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Thermalization time of thin metal film heated by short pulse laser*

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Based on the hyperbolic two-step heat conduction model, using the Laplace transform and numerical inverse transform method (Riemann-sum approximation method), the thermal behaviour of thin metal films has been studied during femtosecond pulse laser heating. Also the thermalization time, which is the time for the electron gas and solid lattice to reach thermal balance, has been studied in detail. The values of thermalization time for silver (Ag), gold (Au), copper (Cu) and lead (Pb) are obtained. The effects of material parameters of the thin metal film on the thermalization time are considered for the four kinds of metals by changing one of the parameters and regarding the other parameters as constant. For a typical metal material, the order of the thermalization time is of the order of hundreds of picoseconds. The thermalization time decays exponentially with the increase of phonon–electron coupling factor or electron gas thermal conductivity, and it increases linearly with the increase of the ratio of lattice heat capacity to electron gas heat capacity. However, the relaxation time of the electron gas has very little effect on the thermalization time.

Keywords: non-equilibrium thermal behaviour, thermalization time, hyperbolic two-step model, short pulse laser

PACC: 6780G, 7215L, 4410, 4255V

1. Introduction

To date, the laser pulse can be shortened to the range of femtosecond (10^{-15}s),[1,2] so as to make controls of the penetration depth and processing time of a material more effective and accurate. Because of the advancement of short-pulse laser technologies and their applications to modern microfabrication technologies, high-rate heating of thin metal films is a rapidly emerging area in heat transfer.

In applications involving high-rate heating, when a thin film is heated very rapidly, such as heated by a short-pulse laser, the typical response time is of the order of picoseconds,[3] which is comparable to the phonon–electron thermal relaxation time. Under these situations, thermal equilibrium between the solid lattice and the electron gas cannot be assumed and heat transfer in the electron gas and the metal lattice needs to be considered separately. Two microscopic heat conduction models describing the non-equilibrium thermal behaviour in such cases are available in the literature. The first one is the parabolic two-step model pioneered by Anisimov and advanced later by Fujimoto *et al.*[1] The second one is the hyperbolic two-step model introduced by Qiu and Tien,[3] based on the macroscopic averages of the electric and heat currents carried by electrons in momentum space.

The parabolic two-step model involves two coupled energy equations governing the heat transfer in the electron gas and the solid lattice. Solutions for this model can be found in the literature for different operating and boundary conditions by using different solutions methodologies.[3–14] Based on the parabolic two-step heat conduction model, Wang and Zhang[4] studied the thermal behaviour of thin metal films under harmonic thermal boundary conditions.

On the other hand, the hyperbolic two-step model, in its simplest form, involves three coupled equations. This model does not account for the conduction of heat by phonons and for the absorption of the incident laser energy by the electron gas.[5,6]

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Qiu and Tien[7] studied the thermal behaviour of multi-layer metals by numerical method (semi-implicit Crank–Nicholson scheme) and experiments. Using a perturbation technique, Al-Nimr *et al*[10,11] eliminated the coupling between the energy equations, which have the same order as the original coupled equations. During ultrafast laser heating, a simple single-layer metal film could be solved analytically by the proposed perturbation technique. By using the same method, the heat transfer mechanism of two thin metal films in perfect thermal contact was studied, and the analytical solution has been obtained employing Green's function. Using the Laplace transform method, Song *et al*[12] investigated the effects of convective thermal losses on the thermal behaviour of thin metal films. A finite-difference algorithm was presented for obtaining the solution of the hyperbolic two-step heat conduction model.[13] The uncoupled characteristic equations are derived from the governing equations of the temperature in the metal film, and the Godunov scheme is applied to solve the characteristic equations, and thus the thermal responses are obtained from the relation between the characteristic equations and the governing equations. Employing the hyperbolic two-step heat conduction model, Al-Nimr *et al*[14] investigated the effect of radiative thermal losses on the thermal performance of a thin metal film. Here he considered the thermal losses under different operating conditions, different geometrical parameters and different metal properties.

However, according to the studies of Al-Nimr, the proposed perturbation technique is only suitable for metal films with very high phonon–electron coupling factor because it demands that the thermalization time be very short. But according to the works of Song *et al*[12] and Tzou,[5,6] for most typical metals, such as Au, Ag, Cu and Pb, the thermalization time is much longer than one picosecond. Unfortunately, there are few quantitative data available to describe the thermalization time for most typical metals during short pulse laser heating. And how does the thermalization time depend on the film material parameters quantitatively? To the author's knowledge, there have not been papers on this subject yet.

In order to obtain the thermalization time to study the effects of metal material parameters on it, in this work, based on the hyperbolic two-step heat conduction model and using the Laplace transform and numerical inverse transform method (Riemann-sum approximation method), the thermal behaviour in the thin metal film during femtosecond pulse laser heating is studied. In terms of this microscopic two-step model, the heating process is investigated as follows: first, the deposition of radiation energy on electrons; second, the transport of energy by electrons; and then the heating of the material lattice through electron–phonon interactions. The effects of material parameters of the thin metal film on the time for phonon–electron thermal equilibrium are studied. As samples, four kinds of metals such as Ag, Au, Cu and Pb are discussed in detail.

2. Mathematic formulae and solutions in Laplace transform domain

Consider an infinite thin film of thickness L, which occupies a space of $0 \leq x \leq L$, and is heated by a pulse laser at the surface $x=0$. The pulse laser is in a Gaussian distribution as follows:[7]

$$Q = 0.94J\frac{1-R}{t_{\mathrm{p}}\delta}\mathrm{e}^{-\frac{x}{\delta}-a\frac{|t-2t_{\mathrm{p}}|}{t_{\mathrm{p}}}}, \tag{1}$$

where J is laser fluence, which is the total energy, carried by a laser pulse divided by the cross-section of the laser spot. R is the reflectivity of the film, t_{p} is the full-width-at-half-maximum (FWHM) duration of the laser pulse, δ is the radiation penetration depth, and a is a constant.

Qiu and Tien[3] presented a microscopic two-step model:

$$C_{\mathrm{e}}(T_{\mathrm{e}})\frac{\partial T_{\mathrm{e}}}{\partial t} = -\nabla q - G(T_{\mathrm{e}} - T_{\mathrm{l}}) + Q, \tag{2}$$

$$C_{\mathrm{l}}(T_{\mathrm{l}})\frac{\partial T_{\mathrm{l}}}{\partial t} = G(T_{\mathrm{e}} - T_{\mathrm{l}}), \tag{3}$$

$$\tau_{\mathrm{F}}\frac{\partial q}{\partial t} + k_{\mathrm{e}}(T_{\mathrm{e}})\nabla T_{\mathrm{e}} + q = 0, \tag{4}$$

where T_{e}, T_{l}, and q represent electron temperature, solid lattice temperature and heat flux, respectively. C_{e} and C_{l} are heat capacities of the electron gas and the lattice, respectively; k_{e} is electron heat conductivity, τ_{F} is the relaxation time of the electron gas; x and t are space and time coordinates, respectively. G is phonon–electron coupling factor.

In the simple case of constant thermal property of the material, the one- dimensional non-dimensional governing equations are

$$\frac{\partial T_{\mathrm{e}}^*}{\partial t^*} = -\frac{\partial q^*}{\partial x^*} - (T_{\mathrm{e}}^* - T_{\mathrm{l}}^*) + Q^*, \tag{5}$$

$$C_{\mathrm{R}}^*\frac{\partial T_{\mathrm{l}}^*}{\partial t^*} = (T_{\mathrm{e}}^* - T_{\mathrm{l}}^*), \tag{6}$$

$$\tau_{\rm F}^*\frac{\partial q^*}{\partial t^*}+k_{\rm e}\frac{\partial T_{\rm e}^*}{\partial x^*}+q^*=0, \tag{7}$$

where

$$T^*=\frac{T-T_0}{T_0},\quad x^*=\frac{x}{L},\quad q^*=\frac{q}{GT_0L},$$

$$k_{\rm e}^*=\frac{k_{\rm e}}{L^2G},\quad \tau_{\rm F}^*=\frac{G\tau_{\rm F}}{C_{\rm e}},$$

$$Q^*=\frac{Q}{GT_0},\quad C_{\rm R}^*=\frac{C_{\rm l}}{C_{\rm e}},$$

T_0 is initial temperature and L is the thickness of the film.

The non-dimensional initial and boundary conditions can be described as

$$\begin{aligned}&T_{\rm e}^*(x^*,0)=T_{\rm l}^*(x^*,0)=0,\\ &\frac{\partial T_{\rm e}^*}{\partial t^*}(x^*,0)=\frac{\partial^2 T_{\rm e}^*}{\partial t^{*2}}(x^*,0)=0,\\ &\frac{\partial T_{\rm l}^*}{\partial t^*}(x^*,0)=\frac{\partial^2 T_{\rm l}^*}{\partial t^{*2}}(x^*,0)=0,\end{aligned} \tag{8}$$

$$\begin{aligned}\left.\frac{\partial T_{\rm e}^*}{\partial x^*}\right|_{x^*=0}&=\left.\frac{\partial T_{\rm e}^*}{\partial x^*}\right|_{x^*=1}=0,\\ \left.\frac{\partial T_{\rm l}^*}{\partial x^*}\right|_{x^*=0}&=\left.\frac{\partial T_{\rm l}^*}{\partial x^*}\right|_{x^*=1}=0.\end{aligned} \tag{9}$$

Now, one can obtain the energy equation for lattice temperature by eliminating electron gas temperature $T_{\rm e}^*$ and heat flux vector q^* in Eqs.(5)–(7):

$$\begin{aligned}&(1+C_{\rm R}^*)\frac{\partial T_{\rm l}^*}{\partial t^*}+[C_{\rm R}^*+\tau_{\rm F}^*(1+C_{\rm R}^*)]\frac{\partial^2 T_{\rm l}^*}{\partial t^{*2}}\\ &+\tau_{\rm F}^*C_{\rm R}^*\frac{\partial^3 T_{\rm l}^*}{\partial t^{*3}}\\ =&k_{\rm e}^*\frac{\partial^2 T_{\rm l}^*}{\partial x^{*2}}+k_{\rm e}^*C_{\rm R}^*\frac{\partial^3 T_{\rm l}^*}{\partial x^{*2}\partial t^*}+Q^*+\tau_{\rm F}^*\frac{\partial Q^*}{\partial t^*}.\end{aligned} \tag{10}$$

By using the initial conditions in Eq.(8), the Laplace transform equation is obtained. In the following, the superscript, a bar, denotes variables in the Laplace transform domain. For convenience, the superscript, *, is omitted:

$$\frac{\partial^2\bar{T}_{\rm l}}{\partial x^2}-\lambda^2\bar{T}_{\rm l}=\frac{(1+\tau_{\rm F}p)\bar{Q}-\tau_{\rm F}Q_0}{k_{\rm e}(1+C_{\rm R}p)}, \tag{11}$$

where

$$\begin{aligned}\lambda=&\sqrt{\frac{p(1+C_{\rm R}+C_{\rm R}p)(1+\tau_{\rm F}p)}{k_{\rm e}(1+C_{\rm R}p)}},\\ Q_0=&S_0{\rm e}^{-2a}{\rm e}^{-x/\delta},\\ \bar{Q}=&S_0S_b{\rm e}^{-x/\delta},\\ S_0=&0.94J\frac{1-R}{t_{\rm p}\delta},\end{aligned}$$

$S_b=t_{\rm p}\left[\dfrac{{\rm e}^{-2a}-{\rm e}^{-2pt_{\rm p}}}{pt_{\rm p}+a}+\dfrac{{\rm e}^{-2pt_{\rm p}}}{pt_{\rm p}-a}\right]$ and $\delta, t_{\rm p}, x$ in the above equation are dimensionless quantities.

Using Eq.(11) and boundary conditions (9), we can obtain the lattice temperature in the Laplace transform domain:

$$\bar{T}_{\rm l}(x,p)=C\left[\frac{{\rm e}^{-1/\delta-\lambda x}-{\rm e}^{-(x+1)\lambda}+{\rm e}^{-1/\delta+\lambda x}-{\rm e}^{-(1-x)\lambda}}{\delta\lambda({\rm e}^{\lambda}-{\rm e}^{-\lambda})}-{\rm e}^{-x/\delta}\right], \tag{12}$$

where

$$C=\frac{S_0\left[\tau_{\rm F}{\rm e}^{-2a}-(1+\tau_{\rm F}p)S_{\rm b}\right]}{k_{\rm e}(1+C_{\rm R}p)(1/\delta^2-\lambda^2)}.$$

Also, the electron gas temperature in Laplace transform is obtained, as follows:

$$\bar{T}_{\rm e}=(1+C_{\rm R}p)\bar{T}_{\rm l}. \tag{13}$$

3. Numerical inversion Laplace transform method

In order to invert the Laplace transform in the above equations, a numerical technique is used based on Fourier expansion of functions. Let $\bar{g}(s)$ be the Laplace transform of a function $g(t)$. The inversion formula of Laplace transform states is

$$g(t)=\frac{1}{2\pi i}\int_{b-{\rm i}\infty}^{b+{\rm i}\infty}\bar{g}(s){\rm e}^{st}{\rm d}s, \tag{14}$$

where b is an arbitrary constant greater than all real parts of the singularities of $g(t)$. Taking $s=b+{\rm i}y$, we have

$$g(t)=\frac{{\rm e}^{bt}}{2\pi}\int_{-\infty}^{+\infty}{\rm e}^{{\rm i}ty}\bar{g}(b+{\rm i}y){\rm d}y. \tag{15}$$

The Fourier integral thus obtained can be approximated by its Riemann sum. Denoting y as the wave frequency and t_1 the half-period of its oscillations, i.e. $y=j\pi/t_1$ for the nth wave mode and $\Delta y_n=\pi/t_1$ for all modes, we can obtain

$$g(t)=\frac{{\rm e}^{bt}}{t_1}\left[\frac{1}{2}\bar{g}(b)+{\rm Re}\left(\sum_{j=1}^{\infty}{\rm e}^{ij\pi t/t_1}\bar{g}(b+ij\pi/t_1)\right)\right]. \tag{16}$$

For numerical purposes this is approximated by

the function

$$g_N(t)\approx\frac{\mathrm{e}^{bt}}{t_1}\left[\frac{1}{2}\bar{g}(b)+\mathrm{Re}\left(\sum_{j=1}^{N}\mathrm{e}^{ij\pi t/t_1}\bar{g}(b+ij\pi/t_1)\right)\right], \tag{17}$$

where N is a sufficiently large integer chosen such that

$$\mathrm{e}^{bt}\mathrm{Re}\left[\mathrm{e}^{\mathrm{i}N\pi t/t_1}\bar{g}(b+\mathrm{i}N\pi t/t_1)\right]<\xi, \tag{18}$$

in which ξ is the chosen small positive number that corresponds to the degree of accuracy to be achieved. Equation (18) is the numerical inversion formula valid for $2t_1 \geq t \geq 0$.[15] In particular, we choose $t = t_1$, and obtain

$$g_N(t)\approx\frac{\mathrm{e}^{bt}}{t_1}\left[\frac{1}{2}\bar{g}(b)+\mathrm{Re}\left(\sum_{j=1}^{N}(-1)^j\bar{g}(b+ij\pi/t_1)\right)\right]. \tag{19}$$

4. The solution of lattice temperature and electron gas temperature in physics domain and the discussions of thermalization time

Using the above numerical method, we obtain the electron gas temperature and the lattice temperature in the physics domain. As an example, the temperature profiles along the thickness direction and its time history are calculated for gold film. The numerical results are listed in Figs.1 and 2. The thermalization times of the four kinds of metals, Ag, Au, Cu and Pb, are obtained. They are 0.9, 0.915, 0.7525 and 0.4657ns, respectively. By changing one of the material parameters of the thin film, such as G, k_e, τ_F and C_R, and regarding the other parameters as constant, the effects of these parameters on thermalization time are considered.

In the calculation, the pulse laser parameters and the material parameters for the four kinds of metals are listed in Tables 1 and 2.[6] In each calculation, the film thickness, L, is set to be 0.1μm and the initial temperature, T_0, is taken to be 300K.

Table 1. The pulse laser parameters in the calculation.

Laser parameters	J/Jm^{-2}	R	δ/nm	t_p/fs	a
Values	13.4	0.93	15.3	100	1.88

Table 2. The material parameters of the metal films in the calculation.

	$k_\mathrm{e}/\mathrm{Wm}^{-1}\mathrm{K}^{-1}$	$C_\mathrm{l}/10^6\mathrm{Jm}^{-3}\mathrm{K}^{-1}$	$C_\mathrm{e}/10^4\mathrm{Jm}^{-3}\mathrm{K}^{-1}$	$G/10^{16}\mathrm{Jm}^{-3}\mathrm{K}^{-1}$	τ_F/ps
Ag	419	2.5	2.1	2.8	0.04
Au	315	2.5	2.1	2.8	0.04
Cu	386	3.4	2.1	4.8	0.03
Pb	35	1.3	2.1	2.4	0.005

Figure 1 shows the dimensionless temperature profile of electron gas (a) and lattice (b) for various durations of the laser pulse. At the early stage, it is easily found that the temperature difference between the front and rear surfaces of the film due to the thermal relaxation time and between the electron gas and the lattice due to the two-step model of energy transfer are distinct. As the duration becomes longer, these temperature differences will disappear. For this example, the time is about hundreds of picosecond.

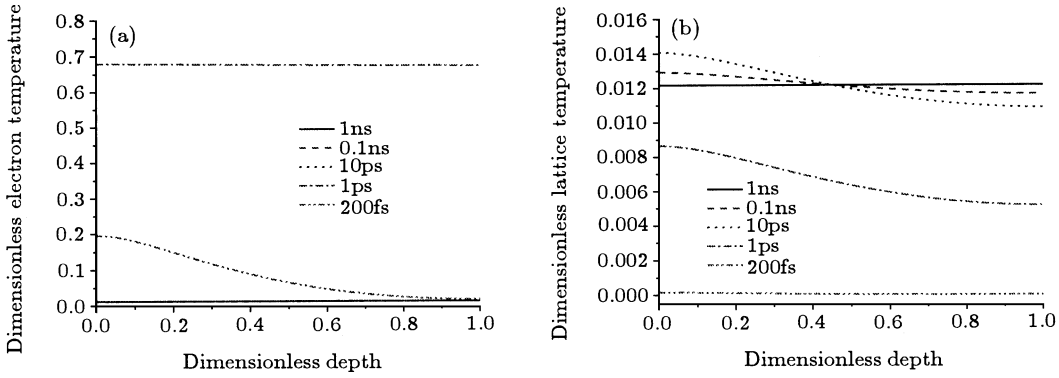


Fig.1. Dimensionless temperature profile of electron gas (a) and lattice (b) for various durations (for 0.1μm thick gold film during 200fs laser pulse heating, J=13.4J/m^2).

Figure 2 presents dimensionless temperature variations of electron gas (a) and lattice (b) in thin film at the front and the rear surface. These results are for τ_F=0.04ps and τ_F=0.7838ps in Fig.2. For τ_F=0.7838ps, the result agrees well with the result in Ref.[13]. From this we can see that if the thermal relaxation time of electron gas is long, the temperature variation phenomenon will appear.

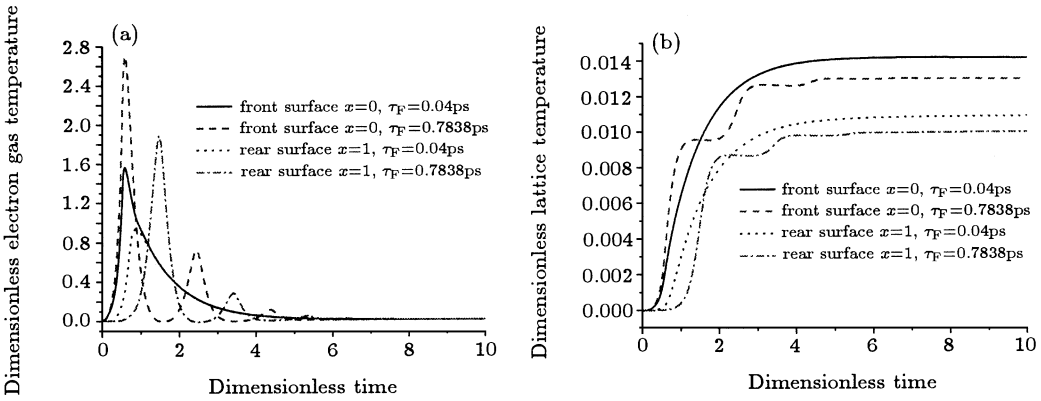


Fig.2. Dimensionless temperature variation of electron gas (a) and lattice (b) in the thin film at the front (x=0) and the rear (x=1) surface (for 0.1μm thick gold film during 200fs laser pulse heating, J=13.4J/m^2).

Figures 3–6 show the effects of film material parameters, such as phonon–electron coupling factor (G), thermal relaxation time of electron gas (τ_F), thermal conductivity of electron gas (k_e), and the ratio of lattice heat capacity to electron gas heat capacity (C_R), on thermalization time. In Figs.3–6, the variation range of G is from 0.1 to 20 times of its real value of the film; the variation range of τ_F, k_e and C_R are all from 0.1 to 2 times of their real values. In the calculations, it is assumed that the thermal balance between electron gas and lattice is reached if the temperature difference between electron gas and lattice is smaller than 10^{-5}, and this duration is taken as the thermalization time.

Also, according to the numerical calculations, the fitted curves are presented. Equations (20)–(22) below are fitting formulations, where A, B, A_1, A_2, A_3, t_1, t_2, t_3 and y_0 are fitting coefficients. Their values are listed in corresponding figures.

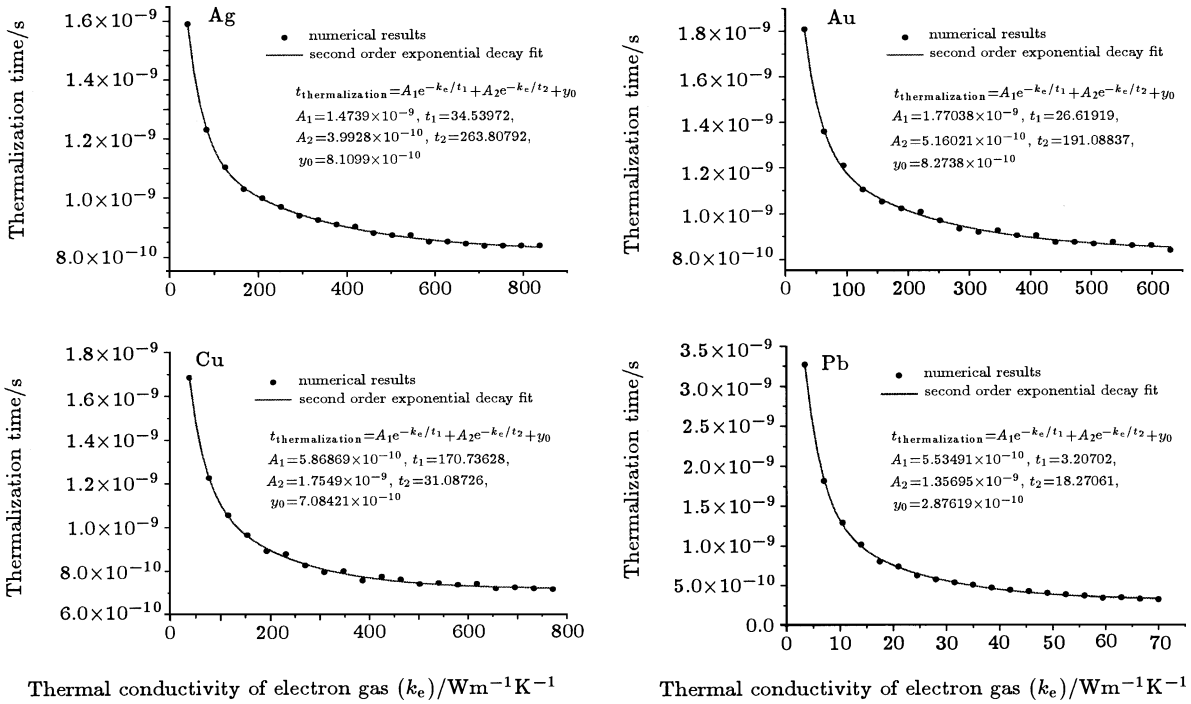


Fig.3. Thermalization time for various thermal conductivities.

Figure 3 shows the effect of the variation of k_e on thermalization time for the four kinds of metals. According to Fig.3, it is shown that the thermalization time decreases with the increase of electron gas thermal conductivity. From the point of view of the physics, the increase of the electron gas thermal conductivity makes the rate of energy exchange between phonon and lattice accelerate and the heat flux propagate more rapidly. So the thermalization time decreases. The second-order exponential decay fits well with the numerical results. The fitting formulation is

$$t_{\text{Thermalization}} = A_1 e^{-k_e/t_1} + A_2 e^{-k_e/t_2} + y_0. \quad (20)$$

Figure 4 shows the effect of the variation of G on the thermalization time for the four kinds of metals. According to Fig.4, it is shown that the thermalization time decreases with the increase of coupling factor. From the point of view of the physics, the increase of phonon–electron coupling factor can accelerate the energy exchange between electron and lattice. As a result, the thermalization time decreases. The third-order exponential decay fits well with the numerical results. The fitting formulation is

$$t_{\text{Thermalization}} = A_1 e^{-G/t_1} + A_2 e^{-G/t_2} + A_3 e^{-G/t_3} + y_0. \quad (21)$$

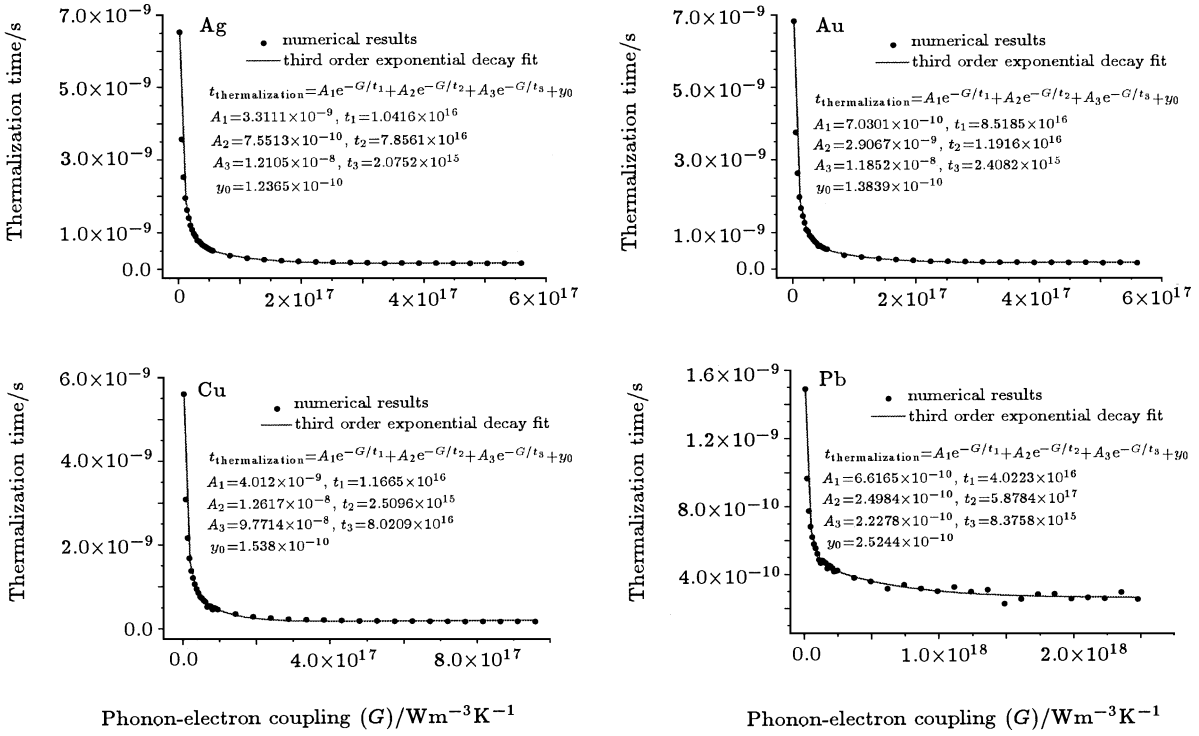


Fig.4. Thermalization time for various coupling factors.

Figure 5 shows the effect of the variation of C_R on the thermalization time for the four kinds of metals. According to Fig.5, it is shown that the thermalization time increases linearly with the increase of the ratio of lattice heat capacity to electron gas heat capacity. From the point of view of physics, in order to raise the lattice temperature, more energy transferred from electron gas is demanded. So the thermalization time increases. The linear curve fits well with the numerical results. The fitting formulation is

$$t_{\text{Thermalization}} = A + BC_R. \quad (22)$$

Figure 6 shows the effect of the variation of τ_F on the thermalization time for the four kinds of metals. From Fig.6, we see that the thermalization time almost keeps constant with the variation of τ_F. Namely, τ_F has very little effect on the thermalization time. In physics, for most typical metallic materials, the relaxation time of electron gas is of the order of 10^{-14}, but the thermalization time is of the order of 10^{-10}. So the effect of relaxation time τ_F on thermalization time may be very small. The fitting formulation has the same form as Eq.(22), but A and B are different and C_R is replaced by τ_F.

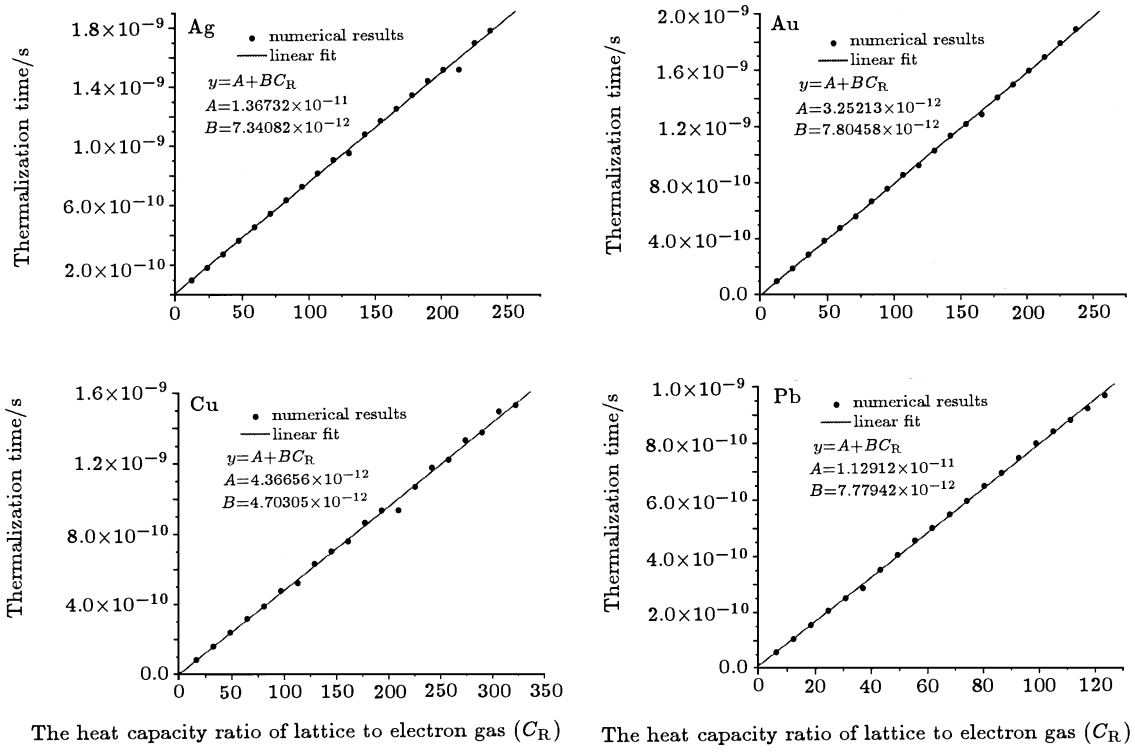


Fig.5. Thermalization time versus heat capacity ratio.

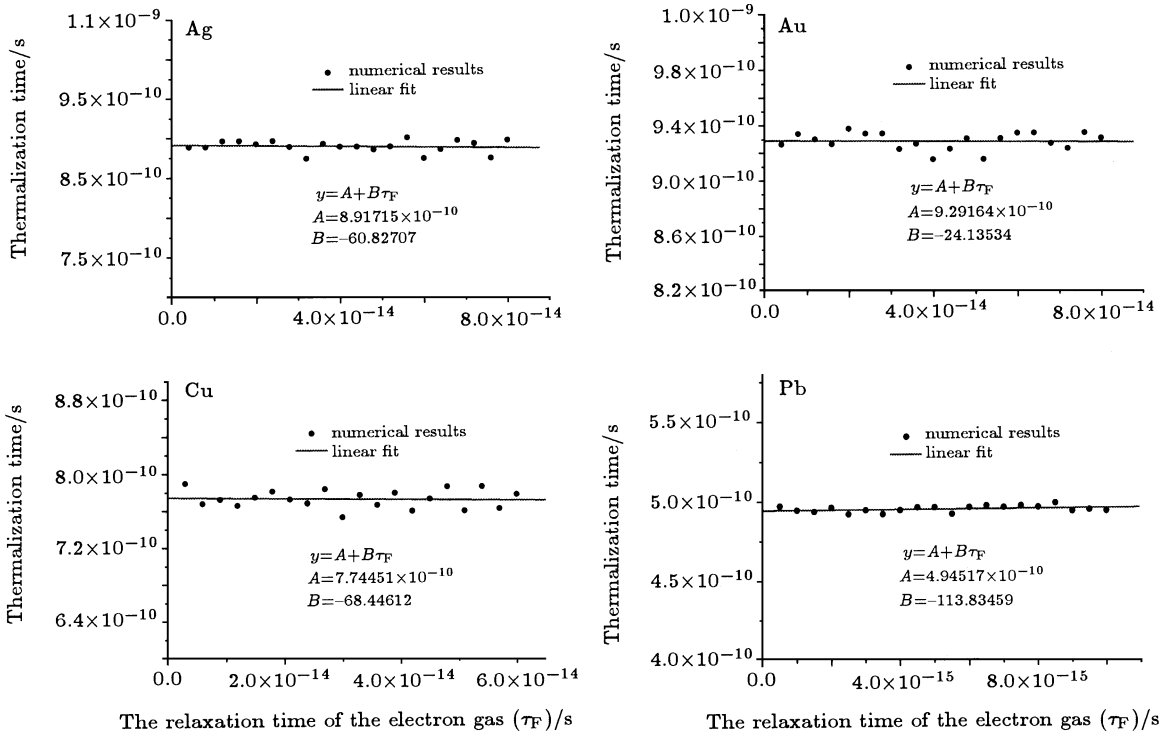


Fig.6. Thermalization time versus relaxation time of the electron gas.

5. Conclusion

Based on the hyperbolic two-step heat conduction model and using the Laplace transform and numerical inverse transform method (Riemann-sum approximation method), the thermal behaviour of thin metal films heated by a femtosecond pulse laser is studied. The analytical solution in the Laplace transform do-

main is obtained. In the physics domain, the numerical results of the temperature profiles of the electron gas and lattice in space coordinate and time coordinate are given by graphs. The effects of thin metal film material parameters on thermalization time are discussed. Four kinds of metals, Ag, Au, Cu and Pb, are used in numerical calculations. The results show that the thermalization time decays exponentially with the increase of phonon–electron coupling factor or electron gas thermal conductivity, and increases linearly with the ratio of lattice heat capacity to electron gas heat capacity, but is not affected by the relaxation time of the electron gas. For a typical metal material, such as Au and Cu, the thermalization time is in the order of hundreds of picosecond. For example, the thermalization times of Ag, Au, Cu and Pb are 900ps, 915ps, 752.5ps and 465.7ps, respectively.

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