Molecular dynamics: some recent developments in classical and quantum mechanical simulation of minerals

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Abstract

We review some of the most recent developments in classical and quantum mechanical molecular dynamics simulations, in particular as applied to Earth-forming phases at conditions prevalent in the Earth's deep interior. We pay special attention to the modelling of high pressures and temperatures, elucidating the problems associated with both the classical and quantum approaches in view of the empirical potentials required for the former, and the limitations of finite temperature calculations for the latter. We show the current status of such calculations for major phases such as $MgSiO_3$ perovskite.

KEYWORDS: computer simulation, molecular dynamics, quantum molecular dynamics, perovskite, mantle minerals.

Introduction

ONE major goal of computational mineral physics is to be able to describe fully the physical and defect behaviour of Earth-forming phases under the conditions found in the Earth's interior. The computational approaches currently used generally employ either static simulation or dynamic simulation techniques to model the mineral properties; in the case of the former, these are calculated using the vibrational frequencies of the atomic oscillations (phonons) via lattice dynamics, whereas in the latter the component ions are given initial explicitly assigned velocities, and their trajectories are calculated via molecular dynamics. For either method to be used successfully, there are two types of methodological problems that have to be overcome: how to model the effect of pressure and temperature accurately, and how to reliably describe the interatomic interactions over a wide range of atomic separations. The solution to these problems differs depending upon the simulation technique used.

In the following section we shall discuss how both lattice dynamics and molecular dynamics can be used to model extreme conditions of pressure and temperature, largely taking examples from work performed by the authors and their collaborators. We will conclude that molecular dynamics techniques are currently most appropriate for modelling the pressure and temperature conditions prevalent in the Earth's interior. We shall then consider how molecular dynamics has been used in association with interatomic potentials to describe the behaviour of silicates at high pressures and temperatures, and will outline how the limitations of such an approach can be overcome by using quantum mechanical methods.

The modelling of pressure and temperature: the case for molecular dynamics

Laboratory experiments on minerals and mineral analogues are currently limited to moderately high pressures or high temperatures, but rarely both. In order to model deep Earth mineral phases, it is essential to be able to simulate systems at extreme conditions of pressure and temperature simultaneously. This can be done using computer simulations techniques; however, the approach adopted depends upon the computational method being used.

Modelling pressure

Modelling the effect of pressure is essential if one is to obtain accurate predictions of phenomena such as phase transformations and anisotropic compression. This problem is now routinely being solved using codes that allow constant stress, variable geometry cells in both static and dynamic simulations. In the case of lattice dynamics, the mechanical pressure is calculated from strain derivatives, whilst the thermal pressure is calculated from phonon frequencies (Parker and Price, 1989):

$$P_{mechanical} = \frac{dU}{d\varepsilon} \; ; P_{kinetic} = \frac{dF(\omega)}{dV} \qquad (1)$$

where U is the static lattice energy, ε is the strain on the cell, $F(\omega)$ is the vibrational free energy, and V is the volume. The balance of these forces is used to determine the variation of cell size as a function of pressure and temperature.

In the case of molecular dynamics, both the particle positions and the volume of the system, or simulation box, can be used as dynamical variables, as is described in detail in Parrinello and Rahman (1980). However, in general, the pressure of the simulated system is calculated from the equation:

$$P = \frac{Nk_B T}{V} - \frac{Nk_B T}{6V} \left(\sum_{i=1}^{N} \sum_{j>i}^{N} r_{ij} \frac{\partial \psi_{ij}}{\partial r_{ij}} \right) \qquad (2)$$

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.

Modelling temperature

In general, the temperature of a simulated system is obtained from kinetic theory via:

$$T = \frac{2 \times \text{average kinetic energy of the system}}{\text{number of degrees of freedom} \times \text{Boltzmann's constant}} \qquad (3)$$

However, for static and dynamic simulations this kinetic energy is obtained in different ways; in the case of lattice dynamics, there are problems in simulating high temperatures, whilst in the case of molecular dynamics the problems arise in the low-temperature régime.

Static calculations normally enable the effect of temperature to be calculated by evaluating the lattice vibrational frequencies and using them in standard statistical mechanics equations to give kinetic energy

and therefore temperature dependent properties such as heat capacity, entropy, etc. (Parker and Price, 1989). This methodology is based on the quasi-harmonic approximation (QHA) which assumes that the lattice vibrational modes are independent. However at high temperatures, where vibrational amplitudes become large, phonon-phonon scattering becomes important as the displacements interact with each other, and the QHA breaks down due to the anharmonicity of the system. Since, at ambient pressure, the QHA is only valid for $T < \theta_D$, the Debye temperature, if we are interested in the extreme conditions of the interior Earth, we need to extend this methodology to accommodate higher temperature simulations well above the Debye temperature of the mineral concerned (see e.g. Ball, 1989).

In the case of molecular dynamics, the methods are essentially classical, and are outlined in detail in Allen and Tildesley (1987), and will be discussed briefly below; however, in principle Newton's equations of motion are solved for a number of particles within a simulation box to generate time-dependent trajectories and the associated positions and velocities which evolve with each timestep. Here the kinetic energy, and therefore temperature, is obtained directly from the velocities of the individual particles. With this explicit particle motion, the anharmonicity is implicitly accounted for at high temperatures; however, in this instance, it is the low temperature quantum effects that cause the problems.

At low temperatures, quantum mechanical effects play a dominant rôle in determining the thermo-dynamic properties of crystals, such as heat capacity (e.g. Cochran, 1973). Molecular dynamics is essentially a classical technique, and therefore the low-temperature quantum behaviour of atomic motions is not adequately described by this method. However, to a first order approximation, this shortcoming can be compensated for, as has been outlined in a study of MgO at zero pressure and 300–2000 K ($\theta_D \approx$ 940 K) by Matsui (1989), who applied a quantum correction to the predicted structural and thermo-dynamical properties via a Wigner-Kirkwood expansion of the free energy in powers of Plancks constant to h^2. He found that although the quantum contribution to the incompressibility was insignificant, for the thermal expansion coefficient and heat capacity, the applied quantum correction became increasingly important as the temperature decreased. Above 500 K, using these quantum corrections, the molecular dynamics simulations gave comparable agreement with the observed experimental data for all structural and thermodynamics properties; however, this was not the case below 500 K where he concluded that the need to include higher order terms in h is essential for accurate predictions of thermal expansion coefficients and heat capacity.

In contrast, at high temperatures, above the Debye temperature for a chosen mineral, molecular dynamics describes the anharmonic effects implicitly and is, in this respect, preferable to the lattice dynamics technique. It is especially important to take these anharmonic effects into account when studying melting and premelting properties of systems where $T \gg \theta_D$.

Matsui et al. (1994) have recently performed a parallel set of lattice dynamical and molecular dynamical calculations on magnesium silicate perovskite in order to investigate the effect of pressure on the validity of the QHA. They found that at zero pressure and 500 K, both molecular dynamics and lattice dynamics agreed well, but as the temperature was increased, the molar volume of $MgSiO_3$ perovskite, as calculated by the lattice dynamical method, was increasingly overestimated. However, at lower mantle pressures (<100 GPa) and temperatures (2000–3000 K) the predicted volumes and incompressibilities of the molecular dynamics and lattice dynamics methods become more comparable (see Fig. 1), but the thermal expansion coefficients are still significantly different due to the increased anharmonicity of this high temperature region. Therefore, to model lower mantle behaviour accurately, we need either high temperature molecular dynamics, or lattice dynamics simulations with a correction for the intrinsic anharmonicity of the system. As discussed above, such corrected lattice dynamics techniques are not currently routinely available, and so the remainder of this review will focus on the application of molecular dynamics to the study of mantle phases.

Classical molecular dynamics and interatomic potentials

In order to calculate the forces required in the solution to Newton's equations of motion, it is necessary to accurately describe the interactions between each of the atoms in the system. Traditionally this has been done using interatomic potentials in which the energy of interaction between the atoms or ions within the system is described as a function of their separation and orientation. In molecular dynamics it is usual to use a two-body potential; many body systems are generally prohibitively complex, although simple three-body corrections may be included. 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:

$$U_L(r_{ij}) = \sum_{ij} \frac{q_i q_i}{r_{ij}} + \sum_{ij} \varphi_{ij} + \sum_{ijk} \theta_{ijk} \qquad (4)$$

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. The second term accounts for the diffuse nature of the electron clouds surrounding the nucleus; it includes the short range interactions associated with 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 be negligible.

In the rigid-ion model, the short range interactions predominantly effect nearest neighbour ions. Short-range potential functions may be represented by pairwise potentials such as the Buckingham potential which takes the form:

$$\varphi_{ij} = A_{ij} e^{-\frac{r_{ij}}{B_{ij}}} - \frac{C_{ij}}{r_{ij}^6} \qquad (5)$$

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. The parameters of the potential given by Eq. 5 are obtained either by fitting to experimental data, or to quantum mechanically calculated energy hypersurfaces, or both.
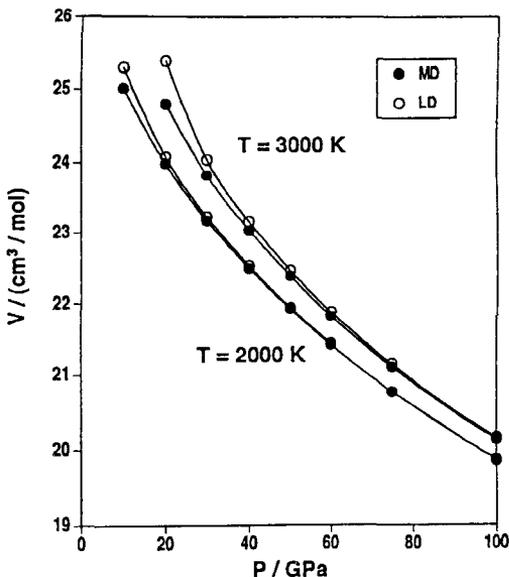

FIG. 1. The lattice dynamics and molecular dynamics simulated molar volumes of $MgSiO_3$ perovskite at the temperatures 2000 and 3000K as a function of pressure up to 100GPa. After Matsui et al., 1994.

Having obtained the optimum potential function that will describe interactions between atoms in a given system, it is possible to calculate the pairwise forces between individual atoms. Newton's laws of motion are then solved to give an evolving trajectory over a period of time-steps for each of the N particles within the system at specified pressures and temperatures, calculating the required dynamic properties iteratively as the system evolves. Periodic boundary conditions applied to the ensemble generate the required infinite system. The ions are initially assigned positions and velocities within the simulation box; their co-ordinates are usually chosen to be at the crystallographically determined sites, whilst their velocities are chosen such that they concur with the required system temperature, and such that both energy and momentum is conserved:

$$\sum_i m_i v_i(0) = 0 \qquad (6)$$

$$\sum_i m_i [v_i(0)]^2 = 3Nk_BT \qquad (7)$$

where k_B is Boltzmann's constant, T is the initial chosen simulation temperature, and m_i and v_i are the mass and velocity of particle i.

In order to calculate subsequent positions and velocities, the forces acting on any individual ion must then be calculated from the first derivative of the potential function, and the new position and velocity of each ion may calculated at each timestep, t, by solving Newton's equation of motion:

$$F = -\frac{\partial U_L}{\partial r} = ma(t) = m\frac{d^2r}{dt^2} \qquad (8)$$

where a is the acceleration. This 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.

In the following section we show how this methodology has been applied to relevant Earth-forming phases at temperatures and pressures prevalent in the lower mantle.

Recent applications of classical molecular dynamics to mantle phases and their analogues

Potential models have been extensively used to simulate the behaviour of mantle phases (e.g. Catlow and Price, 1990). These models are now invariably successful in reproducing known structural and physical properties of mantle silicates. This success has led to potentials being used to predict the behaviour and properties of mantle phases at pressures and temperatures which are currently beyond experimental reach. A recent example of

the use of molecular dynamics to study mantle phases is given in Matsui and Price (1992). These authors applied a simple empirical potential to simulate the structure of six $MgSiO_3$ polymorphs. The simulations successfully predicted both structural and thermo-dynamic properties to within a few percent of the observed values in each case (see Table 1). They further applied the technique to study the existence of a post-protoenstatite high temperature phase and a $C2/c$ high pressure phase, both of which had been previously inferred from experiment. Their predicted co-ordinates and structure for the high pressure $C2/c$ phase were subsequently successfully used by Angel *et al.* (1992) to solve the single crystal X-ray data for this phase when it was later synthesised.

In a previous study Matsui and Price (1991) had used the same empirical potentials to investigate sub-lattice melting and ionic conductivity in $MgSiO_3$ perovskite. Their constant pressure and constant temperature calculations predicted the onset of oxygen sublattice melting and an orthorhombic to cubic phase transition above 10 GPa just prior to melting. They showed that the cubic phase exhibits solid electrolytic behaviour with an electrical conductivity comparable with that inferred for the lower mantle. In a parallel study using different potential models Kapusta and Guillopé (1993) confirmed the high temperature solid electrolyte behaviour of $MgSiO_3$ perovskite but predicted an orthorhombic to tetragonal phase transition in $MgSiO_3$ perovskite, due to the precession of the SiO_6 octahedra, at 2600 K and 310 kbar (see Fig. 2).

If ionic conductivity in $MgSiO_3$ perovskite is significant then it will play an important part in the behaviour of the Earth's lower mantle. To investigate further the nature of sublattice melting in perovskites, Watson *et al.* (1992) modelled the behaviour of fluoride perovskites where experimental data on the
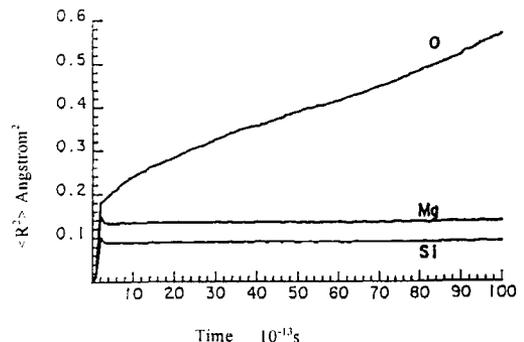

Fig. 2. Mean square ionic displacements in $MgSiO_3$ perovskite for three sublattices Mg, Si an O as a function of temperature at 310 kbar. After Kapusta and Guillopé, 1993.

TABLE 1. Observed and simulated structural and physical properties of the six $MgSiO_3$ polymorphs (P = 0 GPa). After Matsui and Price, 1992

Phase Space group		ortho *Pbca*	clino $P2_1/c$	proto *Pbcn*	garnet $I4_1/a$	ilmenite $R\bar{3}$	perovskite *Pbnm*
Cell lengths, cell angle and molar volume							
a [Å]	Obs	18.227	9.605	9.306	11.501	4.728	4.775
	Calc	18.146	9.600	9.378	11.516	4.740	4.772
b	Obs	8.819	8.813	8.892	11.501	4.728	4.929
	Calc	8.727	8.672	8.820	11.516	4.740	4.925
c	Obs	5.179	5.166	5.349	11.480	13.56	6.897
	Calc	5.262	5.244	5.458	11.523	13.33	6.942
β or γ [°]	Obs	90.0	108.5	90.0	90.0	120.0	90.0
	Calc	90.0	108.6	90.0	90.0	120.0	90.0
V [$cm^3 mol^{-1}$]	Obs	31.33	31.22	31.32	28.58	26.35	24.44
	Calc	31.36	31.14	33.98	28.76	26.03	24.56
Bulk modulus(K_0), volume thermal expansivity (α) and enthalpy (H)							
K_0 [GPa]	Obs	108	–	112	154	212	247
	Calc	84	92	88	137	224	250
α [$10^{-5}K^{-1}$]	Obs	2.5	2.5	4.0	2.2	2.4	3.2
	Calc	3.8	4.1	6.0	2.2	2.8	2.9
H [$kJ\ mol^{-1}$]	Calc	−7187.7	−7187.7	−7186.5	−7151.0	−7157.0	−7150.0

electrical conductivity is known. They found that enhanced fluoride mobility was only predicted in one of the compounds under investigation, $KCaF_3$, but not in either of the other two, $KMnF_3$ or $KZnF_3$, in accord with experiment. These calculations, therefore, confirm that potential models can accurately describe the structural and defect properties of perovskite phases. However, the major shortcoming associated with this type of calculation when applied to silicate perovskites at high pressures and temperatures is the reliance of the quantitative precision of the predicted properties upon the accuracy of the empirical potential used to model the interatomic interactions when sampling interatomic separations which are much shorter or much larger than those used in the development of the potential model. In an attempt to circumvent this principal limitation, molecular dynamics codes are now being developed that explicitly calculate the forces within the system via quantum mechanical methods without the need to employ empirical potential functions.

Quantum molecular dynamics

Density Functional Theory provides a tractable theoretical framework through which one can describe the electronic structure of materials (e.g. Tossel and Vaughan, 1992; Lundqvist and March, 1987). Generally good predictions of the structural

and electronic properties of materials can be obtained by solving self-consistently the one-electron Schrödinger equation for the system. However, in comparison with empirical methods, quantum mechanical molecular dynamics applications are still in their infancy and are limited by the large computer resources required. Nevertheless, significant progress is being made in this area and we shall illustrate this method with some recent examples.

Quantum molecular dynamics (QMD) was first developed by Car and Parrinello (1985) who combined molecular dynamics with density functional theory (DFT) to produce a simulation technique applicable to both covalently bonded and metallic systems. DFT reduces the many-body Hamiltonian in the Schrödinger equation to that for one electron surrounded by an effective potential associated with the interactions of the surrounding crystal. The energy of the system is explicitly calculated by solving Schrödinger's equation for the ensemble at each timestep using DFT to obtain the minimum energy surface and thereby calculate the interatomic forces, which is then combined with classical molecular dynamics techniques to calculate the atomic trajectories and related dynamic properties. The local density approximation (LDA) is used in DFT to simplify the solution to Schrödinger's equation by assuming the correlation energy is purely a function of electron density at any particular point in space, defining the exchange-correlation potential

as a function of electron density at a given co-ordinate position (Kohn and Sham 1965); in the LDA, the exchange-correlation energy of an electronic system is constructed by assuming that the exchange-correlation energy per electron at a point **r** in the electron gas, $\varepsilon_{xc}(\mathbf{r})$, is equal to the exchange-correlation energy per electron in a homogeneous electron gas which has the same density as the electron gas at point **r**.

Once the interaction energies and forces have been calculated, classical molecular dynamics techniques are used to solve for the particle trajectories. In QMD, the Lagrangian is used to define the system dynamics, and the equations of motion are derived by applying Lagrange's equation to this Lagrangian. The Lagrangian has four parts: the kinetic energy for both the internal and strain variables (i.e., all degrees of freedom for ions, electrons, and also the cell), the potential energy of the system from the Kohn and

Shan equations (calculated *ab initio* from DFT), and a pressure-volume term; for a system of N particles of mass, m_i, at position $\mathbf{r}_i$ undergoing strain, ε, to rescaled co-ordinates $\mathbf{q}_i$, the Lagrangian takes the form:

$$\mathcal{L} = \sum_{i=1}^{N} \frac{m_i}{2} \dot{\mathbf{q}}_i g(\varepsilon) \dot{\mathbf{q}}_i + \frac{w}{2} Tr(\dot{\varepsilon}\dot{\varepsilon}^T) - U(\varepsilon, \mathbf{q}_i - P\Omega(\varepsilon)$$

$$(9)$$

where the metric tensor $g(\varepsilon) = (1+\varepsilon)^T(1+\varepsilon)$, $U(\varepsilon, \mathbf{q}_i)$ is the Kohn-Sham energy, P is the constant applied external pressure, and $\Omega(\varepsilon)$ is the variable cell volume; w is a fictitious mass (see Wentzcovitch (1991) for details). The third and fourth terms combine to give the enthalpy which is minimised along the trajectories generated by the following equations of motion, and results in the structural optimization of the evolving system:
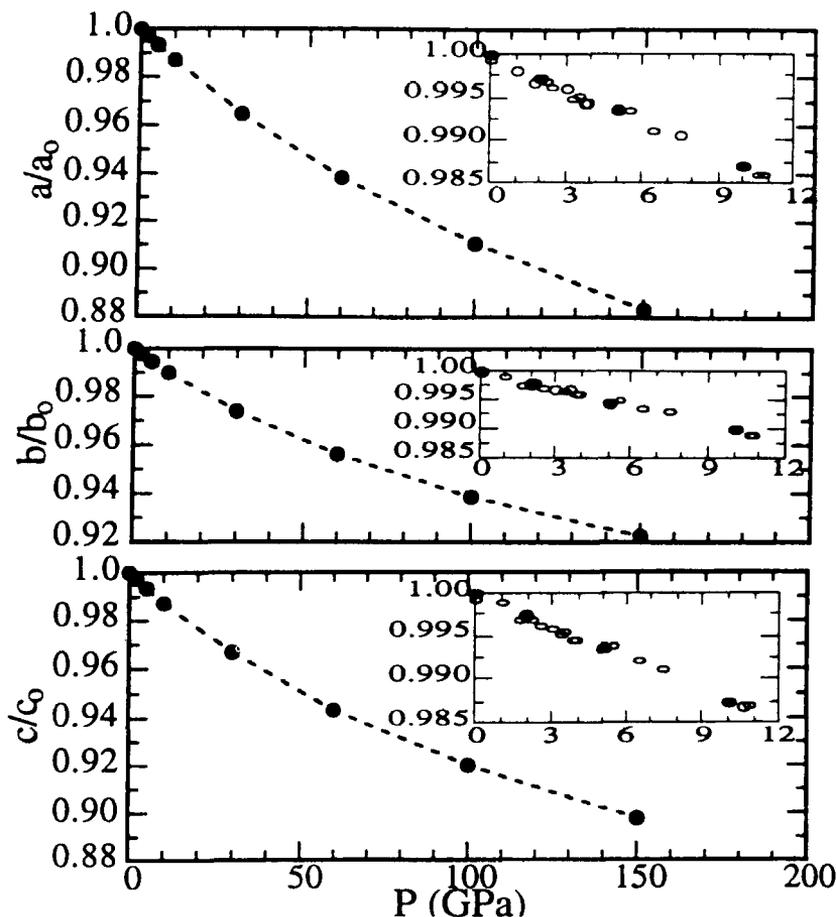

FIG. 3. Pressure dependence of structural parameters for the *Pbnm* phase. After Wentzcovitch *et al.*, 1993.

$$\ddot{q}_i = -\frac{1}{m_i}(1 + \varepsilon)^{-1}\vec{f}_i - g^{-1}\dot{g}\dot{q}_i \qquad (10)$$

$$\ddot{\varepsilon} = \frac{\Omega}{w}(\Pi - P)(1 + \varepsilon^T)^{-1} \qquad (11)$$

where f_i are the Hellmann-Feynmann forces, and the total stress Π is given by:

$$\Pi = \sum_{i=1}^{N}\frac{1}{\Omega}m_i\vec{v}_i\vec{v}_i^T + \Sigma \qquad (12)$$

where v_i $(\varepsilon,q_i) = (1 + \varepsilon)q_i$ and Σ is the quantum mechanical stress tensor.

The above equations would normally be used for finite temperature simulations; however, until recently, calculations have been limited to zero Kelvin studies of simple systems, since the computational power required for finite temperature calculations has been prohibitively time consuming and expensive. Under these conditions a damped dynamics can be used more efficiently, as outlined in Wentzcovitch et al. (1993).

Recent applications in quantum molecular dynamics

An example of recent finite temperature QMD is provided by the study of liquid lithium by Wentzcovitch and Martins (1991). This implementation uses soft separable pseudopotentials (Troullier-Martins) in a self-consistent calculation of forces and stresses on a system of variable cell shape. The pseudopotential function, which describes the core electrons throughout the crystal space, is generated for individual atoms, making the whole calculation more tractable. The efficiency of this method is comparable with that of Car-Parrinello showing a convergence of atomic co-ordinates after ~ 15 timesteps for structural optimisations at zero Kelvin. Wentzcovitch and Martins (1991) method is particularly suited to dealing with simulations involving a cell with variable shape and volume. They found that their method, when applied to liquid lithium, produced results which were in excellent agreement with experiment, and which suggested that their approach would be ideally suited to the study of more complex phases. More recently, Wentzcovitch (1994) has studied the pressure induced hcp to bcc transformation in elemental Mg using a finite temperature QMD simulation. She succeeded in simulating both the hcp to bcc and the bcc to hcp transformation, and found that the mechanism involved was martensitic (diffusionless).

The success in the initial study of lithium led to the investigation of silicate minerals. However, the complexity of such systems prevented their study at finite temperature, but Wentzcovitch et al. (1993) used the established constant pressure QMD to investigate the relative stabilities of the orthorhombic and cubic phases of $MgSiO_3$ perovskite up to 150 GPa, a pressure well beyond the reasonable extrapolation range for empirical potential models. Their low pressure results (<11 GPa) are in excellent agreement with single crystal X-ray observations for orthorhombic perovskite under compression (see Fig. 3 and Table 2), but the calculated relative compressibilities of the orthorhombic axes (a>c>b) are in conflict with those inferred from Brillouin scattering. Calculations on the relative enthalpies of the orthorhombic and cubic perovskite indicate a significant and increasing difference in enthalpy with pressure between these two structures, and suggest that the orthorhombic phase is always more stable than the cubic phase throughout the pressure range of the lower mantle (see Fig. 4).

The type of quantum molecular dynamics described above supercedes the empirical potential method and is currently the best available technique for simulations of high pressure behaviour of silicate structures. However, with the advent of new massively parallel supercomputers, we will soon be able to perform finite temperature calculations on complex systems using quantum mechanical molecular dynamics.

Conclusion

For high-pressure and -temperature studies, QMD is ideal; finite temperature studies on liquid lithium and magnesium show that the technique works, whilst

TABLE 2. Experimental and theoretical parameters of the zero pressure Pbnm phase of $MgSiO_3$. After Wentzcovitch et al., 1993

	Calc.(Pbnm)	Exp.(Pbnm)	Calc.(Pm3m)
a	4.711	4.7787(4)	4.909
b	4.880	4.9313(4)	4.909
c	6.851	6.9083(8)	6.942
Mg_x	0.5174	0.5141(1)	0.500
Mg_y	0.5614	0.5560(1)	0.500
O_x^1	0.1128	0.1028(2)	0.000
O_y^1	0.4608	0.4660(2)	0.500
O_x^2	0.1928	0.1961(1)	0.250
O_y^2	0.1995	0.2014(2)	0.250
O_z^2	0.5582	0.5531(1)	0.500

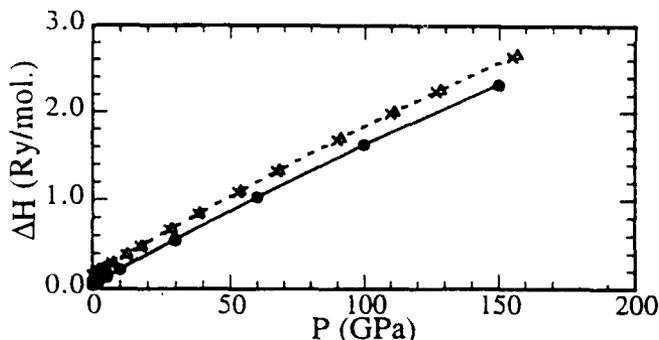| Calc.(Pm3m)	
a'	3.472
a'	3.48

FIG. 4. Change in Enthalpy (H-H$_0$), where H$_0$ is the zero pressure value for the *Pbnm* phase (●). × and △ are results for the cubic phase obtained using 1 and 4 special k points respectively. After Wentzcovitch *et al.*, 1993.

zero Kelvin studies on more complex systems such as MgSiO$_3$ perovskite show that the methodology can well be applied to Earth-forming phases. Indeed, calculations are currently also being performed on Mg$_2$SiO$_4$ olivine containing 28 atoms in the unit cell, and on a monoclinic pyroxene polymorph of MgSiO$_3$ with 40 atoms in the unit cell (Wentzcovitch *et al.*, 1995). However current lack of cpu power limits studies on silicates to zero Kelvin simulations, where the molecular dynamics codes are simply efficient geometry optimisers. Recent developments on machines with massively parallel architecture and enhanced processor speeds, such as the Cray T3D in Edinburgh, will enable finite temperature high pressure QMD simulations of complex minerals to become a realistic prospect within the next few years. It must be noted, however, that to obtain dependable thermodynamic data from MD simulations, large ensemble sizes are required. This will require the simulation of at least 1000 particles, and possibly even more (Winkler and Dove, 1992), and it seems that such very large simulations will be beyond QMD for several years yet to come.

Acknowledgements

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