Z method calculations to determine the melting curve of silica at high pressures

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Abstract. The Z method is a novel technique that allows to calculate the melting temperature of materials at different pressures from the microcanonical ensemble. In this work, we apply this method to study the melting behavior of silica at high pressures, determining melting temperatures and dynamical properties.

1. Introduction

Silica is one of the most studied materials. It makes up most of the composition of the Earth's lower mantle and is one of the basic components of rocky bodies in space. Knowing the properties of silica at different pressures is not only important for physics, but for earth sciences and astrophysics, where the wide variety of extrasolar planets discovered has put challenges in our understanding of how planets are formed and how their interiors evolve. Models for planetary interiors (see figure 1) are constrained by the bulk composition and distribution of chemical species, and they need to include equations of state, such as phase transitions and melting curves at high pressure, for perovskites, magnesiowustites and silicates, which are among the most common rock-forming elements.
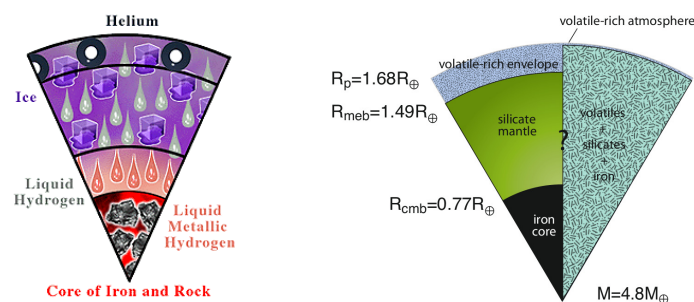
Figure 1. Left: interior of a gas-giant-like planet (Jupiter, Saturn). Right: interior of a super-Earth-like planet (Earth, CoRoT-7b, Kepler 20b) [1, 2].

Since the discovery of stishovite in 1962 by Stishov and Popova, various experimental and theoretical studies have characterized the so-called post-stishovite phases, including $CaCl_2$, α-PbO_2, pyrite, and the recently predicted phases, cotunnite and Fe_2P phases [3, 4]. However, the

melting curve of silica for the pressures corresponding to these phases is poorly constrained, or simply not known. The latter point is of considerable interest for understanding the physical evolution of planetary interiors, such as the process of differentiation of terrestrial planets into a dense metallic core surrounded by a rocky mantle, where the dynamics is driven by the gravitational separation of a liquid phase.

Here we present a study of the melting behavior of silica at high pressures, obtained from first principles molecular dynamics simulations using the Z method. We calculate the melting point of three high pressure phases of silica (pyrite-, cotunnite-, and Fe_2P-type SiO_2) at different pressures.

2. The Z method

The theoretical rationale of the Z method is that, in the NVE (microcanonical) ensemble, with N the number of particles, V the volume, and E the energy of the system, there is a maximum energy E_{LS} that can be given to the crystalline system before it melts. Increasing the energy beyond this point, at which the temperature is the limit of the superheating temperature T_{LS}, the solid spontaneously melts, but due to the increase in potential energy, namely the latent heat of fusion, the temperature decreases. The interesting fact is that the final temperature after melting seems to coincide with the melting temperature T_m obtained from other methods.

Although we still lack of a thermodynamical explanation for the Z method, it has been empirically observed [5–23] that the method works, and the procedure is as follows: at a fixed volume, the (E, T) points from different simulations draw a 'Z' shape, as shown in figure 2. In these Z–shaped curves the sharp inflection at the higher temperature corresponds to T_{LS} and the one at the lower temperature to T_m. Thus, knowledge of the lower inflection point for different densities allows the determination of the melting curve for a particular range of pressures.
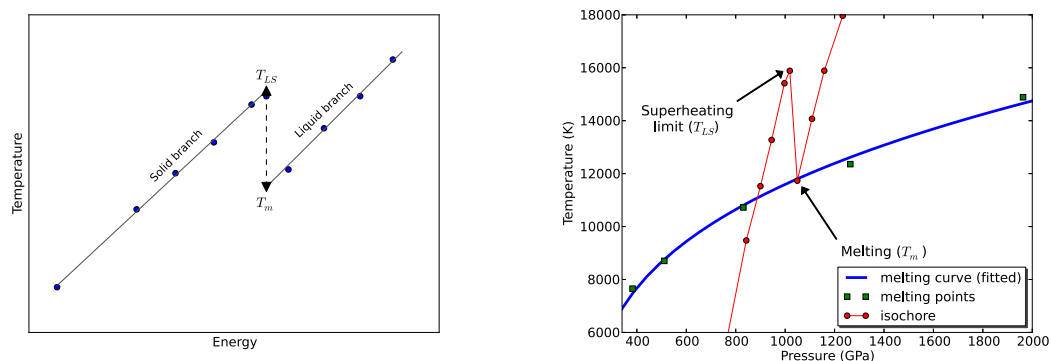
Figure 2. Schematic representation of the isochoric lines in Z-method: Mean temperature versus total energy (left) and temperature versus pressure (right).

3. Ab initio molecular dynamics simulations

The first principles molecular dynamics (FPMD) simulations were preformed in the framework of the Kohn–Sham density functional theory. We worked under the NVE-ensemble, using the Born-Oppenheimer molecular dynamics (BOMD) method, as implemented in the VASP code [24], employing PAW pseudopotential [25], and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [26]. For the plane wave expasion of the wavefunctions, we used a cutoff energy of 900 eV, and k-points convergence tests were performed in order to determine the amount of k-points necessary to perform accurate calculations. The results of these tests

yielded that the Γ point was enough for the sampling in all cases. Due to the high temperatures explored, the fast dynamics of the ions needs a small time step, therefore a time step of $\Delta t = 0.2$ fs was used in all calculations. A total of 5000 steps (1 ps) was used in the simulations, which we discuss in section 4.2.

4. Results

4.1. Size dependance

Since the primitive cell of the Fe_2P-type silica has 9 atoms [3], the most simple supercell ($2 \times 2 \times 2$) contains 72 atoms, a size which might be still insuficient to lead to reliable results. Therefore, we have carried out calculations comparing the predictions of the Z method using 72 and 243 atom cells. In figure 3 we show the temperature as a function of the pressure for both systems. We observe that only a slight difference in the predictions is obtained in the Fe_2P-type silica when the size of the system is increased. At 1920 GPa, the mean temperature is slightly greater in
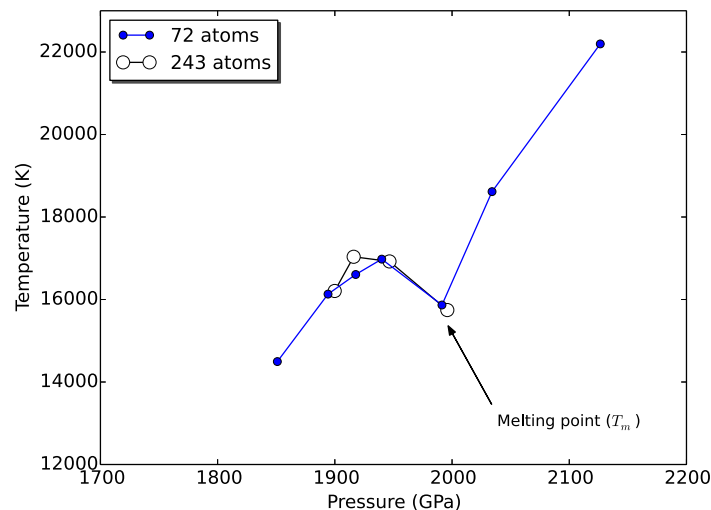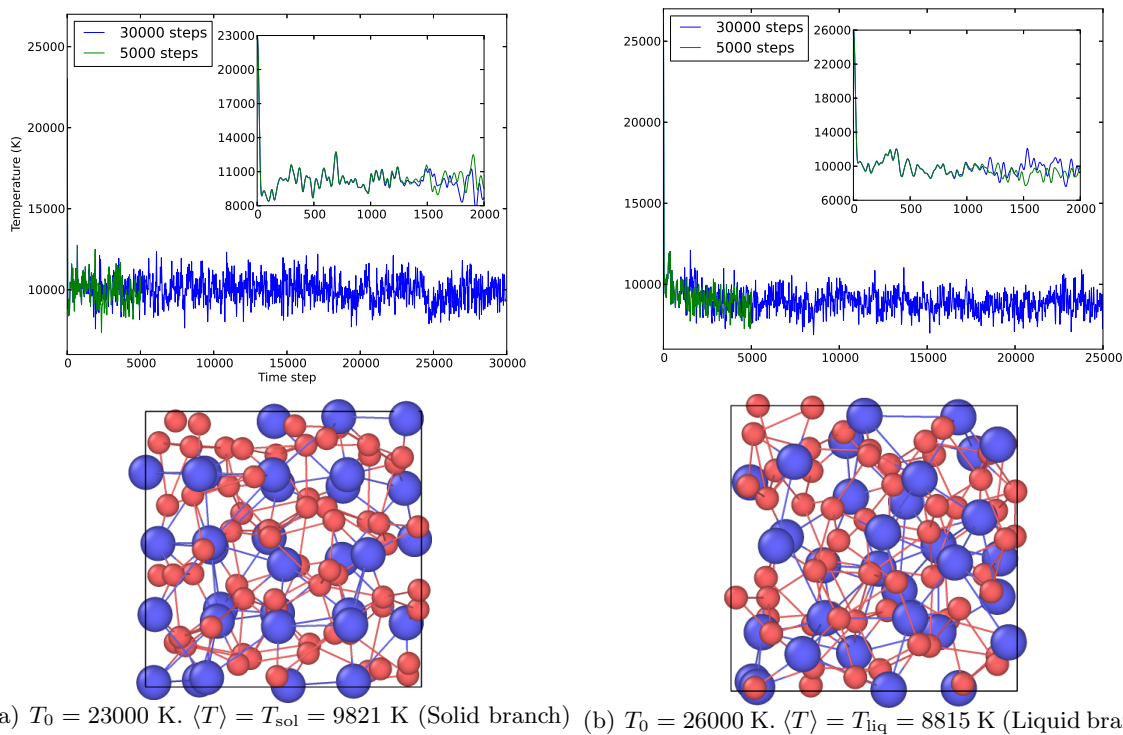

Figure 3. Size dependance of the calculations: isochore for silica in the Fe_2P phase at $V = 2.93$ Å^3/atom ($\rho = 11.33$ g/cm^3).

the system with 243 atoms, but this does not affect the prediction of the melting temperature, which corresponds to $T_m = 15800$ K in both cases. Therefore, we conclude that using a 72 atom cell is enough for our purposes.

4.2. Simulation time dependance

As noticed by Alfè *et al.* [5], the waiting times before the transition to liquid takes place are variable, and sometimes considerably long. Starting from the perfect crystal, and as we know from energy equipartition, the initial temperature T_i drops rapidly about the half of its initial value, and it then fluctuates about a value T_{sol}, and if the energy is greater than E_{LS}, it drops again and fluctuates about a lower steady value T_{liq} when the system melts. However, if T_i is high enough, the system will not be able to remain in solid state and will melt spontaneously, reaching T_{liq} in the first steps of the simulation. The same happens with low initial temperatures, for which T_{sol} will never drop to T_{liq}. Therefore, long simulation times are not needed to get a rough shape of the Z curve and, therefore, a good estimation for T_m.

The evolution of temperature as a function of time in a 96-atom cell of silica in the pyrite phase is shown in figure 4. The initial velocities are randomly assigned, so that they correspond to the a given temperature, leading to different values of instantaneous temperatures in the simulation but the same mean temperature. Homogeneous melting occures for the sample initiated at 26000 K during the first 200 steps (40 fs), while the structure remains as a superheated solid when initiated at 23000 K, where the crystal lattice sites are still identifiable (figure 4, left). The mean temperatures of the superheated solid and the final liquid are $T_{\mathrm{sol}} = 9821$ K and $T_{\mathrm{liq}} = 8815$ K, while the mean pressures are $P_{\mathrm{sol}} = 375$ GPa and $P_{\mathrm{liq}} = 391$ GPa.

(a) $T_0 = 23000$ K. $\langle T \rangle = T_{\mathrm{sol}} = 9821$ K (Solid branch) (b) $T_0 = 26000$ K. $\langle T \rangle = T_{\mathrm{liq}} = 8815$ K (Liquid branch)
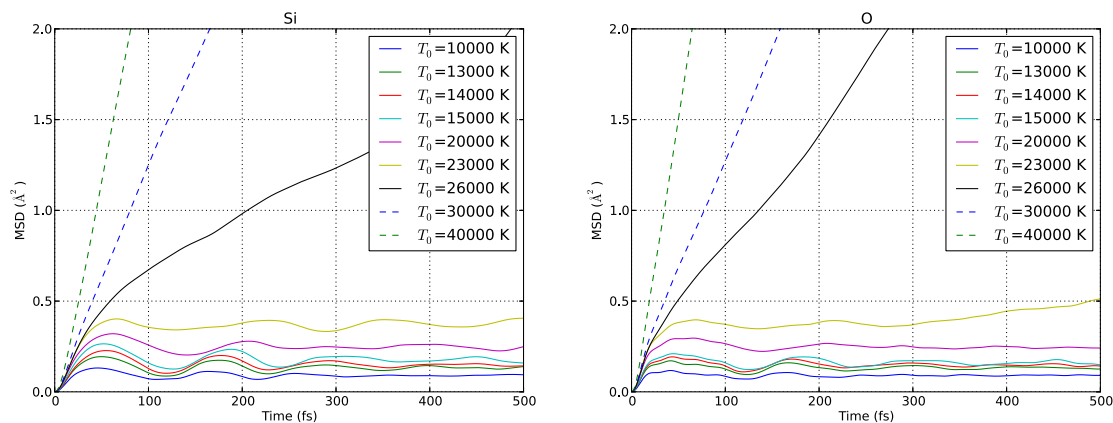
Figure 4. Evolution of temperature as a function of time in four independent simulation runs for a volume $V = 5.06$ Å^3/atom ($\rho = 6.58$ g/cm^3) of the pyrite structure: two initiated at 23000 K (left) and two initiated at 26000 K (right).

4.3. Mean Squared Displacement

In figure 5 we show an isochore of pyrite-like silica, where we observe a temperature drop around $P \sim 380$ GPa. The highest temperature in the solid branch, 9821 K, corresponds to a simulation initiated at 23000 K (the same shown in figure 4, left), which drops to 8815 K when initiated at 26000 K, which we associate to melting. We analyzed the mean squared displacement (MSD) for all simulations in the isochore, which are shown in figure 6. We observe that there is a clear difference in behavior of atoms when the sample is initiated at $T_0 = 26000$ K, respect to lower initial temperatures. Both Si and O show a diffusive behavior, which is steeper for highest temperature, an evidence that the sample is already molten. However, when the sample is initiated at $T_0 = 23000$ K, only the oxigen atoms diffuse, with a slope in the MSD curve that is very small. The MSD shows that superheated solids present this anomalous behavior:
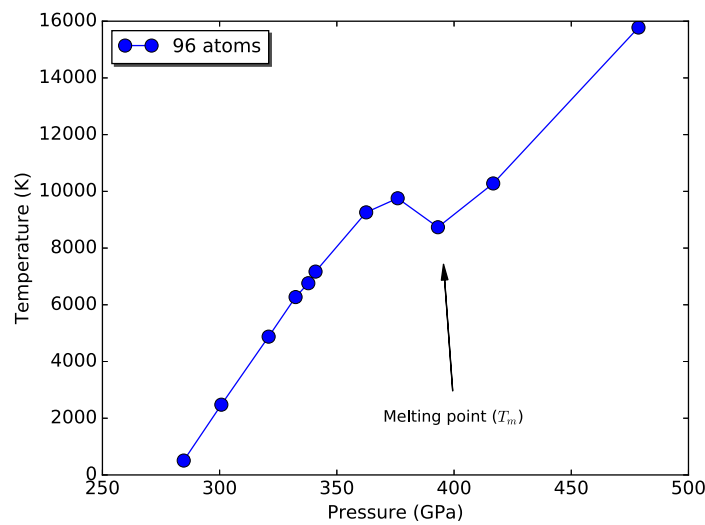
Figure 5. Isochoric of the pyrite-type silica. $V = 5.06$ Å^3/atom ($\rho = 6.58$ g/cm^3). The melting point corresponds to a simulation intiated at $T_0 = 26000$ K.

Figure 6. Mean squared displacement of Si and O atoms in the pyrite-type silica crystal as the initial temperature T_0 is increased.

a non-flat slope MSD curve or an almost-flat zero-slope MSD that adquires a non-zero slope, which sometimes makes it difficult to differentiate between a solid and a liquid.

4.4. Melting points
Using the Z method and the MSD analysis, we have obtained some high pressure melting temperatures for silica, which are depicted in table 1.

5. Conclusions

By using the Z method, we have determined some melting temperatures of silica for pressures higher than 300 GPa. These findings have considerable importance for the field of planetary science, since there still are no constraints for the solid–liquid phase diagram of silica at pressures concerning the interior of massive rocky planets (greater than 1000 GPa), which enable us to

Table 1. Melting temperatures (T_m) of silica in different crystalline phases at high pressures.

Structure	T_m (K)	P (GPa)	V/atom (Å^3)
Pyrite	8815	391	5.06
Cotunnite	12886	1273	3.43
Fe_2P	16922	1946	2.93

build more precise models for their interiors. However, further research must be done in order to constrain the melting points in the Z method, since the precision of the temperature obtained depends on the amount of simulations performed close to the T_{LS}–T_m drop, and the waiting times considered to determine if the system has reached the final equilibrium temperature. Further studies should consider the different structures of silica and determine whether how the melting temperature predicted by the Z method depends on the initial structure used.

Acknowledgments

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