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Characterization of melting properties of several Fe-C model potentials

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ABSTRACT

We use the coexisting phases approach to calculate melting phase diagrams of several Fe-C interaction potentials, such as Embedded Atom Method (EAM) potential of Lau et al. [Phys. Rev. Lett. 98 (2007) 215501], EAM potential of Hepburn and Ackland [Phys. Rev. B 78 (2008) 165115], and two flavours of the Analytic Bond Order potential (ABOP) of Henriksson and Nordlund [Phys. Rev. B 79 (2009) 144107]. Melting of both bcc (ferrite) and fcc (austenite) crystals is investigated with C concentrations up to 5 wt%. The results are compared with the experimental data and suggest that the potential of Hepburn and Ackland is the most accurate in reproducing the melting phase diagram of the ferrite, although the austenite cannot be stabilized at any C concentration for this potential. The potential of Lau et al. yields the best qualitative agreement with the real phase diagram in that the ferrite-liquid coexistence at low C concentrations is replaced by the austenite-liquid coexistence at higher C concentrations. However, the crossover C concentration is much larger and the ferrite melting temperature is much higher than in the real Fe-C alloy. The ABOP of Henriksson and Nordlund without the Ziegler-Biersack-Littmark (ZBL) correction correctly predicts the relative stability of ferrite and austenite at melting, but significantly underestimates the solubility of C in the solid phases, while the same potential with the ZBL correction predicts the austenite to be more stable compared to the ferrite at all C concentrations near the melting transition.

1. Introduction

Iron and iron-based alloys are of considerable interest for the materials modelling community because of the immense technological importance of steels. Understanding the melting properties of these materials is essential since they determine microstructure of steels which is important in applications such as casting and welding. Molecular simulation of such materials can offer insight into the formation and evolution of microstructures during solidification. However, most of the interatomic potentials developed for iron and iron-based alloys are optimized at lower temperatures, and the melting properties of these model potentials are rarely explored.

In this work we investigate the melting properties of several Fe-C model potentials. We study the Fe-C alloy with relatively low C concentrations, up to about 20 at.% (5 wt%), and therefore explore the melting of ferrite and austenite, but not of cementite. The experimental phase diagram of the real Fe-C system is shown in Fig. 1. The key feature of the diagram at temperatures near melting is the interplay between the bcc phase, known as the δ-iron or δ-ferrite, at low C concentrations and the fcc phase, or γ-iron (austenite), at higher C concentrations [1]. For pure iron ($C = 0$), the bcc crystal (δ-ferrite) is stable from the melting temperature of 1811 K down to 1667 K, where it is replaced by a more stable fcc crystal (austenite).

Carbon is an interstitial impurity in both fcc and bcc iron crystals, occupying predominantly octahedral sites (middle of edges and the centre of the fcc unit cell and middle of faces and edges of the bcc unit cell). Since carbon more readily dissolves in the fcc crystal, its presence stabilises the γ phase relative to the δ phase, which is also confirmed in the measurement of relative free energies of bcc and fcc Fe-C crystals in model systems [2]. This manifests itself in the disappearance of the δ phase from the phase diagram at C $\gtrsim$ 0.4 at.% and the replacement of the δ-liquid coexistence with the γ-liquid coexistence at $T < 1766$ K (below the horizontal black line in Fig. 1).

While we do not expect that a model Fe-C potential will reproduce exactly the phase diagram structure of the real system, it would be desirable to obtain at least a qualitative agreement with the experimental results. Unfortunately, to the best of our knowledge, most of the studies to date have focused on the properties of the low temperature α-ferrite [3–5], while those where the melting of Fe or Fe-C systems was considered, only one phase melting was

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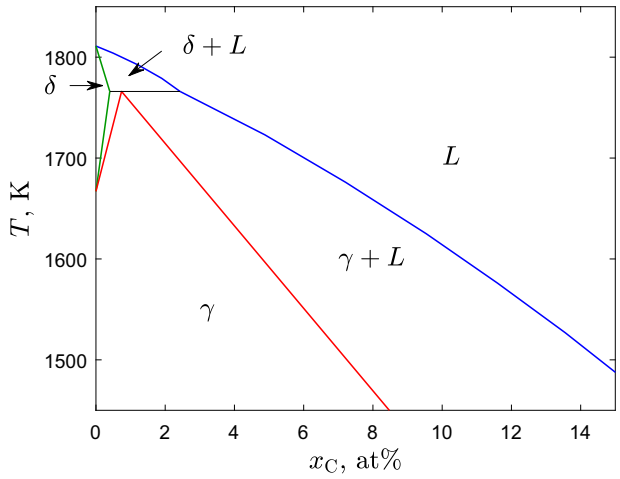

Fig. 1. Experimental temperature-concentration phase diagram of the Fe-C system. Adapted from Ref. [1].

investigated [6]. Therefore, to the best of our knowledge, the present investigation is the first which investigates the interplay between the melting properties of fcc and bcc phases in the Fe-C system.

The rest of the paper is organised as follows. In Section 2 we present the methodology of calculating the solid-liquid coexistence properties of the Fe-C system. In Section 3 we briefly discuss the model potentials which we investigate in this work. The results are presented in Section 4, with conclusions in Section 5.

2. Methodology

Phase diagrams for multicomponent systems can be obtained by a combination of the common tangent construction [7] and the Gibbs-Duhem integration [8]. The common tangent construction requires calculation of Gibbs free energies of different phases as functions of temperature, pressure, and concentrations of various components [9]. Such calculations are usually quite complicated and computationally demanding, especially for dense solid and liquid phases. Nevertheless, they have been used to determine solid-liquid and solid-solid phase boundaries in Fe-based metal alloys. For example, Lopasso et al. [10] used this approach to determine the Fe-Cu phase diagram, while Sak-Saracino and Urbassek calculated the fcc-bcc phase boundary in a model Fe-C alloy [2] with different C concentrations.

A simpler alternative to the evaluation of the Gibbs free energies is to carry out a simulation of the two phases coexisting within the same simulation box and separated by an interface. If the simulation conditions are close to coexistence, then the two phases will remain in relative equilibrium during the simulation. Otherwise, a net melting or freezing will be observed in the simulation, depending on whether the simulation conditions are within the liquid or solid phase, respectively. By performing simulations at a number of different conditions, it is possible to determine the location of the phase coexistence line. This approach was successfully applied to determine the solid-liquid coexistence conditions in hard and soft spheres and Lennard-Jones system [11–13], several models of water [14,15], many metals [6,16,17], as well as more complex molecular crystals [18].

Typically, the method of coexisting phases cannot be used directly to investigate the melting properties of multicomponent materials due to very slow inter-diffusion of the components, especially in the solid phase. However, in the case of the Fe-C alloys with low C concentrations, the direct coexistence method benefits from the fact that carbon diffuses relatively well both in the liquid and solid phases at temperatures close to melting. Therefore, we have used the coexisting phases approach in our simulations.

To set up the coexistence simulations, we first prepared separate solid (fcc or bcc) and liquid systems with given C concentrations. Carbon atoms were initially placed randomly at the octahedral sites in the solid phase. The solid system was equilibrated at given pressure and temperature using Berendsen thermostat and anisotropic barostat, where the simulation box dimensions, L_x, L_y, and L_z were allowed to fluctuate independently. The liquid system was initialised in the same way as the solid, but then melted in a simulation run with the thermostat at 3000 K, followed by an equilibration run at the same temperature as the solid system, with the anisotropic Berendsen barostat where only L_z was allowed to vary. The typical size of the solid and liquid systems was about $L_x \approx L_y \approx 40$ Å, $L_z \approx 80$ Å with about 10,000 Fe atoms. The orientation of bcc and fcc crystals in the solid system was (100). The two systems were then combined in a single simulation volume with 1 Å gaps between the two systems along the z axis, preceded by a small constant volume scaling of the liquid system in order to match the L_x and L_y dimensions of the solid system. Potential energy minimisation was performed in order to remove high-energy states of any solid and liquid atoms that happen to be too close. Coexistence simulations were carried out on the combined solid-liquid system of approximate dimension $L_x \approx L_y \approx 40$ Å, $L_z \approx 160$ Å with about 20,000 Fe atoms. The system size was relatively large in order to have a sufficient range of equilibration through freezing/melting at the solid-liquid interfaces and relatively stable locations of the interfaces in the equilibrated systems, which exhibit capillary fluctuations. In all the simulation runs the barostat pressure was 1 atm.

Coexistence conditions for the solid and liquid phases of the Fe-C system are characterised by the equality of temperature, $T_s = T_l$, pressure $P_s = P_l$, and chemical potentials of the two components: $\mu_{Fe,s} = \mu_{Fe,l}$ and $\mu_{C,s} = \mu_{C,l}$. While temperature and pressure equilibrate to the given thermostat and barostat conditions relatively quickly through the balance of kinetic energies and forces, the equilibration of chemical potentials is achieved through much slower processes of melting/freezing at the solid–liquid interfaces and the diffusion of carbon atoms between the two phases across the interfaces. When the initial conditions are far from coexistence, we observe significant freezing or melting at the interfaces, up to a complete freezing or melting of the whole system. Otherwise, the system reaches equilibrium coexistence conditions after sufficiently long simulations with significant fractions of both phases present in the simulation volume. Typical simulation runs of 8–10 ns were required to reach the equilibrium conditions, but in some cases (especially at lower temperatures) the runs were extended to 20–30 ns in order to allow the C concentrations in the solid and liquid to equilibrate.

In order to ascertain that equilibrium C concentrations were reached in the solid and liquid phases, we also performed control simulations starting from initial C concentrations on the opposite side of the coexistence line. For example, if during equilibration we observed net flow of C atoms from solid to liquid due to initial excess of C atoms in the solid compared to the coexistence concentration, we initiated another simulation run at the same temperature and lower C concentrations in the solid, observing the opposite net flux during equilibration and convergence to the same, within statistical uncertainty, C concentrations in the solid and liquid phases as in the previous run.

Once the equilibrium of the solid-liquid system was reached, the measurements of Fe and C number densities, Γ_{Fe} and Γ_C, in the bulk solid and liquid phases at coexistence were taken during a subsequent 2 ns *NVT* simulation run with the Nosé-Hoover