Quasi–*Ab Initio* Molecular Dynamic Study of Fe Melting

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We have investigated the melting of hcp Fe at high pressure by employing molecular dynamics simulations in conjunction with the full potential linear muffin tin orbital method. Apart from being of fundamental value, the melting of iron at high pressure is also important for our understanding of the Earth. The subject of iron melting at high pressures is controversial. The experimental data for the iron melting temperature can be separated into two regions, "low" and "high." Here we present an *ab initio* simulated iron melting curve which is in agreement with the low temperatures at lower pressures, but is in excellent agreement with the high—mostly shockwave—temperatures at high pressures. A comparison with available data lends support to the presented iron melting curve.

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A reliable simulation of melting requires a considerable number of atoms [1–3] and, therefore, it is somewhat problematic to use *ab initio* molecular dynamics (MD). On the other hand, semiempirical methods allow simulations with a sufficient number of atoms but require tuning to experimental data [4,5]. In a situation such as with iron at extreme conditions, where experimental data on solid iron are scarce (even the crystal structure of iron at high pressure is a controversial issue [5–8]), and data on liquid iron are practically nonexistent, the reliability of semiempirical methods is uncertain. The problem of iron simulation is further complicated by the magnetic nature of the low pressure bcc phase and requires rather artificial restrictions when one attempts to calculate [4] the phase diagram for the whole pressure-temperature range. Therefore, some combination of *ab initio* and semiempirical methods has to be applied to tackle the problem. Since the most controversial part of the iron phase diagram is the melting at high pressures, we decided to restrict our study to a calculation of the iron melting curve at pressures above 60 GPa, where, according to the most recent studies [7,9], iron exists only in hcp and liquid forms and is nonmagnetic in these phases. This allows us to simplify the problem and increases the reliability of our results.

The method applied here is similar to the method [10] which was used to calculate the Al melting curve in very good agreement with experiment. The FPLMTO energy-volume data [4] for hcp and liquid iron were fitted with an EAM (embedded-atom method [11]) potential, because the EAM method has been shown [11] to produce melting temperatures for metals in good agreement with experiment. The FPLMTO data for liquid iron were calculated from configurations consisting of 32 iron atoms obtained using MD simulations with a first order approximation for the EAM iron potential. The particular form of the applied potential is as follows:

$$E_{\text{conf}} = \sum_{i=1}^{N} E_i \,, \tag{1}$$

where

$$E_i = \frac{1}{2} \sum_{j=1, j\neq i}^{N} \phi(r_{ij}) + F(\rho_i) \,, \tag{2}$$

with

$$\rho_i = \sum_{j=1, j\neq i}^{n} \rho(r_{ij}) \,. \tag{3}$$

Here E_{conf} is the potential energy of a system of **N** atoms, E_i is the energy of atom i, ϕ is the pairwise interaction between atoms i and j, r_{ij} is the distance between them, $F(\rho)$ is the embedding function, and ρ is another pairwise interaction leading to the density term ρ_i. The functions ϕ, ρ_i, and $F(\rho)$ are defined as follows:

$$\phi(r_{ij}) = \epsilon \left(\frac{a}{r_{ij}} \right)^n , \tag{4}$$

$$\rho(r_{ij}) = \left(\frac{a}{r_{ij}} \right)^m , \tag{5}$$

$$F(\rho_i) = -\epsilon C \sum_{i=1}^{N} \sqrt{\rho_i} \,. \tag{6}$$

As a result of the fit the adjustable parameters were iterated to be $n = 8.137$, $m = 4.788$, $\epsilon = 0.0173$ eV, $a = 3.4714$ Å, and $C = 24.939$.

Using this potential and the two-phase MD simulation method [1,2,12] we calculated the melting temperatures of hcp iron in the pressure range from 60 to 330 GPa (from the pressure of the triple point [7] to the pressure of the inner-outer core boundary [13]). The two-phase method is equivalent to a calculation of the free Gibbs energies of the solid and the liquid to determine the melting temperature [12]. It was tested earlier for a number of materials including metals and was found to perform very well, producing melting curves in very good agreement with experiment (e.g., $MgSiO_3$ perovskite [1] and NaCl [2]). The resulting melting curve for iron is shown in Fig. 1(a) and compared with experimental diamond anvil cell [7,6,14,15] and shockwave data [15–17]. The earlier shockwave temperatures of solid iron [16] were recalculated using a new equation of state derived from the latest (up to a

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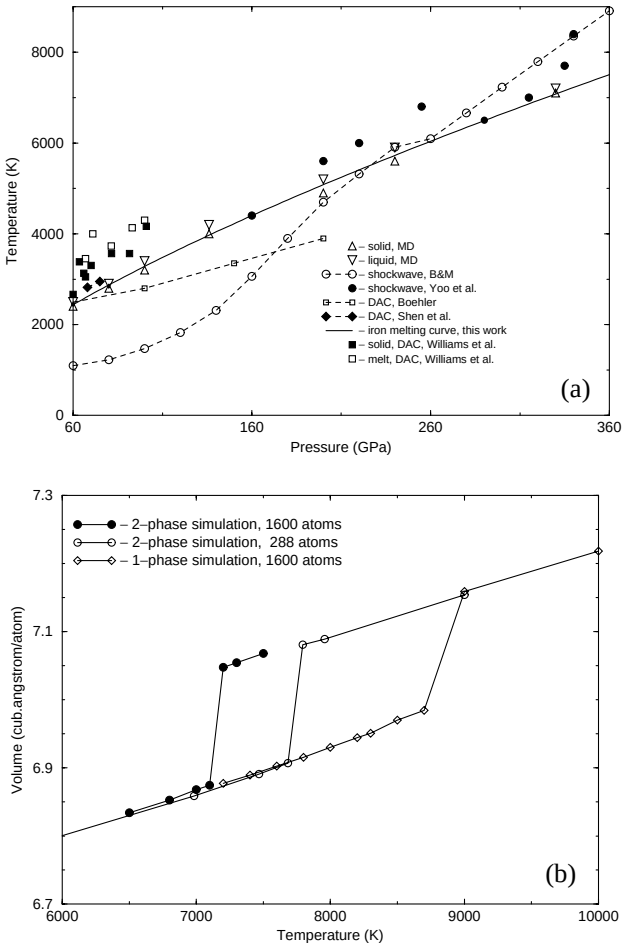

FIG. 1. The calculated iron melting curve compared with experimental data (see text for discussion of the shockwave data) indicated in the legend (a). The calculated melting curve is bracketed by open triangles, which indicate stability either of liquid or solid iron. Panel (b) illustrates how a particular point of the melting curve at a pressure of 330 GPa (the highest pressure in our simulations) was calculated. The melting was determined as the temperature at which the volume of the initial two-phase computational cell containing 1600 atoms showed a discontinuous change. The dependence of volume on temperature is shown by solid circles. The cell contained completely solid iron at the temperature of 7100 K and completely liquid iron at the temperature of 7200 K. Therefore, the melting temperature can be precisely bracketed to be located between 7100 and 7200 K. Other simulations, shown by open circles and open diamonds, are considered as incorrect, either due to an insufficient number of atoms (288) or due to an incorrect method of simulations (one-phase simulation).

pressure of slightly above 300 GPa) experimental data for hcp iron [18]. Therefore, these temperatures should now be considered as experimentally based and not as a result from a theoretical interpretation. One notices [Fig. 1(a)] that in the range of about 60 to 80 GPa the calculated melting temperatures are in agreement with recent diamond anvil cell (DAC) experiments [7]. However, when increasing the pressure, the calculated melting curve gradually diverges from the DAC temperatures [14] and at pressures of 200 to 300 GPa our theoretical melting curve is in agreement with shockwave temperatures. Brown and McQueen [16] claim that iron melts at a pressure of 243 GPa along the Hugoniot. The estimated temperature at this pressure coincides almost exactly with our MD results. Note, that a Hugoniot, crossing a melting curve, exhibits two kinks, coinciding with a melting curve between the kinks [19–21]. The pressure difference between the kinks is not known for iron, but can be roughly estimated as a few dozen GPa. The comparison suggests [Fig. 1(a)] that the Hugoniot follows the melting curve starting from a pressure slightly above 200 GPa and up to a pressure of about 250 GPa. The recalculated temperatures from the Hugoniot data obtained by Brown and McQueen [16] are within the error bars of the data provided by Yoo *et al.* [17]. Figure 1(b) illustrates how each point of the melting curve was determined and shows that simulations with a small number of atoms [22] and, in particular, that one-phase simulations [23,24] may give inaccurate results.

The reliability of our results can be judged from a comparison between calculated and experimental data for hcp iron (Fig. 2) and earlier *ab initio* MD data for liquid iron [25] (Table I). In both cases the comparison is favorable, providing additional support to our calculations.

The most serious discrepancy between our MD simulations and the *ab initio* simulations is that our method does not account for the electronic entropy which may be important at high temperatures [26]. However, as one can see from Fig. 2(b), this effect is probably not that important (because the thermal expansion comes out very similar from experiment and theory). Moreover, the errors, introduced by neglecting electronic entropies both for the solid and the liquid phase, are likely to cancel to a large degree because the coordination numbers in the liquid and solid at high pressure are almost the same.

An important consequence of our calculated melting temperatures is that they provide constraints on the temperature profile in the Earth interior. From the comparison of densities, provided by our MD simulations in combination with recent iron equation of state [18], and the densities from PREM [13] we can conclude that the Earth inner core is almost pure iron with a very small amount of additives. Since these additives are unlikely to change the melting temperatures significantly, we can use estimates of iron melting temperatures in the analysis of temperatures in the Earth inner core. However, the outer core is likely to be enriched with some lighter elements than iron. Assuming the adiabatic temperature gradient in the outer liquid core calculated earlier [4], the temperature at the core side of CMB can be roughly estimated between 4000 and 5000 K. This value is rather close to the melting temperature of the mantle material [27,28] at this pressure (136 GPa). Therefore, a partial melting at the CMB is possible, which can explain the heterogeneous structure of the CMB and the ultralow velocity zone [13].

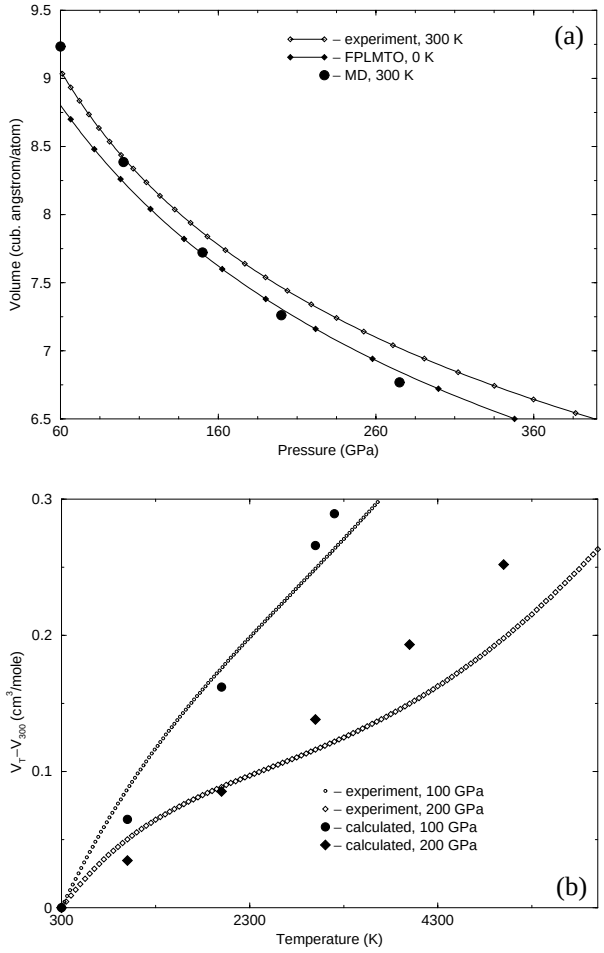

FIG. 2. Comparison (a) between the calculated 300 K isotherm for hcp iron with FPLMTO 0 K and the experimental [18] 300 K isotherms and (b) the volume expansion at pressures of 100 and 200 GPa against experimental data [18]. The difference between experimental and calculated volumes at 300 K (a) is less than 3%. The agreement between the calculated and the experimental volume expansions at 100 GPa (b) is nearly perfect. The somewhat poorer agreement at 200 GPa (b) may be due to an unphysical behavior of the equation of state used for fitting to the experimental data [18].

The temperature at the inner-outer core boundary is calculated to be about 7100 K. The melting temperature in the center of the Earth is about 7400 K. The temperature in the inner core increases from the boundary to the center. It means that the temperature of the whole inner core is very close to the range of temperatures critical for melting.

TABLE. I. Properties of liquid iron.

T (K)	P (GPa)	ρ 10^4 kg m^{-3}		D 10^{-8} m^2 s^{-1}	
		Ref. [25]	This work	Ref. [25]	This work
6000	358	1.33	1.36	0.5	0.32
4300	132	1.07	1.07	0.4	0.58
3500	125	1.07	1.07	0.3	0.35

In conclusion, we would like to emphasize, that the iron melting curve was obtained from as little information as the atomic number, yet yielding a melting curve in remarkable agreement with shockwave data. It is unlikely that the agreement is fortuitous. The close match of these two completely different methods provides strong support to both of them. While the recently obtained iron melting curve [22] is somewhat different from ours due to, probably, certain deficiencies in both methods, there is a consensus that the temperature of iron melting at pressures of the inner core is higher than can be concluded from a number of recent experimental DAC studies.

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