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Computational method for aperiodic systems: Molecular mechanics simulations

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For aperiodic systems with long-range interactions, an algorithm of molecular mechanics (MM) calculations is proposed. In order to treat the aperiodic system as an infinite system containing completely isolated disorder, the crystal structure is described based on the deviation from a periodic system, and potential energy and forces are evaluated as differences from those for the periodic system. The MM calculations for ionic systems containing local impurity atoms have been carried out as test calculations. The obtained lattice relaxation and energy of impurities have been compared with the results of a conventional supercell method performed based on five different sizes of unit cells, and the advantages of the proposed algorithm in terms of computational accuracy and time have been ascertained. For aperiodic systems where the charge neutrality has been lost because of the existence of ionized impurities, this algorithm realizes MM calculations without artificial charge neutral conditions which are usually required in the supercell method. The algorithm also has a possibility of the application to molecular dynamics calculations. [S1063-651X(97)01610-3]

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I. INTRODUCTION

Molecular mechanics (MM) and molecular dynamics (MD) simulations have become recognized as useful tools for research in various scientific fields [1,2]. Recently, their importance has been growing, particularly in applications to complex and large-sized systems. Amorphous structures, impurity systems, liquid crystals, polymers, and so on are mentioned as such systems, and several phenomena such as impurity diffusion, surface adsorption, ion implantation, radiation damage, and fracture are also associated with complex-structured systems. Since a crystallographic periodicity has disappeared in these systems, a supercell method is usually adopted in MM and MD calculations for them. This method is an expedient approach to aperiodic systems, and has been widely applied in both *ab initio* and empirical calculations. Particularly as for the former, well-developed energy band calculations can be directly applied. In the supercell method, aperiodic systems are approximately described by assuming the periodic boundary condition, so that large-sized supercells are required for the computational accuracy in order to diminish interactions with crystal imperfections involved in surrounding cells. However, it is difficult to treat sufficiently large-sized systems because of the restriction of computational time, although computer abilities have been increasing rapidly. Thus the problem of the numerical inaccuracy depending on system sizes still remains unsolved in the supercell method, and several investigations concerning it have been reported [3]. This problem is most serious for long-range interatomic interactions. Generally, imperfections in the above-mentioned aperiodic systems are given as a charged particle, such as impurities in semiconductors, so that it is necessary to treat a Coulomb interaction precisely without the dependence on system sizes. However, to reduce the influence of system sizes and obtain accuracy an order of magnitude higher in the calculation of total energies, one needs a larger system whose constituent atoms are about 10^3 times as many as the prior system because of the long-range r^{-1} interaction, and thus computational time of about 10^6 times longer will be consumed. Although this estimation is rough, it implies that even checking the dependence on system sizes is difficult for Coulomb interacting systems.

As a sophisticated approach to aperiodic systems, a Green-function method to calculate the electronic states of deep levels in semiconductors was developed independently by two groups in the late 1970s [4,5]. In this method, a localized defect, which cannot be described based on expanded Bloch states, is represented by a perturbation potential for a perfect crystal, and this perturbation potential is determined self-consistently so as to coincide with the Green function for the perfect crystal at infinity. This Green-function method is a skillful approach to aperiodic systems. It is, however, necessary to realize a more efficient calculation of forces acting on each constituent atom from the viewpoint of MM and MD calculations.

It is the purpose of this paper to propose a method of MM and MD calculations for aperiodic systems. This algorithm is based on the premise that interatomic interactions have been determined by some method beforehand. Empirical interatomic potentials enable us to perform MM and MD calculations for large-sized systems practically, whereas their function forms directly influence the accuracy of calculated physical quantities. In the present algorithm, when interatomic potential functions have been given, the focus is on how accurately physical quantities of the aperiodic system can be evaluated for an infinite system containing completely isolated disorder. For this purpose, atomic positions of the aperiodic system are described by the deviation from a periodic system, and potential energy and forces are calculated based on this description. As interatomic interactions, typical long-range ones whose function forms are given by r^{-n} are considered. In the MM calculations for ionic systems, advantages with respect to both numerical accuracy and computational time have been ascertained as compared with the conventional supercell method.

This paper is organized as follows: In the next section, the formulation of the present algorithm is described. In Sec. III the MM calculations for ionic systems containing substitu-

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tional impurity atoms are reported as numerical tests, and the obtained lattice relaxation and energy of impurities are compared with those of the supercell method. For more detailed comparisons between the two methods, discussions concerning the computational accuracy and time are given in Sec. IV. Finally, a short summary is presented in Sec. V.

II. FORMULATION

A. Crystal structures

In this paper, aperiodic systems are defined as infinite systems where atomic positions are locally disordered. As such an aperiodic system, a crystal containing local impurity atoms is considered here. Those impurity atoms cause lattice relaxation in a local region, and this relaxation can be described by the deviation from a crystal containing no local impurity atoms, which is called the reference system hereafter. From this viewpoint, the position of the ith atom in the aperiodic system is given by

$$\mathbf{r}(i)=\mathbf{r}^0(i)+\Delta\mathbf{r}(i), \tag{1}$$

where $\mathbf{r}^0(i)$ represents the atomic position in the reference system, and $\Delta\mathbf{r}(i)$ represents the displacement of the ith atom caused by the local impurity atoms.

As mentioned above, it is reasonable to consider a relaxation region centered at the local impurity atoms. This region R_Δ is determined so as to contain all atoms whose $|\Delta\mathbf{r}(i)|$ is not zero. In the center of R_Δ, $|\Delta\mathbf{r}(i)|$ is relatively large, but it becomes negligibly small near the boundary of R_Δ. The number of atoms inside R_Δ is given by N_Δ, and it always shows $N_\Delta > N_{\mathrm{imp}}$, where N_{imp} is the number of the impurity atoms. On the other hand, the reference system does not have any local impurity atoms, so that it has translational periodicity like perfect crystals. Thus $\mathbf{r}^0(i)$ is written also in the following notation:

$$\mathbf{r}^0(i)=\mathbf{r}^0\begin{pmatrix} s \\ l \end{pmatrix}, \tag{2}$$

where $\mathbf{r}^0(\begin{smallmatrix} s \\ l \end{smallmatrix})$ means the position of the sth atom in the lth unit cell in the reference system.

B. Interatomic potentials

In the present algorithm, pair-type potentials are considered as interatomic interactions. The pair-type potential ϕ between the ith and the jth atoms is represented by the following expression:

$$\phi(r_{ij})=\sum_{\xi}\ \phi_\xi(r_{ij})=\sum_{\xi}\ A_\xi(i)A_\xi(j)\psi_\xi(r_{ij}), \tag{3}$$

where r_{ij} is the distance between the atoms i and j which is given by

$$r_{ij}=|\mathbf{r}_{ij}|, \tag{4}$$

$$\mathbf{r}_{ij}=\mathbf{r}(i)-\mathbf{r}(j). \tag{5}$$

In Eq. (3), $A_\xi(i)$ represents the potential parameter of the ith atom, and the subscript ξ specifies the type of interatomic interactions. In the case of Coulomb interaction, ϕ_{Coul} is given by

$$\phi_{\mathrm{Coul}}(r_{ij})=\frac{e^2}{4\pi\varepsilon_0}\frac{q(i)q(j)}{r_{ij}}, \tag{6}$$

where $q(i)$ is the point charge of the ith atom and corresponds to the potential parameter $A_{\mathrm{Coul}}(i)$. Other interactions written by Eq. (3) are multipole-multipole and van der Waals interactions whose potential functions are given by r^{-n}. These interactions with a small value of n, especially the Coulomb one, are well known as a long-range interaction, and the Ewald method is generally required for their lattice sums. As discussed in Sec. I, the problem of the supercell method is most serious in calculations for systems with long-range interactions. Based on Eq. (3), general long-range interactions with r^{-n} function forms can be treated in this algorithm. Interatomic interactions which are not written by Eq. (3) are Born-Mayer-type potential, many-body interactions such as a valence-force field model, and so on. Since these interactions are regarded as short-range ones, there is no problem in evaluating physical quantities based on them by means of a conventional way. Therefore the assumption of Eq. (3) does not impose any restrictions on applications of this algorithm practically.

The potential parameter for the aperiodic system $A_\xi(i)$ obeys the following rule:

$$A_\xi(i)\begin{cases} \neq A_\xi^0(i) & \text{for impurity atoms } (i=1,\ldots,N_{\mathrm{imp}}) \\ =A_\xi^0(i) & \text{otherwise,} \end{cases} \tag{7}$$

where $A_\xi^0(i)$ is the potential parameter of the corresponding ith atom in the reference system, and is also represented by

$$A_\xi^0(i)=A_\xi^0\begin{pmatrix} s \\ l \end{pmatrix}=A_\xi^0\begin{pmatrix} s \\ 0 \end{pmatrix} \quad \text{for all } l, \tag{8}$$

because of the translational periodicity of the reference system. According to values of $A_\xi^0(i)$ and $A_\xi(i)$, all types of impurity atoms (substitutional impurity atoms, interstitial impurity atoms, and defects) can be treated as follows: When $A_\xi^0(i)\neq 0$ and $A_\xi(i)[\neq A_\xi^0(i)]\neq 0$, the atom i in the aperiodic system is given as a substitutional impurity atom. And, an interstitial impurity atom is given by $A_\xi^0(i)=0$ and $A_\xi(i)\neq 0$; a defect is given by $A_\xi^0(i)\neq 0$ and $A_\xi(i)=0$, where the atoms whose potential parameters are zero are called dummy atoms. As for interstitial impurity atoms, dummy atoms are initially positioned in the reference system so as not to change its periodicity, and defects are treated as dummy atoms in the aperiodic system. The consideration of those dummy atoms has no effect on the evaluation of physical quantities for both the reference and the aperiodic systems, because their potential parameters have been set at zero.

C. Energies and forces

In MM and MD simulations, it is necessary to calculate total potential energies and forces acting on constituent atoms. In the present algorithm, these quantities for the aperiodic system are estimated as differences from the reference system. Then, the energy difference ΔE and the force difference $\Delta \mathbf{F}(i)$ are defined as

$$\Delta E = E - E^0 \tag{9}$$

and

$$\Delta \mathbf{F}(i) = \mathbf{F}(i) - \mathbf{F}^0(i), \tag{10}$$

where E and E^0 are the total potential energies for the aperiodic and the reference systems, and $\mathbf{F}(i)$ and $\mathbf{F}^0(i)$ are the forces acting on the ith atom in the aperiodic and the reference systems, respectively. Since E and E^0 represent the total potential energies for the whole systems, their values are divergent. However, the energy difference ΔE has a finite value, which corresponds to the fact that the lattice relaxation occurs only in a local region. Since ΔE represents the energy change caused by local impurities, it is called the impurity energy hereafter.

The impurity energy ΔE and the force difference $\Delta \mathbf{F}(i)$, whose definitions are given by Eqs. (9) and (10), are explicitly calculated from two terms as follows: First, ΔE is written

$$\Delta E = \sum_{\xi} \Delta E_{\xi} = \sum_{\xi} [\Delta E_{\xi}^{(1)} + \Delta E_{\xi}^{(2)}], \tag{11}$$

where

$$\Delta E_{\xi}^{(1)} = \sum_{i}^{N_{\rm imp}} [A_{\xi}(i) - A_{\xi}^0(i)] e_{\xi}^0(i) + \sum_{i}^{N_{\rm imp}} [A_{\xi}(i) - A_{\xi}^0(i)] \times \sum_{j>i}^{N_{\rm imp}} [A_{\xi}(j) - A_{\xi}^0(j)] \psi_{\xi}(r_{ij}^0), \tag{12}$$

$$\Delta E_{\xi}^{(2)} = \sum_{i \in R_{\Delta}}^{N_{\Delta}} A_{\xi}(i) \sum_{j>i}^{\rm all} A_{\xi}(j) \{ \delta r_{ij} \psi_{\xi}^{[1]}(r_{ij}^0) + \tfrac{1}{2} [\delta r_{ij}]^2 \psi_{\xi}^{[2]}(r_{ij}^0) \} + O((\delta r)^3), \tag{13}$$

with

$$\psi_{\xi}^{[k]}(r_{ij}^0) \equiv \frac{d^k}{d[r_{ij}]^k} \psi_{\xi}(r_{ij}) \bigg|_{r=r^0} \tag{14}$$

and

$$\delta r_{ij} = |\mathbf{r}_{ij}| - |\mathbf{r}_{ij}^0|. \tag{15}$$

Second, $\Delta \mathbf{F}(i)$ is written

$$\Delta \mathbf{F}(i) = \sum_{\xi} [\Delta \mathbf{F}_{\xi}(i)] = \sum_{\xi} [\Delta \mathbf{F}_{\xi}^{(1)}(i) + \Delta \mathbf{F}_{\xi}^{(2)}(i)], \tag{16}$$

where the α components of $\Delta \mathbf{F}_{\xi}^{(1)}(i)$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ are given by

$$\Delta F_{\xi,\alpha}^{(1)}(i) = [A_{\xi}(i) - A_{\xi}^0(i)] f_{\xi,\alpha}^0(i) + A_{\xi}(i) \sum_{j}^{N_{\rm imp}} [A_{\xi}(j) - A_{\xi}^0(j)] \psi_{\xi,\alpha}^{\langle 1 \rangle}(r_{ij}^0), \tag{17}$$

$$\Delta F_{\xi,\alpha}^{(2)}(i) = A_{\xi}(i) \sum_{j}^{\rm all} A_{\xi}(j) \left[\sum_{\beta} \Delta r_{ij,\beta} \psi_{\xi,\alpha\beta}^{\langle 2 \rangle}(r_{ij}^0) + \tfrac{1}{2} \sum_{\beta,\gamma} \Delta r_{ij,\beta} \Delta r_{ij,\gamma} \psi_{\xi,\alpha\beta\gamma}^{\langle 3 \rangle}(r_{ij}^0) \right] + O((\Delta r)^3), \tag{18}$$

with

$$\psi_{\xi,\alpha\beta\ldots}^{\langle k \rangle}(r_{ij}^0) \equiv (-1)^k \frac{\partial^k}{\partial r_{ij,\alpha} \partial r_{ij,\beta} \cdots} \psi_{\xi}(r_{ij}) \bigg|_{r=r^0} \tag{19}$$

and

$$\Delta r_{ij,\alpha} = (\Delta \mathbf{r}_{ij})_{\alpha} = (\mathbf{r}_{ij} - \mathbf{r}_{ij}^0)_{\alpha}. \tag{20}$$

In Eqs. (12) and (17), e_{ξ}^0 and $f_{\xi,\alpha}^0$ represent the physical quantities for the reference system, and are given by

$$e_{\xi}^0(i) = e_{\xi}^0\begin{pmatrix} s \\ l \end{pmatrix} = e_{\xi}^0\begin{pmatrix} s \\ 0 \end{pmatrix} = \sum_{s'}^{N^0} \sum_{l'}^{\rm all} A_{\xi}^0\begin{pmatrix} s' \\ l' \end{pmatrix} \psi_{\xi}\left(r^0_{\binom{s\ s'}{0\ l'}}\right) \tag{21}$$

and

$$f_{\xi,\alpha}^0(i) = f_{\xi,\alpha}^0\begin{pmatrix} s \\ l \end{pmatrix} = f_{\xi,\alpha}^0\begin{pmatrix} s \\ 0 \end{pmatrix} = \sum_{s'}^{N^0} \sum_{l'}^{\rm all} A_{\xi}^0\begin{pmatrix} s' \\ l' \end{pmatrix} \psi_{\xi,\alpha}^{\langle 1 \rangle}\left(r^0_{\binom{s\ s'}{0\ l'}}\right). \tag{22}$$

Since the reference system is a periodic one, the notation $\binom{s}{l}$ is adopted in Eqs. (21) and (22), and N^0 means the number of atoms per unit cell. Because of the translational periodicity of the reference system, the Ewald method can be applied to the lattice sums in Eqs. (21) and (22) for the long-range r^{-n} interactions [6,7]. By using $e_{\xi}^0\binom{s}{0}$ and $\mathbf{f}_{\xi}^0\binom{s}{0}$, the total potential energy per unit cell $E_{\rm cell}^0$ and the force acting on the sth atom in the 0th unit cell $\mathbf{F}^0\binom{s}{0}$ are calculated for the reference system as the following expressions:

$$E_{\rm cell}^0 = \sum_{\xi} \left[\frac{1}{2} \sum_{s}^{N^0} A_{\xi}^0\begin{pmatrix} s \\ 0 \end{pmatrix} e_{\xi}^0\begin{pmatrix} s \\ 0 \end{pmatrix} \right] \tag{23}$$

and

$$\mathbf{F}^0\begin{pmatrix} s \\ 0 \end{pmatrix} = \sum_{\xi} \left[A_{\xi}^0\begin{pmatrix} s \\ 0 \end{pmatrix} \mathbf{f}_{\xi}^0\begin{pmatrix} s \\ 0 \end{pmatrix} \right]. \tag{24}$$

According to the framework of this algorithm, there are two kinds of discrepancies between the aperiodic and the corresponding reference systems: one is the discrepancy between the potential parameters and the other is that between the atomic positions. Each of them independently contributes to the two terms in Eqs. (11) and (16) as follows: The first terms $\Delta E_{\xi}^{(1)}$ and $\Delta \mathbf{F}_{\xi}^{(1)}(i)$ are derived from the discrepancy between $A_{\xi}(i)$ and $A_{\xi}^0(i)$, so that the summation in Eqs. (12)

and (17) is running over the N_{imp} impurity atoms only. On the other hand, the second terms $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ are derived from the discrepancy between $\mathbf{r}(i)$ and $\mathbf{r}^0(i)$, and thus are given as a function of δr_{ij} or $\Delta \mathbf{r}_{ij}$ as shown in Eqs. (13) and (18). In these equations, the summation Σ_j^{all} is taken for all atoms interacting with the ith atom inside the relaxation region R_{Δ}. Since the values of δr_{ij} and $\Delta \mathbf{r}_{ij}$ reach zero rapidly as the atom j goes away from the relaxation region R_{Δ}, rapid convergence can be achieved in the calculations of $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$. The aperiodic system is characterized by the infiniteness as a crystal and the local disorder caused by isolated impurities. The infiniteness is taken into account in the first terms $\Delta E_{\xi}^{(1)}$ and $\Delta \mathbf{F}_{\xi}^{(1)}(i)$ through the physical quantities for the reference system $e_{\xi}^{0}\binom{s}{0}$ and $\mathbf{f}_{\xi}^{0}\binom{s}{0}$. And, the local disorder is described by the second terms $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ which are given by the atomic displacements from the reference system.

From the mathematical viewpoint, the first term $\Delta E_{\xi}^{(1)}$ is regarded as the zero-order term in a Taylor expansion of E for δr_{ij}, and $\Delta \mathbf{F}_{\xi}^{(1)}(i)$ is similarly regarded as that of $\mathbf{F}(i)$ for $\Delta \mathbf{r}_{ij}$. And, the second terms $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ correspond to the higher-order terms in those Taylor expansions, which implies that a computational error occurs in the evaluation of $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$, if δr_{ij} and $\Delta \mathbf{r}_{ij}$ become considerably large during MM and MD simulations. We can resolve this problem by changing the atomic positions in the reference system $\mathbf{r}^0(i)$ so as to decrease $|\Delta \mathbf{r}(i)|$. This modification can be carried out by the consideration of dummy atoms in the reference system, such as in the abovementioned case of the interstitial impurity atoms.

In Eqs. (13) and (18), the summation Σ_j^{all} is taken for all atoms interacting with the ith atom inside the relaxation region R_{Δ}. The calculations of $\Delta E_{\xi}^{(2)}$ and $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ converge rapidly, since these terms are given as a function of δr_{ij} or $\Delta \mathbf{r}_{ij}$ whose value reaches zero rapidly as the atom j goes away from the relaxation region R_{Δ}. This rapid convergence is obtained particularly in the calculation of $\Delta \mathbf{F}_{\xi}^{(2)}(i)$. However, in the calculation of $\Delta E_{\xi}^{(2)}$ based on the Coulomb interaction, the convergence is not so easily achieved because of the long-range r^{-1} interaction and the existence of both cations and anions. Thus it is desirable to take the summation so as to satisfy

$$\sum_{j}^{\text{all}} q(j) = \sum_{j}^{N_{\text{imp}}} [q(j) - q^0(j)], \tag{25}$$

which means that the summation Σ_j^{all} in Eq. (13) is taken to keep the charge neutrality except for the impurity atoms, the same as in the Evjen method. From the same reason, the relaxation region R_{Δ} also had better be determined so as to satisfy

$$\sum_{i \in R_{\Delta}}^{N_{\Delta}} q(i) = \sum_{i}^{N_{\text{imp}}} [q(i) - q^0(i)] \tag{26}$$

for energy calculations.

In MM calculations, each atom i is iteratively moved in proportion to the force $\mathbf{F}(i)$ until the equilibrium structure is obtained, and, in MD calculations, the position and the velocity of each atom i at the time $t + \Delta t$ are calculated based on the force $\mathbf{F}(i)$ at the time t by solving Newton's equations. In the present algorithm, the atomic position in the aperiodic system $\mathbf{r}(i)$ is given by Eq. (1) in each iteration step of MM and MD calculations, where the atomic position in the reference system $\mathbf{r}^0\binom{s}{0}$ and the displacement $\Delta \mathbf{r}(i)$ are simultaneously calculated from $\mathbf{F}^0\binom{s}{0}$ and $\Delta \mathbf{F}(i)$, respectively. The iterative calculation for the reference system is not required during the MM calculations, if an optimized crystal structure has been adopted as an initial structure of the reference system. In MD calculations, the atomic velocities $\mathbf{v}(i)$ and $\mathbf{v}^0(i)$ are also considered for the aperiodic and the reference systems, and $\mathbf{v}(i)$ is given by $\mathbf{v}^0(i) + \Delta \mathbf{v}(i)$, the same as in Eq. (1). However, to apply the present algorithm directly to MD calculations, the unit cell of the reference system should be taken much larger than that in MM calculations because of the lattice vibration caused by the temperature effect, and there is a difficulty in realizing a practical MD calculation based on the present algorithm from the viewpoint of the efficiency for computational time. The size of the relaxation region R_{Δ} can be variable during progress of the MM and MD calculations, which means that it is possible to optimize the atomic number N_{Δ} which gives the degree of freedom to describe the lattice relaxation. This variability of the relaxation region R_{Δ} is one of the advantages of the proposed algorithm as compared with the supercell method which does not allow the size of unit cells to be changed during the simulations.

III. MM CALCULATIONS

In this section, the numerical results of MM calculations are presented. In order to make a clear comparison between the present algorithm and the supercell method, the MM calculations have been carried out for ionic systems with the long-range Coulomb interaction. As a typical ionic system, NaCl alkali halide crystal has been chosen here. The interatomic potential for NaCl is given by the Coulomb and the Born-Mayer-type potentials as follows:

$$\phi(r_{ij}) = \frac{e^2}{4\pi\varepsilon_0} \frac{q(i)q(j)}{r_{ij}} + c_1 \exp\left[-c_2 \frac{r_{ij}}{\rho(i) + \rho(j)} \right], \tag{27}$$

where $\rho(i)$ represents the effective radius of the ith ion. The constants c_1 and c_2 are fixed at 1822 eV and 12.364, respectively [8]. The values of the potential parameters $q(i)$ and $\rho(i)$ have been determined as follows: $q(i) = 1$ and $\rho(i) = 1.85$ Å for Na ions, and $q(i) = -1$ and $\rho(i) = 1.85$ Å for Cl ions. According to these potential parameters, the calculated perfect crystal structure is stabilized as a fcc structure with the experimental lattice constant ($a = 5.63$ Å). In the MM calculations based on the present algorithm, the formulation described in Sec. II has been applied to the long-range Coulomb interaction. In the supercell method, the energy change caused by local impurities $\Delta E_{\text{cell}}^{\text{SC}}$, which should be compared with the impurity energy ΔE evaluated in the present algorithm, is defined as

$$\Delta E_{\text{cell}}^{\text{SC}} = E_{\text{cell}}^{\text{SC}} - E_{\text{cell}}^{\text{SC},0}, \tag{28}$$

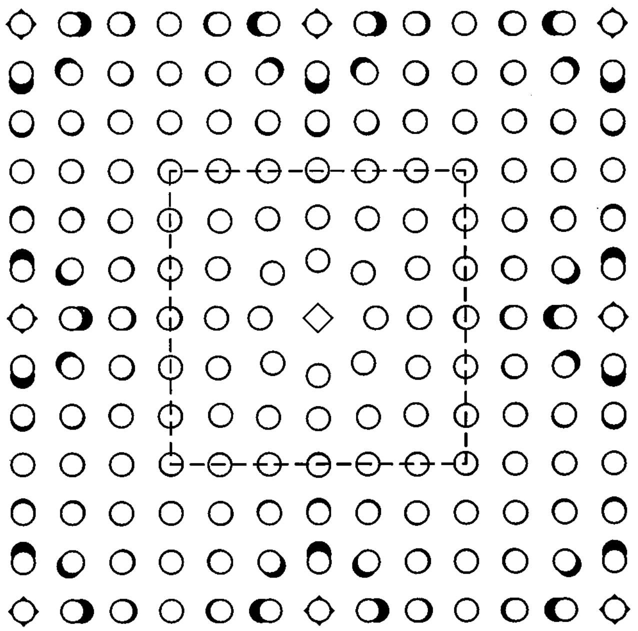

FIG. 1. Cross section of the stable structure of an aperiodic NaCl system containing one substitutional impurity Cl ion (case I) calculated by the present algorithm (open circles), together with that of the supercell method (closed circles). An open diamond shows the impurity ion in the present algorithm, and closed diamonds show impurity ions in neighboring cells in the supercell method. A dashed line indicates a supercell with 216 constituent ions. Na cations and Cl anions are not distinguished in this figure for simplicity.

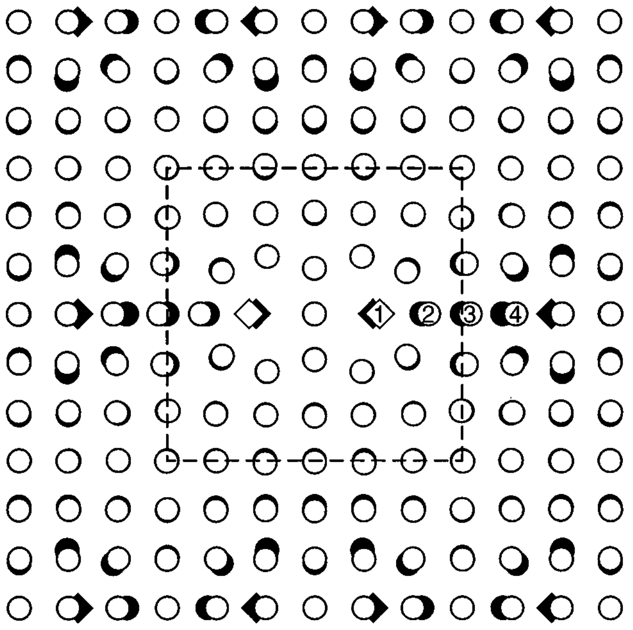

FIG. 2. Cross section of the stable structure of an aperiodic NaCl system containing two substitutional impurity Cl ions (case II) calculated by the present algorithm (open circles), together with that of the supercell method (closed circles). The impurity ions are shown by open and closed diamonds in the results of these two methods. A dashed line indicates a supercell with 216 constituent ions.

where $E_{\text{cell}}^{\text{SC}}$ and $E_{\text{cell}}^{\text{SC},0}$ represent the total potential energies per unit cell for systems with the impurity atoms and without any impurity atoms, respectively.

The MM calculations have been performed for the following two cases: one is a NaCl system where one Na ion has been substituted by one Cl ion (case I), and the other is a NaCl system where two Na ions have been substituted by two Cl ions (case II). For these aperiodic systems, a perfect crystal of NaCl whose cubic unit cell contains eight constituent ions has been considered as the reference system. In the MM calculations performed here, the perfect crystal of NaCl is given as an initial structure, and the same conditions (the constant rate at which each atom is moved and the convergence criterion) are adopted in the two methods for a direct comparison between them. The MM calculations have been judged to be convergent, when the maximum force became 0.01 times that in the initial structure.

Case I. The calculated stable structures of an aperiodic NaCl system containing one substitutional impurity ion are shown in Fig. 1, where open and closed circles indicate the ionic positions obtained by this algorithm and the supercell method, respectively. Whereas only one impurity ion (an open diamond) exists in the structure of the present algorithm, artificial impurity ions (closed diamonds) also exist in neighboring cells in the supercell method. The relaxation region R_Δ having the same size as the unit cell of the supercell method, which is shown by a dashed line, has been considered in the present algorithm. Although the stable structure calculated by the supercell method shows artificial lattice relaxation because of the periodic boundary condition, there is no notable difference between the results of the two methods inside the center unit cell. This result indicates that the lattice relaxation in case I occurs in a relatively small region, and the unit cell used in the supercell method has adequate size to describe such a small relaxation. However, a large difference between the two methods has been obtained for computational time, which means that CPU time consumed by the supercell method is about ten times longer than that of the proposed algorithm. Moreover, whereas the impurity energy ΔE of 6.9 eV is obtained by the proposed algorithm, only $\Delta E_{\text{cell}}^{\text{SC}}$ of 4.3 eV is evaluated by the supercell method. These disagreements are discussed in more detail in the next section.

Case II. The calculated stable structures of aperiodic NaCl system containing two impurity atoms are shown in Fig. 2, where the same notations as in Fig. 1 are adopted. In case II, the two substituted ions cause an anisotropic relaxation which has a larger expansion than that of case I. The relaxation region R_Δ containing 1815 ($=5\times11\times11$) ions has been adopted in the present algorithm. In Fig. 2, the two stable structures obtained give a disagreement which is significant even inside the center cell. This result means that, for aperiodic systems containing a large relaxation such as case II, the supercell with 216 constituent ions is not large enough to investigate the structural stability.

In order to investigate the dependence on the size of supercells and make a comparison between the two methods quantitatively, the MM calculations for case II have been performed by using four more supercells of larger sizes. The calculated displacements of four atoms, which are specified in Fig. 2, are shown in Fig. 3. The solid lines indicate the relaxation ratio to the atomic displacements calculated by the

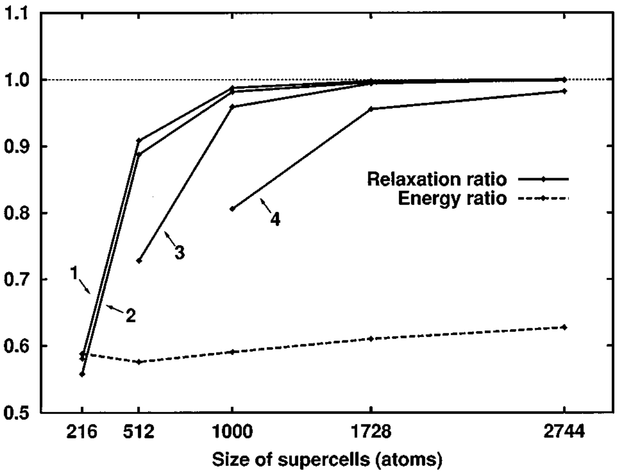

FIG. 3. Atomic displacements and impurity energy for case II obtained by the supercell method are shown as a ratio to the corresponding result calculated by the proposed algorithm. Solid lines show the relaxation ratio of four atoms numbered in Fig. 2, and a dashed line shows the energy ratio. The values of the atomic displacements and the impurity energy calculated by the proposed algorithm are shown as 1.0.

present algorithm. From this figure, it has been found that the relaxation ratio obtained by the small supercell containing 216 atoms reaches only about 55%. With increasing size of supercells, the relaxation ratio of the four atoms approaches the value of 1.0, and a good agreement is given by the supercell with 2744 constituent atoms. However, in the calculation based on this supercell, CPU time which is about 45 times longer than that of the proposed algorithm has been consumed. In Fig. 3, the impurity energy $\Delta E_{\rm cell}^{\rm SC}$ is also shown as a ratio to ΔE of 15.7 eV obtained by the proposed algorithm. Even $\Delta E_{\rm cell}^{\rm SC}$ calculated by the large supercell containing 2744 atoms is 9.9 eV, and this value is only 63% of ΔE as shown in Fig. 3. This result indicates that the asymptotic behavior of energies depending on system sizes is much slower than that of the lattice relaxation, and the supercell containing 2744 constituent atoms is not large enough to calculate the energy change introduced by impurity atoms, although case II has simple lattice relaxation.

IV. DISCUSSIONS

First, let us discuss the numerical accuracy attained by the present algorithm. Since the supercell method assumes the periodic boundary condition, artificial interactions exist between the impurity atoms inevitably positioned in each unit cell. This periodic approximation is not introduced in the present algorithm, and it is capable of evaluating a value which corresponds to the asymptotic solution obtained by the infinite-sized supercell as shown in Fig. 3. Moreover, this algorithm has the following advantage for the Coulomb interaction: For aperiodic systems where the charge neutrality has been broken by local impurity atoms, in the case of the supercell method it is necessary to add a uniform background charge to each constituent atom, in order to keep the charge neutrality in the whole system and avoid a divergence of total potential energies. For example, in case II, uniform charges ($q_{\rm add}=4/N^{\rm SC}$) have been added to all $N^{\rm SC}$ atoms in a unit cell. Since the amount of additional charges is usually small, their existence has no serious effect on the interatomic potential itself and the evaluation of forces. It, however, has a large influence on the evaluation of energies. As shown in Fig. 3, the impurity energy for case II is underestimated by the supercell method, and the deviation from that of the present algorithm is about 5.8 eV. This disagreement is caused by two artificial influences introduced in the supercell method: one originates from impurity atoms periodically positioned in surrounding cells, and the other originates from background charges added to each atom. If only the former influence exists, the energy change $\Delta E_{\rm cell}^{\rm SC}$ will be overestimated because the interaction between the impurities positioned in different supercells is always evaluated as a positive value. On the other hand, since the background charge has the opposite sign of the impurity ions, the interaction between them is given as a negative value and consequently causes the above-mentioned underestimation. In addition, the approach of $\Delta E_{\rm cell}^{\rm SC}$ to the asymptotic value is very slow as shown in Fig. 3, which implies that it is difficult for the supercell method to even estimate the exact value for completely isolated impurities. In contrast to this conventional method, since the proposed algorithm does not need any artificial corrections for charge distribution, impurity energies for ionic aperiodic systems can also be evaluated exactly.

Next, the computational time is discussed as the second advantage of the present algorithm. The efficient MM calculations reported in Sec. III are due to the calculation of forces which is given by the two terms with the following characteristics: The first term $\Delta\mathbf{F}_{\xi}^{(1)}(i)$ shown in Eq. (17) is evaluated from the physical quantity for the reference system $\mathbf{f}_{\xi}^{0}(i)$ given by Eq. (22). Then, the amount of calculations for $\Delta\mathbf{F}_{\xi}^{(1)}(i)$ becomes small, and its order is given by $N^0N_{\rm all}$, where $N_{\rm all}$ means the number of all atoms interacting on N^0 atoms. In this order estimation, the second term in Eq. (17) is negligible since $N_{\rm imp} \ll N^0N_{\rm all}$. The value of $N_{\rm all}$ is related to the lattice sum in Eq. (22), and the Ewald method can be applied to this summation for the long-range r^{-n} interactions. The second term $\Delta\mathbf{F}_{\xi}^{(2)}(i)$ given by Eq. (18) is written in a function of $\Delta\mathbf{r}_{ij}$, and its amount of calculations is estimated as $N_{\Delta}N'_{\rm all}$. In contrast to the force whose function form is given by $r^{-(n+1)}$, the force difference introduced in the proposed algorithm roughly shows $\Delta r r^{-(n+2)}$. This function form causes the rapid convergence of Eq. (18), and we can obtain $N'_{\rm all} \ll N_{\rm all}$. As for case II, the amount of calculations in the present algorithm is roughly given by $N^0N_{\rm all} \sim 10\times 6000$ and $N_{\Delta}N'_{\rm all} \sim 2000\times 3000$. In MM simulations, it is not necessary to calculate the first term $\Delta\mathbf{F}_{\xi}^{(1)}(i)$ during iteration steps, if the initial structure of the reference system has been optimized before the simulation. Thus $N^0N_{\rm all}$ can be omitted in the computational time estimation for MM simulations. On the other hand, the calculation based on the supercell method has the order of $N^{\rm SC}N_{\rm all}$, where the Ewald method is also applied to the lattice sum for the long-range r^{-n} interactions. In the calculation for case II by using the supercell containing 2744 constituent atoms, $N^{\rm SC}N_{\rm all}$ becomes about $3000\times 75\,000$. Consequently we obtain $(N^{\rm SC}N_{\rm all})/(N_{\Delta}N'_{\rm all}) \sim 40$, which indicates that the MM calculation based on the proposed algorithm is accelerated about 40 times as fast as in the supercell method. This rough estimation corresponds to the result reported in Sec. III, and it has been ascertained that the proposed algorithm achieves the saving of much computational time as compared with the conventional supercell method. A similar estimation is possible for the calculation of energies. However, it should be noted that the energy difference $\Delta E_{\xi}^{(2)}$ based on the Coulomb interaction does not converge as rapidly as $\Delta \mathbf{F}_{\xi}^{(2)}(i)$ because of the long-range r^{-1} interaction and the existence of both cations and anions, so that N'_{all} is required to have a larger value than the force difference as mentioned in Sec. II C.

V. CONCLUSIONS

In this paper, an algorithm of MM and MD calculations has been presented for aperiodic systems with long-range interactions. Since this algorithm is particularly effective for the long-range Coulomb interaction, the MM calculations have been carried out for ionic systems containing local impurity atoms. The calculated lattice relaxation and impurity energy have been compared with the results calculated by the conventional supercell method.

A characteristic of this algorithm is that it describes the crystal structure of the aperiodic system based on the deviation from a periodic system. According to this description, two characteristics of the aperiodic system, the infiniteness and the local disorder, are simultaneously taken into account, and physical quantities can be evaluated for completely isolated impurities. Moreover, for aperiodic systems where the charge neutrality has been lost, the present algorithm does not need any additional background charges, which enables us to perform MM and MD simulations for ionic aperiodic systems with real charge distribution.

According to the above-mentioned description of crystal structures, the impurity energy and the force difference are evaluated from the two terms. These two terms, which are characterized by a small amount of calculations and a rapid convergency, achieve efficient MM simulations. In the test calculations, the computational time which is several tens of times faster than that of the conventional supercell method has been obtained. This result implies that there is a possibility of applications to systems whose number of constituent atoms is more than an order of magnitude larger than present systems.

In this paper, only the implementation of the MM calculations based on the proposed algorithm has been reported. The extension for MD calculations is now in progress. Furthermore, from the viewpoint of practical applications, it is important to combine this algorithm with *ab initio* calculations, which is an open and interesting problem for a future study.

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