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Application of shell model in molecular dynamics simulation to MgO*

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The P–V–T equation of state of MgO has been simulated under high pressure and elevated temperature using the molecular dynamics (MD) method with the breathing shell model (BSM). It is found that the MD simulation with BSM is very successful in reproducing accurately the measured molar volumes of MgO over a wide range of temperature and pressure. In addition, the MD simulation reproduces accurately the measured volume compression data of MgO up to 100GPa at 300K. It is demonstrated that the MD simulated P–V–T equation of state of MgO could be applied as a useful internal pressure calibration standard at elevated temperatures and high pressures.

Keywords: equation of state, breathing shell model, molecular dynamics, MgO
PACC: 6400, 2160C, 6185, 7115Q, 9160

1. Introduction

Accurate equations of state for crystalline materials are very important in many applications involving high pressure and elevated temperature. Such areas include geophysical studies of planetary cores, the behaviour of shocked condensed matter, explosives technology, materials processing, and studies of nuclear fuels. MgO is a 'classic' ceramic material and also a dominant mineral material of the Earth's lower mantle.[1] Therefore, the thermodynamic properties of MgO at elevated temperatures and pressures are of great interest to the geophysicist.

In experiment, based on ultrasonic interferometric measurements on MgO single crystals up to 3GPa, Jackson and Niesler [2] presented the accurate values of the isothermal bulk modulus and its pressure derivative of MgO. Using the shock compression data for MgO at pressures up to 199GPa, together with the Mie–Grüneisen equation, Duffy *et al*[3] reduced the isothermal volume compression relation at 300K. Recently, Fei [4] carried out the diamond-anvil-cell static compression experiments of MgO up to 23GPa at 300K. Dubrovinsky and Saxena [5] measured the volume thermal expansivity of MgO over a wide temperature range between 300 and 3000K at zero pressure. It is difficult to measure available results at the extremes condition of higher pressure and temperature. Therefore, computer simulations based on interionic interactions have been applied extensively to investigate the microscopic structures of a wide variety of chemical and physical properties.

In theory, Allan *et al*[6] calculated the 300K isotherm using two-body potentials and a simple shell model; Mehl *et al*[7,8] studied the 300K isotherm with potential-induced breathing model; Wolf and Bukowinski [9] investigated the 300 K isotherm with electron-gas model; and Matsui *et al*[10] simulated the structural and thermodynamic properties of crystals by combining the molecular dynamics (MD) method with quantum corrections to the MD values over a wide range of temperature and pressure. All the studies have shown that numerical computations are particularly useful and powerful for problems that may inaccessible to direct experimental studies. The Monte Carlo (MC) and MD simulations for ionic systems usu-

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ally use pairwise additive rigid-ion models for treating interactions in the crystal. However, it is often pointed out that noncentral forces are very important in ionic system composed of ions with large polarizabilities, like oxides.[11–13]

In this work, the breathing shell model (BSM) is introduced into the MD simulation; we include the breathing shell of each ion as an additional degree of freedom by means of an extended Lagrangian formalism, in which fictitious kinetic-energy terms are added to the usual Lagrangian equation. We simulate the volume thermal expansivity, the volume compression and equation of state for MgO, and compare our results with available experimental results. In addition, we propose that the MD simulated P–V–T equation of state of MgO could be applied as a useful internal pressure calibration standard at elevated temperatures and high pressures.

2. Theoretical method

We carried out a way of performing MD simulation using the BSM to treat noncentral forces in crystals.[14] In BSM the repulsive radii of ions are allowed to deform isotropically under the effects of other ions being linked in the crystal, with the core and breathing shells of each ion being linked by a harmonic potential, which was called harmonic BSM.

We have applied the shell-model MD simulations at high pressures and temperatures with the empirical potential given in the following form:

$$V(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6}, \qquad (1)$$

where the right-hand side terms represent Coulomb, repulsive interactions, and Van der Waals force, respectively; Z_i (or Z_j) is an effective charge of the ith atom, e the electronic unit charge, A_{ij} the magnitude of the repulsion force, B_{ij} the softness parameter, and C_{ij} the Van der Waals coefficient of the ith ion. Here r_{ij} is the interionic distance between the ith and the jth atoms. The optimized potential parameters obtained in this work are listed in Table 1.

Table 1. The optimized potential parameters used for our simulations.

	A/eV	B/eV	C/(eV·nm^6)
Mg–O	1822.0	3.08185	0.0
O–O	17.226	1.52290	1.1×10^{-7}

For BSM-MD calculations, an extended Lagrangian[15] includes kinetic and potential energies, $U_{\rm bre}$ terms associated with the breathing shell of the ith ion as

$$L = L^0 + 1/2\sum_i m_{b,i}(\mathrm{d}A_i/\mathrm{d}t)^2 - U_{\rm bre}, \qquad (2)$$

where L^0 is the ordinary Lagrangian without breathing energy terms, and $m_{b,i}$ is the 'fictitious' mass of the ith breathing ion. The kinetic-energy term $(1/2)\sum_i m_{b,i}(\mathrm{d}A_i/\mathrm{d}t)^2$ in Eq.(2), which has no direct physical meaning, is just introduced to generate Lagrangian equations of motion for the breathing shell. Similar fictitious kinetic-energy terms have previously been introduced by Mitchell and Fincham[16] for performing MD simulations using polarizable ion models.

In harmonic BSM, $U_{\rm bre}$ is written as

$$U_{\rm bre} = \frac{1}{2}\sum_i k_i(A_i - A_{0,i})^2, \qquad (3)$$

where k_i is the force constant for the ith breathing ion, A_i and $A_{0,i}$ are the breathing repulsive radius of the ith ion, and the repulsive radius of the ith free-ion, respectively.

When simulating the structure and physical properties of a crystal under a desired T and P condition, we have used the combination of the constant-temperature MD method proposed by Nosé,[17] and the constant-stress MD technique by Parrinello and Rahman.[18] We have taken the MD molar volume of 11.3cm^3/mol, containing 216 ions.[5] A fifth-order predictor–corrector algorithm with a time increment Δt of 0.001ps solves the equations of motion. The fictitious mass constant $m_{\rm b}$ for breathing O is fixed at $m_{\rm b}$=7.2 amu.

3. Results and discussions

In Fig.1, we illustrate the simulated temperature dependence of molar volume V of MgO over the wide temperature range between 300 and 3000K at zero pressure. The simulated molar volume V_0 (=11.264cm^3/mol) value agrees well with experimental data[5] within 0.25% at 300K and zero pressure. The volume thermal expansivity has been obtained by fitting the computed T–V results to the equation $\alpha = \alpha_0 + \alpha_1 T + \alpha_2/T^2$, where α_0, α_1 and α_2 are the coefficients of thermal expansion. The MD α value at 500K are estimated to be 3.83/K, which compare very well to the measured value[5] of 3.86/K.

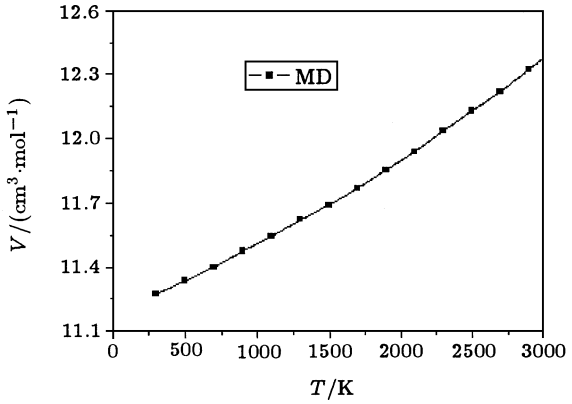


Fig.1. Simulated molar volumes as a function of temperature at 0 GPa for MgO.

The observed and simulated volume compressions of MgO up to 100GPa at 300K are shown in Fig.2. Duffy *et al*[3] carried out the diamond-anvil-cell volume compressions experiments of MgO up to 227GPa at 300K. As is shown, the agreement between the observed and the simulated volume compressions is very good. The volume compression of MgO is simulated to be 8.167cm^3/mol at 90GPa and 300K, which is found to be 2.3% smaller than the corresponding measured value.[3] In addition, we have also simulated the volume compressions of MgO at 600, 1200, 2000, and 3000 K, respectively, which are illustrated in Fig.3.

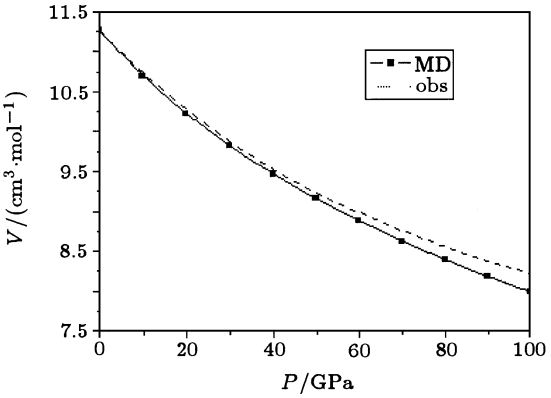


Fig.2. The observed and MD simulated molar volume compression of MgO at 300K.

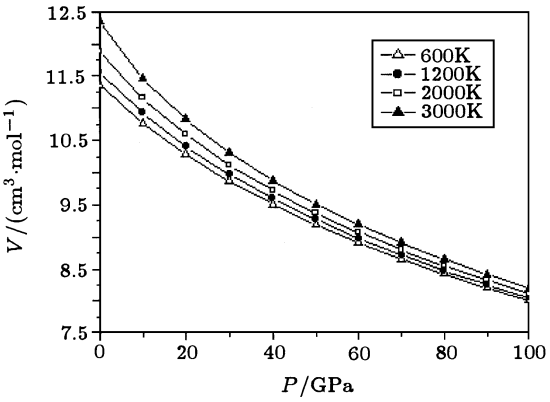


Fig.3. The simulated molar volume compressions of MgO at 600, 1200, 2000 and 3000K, respectively.

In elevated temperature and high pressure experiments, the P–T–V equations of state obtained for standard materials are usually used to measure the pressure of the system. Hence, accurate pressure measurements require attentive cross-checking of these pressure calibration standards. We have demonstrated that the BSM-MD simulation is especially successful for MgO in reproducing accurately not only the measured molar volume up to 3000K and zero pressure, but also the observed volume compression data up to 100GPa at 300K. Such excellent agreements lend us much credibility in the predicted MD results on the P–T–V equation of state of MgO at elevated temperatures and high pressures. Thus, we propose to use MgO as an additional pressure calibration at elevated temperatures. The MD computed V/V_0 values, where V_0 (=11.264cm^3/mol) is the molar volume at 300K and 0GPa, are listed in Table 2 up to 3000K and 100GPa. Experimental V/V_0 data as a function of temperature at 0GPa,[5] and those as a function of pressure at 300K[3] are also listed in Table 2 for comparison. The simulated P dependence of V/V_0 at 300K is in agreement with the experimental value, as shown in Fig.4, where we note the slight underestimations in the simulated V/V_0 values at high pressures and 300K with an error of 0.4% at 50GPa.

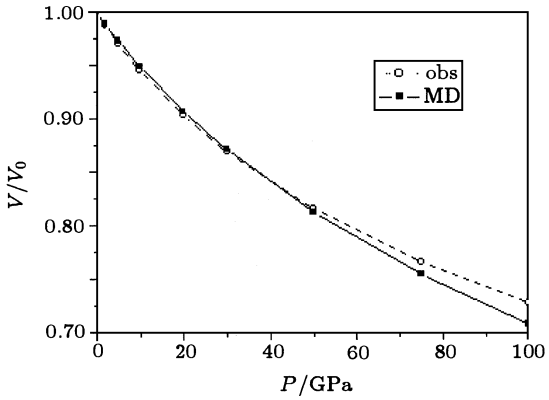


Fig.4. The observed and MD simulated values of V/V_0 against pressure for MgO at 300K.

4. Conclusions

The Monte Carlo and the MD simulations for ionic systems usually use pairwise additive rigid-ion models to treat the interactions in the crystal. However, it is often pointed out that noncentral forces are very important in an ionic system composed of ions with large polarizabilities. Therefore, we have performed MD simulation using the BSM to treat noncentral forces in crystals. In BSM the repulsive radii

of ions are allowed to deform isotropically under the effects of other ions in the crystal. The simulated molar volume, the volume compressions and equation of state for MgO are in good agreement with the available experimental data over wide temperature and pressure ranges, respectively. Hence, we propose that the MD simulated P–V–T equation of state of MgO could be applied as a useful internal pressure calibration standard at elevated temperatures and high pressures.

Table 2. The observed and MD simulated values of V/V_0 versus P and T for MgO.

P/GPa		T/K							
		300	600	900	1200	1500	2000	2500	3000
0	Obs*	1.0000	1.0118	1.0246	1.0383	1.0533	1.0812	1.1138	1.1520
	MD$^+$	1.0000	1.0088	1.0180	1.0273	1.0378	1.0553	1.0763	1.0991
2	Obs	0.9877							
	MD	0.9889	0.9969	1.0060	1.0144	1.0247	1.0416	1.0601	1.0791
5	Obs	0.9706							
	MD	0.9730	0.9808	0.9884	0.9974	1.0058	1.0213	1.0353	1.0533
10	Obs	0.9452							
	MD	0.9491	0.9557	0.9629	0.9696	0.9767	0.9900	1.0042	1.0181
20	Obs	0.9029							
	MD	0.9097	0.9124	0.9174	0.9232	0.9291	0.9392	0.9496	0.9613
30	Obs	0.8685							
	MD	0.8712	0.8754	0.8799	0.8847	0.8888	0.8974	0.9054	0.9150
50	Obs	0.8150							
	MD	0.8119	0.8153	0.8188	0.8219	0.8252	0.8314	0.8382	0.8433
75	Obs	0.7652							
	MD	0.7541	0.7566	0.7591	0.7614	0.7640	0.7685	0.7729	0.7777
100	Obs	0.7269							
	MD	0.7077	0.7097	0.7117	0.7138	0.7155	0.7190	0.7226	0.7257

*The observed data from Ref.[5] for high temperatures at 0GPa and from Ref.[3] for high pressures at 300K.

$^+$Present study V_0=11.264cm^3/mol

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