Review of the Two-Temperature Model for Laser-Material Interactions in Metals

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Abstract: A review is made of the two-temperature model (TTM) for ultrafast laser-material interactions in metals. The TTM was first developed in the Soviet Union for laser-material interactions with picosecond pulses. It is now applied to studies of metals heated with subpicosecond pulses: the ultrafast regime. Qualitatively, the TTM distinguishes between the temperatures of a material's free electrons and lattice. With ultrafast pulses separate diffusion mechanisms for the electrons and the lattice lead to nonequilibrium in the material. Since its first proposal many variations of the TTM have been developed. The core mathematical basis of the model is discussed as well as some of these variations. Also explored is the TTM's use in analysis of ablation drilling processes which extend as far as full 3D simulations. While the TTM has proven useful for studies of a wide range of materials including semiconductors and dielectrics, there is still work to be done to make the TTM useful for quantitative analysis in some cases.

1. Introduction

Originally motivated by studies on picosecond-length or "ultrashort" laser pulse interactions with metals which took place in the USSR, the two-temperature model (TTM) has seen continued use and development for similar purposes. The main difference is that technology now allows applications with subpicosecond length pulses and focus is on ablation drilling of materials. Much of the drive for this change has come from the semiconductor industry, where the push for ever smaller electronic devices and larger through-puts has demanded advances in material processing technology. Here the TTM plays a role in the underlying theory for predicting technology performance and needs.

The TTM distinguishes between electron temperature and lattice temperature in solid-state materials when the two aren't in equilibrium. This is generally the case for metals irradiated with laser pulses with subpicosecond length [1]. These ultrafast pulses lead to two nonequilibrium heat diffusion effects in the material: ballistic electron collisions and electron-phonon coupling [2]. For longer pulse durations, particularly of nanosecond length or longer, the period of nonequilibrium can be neglected, but for ultrafast pulses the non-equilibrium becomes significant because the pulse duration is on the order of the time taken to reach equilibrium [3]. For those situations the TTM is needed to model the thermal state of the material.

Applications of the TTM have been focused on predicting melt and ablation thresholds in materials as well as simulating the dynamics for 3D visualizations. Understanding melt thresholds is often useful for finding the size of thermal damage zones while ablation thresholds indicate the minimum fluence needed to remove material. Simulations which have seen success include hydrodynamic models, molecular dynamic models, and hybrids of the two [1]. Work has been done to extend the TTM to other materials such as semiconductors and dielectrics, but the focus here is on metals [1].

Some confusion may be caused by the reference to the TTM as a singular model, when in fact a multitude of formulations exist and the concept of non-equilibrium thermal states is not limited to laser-material interactions. Nevertheless, most contemporary references to a "two-temperature model" are in connection to laser-material interactions. Whether these variations–which pursue the same purpose–should be considered separate models or different versions of the same model is a debate of semantics, however. Hopefully this paper provides the context needed to understand

the common basis between the various models used in the literature.

2. Theoretical Development

In 1974 the TTM was used by S. I. Anisimov et al. to approximate the flux threshold for ultrashort laser pulses at which both thermionic and photoelectric emission could theoretically be observed in metals [4]. This is sometimes considered the point at which the TTM was first proposed. However, they say the TTM was suggested as early as the 1950s in papers by M. I. Kaganov et al. and V. L. Ginzburg [4].

Following the initial proposition of the model, the results of an experiment demonstrating non-equilibrium heating of copper from ultrafast laser pulses was published by H. E. Elsayed-Ali et al. in 1987 [5]. Soon after in 1993 the TTM was, in their own words, "rigorously derived" by T. Q. Qiu and C. L. Tien. Their derivation was based on the Boltzmann transport equation and outlined the limiting cases where the TTM reduces to a single-temperature model (STM) [3].

Before diving into the mathematics let's consider a qualitative picture of the diffusion mechanisms of the TTM for a metal heated with ultrafast laser pulses. Energy from the laser pulse is first absorbed by electrons in the metal. These electrons penetrate into the material where they undergo electron-electron (e-e) collisions [2]. Meanwhile, electron-phonon (e-p) coupling causes diffusion to occur through the lattice of the metal [2, 6]. Over time, the two diffusion mechanisms approach equilibrium [2]. The electrons and lattice diffusion are illustrated in Fig. 1.

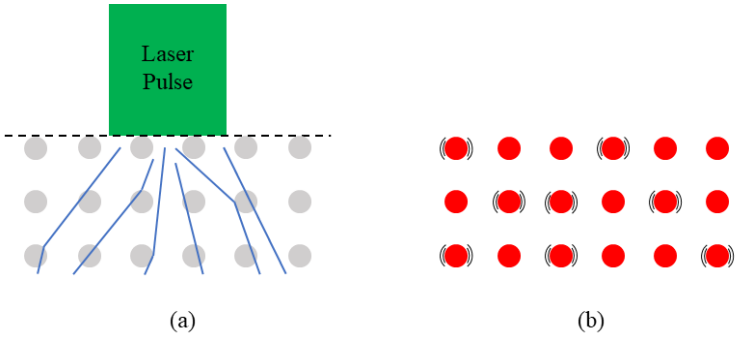

Fig. 1. (a) The laser pulse is absorbed by electrons in the material which then travel at ballistic speeds while colliding with other electrons. (b) Over time coupling between electrons and phonons leads to heat diffusion through the lattice.

There are two parameters which are key to understanding the relative time scales of each step in the process: the relaxation time and the thermalization time. Relaxation time is the mean time for electrons to change their state as in ballistic collisions. This is relevant to both e-e and e-p interactions [3]. Thermalization time is the time needed for the two diffusion processes to reach equilibrium. Generally for metals, the relaxation time is ~0.01 ps and the thermalization time is ~0.1 ps [3]. These approximations indicate the importance of the TTM for the ultrafast pulse regime, where energy deposition from the laser occurs on the same time scale as the time needed to reach equilibrium between the two diffusion mechanisms.

Let's now consider the mathematics of the TTM by starting with the base formulation presented by S. I Anisimov et al. Their heating equations for the electrons and the lattice are given respectively in Eqs. 1 & 2 [4].

$$c_e(T_e)\frac{\partial T_e}{\partial t} = \chi \Delta T_e - \alpha(T_e - T_i) + f(\mathbf{r}, t) \tag{1}$$

$$c_i \frac{\partial T_i}{\partial t} = \alpha(T_e - T_i) \tag{2}$$

The subscript e is used for the electron parameters and i is used for lattice parameters. On the LHS specific heat capacity is represented by c and temperature by T. Looking at the RHS of Eq. 1, the first term likely comes from the Fourier heat equation with χ being thermal diffusivity. The second term is for heat transfer from e-p coupling with α being an e-p coupling parameter. Laser heating is given by the third term which represents the laser intensity distribution in three dimensions. Eq. 2 has only one term on the RHS which is the negation of the second term in Eq. 1 since heat is flowing from the electrons to the lattice.

A key simplification can be made by reducing the problem to one dimension. This is justified due to the low heat penetration depth of short laser pulses and the relatively large size of the beam [3,4]. Qiu and Tien presented the one-dimensional formulation of the model cleanly in their derivation. Their results are summarized in Eqs. 3-5.

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \frac{\partial}{\partial x}\left(\kappa\frac{\partial T_e}{\partial x}\right) - G(T_e - T_l) + S \tag{3}$$

$$C_L\frac{\partial T_l}{\partial t} = G(T_e - T_l) \tag{4}$$

$$S = (1-R)I\alpha\exp\left[-\alpha x - 2.77(t/t_p)^2\right] \tag{5}$$

Heat capacity C is used rather than specific heat capacity. The Fourier term shows the one-dimensional nature of the model and is in the form for thermal conductivity κ rather than thermal diffusivity. In the second term G takes the place of α for the e-p coupling parameter.

For the laser heating term S they derived an expression for the one-dimensional case under the assumption of no temperature dependence for the optical properties of the material [3]. The laser heating depends on the reflectivity of the material surface R, the intensity of the pulse I, the radiation absorption coefficient α, and the pulse duration t_p. They assume the intensity distribution of the laser pulse is uniform [3].

Qiu and Tien described Eqs. 3 & 4 as the parabolic TTM. It is a special case of their hyperbolic TTM where the electron relaxation time is much shorter than the pulse duration [3]. On the other hand, if the thermalization time is also much shorter than the pulse duration, the parabolic TTM reduces to the parabolic STM shown in Eq. 6 [3].

$$C\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(\kappa_{eq}\frac{\partial T}{\partial x}\right) + S \tag{6}$$

Where κ_{eq} is thermal conductivity at equilibrium between the electrons and lattice.

Since the electron relaxation time for metals is generally on the order of 10 fs the parabolic TTM is a good approximation for ultrafast laser applications on the longer end of the regime. References to the TTM sometimes assume the parabolic version.

3. Current State of the Art

The TTM as developed by S. I. Anisimov et al. and Qiu and Tien still sees use. Examples include a study published in Nature on the controversial topic of "ablation-cooling" in 2016 [7] and a study by S.-S. Wellershoff et al. on damage to metals by femtosecond pulses [2]. There have been some developments to the model, though, to improve it's accuracy in certain special applications. These include processing of "thick" materials, laser pulse durations in the short end of the ultrafast regime, and cases where lattice diffusion plays a significant role alongside electron diffusion.

Analysis of thick materials has prompted the development of a three-dimensional TTM. The reduction to one-dimension is based on the assumption that the heat penetration depth of the laser is limited to the surface of the material and that the spot size of the laser pulse can be assumed to be constant. While the first assumption holds true for transition metals [2], the second

assumption can be dependent on the material thickness. In particular, laser drilling of holes with depth greater than the Rayleigh range of the laser leads to appreciable change in intensity as a function of depth [8].

Represented in three dimensions the electron heating equation becomes,

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla(\kappa_e \nabla T_e) - G(T_e - T_l) + S(x, y, z, t). \tag{7}$$

The Fourier conduction term becomes a function of all three dimensions as does the laser heating term. No change is required to the e-p coupling term so the lattice heating equation is also unchanged. For their study of drilling in thick metal films, J. Zhang et al. decoupled the laser heating term into an intensity function dependent on position and a temperature function dependent on time [8].

Advances in laser technology have lead to ever smaller pulse durations, even approaching atto-second length [6]. This has brought the validity of the parabolic TTM as a good approximation into question for some ultrafast laser pulse studies.

The parabolic TTM is based on the Fourier heating law which assumes instantaneous heat transport [9]. Limitations of using the Fourier law were recognized by Qiu and Tien and motivated their development of the hyperbolic TTM. Using a hyperbolic heat equation as a basis, the goal was to address the shortcomings of the hyperbolic approach.

However, the hyperbolic TTM still assumes a temperature can be defined for the ballistic electrons. As pointed out by B. Rethfeld et al., a temperature shouldn't be assumed for the electrons when the laser pulse duration is on the order of their relaxation time since there isn't time for the electron gas to come into equilibrium with itself [1]. Rather than using a hyperbolic model, they recommend kinetic representations where the individual electrons are treated independently [1].

Lattice diffusion is a frequently omitted component of the TTM. This is because for metals, lattice conduction is usually negligible compared to electron conduction [2]. The much faster electron relaxation process compared to lattice conduction allows a constant lattice temperature to be assumed [1].

Still, this assumption is worth noting for cases where lattice diffusion may not be negligible. Inclusion of the Fourier conduction term for the lattice gives Eq. 7 for the lattice heating equation.

$$C_l\frac{\partial T_l}{\partial t} = \frac{\partial}{\partial x}\left(\kappa_l\frac{\partial T_l}{\partial x}\right) + G(T_e - T_l) \tag{8}$$

A study on ultrafast laser heating of gold films on a glass substrate by P. Bresson et al. gives an example of a case where inclusion of the lattice conduction term proved important. By including the lattice term in their model they were able to make accurate predictions over the timescale of e-p interactions in addition to the timescale of e-e interactions [10].

4. Technology

Most applications of the TTM for metals use it to make predictions about ablation drilling processes. These predictions can be used to find process parameters directly or can be part of detailed 3D simulations.

In a study by S.-S. Wellershoff et al. the TTM was used to predict threshold fluence for gold, molybdenum, and nickel films exposed to ultrafast laser radiation as a function of pulse length and the film thickness [2]. Analysis of ablation rates for copper drilled with ultrafast pulses was done by S. Nolte et al using the TTM [11]. Threshold fluence is a key parameter in determining minimum energy requirements while ablation rate is a limiting factor in drilling speed.

In 3-D simulations the TTM is one of the pieces of the overall model. These 3-D simulations for ablation processes can be separated into hydrodynamic models, molecular dynamic models,

and hybrids of the two [1]. In hydrodynamic models the material heated by the laser is treated in bulk as warm dense matter. For molecular dynamic models the kinetics of the individual atoms and electrons is considered. Hybrids of the two models are sometimes used to overcome some of their limitations. Use of molecular dynamics avoids assumptions about phase transitions by making nucleation kinetics inherent, while hydrodynamic models can more easily predict the initial stage of electron excitation. [1].

The TTM has played a role in models of material processing by ultrafast lasers. The parabolic version was used by Kerse et al. to numerically validate their toy model for ablation-cooled laser processing [7]. The mechanism in the model for material removal was critical phase point separation, where material was assumed to be removed after reaching a separation temperature [7]. Given the ultrafast regime of the study the TTM was needed to accurately determine that temperature in the model.

At MKS Instruments Inc. the TTM has seen use in simulations of punch and line scribing processes [12]. Punching is the use of a stationary beam to drill holes whereas line scribing uses a scanning beam to remove material in a line. The simulations were hydrodynamic based and used the TTM as one component in the material removal process alongside software and the Navier Stokes equations to model the fluid dynamics [12].

5. Future Directions

While the TTM may be a good qualitative description of ultrafast laser-material interactions in metals, there are some challenges to using the model for quantitative analysis. One of these challenges is obtaining the physical parameters needed for the model. Kerse et al. encountered difficulty finding references for all the parameters needed to model ablation drilling of copper and instead used data for nickel [7].

The e-p coupling parameter is one the physical parameters which can be difficult to obtain. This may be due to measurement difficulties. A common method to obtain electron-phonon coupling data is by ultra-low temperature resistivity measurements [13]. However, this method isn't suitable for use with the TTM due to the high temperatures of the electrons and lattice in the laser heating process. Better access to relevant physical parameters would improve the quantitative usefulness of the TTM.

Much of the use for the TTM is in the semiconductor laser drilling industry. Because of this, laser-material interactions with semiconductors and dielectrics are important considerations as well. Work has been done at MKS Instruments Inc. to investigate drilling of silicon and glass using ultrafast lasers [14, 15].

In general, applications of the TTM to non-metals requires modifications due to the change in electronic structure. In combined TTM and molecular dynamic simulations for semiconductors and dielectrics the density of conduction band electrons can't be treated as constant as it is in metals [1]. Models have been developed which take into account this difference by using a density dependent version of the TTM [16, 17]. Still, there is an absence of models for semiconductor materials which consider the change in potential energy on the surface from electron excitation [1]. There may be more work to do to extend the usefulness of the TTM to non-metal materials.

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