

Ab initio study of the phase separation of argon in molten iron at high pressures

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[1] Using first-principles molecular dynamics (MD) simulations, we study the solubility of argon in molten iron at high pressures and temperatures. In particular we explore whether the low pressure immiscibility of liquid Fe and Ar persists to high pressure (130 GPa) and temperature (4500K), or whether they mix. Starting from a variety of Fe/Ar mixtures we find that they always separate rapidly into two liquids. We conclude that there is no evidence for a significant increase in the solubility of Ar in Fe at these conditions. We cannot, therefore, attribute the lower melting temperatures of Fe obtained from DAC experiments compared to those obtained from ab initio calculations and shock experiments, to eutectic melting between Fe and the Ar pressure medium. **Citation:** Ostanin, D., S. Alfè, D. Dobson, L. Vočadlo, J. P. Brodholt, and G. D. Price (2006), Ab initio study of the phase separation of argon in molten iron at high pressures, *Geophys. Res. Lett.*, 33, L06303, doi:10.1029/2005GL024276.

1. Introduction

[2] Seismological studies show the Earth's core consists of iron (plus nickel) with a few weight percent of light element(s). Furthermore, the boundary between the solid inner core and liquid outer core (ICB), at 5150 km depth (330 GPa), is on the melting curve. A knowledge of the melting temperature of iron at pressures of the Earth's core would, therefore, provide important constraints on the thermal structure and heat budget of the Earth. Despite several decades of effort to experimentally determine the Fe-melting curve at core-pressures it is still the subject of considerable debate [Boehler, 1993].

[3] Laser-heated diamond anvil cell (DAC) measurements to 197 GPa [Saxena *et al.*, 1994; Yoo *et al.*, 1997; Shen *et al.*, 1998; Ma *et al.*, 2004] imply a melting temperature, T_m , for Fe of $5,000 \pm 500$ K at the ICB, whereas shock experiments to 260 GPa [Brown and McQueen, 1986; Nguyen and Holmes, 2004] suggest the T_m for pure iron nearer to 6000–7000 K under ICB conditions. Ab initio simulations of Fe-melting, using thermodynamic and phase coexistence approaches, are in good agreement with shock melting temperatures [Alfè *et al.*, 1999a], with a predicted ICB temperature of around $6,300 \pm 600$ K, but the cause of the discrepancy with DAC results is currently unclear. In DAC experiments, the sample is contained in a pressure medium, which transfers the stress from the diamond anvils and should not react with the sample.

In ultra-high-pressure DAC experiments below 80 GPa this pressure medium is often argon [Boehler, 2000; Boehler *et al.*, 2001] or Al_2O_3 which is used to above 100 GPa. Errandonea *et al.* [2001] have demonstrated that the use of Al_2O_3 must not change the DAC melting curve compared to that observed with the Ar pressure media. One possible cause of the low observed Fe T_m in DAC experiments would be if the pressure medium was soluble in liquid iron, resulting in eutectic melting between the sample and pressure medium. A eutectic depression of 1500 K in Fe-alloys at 200 GPa would be large, but not impossible [Alfè *et al.*, 2002]. Under ambient pressure, Fe and Ar liquids are immiscible but their behaviour may change at high pressures and temperatures. We have therefore performed ab initio simulations of Ar solubility in liquid Fe under the Earth's core conditions.

2. Methods

[4] We used first-principles molecular dynamics simulations as implemented within the Vienna Ab initio Simulation Package (VASP) [Kresse and Furthmüller, 1998]. This method has been shown to describe accurately the various properties of liquids including Fe/O [Alfè *et al.*, 1999b] and Fe/S [Vočadlo *et al.*, 2000]. The electron orbitals were represented using plane-waves, with a cut-off energy of 350 eV, while the electron-ion interactions were described by ultrasoft Vanderbilt pseudopotentials [Vanderbilt, 1990], within the local density approximation (LDA) and generalised-gradient approximation (GGA). The Fe GGA pseudo-potential was used in our earlier works and, hence, its quality has been verified elsewhere [Vočadlo *et al.*, 2000]. In the case of Ar, as Figure 1 shows, GGA overestimates the equilibrium volume at $P = 0$ compared with the low- [Anderson and Swenson, 1975] and room temperature [Ross *et al.*, 1986] experimental data and yields gradually worsening agreement when $P > 30$ GPa. Consequently, the LDA results are better. We have, therefore, tested both these approximations for the mixtures and find that the conclusions of this work are completely unaffected by the choice of LDA or GGA.

[5] We use the supercell approach with periodic boundary conditions, and Γ -point Brillouin-zone sampling. Starting from the simulations of pure liquid iron we replace 12-, 25- and 50-at.% of Fe by Ar. We have examined the size of supercell repeating the 157-atom simulations for the various compositions. Regarding the structural properties and phase stability of binary liquids, the 157-atom simulations yield essentially the same results as those of the 64-atom cell. The time step used in our simulations was 1 fs. To obtain adequate statistics for thermodynamic equilibrium, we run the simulations for a time of 10 to 12 ps.

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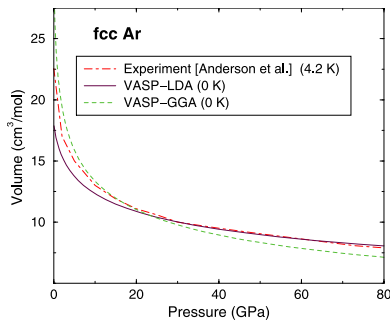


Figure 1. Equation of state for Ar: the present calculations are compared with experiment [Anderson and Swenson, 1975] at 4.2 K.

Simulations were started from artificially well mixed systems (see below).

3. Results and Discussion

[6] A snapshot of the 25 at.-%-Ar Fe/Ar composition is shown in the top panel of Figure 2 and shows that the liquid is in fact mixed. To keep this under control the calculated average distance between impurities (Ar–Ar) was compared to that of Fe/O, a reference mixture at the same P-T conditions. The pressure is about 130 GPa and $T \approx 4500$ K which is higher than T_m of Ar while $T_m^{Ar} > T_m^{Fe}$ [Jephcoat and Besedin, 1996]. The second panel of Figure 2 is a snapshot toward the end of the simulation and shows that the Ar atoms have coalesced into a compact cluster. This is the

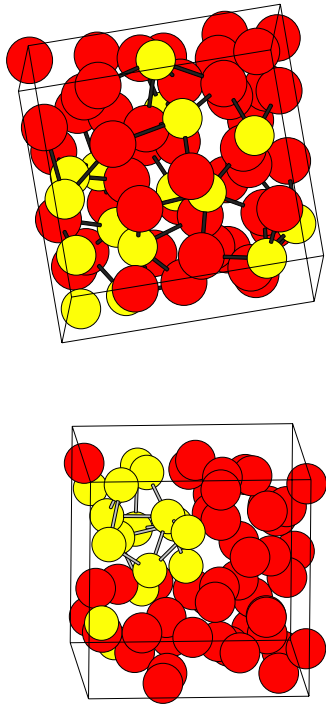


Figure 2. Snapshots of the 25 at.-%-Ar Fe/Ar liquid simulated at the CMB conditions. Large and small spheres represent iron and argon atoms, respectively. (top) A starting configuration when Ar were displaced as far as possible from each other in the box. (bottom) The atomic configuration and Ar–Ar bonds after 10 ps of simulations.

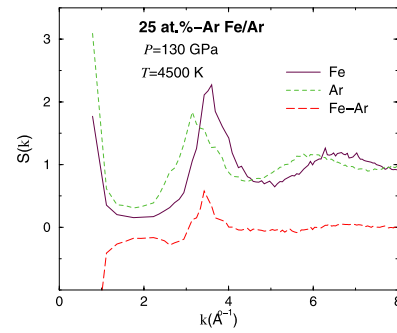


Figure 3. Partial structure factors $S_{\alpha\beta}(k)$ of the 25 at.-%-Ar Fe/Ar calculated at the CMB conditions.

case for all simulations, regardless of the starting conditions and concentration of Ar. Phase separation was always clearly obtained within 10 ps. We infer from this that there is no evidence for significantly increased mixing of Fe, even under these extreme P-T conditions.

[7] To study the phase separation in more detail, we calculated the static partial structure factor $S_{\alpha\beta}(\mathbf{k}) = \langle \rho_{\alpha}^*(\mathbf{k}) \rho_{\beta}(\mathbf{k}) \rangle$, evaluated in practice as the time average. Here, $\rho_{\alpha}(\mathbf{k})$ is the Fourier component of the number density of species α at wavevector \mathbf{k} . For the 25 at.-%-Ar composition, the calculated $S_{\alpha\beta}(k)$ are plotted in Figure 3. In Figure 3, one can see that the S_{Fe-Fe} and S_{Ar-Ar} show prominent peaks associated with a spatial packing of the atoms at $k \sim 3.6 \text{ \AA}^{-1}$ and $k \sim 3.15 \text{ \AA}^{-1}$, respectively. The divergence of the structure factors at $k < 1 \text{ \AA}^{-1}$ is a clear signature of phase separation [Alfè et al., 1999b].

[8] Further evidence of phase separation in the liquid alloy can be obtained by examining probability distributions for Ar atoms around Fe atoms, as demonstrated by Alfè et al. [1999b]. Using a cut-off distance $r_{\alpha\beta}^c$ of the first coordination shell obtained from radial distribution functions (not shown) we count how many neighbours of species β (Ar) has each atom of species α (Fe) at each time step. We then evaluate the function $P_{\alpha\beta}(n, r_{\alpha\beta}^c)$ as the probability that an α -atom has n β -neighbours. For a 25 at.-%-Ar Fe/Ar composition, simulated at the CMB

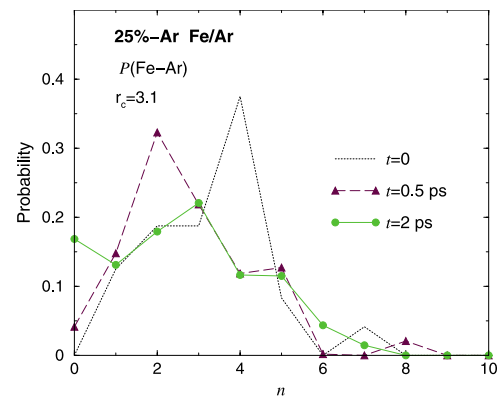


Figure 4. Probability distributions $P(n, r_c)$ for number n of α neighbours ($\alpha = \text{Ar}$) surrounding β -atom ($\beta = \text{Fe}$) calculated for 25 at.-%-Ar Fe/Ar liquid at the CMB conditions. Results are average values for the three windows of 0.1 ps each calculated at $t = 0$, $t = 0.5$ ps and $t = 2$ ps.

conditions, the probability distribution functions $P_{\alpha\beta}(n, r_{\alpha\beta}^c)$ are plotted in Figure 4. The figure shows $P(\text{Fe-Ar})$ calculated by averaging over three short windows of 0.1 ps at $t = 0$ (i.e., just after the artificial mixture was created), and at $t = 0.5$ ps and $t = 2$ ps into the simulation. The $P(\text{Fe-Ar})$ function calculated at $t = 0$ reveals a pronounced peak at $n = 4$, indicating that most Fe atoms have four Ar atoms in the first shell. In addition, there is a zero probability of Fe atoms having no Ar atoms in the first shell. In other words, no Fe atoms are coordinated only by other Fe atoms and most have three or four Ar atoms in the first shell. This is exactly as we would expect for a well-mixed starting system. As the simulation progresses, the Ar and Fe atoms rapidly start to separate. This is evident in Figure 4 from the fact that the probability of having Fe atoms with no Ar neighbours increases, and the large peak at $n = 4$ moves to $n = 2$ after only 0.5 ps, and disappears altogether by 2 ps. A positive probability of Fe atoms having one or more Ar atoms around them still persists but this is due of the finite size of the simulated systems; the cluster of Ar atoms is still quite small so the ratio of surface area to volume is still quite high and Fe-Ar contacts at the surface of the cluster make up a large proportion of the system. In a macroscopic systems the probability of these surface contacts vanishes.

4. Conclusions

[9] In summary, our simulations of Fe/Ar liquids at high temperatures and pressures based upon ab initio MD simulations, show convincing evidence of phase separation, regardless of how we start the simulations. In other words, there is no evidence for a strong change in the properties of the Fe-Ar system at high pressures and temperatures from those at ambient conditions. It is likely that Fe and Ar liquids remain essentially immiscible to very high pressures. A consequence of this is that the solids do not produce a eutectic melt. The lower solidus temperatures of Fe measured in the DAC relative to temperatures obtained from shock experiments and ab initio simulations are, therefore, not a consequence of eutectic melting of Fe with the Ar pressure medium.

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