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A simple model for high fluence ultra-short pulsed laser metal ablation

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Abstract

The ultra-short laser metal ablation is a very complex process, the complete simulation of which requires applications of complicated hydrodynamics or molecular dynamics models, which, however, are often time-consuming and difficult to apply. For many practical applications, where the laser ablation depth is the main concern, a simplified model that is easy to apply but at the same time can also provide reasonably accurate predictions of ablation depth is very desirable. Such a model has been developed and presented in this paper, which has been found to be applicable for laser pulse duration up to 10 ps based on comparisons of model predictions with experimental measurements.

Keywords: Ultra-short pulsed laser; Laser ablation; Modeling of laser ablation

1. Introduction

The ultra-short laser pulse is very attractive for precise micromachining and many other applications due to the special features of its interaction with matter such as the negligible heat affected zone, etc. [1,2]. A lot of efforts have been devoted to the experimental and theoretical studies of the ultra-short laser-matter interactions in recent years, and numerical models based on comprehensive hydrodynamics [2–5] or molecular dynamics [6–14] have been developed. These models can provide a lot of useful information in many aspects for scientific studies of laser ablation. However, they are not easy to apply due to the serious theoretical and numerical difficulties, and they are often computationally very expensive. For many practical applications, such as micromachining, where the laser ablation depth is the main concern, a numerical model that is easy to apply but at the same time can also provide reasonably accurate predictions of ablation depth is very desirable. However, this kind of model has been rarely reported in literature.

Several different physical mechanisms have been proposed in literature to explain the complicated ultra-short laser ablation process, such as spallation, phase explosion, critical-point phase separation, fragmentation, etc. [3–14]. The dominant physical mechanism for material removal may depend on the type and properties of materials, laser fluence, and laser pulse duration, etc.

The hydrodynamic simulations in Ref. [3] and the molecular dynamic simulations in Ref. [6] suggest that the critical-point phase separation (CPPS) is the dominant physical mechanism for material removal during ultra-short laser ablation of metals at high fluences (around 0.6–1 J/cm^2 or higher for nickel [6]). Despite the many complex physical processes involved, there are some features of the high fluence ultra-short laser metal interactions that make the development of a simplified but reasonable model possible. It has been found in Ref. [3] that during the ultra-short laser ablation the thermodynamic trajectories of the material cells near the surface can often be roughly divided into two stages. During the first heating stage, the material cells are heated very rapidly to around their maximum temperatures while their densities do not change very significantly. After that, the densities of the material cells will decrease following approximately $T \propto \rho^{2/3}$, the adiabat for perfect gases. It has also been found in Ref. [3] that the material cells, whose expansion trajectories enter the unstable zone near the critical point, will then transform into a bubbles–droplets transition layer as a result of thermodynamic instabilities. The mass above these material cells will be ablated, while mass below will condense back onto the target. Therefore, the original depth of these material cells is the ablation depth. This process is the so-called critical-point phase separation [3]. Fig. 1 shows the rough schematic diagram

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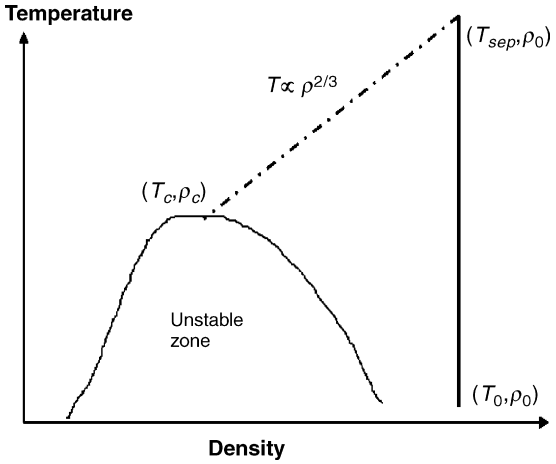

Fig. 1. The rough schematic diagram of the approximate thermodynamic trajectory of the material point entering the unstable zone near the critical point.

of the approximate thermodynamic trajectory of the material point entering the unstable zone near the critical point. Initially, the material point is in a state of the room temperature and normal density (T_0, ρ_0), and then the material point is heated to around its maximum temperature T_{sep}, which will be called the ''separation temperature'' in this paper, and then the state changes following approximately $T \propto \rho^{2/3}$. The separation temperature can be related to the critical temperature as follows

$$\frac{T_{sep}}{T_c} = \left(\frac{\rho_0}{\rho_c}\right)^{2/3} \tag{1}$$

Based on the material critical temperature and density, the separation temperature can be calculated.

Based on the above analysis, since the density of material points generally does not change very significantly during the first heating stage, a simplified but reasonable model for high fluence ultra-short laser metal ablation can be developed, where only the two-temperature heat conduction equations need to be solved to locate the material point whose maximum temperature is equal to the ''separation temperature'', which will be called the ''separation point'' in this paper, and then the depth of the separation point can be taken as the ablation depth approximately. This model will be much easier to apply than the comprehensive hydrodynamics or molecular dynamics model, and its applicable range will be discussed later after the comparisons between model predictions and experimental measurements.

It should be noted that the above-mentioned temperature refers to the lattice temperature of metals.

2. Model

Under the radiation of ultra-short laser pulses, the laser energy is first absorbed by electrons in metal, which then transfer the energy to the lattice owing to the electron–phonon coupling [1,4]. Due to the short duration of the laser pulses, the electrons and the lattice may not always be in thermal equilibrium, and the heat diffusion process should be described by the well-known two-temperature model [1,4]:

$$C_e \frac{\partial T_e}{\partial t} = \frac{\partial}{\partial z}\left(k_e \frac{\partial T_e}{\partial z}\right) - G(T_e - T_i) + S \tag{2}$$

$$C_i \frac{\partial T_i}{\partial t} = G(T_e - T_i) \tag{3}$$

where T_e, T_i, C_e and C_i are the temperatures and the volumetric heat capacities of electrons and the lattice, respectively, k_e the electron thermal conductivity, and G denotes the electron–phonon coupling, following Ref. [4], given by $G = C_e/\tau_\varepsilon$, where τ_ε is the mean energy exchange time for electrons and the lattice. The laser energy source term can be calculated as

$$S = (1 - R)\alpha I \exp(-\alpha z) \tag{4}$$

where R is the surface reflectivity, α the absorption coefficient, and I is the laser power density reaching the target surface.

Following Refs. [3,4], the electron and lattice heat capacities are calculated from the widely used QEOS model [15] at the normal density of metals. In the QEOS model, the thermodynamic functions, such as energy, are obtained from the Helmholtz free energy, which is given by with the additive assumption:

$$F = F_i + F_e + F_b \tag{5}$$

where F_i, F_e and F_b are the ion free energy, semiclassical electron free energy and the semiempirical correction for chemical bonding effects in the solid state, respectively.

For the ion part, the Cowan model is applied, which can be divided into two parts, a ''structural part'' which gives thermodynamic functions on the basis of assumed expressions for melting and Debye temperatures, and a ''phenomenological part'' which attempts to predict the melting and Debye temperatures for any material [15].

The electronic properties are obtained from a modified Thomas–Fermi statistical model. In Thomas–Fermi theory, the electrons are treated as a charged fluid surrounding the nucleus and the properties of this electron gas are obtained from finite-temperature Fermi–Dirac statistics. Numerically, the electron free energy is relatively difficult to obtain. Fortunately, the scaling law can relate properties of an arbitrary element (atomic number Z, atomic weight A) to those defined by the case $Z = A = 1$.

The input of the QEOS model includes the material atomic number, bulk modulus, normal solid density, etc., based on which the equation of state of the material can be generated. The QEOS has been widely applied in the studies of ultra-short laser-matter interactions [3,4,16].

The transport properties of metals, such as thermal and electrical conductivities can be obtained using the model of Lee and More [17,18], which is based on the Boltzmann transport equation in the relaxation time approximation. The model is applicable over a wide range of temperature and density, and is expressed in computationally simple forms, which makes it relatively easy to apply.

In Ref. [17] the conductivity model has been compared with some available experiments, which shows that the model gives

results that are sufficiently accurate for many practical applications. The Lee–More conductivity model has also been widely applied in many investigations of ultra-short laser-matter interactions [3,4,16].

Based on the dc electrical conductivity obtained using the model of Lee and More, the complex index of refraction and absorption coefficient of metals can be obtained based on the Drude theory [3,19,20]:

$$\nu = \frac{n_e e^2}{m' \sigma_0} \tag{6}$$

$$w_p = \sqrt{\frac{n_e e^2}{m' \varepsilon_0}} \tag{7}$$

$$n_r^2 - n_i^2 = 1 - \frac{w_p^2}{w^2 + \nu^2} \tag{8}$$

$$2 n_r n_i = \frac{\nu w_p^2}{w(w^2 + \nu^2)} \tag{9}$$

$$\alpha = 2 \frac{w}{c} n_i \tag{10}$$

where w_p is the plasma frequency, ν the electron collision frequency, σ_0 the dc electrical conductivity, ε_0 the permittivity of vacuum, n_e the electron number density, e the electron charge, m' the mass of electrons, n_r and n_i the real and imaginary parts of the complex index of refraction, w the laser frequency, c the speed of light, and α is the absorption coefficient.

Based on the index of refraction, the metal surface reflectivity can be calculated as

$$R = \frac{(n_r - 1)^2 + n_i^2}{(n_r + 1)^2 + n_i^2} \tag{11}$$

The above equation is for the case of normal incidence of laser radiation, and the reflectivity at other incident angels for p- and s-polarized radiation can also be calculated based on the Fresnel formulas [21].

Eqs. (2) and (3) can be easily solved using a finite volume method, which makes this model much easier to apply than the comprehensive hydrodynamic or molecular dynamics models.

3. Simulation results and comparisons to experimental measurements

Under the intense radiation of the ultra-short laser pulses, the reflectivity of metal targets may be significantly different from the normal values. The reflectivity determines the laser energy penetrated into the target, for which the comparisons between model predictions and experimental measurements will be first made. Fig. 2 shows the reflectivity as a function of the angle of the incidence for s- and p-polarized radiation for an aluminum target under the radiation of 250 fs laser pulses. When the incident angle is 0°, the reflectivity is around 0.6, and as the angle increases to 50°, the reflectivity for s-polarization increases to around 0.7 while it decreases to around 0.4 for p-polarization. The agreement between the experimental measurements [22] and the predictions from the simplified model is reasonably good, which can be seen from Fig. 2.

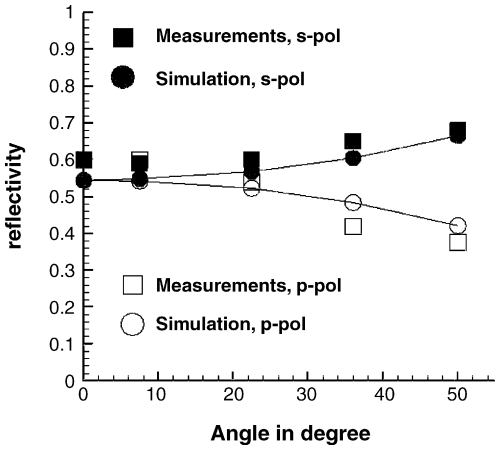

Fig. 2. The total reflectivity as a function of the angle of the incidence for s- and p-polarized radiation, measurements from Ref. [22] (aluminum target, pulse duration: 250 fs, 248 nm, power density: 10^{14} W/cm^2).

Next, the model predicted ablation depth will be compared with experimental measurements under a variety of pulse durations to verify the model and obtain its applicable range. The ablation depth is chosen as the main validation of the model, because it is the major concern in many practical applications, and also it is relatively easy to measure and therefore has often been chosen as the main parameters to compare between simulations and experiments in many papers in this field such as Refs. [5,9,14].

Using Eq. (1) the "separation temperature" T_{sep} can be obtained based on the metal critical temperatures and densities taken from Ref. [23]. By solving Eqs. (2) and (3), the transient temperature fields of the metal target under ultra-short laser pulses can be obtained. For sufficiently intense laser radiation, the maximum lattice temperature at the target surface may be much higher than the "separation temperature", and it decreases as the depth of material points increases. The peak lattice temperature of the material point at certain depth will be

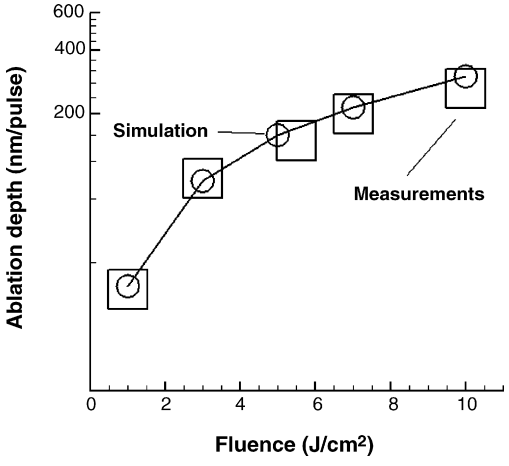

Fig. 3. The variation of ablation depth with laser fluence for copper, laser pulse duration: 70 fs, measurements from Ref. [24].

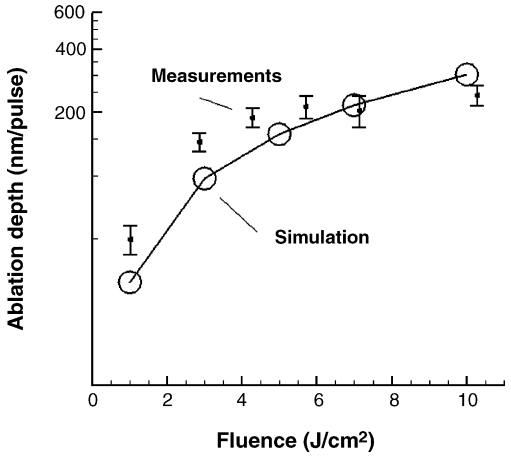

Fig. 4. The variation of ablation depth with laser fluence for copper, laser pulse duration: 150 fs, measurements from Ref. [1].

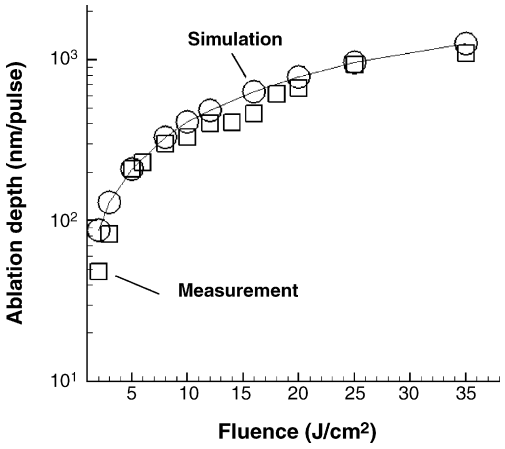

Fig. 6. The variation of ablation depth with laser fluence for aluminum, laser pulse duration: 170 fs, measurements from Ref. [5].

equal to the ''separation temperature'', and in this paper this material point will be called the ''separation point'', whose expansion thermodynamic trajectory in the $T \sim \rho$ plane will eventually enter the unstable zone near the critical point (see Fig. 1). The mass above the ''separation point'' will eventually be ablated and the mass below it will condense back onto the target. Therefore, the depth of the ''separation point'' gives the ablation depth. In a word, the ablation depth can be easily obtained by solving Eqs. (2) and (3) to locate the material point whose maximum lattice temperature is equal to the ''separation temperature''.

Figs. 3–6 show the ablation depth for copper or aluminum under the radiation of laser pulses with durations less than 1 ps. In Fig. 3, the laser pulse duration is 70 fs, and most model prediction points are close to the experimental measurement points. The ablation depth increases from around 30 nm at 1 J/cm^2 to around 250 nm at 10 J/cm^2, indicating that increasing laser pulse fluence in this range can increase the laser ablation depth very effectively. The differences between model predictions and measurements get a little bit larger for longer pulses as shown in Figs. 4–6. However, the agreement is still reasonably good, compared with many existing complicated molecular dynamics and hydrodynamics models (such as those in Refs. [5,14]) in spite of the fact that the model is a self-closed (with no free adjustable variables) and simplified one such that it is very easy to apply and is computationally very fast.

The differences between calculations and measurements increase as the laser pulse duration increases to the range of 1–10 ps, as can be seen from Figs. 7–9. The overall accuracy of the model for Fig. 7 is about the same as Fig. 8, which is slightly better than Fig. 9. Although the accuracy deceases, the model is still capable of giving a good estimation of the ablation depth. However, when the laser pulse duration is longer than 10 ps, the differences between model predictions and experiments become quite big, as can be seen from Fig. 10, and the model is not very applicable in this range.

The above comparisons show a very clear trend that as the laser pulse duration increases, the model accuracy decreases, and for pulse durations above 10 ps the model is not very applicable. One of the main possible reasons could be that as the laser pulse duration increases, the effect of hydrodynamic motion of target metals on the laser energy deposition and

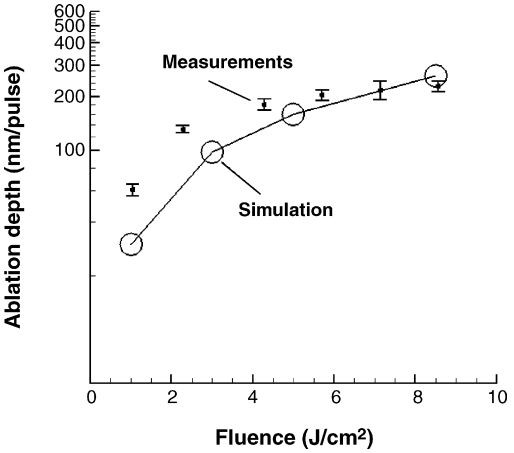

Fig. 5. The variation of ablation depth with laser fluence for copper, laser pulse duration: 500 fs, measurements from Ref. [1].

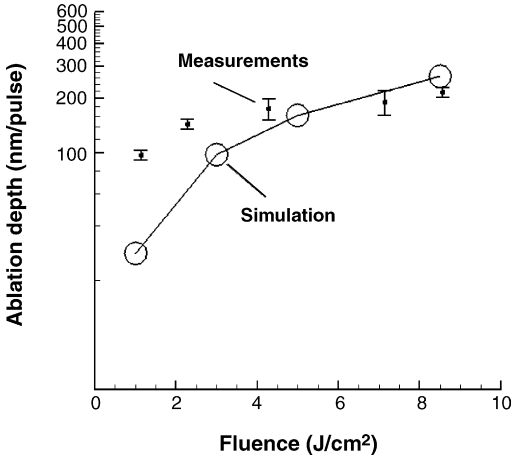

Fig. 7. The variation of ablation depth with laser fluence for copper, laser pulse duration: 2 ps, measurements from Ref. [1].

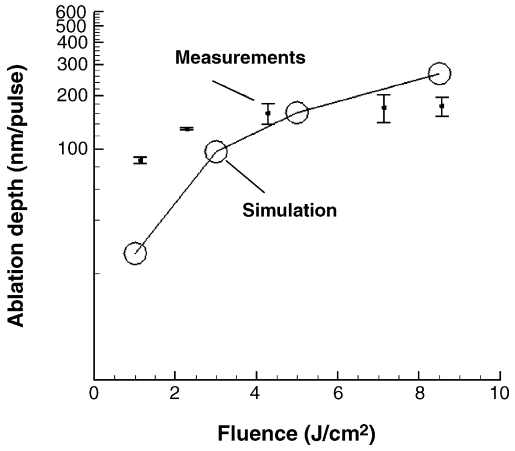

Fig. 8. The variation of ablation depth with laser fluence for copper, laser pulse duration: 4.8 ps, measurements from Ref. [1].

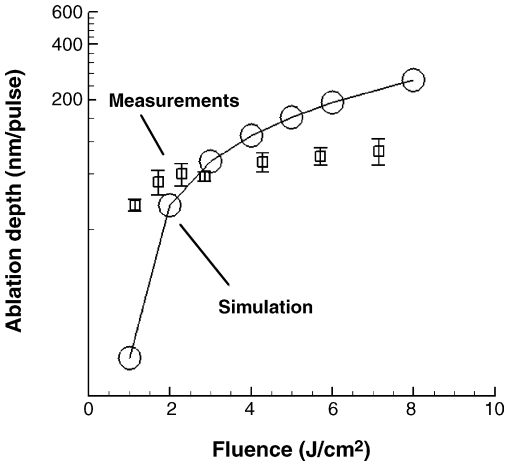

Fig. 10. The variation of ablation depth with laser fluence for copper, laser pulse duration: 22.4 ps, measurements from Ref. [1].

distribution becomes larger. In the simplified model, only the two-temperature heat conduction equations have been solved, and therefore its accuracy decreases as laser pulse duration increases.

To the authors' best knowledge, the critical temperatures and densities of many common metals have not been conclusively determined. In this paper, the values from Ref. [23] have been used, which have some uncertainties. A better knowledge of the material critical temperature and density, which may be obtained in the future research, will certainly benefit the model calculations in this paper and it will also benefit the whole research area of laser-matter interactions.

Although the hydrodynamic simulations in Ref. [3] and the molecular dynamic simulations in Ref. [6] suggest that critical-point phase separation (CPPS) is the dominant physical mechanism for material removal for ultra-short laser ablation of metals at high fluences, the CPPS theory has not been completely validated through experiments. Some molecular dynamic studies, such as those in Refs. [10,11], seem to contradict CPPS theory in some aspects, which do not have conclusive experimental supporting evidence either to authors' best knowledge.

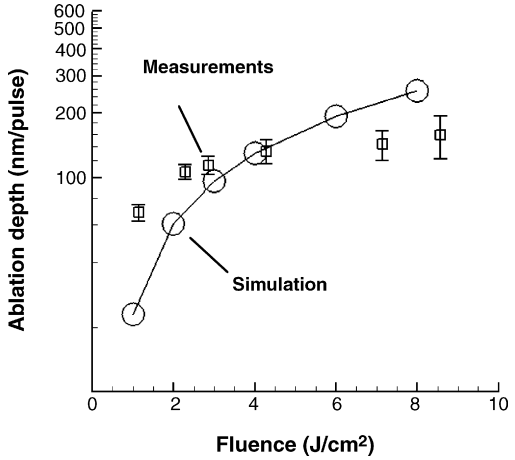

Fig. 9. The variation of ablation depth with laser fluence for copper, laser pulse duration: 9.6 ps, measurements from Ref. [1].

It should not be concluded that the CPPS theory is completely valid based on the good agreement between simulations and measurements shown in this paper for pulse duration below 1 ps. The complete verification of the CPPS theory requires much more detailed theoretical and experimental work, which is beyond the scope of this paper. However, it should be noted that that although the basic idea of the model in this paper mainly comes from CPPS theory, its applicability does not completely depend on the validity of CPPS theory. That is, even though it turns out that CPPS theory is not completely valid through further investigations in the future, it is still very possible that the model can still be applied to predicting ablation depth with acceptable accuracy at high laser fluence. This is because: no matter if or not CPPS theory is completely valid, as laser fluence increases, the maximum temperature of metal materials during the first nearly constant-volume heating stage will be higher. Therefore, at sufficiently high laser fluence, it is very possible that the amount of the material whose maximum temperature during the first nearly constant-volume heating stage exceeds the "separation temperature" (determined through Eq. (1)) is close to the actual total amount of the ablated material, and therefore the ablation depth predicted by our model should be close to the actual ablation depth.

It should be noted that most of the MD studies that contradict CPPS theory are performed for Lennard–Jones system or silicon [10,11], while the MD and hydrodynamic studies supporting CPPS theory are performed for metals [3,6]. Since the purpose of this paper is to develop a model for high fluence laser ablation of metals, it is a slightly better choice (at least not a much worse one) to assume CPPS theory than to apply other theories contradicting CPPS such as those in Refs. [10,11], when the theories on both sides do not have conclusive experimental supporting evidence. This is because different types of materials may have very different properties. For example, for aluminum the power density threshold for the observation of liquid droplet ejection induced by nanosecond

laser ablation is close to that for nickel [25,26], which is, however, about two to three orders of magnitude smaller than that for silicon [27,28]. The huge difference in the value of this threshold between silicon and metals (such as aluminum and nickel) indicates a very significant difference in some of the material properties between silicon and metals. The differences in some of the properties between Lennard–Jones system and metals may also be very large. The big differences in some of the properties between metals and silicon (or Lennard–Jones system) may possibly affect the fundamental physical mechanisms for material removal although some phenomena may be found to be similar for different materials in ultra-short laser ablation.

Further theoretical and experimental investigations are needed to conclusively determine the dominant physical mechanism of material removal for high fluence ultra-short laser ablation of metals. Fortunately, as mentioned earlier, although the basic idea of our model mainly comes from CPPS theory, its applicability does not completely depend on the validity of CPPS theory.

4. Conclusions

A simplified model has been developed for high fluence ultra-short laser metal ablation, which is much easier to apply than the comprehensive hydrodynamic models or molecular dynamics models. The comparisons between model predictions and experimental measurements indicate that the model is reasonably accurate for laser pulse duration below 1 ps, and can still produce good estimations of ablation depth when the pulse duration is in the range of 1–10 ps, and the model is not very applicable for pulse duration above 10 ps. The simplified model may not be suitable for fluences smaller than around 1 J/cm^2, where the dominant physical mechanisms may be phase explosion or other mechanisms [6,8,9] instead of the CPPS process.

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