

Molecular-Dynamics Study of the α to β Structural Phase Transition of Quartz

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(Received 26 April 1989)

A molecular-dynamics simulation with a first-principles interatomic potential is used to study the phase transition of quartz from the α to the β phase. The phase transition, successfully reproduced at about 850 K, is shown to have a peculiar dynamical character in that, although the probability distribution for atomic positions mimics, when averaged over a long time, a displacive shift to the β structure, atoms in fact hop between the two equivalent α_1 and α_2 structures by anharmonic motions with a temperature-dependent correlation time.

PACS numbers: 61.50.Ks, 63.75.+z, 65.70.+y

The thermally induced structural phase transition of crystals is one of the best testing grounds for molecular-dynamics (MD) simulations, since large fluctuations in the atomic motion inherent in the critical phenomena can be treated, as compared with the lattice-dynamics method. An MD simulation has been applied by Schneider and Stoll to a simplified model to investigate order-disorder and displacive phase transitions.¹ Kerr and Bishop also studied the dynamics of a phase transition in a two-dimensional model.² In these studies, however, thermal expansion of the system was completely neglected, whereas the interatomic forces are in fact sensitive to the density of the system. Recently an MD simulation was used by Billesbach, Edwardson, and Hardy³ to determine the structures above and below the phase transition for Rb_2CaCl_4 with *ab initio* interatomic potentials, although the system size studied was rather small to obtain a clear picture of the transition, and no experimental results have been reported on this material.

In this Letter, we report an MD study of the structural transition of quartz, an ordinary polymorph of silica (SiO_2), using a nonempirical interatomic potential. There is a long history of experimental study on the phase transition in quartz.⁴⁻⁷ At room temperature, quartz assumes a low-temperature phase of space group $P3_121$, which is called low quartz or α -quartz, while it transforms into a high-temperature phase of space group $P6_222$ (high quartz or β -quartz) when it is heated above 846 K. The soft mode of the phase transition was first detected by Raman scattering⁵ below T_c and by inelastic neutron scattering⁶ above T_c . There has been a controversy as to the structure of β -quartz: the question is whether the atoms in the β phase vibrate around the idealized position⁴ or fluctuate between the α_1 and α_2 phases.^{8,9} Thus an MD study of the transition is particularly desirable. The MD method is suitable since (i) effects of dielectric polarization of electrons should not be significant in this transition, which is not a ferroelectric transition, so that we can employ a rigid-ion poten-

tial approximation in a first approximation, and (ii) the transition temperature is much higher than the Debye temperature (470 K), so that the classical dynamics is applicable. Establishing the high-temperature phase is also important for characterizing the incommensurate phase,⁷ which was recently observed to occur in a narrow temperature range (< 2 K); we do not discuss the incommensurate phase here, since it would require a study with larger system sizes.

Here we employ the interatomic potential recently derived from a first-principles many-body cluster calculation, which has been successfully applied to an MD simulation of silica.¹⁰ Although the potential is fitted with a pairwise functional form, the structures and bulk moduli of virtually all the known polymorphs of silica have been reproduced with the potential.¹¹

The functional form of the interatomic potential is expressed as

$$U_{ij}(r) = Q_i Q_j / r + f_0(b_i + b_j) \exp[(a_i + a_j - r)/(b_i + b_j)] - C_i C_j / r^6, \quad (1)$$

where r is the distance between the i th and j th atoms, and details are described in Ref. 10. With this interatomic potential we have performed an MD simulation of quartz under normal pressure (1 bar) with prescribed temperatures using both the constant-pressure algorithm by Parrinello and Rahman¹² and the constant-temperature algorithm by Nosé.¹³ The number of atoms in the system is 432 (containing $4 \times 4 \times 3 = 48$ unit cells). We impose periodic boundary conditions in all directions and the Ewald sum method is used for evaluating the long-ranged Coulomb interaction. Starting from the ideal crystal configuration and random velocities for atomic positions, we obtain the equilibrium configuration at 300 K. Then the temperature of the system is gradually increased (by 200 K at lower temperatures and 10–50 K near the critical temperature). Physical quantities are averaged over 12 psec (6000 MD steps) after at

least a 4-psec run for equilibration at each temperature.

The result [open squares in Fig. 1(a)] shows that, as the temperature is increased, the expansion coefficient abruptly changes at $T_c = 850\text{--}900\text{ K}$ and remains almost zero above T_c . This is clear-cut evidence for a phase transition and the behavior agrees with the experimental results,¹⁴ also shown in the figure, in which the expansion coefficient shows an abrupt change at $T_c = 846\text{ K}$ when the system changes into β -quartz. The absolute value for the equilibrium density of the simulated α -quartz at 300 K is 2.47 g/cm^3 , which agrees within 7% with the experimental value (2.65 g/cm^3). The phase transition is experimentally shown to be first order but very close to second order.⁷ No appreciable hysteresis is observed in the MD simulation around T_c either. The

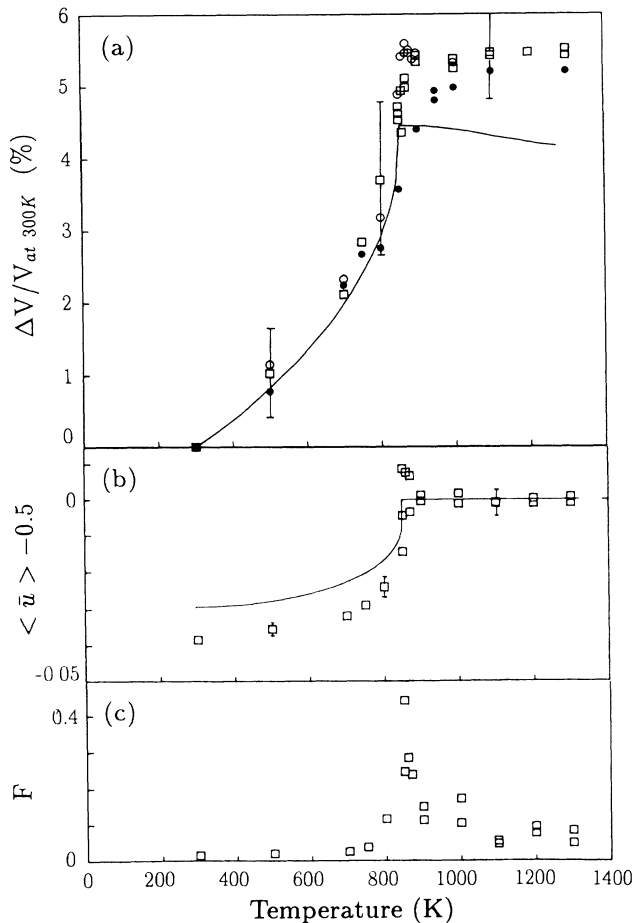


FIG. 1. (a) The MD result for the thermal expansion of quartz. Open squares represent the 432-particle system, with a typical magnitude of the fluctuation in $\Delta V/V$, while filled circles represent the 324-particle system and open circles, the 576-particle system. The experimental result (Ref. 14) is also shown by a solid curve. (b) The MD result (squares) for the temperature dependence of the u parameter of silicon averaged over the unit cells and time (12 psec). The solid curve is an experimental result (Ref. 4). (c) The MD result for the correlation function, F .

anisotropy of the expansion coefficient is also reproduced, although not shown here.

We first define the order parameter of the phase transition in the following way. The internal coordinates of atoms in α - and β -quartz can be specified by the symmetry operation of the space group $P3_121$ on a representative position of silicon at $\mathbf{r} = (u, 0, 0)$ and an oxygen in the hexagonal unit cell (with three silicon atoms and six oxygen atoms). In the low-temperature phase (α -quartz), there are two equivalent phases called a_1 and a_2 , respectively, which are rotated by 180° around the c axis from each other. The values at 300 K determined experimentally⁴ are $u = 0.4705(3)$ for a_1 and $u = 1 - 0.4705 = 0.5295$ for a_2 . In the idealized β -quartz, on the other hand, we have exactly $u = \frac{1}{2}$ from symmetry restrictions.⁴ We can thus choose $u - \frac{1}{2}$ as an order parameter of the phase transition. The positional parameters of oxygen are highly correlated with u to preserve the SiO_4 tetrahedra, which will be discussed elsewhere.

In the MD simulation, we monitored the u parameter averaged for the three silicon atoms in each unit cell at each time step. We denote the u parameter averaged over all the unit cells in the system by \bar{u} (which is a function of time), while the u parameter averaged over all the cells and all the time steps is denoted by $\langle \bar{u} \rangle$. The averaged order parameter, $\langle \bar{u} \rangle - \frac{1}{2}$, is shown in Fig. 1(b) against temperature. Although the simulation started from the a_1 phase at 300 K, the a_2 phase also appears as the temperature is raised. Above T_c , which corresponds to the kink in the volume-temperature relation [Fig. 1(a)], $\langle \bar{u} \rangle - \frac{1}{2}$ indeed vanishes.

If we look at a short-time average of u , however, it fluctuates substantially even above this temperature. If we trace the MD history of the atomic configuration at 850 K, the system alternates between a period of predominantly a_1 phase and a period of a_2 phase. When these periods cross over, a phase boundary of a_1 and a_2 appears in the system, when the density drops below that for the pure a phase and u averages $\frac{1}{2}$. As the temperature is increased, the period (correlation time) during which the system is in one of a_1 or a_2 becomes shorter. The domain size (correlation length) for the a_1 and a_2 phases is also a function of temperature.

To characterize these atomic motions, we show in Fig. 1(c) the ratio of the temporal variance in u to its spatiotemporal variance as defined by

$$F = (\langle \bar{u}^2 \rangle - \langle \bar{u} \rangle^2) / (\langle \bar{u}^2 \rangle - \langle \bar{u} \rangle^2). \quad (2)$$

F is close to unity if the atomic motions in different cells are strongly correlated, while $F \sim 0$ when motions are uncorrelated. F is seen to be singular at 850 K. Since the correlation length and time vary continuously with T , the a_1 - a_2 phase and β phase cannot be strictly discriminated, although the critical fluctuation becomes small as T departs from T_c . Above 900 K, the correlation length becomes smaller than the sample size studied in the

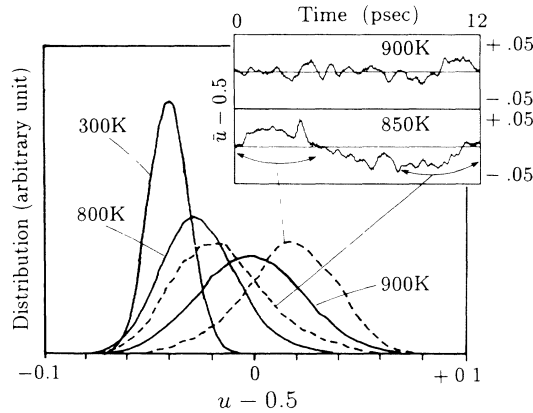


FIG. 2. The distribution of the u parameter of silicon. The data were accumulated over 12 psec (full lines) or 4 psec (dashed lines) at different intervals at 850 K. Inset: A typical trace of the u parameter, averaged over all the cells, against MD step.

simulation. Then phase boundaries appear within the system, which expands the system volume as reflected in the flat (saturated) $\Delta V/V$ behavior in Fig. 1(a). In this context we note that, in the case of a smaller, 324-particle system ($3 \times 4 \times 3 = 36$ unit cells), the whole system tends to stay in a single α phase even above 900 K, so that F becomes large in a wider region of temperature, and the kink in the temperature dependence of the volume is smeared around T_c as shown by the filled circles in Fig. 1(a). This is the origin of the sharper kink in the volume-expansion relation in a larger system with 576 particles ($4 \times 4 \times 4 = 64$ unit cells) as shown by open circles in Fig. 1(a).

We can characterize the structure by the distribution function of u accumulated for all the cells (Fig. 2). At lower temperatures, the motion of each particle is nearly harmonic, so that the distribution function is Gaussian. As the temperature increases, the distribution first becomes asymmetric, and then symmetric again above T_c with the peak shifted to $u = \frac{1}{2}$, although the distribution is no longer Gaussian as discussed later.

On the other hand, the distribution function for u averaged over a period shorter than the correlation time, which is about 4 psec at 850 K in the simulation, is shown in Fig. 2 by dashed lines. Depending on the interval at which the average is taken, the distribution exhibits either α_1 or α_2 behavior, while when averaged over a long time, the distribution function at 850 K already exhibits a single peak like that at 900 K. When seen locally, α_1 and α_2 phases switch to each other even at 900 K (Fig. 3), at which temperature the system comprises α_1 and α_2 domains. Thus the β -quartz structure is only realized as an average of the structure dynamically hopping between α_1 and α_2 with a T -dependent correlation length and time. The β -quartz structure is actually shown to be statically unstable in that the potential bar-

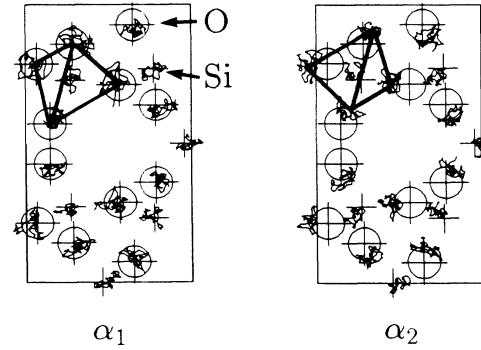


FIG. 3. The trajectory (at every 5 MD steps over 1 psec) of atomic positions in a part of the system projected to the x - y plane at $T = 900$ K. The two frames, taken at different time intervals in the same run, correspond to α_1 and α_2 phases, respectively. Typical SiO_4 tetrahedra are shown with thick lines and the idealized positions of the α_1 phase are indicated with crosses and circles.

rier separating the α_1 and α_2 phases survives above T_c within the static-lattice-energy calculation.

A conspicuous feature in the α - β phase transition as found here is the anharmonic motion of atoms. From the MD result it is quantitatively shown that the non-Gaussian parameter,¹⁵ which is a measure of the anharmonicity and closely related to the dynamical structure factor, exhibits a singular behavior around the transition. In crystals, we can define the one-dimensional non-Gaussian parameter for each internal coordinate as

$$\alpha_v = \langle \delta v^4 \rangle / 3 \langle \delta v^2 \rangle^2 - 1, \quad (3)$$

where $v (=x, y, z)$ is an internal coordinate of silicon or oxygen. It can easily be shown that α_v is zero if the distribution of v is Gaussian, that is, when the atomic motion in that mode is harmonic, while it is negative for clumpier distributions or positive for asymmetric distributions. The temperature dependence of the non-Gaussian parameters is shown in Fig. 4. The non-Gaussian parameters become nonzero around T_c for $\text{Si}(x, y)$ and $\text{O}(y, z)$ internal coordinates, which implies quite anisotropic anharmonicities in the atomic motion. This may be observed experimentally by neutron inelastic scattering.

In summary, we have shown that the α to β phase transition of quartz is reproduced by a molecular-dynamics simulation using a nonempirical pairwise potential. The β -quartz structure elucidated by the simulation has a peculiar dynamical character. Bruce and Cowley¹⁶ proposed a picture of clusters of two low-temperature structures for the transition based on numerical simulations in a simplified model.¹ Broadly speaking, the present result, obtained for a realistic model, for T -dependent correlation length and time for α_1 and α_2 phases, provides a basis for the cluster picture. The dynamical character stressed here is also consistent

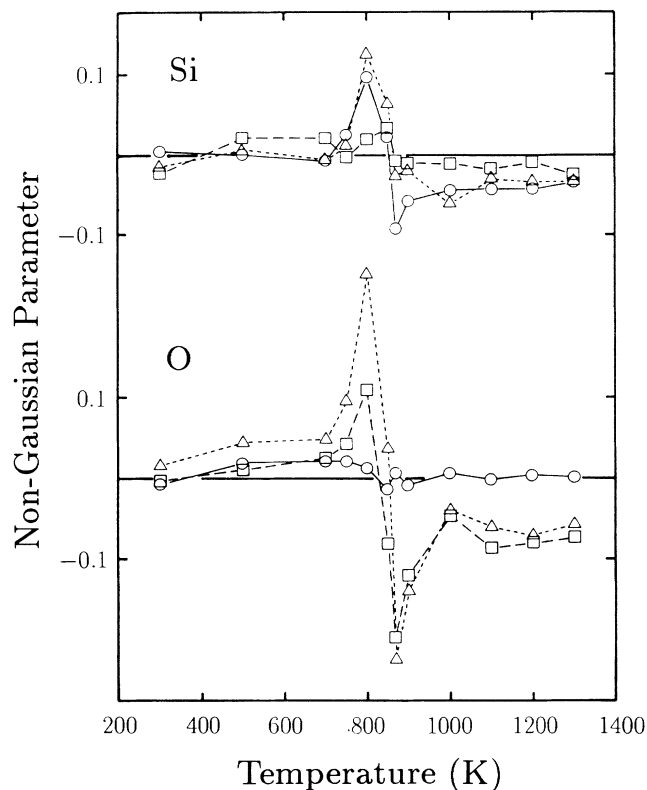


FIG. 4. Temperature dependence of the one-dimensional non-Gaussian parameters of silicon and oxygen for x (O, solid line), y (Δ , dashed line) and z (\square , long-dashed line) fractional coordinates.

with the experimental observations by van Tendeloo, van Landuyt, and Amelinckx⁸ and by Wright and Lehmann⁹ that the electron microscopy, electron diffraction, and neutron diffraction results indicate fluctuations between α_1 and α_2 structures. Physically, the competing factors are the thermal energy and the potential barrier separating the α_1 and α_2 structures. The potential surface is sensitive to the volume, which is exactly why the consideration of the thermal expansion is essential in this problem. Inclusion of core-polarization effects by some nonempirical method may be an interesting future problem.

We thank Dr. S. Nosé and Dr. M. Matsui for providing and helping us modify the MD programs, and Dr. K. Kawamura for useful discussions. Numerical calculations were performed at the Institute for Study of the Earth's Interior, Okayama University, and the Computer Centre, University of Tokyo. This work was supported in part by a Grant-in-Aid (No. 63302020) from the Ministry of Education, Science and Culture, Japan.

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