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MELTING AT HIGH PRESSURE: COMPARATIVE ANALYSIS
OF EXPERIMENTAL AND THEORETICAL RESULTS

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*Theoretical and experimental data on melting at high pressure are often controversial. This is because of difficulties of performing experiments at extreme conditions and difficulties with verification of theoretical models. In this paper, we look into details of mostly theoretical studies and compare different approaches to predict and/or describe melting pressure–temperature curves. Some experimental problems are also addressed. Recent results for melting of alkali halides, some oxides and metals (LiF, MgO, MgSiO₃, Cu, and Fe) obtained using molecular dynamic method and diamond anvil cell technique are analyzed.*

### Introduction

Studies of melting at a high pressure, apart from practical importance, are of fundamental interest. Generally, a high pressure allows to probe distances between atoms which are much shorter than at ambient conditions. Therefore, the information from high-pressure experiments provide a stringent tests for models of a condensed matter, inspires further development of condensed matter theory which, in turn, give a new challenge to high pressure experiment. However, models of solid, being of value, could not be considered as a general ones until they checked for a different states of a matter. Naturally, to test universality of such models, one can try to apply them for studying a melting transition.

There are two things, which hinder direct verification of theoretical models of a condensed matter against experiment. The first one is the possibility of an experiment to be wrong. Such possibility increases when experimental conditions become extreme, as is the case with melting at high pressure, in particular when melting temperatures are high. The second one is that there is an intermediate stage between a model itself and a final result such as a melting temperature – and this is the particular method, which has to be applied to calculate a melting temperature using a model which needs to be verified. These two are indeed serious obstacles. As we will see further, good agreement between theory and experiment does not guarantee that the model is good and, a disagreement between theory and experiment does not necessarily mean that the model is bad. In both cases, careful analysis of an experiment and theory is required.

In this paper, we will concentrate mostly on the second obstacle, i.e. how to correctly calculate melting temperature having a model. When we are saying «correctly» it does not necessarily mean that the calculated temperature will be in agreement with

experiment. «Correctly» means that this is the temperature, which is correct for a given model.

The paper consists of the following parts. First, we discuss different methods for calculating melting temperatures. Second, we discuss a number of examples of calculations for a number of particular substances. We show which results should be considered as correct (in the sense given above). Finally, we provide recommendations on which methods one can trust and provide possible explanations of existing controversial experimental results.

## Description of methods for melting temperature calculation

In what follows we will consider only atomistic approaches to the problem of calculating melting temperatures ($T_m$), i.e. models, which treat a solid as an ensemble of atoms. Further, we restrict the consideration of methods for calculating melting temperature by molecular dynamics (MD). Molecular dynamics method is the technique which solves equations of motion for an ensemble of atoms interacting according to some potential model. A detailed description of this method can be found elsewhere (Allen and Tildesley 1987). There are several particular ways to calculate $T_m$ within general MD method.

1. The most straightforward method to calculate $T_m$ using MD techniques is to gradually increase temperature until the crystal structure becomes unstable and undergoes to liquid structure. This method was applied in a number of works (e.g. Cavazzoni et al., 1999; Chaplot et. al., 1998; Matsui and Price, 1991; Vocadlo and Price, 1996) and even though it is recognized that the method overshoot $T_m$, it is still used by a number of researchers because of its simplicity. However, it would be quite erroneous to believe that this method produces $T_m$, because it does not. The difference between the temperature of thermal instability ($T_{inst}$) is about 10-20% of $T_m$ at zero pressure ($P$) and increases with pressure with $T_{inst}$ always being higher than $T_m$. The method is quite suitable to get a rough estimate of $T_m$. If the empirically known correction is applied one can get a decent estimate of $T_m$. Still, it is important to remember that $T_{inst} > T_m$. If $T_{inst}$ is close to experimental melting temperature, it means that the correct theoretical $T_m$ is substantially lower than the experimental $T_m$ and, therefore, the model is not very good. However, in some cases erroneous conclusions have been made. Because in each individual case the difference between $T_{inst}$ and $T_m$ is not known, this method is not advised to apply unless one needs a rough estimate.

2. Another method is based on the Clausius–Clapeyron equation, which is valid at a phase transition. According to the CC equation

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}.$$

(1)

Because the $\Delta H$ and $\Delta V$ can be calculated directly from the simulation, this allows to calculate the derivative $dT/dP$. The problem is that, to solve Eq. 1, one has to have

an initial value of $T_m$ at some temperature for this model. Another problem is that, to solve Eq. 1 with an acceptable precision, one has to carry out a significant number of simulations which in some cases might be very difficult because of technical restrictions. While this method is thermodynamically valid the results are uncertain because if the initial $T_m$ is not known exactly the error might propagate and increase with increasing pressure, does not matter how small the pressure step of simulations is.

3. The most rigorous way to calculate $T_m$ comes from the requirement that Gibbs free energies of a solid and a liquid are equal at the temperature of solid–liquid phase transition, i.e.

$$\Delta G_{\text{solid}}(T_m, P) = \Delta G_{\text{liquid}}(T_m, P). \tag{2}$$

Because

$$G = F + PV, \tag{3}$$

where $F$ – free Helmholtz energy, and $V$ – volume, and $P$ and volume can be calculated directly from MD simulations, the problem is to calculate $F$. Usually, this is done using the relation (Morris et al., 1994)

$$F = F_0 + \int_0^1 d\lambda \langle U - U_\lambda \rangle_\lambda, \tag{4}$$

where $F$ is the true free energy calculated from the potential energy $U$, and $F_0$ is the free energy of some exactly solvable system corresponding to a potential $U_0$. This relation may be derived simply from the canonical ensemble; note that the average in Eq. (4) is calculated with respect to the potential $U_\lambda = \lambda(U - U_0)$. The average in the integrand may be calculated for a given value of $\lambda$ by performing a simulation of the system with the potential $U_\lambda$. Using a series of these values, an approximate value of the free energy may be calculated. Once the $F$ of the system is known at a given $T$, a similar process may be followed to find $F$ at other $T$ using the relation

$$\frac{F}{T} - \frac{F_0}{T_0} = \int_{T_0}^{T} d\tau \frac{E(\tau)}{\tau^2}. \tag{5}$$

While the use of Eq. (2)–(5) is straightforward, there are a number of problems in this method. Problems are related with choosing a reference system (potential $U_0$). While for a solid phase the reference system might be chosen as, e.g., Einstein solid (Mei and Davenport, 1992), the situation with a liquid phase is more complicated. This is because the integration path in Eq. 4 must be reversible. If one chooses an ideal gas as a reference system for the liquid then one somehow has to deal with the liquid–vapor transition. The normal practice is to turn off the attractive part of the interactions and then perform a slow expansion to a weakly interacting gas. This allows to avoid the liquid–vapor transition and is a reversible path.

Concluding, we should say that this method is, in principle, quite correct. However, it involves a number of intermediate steps, which might lead to an accumulating of errors.

4. There are several other methods, which are based on empirical observations of a particular behavior of various calculated properties at melting. Such observations could be a certain behavior of structure prior to melting, integration of Van der Waals loop, special behavior of pressure–volume curve etc. While these methods might be rather precise in certain cases (e.g. Belonoshko, 1992; 1994a), there is no justification why they should work in a general case. Therefore, each particular case of an application of such a method must be carefully verified, which, sometimes, is simply not possible (e.g. there are no experimental data in the $PT$ range of interest).

5. Finally, we come to the description of the so-called two phase method which we consider to be the most reliable one. In this method, the initial configuration of atoms consists of two major parts, one is a pre-simulated solid and another one is a pre-simulated liquid. These parts are put together so they have a common solid–liquid interface. All MD simulations of freezing/melting start from this configuration and continue until a monophase state is reached. If at some pressure $P$ and temperature $T_1$ this monophase is solid then it means that the $T_1$ is less than $T_m$. If the monophase is liquid then $T_1$ is larger than $T_m$. Proceeding in this way one can make the temperature brackets very narrow. This allows to determine the $T_m$ quite precisely. Morris et al. (1994) showed that this method is equivalent to calculating the Gibbs free energy and, therefore, is thermodynamically grounded. We applied this method successfully for a number of materials (Ahuja et al., 1998; Belonoshko 1994b,1998; Belonoshko et al., 2000a, 2000b, 2000c; Belonoshko and Ahuja, 1997; Belonoshko and Dubrovinsky, 1995, 1996a,b,c).

## Comparison of MD calculated and experimental melting curves

### Perovskite (MgSiO₃)

This is a good example of how a very good model of interatomic interaction being applied incorrectly can produce an impression of poor performance. Matsui and Price (1991) developed a model for perovskite ($MgSiO_3$), which allowed to calculate a number of properties in good agreement with experiment. They applied the model to calculate the $PT$ melting curve (Fig. 1). In fact, instead of $T_m$ they calculated $T_{inst}$ – temperature of thermal instability, as did more recently Chaplot with co-authors (1998). Zerr and Boehler (1993) measured $T_m$ of (Mg,Fe)SiO₃-perovskite and their $PT$ curve appeared to be much lower than the Matsui and Price prediction. Belonoshko (1994) applied the Matsui and Price model using two-phase simulation. The calculated $PT$ curve is in very good agreement with experiment, especially taking into account that $MgSiO_3$-perovskite with some addition of iron should melt at lower temperatures. This is an instructive example of how an improper choice of a method can lead to a wrong conclusions and how important is a choice of a proper method. Matsui and Price (1991) and later Chaplot et al. (1998) observed also orthorhombic to cubic transition in perovskite above melting. From their point of view they observed the transi-
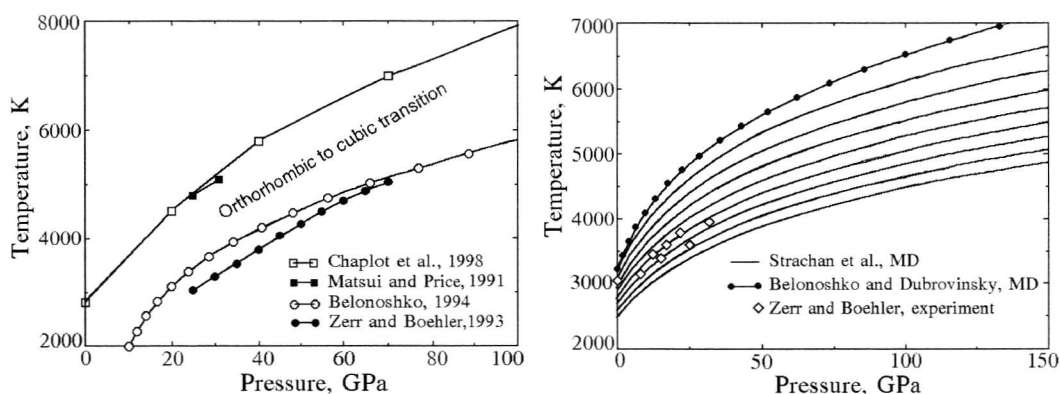
**Fig. 1.** Pressure dependence of melting temperatures of MgSiO$_3$-perovskite as suggested in the studies indicated on the legend. Matsui and Price (1991) and Chaplot et al. (1998) calculated curves provide temperatures of thermal instability. 2-phase simulations by Belonoshko (1994) for Matsui and Price (1991) model produces melting temperatures in close agreement with experiment (Zerr and Boehler, 1993). The text «orthorhombic to cubic transition» is located in the range where it was calculated by Matsui and Price (1991) and Chaplot et al. (1998)

**Fig. 2.** Melting temperatures ($T_m$) of MgO as a function of pressure from different sources. The solid lines are $T_m$ as it comes from Strachan et al. (1999) assuming different $T_m$ at $P = 0$. The only correctly calculated MgO melting curve (Belonoshko and Dubrovinsky, 1996a) and experimental data are marked as indicated in the legend

tion prior to melting. One can see from this, that it is important to know $T_m$ of a model, otherwise it is not clear if the model does produce phase transition or not. Similar ambiguity was reported in the study of Cavazzoni with co-authors (1999) when simulating H$_2$O melting. They observed superionic transition in ice prior to «melting». It is not clear if that transition is real or occurs above correctly calculated melting temperature.

### Periclase (MgO)

Periclase is known to have a very high melting temperature at zero pressure, in excess of 3000 K. Therefore, it is technically difficult to measure $T_m$ at high pressure. There is only one experimental study (Zerr and Boehler, 1994). MgO melting have been studied theoretically rather extensively (Belonoshko and Dubrovinsky, 1996; Cohen and Weitz, 1997; Strachan et al., 1999; Vocadlo and Price, 1996). While Belonoshko and Dubrovinsky (1996a) applied correct two-phase method, Cohen and Weitz (1998) and Strachan with co-authors (1999) used the method based on Eq. (1). Vocadlo and Price (1996) calculated $T_{inst}$ instead of $T_m$. Because the method based on Eq. (1) does not allow to determine melting $PT$ curve but merely its derivative, one can get a set of melting $PT$ curves depending on the assumed $T_m$ at zero pressure (Belonoshko, 2000d). This set is shown in Fig. 2. One can see, that Strachan's work does not provide narrow constraints on the MgO melting curve. The common feature of all published works on MgO melting is that calculated melting curves are all substantially higher than the experimental one; (Zerr and Boehler, 1994) one. Also, the d$T$/d$P$ at zero pressure is considerably lower than for all other similar substances. It could be that all theoretical curves are wrong. However, we can not rule out the possibility of imprecise experimental data (see discussion below).

## LiF, NaCl

This is, probably, the most instructive example. Normally, good agreement between experimental and theoretical data is considered as a good support both for an experimental and a theoretical result, because fortuitous agreement of two quite different methods is unlikely. Boehler et al. (1997) have measured and calculated melting curve of LiF up to pressure of 1 Mbar and claimed very good agreement between theory and experiment. The melting curve for LiF in their study was obtained as temperatures of thermal instability, which is not correct. Close examination (Belonoshko et al., 2000c) revealed that the *PT* melting curve for LiF calculated correctly for the model accepted by Boehler et al. (1997) is much lower than the experimental *PT* melting curve. We (Belonoshko et al. 2000) developed a new very simple model using *ab initio* calculated data for 0 K isotherm. Absolute values of melting temperatures are considerably lower than experimental ones (Fig. 3). However, pressure dependence is of value. It was discovered that at the pressure of about 1 Mbar LiF undergoes phase transition from *B*1 to *B*2 structure. *B*2 LiF crystal melts at higher temperatures than *B*1. This allows to reconcile the diamond anvil cell and shockwave data.
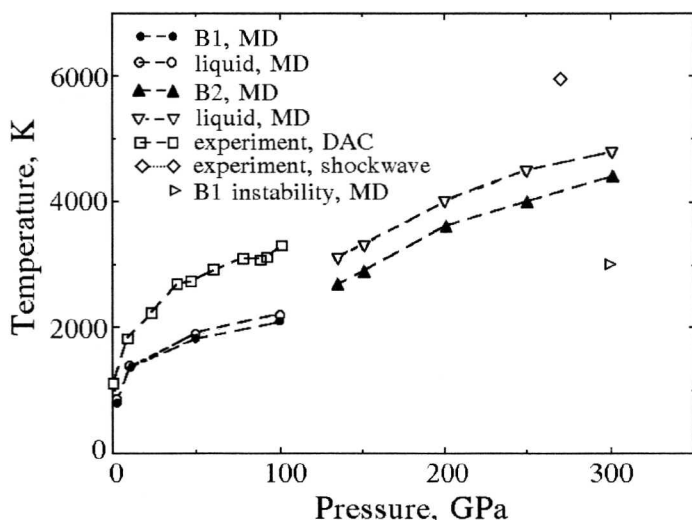


**Fig. 3.** Melting temperatures of LiF. The theoretical curve for LiF in *B*1 structure is lower than the experimental one by about 1000 K at the highest experimental pressure of 1 Mbar. About the same difference is between the shockwave melting point and theoretical curve for LiF in *B*2 structures. This suggests that the experimental data from diamond anvil cell (if extrapolated) might be in agreement with the shockwave melting point at about 2.8 Mbar. This is because stability of *B*2 phase increases the slope of melting curve at the triple *B*1–*B*2–liquid point. This point is located at the pressure 1.0–1.3 Mbar

Boehler et al. (1997) have also extended the pressure range of melting studies for NaCl. Their latest measurements are in agreement with our earlier calculations (Belonoshko and Dubrovinsky 1996).

## Metals (Cu, Fe)

MD calculations of Cu melting curve are a good illustration of the case, when two different methods (Belonoshko et al., 2000a; Moriarty, 1986) being applied correctly produce melting curves in very good agreement. Moriarty calculated Cu melting curve from calculation of the Gibbs free energies for liquid and solid Cu (Eq. 2–5). Belonoshko et al. (2000a) calculated the Cu curve with two-phase method. It is quite rare to see (Fig. 4) such a good agreement between two curves, especially if calculations are based on different models of interatomic interaction. Such agreement provides strong mutual support to both determinations of melting transition.
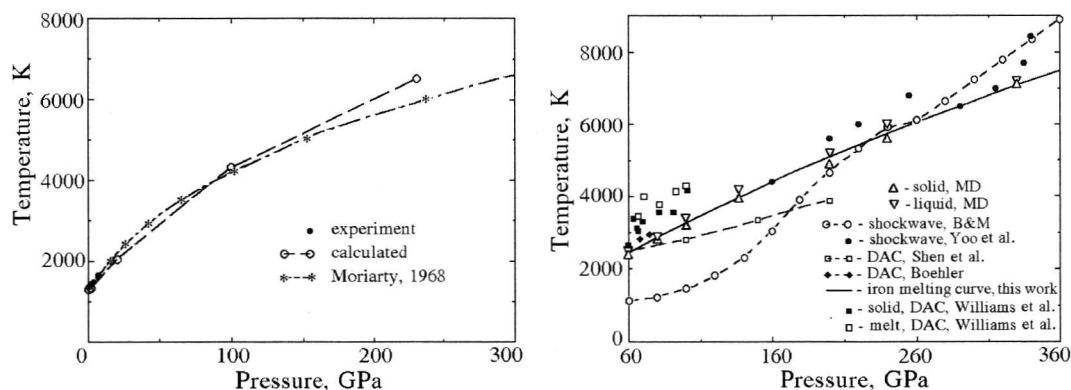


**Fig. 4.** Melting curve of Cu. Static experimental data exist up to the pressure of 70 kbar. The curve, indicated as «calculated» on the legend is due to Belonoshko et al. (2000a). The agreement between all sources of data is quite good

**Fig. 5.** The melting curve for Fe (Belonoshko et al., 2000b) compared with a number of experimental data as indicated on the legends. There is a good agreement between Fe melting curve calculated by two-phase method and the latest data by Shen et al. (1998) obtained with diamond anvil cell technique with *in situ* X-ray determination of Fe structure. The calculated curve is also in good agreement with shockwave data by Brown and McQueen (1986). The melting curve obtained by Boehler (1993) deviates from the calculated one with increasing pressure. Note, that measurements by Boehler (1993) are based on visual determination of melting

It is important to know melting curve for Fe from geophysical point of view, for it is believed that the Earth's core consists of iron. While inner core is solid the outer core is liquid. The boundary between them is the boundary of the solid–liquid transition. Since the pressure of this boundary is known rather precisely, a knowledge of the melting temperature of Fe at that pressure would allow to know temperature inside the Earth. This is an extremely important information, because many Earth models are based on various assumptions on temperature distribution within the Earth. No surprise, that considerable amount of theoretical and experimental effort has been put into study of iron phase diagram at extreme pressures and temperatures (Belonoshko and Ahuja, 1998; Belonoshko et al., 2000b; Boehler, 1993; Brown and McQueen, 1986; Shen et al., 1998; Williams et al., 1987; Yoo et al., 1993). Despite all these efforts, the melting transition in iron at extreme pressures is still rather contradictory

subject (Fig. 5). We performed MD two-phase simulations to determine the Fe melting curve in the pressure range above 60 GPa, where iron is believed to have *hcp* structure. We applied the embedded-atom model based on the *ab initio* calculated properties of iron. Our melting curve is in agreement (Fig. 5) with the most recent diamond anvil cell data (Shen et al., 1998) and shockwave data by Brown and McQueen (1986). Note, that the BM shockwave data is based on the determination of velocity of the rarefaction wave behind the shock front, which is rather unique and provides better precision than traditional shock wave studies, where velocity of the shock front only is measured.

## Discussion

As we see, the numerical studies, if applied correctly, can provide valuable information on a liquid–solid transition. The obtained knowledge is not restricted by the calculation of $T_m$ at certain pressure. Practically any information can be obtained with MD method, such as structure, diffusion coefficients, kinetics of a phase transition, any equilibrium thermodynamic parameter.

On the other hand, improper methods can considerably add to confusion. Indeed, for a non-expert to distinguish between correctly and incorrectly applied MD method might be an impossible task. Hopefully, this paper can help to facilitate the solution.

The most often mistake which have been made in calculating $T_m$ is application of MD to calculate temperature of thermal instability ($T_{inst}$, see also above) instead of melting. We have direct comparison of these two methods when calculated $T_m$ for corundum ($Al_2O_3$) (Belonoshko, 1998; Ahuja et al., 1998) and copper (Cu) (Belonoshko et al., 2000a). Fig. 6 shows the difference between $T_m$ (calculated with two-phase method) and $T_{inst}$ (calculated by «heat-until-it-melts» method) at zero pressure. One can see the difference in excess of 200 degrees. The difference increases with pressure and can reach more than 1500 K at even comparably low pressures of 500 kbar as is the case with perovskite (Belonoshko 1994). Fig. 6 shows also that even two-phase method is not a guarantee of a correct result. For example, small number of atoms in computational cell can produce considerably different $T_m$. If a paper on molecular dynamics does not say explicitly that results are carefully checked against influence of such parameters as system size, cut-off for interatomic interaction calculation, size of time step etc. then it is not clear if that check has been done. And if the check has not been done, the results might be erroneous.

However, what if the method is applied correctly, the model performs very well for calculating a number of properties, and still calculated and experimental melting curves are different? An assumption of an experimental error is, of course, the last resort for a theoretician. However, when there is a strong evidence for theory to be correct, one has to look carefully for errors in experimental data. Rather often, it is obvious that there are experimental errors, as is the case with data on Fe melting (Fig. 5) where we have a number of contradictory experiments. In some melting experiments, melting is determined visually, by appearance of particular features at a surface of sample, particular behavior of temperature as a function of laser heating power and so on. In our opinion, such determination might be subjected to errors. One
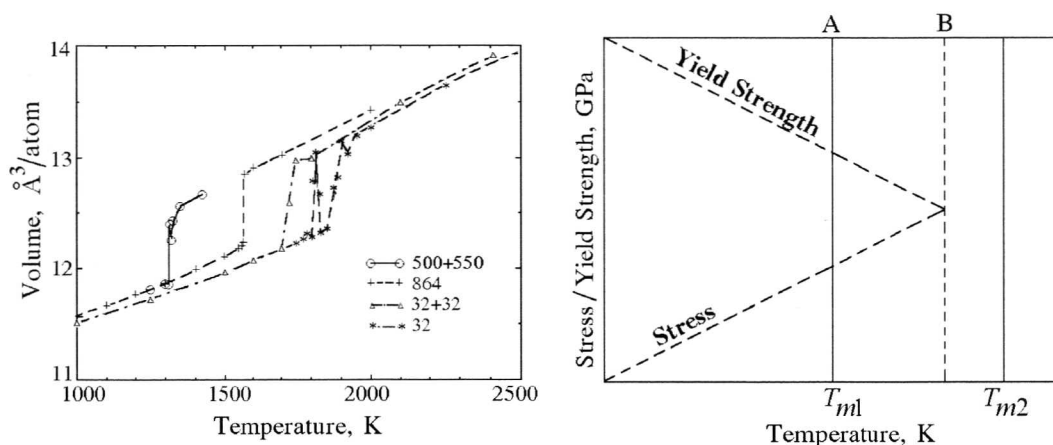
**Fig. 6.** Volume of copper calculated by MD method at zero pressure as a function of temperature. The curves marked by «*N + N*», where *N* – number of atoms calculated by two-phase method. The curves marked by «*N*» are results from conventional «one-phase» MD. The discontinuity is either melting transition (in case of two-phase simulations) or thermal instability

**Fig. 7.** Two possible scenarios in melting diamond anvil experiment. If stress becomes larger than yield strength before melting temperature ($T_{m2}$), visual determination of melting might be not good criteria. If a material melts before that event, the melting temperature ($T_{m1}$) might be determined correctly

has to have a very small sample to be able to reach a very high pressure. It is not possible to avoid non-hydrostaticity completely. Therefore, as temperature increases and material strength decreases (Fig. 7), a sample might yield and give an impression of melting (Belonoshko and Dubrovinsky, 1997). This might produce melting curves with extremely low $dT/dP$ derivative, as is the case with Fe (Boehler, 1993) and MgO (Zerr and Boehler, 1994).

Generally speaking, when a sample is not under hydrostatic pressure, then instead of two (*T* and *P*) intensive variables we have three (*T*, *P*, and stress). One can not exclude that under such circumstances even liquid-solid coexistence is possible in certain temperature range, according to the Gibbs phase rule.

## Conclusions

We have listed a number of different approaches within general molecular dynamics method to melting temperatures calculations. Only two of them are rigorous methods, namely, the Gibbs free energy calculations and two-phase simulation method. While the former is computationally much more expensive and has a tendency of accumulating errors, the latter, being as rigorous as the former one, is computationally comparably cheap, simple, and straightforward. Much of the controversy between various calculated melting curves for a number of compounds (e.g. $MgSiO_3$, MgO, Fe) can be attributed to application of an incorrect method.

A reliability of molecular dynamics method does not depend on the pressure-temperature conditions of application. In fact, high pressure makes situation somewhat simpler, eliminating a variety of structural forms, which is characteristic, mostly, of

low pressure range. On the other hand, experiments face considerable technical problems when conducted at extreme pressures. Notwithstanding the fact that experiment is a primary and ultimate source of information, one has to be aware of unexpected phenomena at the extreme experimental conditions. An ignorance of these phenomena might lead to an erroneous interpretation of experimental data.

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