Thermoelectric Effects of Metals within Small-Scale Regimes: Theoretical Aspects

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The hyperbolic-two-step (HTS) model and the dual-phase-lag (DPL) model are revisited in the current work. A macroscopic delayed model of thermoelectricity is proposed on a basis of the microscopic HTS-model with thermoelectric properties. Along with the temperature gradient and the induced electric field, it is found that the electric current may depend on its rate and the temperature gradient rate. A new phase-lag in the electric current density is revealed. By direct correlations with the thermoelectric HTS-model, the electric current phase-lag is found to be nothing but the relaxation time at the Fermi level. In the absence of an electric field, the model proposed is studied. The effect of the figure of merit and the electric current phase lag on the temperature and the electric current is examined.

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I. INTRODUCTION

Solid state energy conversion devices are a rapidly emerging area in nanotechnologies, as well as fundamental scientific studies. Developing the efficiency of these devices is a main issue in the manufacturing of thermoelectric devices [1–3].

The performance of thermoelectric devices depends heavily on the material intrinsic property, \( Z \), known as the figure of merit and defined by

\[
Z = \frac{\sigma S^2}{k},
\]

where \( \sigma \), \( S \), and \( k \) are, respectively, the electrical conductivity, thermoelectric power, and thermal conductivity. Increasing the parameter \( Z \) has a positive effect on the efficiency of thermoelectric device.

In order to achieve a high figure of merit, one requires a high thermopower \( S \), a high electrical conductivity \( \sigma \), and a low thermal conductivity \( k \). However, this process is not as easy as writing the sentence. The direct proportionality between \( \sigma \) and \( k \), and the inverse proportionality between \( S \) and \( \sigma \) yields a difficulty in improving the efficiency \( \eta \), see [4, 5].
In spite of the negligibility of thermoelectric effects in single metals, the contributions of magnesium and lead in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) thin films, see [6, 7], copper in Cu\(_2\)Se, see [8–10], and barium in BaSi\(_2\), see [11], might suggest giving some attention to the individual thermoelectric properties of a single metal, particularly if the short-scale temporal regime is of interest. The review article [12], among others, contains recent developments, exhaustive discussions, and results on the subject matter.

On the heat transfer side, because of the rapid development and growing interest in the high-rate heating processes (such as a laser beam with pulse duration ranging from 10\(^{-9}\)–10\(^{-15}\) seconds), great effort was theoretically and experimentally directed to evaluating the energy exchange between the electrons and phonons during such heating processes and introducing a governing law to measure the electron and lattice temperatures, see [13–17]. These works, until the end of the last century, were not based on a rigorous thermodynamic foundation. This was the main aim of the papers due to Qiu and Tien [18, 19], to introduce a thermodynamic derivation for the phenomenological laws which were the axial subject of the paper [14], see also Tamma and Zhou [20]. With shortening the response time of materials, the conventional Fourier and Cattaneo-Vernotte models [21, 22] fail to predict the correct trends of thermal propagation, which enhances the models proposed by Anisimov et al. [14] and thermodynamically derived and modified by Qiu and Tien [19], currently known as the HTS or Qiu-Tien model.

Despite these tremendous advancements in the theoretical microscopic heat transfer, which were mentioned above, there was a gap between the macroscopic and the microscopic research efforts. The works of Tzou [23, 24] played a great role in closing the distance between these two approaches. The lagging behavior, proposed in [22, 23], successfully incorporated the microscopic effects within the familiar macroscopic model, and thus involved many researchers in this growth of microscale heat transfer. One refers to some refined aspects given by Awad [25]. As far as we are aware, although the work of Qiu and Tien [19] put a rigorous thermodynamic derivation for the explicit nonequilibrium case between electron and phonons during the ultrafast heating processes, it did not give enough attention to the thermoelectric properties of metals.

The present work aims to propose, theoretically, a delayed model of thermoelectricity by relying on some results given in the Qiu-Tien model. A general background on the thermoelectric effects in metals, and its thermodynamic derivation will be done in the next section. A connection between the classical derivation and the Qiu-Tien model will be given in the third section. The heating of a micro-scale metal film will be studied in Sections IV and V in the framework of the model proposed in Section III. In Section IV, a one dimensional simulation in the absence of the induced electric field will be considered. The variables are plotted against the spatial and temporal variables to show the way in which these variables decay, see [26, 27], and the domain in which the heat and electricity have influence, see [28–30].
II. GENERAL BACKGROUND

If a metal film is subject to an electric field \( \vec{E} \), a temperature gradient \( \nabla T \), or a concentration gradient \( \nabla n \) (and thus a chemical potential gradient \( \nabla \mu \)), its electrons undergo a non-equilibrium thermodynamic transition. Throughout this short review, we shall neglect the heat conduction by the lattice. Let \( f(\varepsilon, T) \) denote the distribution function of electrons, where \( \varepsilon = \frac{1}{2} m v^2 \) is the electron energy, \( m \) is the electron mass, \( v \) the electron velocity, and \( T \) is the absolute temperature. The number of electrons with energy between \( \varepsilon \) and \( \varepsilon + d\varepsilon \) is \( f(\varepsilon, T)D(\varepsilon)d\varepsilon \), where \( D(\varepsilon) \) is the density of states [1–3]. The distribution function of electrons at the equilibrium case is nothing but the Fermi-Dirac distribution [1–3]. Two approaches were already employed to solve this problem. The first (classical) approach assumes that both the lattice and electrons are heated simultaneously. In other words, there is no difference between the lattice and electron temperatures. This approach leads to the familiar Ohm’s and Fourier’s laws, see [1–3], [12], and [31]. The second approach [19] assumes that during the ultrafast heating process the lattice and electron subsystems have two distinct temperatures \( T_l \) and \( T_e \), respectively, and they need a finite time (thermalization time) to reach an equilibrium state. As soon as the equilibrium state is reached, \( T_l = T_e \), there is no need for this assumption. The Fermi-Dirac distribution functions, in these approaches, are defined by

\[
f_i(\varepsilon, \phi_i) = \frac{1}{1 + \exp \left( \frac{\varepsilon - \mu}{k_B \phi_i} \right)},
\]

where \( i = 0, 1 \), \( f_0(\varepsilon, \phi_0) \) is the Fermi-Dirac function of the first approach, \( f_1(\varepsilon, \phi_1) \) is the Fermi-Dirac function of the second approach, \( \phi_0 = T \), \( \phi_1 = T_e \), and \( k_B \) is the Boltzmann constant. In metals \( \mu \) is assumed constant and is equal to the Fermi energy \( \mu_F \) (\( \mu \approx \mu_F \)).

The transport of energy carriers (electrons) can be modeled by the Boltzmann transport equation (BTE) (in the \( x \)-direction):

\[
\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + \frac{F_x}{m} \frac{\partial f}{\partial v_x} = \left[ \frac{\partial f}{\partial t} \right]_{\text{scatt}},
\]

where \( x \) and \( t \) are the spatial and temporal variables, respectively, \( F_x \) is the force field, and \( \left[ \partial f/\partial t \right]_{\text{scatt}} \) is the scattering term expressing the total change rate of the electron number. The classical approach, [1–3], [12], and [31], used for solving the BTE (2) depends on three basic assumptions: (a) the relaxation time approximation, (b) the steady state approximation, and (c) the near-equilibrium approximation. These approximations lead to

\[
f(\varepsilon, T) = f_0(\varepsilon, T) + v_x \tau \left[ \frac{\varepsilon - \mu}{T} \frac{\partial T}{\partial x} + eE_x \right] \frac{\partial f_0}{\partial \varepsilon},
\]

where \( \tau = \tau(\varepsilon) \) is the relaxation time, \( F_x = -eE_x \), \( -e \) is the electron charge, and \( \partial \mu/\partial x \) is disregarded. Equation (3) is thus the approximate solution of the BTE (2). Furthermore, the electric and heat fluxes carried by the electrons are then determined through

\[
J_x = -e \int_{0}^{\infty} v_x f(\varepsilon, T)D(\varepsilon)d\varepsilon, \quad q_x = \int_{0}^{\infty} v_x (\varepsilon - \mu) f(\varepsilon, T)D(\varepsilon)d\varepsilon.
\]
Upon combining (3) and (4), the vector forms of the electric current density and the heat flux are given by [1–3], [12], and [31]:

\[
\vec{J}(\vec{r}, t) = \sigma_0 \left[ \vec{E}(\vec{r}, t) - S_0 \nabla T(\vec{r}, t) \right],
\]

(5)

\[
\vec{q}(\vec{r}, t) = -k \nabla T(\vec{r}, t) + \pi_0 \vec{J}(\vec{r}, t),
\]

(6)

where \( k \) denotes the thermal conductivity, \( \sigma_0 \) the electrical conductivity, \( S_0 \) the Seebeck coefficient, and \( \pi_0 \) the Peltier coefficient, with approximate values

\[
k = \frac{2\pi^2 k_B^2 \mu_F \tau_F D_F T}{9m} \left[ 1 - 3 \left( \frac{\pi k_B T}{2\mu_F} \right)^2 \right], \quad \sigma_0 = \frac{2e^2}{3m} \mu_F \tau_F D_F, \quad S_0 = -\frac{\pi^2 k_B^2 T}{2e \mu_F},
\]

(7)

where \( \tau_F = \tau(\mu_F) \), \( D_F = D(\mu_F) \). In order to obtain the relations (7), the approximation \( \partial f_0 / \partial \varepsilon = -\delta(\varepsilon - \mu_F) \) has been used, where \( \delta(\cdot) \) denotes the Dirac delta function. The Seebeck coefficient \( S_0 \) requires that \( \tau(\varepsilon) = \tau_F \varepsilon^\varsigma \), \( \varsigma \) is a real number, however it was taken to be zero in the former calculations. The Wiedemann-Franz law is another important relation that can be simply derived from the ratio between the thermal conductivity and the electrical conductivity, namely,

\[
(k_\sigma)_0 = \frac{k}{\sigma_0} = LT,
\]

(8)

where \( 1 - 3 \left( \frac{\pi k_B T}{2\mu_F} \right)^2 \cong 1 \), and \( L = \frac{\pi^2 k_B^2}{3e^2} = 2.45 \times 10^{-8} \text{ W} \Omega/\text{K}^2 \) is the Lorentz number.

Evidently, Equation (5) expresses the generation of induced electric current/field resulting from the temperature difference between two points, known as the Seebeck effect, whilst, Equation (6) shows how the passing of electric current contributes in the generation of heat flux (Peltier effect). In the absence of electric currents, Equations (5) and (6) result in the well-known Fourier law

\[
\vec{q}(\vec{r}, t) = -k \nabla T(\vec{r}, t).
\]

(9)

The energy equation associated with (9) is given via

\[
-\nabla \cdot \vec{q}(\vec{r}, t) = C_p \frac{\partial T}{\partial t}(\vec{r}, t),
\]

(10)

where \( C_p \) is the heat capacity. Equations (9) and (10) give the diffusion equation

\[
\nabla^2 T = \frac{1}{\alpha} \frac{\partial T}{\partial t},
\]

(11)

where \( \alpha = k/C_p \) is the thermal diffusivity.
In the ultrafast heating processes, where the duration and penetration depth of the heating are very short and fully controlled (or in those situations in which the short-scale time regime is of interest), energy deposits firstly on electrons (because of the variation of the heat capacities of the electrons and phonons). Then, during the electron-phonon scattering process, the electron energy transforms later to an internal energy of the metal. One can readily infer the nonequilibrium case between electrons and phonons, and that there are two distinct temperatures, the lattice temperature, $T_l$, and the electron temperature, $T_e$. The other scattering processes (such as electron-electron, electron-impurity, and electron-boundary) will be excluded from this review, in accordance with Ref. [19]. Qiu and Tien [19] gave a justification that the three approximations used for solving the BTE in the case of one temperature are open to debate. However, the near-equilibrium approximation is still indispensable. Upon summing all possible transitions among energy levels to determine the scattering term and employing the near-equilibrium approximation, they introduced a solution to the BTE (2) in the form

$$f(ε, T_e) = f_1(ε, T_e) + v_x τ \left[ \frac{ε - μ \partial T_e}{T_e} + e E_x \right] \frac{∂f_1}{∂ε} - τ δ(ε - μ_F),$$

where $∂f/∂t$ has been expressed in terms of the delta function (refer to the last term of the right hand side of (12)). By inserting the distribution function $f(ε, T_e)$ into the fluxes (4), one can obtain the heat and electrical fluxes in the vector forms

$$\vec{j}(\vec{r}, t) + τ_F \frac{∂\vec{j}(\vec{r}, t)}{∂t} = \sigma_e \left[ \vec{E}(\vec{r}, t) - S_e \nabla T_e(\vec{r}, t) \right],$$

$$\vec{Q}(\vec{r}, t) + τ_F \frac{∂\vec{Q}(\vec{r}, t)}{∂t} = -k_e \nabla T_e(\vec{r}, t) + π_e \left[ \vec{j}(\vec{r}, t) + τ_F \frac{∂\vec{j}(\vec{r}, t)}{∂t} \right],$$

where $\sigma_e$, $S_e$, $k_e$, and $π_e$ are, respectively, the effective electrical conductivity, the Seebeck coefficient, the thermal conductivity, and the Peltier coefficient. The approximate formulae of the effective coefficients are

$$k_e = \frac{2π^2 k_B^2}{9m} \mu_F^2 D_F T_e \left[ 1 - 3 \left( \frac{πk_B T_e}{2μ_F} \right)^2 \right], \quad σ_e = \frac{2e^2}{3m} \mu_F^2 D_F, \quad S_e = -\frac{π^2 k_B^2 T_e}{2eμ_F},$$

$$π_e = S_e T_e.$$

Returning to Equation (13), we could see that the current density $\vec{j}(\vec{r}, t)$ depends not only on the electric field and electron temperature gradient, but also depends on its rate, $\frac{∂\vec{j}(\vec{r}, t)}{∂t}$. In fact Equation (13) is a version of non-Ohm’s law which includes the Seebeck effect. Moreover, the Seebeck effect, according to (13), depends on the electron temperature difference at two different points, and is independent of the lattice temperature, in contrast to (5). Equation (14) emphasizes that it is not only $\vec{j}(\vec{r}, t)$ which could produce a heat flux, but also $\frac{∂\vec{j}(\vec{r}, t)}{∂t}$ that contributes in this production, which may entirely change the familiar
insight of Peltier effect in the high rate heating. Actually, the work of Qiu and Tien [19] focused on the heat propagation without electric currents; alternatively, they neglected the possibility of activation of the thermoelectric properties in the metal film, and thus its contribution to the heat production. In view of the effective and the classical coefficients, one can deduce that if $k_BT \ll \mu_F$ or $k_BT_e \ll \mu_F$,

$$k_e = \left(\frac{T_e}{T_l}\right)k, \quad \sigma_e = \sigma_0, \quad S_e = \left(\frac{T_e}{T_l}\right)S_0, \quad \pi_e = \left(\frac{T_e}{T_l}\right)^2\pi_0.$$  \hspace{1cm} (16)

The relation (16), had been already deduced by Qiu and Tien (refer to Equation (22) in [19]). It is worthwhile writing the Wiedemann-Franz law in the Qiu-Tien model:

$$(k_e/\sigma_e) = LT_e,$$  \hspace{1cm} (17)

where, again, we assume that $1 - 3\left(\frac{\pi k_BT_e}{2\mu_F}\right)^2 \approx 1$. In the absence of electric currents, Equations (13) and (14) render the non-Fourier law

$$\tilde{Q}(\vec{r}, t) + \tau_F \frac{\partial \tilde{Q}(\vec{r}, t)}{\partial t} = -k_e \nabla T_e(\vec{r}, t).$$  \hspace{1cm} (18)

In spite of the resemblance between Equation (18) and the Cattaneo-Vernotte equation [20–22], due to both resulting from the existence of the term $\partial f/\partial t$ in the BTE (2), see pp. 252–253 in [3], they are completely different, because of the following reasons: First, Equation (18) has been derived based on the assumption that there are two distinct temperatures for the electrons and the lattice, which renders the electron temperature gradient in the right hand side. Second, the energy equation associated with (18), and thus (14), is dissimilar to that attached to (9) (refer to Equation (10)), and hence the Cattaneo-Vernotte equation. The energy equation related to (14) and (18) was firstly proposed by Anisimov et al. [14]. They suggested that the laser heating process (or generally ultrafast heating) occurs during two main steps; the first is the heating of electron subsystem by the lighting source, which can be expressed through, see also [23–25],

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -\nabla \cdot \tilde{Q} - G(T_e - T_l) + I,$$  \hspace{1cm} (19)

where $C_e$ is the heat capacity of the electron, $I$ is the laser source, and $G$ denotes the electron-phonon coupling factor given by [18, 19] $G = \pi^4(nv_s k_B)^2/18k$, where $n$ is the electron number density, and $v_s$ is the speed of sound. The second step is the heating of the metal lattice during the electron-phonon interaction, represented by

$$C_l(T_l) \frac{\partial T_l}{\partial t} = G(T_e - T_l),$$  \hspace{1cm} (20)

where $C_l$ is the heat capacity of the lattice. The reader can consult the literature due to Tzou [32–35] for further discussions about the Lagging Behavior phenomenon.
III. LAGGING BEHAVIOR IN THERMOELECTRICITY

In view of the HTS-model with thermoelectric properties, it consists of the non-Ohm's law (13), the non-Fourier law (14), and the energy equations (19) and (20). We shall consider again the case in which all the coefficients are computed at room temperature $T_0$. As such, the following relations hold true:

$$
k_e = k, \quad \sigma_e = \sigma_0, \quad S_e = S_0, \quad \pi_e = \pi_0,
$$
$$
C_e (T_e) = C_e, \quad C_l (T_l) = C_l, \quad G (T_e, T_l) = G.
$$

(21)

An exploration of the wave structure of the lattice temperature requires an elimination of the heat flux $\vec{Q}$, electric current $\vec{j}$, and the electron temperature $T_e$ among (13), (14), (19), and (20). This leads, after setting $I = 0$ and $T_l = T$, to

$$
(1 + ZT_0) \left( 1 + \frac{C_l}{G} \frac{\partial}{\partial t} \right) \nabla^2 T - \frac{\sigma_0 \pi_0}{k} \nabla \cdot \vec{E} = \frac{C_i + C_e}{k} \frac{\partial T}{\partial t} + \left( \frac{\tau_F (C_i + C_e)}{k} + \frac{C_i C_e}{kG} \right) \frac{\partial^2 T}{\partial t^2} + \tau_F \frac{C_i C_e}{kG} \frac{\partial^3 T}{\partial t^3},
$$

(22)

where $ZT_0 = \sigma_0 \pi_0 S_0 / k$ is the figure of merit of the metal material. Equation (22), in essence, contains two unknowns, $T$ and $\vec{E}$. The electric field $\vec{E}$ is composed of two vectors, the externally applied electric field and the thermally-induced electric field. The non-Ohm’s equation (13) should be solved instantaneously with (22). The Maxwell equations governing the induced electromagnetic fields are then unavoidable for such types of problems:

$$
\nabla \times \vec{H} = \vec{j} + \epsilon_0 \frac{\partial \vec{E}}{\partial t}, \quad \nabla \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t}, \quad \nabla \cdot \vec{H} = 0, \quad \nabla \cdot \vec{E} = \frac{\rho_e}{\epsilon_0},
$$

(23)

where $\vec{H}$ is the induced magnetic field, $\epsilon_0$ and $\mu_0$ are respectively the vacuum permittivity and magnetic permeability, and $\rho_e$ is the induced charge density.

The electron temperature, for the sake of convenience, should be eliminated from Equation (13) by using (20) and (21), i.e.,

$$
\left( 1 + \tau_F \frac{\partial}{\partial t} \right) \vec{j} (r, t) = \sigma_0 \left[ \vec{E} (r, t) - S_0 \left( 1 + \frac{C_l}{G} \frac{\partial}{\partial t} \right) \nabla T (r, t) \right].
$$

(24)

A question arises, could we convert the classical statistical system used in deriving Ohm’s and Fourier’s laws into another complicated system, such as that used by Qiu and Tien. This question was answered previously by Tzou, and shall be emphasized here, by recalling the classical macroscopic model (5)–(6), and viewing the microscopic effects as retarding sources at the macroscopic level. This of course leads to the lagging behavior in the thermoelectric model of heat conduction. We suggest that Equation (5)–(6) take the form:

$$
\vec{J} (r, t + \tau_j) = \sigma_0 \left[ \vec{E} (r, t) - S_0 \nabla T (r, t + \tau_F) \right],
$$

(25)
\[
\vec{q}(\vec{r}, t + \tau_q) = -k \nabla T(\vec{r}, t + \tau_T) + \pi_0 \vec{J}(\vec{r}, t + \tau_j), \tag{26}
\]

where \( t, t + \tau_j, t + \tau_q, \) and \( t + \tau_T \) are four different instants at which the variables \( \vec{E}, \vec{J}, \vec{q} \) and \( \nabla T \) occur. \( t \) is called the physical time, which is observed practically. \( \tau_j \) is a phase-lag in the induced electric current. \( \tau_q \) and \( \tau_T \) preserve their original meaning. By applying a Taylor's series expansion in (25)–(26) such that \( O(\tau_j^2), O(\tau_q^3) \) and \( O(\tau_T^2) \) are neglected, one obtains

\[
\begin{align*}
(1 + \tau_j \frac{\partial}{\partial t}) \vec{J}(\vec{r}, t) &= \sigma_0 \left[ \vec{E}(\vec{r}, t) - S_0 \left( 1 + \tau_T \frac{\partial}{\partial t} \right) \nabla T(\vec{r}, t) \right], \\
(1 + \tau_q \frac{\partial}{\partial t} + \frac{\tau_q^2}{2} \frac{\partial^2}{\partial t^2}) \vec{q}(\vec{r}, t) &= -k \left( 1 + \tau_T \frac{\partial}{\partial t} \right) \nabla T(\vec{r}, t) + \pi_0 \left( 1 + \tau_j \frac{\partial}{\partial t} \right) \vec{J}(\vec{r}, t). \tag{27}
\end{align*}
\]

In order to derive the energy equation in terms of the temperature \( T \), we first eliminate the heat flux \( \vec{q} \) between (10) and (28), which yields

\[
\begin{align*}
(1 + \tau_T \frac{\partial}{\partial t}) \nabla^2 T - \frac{\pi_0}{k} \left( 1 + \tau_j \frac{\partial}{\partial t} \right) \nabla \cdot \vec{J} &= \frac{1}{\alpha} \frac{\partial T}{\partial t} + \frac{\tau_q}{\alpha} \frac{\partial^2 T}{\partial t^2} + \frac{\tau_q^2}{2\alpha} \frac{\partial^3 T}{\partial t^3}. \tag{29}
\end{align*}
\]

Then we use (27) to eliminate the current density \( \vec{J} \) in (29):

\[
(1 + ZT_0) \left( 1 + \tau_T \frac{\partial}{\partial t} \right) \nabla^2 T - \frac{\sigma_0 \pi_0}{k} \nabla \cdot \vec{E} = \frac{1}{\alpha} \frac{\partial T}{\partial t} + \frac{\tau_q}{\alpha} \frac{\partial^2 T}{\partial t^2} + \frac{\tau_q^2}{2\alpha} \frac{\partial^3 T}{\partial t^3}. \tag{30}
\]

Clearly, Equations (22) and (30) are identical if and only if the Tzou conditions

\[
\alpha = \frac{k}{C_l + C_e}, \quad \tau_T = \frac{C_l}{G}, \quad \tau_q = \tau_F + \frac{1}{G} \left( \frac{1}{C_l} + \frac{1}{C_e} \right)^{-1}, \quad \tau_j = \tau_F, \tag{31}
\]

are met. While the first three relations of (31) assure the Tzou conditions [24], the fourth relation determines the physical value of the electric current phase-lag to be equal to the relaxation time at the Fermi level. Reviewing Equations (31), the following inequalities:

\[
0 \leq \tau_j \leq \tau_q \leq \tau_T; \tag{32}
\]

hold true. Inequalities (32) determine the temporal order by which the relevant variables occur. In the constitutive Equation (25), for instance, while the electric field occurs at the physical time \( t \), the electric current occurs at the instant \( t + \tau_j \) and the temperature gradient establishes at \( t + \tau_T \). Moreover, if the electric field is absent, Equation (25) shows that the induced electric current establishes earlier than the temperature gradient. The delayed Equation (26), on the other hand, in addition to proving the heat flux established results from two ways, the temperature gradient and the passing current density, it further shows that the resulting heat flux, temperature gradient and the electric current occur at different instants of time. Along with the known result that [23, 24] the heat flux resulting...
from the temperature gradient establishes at \( t + \tau_q \), whilst the temperature gradient occurs at later instant \( t + \tau_T \), the heat flux resulting from the electric current establishes at \( t + \tau_q \), however, the electric current occurs at early instant \( t + \tau_j \). It is worth noting that the energy Equation (10), the Maxwell's equations (23) and the electric and thermal fluxes (27)–(28) occur at the same physical time \( t \), however, Equations (25)–(26) are of a delayed type. For this reason, a combination of (10), (23), (25), and (26) is impossible. An alternative version of the energy Equation (30) can be concluded by eliminating the current density \( \vec{J} \) from (29) by using Equation (23), which yields

\[
\left( 1 + \tau_T \frac{\partial}{\partial t} \right) \nabla^2 T + \frac{\pi_0 e_0}{k} \left( \frac{\partial}{\partial t} + \tau_j \frac{\partial^2}{\partial t^2} \right) \nabla \cdot \vec{E} = \frac{1}{\alpha} \frac{\partial T}{\partial t} + \tau_q \frac{\partial^2 T}{\partial t^2} + \frac{\tau_q^2}{2\alpha} \frac{\partial^3 T}{\partial t^3}.
\]

(33)

Although the energy Equations (30) and (33) seem to have different forms, they must give identical results in the sequel.

IV. ONE-DIMENSIONAL EXAMPLE

The thermal shock heating of metal films has been studied in many works in the literature, see for example [23], [25], and [34–37]. We shall consider a metal film lying on the \( yz \)-plane, with thickness \( \ell \), and subjected to an increase of temperature on the upper surface, whereas the lower surface is kept at the room temperature. Mathematically,

\[
T(0,t) = T_w, \quad T(\ell,t) = T_0.
\]

(34)

Two superconductor plates are linked to the upper and lower surfaces of the film and measure any potential difference between these surfaces. It is helpful to use the absolute values of the Seebeck and Peltier coefficients. Thus all variables will be functions of \( x \) and \( t \) and independent of \( y \) and \( z \). Moreover,

\[
\vec{q} = (q,0,0), \quad \vec{J} = (J,0,0).
\]

(35)

The following initial conditions are assumed

\[
T(x,0) = T_0, \quad \frac{\partial T}{\partial t}(x,0) = 0, \quad \frac{\partial^2 T}{\partial t^2}(x,0) = 0.
\]

(36)

Assuming that the contribution of the induced electric field can be disregarded in the one-dimensional formulation, the governing equations are given as

\[
(1 + ZT_0) \left( 1 + \tau_T \frac{\partial}{\partial t} \right) \frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t} + \frac{\tau_q}{\alpha} \frac{\partial^2 T}{\partial t^2} + \frac{\tau_q^2}{2\alpha} \frac{\partial^3 T}{\partial t^3},
\]

(37a)

\[
\left( 1 + \tau_j \frac{\partial}{\partial t} \right) J = -\sigma_0 S_0 \left( 1 + \tau_T \frac{\partial}{\partial t} \right) \frac{\partial T}{\partial x}.
\]

(37b)
\[
\left(1 + \tau_q \frac{\partial}{\partial t} + \frac{\tau_q^2}{2} \frac{\partial^2}{\partial t^2}\right) q = -k \left(1 + \tau_T \frac{\partial}{\partial t}\right) \frac{\partial T}{\partial x} + \pi_0 \left(1 + \tau_j \frac{\partial}{\partial t}\right) J. \tag{37c}
\]

An introduction of the following dimensionless quantities will help in implementing the numerical calculations:
\[
\theta = \frac{T - T_0}{T_w - T_0}, \quad x' = \frac{x}{\ell}, \quad t' = \frac{t}{\ell^2/\alpha}, \quad \tau_j' = \frac{\tau_j}{\ell^2/\alpha}, \quad \tau_q' = \frac{\tau_q}{\ell^2/\alpha}, \quad \tau_T' = \frac{\tau_T}{\ell^2/\alpha},
\]
\[
q' = \frac{\ell q}{kT_0}, \quad J' = \frac{\ell J}{\sigma_0 \pi_0}. \tag{38}
\]

Next, by using (38) to simplify (34), (36), and (37), and dropping the primes of the dimensionless quantities for convenience, and making use of the Laplace transform, Equations (37) can be transformed to the forms
\[
\theta(x, s) = A(s) \exp(\beta x) + B(s) \exp(-\beta x), \tag{39a}
\]
\[
\bar{J}(x, s) = -\frac{\gamma_0 \beta (1 + \tau_T s)}{1 + \tau_j s} \left[A(s) \exp(\beta x) - B(s) \exp(-\beta x)\right], \tag{39b}
\]
\[
\bar{q}(x, s) = -\frac{\gamma_0 \beta (1 + ZT_0) (1 + \tau_T s)}{1 + \tau_q s + (\tau_q s)^2/2} \left[A(s) \exp(\beta x) - B(s) \exp(-\beta x)\right], \tag{39c}
\]
\[
A(s) = -\frac{\exp(-\beta)}{2s \cdot \sinh(\beta)} \quad \text{and} \quad B(s) = \frac{\exp(\beta)}{2s \cdot \sinh(\beta)}, \tag{39d}
\]
\[
\beta = \sqrt{\frac{s \left[1 + \tau_q s + (\tau_q s)^2/2\right]}{(1 + ZT_0) (1 + \tau_T s)}}, \tag{39e}
\]
where \(\gamma_0 = (T_w - T_0)/T_0\), \(s\) denotes the Laplace parameter, and \(\bar{J}(s)\) denotes the Laplace transform of the function \(f(t)\). Equations (39a)–(39e), in fact, complete the solution of the thermal-shock heating of a metal film in the Laplace transformed domain. In order to obtain the solution of the present application in the physical domain, we firstly apply the well-known formula
\[
f(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \bar{f}(s) e^{st} \, ds \tag{40a}
\]
to Equations (39a) and (39c) and use Equations (39d)–(39e). Secondly, we adopt a numerical inversion method based on the Fourier series expansion, by which the integral (40a)
can be approximated as a series:

\[
 f(t) = \frac{e^{ct}}{t_1} \left[ -\frac{1}{2} \text{Re}\{f(c)\} + \sum_{j=0}^{\infty} \text{Re}\left( \tilde{f}\left(c + \frac{ij\pi}{t_1}\right) \right) \cos\left(\frac{j\pi}{t_1}\right) \\
 - \sum_{j=0}^{\infty} \text{Im}\left( \tilde{f}\left(c + \frac{ij\pi}{t_1}\right) \right) \sin\left(\frac{j\pi}{t_1}\right) \right] \\
 - \sum_{j=1}^{\infty} e^{-2cjt_1} f(2jt_1 + \eta),
\]

for \(0 \leq t \leq 2t_1\), \(ct \approx 4.7\). The above series (40b) is called the Durbin formula, and the last term in it is called the discretization error. Honig and Hirdes [38] developed a method for accelerating the convergence of the Fourier series and a procedure that computes approximately the best choice of the free parameters. Further, they established a FORTRAN subroutine that helps in carrying out the series (52). We shall consider that \(T_w = 2T_0\), so that \(\gamma_0 = 1\).

Figure 1a shows the distributions of the temperature at different values of the dimensionless figure of merit \(ZT_0\) (zee-tee). The sharp wave front, that characterizes the conventional DPL (\(ZT_0 = 0.0\)) due to the existence of \(\tau_q^2\), is preserved in the thermoelectric DPL-model (Triple-Phase-Lag model or TPL). It appears that the heat affected zone is prolonged, and the temperature level slightly increases with zee-tee. Not only is the ratio \(\tau_T/\tau_q\) the reason behind the propagation of the sharp thermal wave front (see Figures 2 and 3 in [24]), but also the thermoelectric properties of the medium may be. The general behavior of the DPL-model does not qualitatively change; the change is only quantitative.

Figure 1b emphasizes the same insights expressed in Figure 1a. It displays the variations of the temperature at the middle point of the micro-film with the passing of time. For long values of time, the effect of zee-tee becomes of no importance.

The spatial decay of the heat flux with varying of \(ZT_0\) is shown in Figures 2a. Just like the temperature behavior, the heat flux in both the thermoelectric DPL and classical models records the same trend. The differences between the thermoelectric DPL and classical models are significant. The temporal decay, on the other hand, is presented in Figure 2b.

The thermally-induced electric current density variations, in the framework of the thermoelectric DPL and classical models, are plotted in Figures 3a for different values of the figure of merit \(ZT_0\).

In the classical model of thermoelectricity, the current density depends on the Seebeck coefficient as well as the temperature gradient. Thus, if \(S_0 > 0\) (like antimony, nichrome, gold, silver, copper) and \(T_w > T_0\) (i.e., \(\frac{dT}{dx} < 0\)), it yields that \(J > 0\) (i.e., the current flows from the high temperature region to the lower). On the other hand, if \(S_0 < 0\) (such as bismuth, constantan, nickel, potassium) and \(T_w > T_0\), it yields that \(J < 0\) (i.e., the electric current flows from the low temperature to the high temperature regions). In the current numerical model, we choose \(S_0 > 0\) and \(T_w > T_0\), therefore, according to the classical model, \(J\) is predicted to be in the opposite direction to the temperature gradient (\(J\) is
FIG. 1: (a) Variation of the temperature with the dimensionless depth at the dimensionless time 0.001 and different values of the figure of merit. (b) Variation of temperature with the dimensionless time at the dimensionless depth 0.5 and different values of the figure of merit.

parallel to the positive $x$-direction). This is what has been revealed by the curves of the classical thermoelectric model laying upwards of the $x$-axis of Figure 3a.

In the thermoelectric DPL-model, $J$ further depends on its rate $\partial J/\partial t$ and $\partial^2 T/\partial t \partial x$, which may disturb the total value of $J$. Indeed, the electric current density reverses its conventional trend and records values higher than that recorded by the classical model of thermoelectricity. It seems that the increase of $ZT_0$ causes a larger electricity-affected zone and lower peaks for the electric current density for both the classical and DPL models of thermoelectricity.

The effect of the three phase lags, $\tau_j$, $\tau_q$, and $\tau_T$, on the electric current density is shown in Figures 3b, 3c, and 3d, respectively. One can easily see that they have different
effects on the electric current behavior. An increase of $\tau_j$ causes an increase in the $J$-levels, an increase of $\tau_q$ prolongs the electricity-affected area and lowers the peak of $J$, and an increase of $\tau_T$ lowers both the peak electric current and the electricity-affected region.

V. SUMMARY

In this work, light has been shed on the HTS-model and the DPL-model. The thermoelectric properties of metals have been studied in the framework of the HTS-model.
FIG. 3: (a) Variation of the induced electric current with the dimensionless depth at the dimensionless time 0.001 and different values of the figure of merit. (b) Variation of the induced electric current with the dimensionless depth at the dimensionless time 0.001 and different values of the electric current phase-lag. (c) Variation of the induced electric current with the dimensionless depth at the dimensionless time 0.001 and different values of the heat flux phase-lag. (d) Variation of the induced electric current with the dimensionless depth at the dimensionless time 0.001 and different values of the temperature gradient phase-lag.

By employing the lagging behavior, it is found that the macroscopic thermoelectric model can include the microscopic effects associated with the high-rate heating situations or the shortening of response time cases. In the new model, the electric current depends on its rate and the temperature gradient rate, in addition to the electric field and the temperature gradient. An example has been considered by taking into account the proposed model. It describes the thermal-shock heating of a metal film, without induced electric field, so that the resulting heat flow can be modeled as a one-dimensional example. The effect of the figure of merit on the temperature, the heat flux, and the electric current is studied. The electric current phase lag changes the profile of the current in the small-scales of time. For
relatively large values of time, the TPL-model (Triple-Phase-Lag) reduces to the classical thermoelectric model with DPL.

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References

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