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The Local-Nonequilibrium Temperature Field Around the Melting and Crystallization Front Induced by Picosecond Pulsed Laser Irradiation[1]

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The local-nonequilibrium model for heat transport around melting and crystallization zone induced by ultrafast laser irradiation is considered. The model predicts strong overheating during melting of the material near the interface. Moreover, the local-nonequilibrium effects lead to an interface temperature gradient steeper than expected from the classical heat flow calculations. Possible modification of the kinetics of melting to include the relaxation effects is also discussed.

KEY WORDS: hyperbolic heat conduction; local-nonequilibrium effects; melting; overheating; pulse heating; Stefan problem; ultrafast heat transport.

1. INTRODUCTION

Pulse laser processing of materials, especially semiconductors, is a field of condensed matter physics and materials science that has developed rapidly over the recent years. It has proved to be of considerable interest in both applied and fundamental research for a variety of reasons discussed extensively in the literature [1–13]. Irradiation of materials with laser pulses in the nanosecond to picosecond range extends traditional studies of melting–solidification kinetics and thermodynamics to extreme velocities. It provides a unique tool for well-controlled studies of physical processes occurring far from thermodynamic equilibrium. Most existing theoretical models [1–3] rely on equilibrium thermodynamics and assume a local equilibrium at the solid–liquid interface. For low interface velocities this assumption is valid. However, the motion of phase interface induced by

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laser pulses in the nanosecond to picosecond range can be so rapid [4–10] that the local equilibrium assumption is no longer valid and deviations from local equilibrium at the interface must be considered. The hyperbolic [11, 12, 16] and two-temperature [13, 16] phase change problems, which go beyond the local-equilibrium assumption, have received little attention in the literature.

The most active branch in phenomenological nonequilibrium thermodynamics, which does not adopt the local-equilibrium assumption, is the so-called extended irreversible thermodynamics (EIT) [14]. EIT introduces a phenomenological generalized entropy, as well as other thermodynamic functions, which, in addition to the usual local-equilibrium variables, encludes dissipative fluxes as independent variables.

The motion of phase interface during pulsed laser irradiation is determined by two distinct processes: (i) interface kinetics, i.e., the rate at which atoms leave and join phases, and (ii) heat-flow balance between conduction into the substrate, energy of a laser pulse, and enthalpy change at the interface. The objective of this paper is to provide a conceptual foundation, and a mathematical model based on it, for the study of the heat transport and interface kinetics associated with rapid melting and solidification during pulsed laser irradiation. This is achieved by using the concepts of EIT.

2. LOCAL-NONEQUILIBRIUM TEMPERATURE FIELD

2.1. Equations

According to EIT, the heat flux q is an independent variable, and in the simplest case its evolution is governed by the Maxwell–Cattaneo equation [14] (see also Refs. 15 and 16),

$$q+\tau\frac{\partial q}{\partial t}=-\lambda\,\nabla T \tag{1}$$

where τ is the relaxation time of q, T is the temperature, and λ is the thermal conductivity. Introducing Eq. (1) into the energy balance equation

$$cp\frac{\partial T}{\partial t}=-\nabla q+W \tag{2}$$

one is led, for constant coefficients τ, λ, and C, to the hyperbolic heat conduction equation (HHCE)

$$cp\frac{\partial T}{\partial t}+\tau cp\frac{\partial^2 T}{\partial t^2}=\lambda\,\nabla^2 T+W+\tau\frac{\partial W}{\partial t} \tag{3}$$

where c is the specific heat, p is the mass density, and W is the heat source due to the laser pulse. The hyperbolic equation, Eq. (3), differs from the usual heat conduction equation of the diffusion type by having two additional terms: a second-order time derivative of the temperature, $\partial^2 T/\partial t^2$, and a first-order time derivative of the heat source, $\partial W/\partial t$. The presence of the second-order time derivative is conceptually important because it allows one to avoid the paradox of propagation of thermal disturbances with an infinite velocity [14, 15]. Although the presence of the time derivative of the intensity of the heat source, $\partial W/\partial t$, in Eq. (3), does not affect the total energy balance of the system, it does significantly influence the shape of the pulse of energy absorbed by the system, i.e., the shape becomes $W + \tau\, \partial W/\partial t$. The additional time derivatives $\partial^2 T/\partial t^2$ and $\partial W/\partial t$ in Eq. (3) can be described as a thermal "inertia" [14–16]. Note that the presence of the second-order derivative in time makes it necessary to supplement Eq. (3) with the additional initial condition $\partial T/\partial t\,|_{t=0}$.

Eliminating T from Eqs. (1) and (2), one can derive an equation for the heat flux q, and like Eq. (3), this equation is of the hyperbolic type:

$$\frac{\partial q}{\partial t} + \tau \frac{\partial^2 q}{\partial t^2} = a\,\nabla(\nabla q) - a\,\nabla W \tag{4}$$

where $a = \lambda/cp$ is the thermal diffusivity. Both Eq. (3) and Eq. (4) imply a finite speed of thermal disturbances,

$$U = (a/\tau)^{1/2} \tag{5}$$

Note that the heat flux q is now an independent variable and one needs to supplement Eq. (4) with two initial conditions, $q\,|_{t=0}$ and $\partial q/\partial t\,|_{t=0}$.

2.2. Interface Conditions

To derive the interface conditions, we integrate Eqs. (1) and (2) over an infinitesimal zone that includes the interface. For the sake of simplicity, we assume that the parameters C, p, and λ do not change at the interface. In such a ease, the interface conditions are given as [16]

$$[T] = \frac{V}{U^2}\frac{Q}{cp}\left(1 - \frac{V^2}{U^2}\right)^{-1} \tag{6}$$

$$[q] = Q\left(1 - \frac{V^2}{U^2}\right)^{-1} \tag{7}$$

where brackets denote the difference in a value ahead of and behind the interface, V is the interface velocity, and Q is the total heat released at the interface. The interface conditions, Eqs. (6) and (7), for the hyperbolic phase change problem, Eqs. (3) and (4), clearly demonstrate that the interface is a surface of strong discontinuity, i.e., there are jumps in temperature, Eq. (6), and heat flux, Eq. (7), at the interface. If $\tau \to 0$ and, hence, $U \gg V$, the jump conditions, Eqs. (6) and (7), reduce to the classical interface conditions $[T]=0$ and $[q]_{\text{eq}}=Q$. In such a case the temperatures ahead of the interface T_1 and behind the interface T_2 are equal to the temperature of the equilibrium phase transition (melting temperature) T_{m}. For a relatively high interface velocity $V \sim U$, the local-nonequilibrium nature of heat transport under extreme conditions leads to the temperature jump $[T]=T_1-T_2 \neq 0$ at the interface. Note that the jumps in temperature, Eq. (6), and heat flux, Eq. (7), at the interface result from the assumption of the infinitely thin region of phase change. In the case of the interface of finite width, Eq. (6) and (7) give the temperature and heat flux change over the interface width [16]. The temperature discontinuity can also be smoothed by introduction in HHCE, Eq. (3), the effective "temperature viscosity," i.e., an additional mixed derivative $\partial^3 T/\partial t\, \partial X^2$ [15]. Such an additional mixed derivative arises in the two-temperature heat conduction model [13, 16] and in EIT [14] due to spatial nonlocal effects.

Taking into account the energy balance at the interface, the jump condition, Eq. (6), can be written in another form:

$$\frac{T_1-T_2}{T_2-T_0}=\frac{V^2}{U^2}\left(1-\frac{V^2}{U^2}\right)^{-1} \tag{8}$$

where T_0 is the initial temperature. At reasonable values for $U \sim 10^3 \text{m} \cdot \text{s}^{-1}$ [7] and $V^2/U^2=0.3$, which corresponds to the laser heating experiments [6–10, 17], the jump condition, Eq. (8), gives strong interface overheating $T_1-T_2=0.43(T_2-T_0)$. In the approximation $T_2 \approx T_{\text{m}}$ and $T_{\text{m}} \gg T_0$, we obtain $T_1-T_{\text{m}}=0.43T_{\text{m}}$, which is in agreement with the experimental results [6–10, 17].

The interface conditions, Eqs. (6) and (7), are written in terms of both T and q. Eliminating q between Eq. (1) and Eq. (7), the interface condition for the temperature field is found:

$$-\lambda\frac{\partial T_1}{\partial X}=-\lambda\frac{\partial T_2}{\partial X}+A+\tau\dot{A}-L(V+\tau\dot{V}(1+2V^2/U^2))(1-V^2/U^2)^{-1} \tag{9}$$

where A is the heat flux due to an external heat source, L is the latent heat of phase transition, and the superscript dot implies differentiation with respect to time. The new interface condition, Eq. (9), includes not only the interface velocity and the external heat flux, but also the interface acceleration and the time derivative of the flux. This is also a consequence of a thermal "inertia" in local-nonequilibrium systems.

The interface condition, Eq. (7), limits the value of possible velocities of the interface V. At $[q] \to \infty$, the interface condition, Eq. (7), implies that $V \to U$, in contrast to the classical case where $V \to \infty$. Such a limitation is valid for the phase-change wave with thermal mechanism of propagation due to heat conduction. Other types of phase-change waves with nonthermal mechanism of propagation, for example, shock waves, can propagate with $V > U$. EIT limits the value of heat flux itself and yields a maximum value for the heat flux at a given energy density $q_{\max} = c\rho TU$ [18]. Hence, the maximum value for $V = V_{\max}$ is less than U and can be estimated from

$$c\rho TU = LV_{\max}(1 - V_{\max}^2/U^2)^{-1}.$$

2.3. Steady-State Regime

Let us consider the interface moving with a constant velocity V. Such a steady-state regime can be described by HHCE, Eq. (3), in a frame of reference moving with velocity V in the X direction:

$$\left(1 - \frac{V^2}{U^2}\right)\frac{d^2T}{dX^2} + \frac{V}{a}\frac{dT}{dX} + \frac{1}{\lambda}\left(W - \tau V\frac{dW}{dX}\right) = 0 \tag{10}$$

Ahead of the interface $X > 0$ there is no external heat source, i.e., $W = 0$, and this equation results:

$$T(X) = (T_1 - T_0)\exp(\mu X) + T_0$$

$$\mu = -\frac{V}{a}\left(1 - \frac{V^2}{U^2}\right)^{-1} \tag{11}$$

These expressions describe the steady-state temperature profiles ahead of the interface $X > 0$ in a moving reference frame (its origin $X = 0$ fixed on the interface). The characteristic dimension X^* of the heated layer ahead of the interface is determined by the following relation:

$$X^* = \mu^{-1} = \frac{a}{V}\left(1 - \frac{V^2}{U^2}\right) \tag{12}$$

It follows from Eq. (12) that $X^* \to 0$ as $V \to U$. This result differs fundamentally from the classical case, where $X^* \to 0$ only when $V \to \infty$.

In the classical case $V \ll U$, Eqs. (8) and (11) yield a continuous temperature profile without overheating:

$$T(X) = (T_m - T_0)\exp(-VX/a) + T_0 \tag{13}$$

At a high melt-front velocity, $V^2/U^2 = 0.3$, the temperature profiles differ substantially from those predicted by the classical theory at $V \ll U$, in Eq. (13). First, the local-nonequilibrium effects lead to strong overheating of the solid. Second, the heated layer, Eq. (12), is much less than the classical heated layer a/V [see Eqs. (11)–(13)]. Third, the local-nonequilibrium heat transport results in the temperature gradient at the interface steeper than expected from classical consideration. Differentiating Eqs. (11) and (13) with respect to X, one obtains

$$\left.\frac{dT}{dX}\right|_{\text{hyp}} = \left.\frac{dT}{dX}\right|_{\text{par}} \left(\frac{T_1 - T_0}{T_m - T_0}\right)\left(1 - \frac{V^2}{U^2}\right)^{-1} \tag{14}$$

At $V^2/U^2 = 0.3$, the hyperbolic model predicts that the interface temperature gradient is twice as high as the temperature gradient expected from the classical, parabolic model [see Eq. (14)]. This effect, i.e., the temperature gradient steeper than expected from the classical heat flow calculations, has been observed in the pulsed laser melting of germanium [8].

3. KINETICS OF LOCAL-NONEQUILIBRIUM MELTING

The phenomenological theory of melting [2] expresses the velocity of a liquid–solid interface as the difference between a melting and a freezing flux, i.e.,

$$V_{\text{sl}} = K_{\text{sl}} - K_{\text{ls}} \tag{15}$$

K_{sl} is the rate (in velocity units) at which atoms leave the solid (subscript s) and join the liquid (subscript l), while K_{ls} is the rate for the reverse process. It is assumed that K_{sl} and K_{ls} represent activated processes and are written as

$$K_{\text{sl}} = \nu_s f_s h_s \exp(-E_2/RT_2) \tag{16}$$

$$K_{\text{ls}} = \nu_l f_l h_l \exp(-E_1/RT_1) \tag{17}$$

where E_2 and E_1 are the activation energies, i.e., the effective barrier heights against $s \to 1$ and $1 \to s$ jumps, respectively; ν_i $(i = \text{s, l})$ is the atomic vibration, or attempt frequency; h_i is the average jump distance; and f_i is the fraction of interracial sites at which attachment can occur. Thus, an expression for melt-front velocity can be obtained in the form [see Eqs. (15)–(17)]

$$V_{sl} = U_s \exp(-E_2/RT_2) - U_l \exp(-E_1/RT_1) \tag{18}$$

in which $U_s = v_s f_s h_s$ is the limit (maximum) for the melting velocity and $U_l = v_l f_l h_l$ is the limit for the crystallization velocity. Here, U_s is of the order of the speed of sound in the solid, which, in turn, is of the order of the speed of heat wave U [see Eq. (5)]. In the equilibrium, i.e., at $V = 0$ and $T_l = T_2 = T_m$, Eq. (18) reduces to

$$U_s \exp(-L/RT_m) = U_l \tag{19}$$

where $L = E_2 - E_1$ is the latent heat of melting at the equilibrium temperature $T = T_m$. Equation (19) clearly demonstrates that the maximum freezing rate U_l is lower than the maximum melting rate U_s by the factor $\exp(-L/RT_m)$. Such "asymmetric" behavior is consistent with the measurements of melting and freezing velocities of amorphous Si and has been interpreted by taking the entropy as the barrier to crystallization and the enthalpy as the barrier to melting [10]. The kinetic approach interprets the asymmetry in terms of the different heights of the effective barriers and different maximum rates for melting and freezing. The rate of melting can be written in the form

$$V_{sl} = U_s\left(1 - \exp\left(-\frac{L}{RT_m} - \frac{E1}{RT_1} + \frac{E_2}{RT_2}\right)\right)\exp\left(-\frac{E_2}{RT_2}\right) \tag{20}$$

In the same way, the rate of freezing can be given as

$$V_{ls} U_l\left(1 - \exp\left(\frac{L}{RT_m} + \frac{E_1}{RT_1} - \frac{E_2}{RT_2}\right)\right)\exp\left(-\frac{E_1}{RT_1}\right) \tag{21}$$

If the system is not far from local-equilibrium, then $T_l = T_2$ and $E_2 - E_1 = L$. In such a case, Eqs. (20) and (21) reduce to

$$V_{sl} = U_s\left(1 - \exp\left(-\frac{L}{RT_m^2}\left(T - T_m\right)\right)\right)\exp\left(-\frac{E_2}{RT_2}\right) \tag{22}$$

$$V_{ls} = U_l\left(1 - \exp\left(\frac{L}{RT_m^2}\left(T - T_m\right)\right)\right)\exp\left(-\frac{E_1}{RT_1}\right) \tag{23}$$

with $T > T_m$ for melting, and $T < T_m$ for solidification. If the interface moves with a high velocity $V \sim U$, then the system is far from local-equilibrium at the interface and the temperature difference $T_2 - T_1$ is determined by the relaxational conditions, Eqs. (6) or (8). According to EIT [14], the generalized Gibbs equation and entropy production equation have the form

$$dS = dS_{\mathrm{eq}} - \frac{\tau}{2\lambda T^2} q \cdot q \tag{24}$$

$$\sigma = \sigma_{\mathrm{eq}} - \frac{\tau}{\lambda T^2} q \cdot \dot{q} \tag{25}$$

where s_{eq} and σ_{eq} are the equilibrium entropy and entropy production, respectively. The nonclassical terms [i.e., the last terms in Eqs. (24) and (25)] come into play when the system is far from local equilibrium, i.e., when the relaxation time τ, is of the order of the characteristic time of the process. In terms of an interface velocity V, the system is far from local equilibrium if $V \sim U$ [16]. In the steady-state regime, i.e., when the interface moves with a constant velocity $V = \mathrm{const}$, Eq. (25) can be rewritten as

$$\sigma = \sigma_{\mathrm{eq}} - \frac{V}{U^2 T^2 cp} q \cdot \frac{dq}{dX} \tag{26}$$

Thus, in the local-nonequilibrium case, the entropy production depends on the interface velocity V. It implies that all the thermodynamic functions (entropy, Gibbs free energy, chemical potential) as well as the effective barrier heights in Eqs. (20) and (21) are velocity dependent. The effective barrier change $\Delta E = E_2 - E_1$ and the Gibbs free energy change ΔG, which is considered as the driving force for crystallization [1, 7, 19], can be expressed in the form

$$\Delta E = \Delta E_{\mathrm{eq}} + \Delta E(V) \tag{27}$$

$$\Delta G = \Delta G_{\mathrm{eq}} + \Delta G(V) \tag{28}$$

where ΔE_{eq} and ΔG_{eq} are the classical terms, and $\Delta E(V)$ and $\Delta G(V)$ are the local-nonequilibrium terms. $\Delta E(V)$ and $\Delta G(V)$ may be complicated functions of V, but they must go to zero as $V \to 0$ and to their maximum values at $V \to U$. The expressions for $\Delta E(V)$ and $\Delta G(V)$ can be obtained in the framework of EIT [14] and it is planned to be reported in future papers. Thus, the relaxation process leads to velocity-dependent thermodynamic functions, i.e., it applies feedback from the interface velocity to driving force for solidification.

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