International Journal of Thermophysics, Vol. 11, No. 4, 1990

Theoretical Considerations of the Effects of Rapid Heating of Solids on Their Apparent Thermal Properties[1]

P. G. Klemens[2]

The conditions are investigated for thermal properties to change from their normal values when solids are heated very rapidly. The properties considered are specific heat, thermal expansion, thermal conductivity, and thermal diffusivity. Over times which may be as long as a microsecond, the heated solid is unable to expand: the appropriate values of specific heat and thermal conductivity are then those at constant volume rather than constant pressure. In those alloys where thermal equilibrium requires diffusion, its establishment is delayed, and if solids do not have time to expand, the diffusion coefficient is reduced. For heating times below nanoseconds, the electrons and the lattice may be at different temperatures, particularly if the energy is initially imparted to the electrons. The temperature of the electron gas of metals may then approach the degenerary temperature. The apparent specific heat of a decoupled system departs from the steady-state value in a manner which depends on how temperature is measured. In such a decoupled system the concepts of thermal conductivity and thermal diffusivity must be used with care.

KEY WORDS: diffusion; electrons; expansion; phonons; rapid heating; relaxation times; specific heat; thermal conductivity.

1. INTRODUCTION

In the description of the thermal properties of matter one usually assumes that the system is in thermal equilibrium. Alternatively, in the case of transport properties, one assumes that the departures from thermal equilibrium are very small, so that the various currents are linear functions

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[1] Paper presented at the First Workshop on Subsecond Thermophysics, June 20–21, 1988, Gaithersburg, Maryland, U.S.A.

[2] Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, U.S.A.

of the driving forces which cause them, i.e., gradients in temperature or in electric or in chemical potentials. This raises the question of under what conditions the apparent thermal properties depend upon heating rates and when nonlinear effects become important in transport properties.

The thermal properties of solids may be described in terms of a superposition of excitations, in particular, lattice vibrations, free electrons, and electromagnetic waves, and also localized excitations such as electronic energy levels of atoms or groups of atoms and atomic configurations. Energy exchange between these various excitations takes place continuously, and as a result of the size and complexity of the system on a microscopic scale, these interactions tend to bring the excitations into a state of mutual equilibrium or to a common temperature. The rate at which this thermal equilibrium is established can be characterized by one or more relaxation times. These are defined by the rate with which mutual equilibrium would be restored if the various excitations had been thrown out of equilibrium at some instant and if the system were then left to return to equilibrium in the absence of any further disturbances.

The relaxation rate also provides an upper limit of the rate at which a solid can be heated without its apparent thermal properties departing significantly from those measured under steady-state conditions.

Relaxation times are generally functions of temperature and increase as the temperature is lowered. At very low or cryogenic temperatures they can be quite long, so that temperature differences can be established and maintained between different subsystems (e.g., spins and phonons) over times comparable to those of laboratory measurements. In fact, it is sometimes difficult to bring all parts of a system to a common temperature at low temperatures. Apparent thermal properties are then influenced by the time scale of measurements. In many cases only a metastable equilibrium is reached. At ordinary temperatures the relaxation times are usually short, and equilibrium is attained rapidly, although metastable equilibria are sometimes encountered. At high temperatures the relaxation times are generally quite short, and different parts of the system, such as electrons and lattice vibrations, will be at different temperatures only at very high heating rates. Nevertheless, except for this differences in time scale, similar principles govern the establishment of equilibrium during rapid heating.

There is, however, one important difference between low and high temperatures. Heating causes thermal stresses, and true equilibrium requires thermal expansion, which eliminates these stresses. The rate at which this occurs depends on the dimensions of the heated regions and on the velocity of elastic waves. The times required for elastic relaxation show less temperature sensitivity than the internal relaxation times, so that at high temperatures true equilibrium is often delayed by these inertial effects.

Furthermore, the differences between properties at constant volume and at constant or zero stress become more pronounced the higher the temperature. The most obvious dependences of thermal properties on heating rate above room temperature are therefore owing to this delay in thermal expansion.

The establishment of thermal equilibrium always takes a long time if it requires atomic movement, such as the destruction of long-range and short-range order on heating alloys, the dissolution of segregated phases, and the reduction of solute atmospheres around dislocations. Alloys thus respond frequently more slowly to temperature changes than pure metals. In the case of very rapid heating, when the material has no time to expand and diffusion occurs at a constant volume, this process is even more slow.

Similar considerations apply to conduction properties such as thermal conductivity and thermal diffusivity. One defines a mean free path of the mobile carriers, such as electrons and phonons, proportional to their relaxation time. These mean free paths are quite short, ranging from 10 to 100 Å. Departures from Fourier's law in thermal conduction can be expected only for such high temperature gradients that the fractional change in absolute temperature is appreciable over comparable distance. This condition is rarely attained, except in the case of radiative heat transfer through partially transparent media.

2. INERTIAL EFFECTS

When a solid is heated under quasi-equilibrium conditions at constant pressure, it expands, but when it is heated very rapidly, the inertia of the material can delay the expansion. In the extreme case of rapid heating, the volume stays constant and the pressure increases by ΔP, where

$$\Delta P = \alpha K_{\mathrm{B}} \Delta T \tag{1}$$

Here ΔT is the temperature rise, K_{B} the bulk modulus, and α the volumetric coefficient of thermal expansion.

The time t_X required for the pressure to relax and for the heated material to reach its equilibrium volume depends on the inertia of the body, its dimensions, and how the body is constrained by other bodies. One expects t_X to be given approximately by

$$t_X \simeq L/v_{\mathrm{s}} \tag{2}$$

where L is the distance from the point where heat is deposited to the nearest free surface, and where v_{s} is the velocity of compressional waves. Since sound velocities in solids depend primarily on density rather than pressure, decreasing with increasing volume, v_s is never larger than the sound velocity of the cold or unexpanded material, and t_X will be determined by that value of v_s.

For example, if energy deposition is about 10^{-5} cm below the surface, since v_s is typically around $3 \times 10^5\ \text{cm} \cdot \text{s}^{-1}$, the expansion time t_X is around 3×10^{-11} s. In cases where the energy is deposited deep within the body, such as by gamma rays or by electric currents, L can be much larger and t_X would be correspondingly increased. For a wire of 0.6-mm diameter, rapidly heated by current, t_X would be as long as 10^{-7} s.

There are several consequences of delayed expansion. All properties—equilibrium as well as conduction properties—which are normally measured as a function of temperature at atmospheric pressure must now be regarded as changing with temperature at constant volume, at least initially, rather than at constant pressure. This will tend to decrease the specific heat and tend to increase electrical conductivities as well as thermal conductivities and thermal diffusivities.

3. ATOMIC DIFFUSION

One mechanism which yields relatively long times for the establishment of thermal equilibrium is that of atomic diffusion. Changes in temperature are sometimes accompanied by changes in the equilibrium positions of atoms, which needs diffusion. This is the case when alloys change their degree of order with temperature, when segregated solute atoms move into the matrix on heating, or when there are solute atmospheres around dislocations.

One can write the diffusion coefficient in the form [1]

$$D = D_0 \exp(-H/kT) \tag{3}$$

where $D_0 \sim a^2 \omega_D$, a being the interatomic distance and ω_D the (circular) Debye frequency, typically around $5 \times 10^{13}\ \text{s}^{-1}$. Also, H is an activation energy, k the Boltzmann constant, and T the absolute temperature. Typical activation temperatures H/k range from 10,000 K up. If the change in atomic order involves movements over distances of $3a$, the time required to establish equilibrium by diffusion is

$$t_D \simeq (3a)^2/D = 10(\omega_D)^{-1} e^{H/kT} \tag{4}$$

and is strongly dependent on H/kT. For example, if $T = 1000$ K, $H/k = 10{,}000$ K, $\omega_D = 5 \times 10^{13}\text{s}^{-1}$, then $t_D \simeq 5 \times 10^{-9}$ s. If the establishment of equilibrium required motion over longer distances, such as when solute atoms move from precipitates into solid solution, the equilibrium time is correspondingly lengthened and may even be comparable to the time needed for thermal expansion.

Another point to consider is that diffusion rates are sensitive to volume. If the solid is unable to expand because of inertial constraints, the time required for diffusion will, in some cases, be controlled by the expansion of the heated material.

The diffusion coefficient, as a function of pressure, is

$$D(P) = D(0)\exp(-\Delta H/kT) \tag{5}$$

where the increase in the activation enthalpy H is

$$\Delta H = V_a P \tag{6}$$

and where V_a is a volume of the order of the volume per atom. One can express thermal expansion in the form

$$\Delta V/V = \gamma CT/K_B \tag{7}$$

where γ is the Grüneisen constant, K_B the bulk modulus, and C the specific heat per unit volume. If expansion is prevented, the pressure which is generated is

$$P = K_B\,\Delta V/V = \gamma CT \tag{8}$$

so that

$$H/kT = \gamma C V_a/k \tag{9}$$

Thus $\Delta H/kT$ is only weakly dependent on temperature and $D(P)$, the diffusivity at constant volume, is related to $D(0)$, that at zero pressure, by

$$D(P) = D(0)\exp(-\gamma C V_a/k) \tag{10}$$

Taking C as $3\ \mathrm{J \cdot cm^{-3} \cdot K^{-1}}$, γ as 2, and V_a as $1 \times 10^{-23}\ \mathrm{cm}^3$, so that $\Delta H/kT = 4.3$, $D(P) \simeq 0.014\ D(0)$. Thus diffusion rates are decreased by a factor 50 to 100 relative to those at zero pressure.

In the numerical example selected above, t_D was 5×10^{-9} s, but using $D(P)$ in place of $D(0)$, it would be around 3×10^{-7} s. If t_X of Eq. (2), the time required for thermal expansion, were to fall between those two limits, t_D should actually be equated to t_X, for diffusion would be inhibited until the material attained its expanded state.

4. LOCAL EQUILIBRIUM IN SOLIDS

In addition to the effects of delayed equilibrium due to the need for atomic movement and for the movement of macroscopic elements of the material, there is the need to establish equilibrium between different microscopic modes of excitation at each location of the solid. The corresponding relaxation times are quite short.

We picture the thermal energy of a solid to reside in subsystems such as lattice vibrations or phonon gas, and the gas of free electrons in the case of metals. There may be other excitations such as magnetic moments, other localized electron states, changes in configuration, etc. These subsystems must come to a new equilibrium, each within itself and also with each other. The time needed to do so can be described by a set of relaxation times.

Most of our information about relaxation times in solids is derived from the measured electrical and thermal conductivities. The electrical conductivity can be expressed as

$$\sigma = (N/m)e^2\tau_e \tag{11}$$

where for free electrons m is the electron mass and N the electron density. In a solid N/m takes on an effective value. Also, e is the electronic charge, while τ_e is the relaxation time. Some values of τ_e for simple metals are given in Table I.

The relaxation time τ_e is a measure of the time required by the electron gas to lose excess momentum supplied by the electric field. In pure metals this occurs by means of electron–phonon interactions; in alloys the scattering of electrons by the solute atoms makes an additional and major contribution to the relaxation rate. In the electron–phonon interaction an electron loses memory of its direction and, also, changes its energy by $k\theta$, where θ is the Debye temperature [2].

In order for an electron to come into energy equilibrium with the lattice vibrations, it must randomly change its energy by an amount kT. Near the Debye temperature this is achieved by a single electron–phonon interaction, but at very high temperatures it takes several steps of order $k\theta$ to

Table I. Relaxation Times (in seconds)

Metal	T(K)	τ_e	τ_{th}
Cu	300	3×10^{-14}	3×10^{-14}
Cu	1400	6×10^{-15}	1.5×10^{-13}
Al	300	1×10^{-14}	1×10^{-14}
Al	900	3×10^{-15}	2×10^{-14}
Ti	300	1×10^{-15}	1×10^{-15}
Ti	1500	2×10^{-16}	5×10^{-15}

change its energy by kT. In this random walk along the energy coordinate, the number of steps required is $(T/\theta)^2$, so that the relaxation time of the electron gas for the attainment of thermal equilibrium is, if $T \gtrsim \theta$,

$$\tau_{\mathrm{th}} = \tau_{\mathrm{e}}(T)(T/\theta)^2 = \tau_{\mathrm{e}}(\theta)(T/\theta) \tag{12}$$

The latter result follows because $\tau_{\mathrm{e}} \propto 1/T$.

In alloys the thermal relaxation time is the same as in a pure metal, since the scattering by solute atoms is elastic [2] and does not contribute to thermal relaxation.

As seen from Table I, electronic relaxation times are very short, and even though τ_{th} at high temperatures is an order of magnitude larger, the longest relaxation time is around 10^{-13} s. It is only when energy is deposited directly into the electron gas, so that the electron temperature can exceed the lattice temperature by an order of magnitude, that the relaxation time can approach 10^{-12} s, a time scale which has become recently accessible to observation [3].

The relaxation times for the establishment of mutual equilibrium between different groups of lattice waves are also very short. They can be derived from observed lattice thermal conductivities or from the theory of anharmonic three-phonon interactions. Most of the vibrational energy resides in lattice modes of high frequency, near and just below the Debye frequency

$$\omega_{\mathrm{D}} = 2\pi k\theta/h \tag{13}$$

where h is the Planck constant. From theory, for modes of that frequency [4]

$$1/\tau_{\mathrm{th}} = A\omega_{\mathrm{D}}(1 + T/\theta) \tag{14}$$

Here $A = 2\gamma^2 k\theta/\mu a^3$, γ being the Grüneisen constant and μ the shear modulus, so that typically $A \simeq 0.1$. Thus with $\omega_{\mathrm{D}} \sim 3 \times 10^{13}\ \mathrm{s}^{-1}$, τ_{th} for phonons is typically around 10^{-12} to 10^{-13} s.

5. HEAT CAPACITY

We now wish to examine the consequences to the apparent thermal properties of a finite relaxation time between subsystems of a solid. The most important property is the heat capacity.

Consider for simplicity a system which consists of only two loosely coupled subsystems, labeled 1 and 2, with heat capacities C_1 and C_2 and with relaxation times τ_1 and τ_2, respectively. If they are at slightly different temperatures, the same amount of energy per unit time would be transferred between them during their approach to equilibrium, so that

$$C_1/\tau_1 = C_2/\tau_2 \tag{15}$$

Now assume that energy is deposited from an external source at a rate W per unit time and that only subsystem 1 receives external energy directly. The two subsystems are consequently at different temperatures T_1 and T_2; energy balance requires

$$C_1(dT_1/dt) = W - (C_1/\tau_1)(T_1 - T_2) \tag{16}$$

$$\begin{aligned} C_2(dT_2/dt) &= (C_1/\tau_1)(T_1 - T_2) \\ &= (C_2/\tau_2)(T_1 - T_2) \end{aligned} \tag{17}$$

and also

$$W = C_1(dT_1/dt) + C_2(dT_2/dt) \tag{18}$$

The apparent specific heat will depend on which subsystem receives energy (i.e., plays the role of subsystem 1) and whether the "thermometer" is attached to system 1 or system 2 and, thus, measures T_1 or T_2.

If τ_1 and τ_2 are sufficiently short, $\Delta T = T_1 - T_2$ will be small, and the apparent specific heat, defined by

$$C(dT/dt) = W \tag{19}$$

will be $C = C_1 + C_2$, irrespective of whether T is identified with T_1 or T_2.

If the relaxation times are long, ΔT is no longer negligible. Let us consider the case when the thermometer measures T_1. The apparent specific heat, defined by Eq. (19) with $T = T_1$, now lies between C_1 and $C_1 + C_2$. From Eqs. (15) and (16)

$$W - C_1(dT_1/dt) = C_2(dT_2/dt) = C_2 d(T_1 - \Delta T)/dt \tag{20}$$

and from Eqs. (15) and (17)

$$\Delta T/\tau_2 = dT_2/dt = dT_1/dt - d(\Delta T)/dt \tag{21}$$

If $\Delta T = 0$ at $t = 0$, the solution to Eq. (21) makes ΔT increase as a function of time. In the special case when dT_1/dt is constant, Eq. (21) yields

$$\Delta T = \tau_2(dT_1/dt)[1 - e^{-t/\tau_2}] \tag{22}$$

so that ΔT eventually reaches a constant value. Other solutions can be constructed by superposition.

Using Eq. (18) and defining $C = W/(dT_1/dt)$, one obtains

$$C = C_1 + C_2 - C_2(d\Delta T/dt)/(dT_1/dt) \tag{23}$$

This makes the apparent specific heat depend on time. In the special case above when dT_1/dt is constant, and ΔT is given by Eq. (22),

$$C = C_1 + C_2[1 - e^{-t/\tau_2}] \tag{24}$$

It may be possible to shape $W(t)$, the energy deposition as a function of time, to make dT_1/dt constant, and to use this simple equation to extract C_1, C_2, τ_2, and τ_1 from $C(t)$. Alternatively, one can use Eq. (21) and the observed time dependence of $T_1(t)$ to calculate ΔT and τ_2 numerically and then to calculate C_1 and C_2 from Eq. (20).

In the case when the thermometer measures T_2 and with similar assumptions, one obtains in place of Eq. (24)

$$C = W(dT_2/dt)^{-1} = C_2 + C_1[1 - e^{-t/\tau_2}] \tag{25}$$

5.1. Energy Deposited into Electron Gas

Consider a metal or alloy heated rapidly at constant volume by energy deposition directly into the electron gas, as in the case of incident electromagnetic radiation. Thus T_1 is the temperature of the electron gas, and T_2 that of the lattice. The two component of specific heat, C_E and C_P, are at the ratio [1]

$$\begin{aligned} C_\text{E}/C_\text{P} = C_1/C_2 = T_1/T_\text{F} \qquad & \text{if} \quad T < T_\text{F} \\ \simeq \tfrac{1}{2} \qquad & \text{if} \quad T > T_\text{F} \end{aligned} \tag{26}$$

where T_F is of the order of the degeneracy temperature of the electron gas.

To obtain τ_1, one must generalize τ_th of Eq. (12) to the case when the electron temperature T_1 differs from the lattice temperature T_2, i.e.,

$$\tau_1 = \tau_\text{e}(T_2)(T_1/\theta)^2 = \tau_\text{e}(\theta)\, T_1^2/\theta T_2 \tag{27}$$

Using Eqs. (26) and (15)

$$\tau_2 = \tau_\text{e}(\theta)\, T_\text{F} T_1/\theta T_2 \qquad \text{if} \quad T_1 < T_\text{F} \tag{28a}$$

$$= 2\tau_\text{e}(\theta)\, T_1^2/\theta T_2 \qquad \text{if} \quad T_1 > T_\text{F} \tag{28b}$$

Thus from Eq. (28a), taking $\tau_\text{e}(\theta) = 10^{-14}$ s and $T_\text{F} = 100\,\theta$, one finds $\tau_2 \simeq 10^{-12}(T_1/T_2)$ s. If $T_1 = 30{,}000$ K and $T_2 = 300$ K, the relaxation time τ_2 in Eq. (24) will initially be as long as 10^{-10} s. Of course, τ_2 will decrease as

T_2 increases, so that the time-dependent term in Eq. (24) is not really an exponential, but the growth of the C_2 term is essentially governed by the initial value of τ_2.

In addition to the delayed appearance of the lattice specific heat C_2, which represents a large change in the specific heat, albeit short-lived, there will be the effect due to delayed thermal expansion. The appropriate delay time t_X of Eq. (2) depends on the depth of energy deposition, and can range from 10^{-9} to 10^{-6} s. The change in specific heat, being the difference between specific heat at constant pressure and that at constant volume, is given by

$$\Delta C = C_{\text{p}} - C_{\text{v}} = T\alpha^2 K_{\text{B}} = \gamma^2 C^2 T / K_{\text{B}} \tag{29}$$

where α is the coefficient of thermal expansion, γ the Grüneisen coefficient. This change is much smaller, being only about 10% at 1000 K, but persists over a longer time than that due to the delay in heating the lattice.

6. THERMAL CONDUCTIVITY AND THERMAL DIFFUSIVITY

The thermal conductivity of metals and alloys is additively composed of contributions from electrons and phonons [4], i.e.,

$$\lambda = \lambda_{\text{E}} + \lambda_{\text{P}} \tag{30}$$

while nonmetals have only the phonon contribution λ_{P}. Now

$$\lambda_{\text{E}} = (1/3) C_{\text{E}} v_{\text{E}} l_{\text{E}} \tag{31}$$

$$\lambda_{\text{P}} = (1/3) C_{\text{P}} v_{\text{P}} l_{\text{P}} \tag{32}$$

where C_{E} and C_{P} are the specific heats (per unit volume) of the electron gas and of the lattice waves or phonons. Also, v_{E} and v_{P} are the electron and phonon velocities, and l_{E} and l_{P} their mean free paths, which are related to the relaxation times by $l_{\text{E}} = v_{\text{E}} \tau_{\text{E}}$ and $l_{\text{P}} = v_{\text{P}} \tau_{\text{P}}$.

In most cases λ_{E} is related to the electrical conductivity σ by the Sommerfeld value of the Lorenz ratio

$$\lambda_{\text{E}} / \sigma T = (\pi^2/3)(k/e)^2 \tag{33}$$

where k is the Boltzmann constant and e the electronic charge. Equation (33) is based on two assumptions: T is well below the degeneracy temperature T_{F}, and the relaxation time τ_{E} is the same as for electrical conduction.

Now τ_{E} is limited either by the time it takes for electrons to dissipate their momentum or by the time required for the electron gas to come to a common temperature [2]. Thus if τ_e is the relaxation time in σ, τ_E for thermal conduction is given by

$$1/\tau_E = 1/\tau_e + 1/\tau_{th} \tag{34}$$

where τ_{th} is given by Eq. (12). At sufficiently high temperatures τ_E is thus less than τ_e, and τ_E is less than given by Eq. (33). Electron–electron interactions, which are also more effective for thermal relaxation than for electrical resistance, will reinforce this trend at higher temperatures. On the other hand, departures from high degeneracy—as T approaches T_F—will usually work in the opposite sense.

At high temperatures it is difficult to measure thermal conductivity by steady-state methods, and transient measurements are frequently used. These yield the thermal diffusivity

$$D_t = \lambda/C = (\lambda_E + \lambda_P)/(C_E + C_P) \tag{35}$$

In the definition of D_t it is implied that the electron gas and the phonon gas are everywhere at a common temperature, even though each component contributes independently to the heat current. This holds provided heating is slow compared to the relaxation time τ_{th} and provided the temperature gradient is small so that $v_E \tau_E$ grad T is small compared to T.

At high heating rates one first encounters conditions such that the inertial constraints keep the material at constant volume rather than permit the normal thermal expansion. This will change both the thermal and the electrical conductivities, but not the Lorenz ratio, and also the specific heat. The change in thermal diffusivity D_t will be somewhat larger than that in λ. Because electrons and phonons remain at a common temperature, thermal diffusivity as defined by Eq. (35) is still a valid concept, and λ can be deduced from D_t, provided the value of C is estimated from the amount of thermal expansion allowed during the time of thermal diffusion.

6.1. Thermal Conductivity at Constant Volume

At heating rates such that $(1/T)dT/dt$ exceeds $1/t_X$, i.e., typically $10^7\ \mathrm{s}^{-1}$, thermal expansion is surpressed and the conductivities change with temperature at constant volume.

The electrical resistivity at zero pressure has the form [5]

$$\rho = AT(1 + \delta\alpha T) \tag{36}$$

where α is the volume coefficient of thermal expansion, and

$$\delta = (V/\rho)\, d\rho/dV \tag{37}$$

For simple metals, δ ranges from 6 to 8, and it is somewhat smaller for alloys. The change in λ_E is proportional to that in σ [6], so that, for a temperature increase ΔT

$$\Delta\lambda_E = \alpha\delta\,\Delta T\lambda_E \tag{38}$$

There is a similar change in λ_P, with a value of δ typically around 8.

For a temperature increase of $\Delta T = 1000\,\mathrm{K}$ with $\delta = 6$ and $\alpha = 7 \times 10^{-5}\,\mathrm{K}^{-1}$, the fractional change in thermal conductivity due to heating at constant volume is $\Delta\lambda/\lambda = \alpha\delta\,\Delta T = 0.4$. The corresponding decrease in specific heat, estimated from Eq. (29), is 0.12, so that the thermal diffusivity is increased by almost 60%.

6.2. Electrons and Phonons Decoupled

At very high heating rates, such that $(1/T)\,dT/dt$ becomes comparable to $1/\tau_2$ of Eq. (28), electron and lattice temperatures will begin to diverge; the electrons and phonons will have different temperature distributions in space. Under these conditions, the concept of thermal diffusivity becomes inappropriate and must be carefully defined. In place of D_t of Eq. (35) one must define individual thermal diffusivities $D_E = \lambda_E/C_E$ and $D_P = \lambda_P/C_P$. Since the two excitations have different temperature gradients, one must use two equations of thermal conduction, linked by a source term, respectively sink term, describing the heat transfer from one system to the other.

In particular, if heat is initially deposited into the electron gas, it may be possible to neglect λ_P. However, the time-dependent conduction equation for the electronic heat must have a sink term proportional to the instantaneous temperature difference $T_E - T_P$. Also, in λ_E the term $1/\tau_{th}$ of Eq. (34) must be modified, as in Eq. (27), so that

$$\tau_{th} = \tau_e(\theta)\,T_E^2/T_P\theta \tag{39}$$

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