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The Thermal Inertia of Materials Heated with a Laser Pulse Faster than Relaxation Time[1]

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The nonlocal hyperbolic heat conduction equation is used to describe the thermal inertia of thin metal films (TMF) heated with femtosecond laser pulses. It is shown that for TMF the signatures of thermal inertia are (i) the delay of the heating process and (ii) the strong localization of the thermal energy in TMF.

KEY WORDS: hyperbolic heat transfer; thermal inertia; thin metal films; pulse heating.

1. INTRODUCTION

The differential equations of thermal energy transfer should be hyperbolic so as to exclude action at distance; yet the equations of irreversible thermodynamics—those of Navier–Stokes and Fourier are parabolic.

In the present paper, the dynamics of the heat transfer in thin metal films is investigated. When an ultrafast laser pulse (femtosecond pulse) interacts with a metal surface, the excited electrons become the main carriers of the thermal energy. For a femtosecond laser pulse, the duration of the pulse is of the same order as the electron relaxation time. In this case, the hyperbolicity of the thermal energy transfer plays an important role.

In this paper, the theoretical as well as the experimental aspects of the hyperbolic heat conduction equation (HHC) are discussed. First, the mathematical structure of HHC is discussed. The different approaches to the

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derivation of HHC (e.g., memory function of the system) are presented. It is shown that the inherent feature of the solution of HHC is the inertia of the heat transfer. The signatures of the inertia are (i) the delay of the heating process in comparison to the external thermal perturbation and (ii) the strong localization of the thermal excitation.

2. FUNDAMENTALS OF RAPID THERMAL PROCESSES

Radiation deposition of energy in materials is a fundamental phenomena to laser processing. It converts radiation energy into material's internal energy, which initiates many thermal phenomena such as heat pulse propagation, melting, and evaporation. The operation of many laser techniques requires an accurate understanding and control of the energy deposition and transport processes.

Recently, radiation deposition and the subsequent energy transport in metals have been investigated with picosecond and femtosecond resolutions [1–7]. Results show that during high-power and short-pulse laser heating, free electrons can be heated to an effective temperature much higher than the lattice temperature, which in turn leads to both a much faster energy propagation process and a much smaller lattice-temperature rise than those predicted from conventional radiation heating model. Corkum et al. [8] found that this electron-lattice nonequilibrium heating mechanism can significantly increase the resistance of molybdenum and copper mirrors to thermal damage during high-power laser irradiation when the laser pulse duration is shorter than one nanosecond. Clemens et al. [9] studied thermal transport in multilayer metals during picosecond laser heating. The measured temperature response in the first 20 ps was found to be different from predictions of the conventional Fourier model. Due to the relatively low temporal resolution of the experiment ($\sim$4 ps), however, it is difficult to determine whether this difference is the result of nonequilibrium laser heating or is due to other heat conduction mechanism, such as non-Fourier heat conduction, or reflection and refraction of thermal waves at interfaces.

Heat is conducted in solids through electrons and phonons. In metals, electrons dominate the heat conduction, while in insulators and semiconductors, phonons are the major heat carriers. Table I lists important features of the electrons and phonons. The traditional thermal science, or macroscale heat transfer, employs phenomenological laws, such as Fourier's law, without considering the detailed motion of the heat carriers. Decreasing dimensions, however, has brought an increasing need of understanding the heat transfer processes from the microscopic point of view of the heat carriers.

Table I. General Features of Heat Carriers

	Free electron	Phonon
Generation	Ionization or excitation	Lattice vibration
Propagation media	Vacuum or medium	Medium only
Statistics	Fermion	Boson
Dispersion	$E=h^2q^2/(2m)$	$E=E(q)$
Velocity ($m \cdot s^{-1}$)	$\sim 10^6$	$\sim 10^3$

In earlier papers [10, 13], the microscopic picture of the heat transport in thin metal films was developed and applied to gold film irradiated with femtosecond laser pulses.

The response of the electron and phonon gases to the external perturbation initiated by laser irradiation can be described with the help of a memory function of the system. To that aim, let us consider the generalized Fourier law:

$$q(t) = -\int_{-\infty}^{t} K(t-t')\,\nabla T(t')\,dt' \tag{1}$$

where $q(t)$ is the density of a thermal energy flux, $T(t')$ is the temperature of electrons, and $K(t-t')$ is a memory function for thermal processes. The density of thermal energy flux satisfies the following equation of heat conduction:

$$\frac{\partial}{\partial t} T(t) = \frac{1}{\rho c_v} \nabla^2 \int_{-\infty}^{t} K(t-t')\,T(t')\,dt' \tag{2}$$

where ρ is the density of charge carriers and c_v is the specific heat of electrons in a constant volume. We introduce the following equation for the memory function describing the Fermi gas of charge carriers:

$$K(t-t') = K_1 \lim_{t_0 \to 0} \delta(t-t'-t_0) \tag{3}$$

In this case, the electron has a very "short" memory due to thermal disturbances of the state of equilibrium. Combining Eqs. (3) and (2), we obtain

$$\frac{\partial}{\partial t} T = \frac{1}{\rho c_v} K_1 \nabla^2 T \tag{4}$$

Equation (4) has the form of the parabolic equation for heat conduction (PHC). Using this analogy, Eq. (4) may be transformed as follows:

$$\frac{\partial}{\partial t} T = D_{\mathrm{T}} \nabla^2 T \tag{5}$$

where the heat diffusion coefficient D_{T} is defined as follows:

$$D_{\mathrm{T}} = \frac{K_1}{\rho c_{\mathrm{v}}} \tag{6}$$

From Eq. (6), we obtain the relation between the memory function and the diffusion coefficient:

$$K(t - t') = D_{\mathrm{T}} \rho c_{\mathrm{v}} \lim_{t_0 \to 0} \delta(t - t - t_0') \tag{7}$$

In the case when the electron gas shows a "long" memory due to thermal disturbances, one obtains for memory function

$$K(t - t') = K_2 \tag{8}$$

When Eq. (8) is substituted into Eq. (2), we obtain

$$\frac{\partial}{\partial t} T = \frac{K_2}{\rho c_{\mathrm{v}}} \nabla^2 \int_{-\infty}^{t} T(t')\, dt \tag{9}$$

Differentiating both sides of Eq. (9) with respect to t, we obtain

$$\frac{\partial^2 T}{\partial t^2} = \frac{K_2}{\rho c_{\mathrm{v}}} \nabla^2 T \tag{10}$$

Equation (10) is the hyperbolic wave equation describing thermal wave propagation in a charge carrier gas in a metal film. Using a well-known form of the wave equation,

$$\frac{1}{v^2} \frac{\partial^2 T}{\partial t^2} = \nabla^2 T \tag{11}$$

and comparing Eqs. (10) and (11), we obtain the following form for the memory function:

$$\begin{aligned} K(t - t') &= \rho c_{\mathrm{v}} v^2 \\ v &= \text{finite}, \qquad v < \infty \end{aligned} \tag{12}$$

As the third case, "intermediate memory" is considered:

$$K(t-t') = \frac{K_3}{\tau} \exp[-(t-t')/\tau] \tag{13}$$

where τ is the relaxation time of thermal processes. Combining Eqs. (13) and (2), we obtain

$$c_v \frac{\partial^2 T}{\partial t^2} + \frac{c_v}{\tau} \frac{\partial T}{\partial t} = \frac{K_3}{\rho\tau} \nabla^2 T \tag{14}$$

and

$$K_3 = D_\tau c_v \rho \tag{15}$$

Thus, finally,

$$\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau} \frac{\partial T}{\partial t} = \frac{D_T}{\tau} \nabla^2 T \tag{16}$$

Equation (16) is the hyperbolic equation for heat conduction (HHC), in which the electron gas is treated as a Fermion gas. The diffusion coefficient D_T can be written in the form [14]

$$D_T = \tfrac{1}{3} v_F^2 \tau \tag{17}$$

where v_F is the Fermi velocity for the electron gas in a semiconductor. Applying Eq. (17) we can transform the hyperbolic equation for heat conduction, Eq. (16), as follows:

$$\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau} \frac{\partial T}{\partial t} = \frac{1}{3} v_F^2 \nabla^2 T \tag{18}$$

Let us denote the velocity of disturbance propagation in the electron gas as s:

$$s = \sqrt{1/3}\, v_F \tag{19}$$

Using the definition of s, Eq. (18) may be written in the form

$$\frac{1}{s^2} \frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau s^2} \frac{\partial T}{\partial t} = \nabla^2 T \tag{20}$$

For the electron gas, treated as the Fermi gas, the velocity of sound propagation is described by the equation [15]

$$v_S = \left(\frac{P_F^2}{3mm^*} (1 + F_0^S) \right)^{1/2}, \qquad P_F = m v_F \tag{21}$$

where m is the mass of a free (non-interacting) electron and m^* is the effective electron mass. Constant F_0^S represents the magnitude of carrier–carrier interaction in the Fermi gas. In the case of very weak interaction, $m^* \to m$ and $F_0^S \to 0$, so according to Eq. (21),

$$v_S = \frac{mv_F}{\sqrt{3}\,m} = \sqrt{\frac{1}{3}}\,v_F \tag{22}$$

To sum up, we can make a statement that for the case of weak electron–electron interaction, sound velocity $v_s = \sqrt{1/3}\,v_F$ and this velocity is equal to the velocity of thermal disturbance propagation s. From this we conclude that the hyperbolic equation for heat conduction, Eq. (20), is identical as the equation for second sound propagation in the electron gas:

$$\frac{1}{v_S^2}\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tau v_S^2}\frac{\partial T}{\partial t} = \nabla^2 T \tag{23}$$

Using the definition, expressed by Eq. (17), for the heat diffusion coefficient, Eq. (23) may be written in the form

$$\frac{1}{v_S^2}\frac{\partial^2 T}{\partial t^2} + \frac{1}{D_T}\frac{\partial T}{\partial t} = \nabla^2 T \tag{24}$$

The mathematical analysis of Eq. (23) leads to the following conclusions.

(1) In the case when $v_S^2 \to \infty$, τv_S^2 is finite, Eq. (24) transforms into the parabolic equation for heat diffusion:

$$\frac{1}{D_T}\frac{\partial T}{\partial t} = \nabla^2 T \tag{25}$$

(2) In the case when $\tau \to \infty$, v_S is finite, Eq. (24) transforms into the wave equation:

$$\frac{1}{v_S^2}\frac{\partial^2 T}{\partial t^2} = \nabla^2 T \tag{26}$$

Equation (26) describes propagation of the thermal wave in the electron gas. From the point of view of theoretical physics, condition $v_S \to \infty$ violates the special theory of relativity. From this theory we know that there is a limited velocity of interaction propagation and this velocity

$v_{\text{lim}} = c$, where c is the velocity of light in a vacuum. Multiplying both sides of Eq. (24) by c^2, we obtain

$$\frac{c^2}{v_S^2}\frac{\partial^2 T}{\partial t^2} + \frac{c^2}{D_T}\frac{\partial T}{\partial t} = c^2 \nabla^2 T \tag{27}$$

Denoting $\beta = v_S/c$, Eq. (27) may be written in the form

$$\frac{1}{\beta^2}\frac{\partial^2 T}{\partial t^2} + \frac{1}{\tilde{D}_T}\frac{\partial T}{\partial t} = c^2 \nabla^2 T \tag{28}$$

where $\tilde{D}_T = \tau\beta^2$, $\beta < 1$.

On the basis of the above considerations, we conclude that the heat conduction equation, which satisfies the special theory of relativity, acquires the form of the partial hyperbolic Eq. (28). The rejection of the first component in Eq. (28) violates the special theory of relativity.

3. THE RELAXATION DYNAMICS OF ULTRAFAST THERMAL LASER PULSES

Heat transport during fast laser heating of solids has become a very active research area due to the significant applications of short pulse lasers in the fabrication of sophisticated microstructures, syntheses of advanced materials, and measurements of thin film properties. Laser heating of metals involves the deposition of radiation energy on electrons, the energy exchange between electrons and the lattice, and the propagation of energy through the media.

Ultrafast dynamics of hot electrons in metals has become an area of active theoretical investigation. The theoretical predictions showed that under ultrafast excitation conditions the electrons in a metal can exist out of equilibrium with the lattice for times of the order of the electron energy relaxation time [2, 5]. Model calculations suggest that it should be possible to heat the electron gas to temperature T_e of up to several thousand degrees for a few picoseconds while keeping the lattice temperature T_l relatively cold. Observing the subsequent equilibration of the electronic system with the lattice allows one to directly study electron–phonon coupling under various conditions.

Several groups have undertaken investigations relating dynamics changes in the optical constants (reflectivity, transmissivity) to relative changes in electronic temperature. But only recently, the direct measurement of electron temperature has been reported.

In an earlier investigation [2, 5], the temperature of hot electron gas in thin gold film ($l = 300$ Å) was measured, and a reproducible and systematic deviation from a simple Fermi–Dirac (FD) distribution for short time $\Delta t \sim 0.4$ ps were obtained. As stated in Ref. 5, this deviation arises due to the finite time required for the nascent electrons to equilibrate to a FD distribution. The nascent electrons are the electrons created by the direct absorption of the photons prior to any scattering.

In earlier papers [10, 12, 13], the relaxation dynamics of the electron temperature with the hyperbolic heat conduction equation (HHC), Eq. (24), was investigated. Conventional laser heating processes which involve a relatively low-energy flux and long laser pulse have been succesfully modeled in metal processing and in measuring thermal diffusivity of thin films [16]. However, the applicability of these models to short-pulse laser heating is questionable [2, 5, 10–13]. As is well known, the Anisimov model [16] does not properly take into account the finite time for the nascent electrons to relax to the FD distribution. In the Anisimov model, the Fourier law for heat diffusion in the electron gas is assumed. However, the diffusion equation is valid only when the relaxation time is zero, $\tau = 0$, and the velocity of the thermalization is infinite, $v \to \infty$.

The effects of ultrafast heat transport can be observed in the results of front-pump back probe measurements [2, 5]. The results of these type experiments can be summarized as follows. First, the measured delays are much shorter than would be expected if heat were carried by the diffusion of electrons in equilibrium with the lattice (tens of picoseconds). This suggests that heat is transported via the electron gas alone and that the electrons are out of equilibrium with the lattice on this time scale. Second, since the delay increases approximately linearly with the sample thickness, the heat transport velocity can be extracted, $v_h \simeq 10^8\ \mathrm{cm \cdot s^{-1}} = 1\ \mu\mathrm{m \cdot ps^{-1}}$. This is of the same order of magnitude as the Fermi velocity of electrons in gold, $1.4\ \mu\mathrm{m \cdot ps^{-1}}$.

Since heat moves at a velocity comparable to v_F—Fermi velocity of the electron gas, it is natural to question exactly how the transport takes place. Since those electrons which lie close to the Fermi surface are the principal contributors to transport, the heat-carrying electrons move at v_F. In the limit of lengths longer than the momentum relaxation length, λ, the random walk behavior is averaged and the electron motion is subject to a diffusion equation. Conversely, on a length scale shorter than λ, the electron move ballistically with a velocity close to v_F.

The importance of the ballistic motion may be appreciated by considering the different hot-electron scattering lengths reported in the literature. The electron–electron scattering length in gold, λ_{ee} has been calculated in Ref. 17. They find that $\lambda_{ee} \sim (E - E_F)^2$ for electrons close to

the Fermi level. For 2-eV electrons $\lambda_{ee} \approx 35$ nm, increasing to 80 nm for 1 eV. The electron–phonon scattering length λ_{ep} is usually inferred from conductivity data. Using Drude relaxation times [14], λ_{ep} can be computed, $\lambda_{ep} \approx 42$ nm at 273 K. This is shorter than λ_{ee}, but of the same order of magnitude. Thus, we would expect that both electron–electron and electron–phonon scattering are important on this length scale. However, since conductivity experiments are steady-state measurements, the contribution of phonon scattering in a femtosecond regime experiment, such as pump-probe ultrafast lasers, is uncertain.

In the usual electron–phonon coupling model [16], one describes the metal as two coupled subsystems, one for electrons and one for phonons. Each subsystem is in local equilibrium so the electrons are characterized by a FD distribution at temperature T_e and the phonon distribution is characterized by a Bose–Einstein distribution at the lattice temperature T_l. The coupling between the two systems occurs via the electron–phonon interaction. The time evolution of the energies in the two subsystems is given by the coupled parabolic differential equations (Fourier law).

For ultrafast lasers, the duration of pump pulse is of the order of relaxation time in metals [14, 17]. In that case hyperbolic heat conduction equation, Eq. (24) must be used.

In an earlier paper [13], it was shown that for thin gold film ($l = 0.03\,\mu$m) irradiated with a short laser pulse ($\Delta t = 0.4$ ps), the nonstationary temperature profiles can be well described with the help of HHC. When the experimental data [5] and theoretical calculations are compared, the following values of the thermal wave velocity $v_S = 0.15\,\mu\text{m} \cdot \text{ps}^{-1}$ and relaxation time $\tau = 0.12$ ps are obtained. Considering that for electron Fermi gas the electron mean free path can be calculated according to the equation

$$\lambda = v_S \tau \tag{29}$$

and using the above-mentioned values for v_S and τ, one can obtain for $\lambda = 180$ nm, which is of the same order as the value obtained in an earlier paper [17]. However, it must be stressed that our values were obtained for a nonstationary heating process.

4. THE THERMAL INERTIA OF MATERIALS HEATED WITH ULTRAFAST LASER PULSES

According to the constitutive relation in the thermal wave model, heat flux $\vec{q}$ obeys the relatio [10]

$$\vec{q}(\vec{r}, t+\tau) = -k\,\nabla T(\vec{r}, t) \tag{30}$$

where τ is the relaxation time (a phase lag) and k is the thermal conductivity. The temperature gradient established in the material at time t results in a heat flux that occurred at a later time $t+\tau$ due to the insufficient time of response. For combining with the energy equation, however, all the physical quantities involved must correspond to the same instant of time. The Taylor's series expansion is thus applied to the heat flux $\vec{q}$ in Eq. (30) to give

$$\vec{q}(\vec{r}, t)+\frac{\partial \vec{q}(\vec{r}, t)}{\partial t}\tau+\frac{\partial^2 \vec{q}(\vec{r}, t)}{\partial t^2}\frac{\tau^2}{2}=-k\,\nabla T(\vec{r}, t) \tag{31}$$

In the linearized thermal wave theory, the phase lag is assumed to be small and the higher-order terms in Eq. (31) are neglected. By retaining only the first-order term in τ, Eq. (31) becomes

$$\vec{q}(\vec{r}, t)+\tau\frac{\partial \vec{q}(\vec{r}, t)}{\partial t}=-k\,\nabla T(\vec{r}, t) \tag{32}$$

After combining Eq. (32) with the energy conservation equation

$$-\nabla\cdot\vec{q}=\rho C_v\frac{\partial T}{\partial t} \tag{33}$$

one obtains the HHC, Eq. (24). Equation (32) can be compared to the equation of the motion for particle with mass m in a resistive medium,

$$\gamma\vec{v}+m\frac{d\vec{v}}{dt}=\vec{P}(\vec{r}, t) \tag{34}$$

where γ is a resistive cofficient, $\vec{v}$ denotes the velocity, and $\vec{P}(\vec{r}, t)$ is the external force. Comparing Eqs. (32) and (34) we conclude the correspondence

$$\begin{aligned} -\nabla T(\vec{r}, t) &\to \vec{P}(\vec{r}, t)\\ \vec{q}(\vec{r}, t) &\to \vec{v}\\ k^{-1} &\to \gamma\\ \tau/k &\to m \end{aligned} \tag{35}$$

For the steady-state case, Eq. (34) reduces to

$$\gamma\vec{v}=\vec{P}(\vec{r}, t) \tag{36}$$

and Eq. (31) reduces to the Fourier law.

From the relations, given by Eq. (35), we conciude that the greater relaxation time corresponds to the greater mass $\equiv$ greater inertia. It seems

quite resonable to treat the relaxation timer as the measure of the degree of the thermal inertia.

In earlier papers [10–13], it was shown that for the thermal processes with characteristic time $\Delta t \geqslant \tau$, the heat transfer is well described by Fourier law. In another way, for $\Delta t \geqslant \tau$ the thermal processes can be called

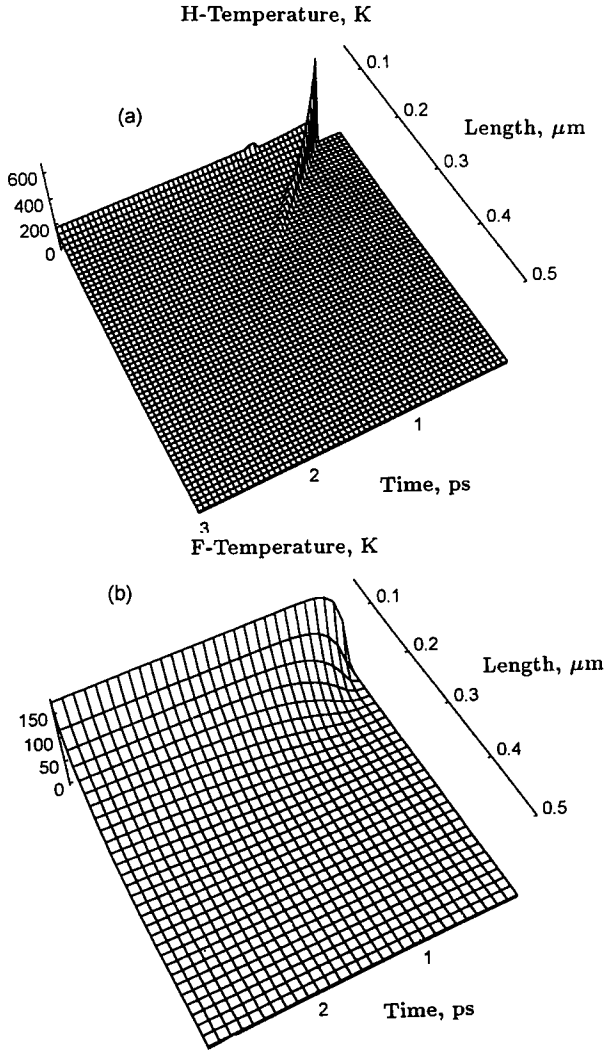

Fig. 1. (a) The solution of HHC for $v_S = 0.15\ \mu m \cdot ps^{-1}$, $\tau = 0.12$ ps, Δt-pulse duration $= 0.06$ ps. (b) The solution of PHC for the same values of v_S, τ and $\Delta t = 0.06$ ps.

inertia-free processes. On the other hand, for thermal processes with $\Delta t < \tau$ the thermal inertia plays an important role.

In Figs. 1 and 2, the 3D solutions of HHC and PHC equation are presented. The solutions are obtained for $v_S = 0.15\ \mu\text{m} \cdot \text{ps}^{-1}$ and $\tau = 0.12$ s [13] and for $\Delta t = 0.06$ and 0.02 ps. As can easily be seen, the solutions of

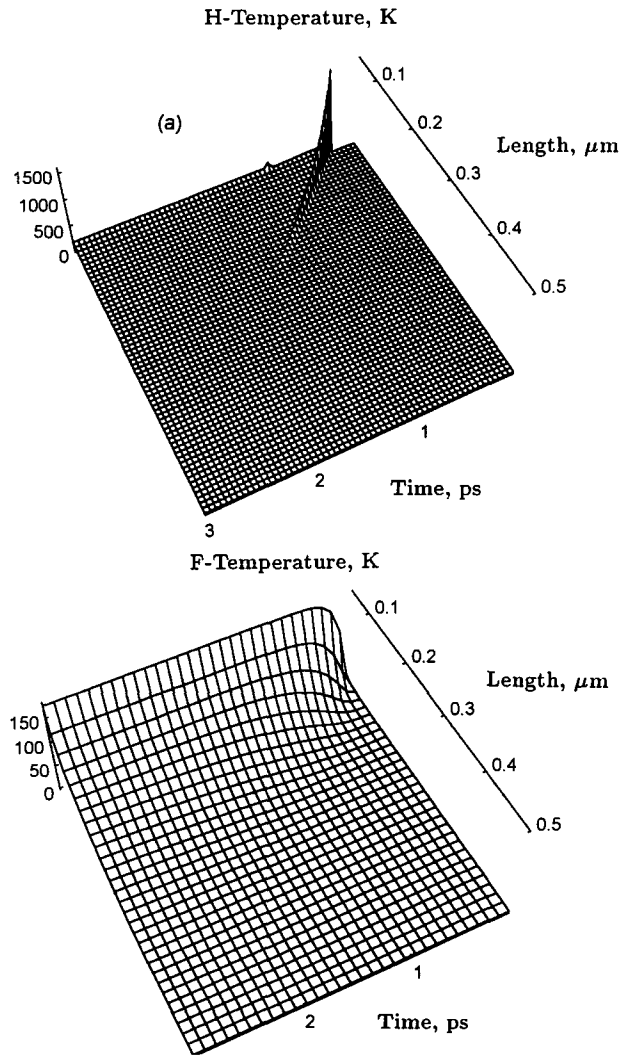

Fig. 2. (a) The same as Fig. 1a but with Δt-pulse duration = 0.02 ps. (b) The same as Fig. 1b, but with $\Delta t = 0.02$ ps.

HHC equations (Figs. 1a and 2a) show the retardation of the response of the system to the external thermal perturbation. The temperature surface shows the effect of the thermal inertia. Moreover, the shorter the Δt, the more localized is the temperature surface. For the solution of PHC (Figs. 1b and 2b) the instant heating of the system is observed without any signature of the inertia of the system, and the temperature in system is smeared out.

5. CONCLUSION

In the present paper the thermal inertia of the heat carriers in thin metal films was investigated. It was shown that the inherent feature of the solution of HHC is the inertia of heat transfer. The signatures of the inertia are (i) the retardation of the heating process in comparison to the time of the external perturbation and (ii) the strong localization of the thermal excitation.

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