_l \text{ for } 0 \le r \le r_l \le r_s \\ 0 \text{ for } r > r_i, \end{cases}$$
(3)

where $Q_i = \alpha_s W_i / \pi r_i^2$, α_s is the absorption coefficient of the solid, W_i is the power of the beam of radiation, and r_i is the effective radius of the collimated beam. The radius of the cylindrical sample is r_s and the radius of the outer cylinder (heat sink) is r_i . The thermal diffusivity $k = K/\rho C$, where K is the thermal conductivity, ρ is the density, and C is the specific heat at constant volume. The subscript s denotes quantities for the solid and the subscript g denotes quantities for the gas.

The boundary conditions are that

$$v_a(r_i) = T_0, \tag{4}$$

where T_0 is the temperature of the heat sink. Continuity of temperature across the solid-gas interface at $r=r_s$ gives,

$$v_s(r_s) = v_g(r_s), \qquad (5)$$

and conservation of heat flow across the solid-gas

interface at $r = r_s$ gives,

$$K_s \frac{dv_s}{dr} \bigg|_{r=r_s} = K_g \frac{dv_g}{dr} \bigg|_{r=r_s}.$$
(6)

Rearranging eq (1) and eq (2) yields, respectively,

$$\frac{d}{dr}\left(r \ \frac{dv_s}{dr}\right) = -\frac{rQ_s(r)}{K_s} \tag{7}$$

and

$$\frac{d}{dr}\left(r\frac{dv_g}{dr}\right) = 0; \tag{8}$$

and integrating these equations twice yields the steady state solutions;

$$v_{s}(r) = v_{s}(0) - \frac{Q_{l}}{4K_{s}} \begin{cases} r^{2} & \text{for } 0 \leq r \leq r_{l} \\ r_{l}^{2} [1 + 2\ln(r/r_{l})] & \text{for } r_{l} \leq r \leq r_{s'} \end{cases}$$
(9)

and

$$v_g(r) = C_{1g} \ln r + C_{2g} \text{ for } r_s \le r \le r_i$$
, (10)

where C_{1g} and C_{2g} are constants of integration and where the limit that

$$\lim_{r \to 0} r \frac{dv_s}{dr} = 0 \tag{11}$$

is invoked to obtain eq (9) (i.e., that v_s remains finite at r=0).

Boundary conditions (4), (5), and (6) require that the temperature at the center of the cylinder r=0 is

$$v_s(0) = T_0 + \frac{Q_l r_l^2}{4K_s} \left\{ 1 - \frac{2K_s}{K_g} \ln \left(\frac{r_s}{r_l} \right) + 2 \ln \left(\frac{r_s}{r_l} \right) \right\}, (12)$$

and that the temperature in the gas is

$$v_g(r) = T_0 - \frac{Q_l r_l^2}{2K_g} \ln\left(\frac{r}{r_i}\right).$$
(13)

3. Transient Solution – Cylinder

The transient temperature u(r, t) for times $t \ge 0$ is given in [3] by the diffusion equations

$$k_s \frac{\partial^2}{\partial r^2} u_s(r,t) + \frac{k_s}{r} \frac{\partial u_s(r,t)}{\partial r} = \frac{\partial u_s(r,t)}{\partial t}$$
(14)

and

$$k_g \frac{\partial^2}{\partial r^2} u_g(r, t) + \frac{k_g}{r} \frac{\partial u_g(r, t)}{\partial r} = \frac{\partial u_g(r, t)}{\partial t}.$$
 (15)

At time t=0, the sum of the transient and steadystate temperatures is everywhere equal to the ambient temperature T_0 ,

$$T(r, 0) = u(r, 0) + v(r) = T_0;$$
(16)

and at any time t the temperature at the heat sink $r=r_i$ is T_0 , i.e.,

$$u_g(r_i, t) = 0, \tag{17}$$

because

$$\lim u(r, t) = 0,$$

by the definition of transient solutions and because $v_g(r_i) = T_0$.

A general separable solution to an equation having the form of either eq (14) or (15) is

$$u(r, t) = R(r)\tau(t) = [AJ_0(\xi r) + BY_0(\xi r)] exp(-\xi^2 kt), \quad (18)$$

where J_n is the *n*th order Bessel function of the first kind, Y_n is the *n*th order Bessel function of the second kind [8], ξ is the constant of separation, and A and Bare constants. The quantities A, B, ξ , and k have the subscript *s* for the solid and the subscript *g* for the gas.

Equation (17) states that

$$R_a(r_i) = 0, \tag{19}$$

and the temperature continuity equation at $r=r_s$, requires that

$$R_s(r_s) = R_g(r_s) \tag{20}$$

and

$$\xi_s^2 = (k_g/k_s)\xi_g^2. \tag{21}$$

Also, the constant $B_s = 0$ because the temperature must be finite for all $r \ge 0$ and t.

Hence, the conservation of heat flow across the solidgas interface

$$K_s \partial u_r(r, t) / \partial r \big|_{r=r_s} = K_g \, \partial u_g(r, t) / \partial r \big|_{r=r_s}$$
(22)

and the other boundary conditions eq (19) and eq (20) yield three homogeneous simultaneous equations for the three unknowns A_s , A_g , and B_g . Solutions for this set of three equations exist if and only if the determinant, D, of their coefficients vanishes; the vanishing of the determinant yields the eigenvalues $\xi_g = \xi_j$, where $j=1, 2 \ldots$. The *j*th eigenvalue ξ_j is that value of ξ_g for which the determinant vanishes for the *j*th time, i.e., $\xi_j < \xi_{j+1}$; namely, det $D(\xi_j) = 0$, where

$$D = \begin{vmatrix} 0 & & J_0(\xi_g r_i) \\ J_0(\xi_s r_s) & -J_0(\xi_g r_s) \\ -K_s \xi_s J_1(\xi_s r_s) & K_g \xi_g J_1(\xi_g r_s) \end{vmatrix}$$

$$\begin{vmatrix} Y_0(\xi_g r_i) \\ -Y_0(\xi_g r_s) \\ K_g \xi_g Y_1(\xi_g r_s) \end{vmatrix}$$
(23)

The eigenvalues ξ_j also determine the characteristic times t_j for the solid-gas system; namely,

$$t_j = (\xi_j^2 k_g)^{-1}. \tag{24}$$

Expressing A_s and B_g in terms of $A_j = A_g$, we obtain,

$$R_{s}(r) = \sum_{j=1}^{\infty} A_{j} F_{0}(\xi_{j}, r_{i}, r_{s}) \{ J_{0}(\overline{\xi}_{j}r) / J_{0}(\overline{\xi}_{j}r_{s}) \}, \qquad (25)$$

for $0 \le r \le r_s$ and

$$R_g(r) = \sum_{j=1}^{\infty} A_j F_0(\xi_j, r_i, r)$$

for $r_s \leq r \leq r_{i'}$ where $\overline{\xi}_j^2 = (k_g/k_s) \xi_j^2$ and where the function F_n is

$$F_{n}(\xi_{g}, r_{i}, r) = \{Y_{0}(\xi_{g}r_{i})J_{n}(\xi_{g}r) - J_{0}(\xi_{g}r_{i})Y_{n}(\xi_{g}r)\}/Y_{0}(\xi_{g}r_{i}).$$
(27)

Relations (25), (26), and (27) are valid only if $J_0(\bar{\xi}_i r_s) \neq 0$ and if $Y_0(\xi_i r_i) \neq 0$.

In terms of the functions $F_n(\xi, r_i, r)$, the eigenvalue equation satisfied by the eigenvalue ξ_j becomes,

$$K_s\xi_jJ_1(\overline{\xi}_jr_s)F_0(\overline{\xi}_j,r_i,r_s)-K_g\xi_jJ_0(\overline{\xi}_jr_s)F_1(\xi,r_i,r_s)=0.$$

We determine the coefficients A_j by using the t=0 relations obtained from eq (16); namely,

$$R_s(r) = T_0 - v_s(r) \qquad \text{for } 0 \le r \le r_s \tag{28}$$

and

$$R_g(r) = T_0 - v_g(r) \qquad \text{for } r_s \leq r \leq r_i.$$
(29)

First, we consider the eigenfunctions for the solidgas system

$$E_{0}(\xi_{j}, r_{i}, r) = \begin{cases} F_{0}(\xi_{j}, r_{i}, r_{s}) \{J_{0}(\bar{\xi}_{j}r)/J_{0}(\bar{\xi}_{j}r_{s})\} & \text{for } 0 \leq r \leq r_{s} \\ F_{0}(\xi_{j}, r_{i}, r) & \text{for } r_{s} \leq r \leq r_{i}. \end{cases}$$

$$(30)$$

Next, we multiply both sides of eq (28) and eq (29) by

$$\frac{K_s}{k_s} r E_0(\xi_i, r_i, r) \quad \text{when } 0 \le r \le r_s$$

and by

$$\frac{K_g}{k_g} r E_0(\xi_i, r_i, r) \quad \text{when } r_s \leq r \leq r_i$$

and then we integrate the resulting expressions over the interval $0 \le r \le r_i$. This procedure yields the following expression for the coefficients A_j

$$\sum_{j=1}^{\infty} A_{j}\Delta(\xi_{j}, \xi_{i})$$

$$= \frac{K_{s}}{k_{s}} \left[\{T_{0} - v_{s}(0)\} \int_{0}^{r_{s}} E_{0}(\xi_{i}, r_{i}, r) r dr + \frac{Q_{l}}{4K_{s}} \left\{ \int_{0}^{r_{l}} E_{0}(\xi_{i}, r_{i}, r) r dr + r_{l}^{2} \int_{r_{l}}^{r_{s}} \{1 + 2 \ln(r/r_{l})\} E_{0}(\xi_{i}, r_{i}, r) r^{3} dr \right\} \right]$$

$$+ \frac{K_{g}}{k_{g}} \left[\frac{Q_{l} r_{l}^{2}}{2K_{g}} \int_{r}^{r_{i}} \ln(r/r_{i}) E_{0}(\xi_{i}, r_{i}, r) r dr \right].$$
(31)

where

$$\Delta(\xi_j, \xi_i) = \frac{K_s}{k_s} \int_0^{r_s} E_0(\xi_j, r_i, r) E_0(\xi_i, r_i, r) r dr + \frac{K_g}{k_g} \int_{r_s}^{r_i} E_0(\xi_j, r_i, r) E_0(\xi_i, r_i, r) r dr.$$
(32)

Appendix A contains the evaluations of the several integrals which occur in eq (31) and eq (32). Using eq

(A4) and the fact that $dB_0(\xi r)/dr = -B_1(\xi r)$, we find that $\Delta(\xi_j, \xi_l)$ vanishes unless $\xi_j = \xi_i$; and when $\xi_j = \xi_i$ the factor $\Delta(\xi_j, \xi_j) = \Delta_j$ becomes

$$\Delta_{j} = \frac{K_{g}r_{s}^{2}}{2k_{g}} \left[\left(\frac{K_{s}k_{g}}{K_{g}k_{s}} - 1 \right) F_{0}^{2}(\xi_{j}, r_{i}, r_{s}) + (r_{i}^{2}/r_{s}^{2})F_{1}^{2}(\xi_{j}, r_{i}, r_{i}) + \left(\frac{K_{g}}{K_{s}} - 1 \right) F_{1}^{2}(\xi_{j}, r_{i}, r_{s}) \right].$$
(33)

Applying eqs (A1) to (A3) to the right-hand side of eq (31), we obtain, after several steps, an expression for the coefficients A_j , namely,

$$A_{j} = -\frac{Q_{l}r_{l}}{k_{s}\bar{\xi}_{j}^{3}} \frac{J_{1}(\bar{\xi}r_{l})F_{0}(\xi_{j}, r_{i}, r_{s})}{\Delta_{j}J_{0}(\bar{\xi}_{j}r_{s})} \cdot$$
(34)

Because we sum in the computer program used in [3] a finite number of terms in such expressions as eq (25) and eq (26), we normalize the A_j 's for $1 \le j \le N$ by using the relation (29) evaluated at $r = r_s$. To accomplish this normalization, we introduce the normalization factor a_N and replace A_j with $a_N A_j(N)$ in the relation (29). This then gives us an expression for the factor a_N ; namely,

$$a_{N} = -\frac{Q_{i}r_{l}^{2}}{2K_{g}} \ln\left(\frac{r_{s}}{r_{i}}\right) / \sum_{j=1}^{N} A_{j}(N)F_{0}(\xi_{j}, r_{i}, r_{s}).$$
(35)

4. Steady-State Solution – Plate

From [5], the steady-state temperature v(z) satisfies the following heat diffusion equations for the proposed device in figure 2:

When $z_2 \leq |z| \leq z_3$,

$$\frac{\partial^2}{\partial z^2} v_s(z) + \frac{Q_l}{K_s} = 0 ; \qquad (36)$$

and when $|z| \leq z_2$,

$$\frac{\partial^2}{\partial z^2} v_g(z) = 0. \tag{37}$$

The temperature in the cell windows is $v_s(z)$ and the temperature in the gas is $v_g(z)$. The power absorbed per unit volume in the cell windows is

 $Q_l = \alpha_s W_l / \pi r_l^2$. The absorption coefficient of the windows is α_s .

The boundary conditions are that

$$v_s(\pm z_3) = T_0, \tag{38}$$

where T_0 is the ambient temperature. Continuity of temperature and conservation of heat flow across the solid-gas interface at $z=\pm z_2$ give, respectively,

$$v_s(\pm z_2) = v_g(\pm z_2) \tag{39}$$

and

$$K_s dv_s/dz \mid_{z=\pm z_2} = K_g dv_g/dz \mid_{z=\pm z_2}.$$
 (40)

We integrate eqs (36) and (37) twice to obtain the general solutions,

$$v_s(z) = -(Q_l z^2 / 2K_s) + C_s |z| + D_s, \qquad (41)$$

and

$$v_s(z) = C_g \mid z \mid + D_g, \tag{42}$$

where the *C*'s and *D*'s are constants of integration.

The absolute value of z occurs in eqs (41) and (42) because v(z) = v(-z) when $\alpha_s |z_3 - z_2| \ge 1$. Also, because $dv_g(z)/dz |_{z=0^+} = C_g$ and $dv_g(z)/dz |_{z=0^-} = -C_g$, the constant C_g must be zero. (If C_g were not zero, then a heat sink or heat source would exist at z=0. This is not the case for the proposed device). The boundary condition (38) at $z=z_3$ and the bound-

ary conditions (39) and (40) at $z=z_2$ yield three inhomogeneous equations for the three unknown coefficients C_s , D_s , and D_g ; namely,

$$C_{s}z_{3} + D_{s} = T_{0} + (Q_{l}z_{3}^{2}/2K_{s}),$$

$$-D_{g} + C_{s}z_{2} + D_{s} = (Q_{l}z_{2}^{2}/2K_{s}),$$

$$C_{s}K_{s} = Q_{l}z_{2}.$$

(43)

A solution for the three equations exists if the determinant of their coefficients does not vanish; i.e.,

$$\det \begin{pmatrix} 0 & z_3 & 1 \\ -1 & z_2 & 1 \\ 0 & K_s & 0 \end{pmatrix} = -K_s \neq 0.$$
 (44)

Using the matrix method to solve the set of equations (43), we obtain the steady-state temperature:

$$v_{s}(z) = T_{0} + (Q_{l}/K_{s}) [z_{3}\{(z_{3}/2) - z_{2}\} - |z| \{(|z|/2) - z_{2}\}], \quad (45)$$

for $z_2 \leq |z| \leq z_3$, and

$$v_g(z) = T_0 + (Q_l/2K_s)(z_3 - z_2)^2$$
(46)

for $|z| \leq z_2$.

5. Transient Solution – Plate

The transient solution u(z, t) for times $t \ge 0$ satisfies the following heat diffusion equations: [5]

$$\frac{\partial^2}{\partial z^2} u_s(z, t) = \frac{1}{k_s} \frac{\partial u_s(z, t)}{\partial t}$$
(47)

for $z_2 \leq |z| \leq z_3$, and

$$\frac{\partial^2}{\partial z^2} u_g(z, t) = \frac{1}{k_g} \frac{\partial u_g(z, t)}{\partial t}$$
(48)

for $|z| \leq z_2$.

At time t=0, the sum of the transient and steadystate temperature at the exterior sides of the cell windows at $|z|=z_3$ is T_0 , i.e.,

$$u_s(\pm z_3, t) = 0, \tag{49}$$

because

$$\lim_{t \to \infty} u(z, t) = 0 \tag{50}$$

by the definition of transient behavior and because $v_s(\pm z_3) = T_0$.

General separable solutions to eqs (47) and (48) are

$$u(z, t) = R(z)\tau(t)$$

where

$$R(z) = [A \exp(i\xi z) + B \exp(-i\xi z)]$$

and

$$\tau(t) = \exp\left(-\xi^2 k t\right).$$

The constant of separation is ξ and the coefficients A and B are constants. The subscripts s and g denote the quantities A, B, ξ , and k respectively for the windows and for the gas.

Equation (49) gives us that

$$R_s(\pm z_3) = 0. \tag{51}$$

The continuity of temperature across the interfaces at $|z| = z_2$ requires that

 $R_{s}(\pm z_{2}) = R_{a}(\pm z_{2})$

and

$$\mathcal{E}_{a}^{2} = (k_{a}/k_{s})\mathcal{E}_{a}^{2}. \tag{52}$$

In addition, the conservation of heat flow across the window-glass interface at $|z| = z_2$ requires that

$$K_{s}(dR_{s}/dz)|_{z=\pm z_{2}} = K_{g}(dR_{g}/dz)|_{z=\pm z_{2}}.$$
(53)

Hence, the boundary conditions (51), (52), and (53) yield six homogeneous simultaneous equations for the six unknown coefficients $A_s^>$, $B_s^>$, A_g , B_g , $A_s^<$, and $B_s^<$, where the superscripts < and > are, respectively, for z < 0 and z > 0. Because $A_s^< = B_s^>$, $B_s^< = A_s^>$, and $A_g = B_g$ by symmetry, these six equations reduce to three equations in three unknowns. $A_s = A_s^>$, $B_s = B_s^>$, and $A = 2A_g$. Solutions for this set of equations exist if, and only if, the determinant D of their coefficients vanishes. The vanishing of the determinant yields the eigenvalues $\xi_g = \xi_j$, where $j = 1, 2, 3, \ldots \infty$.

The *j*th eigenvalue ξ_j is that value of ξ_g for which the determinant vanishes for the *j*th time, i.e., $\xi_j < \xi_{j+1}$; namely,

$$\det D(\xi_j) = 0, \tag{54}$$

where

$$D = \begin{pmatrix} 0 & \exp(i\xi_s z_3) \\ -\cos(\xi_g z_2) & \exp(i\xi_s z_2) \\ \xi_g K_g \sin(\xi_g z_2) & i\xi_s K_s \exp(i\xi_s z_2) \\ & \exp(-i\xi_s z_3) \\ \exp(-i\xi_s z_2) \\ -i\xi_s K_s \exp(-i\xi_s z_2) \end{pmatrix}$$
(55)

and $\xi_s^2 = (k_g/k_s)\xi_g^2$. From eqs (54) and (55), the eigenvalue ξ_j satisfies the following equation

$$(K_g/k_g^{1/2}) \sin (\xi_g z_2) \sin (\xi_s d) = (K_s/k_s^{1/2})$$

 $\cos (\xi_g z_2) \cos (\xi_s d),$

where $\xi_{g} = \xi_{j}$ and $d = (z_{3} - z_{2})$.

Expressing A_s and B_s in terms of $A = A_j$, we have

$$R_g(z) = \sum_{j=1}^{\infty} A_j \cos \left(\xi_j z\right) \text{ for } |z| \le z_2$$
(57)

and

$$R_{s}(z) = \sum_{j=1}^{\infty} \frac{A_{j} \cos(\xi_{j}z_{2})}{2 \sin^{2}(\xi_{j}'d)} \{ \cos(\xi_{j}'(|z|-z_{2})) - \cos(\xi_{j}'(|z|+z_{2}-2z_{3})) \}$$

for $z_2 \leqslant |z| \leqslant z_3$, where $\xi_j' = (k_g/k_s)^{1/2} \xi_j$.

We determine the coefficients A_j by using the t=0 relations obtained from eq (49); namely,

$$R_s(z) = T_0 - v_s(z) \text{ for } z_2 \leq |z| \leq z_3$$
(59)

and

 $\mathbf{n}(\cdot,\cdot)$

$$R_g(z) = T_0 - v_g(z) \text{ for } |z| \le z_2.$$
 (60)

Equations (57) and (58) contain the eigenfunctions for the window-gas system; namely,

$$E(j, z) = \begin{cases} \cos(\xi_j z) & \text{for } |z| \le z_2 \\ \cos(\xi_j z_2) & \{\cos(\xi'_j(|z| - z_2)) \\ -\cos(\xi'_j(|z| + z_2 - 2z_3))\} \\ \hline 2 \sin^2(\xi'_j d) \\ & \text{for } z_2 \le |z| \le z_3. \end{cases}$$
(61)

We multiply both sides of eqs (59) and (60) by

$$K_q(k_s/k_g)^{1/2}E(j, z) \text{ when } -z_2 \leq |z| \leq z_3$$

and by

$$K_s(k_g/k_s)^{1/2}E(j,z) ext{ when } |z| \leq z_3,$$

and we integrate the resulting expressions respectively over the intervals $0 \le z \le z_2$ and $z_2 \le z \le z_3$. This procedure gives us the following expression for the coefficients A_j :

$$\sum_{j=1}^{\infty} A_j \Delta(\xi_j, \xi_i)$$

$$= (T_0 - D_g) K_g(k_s/k_g)^{1/2} \int_0^{z_2} E(i, z) dz$$

$$+ (Q_l/K_s) K_s(k_g/k_s)^{1/2} \int_{z_2}^{z_3} [z\{(z/2) - z_2\} - z_3\{(z_3/2) - z_2\}] E(i, z) dz$$
(62)

where

(56)

(58)

$$\Delta(\xi_j, \xi_i) = K_g(k_s/k_g)^{1/2} \int_0^{z_2} E(j, z) E(i, z) dz + K_s(k_g/k_s)^{1/2} \int_{z_2}^{z_3} E(j, z) E(i, z) dz.$$
(63)

Appendix B contains the evaluations of the several integrals which occur in eqs (62) and (63). Using eq (B4) gives us that $\Delta(\xi_j, \xi_i)$ vanishes unless $\xi_j = \xi_i$. And when $\xi_j = \xi_i$, the factor $\Delta(\xi_j, \xi_j) = \Delta_j$ becomes from eq (B5)

$$\Delta_{j} = \frac{K_{g}(k_{s}/k_{g})^{1/2}}{2} [z_{2} + \{K_{s}k_{g}d \cos^{2}(\xi_{j}z_{2})/K_{g}k_{s} \sin^{2}(\xi_{j}'d)\}].$$
(64)

Applying eq (B1) through eq (B3) repeatedly to the right-hand side of eq (62) gives us an expression for the coefficients A_j ; namely,

$$A_{j} = (K_{g}k_{s}Q_{l}/\xi_{j}^{3}K_{s}k_{g}\Delta_{j}) \{(k_{s}/k_{g})^{1/2}\sin(\xi_{j}z_{2}) - (K_{s}\cos(\xi_{j}z_{2})/K_{g}\sin(\xi_{j}'d)\}.$$
 (65)

Because the computer program in [5] evaluates a finite number of terms in such expressions as eq (57) and eq (58), the coefficients A_j are normalized for $1 \le j \le N$ by using the relation (60) evaluated at $z=z_2$. Replacing A_j with $a_N A_j(N)$ in relation (60), one obtains an expression for the normalization factor a_N ,

$$a_{N} = -\frac{(Q_{l}d^{2}/2K_{s})}{\sum_{j=1}^{N} A_{j}(N) \cos(\xi_{j}z_{2})}$$
(66)

6. Cyclic Heating and Cooling

The Green's function method offers a convenient way for computing the response of the proposed barothermal devices when the beam of radiation is turned on at t=0 and is modulated at angular frequency ω for all times $t \ge 0$. We express the power absorbed per unit volume $Q_l(t)$ by the expression,

$$Q_l(t) = \eta(t) \eta(r_l - r) Q_l(1 + m \cos \omega t), \qquad (67)$$

where $|m| \leq 1$ is the modulation factor for cyclic heating and cooling and where ω is less than the characteristic frequency of the system. The step function $\eta(x)^{\circ}$ is zero for $x \leq 0$ and 1 for x > 0.

6.1. Cylinder

The temperature $T(r_0, t_0) = u(r_0, t_0) + v(r_0) - T_0$, satisfies the heat diffusion for the cylinder and the gas; namely, for times $t_0 \ge 0$,

$$\nabla_0^2 T(r_0, t_0) - k^{-1} (\partial T(r_0, t_0) / \partial t_0) = -\rho(r_0, t_0); \quad (68)$$

where $\rho(r_0, t_0) = \eta(r_l - r_0) (Q_l/K_s) (1 + m \cos \omega t)$ for $r_l \leq r_s$; where ∇_0^2 becomes $\{(\partial^2/\partial r^2) + r_0^{-1}(\partial/\partial r_0)\}$ because the temperature does not depend upon angle θ_0 and coordinate z_0 ; and where k is subscripted with s when $0 \leq r_0 \leq r_s$ and with g when $r_s \leq r_0 \leq r_i$. We subtract the ambient temperature T_0 from the temperature for later convenience in using the boundary condition $T(r_i, t) = 0$.

The Green's function $G(r, t|r_0, t_0)$ for the system satisfies the equation

$$\nabla^{2}G(r, t|r_{0}, t_{0}) - k^{-1}\partial G(r, t|r_{0}, t_{0})/\partial t$$

$$= -\frac{\delta(r - r_{0})\delta(t - t_{0})}{r(K/k)},$$
(69)

where k and K are subscripted with s when $0 \le r \le r_s$ and with g when $r_s \le r \le r_i$. We interpret G to be the temperature which occurs at r and t when an impulse source of heat is introduced at r_0 and t_0 .

The Green's function satisfies a causality condition:

$$G(r, t | r_0, t_0) = 0 \qquad \text{if } t < t_0. \tag{70}$$

In addition, it satisfies a reciprocity condition under time reversal because the causality condition (70) requires a time sequence

$$G(r, t | r_0, t_0) = G(r_0, -t_0 | r, -t), \qquad (71)$$

where the function $G(r_0, -t_0|r, -t)$ gives the temperature at r_0 and $-t_0$ due to a source impulse at r and -t. Because $-t_0 > -t$, the time sequence is properly ordered. Hence, from eq (71) we have that

$$\nabla_{0}^{2} G(r, t | r_{0}, t_{0}) + k^{-1} \partial G(r, t | r_{0}, t_{0}) / \partial t_{0} = -\frac{\delta(r - r_{0}) \delta(t - t_{0})}{r_{0}(K/k)},$$
(72)

where k and K are subscripted with s when $0 \le r_0 \le r_s$ and with g when $r_s \le r_0 \le r_i$.

We shall now express the solutions of the inhomogeneous diffusion eq (68) for the solid and gas in terms of the Green's function G. We first multiply eq (68) by $G(r, t | r_0, t_0)$ and eq (72) by $T(r_0, t_0)$ and then subtract the first product-equation from the second productequation. Keeping in mind that the thermal factor for the solid (K_s/k_s) differs from the thermal factor for the gas (K_g/k_g) , we integrate the above result over the time domain $0 \le t_0 \le t^{-+}$ and over the volume of the solid-gas system.

$$\int dV(\ldots) = \int_0^{r_s} (\ldots) (K_s/k_s) r_0 dr_0$$
$$+ \int_{r_s}^{r_i} (\ldots) (K_g/k_g) r_0 dr_0,$$

where $t^+ = \lim_{\epsilon \to 0} t + \epsilon$.

The differential form of Green's theorem for our special case,

$$r_{0}(T\nabla_{0}^{2}G - G\nabla_{0}^{2}T) = \frac{\partial}{\partial r_{0}} \left(Tr_{0} \frac{\partial G}{\partial r_{0}}\right)$$
$$-\frac{\partial}{\partial r_{0}} \left(Gr_{0} \frac{\partial T}{\partial T_{0}}\right), \qquad (73)$$

enables us to express the temperature in terms of the Green's function. The final result becomes

$$\eta(r)\eta(r_{s}-r)T_{s}(r,t) + \eta(r-r_{s})\eta(r_{i}-r)T_{g}(r,t)$$

$$= \int_{0}^{t^{+}} dt_{0}\frac{K_{s}}{k_{s}} \int_{0}^{r_{s}} \rho(r_{0},t_{0})G(r,t|r_{0},t_{0})r_{0}dr_{0} \quad (74)$$

$$+ \int_{0}^{t^{+}} dt_{0}\frac{K_{g}}{k_{g}} \int_{r_{s}}^{r_{i}} \rho(r_{0},t_{0})G(r,t|r_{0},t_{0})r_{0}dr_{0},$$

where we have used the following initial conditions and boundary conditions:

$$T_{s}(r, 0) = 0, T_{g}(r, 0) = 0, G(r, t|r_{0}, t^{+}) = 0$$

$$T_{s}(r_{s}, t) = T_{g}(r_{s}, t), T_{g}(r_{i}, t) = 0,$$

$$k_{s}^{-1}G(r, t|r_{s}^{-}, t_{0}) = k_{g}^{-1}G(r, t|r_{s}^{+}, t_{0}),$$

$$G(r, t|r_{i}, t_{0}) = 0,$$

$$K_{s}\partial T_{s}/\partial r_{0}|_{r_{0}=r_{s}} = k_{g}\partial T_{g}/\partial r_{0}|_{r_{0}=r_{s}}, \text{ and}$$

 $K_s k_s^{-1} \partial G(r, t | r_0, t_0) / \partial r_0 |_{r_0 = r_s}$

$$= K_{g}k_{g}^{-1}\partial G(r, t|r_{0}, t_{0})/\partial r_{0}|_{r_{0}}=r_{s}^{+}.$$

We now proceed to construct the Green's function $G(r, t/r_0, t_0)$. Referring to eqs (30), (32), and (33), we have that the spatial eigenfunctions of the solid-gas system are

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$$W_{j}(r) = \begin{cases} (K_{s}/k_{s}\Delta_{j})^{1/2}E_{0}(\xi_{j}, r_{i}, r) & \text{for } 0 \leq r \leq r_{s} \\ (K_{g}/k_{g}\Delta_{j})^{1/2}E_{0}(\xi_{j}, r_{i}, r) & \text{for } r_{s} \leq r \leq r_{i}, \end{cases}$$
(75)

where

$$\int_{0}^{r_{i}} r dr W_{j_{1}}(r) W_{j_{2}}(r) = \delta_{j_{1}}, j_{2};$$

$$\sum_{j=1}^{\infty} W_{j}(r) W_{j}(r_{0}) = \{ \eta(r) \ \eta(r_{s}-r) \ (K_{s}/k_{s}) + \eta(r-r_{s}) \ \eta(r_{i}-r) \ (K_{g}/k_{g}) \} r^{-1} \delta(r-r_{0}),$$

and $\nabla^2 W_j(r) + \xi_j^2 W_j(r) = 0.$

Hence, we may expand the Green's function in terms of the above eigenfunctions $W_j(r)$; namely,

$$G(r, t | r_0, t_0) = \sum_{j=1}^{\infty} C_j(t, t_0) W_j(r) W_j(r_0).$$
(76)

Substitution of eq (76) into eq (69) yields the first order differential equation for the coefficients $C_j(t, t_0)$,

$$k_{g}^{-1} \frac{\partial}{\partial t} C_{j}(t, t_{0}) + \xi_{j}^{2} C_{j}(t, t_{0}) = \delta(t - t_{0}).$$
(77)

The solution of eq (77) subject to the condition that $C_i(t, t_0) = 0$ to $t < t_0$ is

$$C_{j}(t, t_{0}) = \eta(t - t_{0}) \exp\{-\xi_{j}^{2}k_{g}(t - t_{0})\}.$$
 (78)

The temperature in the gas $(r_s \leq r \leq r_i)$ for the cyclic heating and cooling described by eq (68) becomes according to eq (74)

$$T_{g}(r,t) = T_{0} + \sum_{j=1}^{\infty} A_{j} F_{0}(\xi_{j}, r_{i}, r) f(\omega, \xi_{j}, k_{g}, m, t)$$
(79)

where we have added the ambient temperature T_0 , where

$$f(\omega, \xi_j, k_g, m, t) = [\{\exp(-\xi_j^2 k_g t) - 1\}$$
(80)

+
$$m\{1 + (\omega/\xi_j^2 k_g)^2\}^{-1}\{\exp(-\xi_j^2 k_g t) - \cos \omega t - (\omega/\xi_j^2 k_g) \sin \omega t\}]$$

where A_j is given by eq (34).

6.2. Plate

The temperature, $T(z_0, t_0) = u(z_0, t) + v(z_0) - T_0$, satisfies the heat diffusion equation for the gas cell; namely, for times $t_0 \ge 0$,

$$\frac{\partial^2}{\partial z_0^2} T(z_0, t_0) - k^{-1} \frac{\partial T(z_0, t_0)}{\partial t} = -\rho(z_0, t_0),$$
(81)

where $\rho(z_0, t_0) = \eta(|z| - z_2) \eta(z_3 - |z|)$ (Q_l/K_s) (1 + $m \cos \omega t$) and where k is subscripted with s when $z_2 \leq |z| \leq z_3$ and with g when $z_2 \geq |z| \geq 0$.

The Green's function $G(z, t | z_0, t_0)$ for the gas cell satisfies the equation,

$$\partial^{2} G/\partial z^{2} - k^{-1} \partial G/\partial t = -\frac{\delta(z - z_{0}) \delta(t - t_{1})}{K(k'/k)^{1/2}},$$
(82)

where, when $0 \leq |z| \leq z_2$, $k = k_g$, $k' = k_s$, and $K = K_g$; and where, when $z_2 \leq |z| \leq z_3$, $k = k_s$, $k' = k_g$, and $K = K_s$. This Green's function for the gas cell obeys causality and conditions similar respectively to eq (70) and eq (71). It also satisfies the adjoint equation similar to eq (72).

Expressing the temperature in terms of the Green's function involves the same steps as those contained in part A of this section. The thermal factors are $K_s(k_g/k_s)^{1/2}$ for the windows and $K_g(k_s/k_g)^{1/2}$ for the gas. The final result is,

$$T_g(z, t) = T_0 + \sum_{j=1}^{\infty} A_j \cos(\xi_j z) f(\omega, \xi_j, k_g, m, t), \quad (83)$$

where A_j is given by eq (65), $f(\omega, \xi_j, k_g, m, t)$ is given by eq (80), and where we have added the ambient temperature T_0 .

7. Conclusions

The mathematical expressions contained in eqs (33), (34), (35) and (79) for cylinders and in eqs (64), (65), (67) and (83) for plates form the basis of the computer programs used in references [3] through [6]. The authors of these references predict by computer programs the performance of the proposed devices for measuring absorption coefficients as functions of their operating parameters.

8. Appendix A. Integrals Occurring in Equation (31) and Equation (32)

If $B_n(\xi r)$ is any one of the functions $J_n(\xi r)$, $Y_n(\xi r)$, or $F_n(\xi, r_i, r)$, then from references [9], [10], and [11], we have that

$$\int B_0(\xi r) r dr = (r/\xi) J_1(\xi r) + \text{constant}, \quad (A1)$$

$$\int B_0(r) r^3 dr = (r/\xi) \left[\left\{ r^2 - (2/\xi)^2 \right\} B_1(\xi r) \right]$$

+
$$(2r/\xi)B_0(\xi r)$$
] + constant, (A2)

$$\int \ln (r) B_0(\xi r) r dr = (r/\xi) \ln (r) B_1(\xi r)$$

$$+ (1/\xi^2)B_0(\xi r) + \text{constant.}$$
 (A3)

If $Z_m(\xi_1 r) = a J_m(\xi_1 r) + b Y_m(\xi_1 r)$ and $X_m(\xi_2 r) = c J_m(\xi_2 r) + d Y_m(\xi_2 r)$ with a, b, c, and d independent of m and r, then

$$(\xi_1^2 - \xi_2^2) \int Z_m(\xi_1 r) X_m(\xi_2 r) r dr$$

= $\xi_2 r Z_m(\xi_1 r) X_{m-1}(\xi_2 r) - \xi_1 r Z_{m-1}(\xi_1 r) X_m(\xi_2 r).$ (A4)

9. Appendix B. Integrals Occurring in Equation (62) and Equation (63)

We tabulate in this Appendix the several integrals which appear in eq (62) and eq (63):

$$\int \cos \{\xi(z+b)\} dz = (1/\xi) \sin \{\xi(z+b)\}$$
(B1)

$$\int z \cos \{\xi(z+b)\} dz = (1/\xi)^2 \cos \{\xi(z+b)\} + \xi z \sin \{\xi(z+b)\}$$
(B2)

 $\int z^2 \cos \{\xi(z+b)\} dz = (1/\xi)^3 [2\xi z \cos \theta]$

$$\{\xi(z+b)\} + (\xi^2 z^2 - 2) \sin\{\xi(z+b)\}].$$
(B3)

When $\xi_1 \neq \xi_2$, we have that

$$\int \cos \left\{ \xi_1(z+b) \right\} \cos \left\{ \xi_2(z+c) \right\}$$
$$= \cos \left\{ \xi_2(b-c) \right\} \left[\frac{\sin \left\{ (\xi_1 - \xi_2) (z+b) \right\}}{2(\xi_1 - \xi_2)} + \frac{\sin \left\{ (\xi_1 + \xi_2) (z+b) \right\}}{2(\xi_1 + \xi_2)} \right]$$
$$+ \sin \left\{ \xi_2(b-c) \right\} \left[\frac{\cos (\xi_1 - \xi_2) (z+b)}{2(\xi_1 - \xi_2)} \right]$$

$$-\frac{\cos\left\{\left(\xi_{1}+\xi_{2}\right)(z+b)\right\}}{2(\xi_{1}+\xi_{2})}]; \qquad (B4)$$

and when $\xi_1 = \xi_2 = \xi$, we have that

$$\int \cos \{\xi(z+b)\} \cos \{\xi(z+c)\} = \frac{\cos \{\xi(b-c)\}}{2\xi} \\ [\xi(z+b) + \sin \{\xi(z+b)\} \cos \{\xi(z+b)\}] \\ + \frac{\sin \{\xi(b-c)\}}{2\xi} \sin^2 \{\xi(z+b)\}.$$
(B6)

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