Two temperature Stefan problem

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Abstract

We consider a two-temperature model for ultrafast melting and solidification observed in pulsed-laser-irradiated materials. The model takes into account energy exchange between the fast relaxing mode related to heat conduction and the slow mode associated with structural rearrangement. Such an anomalous heat transport leads to interface overheating.

1. Introduction

Pulsed laser melting in semiconductors, rapid solidification of undercooled metals, and explosive self-propagating crystallization of amorphous semiconductors have provided an opportunity for studying nonequilibrium heat transport and kinetics of crystal growth under extreme conditions. These processes have attracted attention recently both from the theoretical [1–3] and experimental point of view [4–5].

Theoretical models rely on equilibrium thermodynamics and assume a local equilibrium at the solid–liquid (or solid–solid) interface. For low interface velocities this assumption is valid. However, there is a large volume of experimental evidence proving that laser melting of materials and rapid solidification of undercooled metals may be a highly nonequilibrium process [1–8]. A high melt-front velocity of ~6 m/s is measured in germanium during pulsed laser melting [7]. An explosive crystallization of amorphous Si occurs at a velocity of 10–20 m/s [5,6]. Considerable solidification rates up to 70 m/s are observed for undercooled pure Ni and Cu–Ni alloys [8]. These experiments (see also Refs. [1–3], and references therein) have shown that the motion of the interface can be so fast that the local equilibrium assumption is no longer valid and strong undercooling or overheating of the material must exist in various phases.

The local nonequilibrium conditions at the interface have an effect both on heat transport and kinetics of crystal growth. Previously published models [1–3] take into account only the kinetic nonequilibrium of the process, but make use of classical, local-equilibrium heat transport theory. However, the temperature fields under extreme conditions [9–11], in particular around a fast-moving energy source [11–13], are significantly different from those predicted by the classical Fourier heat conduction model. In this paper we use a phenomenological approach for treating nonequilibrium thermal processes which is based on the two-temperature (or quasi-temperature) model [14,17]. The system is partitioned into two subsystems, which are individually close to internal equilibrium but which are not in equilibrium with each other. Each subsystem can be described by a space–time-dependent quasi-temperature and the flow of energy between subsystems can be described by the generalized heat transfer coefficient α. The idea behind the decomposition of the heat transport pro-
cess under extreme conditions into multiple steps is that different modes relax at different rates. There is thus a number of time scales. For example, ultrafast cooling of the heater dye in a polymer occurs in two stages [15]. Structural rearrangements in very viscous liquids near a glass transition also lead to multiple steps of energy relaxation [16].

The energy of an atom in a solid may be considered as made up of two parts: the cohesive energy associated with the formation of the lattice from isolated atoms and the thermal energy corresponding to the vibrational motion [18]. Hence, deviation from classical heat conduction and a transient nonequilibrium temperature difference between fast relaxing vibrational modes and the slow mode related to structural rearrangement (melting, ablation, recrystallization) are to be expected in the complex phase change behavior observed in pulsed-laser-irradiated materials.

2. Mathematical formulation

When powerful energy sources (laser pulses, for example) act on a solid material, a very high temperature can be achieved and, in most cases, a change of phase, like ablation or melting, or a change of state, like recrystallization, occur. All these circumstances are connected with the absorption of some form of latent heat in correspondence to the displacement of an interface between the phases or two crystalline states of the same substance. These phenomena when investigated within the framework of the Fourier heat conduction equation, originate the classical (parabolic) Stefan problem.

For nonequilibrium pulsed laser melting in systems with multiple steps of relaxation the two-temperature Stefan problem should be introduced. After appending the indices L and S to the quantities relative to the liquid and to the solid, respectively, the two-temperature model to be considered is:

(i) region L:

\[ C_{1L} \frac{dT}{dt} = \frac{\partial}{\partial x} \lambda_L \frac{\partial T}{\partial x} + \alpha_L (\theta - T) + W_L(x, t) , \]  

(ii) region S:

\[ C_{1S} \frac{dT}{dt} = \frac{\partial}{\partial x} \lambda_S \frac{\partial T}{\partial x} + \alpha_S (\theta - T) + W_S(x, t) , \]  

\[ C_{2S} \frac{d\theta}{dt} = \alpha_S (T - \theta) , \]

where \( T \) is the temperature of the fast relaxing subsystem related to heat conduction, \( \theta \) is the temperature (or, to be more exact, quasi-temperature) of the slow mode related to structural rearrangement, \( W(x, t) \) is the heat source term, \( C_1 \) and \( C_2 \) are the heat capacities of the fast and slow modes, respectively, \( \lambda \) is the thermal conductivity. At the interface, the matching conditions are given by

\[ Q = \lambda_L \frac{\partial T}{\partial x} \bigg|_{x=+} - \lambda_S \frac{\partial T}{\partial x} \bigg|_{x=-} , \]

and

\[ \theta(z) = T_{eq} \]

or

\[ V = F(\theta(z)) , \]

where \( Q \) is the latent heat of the phase transition, \( z(t) \) is the location of the moving interface between L and S, \( V = dz/dt \) is the interface velocity, \( T_{eq} \) is the temperature of the equilibrium phase transition. The matching condition (6) is to be used for the quasi-equilibrium kinetics of crystal growth. In the case of a nonequilibrium kinetics, condition (6) is replaced by the matching condition (7) expressing the dependence of the interface velocity on its temperature \( \theta(z) \) [1–3,18]. Unlike the classical Stefan problem with one temperature, the two-temperature model (1)–(7) implies that the heat flux through the interface \( x=z(t) \) is due to the gradient of the temperature of the fast relaxing subsystem but the velocity of the interface depends on the temperature of the slow relaxing subsystem related to structural rearrangement. When an energy source (for example, laser pulse) acts on the system, the energy is first absorbed by the fast relaxing subsystem, which thermalizes very rapidly. Then the subsystem transfers the energy to the slow relaxing mode through the coupling process. This second stage of energy transport heats the mode associated with the structural rearrangement up to a high temperature and a change of phase occurs. In
order to provide the energy flow between the subsystems, the temperature of the fast relaxing subsystem \( T \) must be greater than the temperature of the slow relaxing system \( \theta \). In the case of equilibrium kinetics (6), \( T(z) - \theta(z) = T_{\text{eq}} \). Thus, the multiple steps of energy transport in the two-temperature system lead to overheating of the interface. The same effect may give rise to undercooling during rapid solidification.

Expressing \( \theta \) in terms of \( T \) from (2) and substituting the result into (1), we obtain

\[
\frac{\partial T}{\partial t} + \frac{\partial^2 T}{\partial t^2} = \frac{a}{\partial x^2} + \frac{f}{\partial t} \frac{\partial^3 T}{\partial x^3} + \frac{W}{C_1 + C_2} + \frac{\tau}{C_1} \frac{\partial W}{\partial t}
\]

(8)

where \( \tau = C_1 C_2 / \alpha(C_1 + C_2) \) and \( l = \left( C_1 / \alpha(C_1 + C_2) \right)^{1/2} = (a/\tau)^{1/2} \) are the characteristic time and length, respectively, \( a = \lambda / (C_1 + C_2) \) and \( A_1 = \lambda / C_1 \). Eq. (8) is the third-order parabolic differential equation. In addition to the classical case, it contains two new parameters – the time \( \tau \) and the length \( l \). Physically, \( \tau \) is the relaxation time for internal equilibrium between the modes. The presence of additional higher order derivatives in (8) implies that heat transport in the two-temperature system is nonlocal, both in time and space. In the local limit, i.e. at \( \tau = 0 \) and \( l = 0 \), there is no heat exchange between the modes and Eq. (8) reduces to the classical heat conduction (diffusion) equation. In the case of \( \tau > 0 \) and \( l = 0 \), Eq. (8) gives the hyperbolic heat conduction equation [9–14,19,20].

Note that the space–time nonlocal Eq. (8) has also been obtained by extended thermodynamics with higher-order fluxes [9,21] and by using an effective thermal conductivity [10]. Thus, the two-temperature model based on the coupled classical equations (1) and (2) provides a bridge between the local equilibrium transport theory and nonlocal ones.

3. A steady-state regime

Let us consider the interface moving with a constant velocity \( V \). In a reference frame moving with the interface, Eq. (8) takes the form

\[
2V \frac{\partial^2 T}{\partial x^2} + (a + V^2) \frac{\partial^2 T}{\partial x^2} - \frac{V}{C_1} \frac{\partial T}{\partial x} = 0.
\]

Ahead of the interface \( W = 0 \) and this equation becomes

\[
T(x) = \sum_{i=1}^{3} A_i \exp(\mu_i x), \quad (9)
\]

\[
\mu_{1,2} = \frac{\tau V^2 - a \pm [(a - V^2)^2 + 4V^2l^2]^{1/2}}{2l^2 V},
\]

\[
\mu_3 = 0. \quad (10)
\]

These expressions describe the steady-state temperature profiles ahead of the interface in a moving reference frame (with its origin fixed on the interface). The matching condition (5) takes the form

\[
-q \frac{\partial T}{\partial x} \bigg|_{x=0} = \lambda V \mu_1.
\]

(11)

where \( q \) is the heat flux at the interface due to an external energy source. Using (9)–(11), we obtain the temperature at the interface \( x = 0 \),

\[
T(0) = \frac{q - \lambda V}{\lambda \mu_1}.
\]

When \( V \to 0 \) the modes are in equilibrium with each other and \( T(x) = \theta(x) \). Hence, the overheating of the interface \( x = 0 \) associated with an anomalous heat transport due to multiple stages of relaxation \( \delta T = T(0) - \theta(0) = T(0) - T(0) \mid_{V \to 0} \) is given as

\[
\delta T \mid_{\theta(0)} = \frac{V}{a \mu_1} - 1.
\]

(12)

If \( V \to 0 \), then \( \mu_1 \to V/a \) and \( \delta T \to 0 \). At \( V \sim V_\ast = (a/\tau)^{1/2} \) the relaxation effects play the most important role [11,12] and the interface overheating \( \delta T \) reaches its maximum value \( \delta T_{\text{max}} \).

\[
\delta T_{\text{max}} / \theta(0) = (a/\tau)^{1/2} - 1.
\]

(13)

In the case \( C_1 = C_2, \delta T_{\text{max}} / \theta(0) = 0.4 \). If \( C_2 \gg C_1 \) the overheating is much greater. Thus, the anomalous heat transport in the two-temperature system (1)–(7) can lead to strong overheating of the interface by several hundred K, which has been observed in the experiment [4–7]. At \( V \sim V_\ast, \mu_1 \) is a weak function.
of $V$ and, hence, the interface overheating $\Delta T$ depends linearly on $V$ (see (12)). Thus, the steady-state analysis gives the temperature profiles (9) and (10) in the reference frame moving with the interface, the dependence of interface overheating on its velocity (12), and the maximum interface overheating (13).

4. Conclusion

We have described the conceptual basis of the two-temperature model for treating laser-induced complex melting and solidification phenomena under extreme conditions. The model takes into account a two-stage nature of heat transport in local-nonequilibrium processes. In the first stage, the heat source excites the fast relaxing mode (phonons) related to heat conduction. In the second stage, the fast relaxing mode transfers energy to the slow relaxing mode through the coupling process. When this heat flow acts on the slow mode associated with structural rearrangement, a very high temperature can be achieved and a change of phase, like ablation or melting, or a change of state, like recrystallization, occurs. Such an anomalous, two-stage heat transport leads to interface overheating. This overheating arises due to nonequilibrium energy exchange between the modes during the ultrafast process. Another type of interface overheating described in Refs. [1–3] is associated to nonequilibrium kinetics of crystal growth [18] and has a different physical content. In the general case, both thermal and kinetic nonequilibrium effects should be taken into account. The degree of thermal interface overheating related to nonequilibrium heat transport depends on the interface velocity and takes its maximum value at $V = V^*$. In such a case, the energy exchange between the modes plays the most important role.

Note that the local-nonequilibrium transport theory based on the hyperbolic heat conduction equation also leads to interface overheating [11,12]. Moreover, the hyperbolic model predicts temperature gradients at the interface steeper than expected both from the classical heat conduction and from the parabolic two-temperature model (1)–(7). These effects, i.e. interface overheating and anomalous temperature gradients, have been observed in the experiments by Tischler, Larson and Mills [7]. In such a case, the hyperbolic heat conduction model [11,12] or the "wave" two-temperature model [11,14] are preferable.

References