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The melting of MgO – computer calculations via molecular dynamics

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Abstract Computer calculations based upon molecular dynamics have enabled us to model the melting behaviour of MgO, a significant component of the Earth's lower mantle. We have successfully employed the super-cell method to study the mechanisms governing the melting process at ambient pressure, and this has enabled us to quantitatively predict values for melting temperature as a function of pressure in the range 0–150 GPa. We have performed melting calculations on a constant stress system containing 1728 ions using a variety of potential models, all of which give a good description of the ambient structural, elastic and defect properties of our system. Our results show that the melting temperature of MgO rises from 2900–3400 K at zero pressure to ~8000 K at 150 GPa depending upon the potential model used. Our zero pressure results are comparable with previous calculations and close to the experimental value for zero pressure MgO melting of ~3100 K. We also calculate the melting volume and melting entropy of the system and find our results comparable with zero pressure experimental data for alkali halides but not with the recent high pressure results of Zerr and Boehler (1994) on MgO; the possible sources of this discrepancy are discussed.

Introduction

Melting, the liquid-crystal phase transition, is perhaps the most familiar example of a first order phase transition, but it is also arguably one of the least well understood processes in condensed matter physics. Additionally, melting is a process of fundamental importance to planetary sciences, as it represents the most efficient mechanism for mass and heat transport during planetary evolution. Currently, one of the major challenges in

Earth sciences is to establish the high pressure melting behaviour of lower mantle and core forming phases. The results of high pressure experimental studies for such phases are difficult to constrain precisely; consequently, considerable emphasis has recently been placed on the use of computational and theoretical methods to establish such high P/T behaviour of minerals. In this paper we aim to define the methodology needed to calculate melting curves by using molecular dynamics techniques, and we will use the simulation of the melting of MgO at ambient and then higher pressures as our exemplar.

In the following sections, we initially review the different approaches used to study the phenomenon of melting; we then outline the theory behind the atomic model used in our calculations. Following this we discuss the background to the computer modelling of the solid-liquid phase transition, including a brief description of the molecular dynamics techniques involved, and the criteria governing molecular dynamics melting. We then review the current methodological problems associated with trying to model such melt systems, and assess the validity of a number of potential models at zero pressure. This molecular dynamics approach is extended to investigate the effect of pressure on melting, thus obtaining a high pressure melting curve for MgO. Finally, we examine the predicted thermodynamic properties of melting, revealing the inconsistencies in recent attempts to experimentally determine the high pressure melting curve for MgO.

Melting models

Melting is a fundamental first order phase change from an ordered solid to a disordered liquid. At the macroscopic level, distinct discontinuities occur in free energy, molar volume, entropy, enthalpy, etc.; at the microscopic level, melting occurs when there is a marked and continuous increase in the mean squared displacements of the individual species as their increased energy allows them to dissociate from the solid structure.

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Totally reliable, indisputable melting points and related melting phenomena may only be obtained experimentally, but this is often difficult, especially at high pressures and temperatures. The melting point of MgO has been measured at zero pressure by a number of authors, and generally lies in the range 3060–3125 K. The high pressure melting behaviour of MgO has, until recently, eluded experimentalists due to the difficulty in obtaining simultaneously very high temperatures and very high pressures. However, Zerr and Bohler (1994) have obtained a melting curve for MgO to 35 GPa using the diamond anvil cell technique with CO₂ laser heating on very thin samples in an argon pressure medium. The zero pressure melting point that they determine is 3040 ± 100 K which rises to ~ 3950 K at 35 GPa. No other high pressure experimental data have been reported with which to compare this, although a number of authors infer a significantly higher melting gradient (Jackson and Liebermann 1974; Bollmann 1992). Therefore the high pressure melting behaviour of MgO cannot yet be considered as being fully constrained.

As a result of the experimental difficulties, other approaches have been developed to circumvent the intractable nature of melting. These techniques (which include semi-empirical, theoretical, and computer methods) may be used to predict melting temperatures at ambient pressures, and in some cases as a function of pressure. The semi-empirical Simon equation (Simon and Glatzel 1929) and the Kraut-Kennedy equation (Kraut and Kennedy 1966), both provide simple relations between melting temperature and its variation with pressure or volume; however, their use in this study is not appropriate as they require a number of experimentally fitted parameters which have not been unambiguously determined. Theoretical models are generally based upon the analysis of the stability of the crystal structure at the phase transition, i.e., the development of shear instability, vibrational instability, etc.; in the case of the latter this can lead to a predicted melting temperature dependent on the Debye temperature of the solid and the mean squared displacement of the atomic vibrations via $T_m = f(\Theta_D^2, \langle u^2 \rangle)$ (Lindemann 1910). Although very successful in predicting the melting temperatures of a number of structures (e.g. Poirier 1991), this approach cannot be universally applied since no account is taken of the energetics of the liquid phase. Two further theories have been developed which do not suffer from this limitation as they account for both the energy of the liquid and of the solid: the Lennard-Jones and Devonshire model (1939), developed to study inert gas solids, and dislocation melting models (e.g. Poirier 1991). Of these two models, the dislocation model is likely to be more widely applicable as it attempts to describe the liquid structure in terms of a crystal saturated with dislocation cores. Poirier and Price (1992) successfully used this theory to predict the melting points of a number of metals, but due to the large melting volume for alkali halide structured phases, this theory is inappropriate for use on MgO.

Thus it would appear that each of the above approaches is of limited applicability to the relevant phases and conditions of the Earth's deep interior. An alternative approach is needed that takes the microscopic nature of matter into account, and this may be achieved via computer calculations, using pair potentials to model the interatomic interactions within the system. Using this approach, melting and other related high temperature phenomena may be simulated in a number of ways: Hausleitner and Hafner (1989) used interatomic potentials with statistical thermodynamics to model the melting curve of iron to 1.5 Mbar, Lynden-Bell et al. (1993) used the Monte Carlo method to model the melting and crystallisation of platinum and other ductile metals, whilst a recent study by Cohen and Gong (1994) used molecular dynamics to simulate the behaviour of an MgO crystal; in our study we use classical molecular dynamics to model the bulk melting of MgO to 150 GPa.

The atomistic model

The physical properties of a solid may be established by solving the Schrödinger equation explicitly, thereby obtaining precisely the energy surfaces associated with the interactions of electrons and nuclei within a given system. This *ab initio* approach is not universally practicable due to the size and complexity of the required calculation. A simpler and more approximate treatment is provided through atomistic modelling which describes the interactions between atoms or ions within a crystal structure, as opposed to the finer details of each electronic interaction. Such an approximation is usually based upon the Born model of solids (Born and Huang 1954) where, in this instance, only forces due to ion-ion interactions are included.

In order to model such interatomic interactions, it is first necessary to understand the potential energy functions which describe them. This is achieved initially by considering a two-body system; many body systems are generally prohibitively complex, computer intensive and time consuming. When no net forces are acting on the constituent atoms, the sum of the attractive and repulsive potential energies between each pair of atoms in a crystalline solid at zero Kelvin is termed the *static lattice energy*:

$$U_L(r_{ij}) = \sum_{ij} \frac{q_i q_j}{r_{ij}} + \sum_{ij} \phi_{ij} + \sum_{ijk} \theta_{ijk} \quad (1)$$

The first term on the right hand side is the contribution to the static lattice energy from the long range Coulombic attraction for an infinite array of atoms of charge q , a distance r apart. The second term accounts for the diffuse nature of the electron clouds surrounding the nucleus; it includes the short range interactions from polarisability and Pauli repulsion between neighbouring charge clouds, and the short and long range components of van der Waals attraction. The third term represents three body

interactions which, for severely ionic solids with dominant pairwise interactions, may, to first order, be neglected.

The short range interactions predominantly effect nearest neighbour ions, and may be represented by effective pairwise potentials such as the Buckingham potential which takes the form:

$$\varphi_{ij} = A_{ij} e^{-B_{ij} r_{ij}} - \frac{C_{ij}}{r_{ij}^6} \quad (2)$$

where A_{ij} , B_{ij} and C_{ij} are constants and r_{ij} is the interatomic separation. The first term in φ_{ij} is that due to short range repulsion, while the second is due to van der Waals induced dipole-dipole attraction.

Molecular dynamics

Molecular dynamics is a technique that enables us to use the description of interatomic interactions, given in the previous section, to predict the physical properties of matter. The essence of molecular dynamics calculations (e.g. Allen and Tildesley 1987) is the solution of Newton's laws of motion over a finite time period for a simulation box containing N ions, calculating the dynamic properties iteratively as the system evolves. Normally, periodic boundary conditions applied to the ensemble generates the required infinite system. The ions are initially assigned positions and velocities within the simulation box; their initial coordinates are usually chosen to be at the crystallographically determined sites, whilst their velocities, v_i , are chosen such that they concur with the required system temperature and are such that both energy and momentum is conserved:

$$\sum_i m_i v_i(0) = 0 \quad (3)$$

$$\sum_i m_i [v_i(0)]^2 = 3 N k_B T \quad (4)$$

where m_i are the atomic masses, k_B is Boltzman's constant and T is the initial chosen simulation temperature.

In order to calculate subsequent positions and velocities, the forces acting on any individual ion must be calculated from the first derivative of the potential function, and the new position and velocity of each ion may then be calculated at each timestep by solving Newton's equations of motion:

$$F_i = -\frac{\partial U_L}{\partial r_i} = m_i a_i(t) = m_i \frac{d^2 r_i}{dt^2} \quad (5)$$

where the terms take their usual meaning. Equation (5) may be numerically integrated to generate a set of positions, $r_i(t+\Delta t)$, and velocities, $v_i(t+\Delta t)$, as the system evolves. For an infinitesimally small timestep the updating equations are:

$$r_i(t+\Delta t) = r_i(t) + v_i(t) \Delta t \quad (6)$$

$$v_i(t+\Delta t) = v_i(t) + \frac{F_i(t)}{m_i} \Delta t \quad (7)$$

For a finite timestep, the above equations loose their accuracy and higher powers of Δt are required; in our calculations the equations of motion are solved using the Gear predictor corrector algorithm (Gear 1966) whereby a fourth order Taylor series expansion of the displacements with respect to time generates predicted evolving positions which are then corrected iteratively until a convergent solution to the trajectories and velocities is obtained.

The instantaneous temperatures are calculated at each timestep for a system of N particles from the equation:

$$T = \frac{2}{3 N k_B} E_{\text{kin}} \quad (8)$$

where

$$E_{\text{kin}} = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 \quad (9)$$

The pressure of the simulated system is calculated from the virial theorem thus

$$P = \frac{N k_B T}{V} - \frac{N k_B T}{6V} \left(\sum_{i=1}^N \sum_{j>1}^N r_{ij} \frac{\partial \psi_{ij}}{\partial r_{ij}} \right) \quad (10)$$

where N is the number of particles within the system, V is the volume, r_{ij} is the distance between ions i and j , $\partial \psi / \partial r_{ij}$ is the first derivative of the potential energy of ion i with respect to ion j , and k_B is Boltzmann's constant.

The MDCSPC code used in this study (Smith 1985) employs the Ewald method to calculate the Coulombic term in the potential function more efficiently (Ewald 1921, 1937; Catlow and Norgett 1978), and the Parrinello and Rahman constant pressure algorithm (1980) combined with constant temperature MD (Nosé 1984) for a constant enthalpy $\{N, P, T\}$ ensemble. A timestep of 10^{-15} s is used and the system is allowed to evolve over a large number of timesteps to ensure equilibrium, followed by thermodynamic property averaging over a further several thousand timesteps. Therefore, equilibrium properties can be obtained from the statistical average of the behaviour of the particles over a simulated time period of several picoseconds.

Melting and molecular dynamics

Molecular dynamics is an invaluable technique for high temperature studies such as melting because it incorporates the implicit anharmonicity associated with the development of such a disordered system, and it has been shown to reproduce accurately a number of pre-melting phenomenon. However, there are some problems associated with molecular dynamics when trying to determine exact melting temperatures. Thermodynamically, $T_m = \Delta H / \Delta S$, where ΔH is the melting enthalpy and ΔS is

the melting entropy; but unfortunately, molecular dynamics does not readily enable free energies, entropy, etc., to be determined. Therefore our criteria for melting are, in the first instance, the discontinuity in the cell volume at the transition, and this is corroborated by the observed increase in the atomic root mean square displacements as a function of time. However, when using these criteria, it is necessary to establish whether or not we obtain accurate equilibrium melting temperatures or whether significant superheating occurs. We could establish equilibrium by modelling crystallisation as well as melting, but such calculations are often very time consuming or impossible, since real time nucleation of a crystallisation event often takes longer than several picoseconds. It is therefore generally only viable simply to study the solid→liquid phase transition. Observations indicate that melting nucleates at free surfaces, and we may therefore assume that the presence of a free surface in our calculations will enable us to determine the equilibrium melting temperature at zero pressure for a given potential model. Since nucleation may occur easily on a free surface, superheating effects will be suppressed as the energy activation barrier for nucleation is minimised.

Ideally, therefore, we would like to perform high pressure melting calculations on a solid with free surfaces; unfortunately, such calculations are not routine since the simulation of the high pressure medium required significantly complicates the calculation. However, the absence of a free surface may result in an overestimation of the melting temperature as the energy required to dissociate from the lattice will be significantly greater. We therefore need to assess the effect of surfaces and other relevant factors on the predicted melting temperature and hence establish whether using periodic boundary conditions is a sufficiently accurate technique to enable equilibrium melting points to be established for a model system.

In a parallel study Ferneyhough et al. (1994), using the Lewis and Catlow potential (1985), have shown that calculations containing a free surface (i.e., periodic slab calculations) produce a melting temperature of 3250 ± 200 K for MgO at zero pressure, in good agreement with experiment. It has been suggested that the use of rigid ions may cause the energy of the liquid phase, and therefore the melting temperature, to be overestimated (Matsui and Price 1991) since the diffusion and defect related properties of the system are inadequately accounted for in the rigid-ion model; this implies that there may be insufficient atomic relaxation in the melt phase, thereby increasing the enthalpy of the melt and hence the predicted melting point. However, in that study, Ferneyhough et al. (1994) have shown that the use of the shell model to describe ion polarisability has a negligible effect on T_m ($\Delta T < 100$ K); thus despite the suggestion that the shell model may reduce calculated values of enthalpy for the liquid state, it appears that this effect is negligibly small and therefore, to a first approximation, such polarisability can be ignored.

It is essential to have a variable volume environment when simulating melting; the simulation box must be allowed to fluctuate in size to enable melt nucleation to occur. However, melting calculations on MgO by Fincham et al. (1994) serve to illustrate the importance of the constant *stress* environment. With their constant pressure system on an isotropic box (i.e., constant aspect ratio), also using the Lewis and Catlow potential (1985), they predict a zero pressure melting temperature of $T_m = 4500$ K, which is far higher than the temperature calculated by Ferneyhough et al. (1994). Therefore, in the calculations presented in this paper, we have used a constant stress molecular dynamics code (Smith 1985) whereby the supercell is allowed to change both shape and volume (Parrinello and Rahman 1980). Using the MDCSPC code and the potential model of Lewis and Catlow (1985) with a $6 \times 6 \times 6$ box containing 1728 ions, we predict a zero pressure melting temperature of $T_m \sim 3350 \pm 100$ K, which, within the fluctuations of the MD technique, is comparable with the slab calculations performed by Ferneyhough et al. (1994). Thus, so far, it appears that calculations with a constant stress MD code can give results which are comparable with free surface calculations. However, we need also to investigate the effect of ensemble size on the calculations, as it has been suggested (Winkler and Dove 1992) that this may alter the results of periodic MD calculations by significantly overestimating the melting temperature when small (<1000 atoms) boxes are used.

Ideally one would like to carry out calculations on an extremely large ensemble of atoms (>100 000); however, such calculations are not currently feasible, and this has meant that previous work has often been limited to systems containing only several hundred ions, where there is a danger that the statistical averaging is insufficient for the calculation of meaningful physical properties. The effect of boxsize on melting temperature is not immediately obvious; a larger ensemble would increase the probability of there being an ion with sufficiently large energy to dissociate from the ordered lattice and provide a nucleation point for melting, whereas the argument may be reversed for a smaller ensemble, since, once nucleated, the periodic boundary conditions would generate a higher density of disorder. Figure 1 shows how our calculated melting temperatures for MgO, using the Lewis and Catlow potential (1985), vary as a function of boxsize. The boxes simulated ranged from a $3 \times 3 \times 3$ to a $7 \times 7 \times 7$, i.e., between 64 and 2744 atoms. The uncertainty associated with the melting temperatures arises for two reasons: firstly, there is an effect due to statistical fluctuations associated with the ensemble size, since averaging over more atoms in a larger box will result in a smaller uncertainty in the predicted melting temperature; secondly, because of small fluctuations in temperature, the melting temperature itself cannot be constrained to a sharp volume discontinuity, but only to a region of discontinuity (usually no more than 50 K). It is evident that there is a significant boxsize dependency in the predicted melting temperature which levels off at

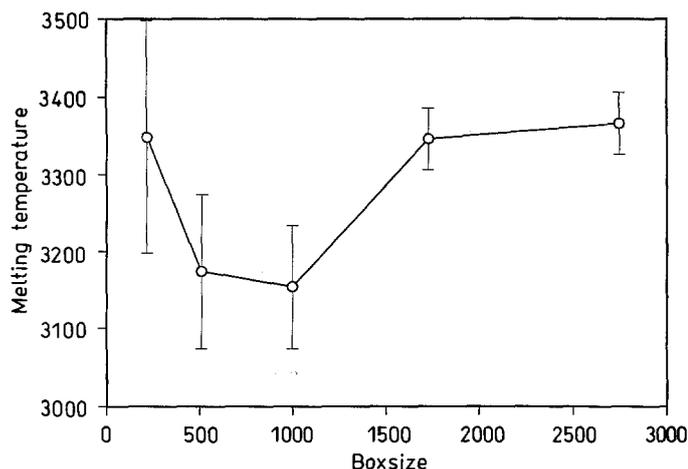


Fig. 1 Melting temperature as a function of ensemble size using the Lewis and Catlow potential (1985)

~1700 atoms. Belonoshko and Dubrovinsky (1995) have also studied the influence of system size on MD results by considering the frequency spectrum within the limits of the Debye approximation; they also found that a small system is less stable and therefore easier to melt than a large system due to the neglect of long wavelength, low frequency vibrations associated with a finite box size. However, they concluded, on the basis of lattice dynamics, that a box of only a few hundred atoms was sufficient. Our calculations show this not to be the case.

We therefore conclude that in order to successfully simulate melting with our supercell methodology, we require >1700 particles and a variable geometry box; this will give a good description of melting for the model system to within ± 100 K.

Molecular dynamics simulation of the melting of MgO

The molecular dynamics calculations are dependent on the quality of the chosen potential, so we have compared the predictions from three sets of short-range potential parameters for the oxygen-oxygen, magnesium-oxygen and magnesium-magnesium interactions (Table 1). The potential parameters used in our calculations were chosen because, using the PARAPOCS lattice dynamics free energy minimisation code (Parker and Price 1989), they were able to accurately reproduce the observed structural and elastic properties of MgO (Table 2). In addition, the potential models used also reproduce the *ab initio* static equation of state calculations of Isaak et al. (1990), and the experimental data summarised in Knittle (1995), as shown in Fig. 2. We note that the calculated values for incompressibility are consistently overestimated for all the potential models used. However, the errors in the equation of state are very small (Fig. 2), and so we believe that our use of these potentials to simulate high pressure melting processes are justified.

Table 1 Parameters for the Buckingham short range potential given by Eq. (2)

	Matsui (1989)	THB 2	Lewis and Catlow (1985)
Ionic Charge	+/-1.4	+/-2	+/-2
Mg-Mg			
A [$\text{J}\times 10^{-16}$]	2097.8	0.0	0.0
B [nm^{-1}]	96.1538	0.0	0.0
C [$\text{Jnm}^6\times 10^{-24}$]	0.0	0.0	0.0
Mg-O			
A [$\text{J}\times 10^{-16}$]	15.8491	1.31636	1.31636
B [nm^{-1}]	49.5050	30.8452	30.8452
C [$\text{Jnm}^6\times 10^{-24}$]	0.0	0.0	0.0
O-O			
A [$\text{J}\times 10^{-16}$]	3.4378	36.4723	36.4729
B [nm^{-1}]	33.3333	67.1141	67.1141
C [$\text{Jnm}^6\times 10^{-24}$]	- 4.8421	- 4.4669	- 3.2637

Table 2 Testing MgO potentials using PARAPOCS (Parker and Price 1989)

Potential	Matsui (1989)	Lewis and Catlow (1985)	THB 2	Observed
a [\AA]	4.1996	4.2195	4.2421	4.2112
K [GPa]	193.25	208.68	207.07	158.36
μ [10^9 Pa]	115	112	114	138

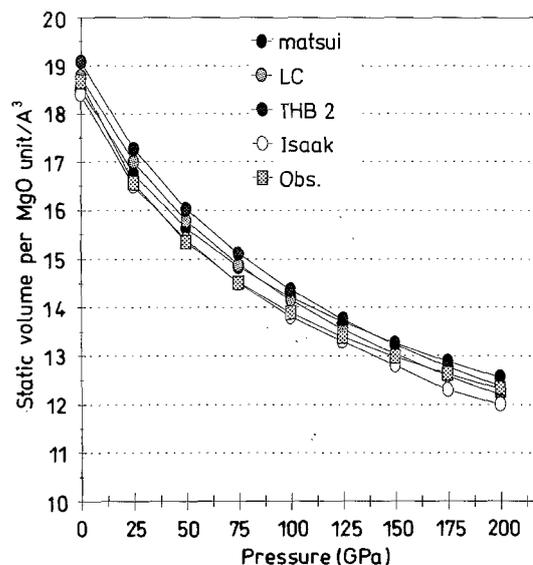


Fig. 2 Equation of state for a $6\times 6\times 6$ MgO ensemble with a number of potential models, compared with the *ab initio* calculations of Isaak et al. (1990), and experimental data (Knittle 1995)

Having found sufficiently good potential models which are robust over a wide range of interatomic separations, we now have to confirm their validity by calculating the zero pressure melting temperatures that they predict using the above methodology. We rigorously tested the temperature region around the melting temperature

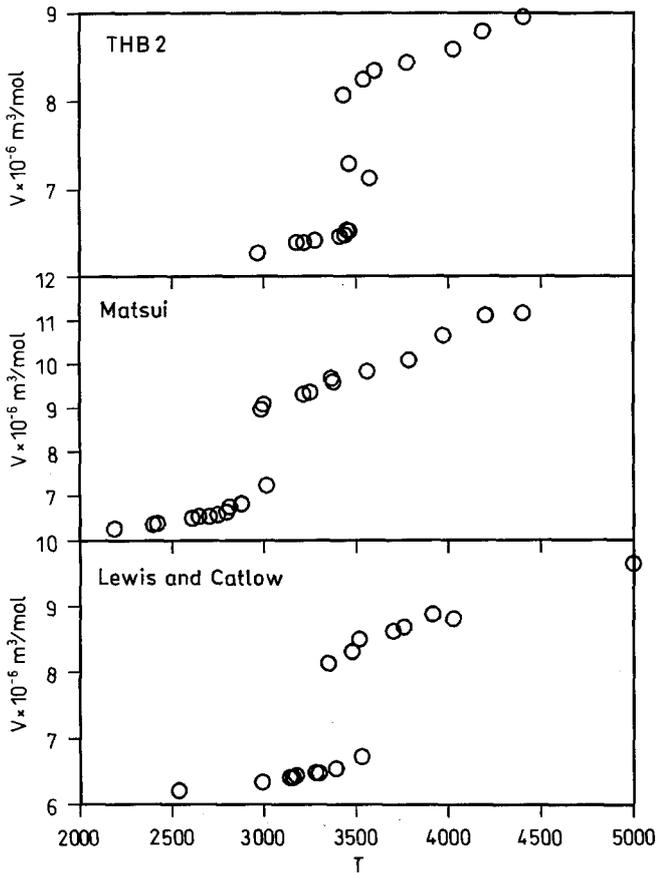


Fig. 3 Zero pressure melting behaviour of MgO for the three potential models; melting occurs at ~ 3430 K, ~ 2990 K, and ~ 3340 K

($\Delta T = 25$ K), and our zero pressure melting results show a discontinuity in volume at 2990 K, 3340 K, and 3430 K (± 100 K) for the potential models used (Fig. 3). The range of predicted results compares well with the experimental values (3050–3150 K). In Table 3 we compare our predicted melting behaviour with previous MD studies of MgO.

Our high pressure melting predictions for each potential are given in Fig. 4, showing an increase in melting temperature with pressure, as one would expect. To confirm that we have obtained fully equilibrated predicted

melting temperatures as a function of pressure, we also performed simulations on partially molten structures generated from restart co-ordinates at a number of pressures. We found that in all cases, these structures *crystallised* at target temperatures below the predicted melting temperature, and became *fully molten* at target temperatures above the predicted melting temperature. Our results show that the high pressure melting behaviour is similar in all cases, rising to a predicted value of $T_m \sim 8000$ K at a pressure of 150 GPa. This is in marked contrast to the experimental results of Zerr and Boehler (1994) who observe high pressure melting rising to ~ 4000 K at 35 GPa, which they extrapolate to ~ 5000 K at 150 GPa (i.e., CMB pressures).

One way in which we can attempt to investigate further this mismatch between the experiments and the calculations is to analyse the thermodynamic properties associated with the melting of MgO. In this subsequent analysis we use only the results obtained with the Lewis and Catlow potential model (1985), since we have shown that the choice of potential model does not significantly affect the results. Figure 5 shows how the melting volume (i.e., the change in volume on melting) varies as a function of pressure. Our calculations predict a zero pressure melting volume of $\sim 26\%$, which agrees well with the experimental observations for alkali halides which range from 15–25% (Ubbelohde 1978), and with a thermodynamic analysis for MgO where $\Delta V_m \sim 21\%$ (Ohtani 1983). Our calculated value decreases significantly with pressure, predicting a melting volume of only a fraction of a percent at 150 GPa, which suggests that the high pressure liquid structure becomes increasingly like that of a crystalline material. This supposition is supported by the fact that our MD prediction of the radial distribution function of the liquid at high pressure shows the first neighbour coordination structure of the liquid and crystalline phases to be virtually identical.

Thermodynamically, melting occurs when the free energy of the solid becomes greater than that of the liquid. From the free energy of the solid at its melting point, the Clausius-Clapeyron relation may be obtained:

$$\frac{dT_m}{dP} = \frac{\Delta V_m}{\Delta S_m} \quad (11)$$

Table 3 Comparative methodologies for the melting of MgO

	Our Calculations	Ferneyhough et al. (1994)	Cohen and Gong (1994)	Finchman et al. (1994)
MD type	Rigid ion	Shell model	PIB	Shell model
System	Supercell	Supercell with slabs	Cluster	Supercell
Surfaces	No	Yes	Yes	No
Number of ions	1728	256	64–1000	216
Minimisation technique	Constant stress	Constant stress	Constant stress	Constant aspect ratio
Potentials used	THB 2, Matsui (1989), Lewis and Catlow (1985)	Stoneham and Sangster (1985), Lewis and Catlow (1985)	MEG potential (see Cohen and Gong 1994)	Lewis and Catlow (1985), Sangster and Stoneham (1985)
Melting T at P=0	3430, 2990, 3340	3250	3200	4500

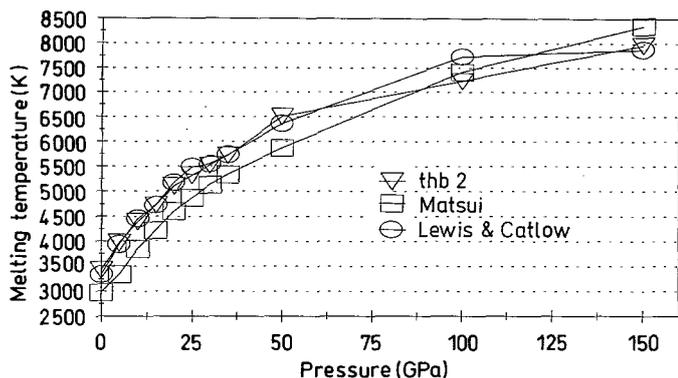


Fig. 4 High pressure melting curve for MgO; calculated melting temperature tends to ~ 8000 K in all cases

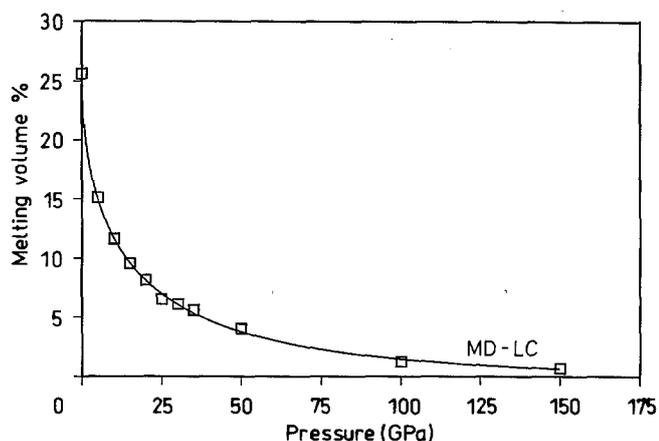


Fig. 5 Melting volume as a function of pressure using the Lewis and Catlow potential (1985); melting volume tends to only a fraction of a percent at high pressures

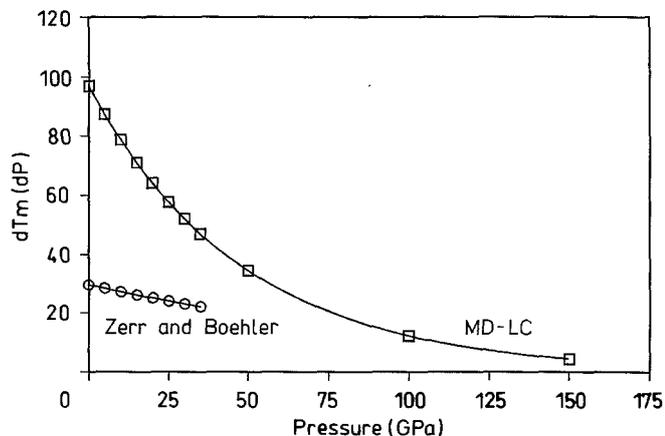


Fig. 6 Calculated and experimental (Zerr and Boehler 1994) melting gradient as a function of pressure

Hence the quantity $\Delta V_m/\Delta S_m$ may be obtained graphically from T_m as a function of P .

Figure 6 shows how the first derivative of our calculated melting curve (dT_m/dP) varies with pressure. The zero pressure value of ~ 98 K GPa $^{-1}$ lies between the experi-

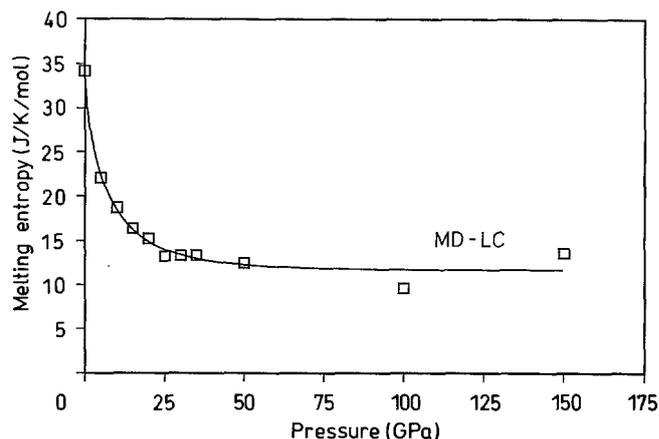


Fig. 7 Calculated melting entropy as a function of pressure; melting entropy tends to ~ 13 J K $^{-1}$ mol $^{-1}$ per MgO unit

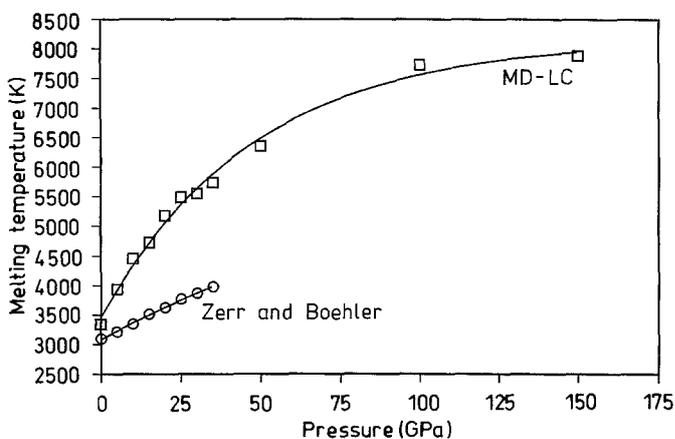


Fig. 8 Mismatch between experimental (Zerr and Boehler 1994) and calculated melting curves

mentally inferred value of ~ 110 K GPa $^{-1}$ (Jackson and Liebermann 1974) and a thermodynamical defect analysis which yields 72–96 K GPa $^{-1}$ (Bollmann 1992). Our calculated value may be used in conjunction with the previous results via Eq. (11) to obtain the melting entropy (Fig. 7). Our predicted zero pressure melting entropy of 34 J K $^{-1}$ mol $^{-1}$ is in fair agreement with the observed experimental value of $\Delta S_m \sim 25$ J K $^{-1}$ mol $^{-1}$ (JANAF 1971), and similar to the melting entropy of other alkali halide materials (e.g., $\Delta S_m \sim 28$ J K $^{-1}$ mol $^{-1}$ for NaCl, Ubbelohde 1978). With increasing pressure this value decreases to ~ 13 J K $^{-1}$ mol $^{-1}$ at 150 GPa. For dense atomic structures where $\Delta V_m \rightarrow 0$, the melting entropy $\Delta S_m \rightarrow R \ln 2$, i.e., ~ 5.8 J K $^{-1}$ mol $^{-1}$ of atoms (Rivier and Duffy 1982); our calculated value is *per MgO unit* and is therefore equivalent to a high pressure value of 6.5 J K $^{-1}$ mol $^{-1}$ of atoms which is in good agreement with this theoretically predicted and widely observed phenomenon (e.g., Poirier and Price 1992).

The recent results of Zerr and Boehler (1994) predict a melting curve for MgO with a significantly different gradient (Fig. 8). However, this slope is improbably low

for if we accept a value for the melting entropy of $\sim 25 \text{ J K}^{-1} \text{ mol}^{-1}$, then the experimental value for the melting volume must be $\sim 3\%$, which is far too low, and nearer that of metals than alkali halide structured phases; yet if we are to have confidence in our melting volume of 26% (not unreasonably given the range of alkali halide values, and the observed MgO value) then this melting curve would result in an experimental melting entropy of $\sim 150 \text{ J K}^{-1} \text{ mol}^{-1}$ which must surely be excessively high. It would therefore appear that there is most certainly some irregularity in these experimental results, possibly as a result of underestimating the observed melting temperature due, perhaps, to the difficulty in measuring temperature at these extreme conditions.

Discussion and conclusion

Using molecular dynamics we have established a methodology for calculating melting curves to extremely high pressures which can be applied to systems of geophysical interest. We have used this methodology to study the MgO structure and find that, provided a reliable potential model is used, ambient pressure melting temperatures can be calculated that are in good agreement with the observed value. The predicted high pressure behaviour for this system shows that T_m tends to 8000 K at the core-mantle boundary.

Despite the discrepancy between the experimental data and our calculations, we have confidence in our high pressure results since they reasonably predict zero pressure thermodynamic melting properties for an alkali halide structure phase, and give reasonable high pressure values for melting volume and melting entropy.

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