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Empirical tight-binding force model for molecular-dynamics simulation of Si

C. Z. Wang, C. T. Chan, and K. M. Ho
Microelectronics Research Center and Department of Physics, Iowa State University of Science and Technology, Ames, Iowa 50011
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A scheme of molecular-dynamics simulation using the empirical tight-binding force model is proposed. The scheme allows the interatomic interactions involved in the molecular dynamics to be determined by first-principles total-energy and electronic-structure calculations without resorting to fitting experimental data. For a first application of the scheme we show that a very simple nearest-neighbor two-center empirical tight-binding force model is able to stabilize the diamond structure of Si within a reasonable temperature range. We also show that the scheme makes possible the quantitative calculation of the temperature dependence of various anharmonic effects such as lattice thermal expansion, temperature-dependent phonon linewidths, and phonon frequency shifts.

I. INTRODUCTION

Molecular-dynamics simulation has been attracting a lot of interest due to its powerful capability in the studies of systems as a function of temperature, in the investigation of kinetics in various processes, as well as in locating the ground state of complex systems with many degrees of freedom. However, the application of the method to real systems is limited by our knowledge of the interaction potentials or forces among the atoms. Modeling the interatomic forces for molecular-dynamics simulation of real systems therefore provides an important goal and a significant challenge to theory. Such is the case, for example, for the molecular-dynamics simulation of tetrahedral silicon.

It is known that no conventional pair potential can stabilize the tetrahedral structure because pair potentials fail to represent the strong electronic covalent binding effects present in such a structure. A number of empirical interatomic potentials recently proposed for the molecular-dynamics simulation of Si had to include three-body interactions.[1-5] Even with the addition of complicated forms for the interaction, it is difficult to find a potential which can satisfactorily describe all the properties of Si.[6] The reason is that the quantum-mechanical and directional nature of the bonding in Si cannot be easily incorporated into these potentials which are based on classical approximations. In addition, even when these potentials reproduce experimental values it is hard to relate the properties of the solid to the underlying electronic structure in order to unearth the microscopic origins of such behavior. On the other hand, much progress has been made during the past decade in the calculation of various structural and vibrational properties of solids in a fundamental first-principles approach with the use of density-functional calculations. However, such calculations are almost always limited to considerations of zero-temperature systems. The investigation of disorder and temperature effects is still a difficult and largely unsolved problem.

In a recent paper,[7] Car and Parrinello proposed a scheme which unifies the approaches of density-functional theory and molecular dynamics and allows the interatomic forces of Si to be calculated by fully quantum-mechanical calculations in the course of molecular-dynamics simulations. This scheme is, in principle, fundamental and superior. However, in practice it requires so much computational effort that, at present, it is restricted to very short simulation times and a small number of atoms. It does represent a method which will become more desirable in the future when computers become even more powerful.

The limitation of the Car-Parrinello scheme is mainly due to two reasons. Firstly, the use of plane waves as a basis to expand the electron wave functions limits the number of atoms used in the simulation due to the large number of basis functions required in the calculation. Secondly, because of the inclusion of degrees of freedom from the electron wave functions (Ψ's) in the molecular dynamics, the simulation time step has to be chosen much smaller than that in simulations with classical potentials (typically ten times smaller).

In this paper, we propose a simplified Car-Parrinello scheme designed for molecular-dynamics simulations involving larger numbers of atoms. This scheme tries to overcome the difficulties in the Car-Parrinello approach by calculating the electronic energies and Hellmann-Feynman forces by an empirical tight-binding method rather than by the density-functional method. Although less rigorous, the empirical tight-binding calculation involves only a few atomic orbitals for each atom to represent the electronic states, thus larger numbers of atoms can be tackled within the present computer capabilities. Also, since the electronic degrees of freedom are not explicitly included in the molecular-dynamics simulation larger time steps can be used. The use of the empirical tight-binding method to simplify the problem is justified by numerous successful applications of the method to the study of surface relaxation and reconstruction, surface vibrations of crystalline Si, as well as geometries of Si clusters and steps on surface.[8-11]

Although our scheme is somewhat simplified, it has the advantage over classical empirical potential models in that the interatomic interactions are determined at the

microscopic level by first-principles total-energy and electronic-structure calculations without resorting to fitting experimental data; also the covalent bonding of the material enters in a natural way from the electronic structure without appealing to three-body potentials.

We arrange our paper as follows. In Sec. II the general features of the empirical tight-binding molecular-dynamics scheme are described. The determination of the potential parameters for the molecular-dynamics simulation of crystalline Si is discussed in Sec. III. Some molecular-dynamics simulation results obtained using the present scheme will be presented in Sec. IV. Finally, we close our paper with concluding remarks in Sec. V.

II. EMPIRICAL TIGHT-BINDING MODEL FOR MOLECULAR-DYNAMICS SIMULATION

We model the interatomic potential for a given configuration of N atoms $\{\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N\}$ by expressing the total potential energy (per atom) of the system as

$$E_{\rm tot}\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}=E_{\rm BS}\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}+U\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}\ , \tag{2.1}$$

where $E_{\rm BS}=N^{-1}\sum_{j=1}^{N}E_j$ is the "band-structure" energy (per atom) consisting of the sum of the eigenvalues E_j for the occupied part of the electronic band structure. In the present scheme, E_j is calculated by the Slater-Koster empirical tight-binding method[12] with the tight-binding parameters determined by fitting the calculated electronic structure of Si:

$$U\{\mathbf{r}_1,\ldots,\mathbf{r}_N\}=\frac{1}{2N}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\phi(r_{ij})$$

is a short-ranged two-body potential representing the sum of the ion-ion repulsion and the correction to the double counting of the electron-electron interaction in the band-structure energy $E_{\rm BS}$. $\phi(r_{ij})$ can be determined by subtracting the volume-dependent band-structure energy $E_{\rm BS}$ from the energy-versus-volume curve obtained from first-principles total-energy calculations.

The potentials modeled as (2.1) are easy to insert into the standard molecular-dynamics routine as illustrated in Fig. 1. The interatomic force necessary for performing the molecular-dynamics run is expressed as a sum of two-body forces of the type of $-(d\phi/dr_{ij})\hat{r}_{ij}$ and a contribution coming from the band-structure energy. In the empirical tight-binding scheme, such electronic forces or Hellmann-Feynman forces are easy to calculate, especially since we employed a two-center approximation for the tight-binding integrals. The force acting on atom n arising from the band-structure energy $E_{\rm BS}$ is given by

$$\mathbf{F}_n=-\sum_j\langle\psi_j|\partial\underline{H}/\partial\tau_n|\psi_j\rangle\ , \tag{2.2}$$

where $\underline{H}$ is the tight-binding Hamiltonian matrix and τ_n is the coordinate of atom n. The sum j is over occupied levels E_j with eigenfunctions ψ_j. For a periodic system, the sum over j is replaced by sums over the band index and wave vector. By writing the eigenfunction in terms

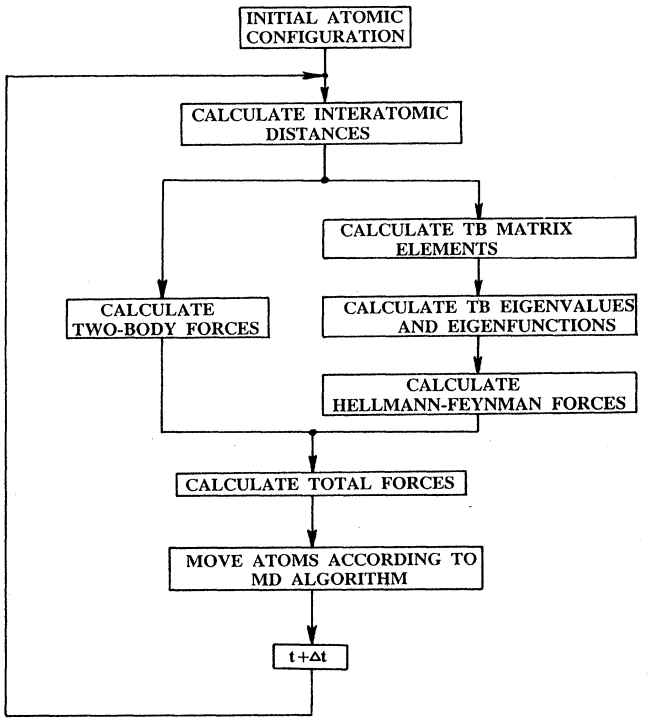

FIG. 1. An illustration of empirical tight-binding molecular-dynamics (ETBMD) routine.

of the basis functions f_m,

$$\psi=\sum_{m,n}\lambda_{mn}f_m(\mathbf{r}-\tau_n)\ , \tag{2.3}$$

it is easy to find

$$\mathbf{F}_n=-\sum_j\sum_m\sum_{m'}\sum_{n'}\lambda^*_{jmn}\lambda_{jm'n'}\,\partial H_{m'n'mn}/\partial\tau_n \tag{2.4}$$

or

$$\mathbf{F}_n=-\sum_{n'}\sum_j\sum_m\sum_{m'}\lambda^*_{jm'n'}\lambda_{jmn}\,\partial H_{m'n'mn}/\partial\tau_n=\sum_{n'}\mathbf{F}_{nn'} \tag{2.5}$$

with

$$\mathbf{F}_{nn'}=-\sum_j\sum_{m,m'}\lambda^*_{jmn}\lambda_{jm'n'}\,\partial H_{m'n'mn}/\partial\tau_n\ . \tag{2.6}$$

The $\mathbf{F}_{nn'}$ appearing in (2.5) is a many-body force because the electronic states sample the environment of the interacting atoms n and n' in the system. Since the quantum-mechanical electronic bonding of the system enters explicitly into our calculation through the tight-binding wave functions, we hope the forces calculated in this way will give a better representation of the true atomic interactions in the real system than previous schemes based on classical approximations. The inclusion of the overlap matrix $\underline{S}$ in a nonorthogonal tight-binding scheme can be taken into account by replacing the Hamiltonian matrix $\underline{H}$ by the $\underline{H}$-$E_j\underline{S}$ matrix in the above formulas.

III. DETERMINATION OF POTENTIALS FOR SI

As a first application of the empirical tight-binding molecular-dynamics (ETBMD) scheme, we study the temperature-dependent properties of diamond-structured Si: temperature-dependent structural stability, thermal expansion, temperature-dependent phonon linewidths, and phonon frequency shifts. As far as we know, there have been no previous molecular-dynamics studies of these properties for Si.

The tight-binding parameters required for describing the electronic structure are obtained from Chadi's previous work on the empirical orthogonal tight-binding model for Si.[8] Explicitly, the electronic states are represented by an orthogonal basis containing four sp^3 orbitals per Si atom. The two-center approximation is used for the expressions for interatomic matrix elements and only nearest-neighbor interactions are taken into account. There are six tight-binding parameters in this model including the on-site energies. These parameters are determined by fitting to the calculated band structure of diamond-structured Si, which gives

$$\begin{aligned} &V_{ss\sigma}(d_0)=-1.94\ \text{eV},\quad V_{sp\sigma}(d_0)=1.75\ \text{eV}\ , \\ &V_{pp\sigma}(d_0)=3.05\ \text{eV},\quad V_{pp\pi}(d_0)=-1.08\ \text{eV}\ , \\ &E_s=-5.20\ \text{eV},\quad E_p=1.20\ \text{eV}\ , \end{aligned} \tag{3.1}$$

after Chadi's work,[8] where d_0 is the $T=0$ equilibrium nearest-neighbor distance. The bond-length dependence of the two-center parameters is assumed to follow Harrison's universal r^{-2} scaling behavior:[11]

$$\begin{aligned} V_{ss\sigma}(r)&=V_{ss\sigma}(d_0)d_0^2/r^2\ , \\ V_{sp\sigma}(r)&=V_{sp\sigma}(d_0)d_0^2/r^2\ , \\ V_{pp\sigma}(r)&=V_{pp\sigma}(d_0)d_0^2/r^2\ , \\ V_{pp\pi}(r)&=V_{pp\pi}(d_0)d_0^2/r^2\ . \end{aligned} \tag{3.2}$$

Although this tight-binding model for Si is very simple, it has been shown by Chadi and by Alerhand and Mele that it describes quite well the $T=0$ structural and dynamical properties of bulk Si as well as various surfaces of Si.[8,9]

Unlike the original Chadi model, which fit the two-body potential to the lattice constant and the bulk modulus of Si, we have determined the two-body potential energy function $U(r)$ by subtracting the ETB band-structure energy function $E_{\rm BS}(r)$ from the first-principles calculated $T=0$ total-energy function $E_{\rm tot}(r)$, i.e.,

$$U(r)=E_{\rm tot}(r)-E_{\rm BS}(r)\ , \tag{3.3}$$

where r is the nearest-neighbor distance of the diamond structure. The total-energy function $E_{\rm tot}(r)$ is taken from the results of Yin and Cohen[13] and fitted to the universal binding-energy curve

$$E_{\rm tot}(r)=E_0[1+(r-r_0)/A\,]\exp[-(r-r_0)/A\,] \tag{3.4}$$

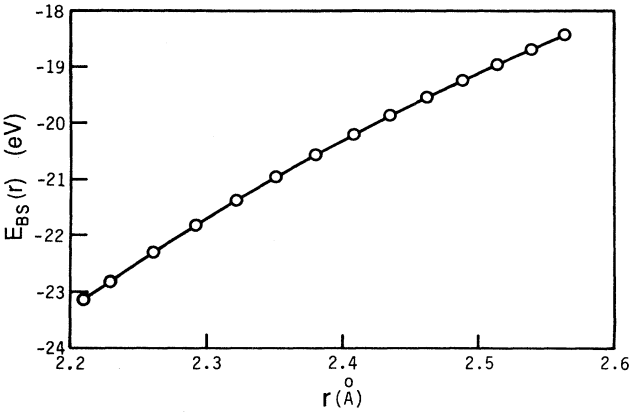

FIG. 3. Band-structure energy $E_{\rm BS}$ (per atom) of Si in diamond structure as a function of nearest-neighbor distance r. The circles are the results of empirical tight-binding calculation; the solid line is the fitting third-order polynomical function.

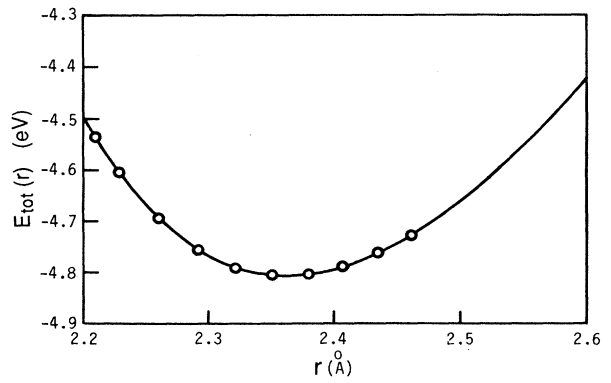

FIG. 2. Total potential energy $E_{\rm tot}$ (per atom) of Si in diamond structure as a function of nearest-neighbor distance r. The circles are the first-principles calculation results. The solid line is the fitting universal binding-energy curve.

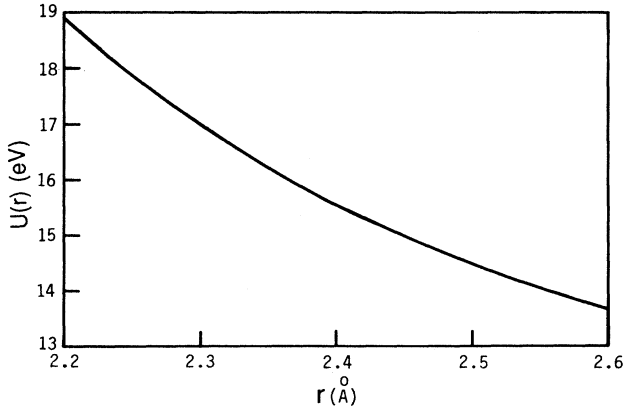

FIG. 4. Two-body potential energy U (per atom) of Si in the diamond structure as a function of nearest-neighbor distance r obtained by subtracting $E_{\rm BS}(r)$ of 3.5 from the total-energy function $E_{\rm tot}(r)$ of 3.4.

TABLE I. $T=0$ K equilibrium properties of diamond Si obtained by the present empirical tight-binding model are compared with the first-principles calculation results and with experiment. The first-principles results are taken from Refs. 13 and 14. The experimental data are also quoted from Ref. 13. A misprint in Table VI of Ref. 13 has been corrected [the values assigned to LOA(X) and TO(X) have been interchanged].

	This work (with 64 atoms)	This work (with 216 atoms)	First-principles calculations	Experiment
Lattice constant (Å)	5.456	5.456	5.456[a]	5.44
B (10^{11} erg/cm^3)	9.20	9.20	9.20[a]	9.78
$C_{11}-C_{12}$ (10^{11} erg/cm^3)	7.25	7.10	9.80[b]	10.12
C_{44}^0 (10^{11} erg/cm^3)	10.26	10.19	11.10[b]	
C_{44} (10^{11} erg/cm^3)	6.16	6.17	8.50[b]	7.96
LTO(Γ) THz	16.95	16.70	15.16[a]	15.53
TA(X) THz	4.96	4.96	4.45[a]	4.49
TO(X) THz	14.71	14.68	13.48[a]	13.90
LOA(X) THz	12.37	12.33	12.16[a]	12.32
$\gamma_{\mathrm{LTO}}(\Gamma)$	0.98	0.99	0.92[a]	0.98
$\gamma_{\mathrm{TA}}(X)$	−1.12	−1.13	−1.50[a]	−1.40
$\gamma_{\mathrm{TO}}(X)$	1.37	1.42	1.34[a]	1.50
$\gamma_{\mathrm{LOA}}(X)$	1.02	1.03	0.92[a]	0.90

[a]Reference 13.
[b]Reference 14.

with $E_0=-4.8060$ eV, $r_0=2.3627$ Å, and $A=0.5076$ Å, as shown in Fig. 2. The ETB results of $E_{\mathrm{BS}}(r)$ can also be fit to a third-order polynomial function

$$E_{\mathrm{BS}}(r)=A_0+A_1(r-r_b)+A_2(r-r_b)^2+A_3(r-r_b)^3 \tag{3.5}$$

with $A_0=-23.37$ eV, $A_1=17.32$ eV/Å, $A_2=-12.42$ eV/Å^2, $A_3=5.25$ eV/Å^3, and $r_b=2.20$ Å as shown in Fig. 3. The resulting $U(r)$ is shown in Fig. 4.

By further assuming that the two-body potential contains only nearest-neighbor interactions and each nearest neighbor contributes equally to the total two-body potential energy, we can extract the pair potential for the molecular-dynamics simulation

$$\phi(r_{ij})=\tfrac{1}{2}[E_{\mathrm{tot}}(r_{ij})-E_{\mathrm{BS}}(r_{ij})] \tag{3.6}$$

which can be expressed analytically via the analytic expression of $E_{\mathrm{tot}}(r)$ and $E_{\mathrm{BS}}(r)$.

Before proceeding to the molecular-dynamics simulation, we have used the constructed potential model to study the $T=0$ properties of Si. The results, compared with first-principles calculations and with experiment, are listed in Table I. The agreement is generally good. In particular, the correct prediction of the negative Grüneisen parameter for the TA(X) mode with our model is quite encouraging. The above represents a well-defined procedure for constructing model potentials that can be applied to any material where information about the electronic structure and total energy versus volume of the ground state system are available from first-principles calculations.

IV. RESULTS FROM MOLECULAR-DYNAMICS SIMULATIONS

The ETB potential model constructed in the preceding section was used for the molecular-dynamics simulations of crystalline Si at finite temperatures. The simulations were performed with 64 Si atoms initially arranged in the diamond structure in a periodic cubic "box." A flow chart indicating the steps performed in our molecular-dynamics simulations with the above scheme is given in Fig. 1. Only the Γ point was used to evaluate the tight-binding electronic structure and Hellmann-Feynman forces. However, because of the 64-atom–supercell geometry, this is equivalent to a **k**-point sampling of 32 points in the Brillouin zone for the primitive diamond-structure cell. The convergence of the sampling grid point is tested by comparing the $T=0$ static properties calculated using the Γ point with 64 atoms per unit cell and with 216 atoms per unit cell (see Table I). The equations of motion of the Si atoms were solved by a predictor-corrector algorithm[15] with time step $\Delta t=1.07\times10^{-15}$ s. This choice of time step conserved the total energy of the system within an accuracy of 4×10^{-6} eV over 18 000 MD steps in the simulation for a microcanonical (N,V,E) ensemble at $T=100$ K.

In order to test the stability of the diamond structure at finite temperature within the ETB potential model, we have run the molecular dynamics for an (N,V,E) ensemble at a number of temperatures ranging from $T=100$ K to $T=1035$ K. The MD steps used for each temperature are over 22,000 steps corresponding to 2.2×10^{-11} s. It can be seen from the temperature-dependent pair-correlation functions of Fig. 5 that the diamond structure is indeed stable in this temperature range. The total energy of the system as a function of temperature shows a

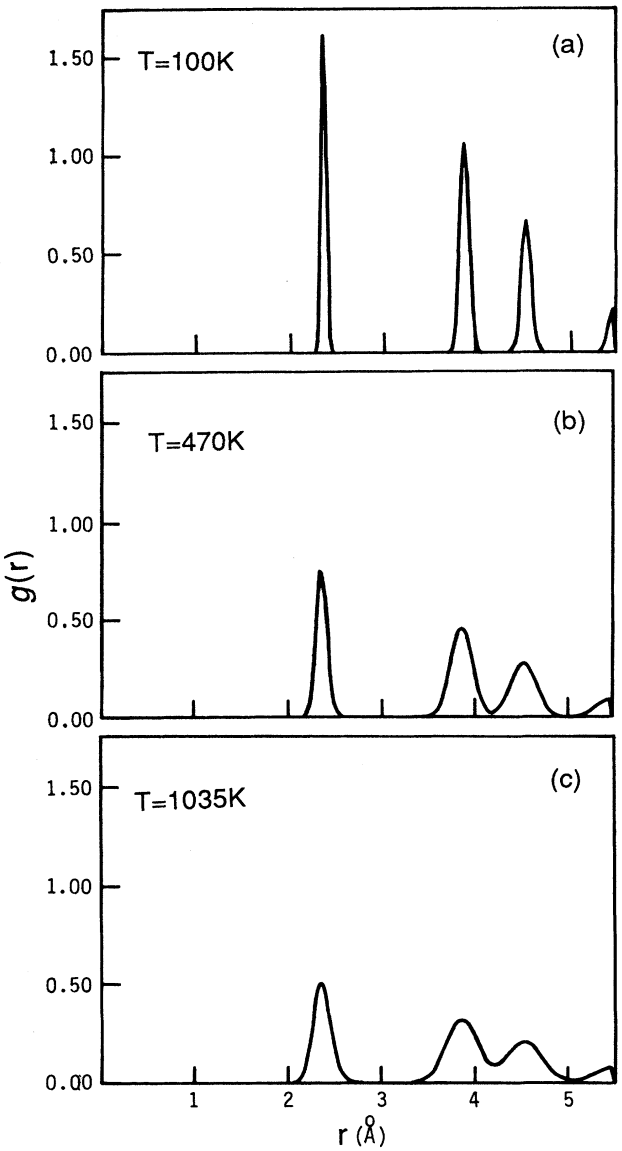

FIG. 5. Molecular-dynamics results of temperature-dependent pair-correlation function.

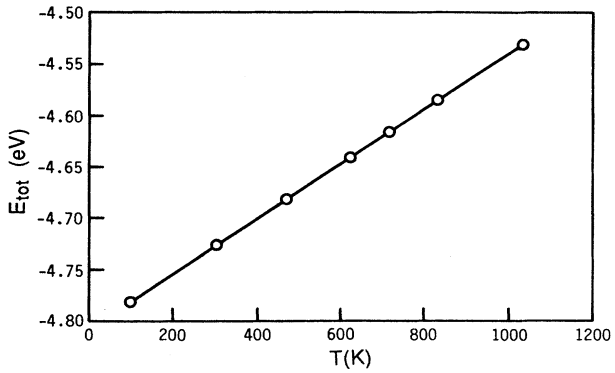

FIG. 6. The total energy (per atom) of the system as a function of temperature obtained from the microcanonical molecular-dynamics simulation.

linear behavior as displayed in Fig. 6. Further evidence is provided by the temperature-dependent dynamics of Figs. 7 and 8. The phonon spectral intensities at each temperature are calculated by taking the Fourier transform of the velocity-velocity autocorrelation function, defined as

$$G(\mathbf{k},\omega)=\int dt\, e^{i\omega t}\sum_n e^{-i\mathbf{k}\cdot\mathbf{R}_n}\frac{\langle \mathbf{v}_n(t)\cdot\mathbf{v}_0(0)\rangle}{\langle \mathbf{v}_n(0)\cdot\mathbf{v}_0(0)\rangle} \quad (4.1)$$

with $\mathbf{K}=(1,1,1)2\pi/a$ for the LTO(Γ) mode and $\mathbf{K}=(0,0,1)2\pi/a$ for the TA(X), TO(X), and LOA(X) modes, respectively, and $\mathbf{R}_n$ is the lattice position of atom n. The results in Figs. 7 and 8 show that all of these high-symmetry modes are very stable even at temperature as high as $T=1035$ K. Slight shifts in frequencies and broadening in the linewidths are due to the effects of the anharmonic interactions.

From the calculated phonon spectral intensities we can extract temperature-dependent phonon frequency shifts and phonon linewidths for the phonon modes of Si at the

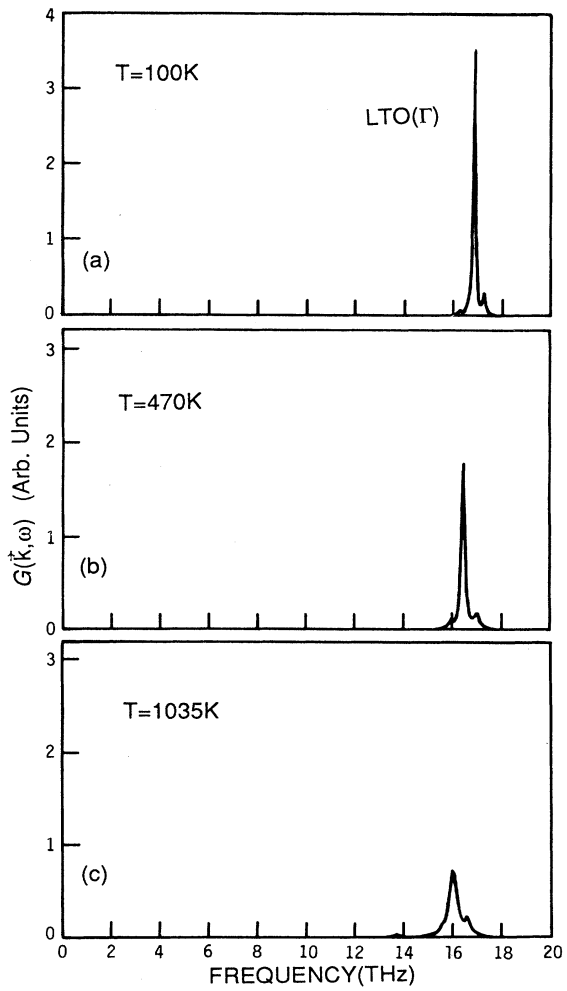

FIG. 7. Molecular-dynamics results of temperature-dependent phonon spectral intensity of the LTO(Γ) mode of Si.

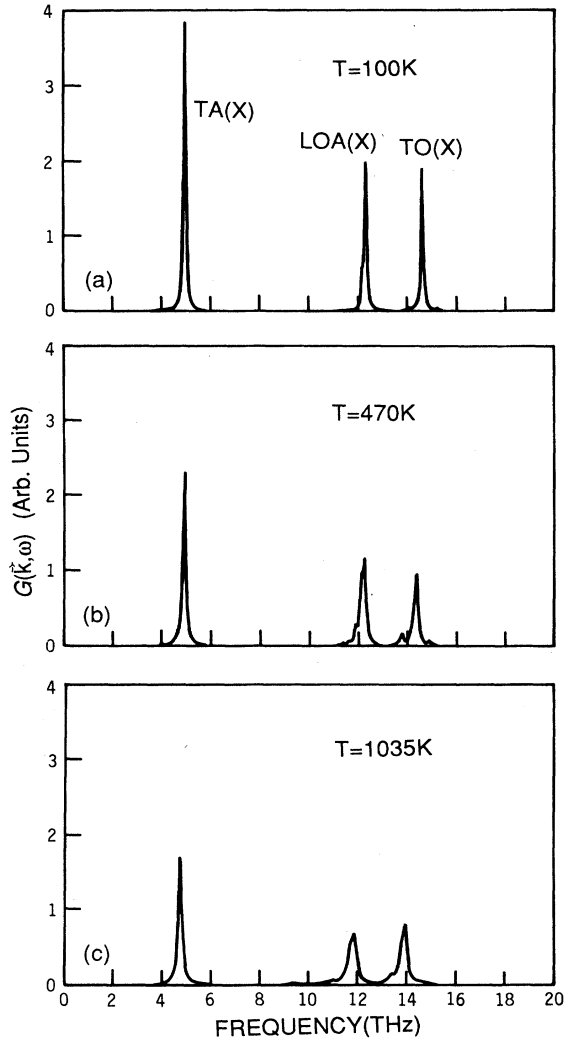

FIG. 8. Molecular-dynamics results of temperature-dependent phonon spectral intensity of the TA(X), TO(X), and LOA(X) modes of Si.

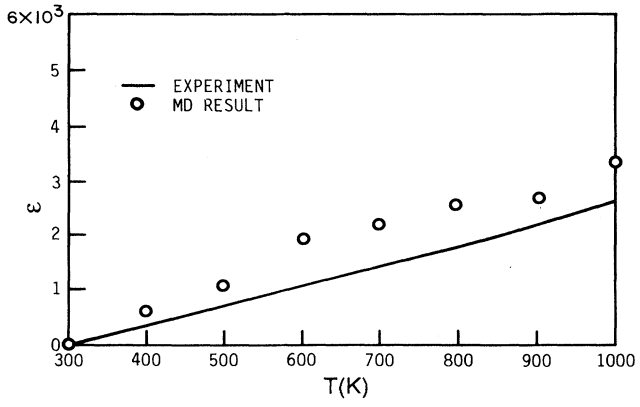

FIG. 9. Lattice thermal expansion behavior of Si. The experimental data are taken from Ref. 18.

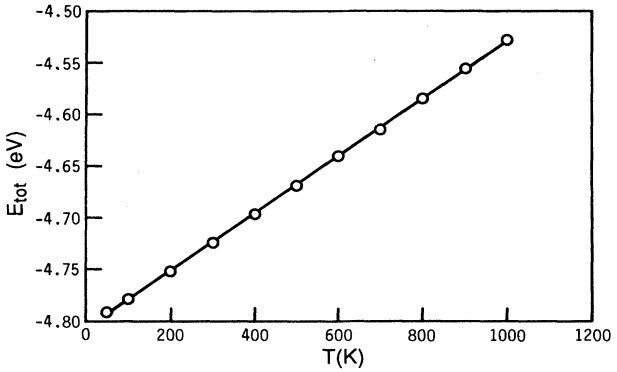

FIG. 10. Total energy (per atom) of the system as a function of temperature obtained from the constant-pressure and constant-temperature molecular-dynamics simulation.

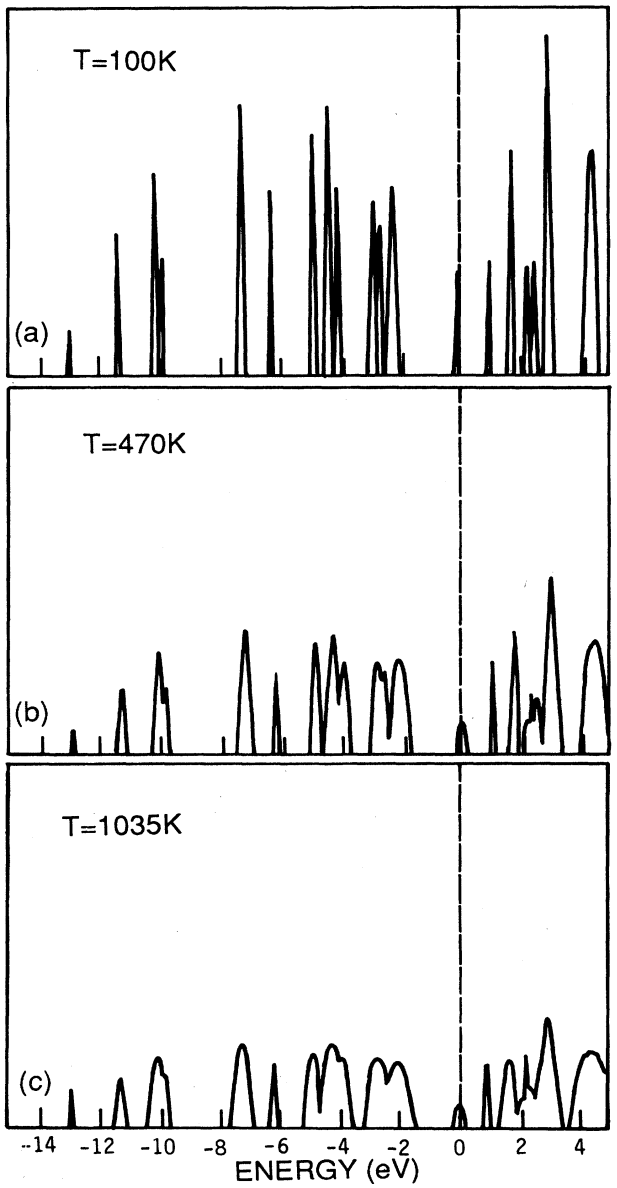

FIG. 11. Temperature-dependent electronic eigenvalues at Γ point of the 64-atom supercell obtained from microcanonical molecular-dynamics simulation.

Γ and X points in the Brillouin zone. The results agree well with available experimental data. Details will be presented in another paper.[16] In this paper we will concentrate on the results we obtained for the thermal expansion and specific heat of Si. Since molecular dynamics treats the motions of the atoms classically, quantum-mechanical corrections to the phonon occupation will be important for thermodynamic quantities like specific heat and thermal expansion below the Debye temperature. Therefore in the present paper, we will display results for temperatures above 300 K (the Debye temperature for Si being 645 K). In our simulation of thermal expansion, the constant-pressure MD method of Rahman and Parrinello[17] was used. The external pressure was set equal to zero in the course of the simulation. The lattice constant at each temperature is evaluated from the average density at that temperature with the averaging performed over 3500 MD time steps. In Fig. 9 we show the MD results for the temperature-dependent thermal expansion parameter ϵ defined as $\epsilon=[a(T)-a(T=300\text{ K})]/a(T=300\text{ K})$. The corresponding experimental quantity is also shown in the same plot for the purpose of comparison. The agreement between the present calculation and experiment is reasonably good.

The total energy of the system as a function of temperature from this simulation is plotted in Fig. 10. From the slope of the energy-versus-temperature curve, we estimate the specific heat of the system to be $C_p \sim 3.22k_B$ at high temperatures. This value is above the Dulong-Petit value of $3k_B$ expected from harmonic crystals, however, it compares very well with experimental data of Si at high temperatures ($C_p \sim 3.3k_B$ at $T=800$ K).[19]

Finally, we would like to point out that with the ETBMD scheme, not only the temperature dependence of lattice properties but also the temperature dependence of the electronic properties can be investigated. For example, we present in Fig. 11 the tight-binding eigenvalues at the Γ point for our 64-atom supercell as a function of temperature. The results have been averaged over the last 18 000 MD steps in a total of 22 000 MD simulated steps at each temperature. The zero of the energy level indicates the top of the valence band for the perfect diamond geometry. We see clearly that thermal disorder broadens the electronic eigenvalues. We also see that the gap between the valence band and the conduction band is narrowed but still well defined at temperatures as high as $T=1035$ K, indicating a stable diamond structure at this temperature. A more quantitative investigation with denser **k**-point sampling to get a better electronic density of states is under way.

V. CONCLUSION

In conclusion, we have shown that a very simple nearest-neighbor two-center ETB force model is able to stabilize the diamond structure of Si within a reasonable temperature range. We also show that the ETBMD scheme makes possible the quantitative calculation of the temperature dependence of various anharmonic effects. At present, the weakness in our method lies in the limited accuracy of the ETB description of the band structure. Work is in progress to remedy this situation to enable us to study Si in more complex systems, including surfaces, amorphous and liquid states, and the effects of impurity and doping. Since the scheme uses only a few atomic orbitals to represent the electronic states on each atomic site, it can be applied to simulate systems involving relatively larger number of atoms without going beyond the present computer capabilities.

ACKNOWLEDGMENTS

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