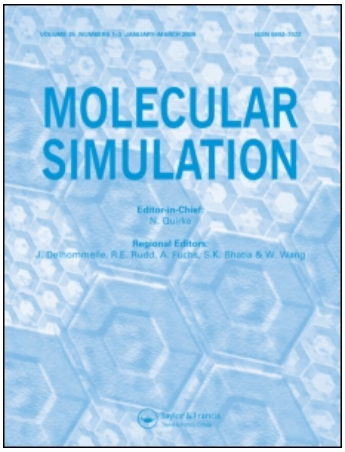

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Promotion of Crystal Phase Transitions by Mass-of-cell Control in Molecular Dynamics Simulations: Phase Transitions in Benzene Crystals

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PROMOTION OF CRYSTAL PHASE TRANSITIONS BY MASS-OF-CELL CONTROL IN MOLECULAR DYNAMICS SIMULATIONS: PHASE TRANSITIONS IN BENZENE CRYSTALS

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The promotion of crystal phase transitions in molecular dynamics (MD) simulations was realized by controlling the momentum of the MD cell. It was implemented by increasing the mass or velocity of the MD cell instantaneously during simulations within the framework of the constant-pressure method by Parrinello and Rahman. This method induced phase transitions in benzene crystals which have not been obtained in conventional MD simulations. This method is useful for the global search of stable (and metastable) crystal structures.

Keywords: Molecular dynamics simulation; Parrinello–Rahman constant-pressure method; Benzene crystal; Phase transition; Global search

1. INTRODUCTION

Benzene crystals have several phases stable at different pressures and temperatures. The phases possess subtle energy differences, since the intermolecular force is relatively weak. The crystal phase first determined at 270 K and atmospheric pressure was orthorhombic *P*bca, and it was named phase I [1]. After that, monoclinic $P2_1/c$ phase was found under 2.5 GPa and named phase II [2]. Later, another monoclinic phase [3] was

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found intermediate between phases I and II; this new phase was designated as phase II, and the former phase II was renamed phase III. Recently, phases III′ and IV also have been reported [3, 4]. The structures of phases I [1] and III [2] have been exactly determined. However, that of phase II has not, in spite of experimental [3] and theoretical [5–13] investigations.

The MD simulation is a useful method to obtain information on the structures and stability of the phases and the transitions between them. Parrinello and Rahman [14] have extended the constant-pressure MD method for isotropic systems [15] developed by Andersen to enable crystals to transfer between different crystal phases. The phase transition from I to III has not been obtained by the Parrinello–Rahman (PR) method despite investigations by Craven *et al.* [7] (In their paper, the phase III was called phase II) and by the authors. This is because the realizability of the phase transition by MD simulation depends not only on the initial and final energies but also on the height of the energy barrier between them. Even if the final state is energetically more stable than the initial state, whether the phase transition is obtained or not depends on the simulation time. If the phase transition is allowed to occur in the simulation under natural conditions, extremely long simulation run times will be required to obtain such an event.

In this paper, we present an MD method which induces phase transitions in crystals. In our approach, the energy barrier between phases is overcome by manipulating the momentum of the MD cell artificially. By increasing the fictitious mass of the cell abruptly during the simulation, the shape of the cell starts to deform significantly from the preceding (*meta-*) stable structure and leads the crystal to a phase transition. We have obtained the transitions from phase I to phase III, from III to II, and from II to III by the method.

2. SIMULATION DETAILS

Our method uses the dynamics of the PR method [14] extended to treat molecular systems [16]. The positions of the center of mass of molecules are scaled by cell matrix **h** as follows:

$$\boldsymbol{r} = \mathbf{h}\boldsymbol{s}, \tag{1}$$

where **h** is the cell matrix given by $\{\boldsymbol{h}_1, \boldsymbol{h}_2, \boldsymbol{h}_3\}$ using side vectors $\boldsymbol{h}_1$, $\boldsymbol{h}_2$, and $\boldsymbol{h}_3$ of the MD cell, $\boldsymbol{r}$ is the position of the center of mass of a molecule in Cartesian coordinates, and $\boldsymbol{s}$ is the internal coordinates of the MD cell for

the molecule. The Lagrangian of the system is expressed as:

$$L=\frac{1}{2}\sum_i m_i \dot{s}_i^t \mathbf{G}\dot{s}_i+\frac{1}{2}\sum_i \omega_i^t \mathbf{I}_i\omega_i-\sum_i\sum_{j>i}\Phi_{ij}+\frac{1}{2}W\mathrm{Tr}(\dot{\mathbf{h}}^t\dot{\mathbf{h}})-P_{\mathrm{ext}}\det\mathbf{h}, \quad (2)$$

where the subscripts i and j denote molecules, m is the mass of a molecule, $\mathbf{G}=\mathbf{h}^t\mathbf{h}$, ω and $\mathbf{I}$ are the angular velocity and the inertia tensor of a molecule, Φ is the interaction potential between molecules, W is the fictitious mass of the MD cell, and P_{ext} is the external pressure. The first and second terms in Eq. (2) are the translational and rotational kinetic energy of the molecules, respectively, the third is the potential energy of the molecules, and the fourth and fifth are the kinetic and potential energy of the MD cell, respectively. The equations of motion for molecules and the MD cell are derived from Eq. (2) as:

$$\ddot{s}_i=\frac{1}{m_i}\mathbf{h}^{-1}\boldsymbol{F}_i-\mathbf{G}^{-1}\dot{\mathbf{G}}\dot{s}_i, \quad (3)$$

$$\frac{d}{dt}(\mathbf{I}_i\omega_i)=\boldsymbol{N}_i, \quad (4)$$

$$\ddot{\mathbf{h}}=\frac{1}{W}(\mathbf{P}-P_{\mathrm{ext}})\boldsymbol{\sigma}, \quad (5)$$

where $\boldsymbol{F}$ and $\boldsymbol{N}$ are the force and the torque acting on a molecule, $\mathbf{P}$ is the internal pressure tensor, and $\boldsymbol{\sigma}=\{\boldsymbol{h}_2\times\boldsymbol{h}_3,\ \boldsymbol{h}_3\times\boldsymbol{h}_1,\ \boldsymbol{h}_1\times\boldsymbol{h}_2\}$. The time evolution of the system is solved by numerically integrating Eqs. (3)–(5). Equation (5) shows that the dynamics of the MD cell explicitly depends on W, which is better to be chosen to reproduce the sound velocity in the material [15]. However, if not necessary to discuss dynamic quantities, W can be chosen so that the system will be equilibrated faster, since static quantities do not depend on it [15, 17, 18].

Usually W is kept constant in the PR method throughout a simulation. However in our approach, it is instantaneously increased at a certain time during simulations. In an equilibrium state, the shape of the MD cell fluctuates around the average one. At this time, if W is instantaneously increased, from Eq. (5) all the absolute values of the accelerations of matrix elements of the MD cell decrease. Thus, the shape of the MD cell starts to deform significantly, depending on the velocities of matrix elements of the MD cell at the moment. As a result, the crystal structure undergoes large changes with keeping its order and, if the energy barrier between phases is overcome, transforms to the other structure.

In the terms of energy, at the moment W is increased, the kinetic energy of the MD cell (the fourth term in Eq. (2)) is discontinuously increased, and the energy barriers between phases are overcome. On the other hand, the kinetic energy of molecules (the first and second terms in Eq. (2)) does not increase discontinuously, and is kept constant if temperature is controlled. Thus, melting of the crystal due to the increase in temperature does not occur. Continuing the simulation after increasing W, the kinetic energy of the MD cell returns gradually to the proper value determined by both the degree of freedom of the MD cell and the target temperature.

The benzene molecule was treated as a rigid body with C—C and C—H bond lengths 1.392 Å and 1.080 Å, respectively. Van der Waals (vdW) interaction sites of H atoms were shifted to a distance 1.027 Å from the C atoms along the direction of the C—H bonds [19]. Intermolecular interactions were calculated by the atom–atom method [20] using the interatomic potential ϕ[21]:

$$\phi(r_{ij}) = f_{ij}\left[-\frac{A_{ij}}{r_{ij}^6} + B_{ij}\exp(-C_{ij}r_{ij})\right] + \frac{q_i q_j}{4\pi\varepsilon r_{ij}}, \tag{6}$$

where $f_{ij} = (Z_i - q_i)(Z_j - q_j)/Z_i Z_j$, the subscripts i and j denote atoms, r is the interatomic distance, A, B, and C are vdW parameters for neutral atoms, q is the net point charge on the atom, ε is the permittivity in vacuum, and Z is the atomic number. The parameters A, B, C, and q for benzene were taken from reference [21]. The cut-off of vdW interaction was 10 Å by interatomic distance base; that of the Coulomb interaction was 13 Å by intermolecular distance base. In computing the Coulomb interaction between neutral molecules such as benzene, instead of the conventional Ewald method, the molecule-based cut-off technique saves substantial computing time without reducing accuracy [22].

The initial structures used for the simulations were those of the experimentally observed phases I [1] or III [2], depending on the purpose. The MD cell for phase I consisted of 27 crystallographic unit cells (3 units along each axis direction) containing 108 molecules; for phase III, 64 crystallographic unit cells (4 units along each axis direction) containing 128 molecules were used. A periodic boundary condition was applied to the MD cell for each direction. The equations of motion were integrated by the Gear's predictor-corrector method [23], with the time step 2 fs. The pressure and temperature were controlled by the PR method and the velocity scaling method [24], respectively.

3. RESULTS

3.1. Preliminary Simulations without Mass Control

Figure 1 shows the time evolution of the shape of the MD cell and the molecular potential energy for the simulation starting from the phase I structure with the condition of $W = 5 \times 10^{-25}$ kg at 270 K under 0 GPa. The crystal structure for the initial 40ps was in good agreement with that experimentally observed for phase I (Tab. I). By changing the conditions to 294 K and 2.5 GPa at 40 ps, the structure was transformed to monoclinic $P2_1/c$ ($N = 2$, $a = 5.54$ Å, $b = 6.57$ Å, $c = 7.17$ Å, $\beta = 124.4$ deg), being distinct from phases I and III. We regard this structure as phase II. It corresponds to the hypothetical phase I-$P2_1/c$ [5, 6] ($N = 2$, $a = 5.45$ Å, $b = 6.55$ Å,

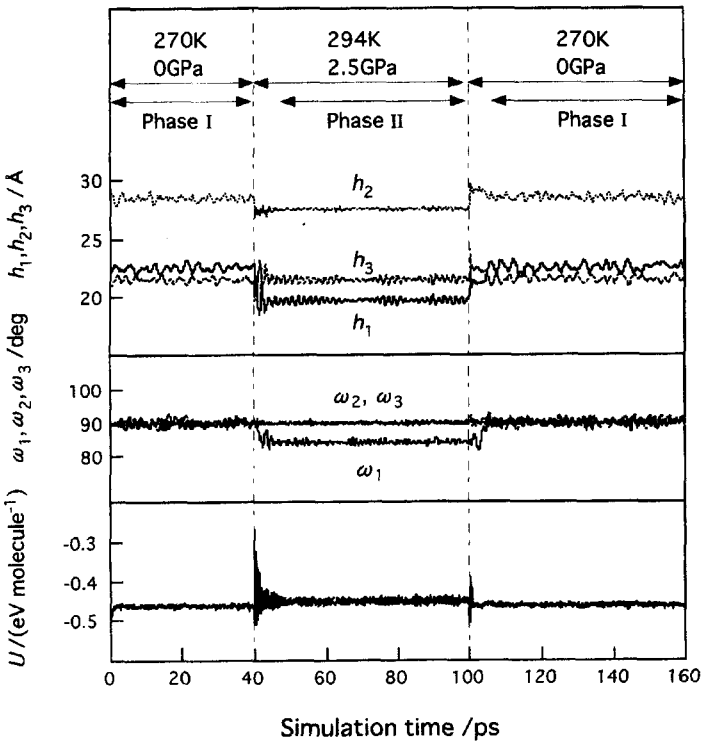

FIGURE 1 Time evolution of the MD cell and the molecular potential energy U. The initial structure is that of the phase I. The temperature and pressure are changed at 40 ps and restored to the original values at 100 ps. The mass, W, of the MD cell is fixed. The symbols, $\boldsymbol{h}_1$, $\boldsymbol{h}_2$, and $\boldsymbol{h}_3$, are the vectors of sides of the MD cell, ω_1, ω_2, and ω_3, are the angles between $\boldsymbol{h}_2$ and $\boldsymbol{h}_3$, $\boldsymbol{h}_3$ and $\boldsymbol{h}_1$, and $\boldsymbol{h}_1$ and $\boldsymbol{h}_2$, respectively, and U is the molecular potential energy.

TABLE I Benzene crystal structures

	Phase I ($N=4$[a]) 270 *K*, 0 *GPa*		*Phase* III ($N=2$[a]) 294 *K*, 2.5 *GPa*	
	Exp.[b]	*This work*	*Exp.*[c]	*This work*
Lattice constants				
a/Å	7.46	7.49	5.42	5.36
b/Å	9.67	9.52	5.38	5.55
c/Å	7.03	7.20	7.53	7.40
α/deg	90.0	89.9	90.0	90.0
β/deg	90.0	89.9	110.0	107.1
γ/deg	90.0	90.1	90.0	90.0
Eulerian angles[d]				
θ/deg	72.3	71.6	135.2	132.3
ϕ/deg	48.1	50.0	−42.6	−41.6
ψ/deg	−87.3	−86.9	33.9	29.7

[a] The number of molecules in a unit cell.
[b] Ref. [1].
[c] Ref. [2].
[d] The orientation of one molecule in a unit cell. Those of the other molecules are determined by the symmetry. The definition of Eulerian angles is the same as in Ref. [21].

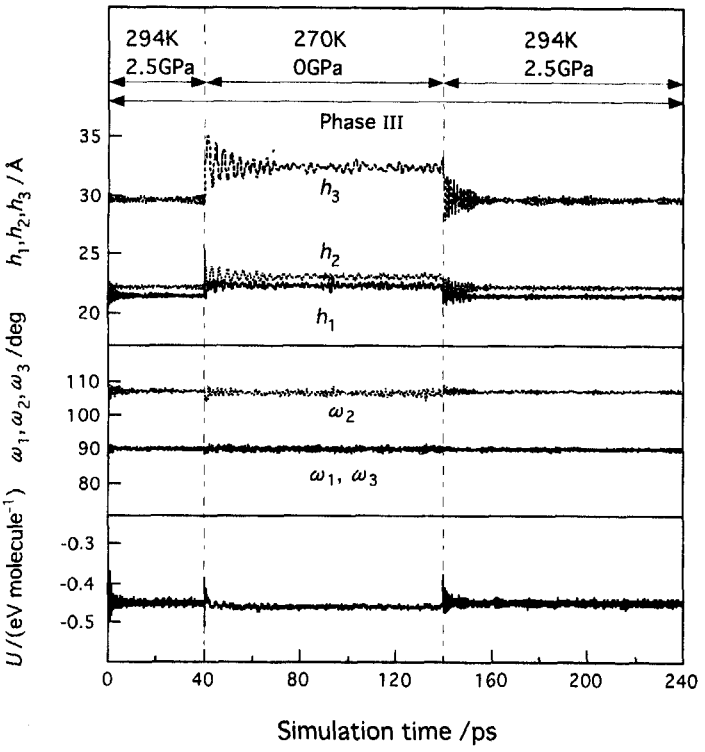

FIGURE 2 Time evolution of the MD cell and the molecular potential energy U. The initial structure is that of the phase III. The temperature and pressure are changed at 40 ps and restored to the original values at 140 ps. The mass, W, of the MD cell is fixed.

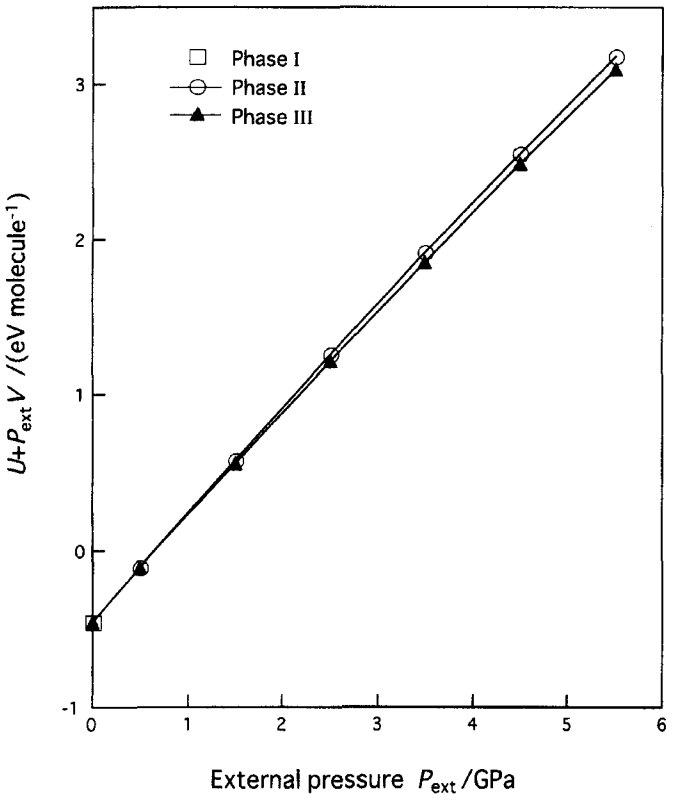

FIGURE 3 Pressure dependence of $U+P_{ext}V$, where V is the volume per molecule. The temperature is 294 K, except for 270 K at 0 GPa.

$c = 6.90$ Å, $\beta = 123.0$ deg), which Dzyabchenko and Bazilevskii have suggested as an intermediate phase between phases I and III (In their papers, the phase III was called phase II). Eight simulations with different timing for the onset of changes in pressure and temperature resulted in transformations to the phase II instead of III without exception. By restoring the initial conditions (*i.e.*, 270 K and 0 GPa) at 100 ps, the structure returned to the original phase I.

Figure 2 presents results similar to those in Figure 1, but the initial condition is the phase III with $W = 5 \times 10^{-25}$ kg at 294 K under 2.5 GPa. The crystal structure, maintained for the initial 40 ps, was in good agreement with that observed experimentally for phase III as shown in Table I. After the conditions were changed to 0 GPa and 270 K at 40 ps, the crystal system remained unchanged, though the cell was slightly expanded. By restoring the

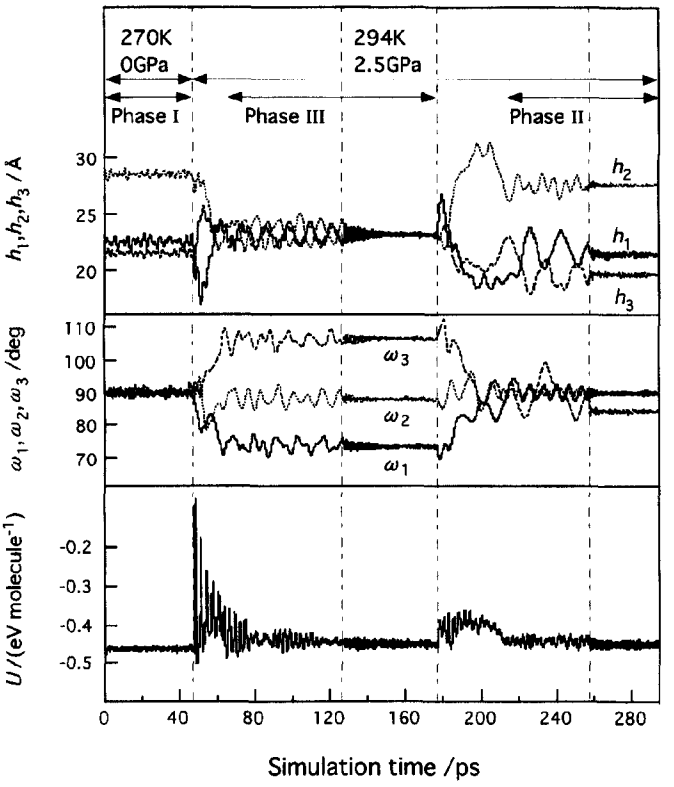

FIGURE 4 Time evolution of the MD cell and the molecular potential energy U. The initial structure is that of the phase I. The temperature and pressure are changed at 47 ps. The mass, W, of the MD cell is increased by hundred times at 47 ps and decreased to the original value at 127 ps, and again increased at 177 ps and decreased at 257 ps.

initial conditions (*i.e.*, 294 K and 2.5 GPa) at 140 ps, the structure returned to the original phase III.

The transitions between phases I and III and between II and III were not obtained at pressures up to 5.5 GPa. The resulting pressure dependence of energy for each phase is shown in Figure 3. Rigorously speaking, phase stability should be evaluated by the Gibbs free energy. However, we discuss phase stability without estimating entropy, since it is difficult to estimate in MD simulations; instead, approximately equal entropy for all phases is assumed. The stabilities of phases I, II and III are nearly equal at low pressures, but phase III becomes more stable than II (and I naturally) at high pressures. Therefore phase transition from II to III is energetically possible at 2.5 GPa, but is not obtained even in a simulation raising the temperature to 1000 K and carried out for 800 ps.

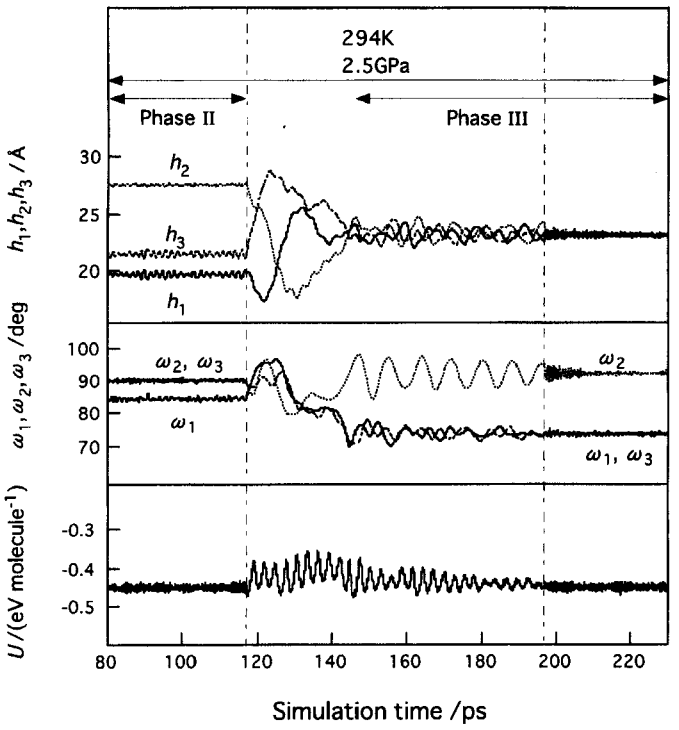

FIGURE 5 Time evolution of the MD cell and the molecular potential energy U. The initial structure is that of the phase I. The mass, W, of the MD cell is increased by hundred times at 117 ps and decreased to the original value at 197 ps.

3.2. Simulations with Mass Control

Figure 4 shows the same sort of results as Figure 1, but with the mass of the cell, W, being changed during the simulation. After the structure was maintained for 47 ps, W was increased one hundred fold at the same time the temperature and pressure were changed to 294 K and 2.5 GPa, respectively. The crystal structure was changed significantly, undergoing large fluctuations, and transforming to the phase III. By restoring W to the original value at 127 ps, the fluctuation was suppressed. Increasing W a second time at 177 ps induced the transformation to the phase II.

Figure 5 shows the time evolution of the MD cell starting from the phase II in Figure 1. As was the case in Figure 4, the increase of W at 117 ps induced a transformation to the phase III followed by the reduction of structure fluctuation after restoring W.

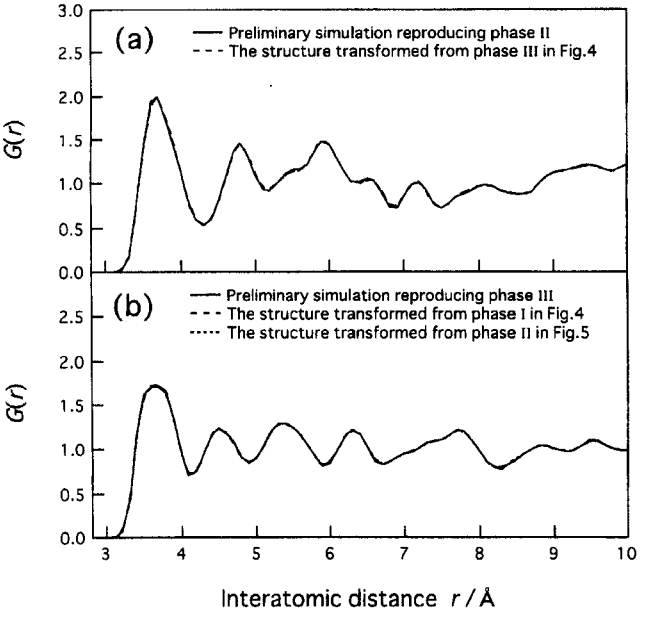

FIGURE 6 Radial distribution functions $G(r)$ for carbon atoms. (a) Phase II, (b) Phase III.

The crystal structures after the three phase transitions in Figures 4 and 5 are compared in Figure 6 with the results of preliminary simulations reproducing the phase II and III structures. The respective structures coincide nearly exactly. The results in Figures 4 and 5 are typical samples from each of 16 simulations starting from the phase I, II, or III structure and changing the timing of mass changes. The displacement of the MD cell and the resulting crystal structure depend on such timing. Resulting structures of all trials are summarized in Table II. The energy relation of these structures at 294 K under 2.5 GPa is shown in Table III. The

TABLE II Resulting structures and the number of their appearance in simulations with mass control

	Starting structures		
	Phase I	*Phase* II	*Phase* III
Resulting structures[a]			
Phase II	11	14	1
Phase III	4(3[b])	1	15
Monoclinic $C2/c$ phase	1(1[b])	1	0

[a] Resulting structures maintained all through the simulation period for 60 ps, after the structures reached each equilibrium states.
[b] The number of structures with plane defects.

TABLE III Energy at 294 K under 2.5 GPa

	$U+P_{ext}V/(eV\ molecule^{-1})$
Monoclinic phase III	1.213 (1.218[a])
Monoclinic phase II	1.251
Monoclinic $C2/c$ phase	1.256 (1.293[a])

[a] Energy for the crystals with plane defects.

phase III is the most stable among the five structures, consistent with the experimental result. The structure with plane defects is as stable as the no-defect phase III, which implies that such defects easily appear in real benzene solids. The monoclinic $C2/c$ phase ($N=4$, $a=11.24$ Å, $b=5.54$ Å, $c=7.45$ Å, $\beta=113.1$ deg), which is identified with the $C2/c$ structure found by Dzyabchenko [25], is comparable to the phase II in energy.

4. DISCUSSION

We have shown that phase transitions are induced by a simple operation, *i.e.*, changing W instantaneously, without changing physical conditions such as pressure or temperature. The fact that the resulting structure depends on the timing of the change in W shows this method is expected to be useful for the global search of (*meta-*) stable crystal structures of unknown materials at arbitrary temperature and pressure. The path of the transition observed in Figure 4 is expected to be one of low energy passes, even if our method contains artificial dynamics. However it is too early to discuss the relation to the results of the transition path theoretically investigated by Dzyabchenko and Bazilevskii [6] using a static method, because of the lack of simulation data.

Another phase [3] (monoclinic: $a=9.80$ Å, $b=4.87$ Å, $c=4.40$ Å, and $\beta=102.1$ deg), experimentally observed at a pressure intermediate between those for phases I and III, was not obtained in these simulations. The structures calculated by static methods [11, 13] do not agree well with the experimental result. There may be an intimate relationship between the calculated results and the experimentally observed result that the transition is a very slow phenomenon under high pressures. As a consequence of this very slow transition, the structure of the experimentally observed intermediate phase has not been measured accurately [11]. On the other hand, the phase II corresponding to the structure, I-$P2_1/c$ [5, 6], was metastable within the simulation time. This coincides with the viewpoint [6, 11] that the phase II is the intermediate phase between phases I and III.

The relation between the amount of change of W (or the rate of changing W) and the possibility of transition inducement was not investigated in this work. However, it is clear that the fluctuation of the MD cell becomes too small to effect a phase transition if the amount of change of W is small. On the other hand, the MD cell becomes unstable for a large change of W. The change of W must be determined considering also the height of the energy barrier for the transition and the external pressure.

Besides changing W, the momentum of the MD cell can be changed by changing the velocity of the MD cell, $\dot{\mathbf{h}}$. The transition from the phase I to III (with plane defects) was obtained by increasing the MD cell velocity. Considered from Eq. (3), this method introduces a discontinuous change in the translational accelerations of molecules that may produce unexpected effects on the dynamics of the entire system, and did not show any superiority to the method scaling W in these simulations. However, the method to scale $\dot{\mathbf{h}}$ offers the promising possibility that individual control of the velocity elements, $\dot{h}_{ij}$, may be able to induce an arbitrary phase transition that would be useful to the active search of crystal phases. A similar outcome may be realized if the Parrinello–Rahman method is extended to express W by the mass elements, W_{ij}, which may be controlled individually.

References

[1] Cox, E. G., F. R. S., Cruickshank, D. W. J. and Smith, J. A. S. (1958). "The crystal structure of benzene at −3°C", *Proc. R. Soc. Lond. A*, **247**, 1.
[2] Piermarini, G. J., Mighell, A. D., Weir, C. E. and Block, S. (1969). "Crystal structure of benzene II at 25 kilobars", *Science*, **165**, 1250.
[3] Thiéry, M. M. and Léger, J. M. (1988). "High pressure solid phases of benzene. I. Raman and x-ray studies of C_6H_6 at 294 K up to 25 GPa", *J. Chem. Phys.*, **89**, 4255.
[4] Cansell, F., Fabre, D. and Petitet, J.-P. (1993). "Phase transitions and chemical transformations of benzene up to 550°C and 30 GPa", *J. Chem. Phys.*, **99**, 7300.
[5] Dzyabchenko, A. V. and Bazilevskii, M. V. (1985). "Theoretical structure of crystalline benzene. III. Hydrostatic pressure effect", *J. Struct. Chem.*, **26**, 553.
[6] Dzyabchenko, A. V. and Bazilevskii, M. V. (1985). "Theoretical structure of crystalline benzene. IV. Calculation of transition states", *J. Struct. Chem.*, **26**, 558.
[7] Craven, C. J., Hatton, P. D. and Pawley, G. S. (1993). "The structure and dynamics of solid benzene. II. Molecular dynamics studies", *J. Chem. Phys.*, **98**, 8244.
[8] Shoda, T., Yamahara, K., Okazaki, K. and Williams, D. E. (1994). "Molecular packing analysis: prediction of experimental crystal structures of benzene starting from unreasonable initial structures", *J. Mol. Struct. (Theochem.)*, **313**, 321.
[9] Shoda, T., Yamahara, K., Okazaki, K. and Williams, D. E. (1995). "Molecular packing analysis of benzene crystals. Part 2. Prediction of experimental crystal structure polymorphs at low and high pressure", *J. Mol. Struct. (Theochem.)*, **333**, 267.
[10] Gibson, K. D. and Scheraga, H. A. (1995). "Crystal packing without symmetry constraints. 2. Possible crystal packing of benzene obtained by energy minimization from multiple starts", *J. Phys. Chem.*, **99**, 3765.

[11] Thiéry, M-M. and Rérat, C. (1996). "High pressure solid phases of benzene III. Molecular packing analysis of the crystalline structures of C_6H_6", *J. Chem. Phys.*, **104**, 9079.
[12] Wawak, R. J., Pillardy, J., Liwo, A., Gibson, K. D. and Scheraga, H. A. (1998). "Diffusion equation and distance scaling methods of global optimization: application to crystal structure prediction", *J. Phys. Chem. A*, **102**, 2904.
[13] van Eijck, B. P., Spek, A. L., Mooij, W. T. M. and Kroon, J. (1998). "Hypothetical crystal structures of benzene at 0 and 30 kbar", *Acta Crystallogr. B*, **54**, 291.
[14] Parrinello, M. and Rahman, A. (1980). "Crystal structure and pair potentials: a molecular-dynamics study", *Phys. Rev. Lett.*, **45**, 1196.
[15] Andersen, H. C. (1980). "Molecular dynamics simulations at constant pressure and/or temperature", *J. Chem. Phys.*, **72**, 2384.
[16] Nosé, S. and Klein, M. L. (1983). "Constant pressure molecular dynamics for molecular systems", *Mol. Phys.*, **50**, 1055.
[17] Haile, J. M. and Graben, H. W. (1980). "Molecular dynamics simulations extended to various ensembles. I. Equilibrium properties in the isoenthalpic-isobaric ensemble", *J. Chem. Phys.*, **73**, 2412.
[18] Haile, J. M. and Graben, H. W. (1980). "On the isoenthalpic-isobaric ensemble in classical statistical mechanics", *Mol. Phys.*, **40**, 1433.
[19] Williams, D. E. (1966). "Nonbonded potential parameters derived from crystalline aromatic hydrocarbons", *J. Chem. Phys.*, **45**, 3770.
[20] Pertsin, A. J. and Kitaigorodsky, A. I., *The Atom–Atom Potential Method*, Springer-Verlag, Berlin, 1987.
[21] Yokoi, K. and Nishikawa, T. (1997). "Revised intermolecular potential with parameters depending on partial atomic charges for aromatic molecular systems", *Mol. Phys.*, **90**, 705.
[22] Yokoi, K. (1995). "Empirical atom–atom potential for a naphthalene crystal and transferability to other polyacene crystals", *Mol. Phys.*, **85**, 449.
[23] Gear, G. W., *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice-Hall, Englewood Cliffs, NJ, 1971.
[24] Woodcock, L. V. (1971). "Isothermal molecular dynamics calculations for liquid salts", *Chem. Phys. Lett.*, **10**, 257.
[25] Dzyabchenko, A. V. (1984). "Theoretical structures of crystalline benzene: the search for a global minimum of the lattice energy in four space groups", *J. Struct. Chem.*, **25**, 416.