High-Pressure Melting of MgSiO$_3$

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The melting curve of MgSiO$_3$ perovskite has been determined by means of *ab initio* molecular dynamics complemented by effective pair potentials, and a new phenomenological model of melting. Using first principles ground state calculations, we find that the MgSiO$_3$ perovskite phase transforms into post perovskite at pressures above 100 GPa, in agreement with recent theoretical and experimental studies. We find that the melting curve of MgSiO$_3$, being very steep at pressures below 60 GPa, rapidly flattens on increasing pressure. The experimental controversy on the melting of the MgSiO$_3$ perovskite at high pressures is resolved, confirming the data by Zerr and Boehler.

The subject of MgSiO$_3$ melting is interesting, important, and challenging. Its importance follows from the fact that MgSiO$_3$ perovskite (Pv) constitutes more than half of Earth's volume [1]. At the early stage of Earth's evolution a significant part of MgSiO$_3$ was molten [2,3]. Therefore, the melting temperature (T_m) as a function of pressure (P) in the P range of the Earth's interior (0–365 GPa) is needed to describe the Earth's evolution. The experimental data on MgSiO$_3$ melting are controversial [4–8]. It is definitely of interest how self-consistent *ab initio* and phenomenolgial methods can help to resolve the controversy. However, an application of these methods to such a structurally and chemically complicated substance as MgSiO$_3$ is far from trivial. The situation became even more complicated when it was discovered [9–12] that Pv transforms to another, so-called post-perovskite phase with *cmcm* symmetry at pressures higher than ~100 GPa at a temperature (T) of 300 K.

The T_m of any substance can be determined using the 2-phase method [13]. However, this method becomes extremely computationally demanding when interactions between particles are described *ab initio*. So far, only systems with few valence electrons have been simulated using the *ab initio* 2-phase method [14,15]. To be reliable, a 2-phase molecular dynamics (MD) simulation has to involve at least several hundred atoms. Computational time scales as N^3, where N is the number of electrons directly involved in the calculations. Therefore, *ab initio* 2-phase MD simulations involving several hundreds of MgSiO$_3$ formula units are much more demanding than the largest ever done 2-phase MD simulation of Al melting, which involved about 1000 atoms [14]. An order N method (e.g., Ref. [16]) might be a useful alternative. However, application of this method to MgSiO$_3$ under high PT conditions requires extensive testing. Besides the 2-phase approach,

there is another way to calculate T_m, namely, by calculating the Gibbs free energies of the solid and liquid phases. This approach involves several intermediate stages where errors are accumulated [17] and it is inferior to the 2-phase method. The difficulties increase enormously if the system in question is polyatomic. To the best of our knowledge, there are no studies in which T_m of a polyatomic system is calculated by equating the Gibbs free energies, even for the case of a classical description of the interatomic interaction. The problem becomes even more difficult if the Gibbs free energies have to be determined by calculating interactions *ab initio*.

Therefore, a rigorous study of MgSiO$_3$ melting is prohibited either by technical problems or by the present state of the theory. This makes the problem of finding T_m of MgSiO$_3$ really challenging. A possible solution is to calculate the T of the thermal instability (T_{inst}) and then estimate the degree of overheating. If one simulates a bulk crystal with periodic boundary conditions (which eliminate surfaces) one finds that on increasing T the crystal does not melt at T_m but, instead, remains metastably solid. Eventually, when T becomes high enough, the crystal melts. This T is called T_{inst}, also known as the T of overheating. Calculation of T_{inst} is a *comparably* simple task. Actually, some time ago [18,19] T_{inst} was erroneously thought to be T_m for Pv. Clearly, a reasonable *ab initio* based estimate of the difference between T_m and T_{inst} for MgSiO$_3$ would be significant progress compared to the previous studies.

The Pv and *cmcm* phases have been studied using a number of *ab initio* methods [10,11,20–23]. Among these methods we have chosen the one which seems to us as being the most robust [11,23,24]. Our *ab initio* ground state calculations and MD simulations at finite temperatures have been carried out using the Vienna *ab Initio* simulation

package (VASP) [24]. The calculations were performed in the framework of the full-potential frozen-core all-electron projector augmented wave method. Exchange and correlation effects were treated in the framework of the generalized gradient approximation [25]. All necessary convergence tests were performed. Using this method, we calculated T_{inst} of the Pv and $cmcm$ phases. The calculations were performed in the NVE (N, number of atoms; V, volume; E, energy) ensemble. The *ab initio* system was comprised of 160 atoms ($2 \times 2 \times 2$ unit cells of 20 atoms). At a given volume, pressures were calculated at a number of temperatures. First, 2000 time steps were chosen for the equilibration, where the velocities were scaled every 5 time steps. The time step was equal to 10^{-15} s. Afterwards, the system evolved without scaling for another 2000 time steps. When the system melts, P increases abruptly due to the difference in volumes of the solid and liquid phases. Therefore, the irregularities in the isochores (Fig. 1) at high T are due to the thermal instability. We calculated three isochores, two for the Pv phase at $V = 37.71$ Å^3/f.u. and $V = 28.23$ Å^3/f.u. and one for the $cmcm$ phase at $V = 28.06$ Å^3/f.u.. The volumes were chosen using ground state calculations to cover comparably low and high P regions. The results are presented in Fig. 1.
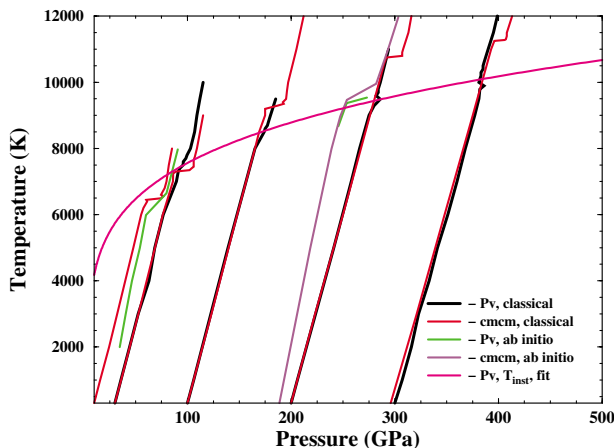

FIG. 1 (color). Isochores of perovskite (Pv) and post-perovskite ($cmcm$) phases calculated by means of MD, using both pair potential [13,18] and *ab initio* interaction models [23,24] shown by different colors as indicated in the legend. The volumes are chosen as described in the text. The irregular behavior of calculated pressures is the indication of thermal instability. Thermal instability temperatures (T_{inst}) of the Pv were fitted by the Simon functional curve (magenta curve). The T_{inst} of the $cmcm$ phase at $P < 100$ GPa is lower than that of perovskite while at higher P the order is reversed. The values of T_{inst} obtained from the AIMD and classical MD calculations are in reasonably good agreement; hence the pair potential model [13] is reliable. Some disagreement at lower P is most likely due to a nearly constant shift between *ab initio* and experimental P of about 12 GPa [23]. Somewhat higher T_{inst} of the classical $cmcm$ phase at P above 100 GPa suggests that a proper correction has to be made for T_m calculated using the classical model.

To calculate both T_m and T_{inst} and, in this way, to estimate T_m in our *ab initio* MD (AIMD) simulations, we have chosen one [18] out of several existing classical models [18,26] describing the interactions in MgSiO$_3$. This model was extensively applied earlier to simulate the melting [18] and properties of the MgSiO$_3$ Pv and liquid phases [13,18,19,27]. Those calculations demonstrated that experimental data [28–30] on Pv and liquid phases are well described by the model [18]. We calculated nine isochores using classical MD, four for the Pv and five for the $cmcm$ phase. The calculations have been performed using exactly the same procedure as in the case of *ab initio* MD, that is, in the NVE ensemble. However, in this case we were able to simulate much larger systems, 2500 atoms in the case of Pv and 1080 atoms for the $cmcm$ phase. We note that MD simulations with larger N lead to somewhat lower T_{inst}, the difference being small, however. The volumes were chosen to cover low and high P range. For the Pv case, these volumes are 36.92, 32.15, 28.55, and 26.26 Å^3/f.u. and 38.75, 36.37, 31.70, 28.17, and 25.99 Å^3/f.u. when simulating the $cmcm$ phase. The results of MD classical simulations on the calculated T_{inst} are presented in Fig. 1.

From the comparison of T_{inst} calculated by *ab initio* and classical methods, we learn the following. At lower pressures (below 100 GPa) the calculated temperatures of the thermal instability are in good agreement if we take into account the P shift of 12 GPa, as suggested in Ref. [23]. At higher pressures the classical model overestimates the stability of the MgSiO$_3$ $cmcm$ phase. Therefore, the classical [18] $cmcm$ T_m should be somewhat higher than the T_m calculated *ab initio*. From Fig. 2 we see that the structures of liquid MgSiO$_3$ obtained by the two models are nearly identical. Further, our *ab initio* method produces an equation of state in good agreement with experiment (see inset in Fig. 2). The ability of the classical model to describe the equation of state of MgSiO$_3$ Pv phase was demonstrated earlier [27]. A somewhat higher T_{inst} of the $cmcm$ phase calculated by the classical MD (in comparison to that from the *ab initio* MD), is likely related to the inability of the classical model to accurately describe the $cmcm$ phase, probably because the model [18] was fitted to the properties of the Pv phase.

Therefore, we can now calculate the melting curve of MgSiO$_3$ using the 2-phase method and classical model, and then ''correct'' it based on the comparison of T_{inst} obtained with the classical and *ab initio* models (Fig. 1). These calculations were performed as described earlier [13]. The simulations were conducted for two systems, namely, $cmcm + liquid$, using the computational cell containing 4800 atoms, and $Pv + liquid$, using a cell with 20 480 atoms. The results obtained for these two phases ($cmcm$ and Pv) are shown in Fig. 3. The melting curves of the $cmcm$ and Pv phases cross at the $P = 142$ GPa and $T = 6200$ K. These conditions represent the $Pv - cmcm - liquid$ triple point. To obtain the phase boundary between
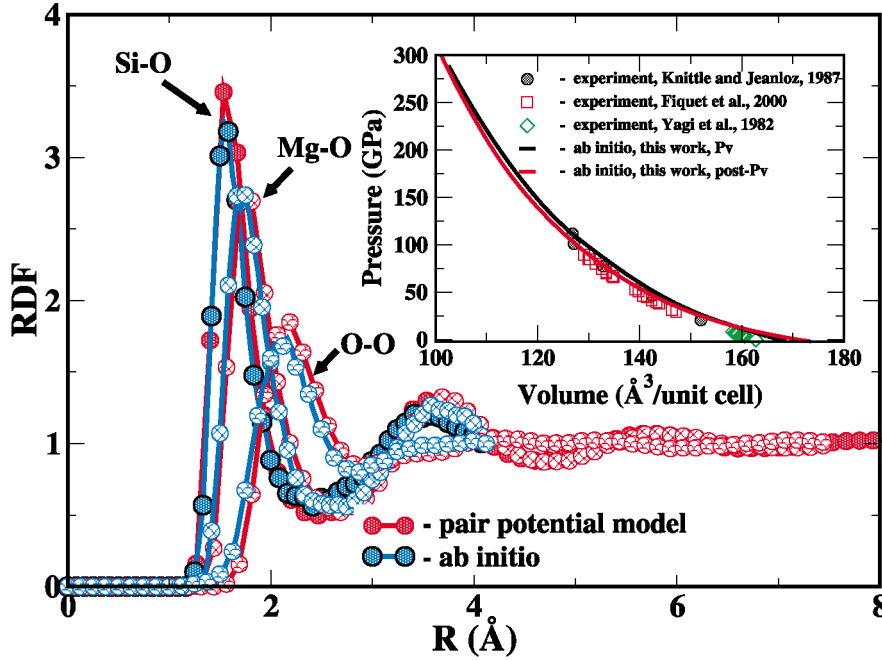
FIG. 2 (color). Si-O, Mg-O, and O-O radial distribution functions (RDF) and the Pv equation of state (EOS) at $T = 0$ K (inset). RDFs are obtained by AIMD at $P = 273$ GPa and $T = 9576$ K, which is a point of thermal instability (Fig. 1), and compared to RDFs calculated using the classical model [13] at the same P and T. The EOS in the inset was calculated using the same *ab initio* method with all the parameters as used in AIMD, and is compared to experimental data [28–30]. The calculated pressures are shifted uniformly upward from the experimental values by 12 GPa. This 12 GPa shift has also been seen in other recent work on Pv [23]. The data support our results on the MgSiO$_3$ melting.

the Pv and *cmcm* phases, we calculated the P of the transition from the Pv to *cmcm* phase at $T = 0$ K *ab initio*. This P is equal to 102 GPa, which is close to the experimental result [9] of 98 GPa. The phase boundary is approximated by a straight line connecting the triple point and the point at $P = 102$ GPa at $T = 0$ K. We note that the position of the triple point can be shifted to higher P if the melting curve of the *cmcm* phase is corrected according to the data in Fig. 1. The exact relation between T_{inst} and T_m is unclear, therefore the magnitude of the correction for the T_m of the *cmcm* phase remains uncertain. However, the data in Fig. 1 tell us that this correction most likely does not exceed 1000 K. The Clapeyron slope of the $Pv - cmcm$ transition calculated in this work ($dP/dT \approx$ 7.0 MPa/K) is somewhat smaller than those obtained earlier (≈ 10.0 [11] and ≈ 7.5 [12] MPa/K). This disagreement is not critical, since a shift of the triple point to higher pressures within 10 GPa will bring our results (Fig. 3) and those from previous calculations [11,12] in to agreement. This shift is equivalent to a correction for T_m of the *cmcm* phase by less than 200 K, which clearly is within the magnitude of the correction to be made (Fig. 1).

It is of interest to find out how our calculations fit into the scope of the melting curve prediction based on the most advanced phenomenological theory [31]. We first derive the theoretical melting curve of MgSiO$_3$ in the $T-\rho$ (ρ-density) coordinates. To this end, we use the computational scheme developed previously in [31]. This scheme has been tested on a number of monatomic substances, and excellent agreement between theory and available experimental data has been found in all cases. MgSiO$_3$ is the first example of the application of this scheme to polyatomic elements. The scheme consists in the calculation of three parameters, γ_1, γ_2, and q, for the melting curve in the form

$$T_m(\rho) = T_m(\rho_m)\left(\frac{\rho}{\rho_m}\right)^{1/3}$$
$$\times \exp\left\{6\gamma_1\left(\frac{1}{\rho_m^{1/3}} - \frac{1}{\rho^{1/3}}\right) + \frac{2\gamma_2}{q}\left(\frac{1}{\rho_m^q} - \frac{1}{\rho^q}\right)\right\}, \quad (1)$$

where $T_m(\rho_m)$ is T_m at a given reference density ρ_m [which is convenient to choose to be that at the normal ($P = 0$) melting point]. The values of the three parameters are obtained based on the $P = 0$ experimental data. Using the published data on enstatite (the $P = 0$ phase of MgSiO$_3$), we obtain $\gamma_1 = 0.76$, $\gamma_2 = 49.3$, and $q = 3.8$. These values, along with those of ρ_m and $T_m(\rho_m)$, being used in Eq. (1), determine the melting curve of MgSiO$_3$ at all densities. Note that as a function of density, the resulting melting curve is continuous (by its construction), so that it also includes metastability regions between the stable solid phases. In the $T-\Pi$ coordinates, however, it becomes a truly continuous function of pressure, which we now calculate for MgSiO$_3$. We use the thermal EOS for the enstatite [32], Pv [33], and *cmcm* (this work) phases of MgSiO$_3$ to convert Eq. (1) into the corresponding $T_m = T_m(P)$ forms. This is done by choosing 7 density points from 2.9 to 3.5 (in g/cm^3) for enstatite [the corresponding pressures range from -0.65 to 23.3 (in GPa)], 9 density points from 4.2 to 5.0 for Pv (P from 33.0 to 112.6), and 17 density points from 5.2 to 6.8 for *cmcm* (P from 132.0 to 389.7) in increments of 0.5, and calculating the corresponding P based on T_m from Eq. (1) and the thermal EOS. Fitting now the Simon functional form to the complete set of 33 data points, with the constraint that $T_m(P = 0) = 1831$ K [34], gives

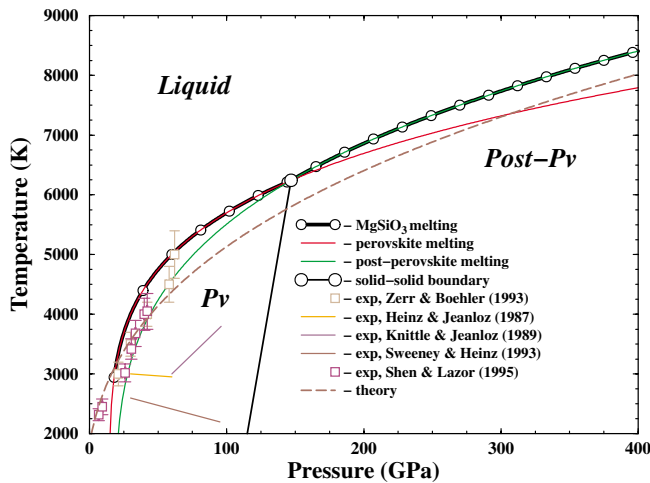$$T_m(P) = 1831\left(1 + \frac{P}{4.6}\right)^{0.33}. \quad (2)$$

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FIG. 3 (color). MgSiO$_3$ phase diagram. Melting temperatures were calculated using the 2-phase MD method [13] with the same model [18] that was used to calculate the overheating (Fig. 1). The melting curves of the Pv and $cmcm$ phases overlay the thick black melting curve of MgSiO$_3$. The $Pv - cmcm$ phase boundary is indicated by a thin black line. The phenomenological melting curve (Eq. (2)) is shown by a dashed line. Experimental melting data are shown by squares [7,8] and solid lines [4–6].

The melting curves [Eq. (2) and the one obtained with MD] are compared in Fig. 3. Though these two are somewhat different, the conclusions that we derive and discuss below are consistent.

First, we notice that both of our melting curves suggest the validity of the experimental data [7,8]. Second, both of the melting curves (Fig. 3) fall below the extrapolations of diamond anvil cell data [7] to higher P. At 135 GPa, the P of the core-mantle boundary, the extrapolations [7] give T_m higher than 7000 K, while our estimate is $T_m = 5900$ K. The slope of the MgSiO$_3$ melting curve becomes low at high pressures. In the calculated P range (at pressures of the Earth's interior) the melting curve of MgSiO$_3$ is higher than the melting curve of iron [35]. Therefore, at the early stage of the Earth's evolution, when the Earth is believed to be largely molten, MgSiO$_3$ would crystallize on cooling first. Since the density of MgSiO$_3$ at the same P is approximately half that of Fe, the MgSiO$_3$ crystals would float, leading to the fast segregation of the mantle and the core.

In conclusion, we have shown how one can approach the problem of calculating the melting curve of a material of high chemical and structural complexity with a high degree of self-consistency characteristic of *ab initio* methods. The T_m correction increases with P but does not exceed 1000 K at the highest P (Fig. 1).

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