

## Unified First Principles Description from Warm Dense Matter to Ideal Ionized Gas Plasma: Electron-Ion Collisions Induced Friction

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Electron-ion interactions are central to numerous phenomena in the warm dense matter (WDM) regime and at higher temperature. The electron-ion collisions induced friction at high temperature is introduced in the procedure of *ab initio* molecular dynamics using the Langevin equation based on density functional theory. In this framework, as a test for Fe and H up to 1000 eV, the equation of state and the transition of electronic structures of the materials with very wide density and temperature can be described, which covers a full range of WDM up to high energy density physics. A unified first principles description from condensed matter to ideal ionized gas plasma is constructed.

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Warm dense matter (WDM), characterized by near or above a solid density and temperature up to 100 eV, is extremely important in shock compression [1], laser or other radiation pulse heating of solid targets [2,3], and astrophysics [4], etc. This matter is partially dissociated, ionized, degenerate, and strongly coupled [5], raising a big challenge in theory to describe the properties of the matter. In this temperature-density regime, semiclassical methods such as Thomas-Fermi molecular dynamics (TFMD) [6], orbital-free molecular dynamics (OFMD) [7], and average atoms molecular dynamics (AAMD) [8], are still far from a regime that is assumed valid. The path integral Monte Carlo method (PIMC) [9,10] is now only applied for the simple elements of H and He. Further, the most widely used database at present, the SESAME table [11], is a patchwork using different methods in the warm dense region. However, the huge demands in experiments, astrophysics, and a lot of other fields require much more accurate results for all elements under extreme conditions. Quantum molecular dynamics (QMD), without requiring any assumption about the potential between atoms, supplies a powerful and accurate tool in this regime [4,12–14]. In principle, QMD can describe the matter at any temperature. However, the application of QMD method has been so far limited to low temperature (usually less than a few 10 eV) mainly because of expensive computational cost, the treatment of core electrons of elements in pseudopotentials (PPs) in *ab initio* code, and insufficient numerical accuracy and convergence [6] in the procedure of QMD. Therefore, it is ultimately necessary to solve these problems and extend QMD into higher temperature and density.

With the development of supercomputers and an efficient QMD [15–17] method, the problems of computational cost and core electrons can be overcome. Moreover, core states in the PPs can be introduced to treat ionization at high temperature [18], and the temperature can be extended to 170 eV for dense hydrogen at 80 g/cm<sup>3</sup> [19]. It is, however, very difficult to apply them to matters at higher temperature around solid density and more com-

plicated elements such as Fe. It is obvious that an adequate treatment of the electron-ion collision is the key for describing the high temperature system. Generally, the subsequent interaction between the electrons and ions is a nonadiabatic effect. In traditional QMD, this interaction is described by the static potentials, losing the information of the dynamical collisions because of the assumption of Born-Oppenheimer approximation. Based on this description, the thermal equilibrium cannot be reached completely at high temperature, suggesting that there should be new physics we have not considered here. In fact, with the increase of temperature, more and more electrons would be delocalized or become free. The time scale of their motions is much less than that of ions, causing many times collisions in one QMD time step. Therefore, within adiabatic framework, the effect of the average electron-ion collisions is of essential and cannot be neglected. Also, the relaxation of the electrons and ions can introduce a significant coupling, which definitely affects the ionic and electronic structures of WDM. This lost physics makes it difficult to describe the dynamical process using QMD in a numerical scale. In order to resolve this issue, here we borrow the idea of Brownian motion, and introduce electron-ion collisions induced friction (EI-CIF) to describe the intrinsic dynamics within adiabatic framework at high temperature up to high energy density physics (HEDP).

In the regime of WDM, matter consists of a plasma where ions are in a liquidlike or gaslike environment. An ion with mass  $M_I$  moves in a dense electronic medium (mass  $m_e$ ), generating friction and random collisions, i.e., EI-CIF, similar to the motion of Brownian particles. The equation of motion is the Langevin equation (LE) and the corresponding equation for the probability is the Fokker-Planck equation (FPE), and the friction coefficient in LE and FPE is the same one. On the one hand, from FPE, the transport properties in dense plasma can be obtained. The energy relaxation and optical absorption can also be investigated by studying the detailed electron-ion collisions [20–22]. On the other hand, from the viewpoint of LE,

the thermodynamic properties can be investigated at the thermal equilibrium state without knowing the nonadiabatic collisional details. Considering small mass of electrons relative to ions, the linear LE for the ions regarding to the ratio of mass  $m_e/M_I$  can be taken here:

$$M_I \ddot{\mathbf{R}}_I = \mathbf{F} - \gamma M_I \dot{\mathbf{R}}_I + \mathbf{N}_I. \quad (1)$$

Where  $\mathbf{F}$  is the force calculated in density functional theory (DFT),  $\gamma$  is a Langevin friction coefficient,  $\mathbf{R}_I$  is the position of ions, and  $\mathbf{N}_I$  is a Gaussian random noise corresponding to  $\gamma$ . This *ab initio* molecular dynamics model based on LE is so-called quantum Langevin molecular dynamics (QLMD). Choosing an appropriate friction coefficient  $\gamma$ , i.e., the noise, is the key point in LE, which affects the dynamical properties and equilibration efficiency. Here,  $\gamma$  contains three parts: the first one is the contribution of electron-ion collisions. For simplification, the EI-CIF can be estimated by the assumption of Rayleigh model [23], i.e.,

$$\gamma_B = 2\pi \frac{m_e}{M_I} Z^* \left( \frac{4\pi n_i}{3} \right)^{1/3} \sqrt{\frac{k_B T}{m_e}}, \quad (2)$$

where  $n_i$  is the ionic number density, and  $Z^*$  is the average ionization degree. Here,  $\gamma_B$  locates generally in the area of 0.000 01 to 0.01 atomic units (a.u.). The second part is the contribution of thermostat, which is an adjuster for the temperature in canonical ensemble calculation,  $\gamma_a$ . And the third one is the contribution of force errors in the efficient QLMD (see details in Ref. [16]),  $\gamma_f$ . In numerical process, these three parts can be combined to the total friction coefficient  $\gamma = \gamma_B + \gamma_a + \gamma_f$ . In fact, the values of the intrinsic friction coefficient  $\gamma_f$  and  $\gamma_a$  do not need to be known but can be bootstrapped by taking a cue from the previous work [15,16]. In this work, we choose the convergent threshold from  $10^{-6}$  to  $10^{-4}$  in all cases with the increase of temperature (see Ref. [16]), which can ensure enough accuracy for all properties.

This method is performed based on the QUANTUM ESPRESSO package [24]. To verify our approach, the equation of state (EOS) of iron on the principal Hugoniot up to 1000 eV [at the temperature-density of (0.1 eV, 10 g/cm<sup>3</sup>), (1 eV, 13.26 g/cm<sup>3</sup>), (5 eV, 18.71 g/cm<sup>3</sup>), (10 eV, 22.5 g/cm<sup>3</sup>), (100 eV, 34.5 g/cm<sup>3</sup>), and (1000 eV, 39.65 g/cm<sup>3</sup>)], and of hydrogen along the 80 g/cm<sup>3</sup> isochore up to 1000 eV are calculated. These objects cover full range of WDM, and they are typical and essential in many fields [5]. These corresponding states are strongly or moderately coupled and partially degenerate [25].

In our calculations, for Fe, PPs with 16 (below 1000 eV) and 24 (at 1000 eV) electrons in the valence [26] are used; For H, a Coulombic pseudopotential is used [26] considering the much dense medium [19]. For the sensitivity of pressure to the plane wave cutoff energy, after carefully testing, enough cutoff for energy is used [27]. All calculations are carried out based on the framework of finite temperature DFT [28] within generalized-gradient ap-

proximation (GGA) [29]. The influence of finite temperature exchange-correlation (xc) functional is not performed [19]. The systems containing 54 Fe atoms below  $T = 100$  eV, 4 Fe atoms at 1000 eV, and 256 H atoms are introduced. More atoms were tested but no difference was found. At 1000 eV, the electron de Broglie wavelength is only about 1 a.u.; therefore, a supercell with about 3 a.u. length (including 4 Fe atoms) is used, which contains enough information for the electronic dynamical properties. Ionic structures are generated using the  $\Gamma$  point for the representation of the Brillouin zone, while more  $k$  points were tested without significant effect. For Fe, the time step is 1 fs at the temperature less than 100 eV, 0.5 fs at 100 eV, and 0.25 fs at 1000 eV. Each temperature point was simulated for at least 1 ps time length for thermal equilibrium, and 500 time steps for picking up the ensemble information such as pressure and ionic positions after thermalization. (For hydrogen, see details in Ref. [19].) Enough band energy corresponding to unoccupied bands are considered to make it higher than at least  $8k_B T$ . With these choices, a total pressure converged to 1%–2%, and all cases can be completed within 10 days using 16 to 128 processors.

Iron is the most important element in the earth, but complicated to deal with in theory. Its EOS is under debate until now since different models give rise to very different results. QMD is considered to be more reliable, but previous QMD calculation without consideration of dynamical electron-ion collisions can only give the results at low temperature ( $T \leq 5$  eV) because of numerical difficulty [6], caused by the lost dynamical ion-electron interactions. At the same time, the semiclassical approach cannot give the accurate EOS at relatively low temperatures where the shell and xc effects are dominant [6,7]. Using QLMD, the principal Hugoniot of Fe up to 1000 eV is calculated from first principles. First, the influence of friction coefficient is tested, as shown in Fig. 1(a). After thermalization, testing for a time length of 0.5 ps, it is obvious that when  $0.0005 \leq \gamma \leq 0.05$ , the pressure of the system is convergent, but for smaller or larger  $\gamma$ , the pressure is dispersed. In this case,  $\gamma_B = 0.001$ , which is a good value to keep the right information and computational efficiency. Here, too small  $\gamma$  cannot capture the EI-CIF, and too large  $\gamma$  destroys the dynamical properties of the system. Only when the  $\gamma$  is in an appropriate range, both the collisions and the dynamical properties can rightly be kept. The pressures along the principal Hugoniot at present are much better than the results of semiclassical methods, as shown in Fig. 1(b), especially at relatively low temperature. At 0.1 eV, the spin polarization might be important, and therefore, the pressure considering electronic spin is a little higher than that of the SESAME table, and much higher than the pressure obtained without spin polarization. When temperature is higher, the contribution from spin polarization can be neglected. The 3s and 3p electrons in Fe play important roles when  $T \geq 1$  eV, where the average ionization degree is very close to 8 from the AA model [30]. Therefore, our results are a little higher than the previous QMD calcula-

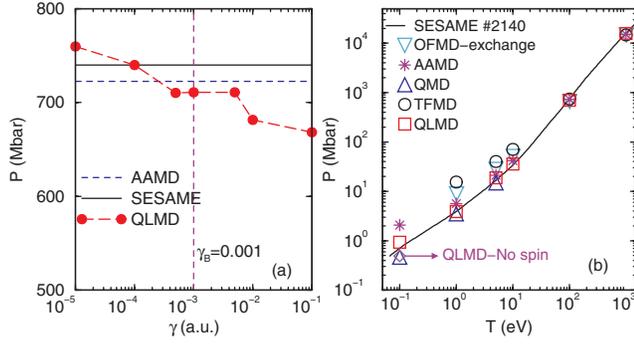


FIG. 1 (color online). (a) Influence of  $\gamma$  on pressure for Fe at a temperature of 100 eV. (b) Principal Hugoniot of Fe, comparing with the results of SESAME EOS No. 2140 [11], OFMD with xc term [7], AAMD [8], previous QMD, and TFMD [6].

tion. Above  $T = 100$  eV, the pressures using different models are in good agreement with each other, indicating our approach can extend the first principles method into the Thomas-Fermi regime.

For hydrogen at the density of  $80 \text{ g/cm}^3$ , and temperature of  $T = 800$  eV (partially degenerate), when empty band energy is higher than  $8k_B T$ , pressure and energy go convergent within 1% difference, and the pressure-temperature curve is also consistent with that using QMD and OFMD [19] and Kerley table [31], shown in Fig. 2(a). OFMD is accurate here because there is no shell effect for H and the very dense medium leads pressure delocalization, but far from SESAME table and QMD results for Fe as in Fig. 1. Furthermore, QLMD will not decrease the dynamical properties. As shown in Figs. 2(b) and 2(c), the radial distribution functions (RDF) at  $T = 5$  eV and  $T = 172$  eV using QLMD are in good agreement with those of one-component plasma (OCP) and QMD [19]. More results calculated by QLMD can be found in Ref. [25].

The figure of change of the electronic structures of dense matter over wide range of temperature is too complicated to be known accurately [32] since there is no good theoretical model before. Using denser  $2 \times 2 \times 2 k$  points, the electronic properties can be shown clearly. The typical electronic projected density of states (PDOS) and charge density distribution at different temperature-density states are shown in Figs. 3 and 4, respectively. It is interesting to find that the process of electronic delocalization and orbital mixing with the increase of density and temperature. In particular, the electronic delocalizing and mixing for  $3s$ ,  $3p$ , and  $3d$  orbitals are more and more obvious, which causes large changes in the compressibility and temperature [32] along the Hugoniot curve. At the temperature of 1000 eV,  $3s$ ,  $3p$ , and  $3d$  orbitals are totally mixed. All electrons except in  $1s$ ,  $2s$ , and  $2p$  orbitals are becoming free electrons, and the corresponding distribution of electrons, as shown in Figs. 3(e) and 3(f), is clearly the discrete energy levels of bound electrons and the Maxwell-Boltzmann (MB) distribution of free electrons. The MB

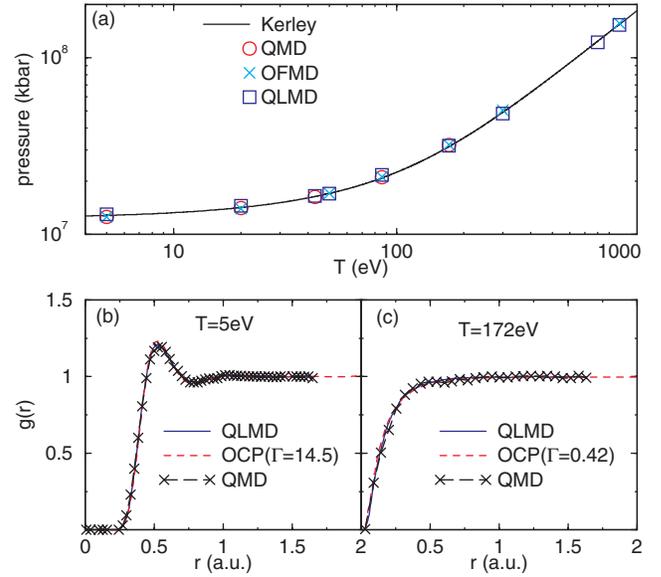


FIG. 2 (color online). (a) Pressure vs temperature for hydrogen at  $80 \text{ g/cm}^3$  compared to the other results. (b),(c) The RDF of hydrogen at different temperature using QLMD compared to the RDF of QMD and OCP [19]. The convergence threshold at 172 eV is  $10^{-4}$ .

free electrons are consistent with the large electron degeneracy parameter (about 5.4) and the matter at this temperature and density is an ideal ionized gas plasma. At this regime, the coupling of the electronic structure and the ionic space motion is not very strong and the ionization balance can be described well by the so-called Saha-Boltzmann formalism [33]. It can be seen that the distribution of free electrons shows more and more “uniform,”

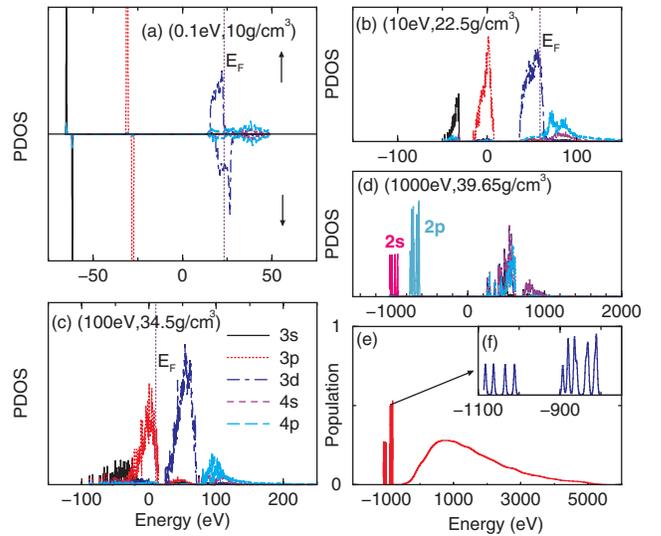


FIG. 3 (color online). (a)–(d) Typical PDOS of different orbitals at different temperature-density points (arbitrary units). The arrows represent spin up and spin down. (e) The electron population distribution at 1000 eV,  $39.65 \text{ g/cm}^3$ ; (f) a slice for the electron population for  $2s$  and  $2p$  electrons.

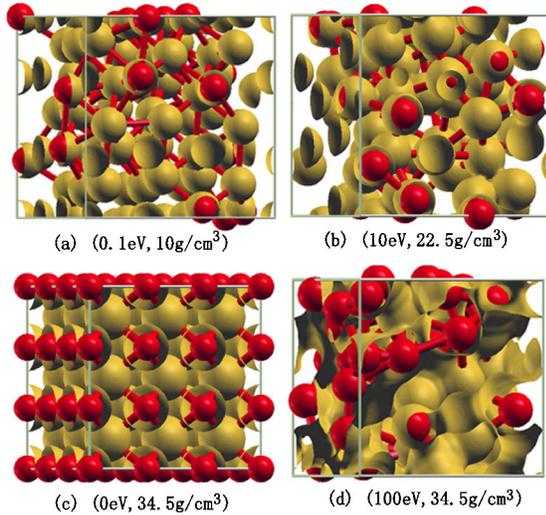


FIG. 4 (color online). Typical plot of the charge density for Fe at typical density and temperature with isovalue of 0.4 a.u.

indicating the decoupling of free electrons from the ionic motion. In Fig. 4, the electrons are more and more delocalized with the increase of temperature and density. In the beginning, at low temperature and low density, the electrons located around the ions. But at high temperature and high density, they are more and more “free.” Comparing the charge density at 34.5 g/cm<sup>3</sup> between zero temperature (crystalline structure) and 100 eV, shown in Figs. 4(c) and 4(d), the contribution of temperature to the electron delocalization is obvious.

In conclusion, the electron-ion collisions are taken as the damping effect (noisy effect) in QLMD. Based on QLMD, we smoothly make the transition between cold dense matter to HEDP going through the warm dense matter regime. It is a real breakthrough in the field of *ab initio* simulations and very complementary to the average-atom model. Also, based on the first principles calculations, accurate changes of the electronic properties, electronic conductivity [12], optical properties such as x-ray absorption [14], EOS of dense matters from low to high temperatures can be known, which have been shown to be very effective and really important in a lot of fields.

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- [1] M. D. Knudson *et al.*, *Phys. Rev. Lett.* **87**, 225501 (2001).  
 [2] U. Zastra *et al.*, *Phys. Rev. E* **78**, 066406 (2008).  
 [3] P. K. Patel *et al.*, *Phys. Rev. Lett.* **91**, 125004 (2003); A. Mančić *et al.*, *ibid.* **104**, 035002 (2010).

- [4] W. Lorenzen, B. Holst, and R. Redmer, *Phys. Rev. Lett.* **102**, 115701 (2009).  
 [5] S. Ichimaru, *Rev. Mod. Phys.* **54**, 1017 (1982).  
 [6] F. Lambert, J. Clerouin, and G. Zerah, *Phys. Rev. E* **73**, 016403 (2006).  
 [7] F. Lambert *et al.*, *Europhys. Lett.* **75**, 681 (2006).  
 [8] Y. Hou and J. Yuan, *Phys. Rev. E* **79**, 016402 (2009).  
 [9] B. Militzer and D. M. Ceperley, *Phys. Rev. Lett.* **85**, 1890 (2000); *Phys. Rev. E* **63**, 066404 (2001).  
 [10] B. Militzer, *Phys. Rev. B* **79**, 155105 (2009).  
 [11] SESAME: The Los Alamos National Laboratory Equation of State Database, edited by S. P. Lyon and J. D. Johnson (Group T-1, Report No. LA-UR-92-3407, 1992).  
 [12] L. Collins *et al.*, *Phys. Rev. E* **52**, 6202 (1995); M. P. Desjarlais, J. D. Kress, and L. A. Collins, *ibid.* **66**, 025401 (R) (2002); S. Mazevet *et al.*, *ibid.* **71**, 016409 (2005); D. A. Horner, J. D. Kress, and L. A. Collins, *Phys. Rev. B* **77**, 064102 (2008).  
 [13] B. Holst, R. Redmer, and M. P. Desjarlais, *Phys. Rev. B* **77**, 184201 (2008).  
 [14] S. Mazevet and G. Zerah, *Phys. Rev. Lett.* **101**, 155001 (2008).  
 [15] F. R. Krajewski and M. Parrinello, *Phys. Rev. B* **73**, 041105(R) (2006); T. D. Kühne *et al.*, *Phys. Rev. Lett.* **98**, 066401 (2007).  
 [16] J. Dai and J. Yuan, *Europhys. Lett.* **88**, 20001 (2009).  
 [17] S. Mazevet *et al.*, *Phys. Rev. E* **75**, 056404 (2007).  
 [18] M. P. Surh, T. W. Barbee, and L. H. Yang, *Phys. Rev. Lett.* **86**, 5958 (2001).  
 [19] V. Recoules *et al.*, *Phys. Rev. Lett.* **102**, 075002 (2009).  
 [20] L. Spitzer, *Physics of Fully Ionized Gases* (Interscience, New York, 1967).  
 [21] M. S. Murillo and M. W. C. Dharma-wardana, *Phys. Rev. Lett.* **100**, 205005 (2008); M. W. C. Dharma-wardana, *ibid.* **101**, 035002 (2008).  
 [22] A. J. Kemp *et al.*, *Phys. Rev. Lett.* **97**, 235001 (2006); A. Grinenko and D. O. Gericke, *ibid.* **103**, 065005 (2009).  
 [23] A. V. Plyukhin, *Phys. Rev. E* **77**, 061136 (2008).  
 [24] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009); <http://www.quantum-espresso.org>.  
 [25] See supplementary material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.104.245001> for parameters, diffusion, and EOS for H, He, Al, and Fe.  
 [26] Fe.pbe-sp-van.UPF and H\_coul.UPF from the QUANTUM ESPRESSO distribution. For Fe at  $T = 1000$  eV, PPs with 24 electrons including 2s and 2p electrons in the valence.  
 [27] Cutoffs of 150 and 200 Ry for wave functions, 1200 and 1600 Ry for the charge density for Fe and H, respectively. For Fe at 1000 eV, cutoffs of 400 Ry for wave functions and 3200 Ry for charge density are adopted.  
 [28] N. D. Mermin, *Phys. Rev.* **137**, A1441 (1965).  
 [29] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).  
 [30] Y. Hou *et al.*, *Phys. Plasmas* **13**, 093301 (2006).  
 [31] G. I. Kerley, Sandia National Laboratory Technical Report No. SAND2003-3613, 2003.  
 [32] M. Ross, *Rep. Prog. Phys.* **48**, 1 (1985).  
 [33] Ya. B. Zel’dovich and Yu. P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamics Phenomena* (Academic Press, New York, 1966), Vol. I.