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P-V-T equation-of-state to the TPa regime for liquid Fe from *ab-initio* simulations

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Abstract

We present a thermodynamic model for liquid iron, based on *ab-initio* molecular dynamics simulations, which is applicable to 2 TPa and beyond 10000 K, conditions that are relevant in the cores of super-Earths. We fit the *V-T-P* results with a self-consistent thermodynamic equation of state formulation combined with a correction formalism that accounts for the known density mismatch of the *ab-initio* molecular dynamics results at ambient pressure. We explore the performance of our thermodynamic potential and various previously published models for liquid iron over a wide range of planetary conditions. The correction significantly improves the agreement of computed properties with experiments and other thermodynamic models that are based on an assessment of the phase diagram at ambient and moderate pressure, showing how *ab-initio* molecular dynamics simulations can be used at par with other thermodynamic techniques. Evaluated along a core-temperature profile in Kepler-36b, differences in density from various models are negligible, showing robust extrapolation of all equation of state models.

1. Introduction

The pressure-volume-temperature (*P-V-T*) equation-of-state (EoS) of liquid iron provides important information (reference adiabat, density ϱ and higher order thermodynamic parameters) in modelling the internal structure of planetary bodies with Fe-based cores. Relevant *P*-conditions range from a few GPa (Moon, Mercury) through the 100 GPa range (Earth) to several TPa (super-Earths). Experimental data on ρ in the liquid stability field are scarce and a thermodynamic assessment of ρ depends on matching Gibbs energy along the melting line which remains controversial to this day and unconstrained above few 100 GPa. The alternative determination of a *P-V-T* EoS based on *ab-initio* simulations provides access to large *P*, but suffer from the fact that ρ at ambient *P* is predicted too large by as much as 20% [e.g., 1].

2. Methods

We perform molecular dynamics simulations based on density functional theory (DFT-MD) using the Vienna Ab-initio simulation package (VASP) and the Perdew-Burke-Ernzerhof generalized gradient approximation to exchange and correlation. The simulations are set up with a 144 atom supercell of liquid iron, covering more than two-fold compression (P~1.4 TPa) and a T-range up to 12000 K. The resulting *V-T-P-E* quadruplets are fit with a thermodynamically self-consistent model for Helmholtz energy [2,3] resulting in an EoS that is reminiscent in its failure to describe the low *P*-behavior near melting to a previous DFT-MD based EoS [1]. In order to correct for this mismatch, we apply the empirical formalism of ref. [4] to adjust the Helmholtz energy expression by fitting it to properties at the melting (T_m) and critical point (T_C).

3. Results and Discussions

Due to the nature of the correction formalism, its most significant influence spans the region between the critical density (ϱ_c~2 g/cm^3) and Earth's outer core (ϱ~12 g/cm^3) [5]. Uncorrected, experimental *P* is systematically underestimated by our DFT-MD simulations and the model EOS fit to the results, a problem it shares with the work using similar underlying DFT-MD results over a narrower *V/T* range and different model parametrization [1]. This discrepancy is resolved by the correction, which is illustrated by the close match of properties at T_m and the single low *P* data point at 4.3 GPa [6] which is not included in the correction or fitting. In this regime, our model performs similarly well as models that are based on the thermodynamic assessment of the phase diagram of iron [7,8].

All models [1,5,7,8] yield similar results on the ϱ-profile along their respective isentrope at *P* of the Earth's outer core, but higher-order or cross derivatives for thermodynamic properties differ significantly between the various models.

Evaluated along a model core T-profile for the super-Earth Kepler-36b [9], all EoS parametrizations [1,5,7,8] yield similar results, within 2% in total core mass (Table 1). This suggests that the various EoS for liquid iron extrapolate well to such conditions at least in terms of P-ϱ-T. This robust extrapolation behaviour suggests that – regardless of the choice of EoS – first order inferences of internal structure based on mass-radius relations or potential observations on the moment of inertia or fluid Love number of super-Earth's will be rather reliable [10].

Table 1: Total mass for the core of Kepler-36b based on the planetary structure model of ref. [9] with a core radius ratio of $R_{core}/R_{planet} = 0.527$ and following their core isentrope

Study	Mass (10^{24} kg)
This study [5]	9.46
Komabayashi [7]	9.42
Dorogokupets et al. [8]	9.52
Ichikawa et al. [1]	9.45
Hakim [10]	9.59

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