Pressure in Electronically Excited Warm Dense Metals

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New emerging physics is connected with formation of warm dense matter (WDM) at the initial transient state of material evolution after energy deposition into electron subsystem with electron temperatures T_e in the range 1-100 eV. Usually WDM forms in ultrafast phenomena and is a non-equilibrium state that makes it very challenging for theory, modelling and simulation. In many cases WDM can be described as a two-temperature (2T) system when electron and ion subsystems can be considered in quasi-equilibrium at $T_e > T_i$.

Both in continuum and in atomistic models it is assumed that the quasi-equilibrium 2T-WDM can be described using thermodynamic concepts. The free energy is represented as $F(\rho;T_i;T_e) = F_e+F_i$, where $F_e = E_b+F_{fe}$, where E_b is the binding energy, F_{fe} is the free energy of free (ionized, delocalized) electrons (that vanishes at $T_e = 0$), F_i is the free energy of the ion subsystem. The corresponding representation of pressure is

$$P = P_e + P_i = P_b + P_{fe} + P_i \,, \quad (1)$$

that is a sum of the cold or binding pressure, the kinetic electronic pressure and the thermal ionic pressure. It is the total pressure P that defines the mass transfer in continuum 2T-WDM models. In the atomistic 2T-WDM models sometimes the so-called blast force [1] is introduced to describe the influence of kinetic electron pressure on the ion subsystem [2,3]. In this work on examples of Al and Au we are making an attempt to analyze the electronic contribution to the total pressure in 2T-WDM metals and to clarify the representation (1). Another question is the separation of electrons into bound and free.

The rigorous wave-functions based theory is very complicated even at $T_e = 0$, the finite temperature case being much farther from applicability in practice. Only recently accurate quantum Monte Carlo approaches have been developed in this field [4]. That is why the finite temperature Kohn-Sham density functional theory (FT KS DFT) method became a tool of choice. In the FT KS DFT framework the free energy of electron subsystem in the external potential of ions is given as $F_e = E_k + E_H + E_{xc} + E_{ei} + E_{ii} – T_eS$. KS electronic states are populated according to the Fermi-Dirac distribution. Each component of F_e gives a contribution to P_e.

We perform FT KS DFT calculations using VASP and ABINIT. The electron-ion interaction for Al and Au is described by PAW potentials. The LDA approximation is used for E_{xc}. We analyze the dependencies on the electronic temperature of the electronic pressure P_e components for fcc aluminum and gold for $T_e = 0–12$ eV. We see the strongest dependence on T_e in the kinetic and non-local pressure components. Using the pDOS-based analysis we decipher the bond hardening effect in fcc Au [5] as a transition of electrons from d-like states into s- and p-like states as well as into the plane-wave like (i.e. free) states. The concept of the homogeneous electron gas (HEG) is a starting point of the DFT-like theories of inhomogeneous systems. Here we deploy the comparison of the HEG model with the FT KS DFT results to understand the 2T-WDM properties better. We also consider the Hellmann-Feynman forces acting on ions in 2T-WDM (with the contributions from the non-local part of the PAW potentials) that are known to be consistent with the FT KS DFT [6]. We are making the following conclusions [7].

The sum of kinetic and non-local DFT pressure components governs the build-up of the electron pressure in FT KS DFT models of warm dense metals. The non-local component of the electron-ion interaction plays an important role in the changes of warm dense metal properties with the increase of electronic temperature.

In the general case the increase of electron temperature in warm dense metal not only causes the free-electron pressure build-up, but also changes the effective interionic forces and hence the binding pressure and the equation of state. Therefore in the representation (1) of the total pressure all three components depend on T_e that should be taken into account in hydrodynamic and atomistic models.

Using effective ion-ion potentials obtained by force-matching for different T_e it is possible to separate the binding component of electron pressure and the free electron like component. This is a method for calculation of the number of free electrons, i.e. the ionization degree of WDM.

Finally we discussed how P_{fe} should be taken into account in ion dynamics (i.e. the need of a blast force).

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