Molecular-dynamics study of anharmonic effects in silicon

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Molecular-dynamics calculations have been performed to study the temperature-dependent linewidths and frequency shifts of selected phonon modes in Si. The results obtained are in excellent agreement with experimental data. Interatomic forces in the calculations are obtained by an empirical tight-binding model with parameters determined completely by first-principles electronic structure and total-energy calculations.

The success of density-functional theory in predicting ground-state properties of solids has paved the way for parallel studies of finite-temperature systems. Recently, Car and Parrinello¹ proposed a scheme combining both the accurate description of the interatomic forces through density-functional theory and the power of the molecular-dynamics techniques for applications to finite-temperature systems. However, applications of this scheme to study temperature-dependent phenomena of real systems have been limited by the large computational effort required. We have developed a molecular-dynamics scheme based on a tight-binding description of the electronic structure that is more efficient than the original Car-Parrinello scheme. In this paper, we will describe an application of this scheme to study phonon frequency shifts and linewidths in bulk Si.

The temperature-dependent anharmonic effects in silicon are important in technical applications and serve as primary examples for understanding the anharmonic interactions in other solids. While many experimental studies on the subject have been reported,²⁻⁴ predictions based on theoretical calculations are scarce. Previous theoretical work was based on perturbation theory with empirical anharmonic force constants fitted to experimental data.^{4,5} While molecular-dynamics (MD) simulation is a natural tool to study this problem,⁶ applications to silicon require an accurate description of the anharmonic interactions at finite temperature.

Applications of the Car-Parrinello scheme are limited to short simulation times and a small number of atoms for two reasons: the use of plane waves to expand the electronic wave function requires a large basis set and the introduction of the electronic degrees of freedom in the simulation limits the time step to be ~ 10 times smaller than in traditional molecular-dynamics studies. Very recently, we have developed a molecular-dynamics scheme treating the electronic calculation by an empirical tight-binding (ETB) method rather than by the density-functional method.⁷ Although less rigorous, the empirical tight-binding calculation uses only a few atomic orbitals for each atom to represent the electronic states. Also the electronic degrees of freedom are not explicitly included in the simulation, allowing larger time steps to be used. We will show that such an approach makes possible the quantitative calculation of various anharmonic

effects in silicon.

Our empirical tight-binding molecular-dynamics (ETBMD) scheme models the interatomic forces in Si by expressing the total potential energy of the system as the sum of a "band-structure" energy consisting of the sum of the eigenvalues for the occupied part of the electronic structure and a short-ranged nearest-neighbor two-body potential, i.e.,

$$E_{\text{tot}}\{\mathbf{r}_1, \dots, \mathbf{r}_N\} = E_{\text{bs}}\{\mathbf{r}_1, \dots, \mathbf{r}_N\} + \frac{1}{2} \sum_{(i,j)} \Phi(r_{ij}). \quad (1)$$

The band-structure energy, E_{bs} , for N Si atoms at $\mathbf{r}_1, \dots, \mathbf{r}_N$ is calculated by Chadi's empirical orthogonal tight-binding model for Si.⁸ The two-body potential $\phi(r_{ij})$ is then determined by the difference between the first-principles calculated volume-dependent total energy⁹ and the ETB calculated volume-dependent band-structure energy of Si in the diamond structure. The procedure allows the interatomic forces to be determined at the microscopic level through first-principles total-energy and electronic structure calculations without resorting to fitting experimental data. The model includes many-body interactions through the electronic forces coming from the derivatives of E_{bs} (via the Hellmann-Feynman theorem). This has an advantage over various classical interatomic potential schemes¹⁰⁻¹³ as the quantum-mechanical nature of the electronic bonding enters naturally into our model. Previous studies showed that the model not only provides a good description for Si at $T=0$,^{8,14} but is also able to stabilize the diamond structure in Si over a reasonable temperature range (at least up to 1035 K) and gives correct thermal-expansion behavior and the correct high-temperature specific heat.⁷ Some $T=0$ dynamical properties of Si from our previous study based on the same model potential are listed in Table I for the purpose of later reference. Other details are contained in another report.⁷

In the present study, we investigate the effect of anharmonicity on the temperature-dependent phonon frequency shifts and phonon linewidths in the crystalline solid. These quantities are calculated through the phonon spectral intensity which is the Fourier transform of the velocity-velocity autocorrelation function in the molecular-dynamics simulation,¹⁷ that is,

TABLE I. Empirical tight-binding calculations of phonon frequencies and Grüneisen parameters for a few selected modes in Si at zero temperature.

Si	LTO(Γ)	TA(X)	TO(X)	LOA(X)
Phonon frequency (THz)				
ETB with 64 atoms	16.95	4.96	14.71	12.37
ETB with 216 atoms	16.70	4.96	14.68	12.33
Experiment ^a	15.53	4.49	13.90	12.32
Grüneisen parameter				
ETB with 64 atoms	0.98	-1.12	1.37	1.02
ETB with 216 atoms	0.99	-1.13	1.42	1.03
Experiment ^b	0.98	-1.40	1.50	~0.90

^aReference 15.

^bReference 16.

$$g(\mathbf{K}, \omega) = \int dt e^{i\omega t} \sum_n e^{-i\mathbf{K} \cdot \mathbf{R}_n} \frac{\langle \mathbf{v}_n(t) \cdot \mathbf{v}_0(0) \rangle}{\langle \mathbf{v}_n(0) \cdot \mathbf{v}_0(0) \rangle}. \quad (2)$$

We report below results with $\mathbf{K}=(1,1,1)2\pi/a$ for the optical modes at Γ , and $\mathbf{K}=(0,0,1)2\pi/a$ for the modes at X . The microcanonical molecular-dynamics simulation is performed with 64 atoms in a cubic "box." Some simulations have been performed with 128 atoms in a tetragonal box for the purpose of testing finite-size effects. Periodic boundary conditions are applied. The volume of the MD cell is fixed at a given temperature but it is allowed to change according to the thermal expansion behavior determined in previous calculations⁷ for different temper-

atures. The Γ point was used to evaluate the electronic structure and Hellmann-Feynman forces in the course of the simulations. The sufficiency of using only a single k point is justified by tests with bigger unit cells (see Table I and Ref. 7). The time step used in the simulation is 1.07×10^{-15} s, which conserves the total energy to an accuracy of 4×10^{-6} eV or better over 18 000 MD steps at $T=100$ K. At each temperature, about 7000 MD steps are used to reach thermal equilibrium followed by 16 384 steps (corresponding to a total time period of 17.5 ps) to evaluate the velocity-velocity correlation function and the phonon spectral intensities. The frequency resolution of the calculated phonon spectra is about 1.3 cm^{-1} , which is the typical resolution of optical experiments.

Typical molecular-dynamics phonon spectra are shown in Fig. 1 corresponding to $\mathbf{K}=(1,1,1)2\pi/a$ at $T=100$, 470, 720, and 1035 K. We have identified the main peak in the spectra as the optical modes at Γ , i.e., the LTO(Γ) mode.¹⁸ Besides that main peak, there are two visible

FIG. 1. Molecular-dynamics results of the temperature-dependent spectral intensity of the LTO(Γ) mode in silicon.

FIG. 2. Temperature dependence of frequency shift of the LTO(Γ) mode in silicon. The experimental data are taken from Ref. 4. The molecular-dynamics results have been renormalized with respect to the experimental data at $T=100$ K.

FIG. 3. Temperature dependence of linewidth of the LTO(Γ) mode in silicon. The experimental data are taken from Ref. 4.

side peaks centered about 0.5 THz away from the main peak present at all temperatures. However, by changing the size of the MD sample from 64 to 128 atoms, we found that while the position of the main peak has been shifted down about 0.15 THz due to the effects of different k points sampled, the absolute positions of the two side peaks remain unaffected. It seems the side peaks are unrelated to the main peak and may be due to the two-phonon states which will be the subject of a future investigation.

It is clear that the main peak in Fig. 1 displays both a shift in frequency and a broadening in linewidth as the temperature is increased. From the spectra we can obtain the frequency shift and the phonon linewidth as a function of temperature. In Figs. 2 and 3, we show the temperature dependence of the frequency shift and linewidth of the LTO(Γ) mode of Si calculated from our molecular-dynamics simulation and compared with the experimental values obtained from Raman-scattering experiments. The agreement between the present theory and experiment is very good. It should be emphasized that in the present calculations, all the parameters are determined by first-principles electronic structure and total-energy calculations—no input from any experimental data has been used. The temperature dependence of the frequency shifts of other modes at the zone boundary X (see Fig. 4) and L (not shown in this paper) from the present calculation also compare very well with the results from two-phonon Raman-scattering experiments.³ Results from tests of size effects as shown in the same figures (the crosses in Figs. 2 and 3) indicate that the phonon frequency shifts and linewidths are well converged with respect to the size of our unit cell and that, while a larger size supercell will provide better agreement with experiment, a cell of 64 atoms is sufficient for providing meaningful results.

The temperature dependence of each phonon frequency can be separated into a quasiharmonic contribution coming from thermal expansion and another part coming

FIG. 4. The contribution of thermal expansion to the frequency shifts (the open circles) and the total frequency shifts (the solid circles) of some selected modes of silicon as a function of temperature.

from anharmonic interactions between phonons.¹⁹ By performing $T=0$ frozen phonon calculations with lattice constants equal to the values actually used in the molecular-dynamics simulations at the various temperatures, we can estimate the contribution of the thermal expansion to the frequency shift at each temperature. The results for the LTO(Γ), TO(X), LOA(X), and TA(X) modes are shown in Fig. 4 together with the total frequency shift obtained from molecular dynamics. We see from the plot that thermal expansion contributes roughly $\frac{1}{3}$ of the total frequency shift. The large frequency shift, particularly at higher temperature, is in fact due to the strong anharmonic phonon-phonon interactions in the system. It is interesting to note that the quasiharmonic contribution is actually opposite in sign from the total frequency shift for the case of the TA(X) mode.

In summary, we have shown that a molecular-dynamics approach based on an empirical tight-binding force model provides a very good description for the temperature dependence of anharmonic effects in silicon. The present scheme provides a general method for studying temperature-dependent anharmonic effects in solids. We also expect that our successful demonstration of combining the empirical tight-binding method with molecular dynamics will stimulate many more fruitful applications in the near future.

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