Numerical estimation of molar volume of MgO periclase crystal

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Mantle of the earth consists mainly magnesium-oxidie. Periclase, MgO, is one of the most important minerals in mantle. The physical properties of periclase crystal have been estimated by experimental[1,2] and numerical[3] methods. I calculated the molar volume of periclase to test the stability of MD program for using VPP-770. The MD program, CTPMD, was made by Matsui.[4] The simulation used the Born-Huggins-Meyer potential as two-body potential model,

$$U(r_{ij}) = \frac{q_i q_j}{r_{ij}} + f(B_i + B_j)\exp\left[\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right] - \frac{C_i C_j}{r_{ij}^6} - \frac{D_i D_j}{r_{ij}^8},$$

where r_{ij} is the interatomic distance between atoms i and j, q_i is the effective ionic charge, A_i, B_i, C_i, and D_i are the energy parameters perculiar to the kind of atom i; f is a standard force of 4.184 kJÅ^{-1}. These parameters followed Matsui[5]; $q_{\mathrm{Mg}} = -q_{\mathrm{O}} = 0.945$, $A_{\mathrm{Mg}} = 0.8940$, $B_{\mathrm{Mg}} = 0.04$, $C_{\mathrm{Mg}} = 40.91$, $A_{\mathrm{O}} = 1.8215$, $B_{\mathrm{O}} = 0.138$, $C_{\mathrm{O}} = 90.61$, $D_{\mathrm{Mg}} = D_{\mathrm{O}} = 0$.

The original CTPMD program can treat 2,000 atoms. The maximum lattice number is $6a_1 \times 6a_2 \times 6a_3$ which composes 216 unit cells of the MgO crystal; then the basic cell contains 864 Mg and 864 O ions. I modified the original program, and the program can treat 30,000 atoms. The simulation condition used constant P-T method. The pressure is 0 Gpa, and temperature is 300 K. Time step of simulation is 1 fsec. The lattice number is changed from 4 to 8. Figure 1 shows snapshot of 8 lattice number. Table 1 shows the mean molar volume and deviation. The σ_{1000} is calculated by

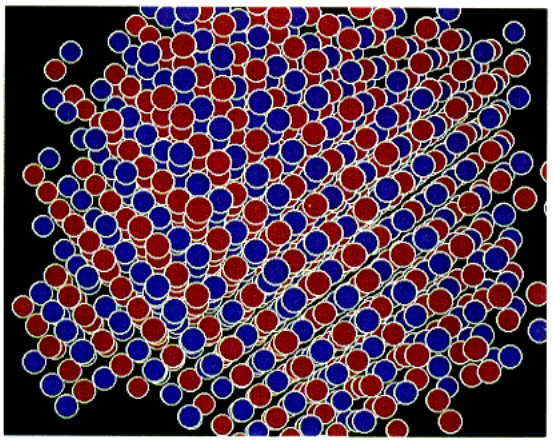

Fig. 1. Snapshot of periclase MD simulation. Blue; Magnesium, Red; Oxigen.

Table 1. The mean molar volume dependence of lattice number.

Lattice number	4	5	6	7	8
Mean volume	10.7640	10.7601	10.7595	10.7598	10.7598
Step/1000	1000	500	300	100	50
σ_{1000}	0.133	0.098	0.076	0.056	0.057

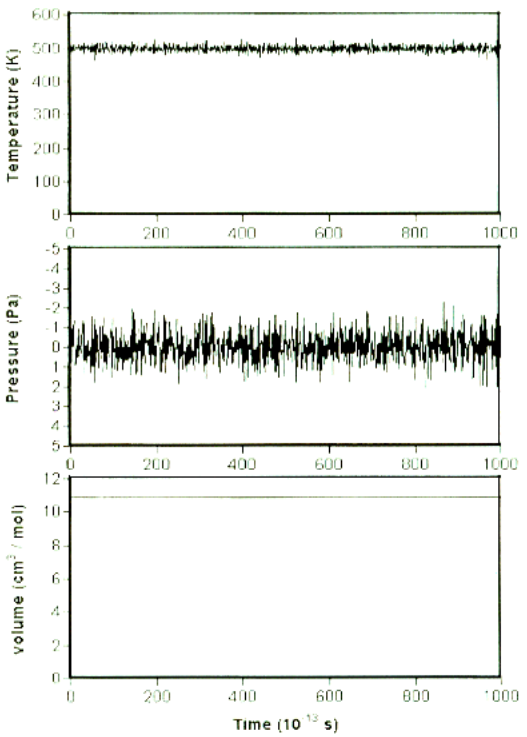

Fig. 2. Time dependence of pressure, temperature and molar volume.

$$\sigma_{1000} = 1000 \times \frac{1}{N}\sum[\bar{V} - V(t)]^2,$$

where V is mean volume, and N is step of calculation. Note the N is different for lattice number (Table 1). The σ_{1000} decreses with lattice size, and mean volume converges to 10.7598 cm^3 mol^{-1}. Figure 2 shows the simulation result of 8 lattice number. These results suggests that the lattice number of 5 is sufficient to estimate the molar volume of periclase crystals.

The mean volume is easy to calculate other physical properties. For example, elastic coefficient[6] is necessary more complex procedure. Next issue, we consider limit lattice number

for other physical properties as same manner. MD simulation in this study uses simple stable ionic crystal. In real earth's mantle, there are vigorous differential stress, and high temperature-pressure environment. To simulate such condition, we need larger lattice number, which includes more than 10,000 atoms.

References

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