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Continuum-atomistic simulation of picosecond laser heating of copper with electron heat capacity from *ab initio* calculation

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ABSTRACT

On the basis of *ab initio* quantum mechanics (QM) calculation, the obtained electron heat capacity is implemented into energy equation of electron subsystem in two temperature model (TTM). Upon laser irradiation on the copper film, energy transfer from the electron subsystem to the lattice subsystem is modeled by including the electron–phonon coupling factor in molecular dynamics (MD) and TTM coupled simulation. The results show temperature and thermal melting difference between the QM-MD-TTM integrated simulation and pure MD-TTM coupled simulation. The successful construction of the QM-MD-TTM integrated simulation provides a general way that is accessible to other metals in laser heating.

1. Introduction

In the past decades, ultrashort laser material processing has been an increasingly hot topic and has drawn lots of attentions from researchers. Numerical modeling and simulation of the laser material interaction ranging from two temperature model (TTM) which assumes the laser energy is firstly absorbed by electron subsystem [1–4], molecular dynamics simulation (MD) which describes the laser heating by scaling the atomic velocity [5], to the quantum mechanics (QM) approach which introduces the Fermi–Dirac distribution of the instantly increased the electron temperature and performs the electron–phonon interaction subsequently [6,7]. Furthermore, there are several MD-TTM combined schemes, which describes the atomic motion by using MD and models the electron subsystem by using a continuum energy equation [8–12]. However, the thermophysical parameters of electron required in the energy equation, such as the electron heat capacity C_e, is necessary in these combined MD-TTM schemes. Due to the strong thermal excitation of the electron subsystem, C_e varies greatly with electron temperature T_e.

Precise knowledge of the electron heat capacity helps to better explain the measurement of material temperature upon laser irradiation, facilitates the theoretical and numerical investigations of melting, vaporization and sublimation. The *ab initio* calculation provides a novel way of obtaining the electron temperature-dependent $C_e(T_e)$ [13–16]. There are limited number of work performing the *ab initio* calculation of $C_e(T_e)$ and plugins it directly into the MD-TTM simulation. Lin and Zhigilei carried out *ab initio* calculations to study C_e for a serials of metals [16], but the variations of electron density of states (EDOS) were not taken into account. Whereas, the EDOS differs a lot at high electron temperature [14]. Bévillon et al. [13] calculated the electron behavior of metals under electron–phonon nonequilibrium resulting from laser irradiation, and the free-electron properties were determined at atomic level. This letter reports the first effort of T_e dependent C_e for copper through the computation in the following section.

2. Computational details

The present letter concentrates on the determination of $C_e(T_e)$ of copper *via* QM and its implementation into the upper scale of MD-TTM coupled simulation to study the ultrashort laser heating of copper film. The electron heat capacity, C_e, of copper is computed by taking derivative of the internal energy of the electron subsystem E_e with respect to T_e, namely $\partial E_e/\partial T_e$. Since the EDOS g is T_e-dependent, the electron heat capacity [16] can be rewritten as

$$C_e(T_e) = \int_{-\infty}^{\infty} \left(\frac{\partial f}{\partial T_e} g + f \frac{\partial g}{\partial T_e} \right) \varepsilon d\varepsilon \tag{1}$$

where f is the Fermi–Dirac distribution function $1/(e^{\varepsilon-\mu/k_B T_e}+1)$, which is a function of T_e and energy level ε. μ is the chemical potential at given T_e. In this letter, the plane wave density functional theory (DFT) code ABINIT [17] was used to perform the massive parallelism calculations of the electron temperature-dependent g

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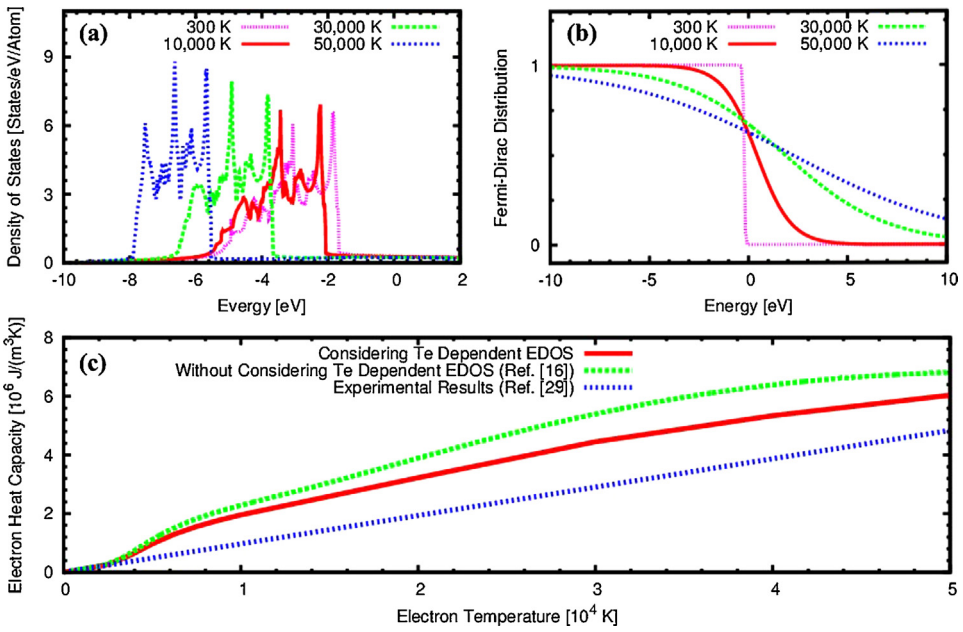

Figure 1. (a) Electron density of states and (b) Fermi–Dirac distribution for electrons at 300 K, 10 000 K, 30 000 K and 50 000 K. (c) T_e-dependent C_e from *ab initio* calculation with and without considering the T_e-dependent EDOS [16] and experimental result [29].

and f [18]. By substituting g and f and their derivatives with respect to T_e into Eq. (1), $C_e(T_e)$ was determined; this approach has not been reported before. The nucleus and core electrons of copper were modeled by the projector-augmented wave (PAW) atomic data [19], which took 11 valence electrons per atom. The local density approximation (LDA) functional developed by Perdew and Wang [20] was included for the exchange and correlation functional. The Brillouin zone was sampled by using the Monkhorts–Pack method [21]. Convergence test results showed the $18 \times 18 \times 18$ k-point grids and cutoff energy of 32 Ha are sufficient to obtain converged energy. Face centered cubic crystal of copper was established. The test result of the PAW atomic data showed the lattice constant of 3.662 Å with a relative error of 1.8% to the experimental value 3.597 Å at 300 K [22], which demonstrated the reliability of the PAW atomic data. In the next step, 50 bands per atom were set to ensure the maximum occupation of electrons. The lattice temperature T_l was kept at room temperature (300 K), while T_e was set at different values range from 300 to 50 000 K.

The energy equation for the electron subsystem is mathematically expressed as:

$$C_e(T_e)\frac{\partial T_e}{\partial t} = \nabla(K_e \nabla T) - G(T_e - T_l) + S(x,t) \tag{2}$$

where K_e and G represent the electron thermal conductivity and electron–phonon coupling factor. Both K_e and G are treated as constant in the present work, which are 400 W/(mK) and 1.0×10^{17} W/(m^{3}K) [23], respectively. Similar treatment of K_e and G are seen in Ref. [9] for aluminum. t represents time, and x denotes the direction of laser incidence, which is perpendicular to y–z plane. S is the source term of incident laser, whose density $S(x, t)$ is given as a temporal- and spatial-dependent (simplified as one dimensional) Gaussian profile

$$S(x,t) = J(1-R)(t_p L_{op}\sqrt{2\pi})^{-1} e^{-x/L_{op}} e^{-(t-t_0)^2/2t_p{}^2} \tag{3}$$

where $J = 21\,333$ J/m^2 is the laser fluence. $R = 0.4$ is the reflectivity and $L_{op} = 14.29$ nm is the optical penetration depth, which is chosen for an incident laser with laser wavelength of ~20 nm [24]. $t_0 = 50$ ps is the temporal center point of the laser beam. $t_p = 10$ ps is the full width of laser pulse at half maximum intensity.

Table 1
Variation of $\mu - \varepsilon_F$ at different T_e.

T_e (K)	$\mu - \varepsilon_F$ (eV)
10 000	0.4266
20 000	1.2756
30 000	1.8427
40 000	2.1332
50 000	2.2180

For the lattice subsystem, the motion of atoms is determined by the

$$m_i d^2\boldsymbol{r}/dx^2 = -\nabla U + \xi m_i \boldsymbol{v}_i^T \tag{4}$$

where the first term in the right side is the spatial derivative of interatomic potential U. The embedded atom method (EAM) potential of copper [25] is adopted in the present work. m_i is the mass of an atom. $\boldsymbol{r}$ is the atom position at given time. ξ in the last term in right side is defined as $1/n_t \sum_{k=1}^{n} G V_N (T_e^k - T_l)/\sum_{j=1}^{N_v} m_j (\boldsymbol{v}_j^T)^2$, which is originally proposed by Inanov and Zhigilei [8] to couple the thermal energy transferring from the electron subsystem to the lattice subsystem. $\boldsymbol{v}_i^T$ is the thermal velocity of atom i. T_e^k is the average electron temperature in each MD time step. The continuum region is divided into $N = 888$ cells with n (variable) atoms in each cell to solve Eq. (2) by using explicit finite difference method (FDM). In order to satisfy the von Neumann stability criterion, the MD time step is set as several times of the FDM time step, namely, $\Delta t_{FDM} = \Delta t_{MD}/n_t < 0.5 \quad \Delta x_{FDM}^2 C_e/K_e$ [26]. In the current letter, a conservative estimation was made by choosing Δt_{MD} as 1 fs and Δt_{FDM} as 0.005 fs.

By combing Eqs. (2)–(5) to solve the laser energy deposition in the electron subsystem and atomic motion in the lattice subsystem, a framework QM-MD-TTM integrated simulation is constructed. The QM-MD-TTM integrated simulation was performed from the revision of the TTM part in the IMD package [27,28].

The entire simulation was performed in three sequential stages. Initially, the entire system was equilibrated at room temperature (300 K) in terms of canonical ensemble (the 1st stage) to keep the lattice temperature constantly for 5 ps. Subsequently, microcanonical ensemble (the 2nd stage) was started to verify whether the