Beyond the Drude model in transport and optical properties of dense plasma of silver

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Abstract. We calculate optical and transport properties of dense silver plasma via quantum molecular dynamics together with the Kubo-Greenwood formalism and compare the results with ones obtained using a semi-analytical Drude-like model. The quantum molecular dynamics highlights an important contribution of d-electrons to the properties of silver, and thus the thermal conductivity is not described by the Drude model. At the same time, the imaginary part of dielectric function can be fitted by the Drude-like model with reasonable accuracy in the optical range of frequencies.

1. Introduction

During last decades, the femtosecond laser ablation of noble metals was a subject of thorough investigations [1, 2]. Numerical modeling can give a deeper insight into the ablation phenomenon when direct measurements are difficult or even impossible. However, simulations require knowledge of optical and transport properties of materials under consideration [3, 4]. Several approaches have been used to obtain material properties at different densities and temperatures [5] including chemical-picture model [6], a model of average atom [7], and a quantum statistical approach [8]. Development of wide-range models of optical and transport properties, covering several orders of magnitude in density and temperature, is a very complex problem. Hopefully, when femtosecond laser pulses interact with condensed targets, the process of matter heating can be considered as isochoric. Thus, the properties of matter, in particular silver, at near-normal density and temperatures from room to several eV are of great interest.

To tackle this problem, there are well elaborated methods based on quantum molecular dynamics (QMD) and the Kubo-Greenwood (KG) formalism. Recently, these approaches were used for calculation of shock Hugoniots [9, 10], phonon spectra [11], and equation of state [12]. In this paper we obtain new data on the transport and optical properties of silver plasma at 10.5 g/cm³ and in the range of temperature from 3000 to 20000 K with the aid of the KG model and QMD. The results are compared with a semi-analytical Drude-like model.
2. Computation technique

2.1. Quantum molecular dynamics and Kubo-Greenwood model

The computation method consists of three main stages: 1) QMD simulation, 2) a precise resolution of the band structure and 3) calculation of transport and optical properties according to the Kubo–Greenwood formula.

At the first stage, the atoms are placed to a supercell with periodic boundary conditions. The size of the supercell is chosen to give a density of 10.5 g/cm³ at a given number of atoms. At each QMD step the electronic structure is calculated within the framework of density functional theory from the solution of the finite–temperature Kohn–Sham equations. The temperature of electrons and ions and the total pressure of electrons and ions. The equilibrium section $T_e$ is set as a parameter in the Fermi-Dirac distribution [13]. The electronic structure is calculated within the Born-Oppenheimer approximation when the electrons are totally adjusted to the current spatial positions of the ions. The Hellmann–Feynman theorem is used to calculate the ionic trajectories via QMD simulation in the $\text{NVT}$-ensemble. Only the one-temperature case $T_e = T_i = T$ is considered in this work, though non-equilibrium case $T_e \neq T_i$ is also possible [14, 15].

As a result of the first stage, we obtain ionic trajectories, temporal dependences of the total energy of electrons and ions and the total pressure of electrons and ions. The equilibrium section of QMD simulation is used to calculate thermodynamic, transport and optical properties.

At the second stage some separate ionic configurations from the equilibrium section of QMD calculation are selected. The finite–temperature Kohn–Sham equations are solved for each chosen configuration. This calculation is similar to the electronic step of the QMD simulation, however, a larger energy cut-off number of $k$-points in the Brillouin zone and number of electron bands may be used. The Kohn–Sham energy eigenvalues $\epsilon_{i,k}$, corresponding wave functions $|\Psi_{i,k}\rangle$ and Fermi-weights $f(\epsilon_{i,k})$ are obtained as a result of the second stage. Here $i$ is the number of an electron band and $k$ is a point in the Brillouin zone.

The first and second stages are performed using Vienna ab initio simulation package (VASP) [16, 17, 18].

At the third stage, the transport and optical properties are calculated. The real part of the dynamic electrical conductivity $\sigma_1(\omega)$ is calculated according to the Kubo-Greenwood formula [19]:

$$\sigma_1(\omega) = \frac{2\pi e^2 \hbar^2}{3m_e^2 \omega \Omega} \sum_{i,j,\alpha,k} W(k) \left| \langle \Psi_{i,k} | \nabla_\alpha | \Psi_{j,k} \rangle \right|^2 \left[ f(\epsilon_{i,k}) - f(\epsilon_{j,k}) \right] \delta(\epsilon_{j,k} - \epsilon_{i,k} - \hbar\omega). \quad (1)$$

Here $\langle \Psi_{i,k} | \nabla_\alpha | \Psi_{j,k} \rangle$ are the matrix elements of the gradient operator, $\alpha$ denotes three spatial directions. $W(k)$ is the weight of the point $k$ in the Brillouin zone, $\Omega$ is the supercell volume, $e$ denotes the electron charge ($e > 0$), $m_e$ is the electron mass, $\hbar$ is the reduced Planck constant.

The calculation according to Eq. (1) is performed for each of the selected ionic configurations. The obtained values of $\sigma_1$ are then averaged for each $\omega$, thus the resulting $\sigma_1(\omega)$ is formed. The imaginary part of dynamic electrical conductivity $\sigma_2(\omega)$ can then be restored using the Kramers–Kronig relation.

To find the thermal conductivity coefficient, we calculate the dynamic Onsager coefficients $L_{mn}(\omega)$ according to the KG as follows:

$$L_{mn}(\omega) = (-1)^{m+n} \frac{1}{e^{m-n}(eT_e)^{n-1}} \frac{2\pi e^2 \hbar^2}{3m_e^2 \omega \Omega} \sum_{i,j,\alpha,k} W(k) \left( \frac{\epsilon_{i,k} + \epsilon_{j,k}}{2} - \mu_e \right)^{m+n-2} \times$$

$$\left| \langle \Psi_{i,k} | \nabla_\alpha | \Psi_{j,k} \rangle \right|^2 \left[ f(\epsilon_{i,k}) - f(\epsilon_{j,k}) \right] \delta(\epsilon_{j,k} - \epsilon_{i,k} - \hbar\omega). \quad (2)$$
The $L_{mn}$ values obtained for different ionic configurations are averaged to form the final $L_{mn}(\omega)$ curve for each $m$ and $n$. Then, the electron transport properties are used to estimate the thermal conductivity $\kappa$:

$$\kappa = L_{22} - \frac{L_{12}L_{21}}{L_{11}}. \quad (3)$$

2.2. Semi-analytical Drude-like model

In metals, according to the Drude approach, the conduction band electrons are considered as a gas, and the optical and transport properties can be estimated for a temperature below the temperature of Fermi, $T_F$. In the present model, the imaginary part of permittivity due to the intraband Drude-like contribution is:

$$\varepsilon_2 = \frac{\omega_{pl}^2 \nu}{\omega^3 + \omega \nu^2}, \quad (4)$$

where $\omega_{pl}$ is the plasma frequency and $\nu$ is the frequency of electron collisions. To take into account a temperature dependence, the frequency of collisions is considered as a sum of electron-phonon and electron-electron parts:

$$\nu = A_1 k_B T / \hbar + A_2 k_B T^2 / (T_F \hbar). \quad (5)$$

Similar, electron thermal conductivity in a metal is calculated according to the Drude formalism as follows:

$$\kappa = \frac{\pi^2 k_B^2 n_e}{3 m_e \nu} T, \quad (6)$$

where $n_e$ is the electron density corresponding to the number of conduction band electrons $Z = 2$. The dimensionless coefficients, $A_1$ and $A_2$, are adjusted to meet the KG results in the best way. These coefficients are different when describe thermal conductivity and dielectric function.

3. Results and discussion

The calculations were performed for silver plasma at normal density 10.5 g/cm$^3$ and temperatures from 3 kK up to 20 kK. The imaginary part of the permittivity $\varepsilon_2(\omega) = \sigma_1(\omega) / (\epsilon_0 \omega)$ calculated via the KG is shown in Fig. 1. The Drude-like fitting is also presented with coefficients of the collisional model (5) $A_1^p = 0.8$ and $A_2^p = 0.5$. As one can see, the results are in reasonable agreement while the real part can be obtained by means of Kramers-Kronig transform and this requires further investigations.

Fig. 2 shows the temperature dependences of thermal conductivity coefficient. The dependence, obtained with the KG formalism is non-monotonic as it decreases at $T < 7$ kK and grows at $T > 7$ kK. This behaviour is different from that for the Drude model where one can observe a monotonic decrease of the value with temperature. The corresponding effective frequency of collisions has the form (5) with coefficients $A_1^t = 1.4$ and $A_2^t = 0.5$ adjusted to meet the room temperature data.

The changes in transport properties are correlated with variations in electron density of states. The static Onsager coefficients $L_{mn}$ are connected with transitions between states with close energy eigenvalues. The transition from an occupied to some other occupied state is impossible, as well as that from an unoccupied to some other unoccupied state. Hence, only the partially occupied states in the vicinity of the chemical potential make contribution to $L_{mn}$. According to our QMD modeling, the $d$-electrons of silver start to contribute to $L_{mn}$ at $T \approx 7$–10 kK. This correlates with the changes in the behaviour of thermal conductivity, Fig. 2. It is worth to mention that in copper (a $d$-metal like silver) we have obtained a monotonically increasing thermal conductivity coefficient in the range of temperatures 2-60 kK [20].
4. Conclusions
We have calculated transport and optical properties of silver at normal density and for temperatures in the range from 3 to 20 kK. The results have been obtained by means of QMD calculations together with the KG formalism. The imaginary part of permittivity in the optical range has the Drude–like shape. The temperature dependence of thermal conductivity is non-monotonic and has a minimum at $T \approx 7$ kK. The transport and optical properties of silver are different from those of previously investigated aluminum at $3 \text{kK} \leq T \leq 20 \text{kK}$ [21] and copper at $2 \leq T \leq 60 \text{kK}$ [20]. The analysis of density of states shows that this behaviour is due to the presence of $d$-electrons.
Acknowledgements
The authors acknowledge the supported by the Presidium of RAS programs on the fundamental research.

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