Molecular Dynamics Study of MgSiO₃ Perovskite

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Abstract. The molecular dynamics (MD) method is applied to the simulations of the structural and physical properties of MgSiO₃ perovskite. The potential energy of our model consists of pairwise additive Coulomb and repulsive terms between atoms, and van der Waals attraction terms for oxygen-oxygen interactions. Required energy parameters are transferred from empirical potentials previously developed for MgSiO₃ perovskite and MgSiO₃ ilmenite based on a static lattice simulation technique. Minor modifications are made for the repulsive radii in the potential to account for thermal vibrational effects in the static description of a crystal lattice. In spite of the simplicity of the potentials used, the MD simulations have succeeded in reproducing pretty well a wide range of structural and physical properties of MgSiO₃ perovskite, including the crystal structure, the compressibilities, the thermal expansivities, and the mean-square atomic displacements. The MD method was further applied to predict the high temperature and high pressure behavior of MgSiO₃ perovskite.

Introduction

Magnesium-rich silicate perovskite is generally accepted as the most abundant mineral in the lower mantle and, therefore, it is of great importance to characterize the structural and elastic properties of MgSiO₃ perovskite at the temperature and pressure conditions of the deep mantle. However, available experimental data is highly insufficient, and it is necessary to construct a reliable computational model of MgSiO₃ perovskite that can be used to extend the information available from experiment.

In a previous study (Matsui et al. 1987) we derived an empirical potential model (MAM potential) applicable for MgSiO₃ perovskite. The energy parameters were adjusted to reproduce the available experimental data of MgSiO₃ ilmenite and MgSiO₃ perovskite as closely as possible. Using the energy-minimization method under external forces (Busing and Matsui 1984) with the MAM potential, the structural and elastic properties of MgSiO₃ perovskite were simulated with good agreement between the observed and calculated values. The validity of this approach and the quality of the MAM potential were further given strong support by the subsequent high-pressure single-crystal X-ray analysis of MgSiO₃ perovskite (Kudoh et al. 1987), in which excellent agreement between the measured and predicted values has been found for the linear compressibilities of the unit cell parameters. The use of this type of simulation, however, has a limitation in modelling temperature effects. Since the technique is based on a static approximation of the crystal lattice, no explicit account of thermal vibrations is included.

The contribution of thermal vibrational motion to the free energy may be included by the lattice-dynamics calculation in the quasiharmonic approximation in which the crystal potential is expanded to second order in the atomic displacement (Born and Huang 1954). Application of such lattice-dynamics calculation to MgSiO₃ perovskite includes publications by Wolf and Bukowinski (1985, 1987), Hemley et al. (1987) and Cohen (1987). Although the quasiharmonic approximation is useful and adequate for solids at temperatures where the atomic displacements are generally small compared to equilibrium interatomic distances (Cochran 1973), it could not be satisfactory for modellings of structural and physical properties of minerals at high temperatures characterizing the lower mantle.

At high temperatures, where anharmonic effects are important and quantum effects are small, molecular dynamics (MD) method has become an important technique for the study of solids (e.g. Nosé and Klein 1983; Kawamura 1984; Ray and Rahman 1985; Schiferl and Wallace 1985; Y. Matsui and Kawamura 1987). In the MD method the Newtonian (or Hamiltonian in general) equations of motion of a system of interacting particles are solved as a function of time, and equilibrium properties are determined from time-averages taken over a sufficient long time interval. Thus the MD techniques treat anharmonicity in solids directly.

The purpose of this paper is to describe the application of the MD method to MgSiO₃ perovskite. We will show that our dynamical simulation can be successfully used to reproduce pretty well the observed crystal structure at ambient conditions (Horiiuchi et al. 1987), the measured linear and volume compressibilities of the lattice (Kudoh et al. 1987), the experimental volume thermal expansivity (Knittle et al. 1986), and the observed mean-square amplitudes of atomic vibrations (Horiiuchi et al. 1987). We will use this model to simulate high temperature and high pressure structural properties of MgSiO₃ perovskite.
Simulation Techniques

Potentials

Following our previous work (Matsui et al. 1987), the potential energy for a lattice configuration was approximated by the sum of pairwise interactions between atoms of the form:

\[ V(r_{ij}) = q_i q_j r_{ij}^{-1} - C_i C_j r_{ij}^{-6} + f(B_i + B_j) \cdot \exp [(A_i + A_j - r_{ij})(B_i + B_j)], \]

where the terms represent Coulomb, van der Waals, and Gilbert-type (1968) repulsion energy, respectively. Here \( r_{ij} \) is the interatomic distances between atoms \( i \) and \( j \), and \( f \) is a standard force of 4.184 kJ Å\(^{-1}\). The effective ionic charges \( q_i \) and the coefficients \( A_i, B_i, \) and \( C_i \) are the energy parameters peculiar of the kind of atom \( i \).

Considering the success of the previous work with the MAM potential (Matsui et al. 1987), the same energy parameters were adopted here, although minor modifications were necessary to account for thermal vibrational effects in the static description of crystal lattices at a finite temperature \( T \). In an attempt to extrapolate the repulsive radii \( A_i \) in the MAM potential to absolute zero, we applied a method, which is similar to that introduced by Busing (1983) for the Born-Mayer type potential \( A \exp(-B r) \), to the present Gilbert-type potential. Consequently, if the values of the repulsive radii have been derived for a static lattice simulation at temperature \( T \), the sum of the repulsive radii of the two atoms \( i \) and \( j \) at absolute zero becomes

\[ A_i(0) + A_j(0) = A_i + A_j - \frac{1}{2} u_{ij}^2(B_i + B_j), \]

where \( u_{ij}^2 \) is the mean-square displacement of the instantaneous distance \( r_{ij} \) from equilibrium value at \( T \). We assume that \( u_{ij}^2 \) is proportional to the sum of the mean-square displacements of the two atoms \( i \) and \( j \),

\[ u_{ij}^2 = u_{ij}^2 + u_{ij}^2, \]

where \( k_{ij} \) is the correlation coefficient for the interaction between the atoms \( i \) and \( j \). Using equations (2) and (3) for the three atom pairs, Mg-O, Si-O and O-O, together with the \( A_i \) and \( B_i \) values in the MAM potential and with the \( u_{ij}^2 \) values from the measured isothermal thermal parameters in MgSiO\(_3\) perovskite (Horiiuchi et al. 1987), we may obtain the required \( A_i(0) \) parameters for Mg, Si and O, if the values of \( k_{ij} \) in equation (3) are known. The coefficients \( k_{ij} \) are arbitrarily assumed to be common to all interactions, and this common coefficient was adjusted such that a short MD calculation at 300 K and 0 GPa reproduces the observed unit cell volume of MgSiO\(_3\) perovskite (Ito and Y. Matsui 1978). We call the resultant potential as MAM0K (Table 1), which is used in this study.

Crystal Structure of MgSiO\(_3\) Perovskite

The atomic arrangement in MgSiO\(_3\) perovskite was first determined by Ito and Y. Matsui (1978) and Yagi et al. (1978) using the powder X-ray diffraction data, and a careful single-crystal X-ray analysis has recently been made by Horiiuchi et al. (1987). The crystal is orthorhombic with space group \( Pbnm \) and four formula units per cell. There are four independent atoms in the asymmetric unit; both Mg and O(1) lie on mirror planes, Si at an inversion center, and O(2) is in a general position. Each Si ion is surrounded by six O ions at distances from 1.783 to 1.801 Å, and each Mg ion is surrounded by eight O ions at distances from 2.014 to 2.427 Å and four more O ions at distances from 2.846 to 3.120 Å (Horiiuchi et al. 1987). Table 2 lists the lattice parameters and the fractional coordinates for the observed structure.

Molecular Dynamics Simulation

In the usual MD simulation a real crystal is considered to be composed of duplicate images of a basic cell which is a super-cell of the unit cell of the crystal. The basic cell size is chosen such that the structural and energetic results are not dependent on the cell size. Equilibrium MD simulations are performed by solving the classical equations of motion of a set of atoms in the basic cell as a function of time. The atom trajectories thus generated are used in statistical mechanical relations to determine static and dynamic properties of the system. We use the combination of a constant-pressure MD method for anisotropic solids developed by Parrinello and Rahman (1981) and a constant-temperature MD method proposed by Nosé (1984). By using this combination, it enables us to simulate the structures of any anisotropic solid at any temperature and pressure. We take a basic cell composed of 48 \((4a \times 4b \times 3c)\) unit cells which contains 960 \([192 \text{Mg, 192 Si, 192 O(1), and 384 O(2)}]\) atoms. In our MD simulation the basic cell is treated as a triclinic lattice and no space group symmetry constraints are imposed on the atomic positions in the basic cell. The electrostatic interactions are handled by the Ewald method and the equations of motion are solved by a fifth-order predictor-corrector algorithm (Rahman and Stillinger 1971) with a time increment of 1.0 fs (\(10^{-15} \text{s}\)). In each MD run a sufficient long period of “aging” (~5000 steps typically) is performed to establish equilibrium of the system under the desired temperature and pressure conditions. After this, the subsequent period of 5000 steps (5 ps) is carried out to calculate time-averages of properties studied here. Equilibrium structures are simulated from the averages, while the pressure or temperature derivatives of the structures were evaluated using a numerical linear interpolation.

Results and Discussion

An important feature of our MD simulation method is that, as described in the preceding section, no explicit symmetry constraints on the atomic positions are assumed. In the simulation procedure, all the atomic coordinates in the basic cell are treated as independent variables and all the six basic cell (not unit cell) parameters are relaxed. The space group symmetry as well as the translational symmetry in the basic cell are determined solely by the interatomic

| Table 1. Energy parameters\(^*\) (MAM0K) used for the calculations |
|-----------------|--------|--------|--------|--------|
| \( q \)         | \( A \)  | \( B \)  | \( C \)  |
| Mg              | +1.565 | 1.0133 | 0.052  | 0      |
| Si              | +2.329 | 0.8436 | 0.040  | 0      |
| O               | -1.298 | 1.7600 | 0.150  | 54     |

\(^*\) Units: \( q \) in \( \text{eJ,Å} \), \( A \) and \( B \) in \( \text{Å}^2 \text{kJ}^{-1/2} \text{mol}^{-1/2} \)

\[ b \] The \( A \) values in the MAM potential (Matsui et al. 1987) are 1.0267, 0.8529 and 1.7652 Å for Mg, Si and O, respectively.