

Dynamic stability of Fe under high pressure

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Abstract. We study the dynamic stability of bcc iron at both high pressure and temperature via Molecular Dynamics in conjunction with three different interatomic potentials constructed within the embedded-atom method. We computed the phonon dispersions, the phonon density of states, as well as the radial distribution functions. It is found that these quantities exhibit different behaviours depending on the potential used. Furthermore it is revealed that the simulated sample remains dynamically stable over a wide range of temperature and pressure for all potentials.

1. Introduction

Iron enjoys a special place in both scientific research and industrial application. It is a transition metal whose physical properties can be augmented by alloying with other chemical elements to produce materials with unique properties, such as high T_c superconductors, stainless steel, etc. Furthermore, it is the most abundant constituent of Earth's outer and inner core. It can be found in many stable crystallographic structures the temperature and the pressure phase diagram (see [1, 2, 3, 4, 5] and references therein).

Ab-initio computations put together with experimental data show that the low temperature phase (at ambient pressure) of Fe is body-centred cubic (bcc), known as α -Fe or ferrite. Increasing the temperature gradually leads to a structural phase change, at about 1185 K, from α - to γ -Fe, which appears to be face-centred cubic (fcc) or austenite. At a higher temperature, about 1667 K, iron transforms again into a stable bcc structure (δ -Fe) and above 1811 K it melts into a liquid phase. On the other hand increasing the pressure to about 13 GPa at room temperature the structure of iron changes into a hexagonal-closed packed (hcp) crystal, known as ϵ -Fe. Moreover there exist some experimental evidences pointing to a β -Fe phase at high-temperatures (exceeding 1500 K) and pressures (above 50 GPa) [5], although it has been thought that this phase has either an orthorhombic structure or a double hcp one (see e.g. [6] and references therein).

Using realistic computer simulations based on quantum mechanical methods to investigate the properties of materials is extremely demanding in terms of memory and/or computer time, restricting the simulations to small samples. To consider systems with very large number of atoms on a large time scale it would be suitable to employ Monte Carlo or Molecular dynamics in conjunction with (semi-)empirical interaction potentials that can be estimated with the aid of relevant experimental data sometimes supported by *ab initio* results. Beside efficiency semi-empirical models need to meet an additional criterion: reliability. First they must be able to reproduce with high accuracy various relevant experimental data, such as elastic, structural and thermal properties. Furthermore the potential must be transferable in the sense that it would predict reasonably well properties that were not used during its construction procedure. By now there



exist several efficient semi-empirical potential formalisms depending on the way their corresponding expressions are derived by quantum mechanical methods. These potentials account for local density profiles of the element under study. These approaches have been successfully applied to model atomic interactions in iron and many interatomic potentials have been proposed so far.

The aim of the present paper is to study the mechanical properties of iron at high temperature and pressure with the aid of an open source code for classical molecular dynamic (MD) simulation, namely LAMMPS [7]. We compute and compare some characteristic physical properties of Fe employing several interatomic potentials [8, 9, 10] (within the embedded atom potential method (EAM) [11]) designed for iron and validated by computing its fundamental physical properties. Moreover some of the potentials were checked for transferability to different atomic structural phases. Here we will turn our attention to the computation of the phonon density of states and the phonon dispersion curves along the high symmetry vectors of the bcc structure at extreme pressures and very high temperatures. Furthermore we will investigate the stability of the structure of iron under these extreme conditions.

The rest of the paper is organized as follows: In Section 2 we introduce the main theoretical models based on EAM and briefly review the computational methodology. In Section 3 we discuss the results of static equilibrium properties, as well as MD simulations. Finally we draw our conclusions in Section 4.

2. Theory and computational technique

The total energy of a monoatomic system within EAM is given by the general expression [11]

$$E_{\text{tot}}^{\text{EAM}} = \sum_i \left[\frac{1}{2} \sum_{j \neq i} \Phi(r_{ij}) + F(\bar{\rho}_i) \right], \quad (1)$$

where $\Phi(r_{ij})$ is the pairwise interaction potential energy among atoms at sites i and j located at distance r_{ij} from each other and F represents the embedding energy of an atom i as a function of the background electron density

$$\bar{\rho}_i = \sum_{j \neq i} \rho(r_{ij}), \quad (2)$$

with $\rho(r)$ the electron density of a single atom. In general this expression may be very complex. It depends on a number of running parameters that need to be optimized by fitting the predictions of some selected properties of specific materials to their target values corresponding to experimental and/or first-principles data. In the EAM formalism, $\bar{\rho}_i$ is a linear superposition of spherically atomic electron densities. For more details the interested reader may consult the article review [12] and references therein.

The EAM potentials constructed for pure iron in references [8, 9, 10] were used to estimate some basic properties, such as the cohesive energy, the equilibrium lattice parameter and elastic constants. Moreover we used MD simulation in the isothermal-isobaric canonical ensemble (NPT) to compute the phonon dispersion curves, as well the phonon density of states (DOS) employing the technique implemented within LAMMPS according to reference [13]. To this end we used a superlattice consisting $16 \times 16 \times 16$ atoms arranged in a bcc-primitive cell. Simulations were performed under periodic boundary conditions on the three space directions, thus neglecting possible surface effects. Equations of motion were integrated using a time step $\delta t = 2 \times 10^{-15}$ s to ensure energy conservation of the trajectories during the simulation process for all potentials under study. The system was equilibrated at the desired temperature and pressure during 0.4 ns. The thermodynamic averages were computed satisfactorily over trajectories lasting 12 ps and measurements were collected every 20 MD steps. Furthermore we deduce temperature dependent elastic constants from the acoustic mode dispersion relations following the method of reference [14]. Let us recall that the elastic constants for cubic metals at finite temperatures are known to obey the following independent inequalities [15]:

$$B = \frac{1}{3} (C_{11} + 2C_{12}) > 0, \quad C' = \frac{1}{2} (C_{11} - C_{12}) > 0, \quad \text{and} \quad C_{44} > 0. \quad (3)$$

3. Results and discussions

In table 1 we present our estimates for some equilibrium (at $T = 0$ K) properties of Fe calculated within the three EAM potentials used in this study along with experimental data [16, 17, 18]. The obtained results show that all the potentials reproduce accurately well the experimental values, except for cohesive energy evaluated with the potential of reference [9] which is about 3.9 % lower. On the other hand the computed relaxed elastic constants C_{11} and C_{12} corresponding to the potentials [8, 9] are in better agreement with the experiment than that of reference [10]. As for C_{44} the closest value to experiment is the one obtained with the potential [8].

Table 1. Lattice properties of iron at equilibrium obtained with the three EAM potentials along and experimental data interpolated to 0 K.

	EAM [8]	EAM [9]	EAM [10]	Experiment
a_0 (Å)	2.8665	2.8553	2.8659	2.87 [16]
E_0 (eV)	-4.28	-4.12	-4.29	-4.28 [17]
C_{11} (GPa)	241.1	243.4	229.7	242.0 [18]
C_{12} (GPa)	146.8	145.0	135.5	146.5 [18]
C_{44} (GPa)	114.0	116.0	116.8	112.0 [18]

Table 2. Lattice properties of iron at finite temperatures obtained for the EAM potentials compared to experiment. Here $\bar{a}_V$ and ρ ($\times 10^3$) are the average atomic volume and density, respectively.

	$T \approx 300$ K and $P \approx 0$ GPa				$T \approx 6000$ K and $P \approx 300$ GPa		
	EAM [8]	EAM [9]	EAM [10]	Exp.	EAM [8]	EAM [9]	EAM [10]
$\bar{a}_V$ (Å ³)	11.92	11.64	11.88	11.77 [19]	7.514	7.175	7.238
C_{11} (GPa)	217.7	210.1	210.7	233.1 [20]	3003	2032	1215
C_{12} (GPa)	135.7	120.8	122.9	135.4 [20]	188.6	1120	1146
C_{44} (GPa)	121.2	117.9	116.0	117.8 [20]	1960	707.7	456.7
ρ (kg/m ³)	7.778	7.966	7.804	7.859 [21]	12.34	12.93	12.81

In table 2 we report results for the lattice properties at two specific cases corresponding to different points on the phase diagram (T, P), namely (300 K, 0 GPa) and (6000 K, 300 GPa). It is obvious that the stability conditions of equation (3) are satisfied in both cases for all potentials. Notice that at 300 K the elastic constants behaves differently for the three potentials, but they follow the same trend as experiment. In general they compare reasonably well with experimental values. At (6000 K, 300 GPa) the stability conditions (3) are fulfilled, but the elastic constants are quite different. This behaviour needs further investigation.

The phonon-dispersion curves measured during MD simulations with the three potentials are shown in figure 1 together with experimental results obtained using inelastic scattering techniques [22] and in table 3, we present our results at the-highest points in the Brillouin zone along with the corresponding experimental ones. It is clearly seen that all three potentials reproduce reasonably well the main features of the experimental curves, apart from some discrepancies at specific points. For the potential [8] this behaviour was already reported in reference [8] where the phonon dispersion curves were obtained using a different method. In the case of higher temperature and pressure however the three potentials lead to completely different behaviours. The maximum value obtained

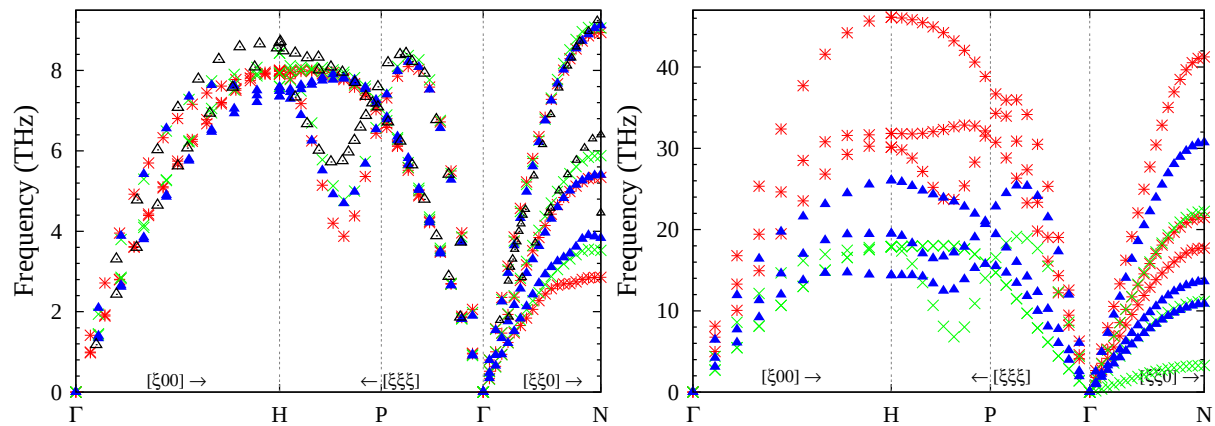


Figure 1. Comparison of the phonon-dispersion curves for iron at low temperature 300 K in the absence of pressure (left) predicted by the three EAM potentials: [8] (stars), [9] (filled triangles) and [10] (crosses). The experimental values (empty triangles) are measured at temperature 295 K [22]. The right panel shows the curves obtained at high temperature 6000 K and pressure 300 GPa with the same symbols as in the case of normal conditions.

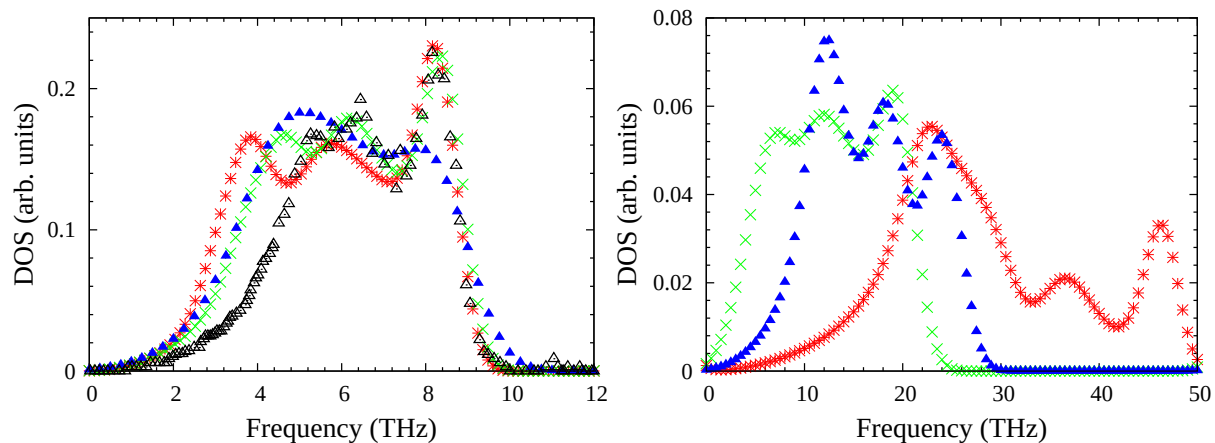


Figure 2. Phonon DOS obtained via MD simulation. Low (left) and high (right) temperature and pressure obtained with the three EAM potentials [8] (stars), [9] (filled triangles) and [10] (crosses) along with the experimental values (empty triangles) measured at temperature 300 K [23].

with the potential [8] lying on the L line in $\Gamma - \Gamma$ region is approximately 2.6 to 3 times larger than those of references [9] and [10], while the maximal value in the region $\Gamma - N$ is 1.9 times larger. In figure 2 we show the corresponding phonon DOS predicted by the three potentials. At 300 K we compare our estimates with experimental measurements obtained by nuclear resonant inelastic scattering of synchrotron radiation [23]. Notice that all EAM potentials reproduce the three main peaks of the experimental DOS. The position of the high frequency peak is found to be in a good agreement with experiment, while the lower ones are beneath those of the experimental ones in agreement with the findings of reference [24]. At high temperature (6000 K) and pressure (300 GPa) the phonon DOS for the different models show different behaviours. This unusual behaviour can be traced back to optimization procedures used to construct each potential and in the absence of experimental results we cannot conclude which potential gives the most accurate results. Despite these differences we

can see from the behaviours of the radial distribution functions (figure 3) that the structure of the final configurations (figure 4) are indeed characteristic of stable bcc like structures, but with different degrees of order. In figure 4 we show the initial, as well as the final configurations of obtained with each potential. One can see that the structure corresponding to the potential [8] is more ordered than the two other potentials, thus confirming the behaviours of the radial distribution functions.

Table 3. Zone boundary phonon frequencies of bcc iron at “normal conditions” and at high temperature and pressure conditions (in THz). The experimental values are measured at 295 K.

	$T \approx 300$ K and $P \approx 0$ GPa				$T \approx 6000$ K and $P \approx 300$ GPa		
	EAM [8]	EAM [9]	EAM [10]	Experiment [22]	EAM [8]	EAM [9]	EAM [10]
H	8.00	7.10	8.10	8.56	46.1	26.1	17.9
N_L	8.95	8.93	9.06	9.24	41.3	30.7	22.2
N_{T_1}	2.87	3.74	3.52	4.35	17.6	10.9	3.26
N_{T_2}	5.34	5.58	5.89	6.40	21.6	13.7	11.2
P	6.96	6.67	7.02	7.20	35.9	21.0	15.4

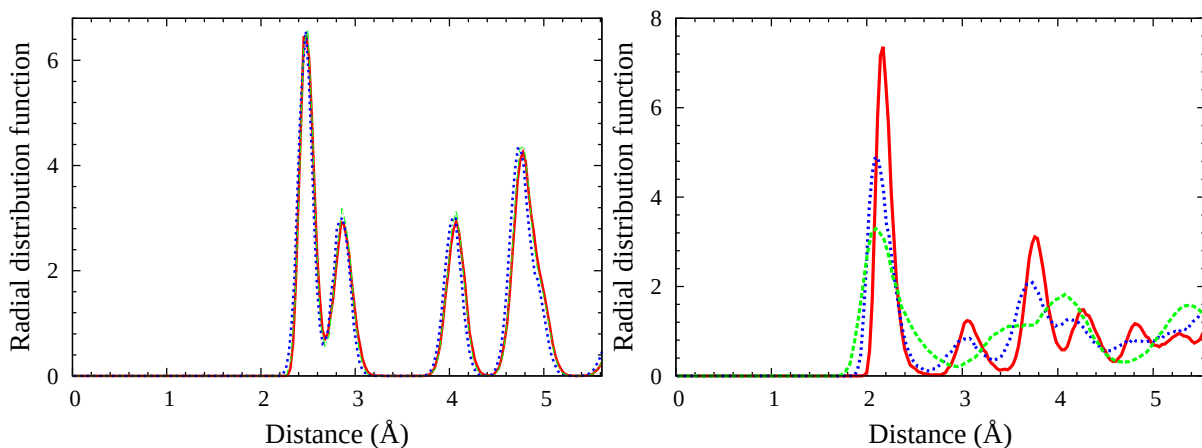


Figure 3. Radial distribution functions of Fe obtained with the EAM potentials [8] (red), [9] (green) and [10] (blue).

4. Concluding remarks

Thermodynamics and structural stability of iron are investigated using three different interatomic potentials [8, 9, 10] within the embedded atom method. Each of the named potentials is constructed by fitting to different physical properties obtained from experimental data and/or first principles results. Minimizing the potential energy of each force field, we computed the equilibrium lattice parameter, cohesive energy and elastic stiffness coefficients. In general it is found that these potentials reproduce accurately the experimental results. Further we performed a molecular dynamics simulation to study the structural stability of iron under high temperature and pressure. To this end we have computed the phonon dispersion curves, the phonon density of states, and well as

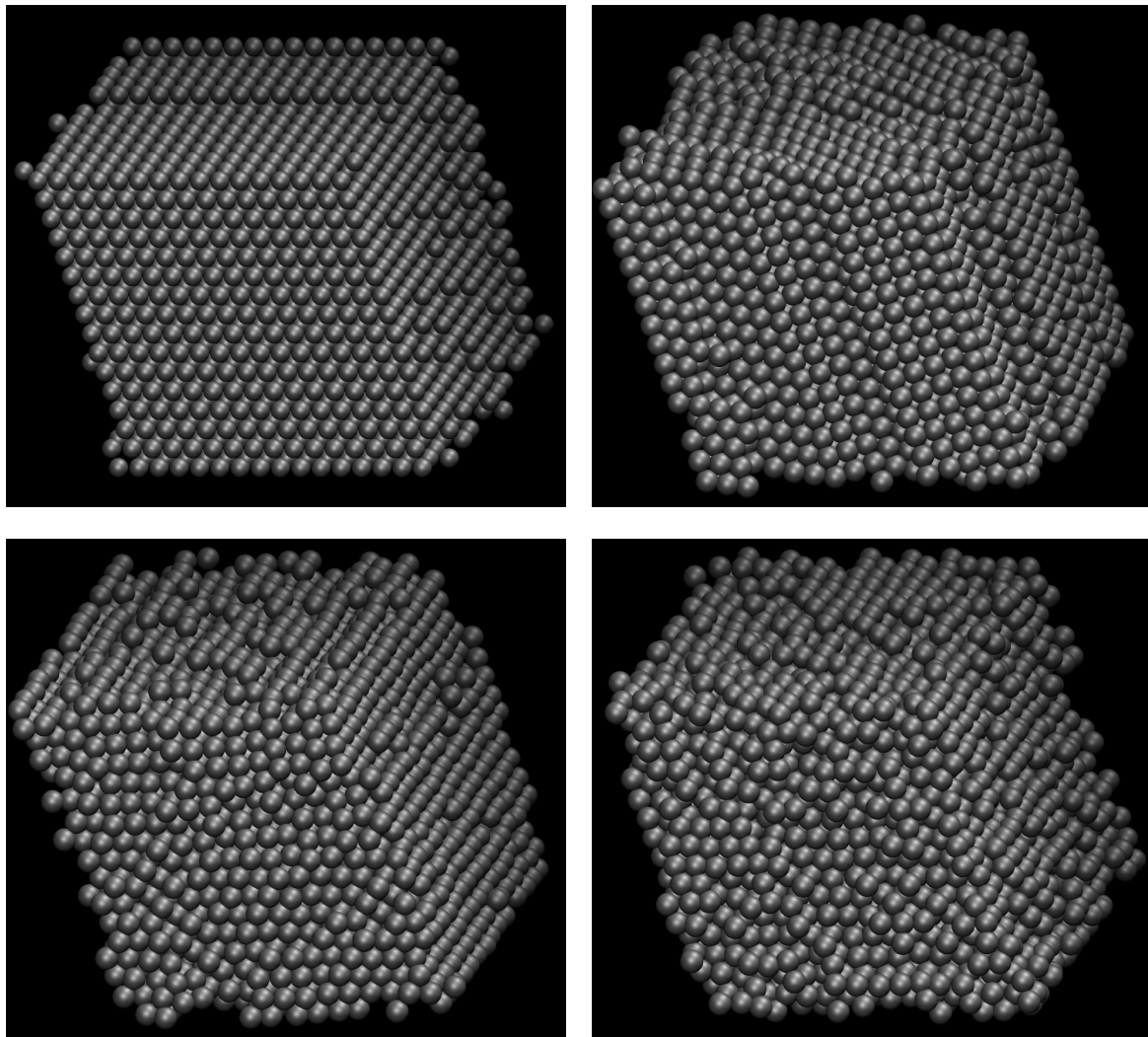


Figure 4. Initial configuration (top left) used for phonon computation at $T = 6000$ K and $P = 300$ GPa, and the final configurations at the very last time step of the simulation corresponding to the different potentials: Top right [8], bottom left [9] and bottom right [10].

the temperature dependent elastic constants. At normal conditions of temperature and pressure our results for the three potentials were found to agree very well with experimental results. To investigate the effect of the high temperature and pressure we have chosen a specific point in the phase diagram of iron, namely 6000 K and 300 GPa. Our results for the phonon dispersion curves and DOS led to completely different behaviours. This is most likely a consequence of the procedures used in the construction of each potential. Despite these discrepancies all potentials predicted stable bcc structures with different degrees of order.

Acknowledgements

Discussions with L. T. Kong are greatly acknowledged. This work was supported by the NSF of Bulgaria Grant DNTS/Germany 01/2 (03.09.2014).

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