if the test is made on the large prototype. On the other hand the test would be much simpler, because one would not be obliged to think about the questions of how to find the right materials or how to increase the lamp intensities or the thermal contact coefficients.

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A MODEL RATE EQUATION FOR TRANSIENT THERMAL CONDUCTION

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NOMENCLATURE

$\vec{a}$,	acceleration of an electron or molecule between 2 collisions;
c,	specific heat;
c_p,	specific heat at constant pressure;
c_v,	specific heat at constant volume;
c_m,	velocity of momentum propagation;
c_w,	velocity of heat propagation;
E,	energy of a molecule or electron;
f,	distribution function;
f_0,	equilibrium distribution function;
K,	thermal conductivity;
k,	Boltzmann's constant;
m,	mass of an electron or molecule;
n,	number of free electrons or molecules;
P,	per unit volume;
p,	pressure;
$\vec{q}$,	heat flux vector;
T,	temperature;
t,	time;
u,	velocity in x direction;
v,	velocity vector;
w,	velocity in z direction;
x, y, z,	coordinate axes.

Greek symbols

α,	thermal diffusivity;
ϕ,	as defined by equation (12);
γ,	c_p/c_v;
μ,	viscosity;
ρ,	density;
τ,	shear stress;
τ_c,	relaxation time.

1. INTRODUCTION

At the present time the analytical treatment of diffusional type of transfer processes is restricted to the domain of the validity of the phenomenological relation given in the form

$$J_i = L_{ij} X_j \tag{1}$$

where J_i represents fluxes and X_j the thermodynamic forces.

Strictly speaking, equation (1) should be applied only to low rate steady-state transfer processes, and all L_{ij} are defined in this manner. However, in practice the validity of relation (1) is successfully extended to the unsteady processes without altering the values of L_{ij}. Phyiscally, there must be a time scale where the validity of (1) is violated. Several investigators [13, 14] having this in mind, tried experimentally, by applying relation (1) to transient heat conduction to show that the heat flow is not only proportional to the temperature gradient, but also rate dependent.

The results of these experiments are not conclusive: the authors in [14] had indicated the possibility of a significant

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departure from prediction based on relation (1), whereas the authors in [13] did not find any discrepancy. (The disagreement could come from a possibly inappropriate measurement technique employed in [14].)

The inadequacy of equation (1) to describe completely the true physical situation was the motivation for discussion [5–10] with some suggestion on modification of phenomenological relation (1) for the case of heat conduction.

Quite recently, the whole problem has been treated more generally by Luikov [4]; by applying the phenomenological theory of thermodynamics of irreversible processes, the author modified (1) for the case when deviation from the equilibrium state is not very large into the following expression:

$$J_i = L_i' \frac{\partial J_i}{\partial t} + L_{ij} X_j + L_{ij}' \frac{\partial X_j}{\partial t}. \tag{2}$$

The author further suggested that in many cases the rate of change of thermodynamic forces is small and hence equation (2) can be approximated by

$$J_i = L_i' \frac{\partial J_i}{\partial t} + L_{ij} X_j. \tag{3}$$

For steady-state processes equation (2) reduces to equation (1). It should be noted that relation (2) or (3) (applied to heat conduction) will produce a hyperbolic type of differential equation for temperature distribution. The thermodynamics of irreversible processes cannot yield any additional information about L_i'. The theoretical derivation of L_i' can be performed with the aid of the kinetic theory or the methods of statistical mechanics, provided that one, by the same method could justify the form of equation (3) for each particular transfer process.

In the following by applying the concept of relaxation time a model equation for heat conduction in metals and gases will be developed.

2. DERIVATION OF THE MODEL EQUATION

We recall that thermal conductivity is defined by the relation:

$$(\vec{q})\,\text{steady state} = -K\nabla T \tag{4}$$

where $\vec{q}$, the heat flux, is the only flux occurring in an isentropic medium. Let $f(\vec{r}, \vec{v}, t)$ represent the distribution function (for molecules, for gases and electrons for metals). Then Boltzmann's equation for the distribution function has the form:

$$\frac{Df}{Dt} = \left[\frac{\partial f}{\partial t}\right]_{\text{coll}}. \tag{5}$$

For certain types of interaction [1–3] one can write the last term of equation (5) as

$$\left[\frac{\partial f}{\partial t}\right]_{\text{coll}} = -\frac{f - f_0}{\tau_c}. \tag{6}$$

The model introduced by this relation was first used for electron gas and also successfully tried in the area of kinetic theory of gases where the model is known as the Krook model. Equation (6) defines relaxation time. f_0 is the equilibrium distribution function.

From equations (5) and (6) it follows:

$$f = f_0 - \tau_c(a\,\text{grad}_{\vec{V}} f + \vec{V}\,\text{grad}_{\vec{r}} f - \tau_c \frac{\partial f}{\partial t} \equiv f_0 - \phi - \tau_c \frac{\partial f}{\partial t} \tag{7}$$

$\vec{a}(a_x, a_y, a_z)$ is the acceleration of an electron (or molecule) between collisions. ϕ, as defined by equation (7), is the contribution of the external forces and the convective terms.

Considering a case when non-uniformity exists in x-direction only, one can write for the heat flux

$$q_x = \iiint_{-\infty}^{+\infty} u\,E\,f\,du\,dv\,dw \tag{8}$$

where E is the energy of a molecule (or electron). From (7) and (8) and the fact that the equilibrium distribution function is an even function of velocity components u, v and w, it follows

$$q_x = -\iiint_{-\infty}^{+\infty} u\,E\,\phi\,du\,dv\,dw - \tau_c \iiint_{-\infty}^{+\infty} u\,E \frac{\partial f}{\partial t}\,du\,dv\,dw. \tag{9}$$

When in writing (9) it was assumed that the relaxation time is not a function of the velocity. From (8) and the assumption that E is a function of velocity only, one obtains directly

$$\frac{\partial q_x}{\partial t} = \iiint_{-\infty}^{+\infty} u\,E \frac{\partial f}{\partial t}\,du\,dv\,dw. \tag{10}$$

At this stage, let us restrict our consideration to processes for which

$$\frac{f - f_0}{f_0} \ll 1 \tag{11}$$

and use this to approximate ϕ as

$$\phi \simeq \tau_c(a\,\text{grad}_{\vec{V}} f_0 + \vec{V}\,\text{grad}_{\vec{r}} f_0). \tag{12}$$

Using equations (10, 12, 4, 9) one readily obtains the rate equation for heat conduction [subject to limitation (11)] as

$$q_x = -K \frac{\partial T}{\partial x} - \tau_c \frac{\partial q_x}{\partial t}. \tag{13}$$

The form of (13) is in agreement with Luikov's general expression (3) as well as with the suggestion proposed in [5, 6].

2.1. *Heat propagation in metals*

Equation (13), together with the conservation of energy equation:

$$\frac{\partial q_x}{\partial x} = -\rho c \frac{\partial T}{\partial t} \tag{14}$$

represent the hyperbolic system of two partial differential equations from which one can obtain the velocity of heat propagation (c_w) as

$$c_w^2 = \frac{k}{\rho c \tau_c} = \frac{\alpha}{\tau_c} \tag{15}$$

where α stands for heat diffusivity. In the case of constant properties (α, τ_c), the temperature distribution is implicitly determined from (13) and (14)

$$\frac{\partial T}{\partial t} + \tau_c \frac{\partial^2 T}{\partial t^2} = \alpha \frac{\partial^2 T}{\partial x^2}. \tag{16}$$

One can relate τ_c to the thermal conductivity K by assuming an appropriate equilibrium distribution for free electrons (f_0) in equation (12) and integrating the relation {which holds for steady state [subject to restriction (11)]}

$$K \frac{\mathrm{d}T}{\mathrm{d}x} = \iiint_{-\infty}^{+\infty} uE\phi \,\mathrm{d}u \,\mathrm{d}v \,\mathrm{d} \tag{17}$$

Using Fermi-Dirac distribution for f_0 and integration of (17) (for condition of zero current flux in x-direction) yields [1]

$$K = \frac{\pi^2}{3} k^2 T \frac{n\tau_c}{m} \tag{18}$$

where k is Boltzmann's constant, n is the number of free electrons per unit volume, m is the mass of an electron.

From (18) and (15) one calculates the velocity of heat propagation in the form:

$$c_w^2 = \frac{\pi^2 k^2 T n}{3\rho c m} \simeq \frac{\pi^2 k T}{9m}. \tag{19}$$

Where in obtaining the last expression on the right hand side of equation (19) we used the fact that for metals (at ordinary temperature) $c = 3Nk/\rho$ where N is the number of atoms per unit volume (approximately equal to the number of free electrons per unit volume). After necessary substitutions, one obtains

$$C_w = 1{\cdot}01 \times 10^4 (\sqrt{T})\,\mathrm{ft/s} \tag{20}$$

where T is in °R.

To illustrate the significance of the new form of the rate equation, one can solve telegraph equation (16) by considering classical transient problem: isentropic semi-infinite body, initially at zero temperature. At time $t = 0$, T is raised to unity at $x = 0$ and it is maintained at unity at that section.

For this boundary and initial conditions the solution of (16) may be written [12] treating c_w and α as constants, in the following form

$$T = 1 - \frac{\exp(-tc_w^2/2\alpha)}{2\alpha} c_w \int_0^x \left[I_0(Y) + \frac{t}{2\alpha} c_w^2 \frac{I_1(Y)}{Y-} \right] \mathrm{d}x; \text{for } x < c_w t \tag{21}$$

and $T = 0$ for $x > c_w t$. The alternative form of the solution is given in (15) for $x > c_w t$

$$T = \exp\left(-\frac{tc_w^2}{2\alpha}\right)\left[I_0(Y) + 2\sum_{n=1}^{\infty} \left(\frac{W}{Y}\right)^n I_n(Y) \right]; \tag{22}$$

where

$$Y \equiv \frac{\sqrt{[(c_w t)^2 - x^2]}}{2\alpha} c_w$$

$$W \equiv \frac{c_w t - x}{2\alpha} c_w.$$

It follows from (21) that when $c_w \to \infty$

$$\lim T_{c_w \to \infty} = 1 - \frac{1}{\sqrt{(t\alpha\pi)}} \int_0^x \exp\left(-\frac{x^2}{4t\alpha}\right) \mathrm{d}x = \operatorname{erfc} \frac{x}{2\sqrt{(\alpha t)}}$$

which is the known solution for the problem when one uses the Fourier rate equation. The temperature "jump" occurring at $x = c_w t$ for a finite value of c_w can be evaluated from equation (21) as

$$\lim T_{x \to c_w t - 0} = \exp\left(-\frac{tc_w^2}{2\alpha}\right). \tag{23}$$

It follows from relation (23) that the discontinuity at $x = c_w t$ will be higher for smaller time (shorter distances). However, even for $t = 10^{-13}$ s which corresponds to the position of the "wave" front at 10^{-6} in [using $c_w = 2{\cdot}26 \times 10^5$ ft/s; see equation (20)]: discontinuity was estimated to be only

$$\lim T_{x_w \to 10^{-6}\mathrm{in} - 0} \simeq 10^{-4}\,°\mathrm{F}$$

($T = 0$ for $x_w^{\rightarrow} \to 10^{-6}$ in $+ 0$).

The value for temperature at the same x and t calculated from the classical solution was $T = 10^{-26}$ °F; i.e. between the values for $x_w - 0$ and $x_w + 0$. Hence, for any reasonable step increase in temperature at the surface $x = 0$ at $t = 0$ (up to 1000°F) the discontinuity at the wave front for $t \geqslant 10^{-13}$ s would be unmeasurable. Moreover, the discrepancy between the two solutions, not only at the front wave, but everywhere, is practically non-existant. From this example (since there is no reason to expect substantial changes between the two solutions for other geometries and boundary and initial conditions) one may conclude that for metals: (a) the use of classical solution is quite sufficient to describe temperature distribution (even at time scale of as small as 10^{-13} s), and consequently (b) it is unreasonable to attempt to verify by experimental methods, discrepancy between the two solutions. Any recorded deviation of experimental results from the prediction based on the classical solutions did not result from the (measurable) inaccuracy of the solution, but rather came as a result of unsophisticated measurement techniques.

It is of some interest to mention here that the above conclusions are obtained based on the model introduced with equation (6) as well as the use of Fermi–Dirac distribution for the equilibrium distribution. With the same model and the equilibrium distribution one can calculate electrical conductivity σ as a function of relaxation time. From expression (19), for thermal conductivity, and value for σ calculated from the model [1] one obtains the value for the Lorenz number as

$$L \equiv \frac{K}{\sigma T} = \frac{\pi^3}{3}\left(\frac{k}{\varepsilon}\right)^2 = 2{\cdot}71 \times 10^{-13} \text{ electrostatic units}$$

$-\varepsilon$ is the charge of an electron.

The observed average value for the Lorenz number in metals was found to be $L = 2{\cdot}72 \times 10^{-13}$ electrostatic units. Based on the good agreement between the predicted value for the Lorenz number and the observed one, one may conclude that the concept of the relaxation time used here could produce reliable results.

2.2. *Model rate equation for gases*

For monatomic gases, assuming the Maxwellian distribution for f_0, and integrating (17) (under the condition of zero net mass flux) one obtains

$$K = \frac{5}{2}\frac{k^2 nT}{m}\tau_c$$

n is the number of molecules per unit volume, m is the mass of a molecule. For gases with internal degrees of freedom, the thermal conductivity can be written as [11]

$$K = \frac{\gamma}{\gamma - 1}\frac{k^2 nT}{m}\tau_c \tag{24}$$

where $\gamma \equiv c_p/c_v$. From equations (24) and (13), using the following relations;

$$\frac{k}{m} = R; \qquad c_p = \frac{\gamma}{\gamma - 1}R; \qquad \rho = mn; \qquad \frac{p}{\rho} = RT,$$

one obtains for the rate equation

$$q_x = -K\frac{\partial t}{\partial x} - \frac{K}{pc_p}\frac{\partial q_x}{\partial t}. \tag{25}$$

It is of some interest to find an estimation for the velocity of heat propagation in a perfect gas. In order to do this we write the energy differential equation in the following form:

$$\rho c_v \frac{DT}{Dt} = -\nabla . \frac{\vec{q}}{A} - p\vec{V}. \tag{26}$$

where $\vec{V}$ is bulk velocity of the gas. For temperature nonuniformity in x-direction only, and stagnant medium ($\vec{V} = 0$), equation (26) reduces to

$$\frac{\partial q_x}{\partial x} = -\rho c_v \frac{\partial T}{\partial t} \tag{27}$$

which together with (13) yields the expression for the velocity of heat propagation

$$c_w^2 = \frac{k}{\rho c_v \tau_c}$$

or, by making use of equation (24)

$$c_w = \gamma\left(\frac{p}{\rho}\right)^{\frac{1}{2}} \tag{28}$$

The above value for the velocity of heat propagation, the same as the velocity of sound, was obtained by approximating energy equation with (27) (which is exact only for stagnant medium—implying also constant density).

On the other hand, by writing the energy equation in the form

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p u \frac{\partial T}{\partial x} = -\frac{\partial q_x}{\partial x} + \frac{\partial p}{\partial t} + u\frac{\partial p}{\partial x}$$

and assuming constant pressure process and neglecting convective term, one would obtain, together with relations (13) and (24), the expression for the velocity of heat propagation

$$c_w = \left(\frac{p}{\rho}\right)^{\frac{1}{2}}. \tag{29}$$

Without claim that either of the expressions given above for the velocity of heat propagation is the exact one, one should notice that both results gave the value for c_w of the expected order of magnitude. Since for both, the heat propagation and the sound propagation in a gas, we have the same mechanism of transport one should expect that those two velocities must be of the same order of magnitude (also order of magnitude of average velocity of a molecule). We want to stress here that the ambiguity connected with the true velocity of heat propagation (related to the energy equation) does not affect the rate equation (25) which is derived directly from the concept of the relaxation time. The significance (or non-significance) of the modified rate equation is not quite apparent. In spite of the claim asserted in reference [4] that the effect of a finite velocity of heat propagation on heat transfer becomes pronounced under conditions of rarefied supersonic flow, it still remains to be shown conclusively that it is really advantageous to use the rate equation which implies a finite velocity of heat propagation instead of the Fourier equation.

It should perhaps be noted here that a model rate equation of the type given by equation (13) could be obtained for the case of heat conduction through dielectric solids where τ_c in equations (13, 15, 16) would then represent relaxation time for latice vibration.

In closing, we would like to mention that the same procedure may be applied to resolve some contradiction in momentum propagation. For example, if one considers a long plate in a fluid, any disturbance of the fluid by a motion of the plate in normal direction will propagate through the fluid by the velocity of sound. On the other hand, if the motion of the plate happened to be in the tangential direction, one would get from the set of equations presently in use to describe the above phenomenon, that the disturbance propagates with an infinite velocity.

For the momentum propagation in a gas, one can show that the similar procedure as used for the heat conduction, would yield the following expression for the shear stress:

$$\tau = \mu \frac{\partial u}{\partial y} - \tau_c \frac{\partial \tau}{\partial t} \tag{30}$$

where μ is the coefficient of viscosity and u is the bulk velocity in x-direction. Relating μ to relaxation time, one obtains [3]

$$\mu = nkT\tau_c. \tag{31}$$

With equation (31) the modified Newton relation (30) can be written as

$$\tau = \mu \quad \frac{\partial u}{\partial y} - \frac{1}{p}\frac{\partial \tau}{\partial t} \tag{32}$$

From (32) and the relation for the conservation of momentum (for bulk velocity in x-direction and its non-uniformity in y-direction only)

$$\frac{\partial \tau}{\partial y} = \rho \frac{\partial u}{\partial t}$$

it is possible to obtain the expression for the velocity of disturbance propagation in y-direction (under stated conditions) as

$$c_m = \left(\frac{p}{\rho}\right)^{\frac{1}{2}}. \tag{33}$$

Again, the result gave the value for the velocity of propagation (c_m) of the expected order of magnitude.

Finally, we want to stress the fact that an identical theoretical approach could modify the rate equation for any diffusion transfer process and hence, resolve inadequacy of relation (1) to describe completely the true physical situation (which is in most cases only of academic importance).

CONCLUSION

The attempt was made here to resolve some inconsistency of the classical rate equations in connection with the description of certain physical situations. The main purpose was not to emphasize the importance of the modified rate equations and the need for their application in practice, but rather to underline the fact (at least for some cases such as transient heat conduction through metals) that the significance of the new relations might be merely academic. The whole work was initiated in order to find justification for some recent experimental research aimed at modification of the Fourier conduction equation.

The conclusion which follows from our finding being that all attempts (with the present measurement technique) to observe discrepancy between experimental results and theoretical predictions based on the classical rate equation is unrealistic, and furthermore, the classical solutions, for all practical purposes, are more than adequate to describe temperature distributions in metals.

The validity of the results presented here, of course, depend on the model and assumptions used in the work. However, the model was already successfully tried (for metals: good prediction of the Lorentz number; for gases: known accomplishments of the Krook model) and hence, in our opinion, there is a basis for confidence in the derived relations. In addition, the results obtained by the model are quite expected (for metals: introduction of finite velocity of heat propagation will not produce any significant changes in the predicted temperature distributions; and for gases: the velocity of heat propagation is of the same order of magnitude as the velocity of sound).

Finally, in connection with the obtained results concerning perfect gases, we want to state that at this stage it is not quite clear what their significance could be and that in this region further work is required before any judgement can be passed.

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