Vibrational and thermoelastic properties of bcc iron from selected EAM potentials

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ABSTRACT

A comprehensive, critical study of the vibrational, thermodynamic and thermoelastic properties of bcc iron is presented, using well established semi-empirical embedded-atom method potentials available in the literature. Classical molecular dynamics simulations are used to address temperature effects, where dynamical matrices are constructed as a time average of the second moment of the atomic displacements. The C_{11}, C_{44}, C' elastic constants are then obtained from the sound velocities along high symmetry directions in reciprocal space. Results are compared to ultrasonic measurements and highlight the limitations of the potentials considered here in describing thermoelastic properties.

1. Introduction

Iron is a transition metal whose relative abundance in the universe is a by-product of stellar activity. It can be found in large quantities in liquid and solid forms in planetary cores like in the case of earth (85% of the composition [1]), thus characterizing the propagation of seismic waves in the interior of our planet. It is also the major constituent of steels which are still of fundamental interest for our economic processes. The complexity of its phase diagram, mainly driven by the co-operative vibrational and magnetic contributions to the free energy [2,3], makes this element particularly challenging to describe via computer simulations. This is valid especially at high temperatures, where these cooperative effects determine a dramatic change in the structural properties of the system. At the Curie temperature of ~1043 K, iron turns from a ferromagnet into a paramagnet experiencing a second order transition ($\alpha \rightarrow \beta$). This transition is then followed at higher temperatures by two other structural transitions, namely a bcc → fcc ($\beta \rightarrow \gamma$) and a fcc → bcc ($\gamma \rightarrow \delta$), before melting at ~1810 K.

Empirical potentials have been extensively tested and used to study the thermodynamic and mechanical properties of iron and its alloys, including phase stability and structural martensitic transitions [4–8], and a vast class of point- or extended defects such as vacancies [9,10], interstitials [11–13], dislocations [14–19], or tip-cracks with brittle to ductile transitions [20–22]. The study of these classes of defects requires the use of accurate potentials that are capable of reproducing

plastic, non-elastic and elastic properties at the same time. In fact, it is known that extended defects induce long-range residual stresses that can directly influence structure and dynamics of their own core-defect region [20,23]. While zero-temperature experimental equilibrium volume and elastic constants are typically well reproduced by most of the embedded-atom method (EAM) potentials available in the literature (due to the fact that, commonly, they are explicitly included in the fitting datasets together with other standard quantities such as lattice parameters, cohesive energies, and defect formation energies from experiments and calculations), there are only a few studies which have been performed to analyze carefully the performance and the accuracy of this kind of potentials at increasingly high temperatures [24,25]. For iron in particular, we are aware of such kind of study for a recent machine learning potential only [26]. For this reason, in this work we perform an extended investigation of the thermo-mechanical response of a selection of popular EAM potentials [27–30] fitted on experimental and ab-intio data. The analysis is performed by means of classical molecular dynamics (MD) calculations throughout the entire range of stability of the α-phase of iron, and can be considered a stringent test for the validation of a potential. Very recently [31], the high pressure/high temperature phase diagram of iron has been derived from a set of EAM potentials, including some of the EAM potentials investigated in our study. The conclusion of Ref. [31] is that the accuracy of the EAM potentials depends strongly on the fitting set (i.e. including or not liquid configurations).

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The paper is organized as follows: in Section 2 we describe the methodology used to calculate thermodynamic quantities, phonons and elastic constants. In Section 3 we analyze convergence issues associated to the methodology adopted for the calculation of the elastic constants. The results are then compared with experimental data available in literature and discussed in Section 4. Summary and conclusions are reported in Section 6.

2. Methods and details of the calculations

EAM potentials [32] are a class of semi-empirical interatomic potentials constructed to provide an improved description of metallic bonding between atoms, compared to that of simple pair-wise interactions. The analytic functional form of such potentials shares similarities with that of the glue model [33], the Finnis-Sinclair [34] approach and effective-medium theory [35]. Specifically, the potential energy of an EAM atom i embedded in a generic atomic environment is given by

$$\epsilon_i = \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}) + \mathscr{F}\left(\sum_{i \neq j} \rho(r_{ij}) \right),$$

(1)

where r_{ij} is the distance between neighboring atoms i and j (j within a sphere centered around i with a local cutoff radius r_{cut}), $\phi(r)$ is a pairwise potential term, and $\mathscr{F}$ a many-body convex nonlinear embedding function depending on an effective local charge density function $n(r_i) = \sum_{i \neq j} \rho(r_{ij})$ due to the atoms surrounding i within a radial distance r_{cut}. Extensive reviews of the EAM approach can be found in Refs. [35,37]. In this work, we focus our attention on the Mendelev03 [27], Meyer98 [28], Ouyang12 [29] and Marchese87 [30] EAM potential parameterizations, which have proven to be successful in the description of a wide range of crystal and defect properties of iron and its alloys (cohesive energy, 0 K elasticity, mono-vacancy formation energy). These potentials differ in the details of the functional form used to describe the embedding, in the pair and effective charge-density functions, and also in the different information included in the datasets.

In particular the Mendelev03 potential (*potential 2* in Ref. [27]) has been fit to both experimental data (including lattice spacing of bcc and fcc at 0 K, bcc cohesive energy, unrelaxed bcc vacancy formation energy, bcc to fcc crystals energy difference, bcc and fcc interstitial formation energies, liquid density) and to the forces obtained from a few snapshots of an ab initio MD simulation of liquid, non-magnetic iron. The Meyer98 potential has been fit to various experimental data sources, including bcc lattice constant, sublimation energy, elastic constants, bcc-to-fcc energy differences, vacancy formation energy and selected phonon frequencies. The Marchese87 potential has been generated starting from an early work by Finnis and Sinclair, and has been fit to experimental cohesive energy, equilibrium volume and elastic constants, in addition to the potential energy along the vacancy migration barrier, but they don't give details of the calculation. Finally, the Ouyang12 EAM potential has been fitted to experimental data, including bcc/bcc lattice parameters, elastic constants, cohesive energies, vacancy formation energies in bcc/fcc, bond-length and dissociation energy of the Fe dimer.

Regardless of the parameterization, low-temperature experimental elastic constants of bcc iron have always been included in the training protocol. These potentials are therefore expected to reproduce such quantities at zero temperature and/or in the low-temperature regime. However, no systematic analysis has been performed to verify accuracy at finite temperature in the whole experimental temperature range of stability of the α ($0 \rightarrow 1043$ K) and β ($1043 \rightarrow 1185$ K) phases, 1185 K being the experimental melting temperature. In order to get a glimpse on the high-temperature behavior of the four potentials, we calculated their melting temperature using the two-phase coexistence method.[2]

The melting temperatures are the following: 1768 ± 16 K (Mendelev03), 2120 ± 17 K (Meyer03), 2404 ± 20 K (Marchese87) and 2276 ± 22 K (Ouyang12). From these results, the Mendelev03 potential, which has been fitted also to the properties of the liquid, provides the best description of melting of solid iron.

The strategy adopted to calculate finite-temperature elastic constants is based on molecular dynamics (MD) simulations:

1. We first compute the thermal expansion from constant pressure MD simulations, and extract the volumetric/linear thermal expansion coefficient $\alpha_V(T)/\alpha_L(T)$ and specific heat at constant pressure $C_P(T)$.
2. Second, we calculate the phonon spectrum for a number of temperatures at their respective calculated equilibrium volumes, using the time average of the second moment of atomic displacements.
3. Then, we compute the C_{11}, C_{44} and C' elastic constants as a function of temperature from the long-wavelength limit of the finite-temperature phonon dispersions. We derive the C_{12} elastic constant and bulk modulus B from standard relationships for cubic crystals.

We now describe these steps in detail. The equilibrium volumes are obtained performing a set of constant pressure/temperature (NPT) runs at vanishing external pressure, at a temperature going from 100 to 1200 K with increments of 100 K. The pressure is controlled through a Parrinello-Rahman barostat [38] while a Nose–Hoover chain thermostat [39] is used to keep constant the average temperature. The equations of motion used to sample trajectories in the position-velocity phase-space of the NPT ensemble are those of Shinoda [40], that combine the Martyna, Tuckerman and Klein correction [41] with the strain energy proposed by Parrinello and Rahman [38], and are solved using the time-reversible measure-preserving Verlet algorithm derived by Tuckerman [42] as implemented in the LAMMPS [43] package. The initial configuration of each MD run consists of a $10 \times 10 \times 10$ cubic supercell with periodic boundary conditions (PBCs) containing 2000 atoms with slightly randomized displacements from the perfect bcc structure. The velocities are initialized according to a Maxwell-Boltzmann distribution. During the simulations, the time-step is fixed at 1 fs, and the relaxation times of the barostat and thermostats are set to be 1 ps and 0.1 ps, respectively. Each simulation is carried out for 10 million steps, equivalent to 10 ns. The first 0.5 ns are used for thermalization and equilibration of the system, while the remaining 9.5 ns are used for accumulating thermodynamics averages. The simulation length and size are chosen to ensure the convergence of the relevant thermodynamic quantities. The volumetric and linear coefficients of thermal expansion are obtained from the temperature derivative of a cubic spline interpolation of the average equilibrium volumes calculated from the MD runs according to Eq. (2),

$$\alpha_V(T) = 3\alpha_L(T) = \frac{1}{V}\frac{\partial V(T,P)}{\partial T}\bigg|_{P=0}.$$

(2)

Similarly, according to Eq. (3), the specific heat is obtained as a temperature derivative of a cubic spline interpolation of the calculated average enthalpy H,

$$C_P(T) = \frac{\partial H(T,P)}{\partial T}\bigg|_{P=0}.$$

(3)

The phonon dispersions at finite temperature are obtained directly through MD runs using the *FixPhonon* fix by Kong [44] implemented into LAMMPS [43]. In this method, the dynamical matrix is obtained through Green's functions [45] calculated as time-averaged second moments of the atomic displacements, assuming thermal equilibrium

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(*footnote continued*)

at different temperature, and monitored the movement of the solid–liquid interfaces. This way, we obtained a rough estimate of the melting temperature. Finally, we performed a constant-enthalpy run and obtained the melting point as the average temperature of the system.

[2] We prepared a 8000 atoms sample, with two solid (bcc)-liquid interfaces, equilibrated