Thermal expansion of c-Si via *ab initio* molecular dynamics

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We show that thermodynamic properties of semiconductors are accessible to first-principles calculations and can be computed with good accuracy.

The *ab initio* calculation of properties of semiconductors is a central issue in present-day theoretical solid-state physics. In the last 10 years major progress has been made with the advent of accurate total-energy calculations based on the local-density approximation for exchange and correlation within density-functional theory (DFT). These calculations have shown that it is possible to predict accurately properties such as the equilibrium lattice structure, the elastic constants, and the phonon spectrum.[1]

However, even relatively simple thermodynamic properties such as the thermal expansion coefficient,

$$\alpha = \frac{1}{3\Omega} \left[\frac{\partial \Omega}{\partial T} \right]_P = \frac{1}{3B} \left[\frac{\partial P}{\partial T} \right]_\Omega , \qquad (1)$$

where Ω is the volume, P the pressure, B the bulk modulus, and T the temperature, have not been calculated with *ab initio* methods. The basic reason is that α is dependent on anharmonic effects and therefore its evaluation can hardly be reduced to a small set of total-energy calculations as has been the case for the properties listed above. Even if one uses the well-known quasiharmonic approximation for α,

$$\alpha = \frac{1}{3B} \sum_{k,s} \frac{-1}{\omega_{k,s}} \frac{\partial}{\partial \Omega} \omega_{k,s} \frac{\partial}{\partial T} \varepsilon(\omega_{k,s}, T) , \qquad (2)$$

where $\varepsilon(\omega_{k,s}, T)$ is the internal energy of an oscillator of frequency $\omega_{k,s}$ at temperature T, one is faced with the difficult task of evaluating, in the whole Brillouin zone (BZ), the phonon frequencies $\omega_{k,s}$ and their volume derivative, i.e., the so-called Grüneisen parameters. The integral over the BZ can be simplified by the use of sets of special points,[2] but still the calculation of phonon frequencies at such points would be difficult since it requires the introduction of prohibitively large supercells. Such difficulty is circumvented by the use of molecular-dynamics (MD) methods[3] that take fully into account anharmonic effects and do not require explicit evaluation of the whole phonon spectrum. Since, however, these methods are based on the classical approximation for the ionic motion, they will correctly determine α only for temperatures T larger than the Debye temperature Θ_D ($\Theta_D \simeq 645$ K for Si), where quantum effects can be neglected. In this limit Eq. (2) predicts a temperature-independent α.

A first-principles MD method has been recently introduced by two of us.[4] In such a scheme one performs a MD simulation in which the interatomic forces are calculated from the electronic ground state using accurate DFT methods. This is at variance with conventional MD where the interatomic potential is determined by empirical means. The method is based on the assumption of a fictitious classical dynamics for the coupled evolution of the ions and of the Kohn-Sham (KS) single-particle orbitals. The dynamics is generated by the Lagrangian

$$L = \sum_i \mu \int_\Omega d^3r |\dot\psi_i|^2 + \sum_I \tfrac{1}{2} M_I \dot{R}_I^2 - E[\{\psi_i\}, \{R_I\}]$$
$$+ \sum_{i,j} \Lambda_{ij} \left[\int_\Omega d^3r \psi_i^*(r)\psi_j(r) - \delta_{ij} \right] , \qquad (3)$$

where M_I and R_I are the ionic masses and positions, $\psi_i(r,t)$ the KS orbitals, μ a fictitious mass associated to them, Λ_{ij} are Lagrangian multipliers used to impose the orthonormality constraints on the ψ_i, and $E[\{\psi_i\}, \{R_I\}]$ is the energy functional

$$E = \sum_i \int_\Omega d^3r \psi_i^*(r)[-(\hbar^2/2m)\nabla^2]\psi_i(r) + V[n(r), \{R_I\}] , \qquad (4)$$

where the functional $V[n(r), \{R_I\}]$ contains the Coulomb repulsion and the effective electronic potential energy including external potential, Hartree, and exchange and correlation contributions. $n(r) = \sum_i |\psi_i|^2$ is the electron density in terms of occupied KS orbitals. The Born-Oppenheimer (BO) potential for the ions, i.e., $\Phi(\{R_I\})$, is given by the minimum of the functional $E[\{\psi_i\}, \{R_I\}]$ with respect to the ψ's subject to the orthonormality condition. The dynamics generated by the Lagrangian L closely reproduce the BO dynamics for the ions, if one starts with ψ's that minimize E and chooses for μ a small enough value. In such a case the ψ's follow adiabatically the ionic motion without acquiring a significant kinetic energy $K_\psi = \sum_i \mu \int_\Omega d^3r |\dot\psi_i|^2$. This has been verified in previous works, and further evidence will be given below.

We used a periodically repeated MD cell with the silicon atoms arranged in the diamond structure. In most of our calculations we used a 54-atom fcc cell and an energy cutoff $E_{\text{cut}} = 8$ Ry for the expansion of the ψ's in plane waves. BZ sampling was performed with the Γ point of the MD cell. The pseudopotential was taken

TABLE I. Convergence study of equilibrium lattice constant and bulk modulus of crystalline silicon. Our results are obtained from pressure calculations within a constant N^{PW} procedure, as in Ref. 9. The experimental values and the theoretical results of Ref. 9 are also presented for comparison.

	$T=0$ lattice parameter (a.u.)		Bulk modulus (Mbar)	
Experimental	10.263		0.992	
theory: Ref. 9	10.204		0.93	
Our results:				
54 atoms fcc cell	s-NL	sp-NL	s-NL	sp-NL
$E_{cut}=8$ Ry	10.00	9.96	1.53	1.32
$E_{cut}=12$ Ry	10.22	10.09	1.21	1.18
$E_{cut}=24$ Ry	10.41	10.21	0.89	0.97
64 atoms sc cell	s-NL	sp-NL	s-NL	sp-NL
$E_{cut}=8$ Ry		9.92		1.35
$E_{cut}=12$ Ry		10.04		1.20

from Ref. 5 considering only s nonlocality and using the Kleinman-Bylander representation.[6] We have checked the convergence of our results by making additional static and dynamic calculations with larger energy cutoffs and including p nonlocality. The dependence of our data on the MD cell was investigated by repeating some of the calculations with a larger 64-atom SC cell. In all our calculations we have kept fixed the number of plane waves (N^{PW}) when varying the volume of the cell.[7] This gives rise to a slower convergence with respect to cutoff than working at fixed E_{cut}.[8] However, in our MD simulations, particularly at constant pressure, we are forced to adopt a fixed N^{PW} scheme.

The results of our static convergence tests, for the lattice parameter and the bulk modulus B at $T=0$, are reported in Table I. The main factor affecting the convergence of our results is E_{cut}, while a better sampling of the BZ as done in Ref. 9 has only minor effects. Indeed our 24-Ry calculation compares well with that of Ref. 9 when we include p nonlocality (sp-NL), whilst using only s nonlocality (s-NL) we overestimate the bond length by $\simeq 2\%$. Similar conclusions on the effect of p nonlocality were obtained in Ref. 10.

The integration of the equations of motion was made with the Verlet algorithm[11] using a fictitious mass $\mu=300$ a.u. and an integration time step $\Delta t \simeq 1.7 \times 10^{-16}$ sec. Such a value is only a factor ~ 2 smaller than the Δt used, for instance, by Broughton et al.[12] in a conventional MD simulation for silicon based on empirical interatomic potentials.

Two kinds of simulations were performed, one at constant volume (CVMD) and the other at constant pressure (CPMD).[13] In the second one the following terms were added to the Lagrangian in Eq. (3):

$$\tfrac{1}{2}W\dot{\Omega}^2+P\Omega \ , \tag{5}$$

where P is the external pressure imposed on the system and W is a parameter of appropriate units adjusted to set the time scale for volume fluctuations. In our simulations we set $P=0$ and took $W=0.05$ a.u. In every run the system has been heated up and then has been equilibrated for at least $500\Delta t$ before taking cumulative averages. An analysis of the data showed that, for the quantities of in-

terest, $3000\Delta t$ were sufficient to compute accurate averages.

In order to check that the BO dynamics can be evaluated correctly from the Lagrangian L, we have calculated the internal energy of the system as a function of temperature. We calculate the ionic internal energy as

$$U(T)=\left\langle \sum_I \tfrac{1}{2}M_I\dot{R}_I^2+E[\{\psi_i\},\{R_I\}]\right\rangle , \tag{6}$$

where the angular brackets indicate temporal average on a convenient finite observation time, and the (ionic) temperature T is related to the equilibrium value of the kinetic energy $\langle K_I \rangle=\langle \sum_I \tfrac{1}{2}M_I\dot{R}_I^2\rangle$ by suitable normalization. In the hypothesis of adiabatic behavior of the coupled dynamics for R_I and ψ's during the observation time, $U(T)$ as defined in Eq. (6) should be a good approximation of $U'(T)=\langle \sum_I \tfrac{1}{2}M_I\dot{R}_I^2+\Phi(\{R_I\})\rangle$. For a classical highly harmonic system, which is the case here, $U'(T)$ is given by the equipartition law $\Delta U'(T)=U'(T)-U'(0)=Nk_BT$, where k_B is the Boltzmann constant and N is the number of degrees of freedom of the (ionic) system. It is seen in Fig. 1 that this is indeed
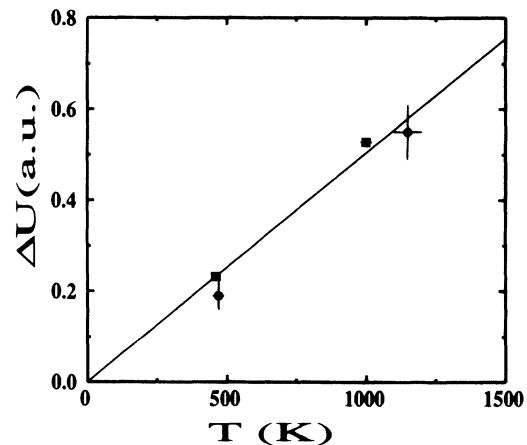

FIG. 1. Variation of the internal energy U of crystalline Si with temperature. Results of both CVMD (solid squares) and CPMD (solid circles) are displayed. Horizontal and vertical bars are error bars. The exact result for a classical harmonic crystal is represented by the straight line.

the case and that CVMD and CPMD give consistent results.

In MD simulations the thermal expansion coefficient can be computed directly from the definition $\alpha = (1/3\Omega)(\partial\Omega/\partial T)_P$ or $\alpha = (1/3B)(\partial P/\partial T)_\Omega$ if CPMD or CVMD are used, respectively. The derivatives are calculated numerically by making a finite temperature change ΔT, either at constant P or at constant Ω, with respect to a reference equilibrium thermodynamic state, which we have chosen to be the state at $T=0, P=0$. This is adequate even at high T since we found that both Ω and P vary linearly with T within the accuracy of our calculations, confirming the prediction of the classical quasiharmonic theory. Notice that both Ω and B vary little with T: for instance, Ω changes by about 1% for $\Delta T \simeq 1000$ K. The results of our calculation are displayed in Fig. 2 together with the experimental curve. The experimental data show for $T < \Theta_D$ a rich structure which also includes at low temperature a region of negative expansivity. This behavior of quantum nature is completely missed by our classical calculation which predicts an approximately constant α. Therefore our data should be compared with experiment only in the high-temperature range $(T > \Theta_D)$. Already with a cutoff of 8 Ry there is a satisfactory agreement between theory and experiment. Furthermore, constant pressure and constant volume data are consistent.

We have checked the stability of our calculation with respect to N^{PW} (E_{cut}) and the size of the MD box. We have also studied the effect of the inclusion of p nonlocality in the pseudopotential. In Table II we summarize our results. These calculations were performed with CVMD simulations because they are slightly less expensive computationally than CPMD (by about 10%).

As to the effect of E_{cut} we note that the variation from 8 to 12 Ry is not dramatic, especially when p nonlocality
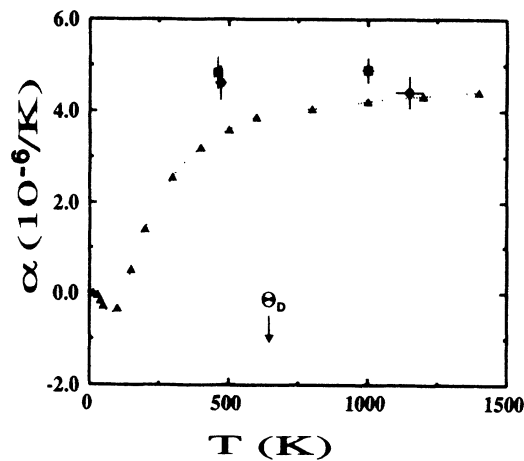

FIG. 2. Thermal expansion coefficient α of c-Si as a function of temperature. Experimental values, indicated with triangles, are taken from Ref. 14; the dotted line is just a guide to the eye. Theoretical values: squares and circles indicate CVMD and CPMD results, respectively. The error bars are also shown. The Debye temperature Θ_D is indicated by the arrow.

TABLE II. Thermal expansion coefficient α of c-Si. Our results are compared with the experimental values for $T \geq \Theta_D$. The theoretical data are from runs at different T in the range 400–1100 K. The result obtained in a computer simulation using the classical Stillinger-Weber (SW) potential [Ref. 12(b)] is also shown.

	$\alpha(10^{-6}$ K$^{-1})$	
Experimental $(T \geq \Theta_D)$	3.9–4.4	
SW potential: Ref. 12(b)	2.0	
Our results:		
54-atom fcc cell	s-NL	sp-NL
$E_{cut} = 8$ Ry	4.9	4.4
$E_{cut} = 12$ Ry	5.6	4.5
64 atoms sc cell	s-NL	sp-NL
$E_{cut} = 8$ Ry		3.1
$E_{cut} = 12$ Ry		3.4

is also included. Although the full convergence in the $T=0$ properties is reached at larger E_{cut}, in the evaluation of α there is a compensation between the variation of B and of $\partial P/\partial T$ with E_{cut}. Therefore the result at 8 Ry can be considered satisfactory even though not fully converged.

The second point that we considered is the importance of a more accurate treatment of the nonlocal part of the pseudopotential with the inclusion of both s and p nonlocality $(sp$-NL). From Table II we see that α is quite sensible to p nonlocality especially for the highest E_{cut} (there is a reduction of 20%), and the agreement with experiment is improved.

Another important feature that one would like to investigate is the dependence of our results on the MD cell. Since computer limitations do not allow at present an extensive study of the size dependence of our simulations, we have only repeated some of the calculations with a 64-atom sc cell. On going from the 54- to the 64-atom cell the variation of the $T=0$ structural properties is very small, while the variation of α is not negligible (more than 20%) and results in a somewhat worse agreement with experiment. We suggest that this is a consequence of the different representation of the phonon spectrum that is achieved with the 54-fcc and with the 64-sc cell, respectively. While the fcc cell samples only phonons in the interior of the diamond BZ, the sc cell samples several zone-boundary phonons which have the largest negative Grüneisen parameters.[14] This leads to a reduction of the calculated α values (Table II). For comparison we also show in Table II the result of a recent calculation of α based on the Stillinger-Weber empirical potential, which leads to a significantly larger underestimate of α.[12(b)]

In summary, we have presented an *ab initio* MD simulation of c-Si at finite temperature. This work indicates that thermodynamic properties of semiconductors are accessible to first-principles calculations.

In particular, the thermal expansion coefficient at high temperature has been calculated with both constant-volume and constant-pressure MD simulations. Consistent values and good agreement with experiment were obtained in the two cases.

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