



ISAS - INTERNATIONAL SCHOOL FOR ADVANCED STUDIES

CRYSTALLINE SILICON AT FINITE TEMPERATURE :
A MOLECULAR DYNAMICS STUDY

Thesis submitted for the degree of
"Magister Philosophiae"

CANDIDATE

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SUPERVISORS

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INTRODUCTION

The Density Functional formalism (DF) within Local Density Approximation (LDA) has been very successful for studying ground state properties of different systems like atoms, molecules and solids, characterized by different kinds of bonding, including covalent bonding.

In particular the determination of the equilibrium geometric configuration, lattice constant, phonon frequencies, bulk moduli, is possible with a high degree of accuracy for several systems. In principle, also structural phase transitions in solids can be studied by the LDA. The computational difficulties which one is faced to have however greatly limited its application in this direction.

If one is interested in finite temperature properties of systems not only in the crystalline phase, but for liquid or amorphous phases also, the Molecular Dynamics (MD) simulation appears to be a rather successful method to predict them, both at equilibrium and out of equilibrium.

The main problem connected with a MD study is the determination of the interatomic forces (potentials). In all MD calculations "empirical" potentials have been used (empirical in the sense that they are fitted to some known properties). Usually the N-body potentials has been written as a

sum of two-body potentials or in some cases of two-body and three-body terms .

This "empirical" approach is appropriate for simple systems (like rare gas solids where the Lennard-Jones interaction works very well) may fail in the case of systems with directional covalent bonds (like tetrahedral semiconductors) . Recently some effort has been paid to construct empirical potentials for silicon [1,2] which contain a combination of pair and triplet interaction ; however from what is known today it is fair to say that existing empirical potentials fail (qualitatively) to give a satisfactory description of local order in silicon . This is related to the strong dependence of the interatomic potential on the electronic structure .

The unified approach for MD and DF developed by R. Car and M. Parrinello [3] overcomes this problem since in this approach the exact (within LDA) many-body interaction potential is evaluated , without any empirical adjustment . In fact the potential derives explicitly from the electronic structure. The mutual ion-electron interaction is taken into account self-consistently within the Born-Oppenheimer (BO) approximation . It means that in such approach is possible to study not only the properties connected to the ionic motion , but also the effect of this motion on the

electronic states .

However it must be emphasized that in all the cases in which non-adiabatic couplings between ions and electrons become important , the BO approximation is nomore valid and then this MD-DF approach cannot give satisfactory results .

In this thesis work we extended the initial formulation of reference [3], combining the MD-DF method with the constant pressure MD due to Andersen [4] , to allow for the MD cell volume to fluctuate .

This generalization should permit to study physical problems for which is necessary to take into account volume fluctuations , like phase transitions . We initially applied this method to the study of finite temperature properties of crystalline silicon , in order to verify the accuracy of this approach and to perform convergence tests .

In particular we have studied the thermal expansion of the crystalline silicon . We looked also at the variation of the direct energy gap with the temperature . Even if in principle it should be possible to obtain this quantity within the present approach , our conclusions on the possibility of studying it are negative because of the necessity to use too large a cell for the present computer capabilities .

We obtain ,completely from first principles, the thermal expansion coefficient in rough agreement with experiment . Note that to obtain this quantity a great precision is required , because we are looking for variation on the lattice parameter of some part on a thousand .

However our results are strongly dependent on the various parameters used in the calculation , as the number of plane waves, the number of k-points , the dimension of the cell . Therefore it has been necessary to perform an accurate study of convergence which is still in progress . In this thesis we present preliminar results of such analysis. Particular attention was devoted in this work to the analysis of the convergence of our results with the number of plane waves used to represent the electronic states .

One of the most relevant results we found is a strong systematic error introduced in all the properties which depend on the volume resulting from the use of a constant number of plane waves , indipendently from the volume variations . This problem is removed if one is able to reach an absolute convergence in the plane waves ; this however requires a prohibitivly large number of plane waves in particular if we want to study the dependence of our results from the size of the MD cell . We think that it should be possible to overcome this problem simply by adding a corrective term in

the total energy . This however remains to be tested.

The outline of this thesis is as follows . In chapter 1 the theoretical framework is discussed : in particular we first describe the MD-DF unified approach ,then we analyze in some detail the constant pressure MD used in this work ; finally we briefly recall the most used theoretical approach to the thermal expansion in solids , i.e. the quasiharmonic approximation . Chapter 2 is technical in nature and deals with the details of our numerical calculations. In chapter 3 the numerical results are presented and discussed . The last section is devoted to the conclusion and to indicate the possible future developments .

CHAPTER 1

THEORETICAL APPROACH

1.1. Unified Approach for Molecular Dynamics and Density Functional theory.

The unified Approach for Molecular Dynamics and Density Functional theory (MD-DF), recently proposed by R. Car and M. Parrinello [3], is able to overcome some limits of both the DF scheme and of MD simulations. In particular this method permits to compute ground-state properties of large and/or disordered systems at the level of state-of-the-art electronic structure calculations and to perform "ab initio" MD simulations. In fact, in this method no assumption about the interatomic interactions is needed: the latter are treated "exactly" within the DF-LD scheme, the only assumption being that the Born-Oppenheimer approximation to separate the nuclear and electronic motion holds.

In a DF-LD framework [5,6], the ground state properties of a given system are computed through the minimization of its total energy,

$$E [\{ \Psi_i \}, \{ R_I \}, \{ \alpha_\nu \}] = \sum_i \int_{\Omega} d^3r \Psi_i^*(\vec{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 \right] \Psi_i(\vec{r}) + U [n(\vec{r}), \{ R_I \}, \{ \alpha_\nu \}] \quad (1.1)$$

with respect to the single particle electronic orbitals $\{\Psi_i\}$ (where the charge density is given by $n(\vec{r}) = \sum_i |\Psi_i(\vec{r})|^2$). Here R_I denote the nuclear coordinates and α_ν indicate all possible external constraints imposed on the system, such as, for example, the volume. The functional U contains the internuclear Coulomb repulsion and the effective electronic potential energy. In the MD-DF method, the parameters $\{\Psi_i\}$, $\{R_I\}$, $\{\alpha_\nu\}$ are taken to be dependent on time and the following Lagrangean is defined :

$$L = \sum_i \frac{1}{2} \mu \int_{\Omega} d\vec{r} |\dot{\Psi}_i|^2 + \sum_I \frac{1}{2} M_I \dot{R}_I^2 + \sum_\nu \frac{1}{2} \mu_\nu \dot{\alpha}_\nu^2 - E[\{\Psi_i\}, \{R_I\}, \{\alpha_\nu\}] \quad (1.2)$$

The $\Psi_i(\vec{r}, t)$ are subject to the holonomic constraints :

$$\int_{\Omega} d\vec{r} \Psi_i^*(\vec{r}, t) \Psi_j(\vec{r}, t) = \delta_{ij} \quad (1.3)$$

In eq. (1.2) the dot indicates time derivative, M_I are the physical ionic masses, whereas μ and μ_ν are arbitrary parameters of appropriate units. From the Lagrangean defined above, the Newtonian equations of motion for the parameters $\{\Psi_i\}$, $\{R_I\}$, $\{\alpha_\nu\}$ are obtained. These are :

$$\mu \ddot{\Psi}_i(\vec{r}, t) = -\delta E / \delta \Psi_i^*(\vec{r}, t) + \sum_K \Lambda_{iK} \Psi_K(\vec{r}, t) \quad (1.4a)$$

$$M_I \ddot{R}_I = -\nabla_{R_I} E \quad (1.4b)$$

$$\mu_\nu \ddot{\alpha}_\nu = -\partial E / \partial \alpha_\nu \quad (1.4c)$$

The Λ_{iK} are Lagrange multipliers introduced in order to satisfy the constraints imposed by eq. (1.3). It can be shown that, once the classical system described by the Lagrangean (1.2) has reached the equilibrium, the eigenvalues of the Λ matrix coincide with the occupied K-S eigenvalues. Different procedures can be employed to minimize the functional E. In the original MD-DF formulation, a dynamical simulated annealing procedure was proposed. However, as far as total energy minimization is concerned, Newtonian dynamics can be conveniently replaced by other type of dynamics [7]. In our work we have adopted a steepest descent minimization method since it was recognized to be computationally more advantageous. We notice that in the MD-DF approach, diagonalization, self-consistency, ionic relaxation and volume relaxation are achieved simultaneously.

The molecular dynamics simulation of a system described within the MD-DF scheme is performed in practice as follows. A situation is realized, in which the ions are allowed to move at a given temperature, following the equations of motions (1.4b), while the kinetic energy of the electronic parameters remains equal to zero. We stress that in this way the first term in equation (1.2), which represents a fictitious kinetic energy, is kept equal to zero. Therefore the ions move under the action of Born Oppenheimer forces, while

the electrons are at any time in their ground state. In order to achieve such a situation an appropriate choice of the μ parameter entering equations (1.2) and (1.4a) must be made. μ must be much smaller than the ionic mass M_I so that during the typical observation time of a MD run, the kinetic energy associated with the ψ_i' 's remains very small compared to the typical variations of the potential energy of the system.

In the original MD-DF formulation, the MD simulation of a system is thought to be performed within the microcanonical ensemble (the volume V , the energy E and the total number of particles N are kept constant). In our application of the MD-DF method, we have instead rewritten the equations of motions (1.4) in order to allow the simulation of a given system in the isobaric-isoenthalpic ensemble.

1.2. Molecular Dynamics at constant pressure.

In the original formulation of the MD simulation method, due to Alder and Wainwright [8], the Newtonian equations of motion of N particles in a fixed MD cell of volume V , are solved numerically. The total energy E of the system is conserved. Time averages calculated in such simulations are then equivalent to averages over the microcanonical ensemble (E, V, N) .

However, one is often interested in the calculation of constant temperature and/or pressure properties in order to have a direct comparison with measured quantities.

In the last few years, a notable effort has been made to generalize the MD method to the study of static and dynamical properties for systems represented by different statistical ensembles, such as, e.g., the isoenthalpic-isobaric (H, P, N) , the canonical (T, V, N) and the isothermal-isobaric (T, P, N) ensembles. The first contribution in this sense is due to Andersen [4]: he has suggested a way of introducing volume fluctuations into MD simulations which allows the description of a given system within the (H, P, N) ensemble. Subsequently, Parrinello and Rahman [9] have extended the Andersen's formulation to allow for changes not only in the volume, but also in the MD cell shape. Recently Nose' [10] has proposed a generalization of the MD method suitable to

study constant temperature properties.

In what follows, we describe in some detail the method introduced by Andersen, which has been implemented in our application of the Car-Parrinello scheme.

The simulation of a system at constant pressure requires the introduction of volume fluctuations. To describe such fluctuations, a MD method can be devised, in which the volume is a dynamical variable rather than a fixed quantity. The result is a way of calculating trajectories so that the trajectory average of any property is equal to the (H,P,N) ensemble average of that property.

In the constant pressure MD method, the system is thought to be in contact with an arbitrary large constant pressure reservoir. The system is imagined to respond instantaneously and homogeneously, rather than locally, to any difference between the external and internal pressure. Each spatial point in the system responds at the same time, so that the volume fluctuations are manifested as uniform pulsations of the system. No local pressure gradients or surface effects are introduced into the system by the reservoir.

Mathematically, this behaviour can be imposed upon the system by an appropriate scaling of the particle positions

\vec{r}_i . These are replaced by the scaled coordinates \vec{q}_i , $i=1,\dots,N$, defined in the following way :

$$\vec{\rho}_i = \vec{r}_i / V^{1/3}, \quad i=1, \dots, N. \quad (1.5)$$

where V is the time dependent volume of the system. The hamiltonian of the system, as expressed through this scaled set of coordinates, is given by :

$$\begin{aligned} \mathcal{H}(\{\vec{\rho}_i\}, \{\dot{\vec{\rho}}_i\}, V, \dot{V}) &= \frac{1}{2} M V^{2/3} \sum_i \dot{\vec{\rho}}_i \cdot \dot{\vec{\rho}}_i \\ &- U(\{V^{1/3} \vec{\rho}_i\}) + \frac{1}{2} M_V \dot{V}^2 - P_e V \end{aligned} \quad (1.6)$$

Here M is the mass of a particle, U is the system potential energy and M_V and P_e are appropriate constants. Dots indicate time derivatives. The Newtonian equations of motion, derived by the Hamiltonian (1.6), and written for the unscaled variables \vec{r}_i are :

$$M \ddot{\vec{r}}_i = -\nabla_{\vec{r}_i} U\{\vec{r}_i\} - \frac{1}{3} M \ddot{V} \left[\frac{2}{3} \left(\frac{\dot{V}}{V} \right)^2 - \frac{\ddot{V}}{V} \right] \quad (1.7a)$$

$$M_V \ddot{V} = -\sum_i \frac{1}{3V} \vec{r}_i \cdot \nabla_{\vec{r}_i} U + \sum_i \frac{M}{3V} \left[\ddot{\vec{r}}_i - \frac{1}{3} \frac{\dot{\vec{r}}_i \cdot \dot{V}}{V} \right]^2 - P_e \quad (1.7b)$$

These equations couple the dynamics of the particles to that of the volume. We notice that if the parameter M_V becomes

infinitely large and the condition $\dot{V}=0$ is satisfied at $t=0$, then eq. (1.7a) reduces to the Newtonian equation for particle i , while eq. (1.7b) expresses the classical virial theorem.

The trajectories defined by eq.(1.7) can be used to calculate time averages of any function $F(r, p, V)$:

$$\bar{F} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt F(r(t); p(t); V(t)) \quad (1.8)$$

Andersen has proved that the resulting time averages for static properties are equivalent, except for negligible errors, to averages in an isoenthalpic-isobaric ensemble in which the pressure is P_c , i.e. :

$$\bar{F} = \langle F \rangle_{NPH} \quad (1.9)$$

We want to stress that the difference between the two different averages is really negligible if a large number of particles N is considered. In fact it has been shown that :

$$\bar{F} = \langle F \rangle_{NPH} + O(N^{-2}) \quad (1.10)$$

for an intensive quantity; and

$$\bar{F} = \langle F \rangle_{NPH} + O(N^{-1}) \quad (1.11)$$

for an extensive quantity.

The introduction of the constant pressure MD in the MD-DF

method is straightforward, once the parameters M_v and P_e are specified.

1.3. Quasi-Harmonic Approximation.

If the potential energy U of a crystal is expanded as a Taylor series in the lattice displacements, it can be written as the sum of three terms:

$$U = U_{eq} + U_{harm} + U_{anh} \quad (1.12)$$

U_{eq} and U_{harm} are respectively the zeroth and second order terms of the expansion. U_{anh} contains all the terms of higher order. Several important physical phenomena are associated with the anharmonic terms. Of these, the most familiar is thermal expansion. In default of adequate information about U_{anh} , the potential energy U of the crystal is approximated by the first two terms of eq. (1.12), where the frequencies of the lattice modes which enter the expression of U_{harm} are assumed to be dependent on volume. This is the so called quasi-harmonic approximation for the potential energy U [11].

The thermal expansion coefficient of a crystal α is defined by :

$$\alpha \equiv \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_P = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{3B} \left(\frac{\partial P}{\partial T} \right)_V \quad (1.13)$$

where l indicates the lattice parameter and B the bulk modulus ($B = V (\partial^2 U / \partial V^2)_T$). In the quasi-harmonic approximation, α can be expressed as follows:

$$\alpha = \frac{1}{3BV} \sum_{q\lambda} \gamma_{q\lambda} \frac{\partial}{\partial T} \epsilon(\omega_{q\lambda}, T) \quad (1.14)$$

Here $\gamma_{q\lambda}$ are the Grüneisen parameters for the mode $q\lambda$:

$$\gamma_{q\lambda} \equiv - \partial \ln \omega_{q\lambda} / \partial \ln V \quad (1.15)$$

$\mathcal{E}(\omega_{q\lambda}, T)$ is the internal energy of an oscillator with frequency $\omega_{q\lambda}$ at the temperature T . According to eq. (1.14), the expansion coefficient should approach a constant value at temperatures higher than the Debye temperature Θ_D ($\Theta_D = 625$ K for Silicon):

$$\alpha = \frac{k_B}{3BV} \sum_{q\lambda} \gamma_{q\lambda} \quad (1.16)$$

where k_B is the Boltzmann's constant .

In the case of Silicon, it has been shown that the quasi-harmonic approximation is a satisfactory one to describe the behaviour of α as a function of temperature in a quite large range of T [12].

Ab initio calculations of the phonon frequencies as functions of the crystal volume allow a first principle estimate of the thermal expansion coefficient at high temperature (see eq. 1.16). Table 1 displays the results of conventional LD calculations [13] of the Grüneisen parameters for Silicon. If these values (together with those for B obtained consistently by the same calculations [14]) are used in eq. (1.16), we obtain $\alpha \approx 20 \times 10^{-7} (\text{K}^{-1})$. This result compares nicely with that derived again by eq. (1.16) when the

Table 1 : Measured and computed phonon frequencies f and Grüneisen parameters γ of Silicon, relative to Γ and X points.

		LTO(Γ)	LOA(X)	TO(X)	TA(X)
f (THz)	EXPT. ^(a)	15.53	12.32	13.90	4.49
	THEOR.	15.16	12.16	13.48	4.45
γ	EXPT. ^(b)	0.98	1.5	0.9	-1.4
	THEOR.	0.9	1.3	0.9	-1.5

(a) from Ref.[14]

(b) from Ref.[15]

experimental values [15,16] for γ and B are used :

$$\alpha = 26 \times 10^{-7} (\text{°K}^{-1}) .$$

CHAPTER 2

DETAILS OF THE CALCULATION

In the following we briefly describe the details of our numerical calculations.

We have performed a constant pressure MD simulation with the external pressure (P_e ; see eq. (1.7b)) fixed equal to zero and used a periodically repeated simple cubic (SC) cell containing 8 Silicon atoms.

We have adopted a pseudopotential framework and used a first-principle nonlocal norm-conserving pseudopotential [17] for the electron-ion interaction. This pseudopotential contains s ($l=0$) and p ($l=1$) angular contributions. Exchange-correlation effects were described within the LDA using the parametrized form proposed by Perdew and Zunger [18].

A plane waves representation was used for the electronic states. There are two procedures to choose basis functions as the linear dimension of the crystal changes: the constant EPW procedure and the constant NPW procedure. In the former case, the basis set contains plane waves up to a kinetic energy cutoff EPW, while in the latter case it contains same number (NPW) of plane waves. NPW and EPW are

related through the equation : $NPW = \frac{1}{6\pi^2} V (EPW)^{3/2}$.

Therefore the NPW and EPW procedures are equivalent, as far as the volume V of the cell is kept constant. Since in our MD simulation V varies with time, the two procedures are no longer equivalent. Though it converges slower than the constant EPW procedure [19], we are forced to choose the constant NPW one in order to have the same number of (time-dependent) expansion coefficients for the electronic wavefunctions, at each MD step.

Only one special \vec{k} -point has been used for the averaging over the supercell Brillouin Zone (BZ). This is the special Baldereschi point [20,21] for a simple cubic Bravais lattice $\vec{K} = (1/4, 1/4, 1/4)$.

We have chosen a value of the parameter μ (see eq. 1.2) equal to 300 electron masses .

In our MD simulation we have used the Verlet algorithm [22] to integrate the equations of motion. Once the NPW parameter of the calculation is fixed, the time step is chosen in order to ensure a desired accuracy for the integration, namely an accuracy which guarantees enthalpy conservation to at least 7 significant figures.

The value of the time step chosen in each of our calculations is of the order of 10^{-16} sec.. About one thousand MD

steps are therefore necessary to observe the system over a time interval of the order of its ionic oscillation, e.g., 10^{-13} sec., as estimated from the phonon frequency values reported in table 1.

The choice of the parameter M_V entering the eq. of motion (1.7b) must satisfy the two following requirements. M_V must be small enough to permit statistically significant variations of the volume [23] ; on the other hand, it must be large enough to allow an accurate integration of the Newtonian equations. The value which we have chosen as a compromise between these two conflicting requirements is 0.05 (mass \times length⁻⁴ in a.u.).

We finally notice that the control of the temperature was achieved by constant rescaling of the velocities.

CHAPTER 3

NUMERICAL RESULTS AND DISCUSSION

3.1. Results for thermal expansion in Silicon

Our calculations for the thermal expansion coefficient of Silicon have been carried out by means of the following steps .

a) We determine the equilibrium lattice parameter (l) at zero temperature via a steepest descent minimization procedure for both the electronic degrees of freedom and the volume , keeping the ionic coordinates fixed in their perfect diamond arrangement .

b) We generate the initial configuration for the MD simulation : in particular we fix l at the value determined in the step a) ; we give an initial small random displacement to the atoms with respect to their equilibrium positions and then we optimize the electronic parameters in order to achieve the point on the B_0 surface relative to that ionic configuration .

c) Starting from the generated configuration , we heat the system up to a certain temperature T via a MD run with a simple rescaling of velocities .

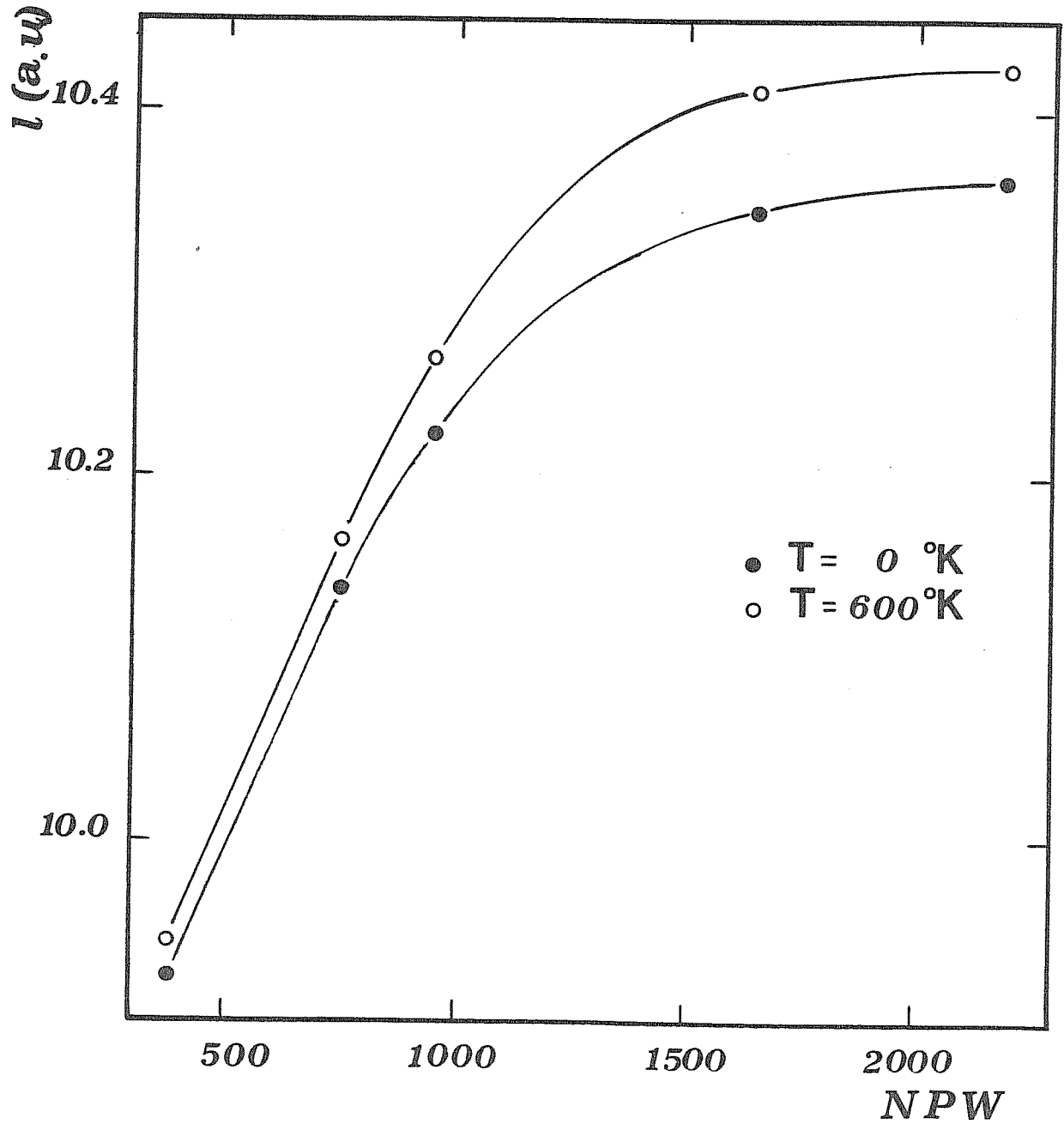


Fig. 1. Behaviour of the lattice parameter (l) of Silicon as a function of the number of plane waves (NPW) employed in the calculation.

d) Finally , we remove the constraint imposed on T in step c), to allow the evolution of the system according to Andersen equations of motions. When the system has reached the thermodynamic equilibrium , its average temperature and lattice constant can be evaluated and then a point of the curve $l(T)$ obtained.

By repeating the steps c) and d), we can obtain other values of l at different temperatures . An interpolation of these points $l(T)$ permits finally to evaluate the thermal expansion coefficient as follows :

$$\alpha = d \ln l / dT$$

We first present the results for the lattice parameter at $T=0$.

A main question we have been faced to is to determine how our results depend on the number of plane waves (NPW) used to describe the electronic states .

In figure 1 we report the lattice parameter at $T=0$ calculated for different values of NPW . Both zero- and finite-temperature results are shown. As we have mentioned in chapter 2, the constant NPW procedure , which we had to choose in our calculations, is usually a slow convergent one. The convergence of our results , as can be seen from fig. 1., is indeed quite slow : the value corresponding to $NPW = 380$, is about 4% of the convergent value . The varia-

tion between the last two points is less than 0.2 % . The convergent value of the lattice constant , as obtained from our calculation with NPW = 2200 (see table 3.1), is 10.362 a.u. . This value agrees with the experimental one , 10.26 a.u., within 1%.

We believe that the discrepancy with the convergent value of 10.26 a.u., determined by Yin [19] within a constant EPW procedure, is due to both the use of only one special k-point in our MD cell of eight atoms ,and to the disregard of the d ($l=2$) nonlocal term in our pseudopotential.

Since a MD analysis of a system regards its ionic motion as governed by the Newton equations , our finite temperature results , must be compared with the experimental ones for high temperatures only ,for which the classical limit holds . We look then at the experimental results for temperatures higher than the Debye temperature Θ_D , which is about 625 ° K for silicon . In this temperature regime α is approximately linear as a function of the temperature and hence α is nearly constant (see table 3.2) .

In principle we should be able to observe the small variations of α still present at high T, because our calculations fully account for anharmonic terms in the potential energy. In practice, the precision with which the values of α are computed does not allow us to account for such

Table 3.1 : Relevant parameters used in our calculations : the energy cutoff EPW, the number of plane waves NPW, the time step Δt , the "Andersen parameter" M_V (see text), the "fictitious mass" μ (see text).

EPW (Ry)	NPW	Δt (a.u.)	M_V (a.u.)	μ (a.u.)
8	380	6	0.05	300
12	750	6	0.05	300
14	950	6	0.05	300
20	1650	4	0.05	300
24	2200	4	0.05	300

Table 3.2 : Measured values of the thermal expansion coefficient α as a function of the temperature in the high temperature regime [27].

$T (^{\circ}\text{K})$	$\alpha (10^{-7}/^{\circ}\text{K})$
600	38.6
700	39.8
800	40.5
1000	42.1
1200	43.3
1400	44.2

Table 3.3 : Calculated values of the lattice constant l as a function of the temperature T , for different values of NPW. The values at $T = 0$ determined by a steepest descent procedure are also indicated.

NPW = 380		NPW = 750	
T	l	T	l
0	9.924 ± 0.002	0	10.139 ± 0.002
860 ± 30	9.951 ± 0.003	600 ± 20	10.165 ± 0.002
1320 ± 20	9.983 ± 0.003	1340 ± 20	10.199 ± 0.002

NPW = 950		NPW = 1650	
T	l	T	l
0	10.222 ± 0.002	0	10.347 ± 0.002
780 ± 30	10.278 ± 0.003	600 ± 10	10.410 ± 0.005
1150 ± 30	10.308 ± 0.003		

NPW = 2200	
T	l
0	10.362 ± 0.002
310 ± 10	10.394 ± 0.002

variations.

We are now going to discuss the results obtained for $l(T)$ at finite temperatures.

In table 3.3 we report the theoretical points $l(T)$ determined by the constant pressure MD simulation, for different values of NPW. The values of l for $T=0$ are also indicated. We have found that the highest is the temperature, the longest is the time needed by the system to reach equilibrium. Hence the number of time steps employed in our calculations is not the same for all the points $l(T)$.

We notice that in order to ensure our calculated properties were evaluated at equilibrium, we did not commence averaging for properties until at least 200 time steps had elapsed.

Figure 2 displays the average temperature \bar{T} and lattice parameter \bar{l} in a MD run where the temperature was initially raised at 1500 °K. About three thousands time steps have been necessary to achieve an accurate estimate of the equilibrium values. By comparison, the same quantities for a MD run in which the initial temperature was 600 °K, are shown in figure 3b. In the latter case only 1000 time steps are necessary to achieve the same accuracy on the average values which one has in figure 2. In figure 3a the instantaneous values of both the temperature and lattice constant are shown. These correspond to the average values of figure 3b.

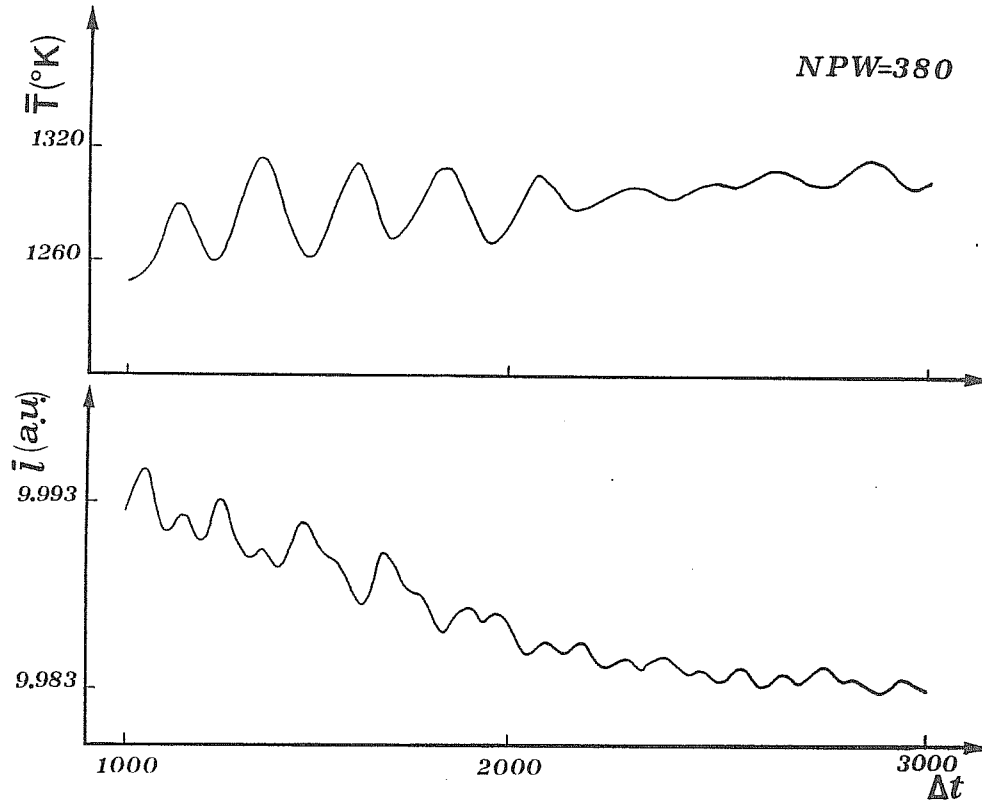


Fig. 2. Average lattice parameter and temperature from a constant pressure MD run in which the temperature was initially raised to 1500 K.

As expected, the dependance of l on the temperature, as extrapolated from the computed values which we report in table 3.3, is linear within the estimated theoretical errors. This is true for each value of the parameter NPW. The straight line fit of the function $l(T)$ allows the evaluation of the lattice constant for any desired value of the temperature. Fig. 1 shows the values of l computed for $T=600$ °K, as function of the parameter NPW. The convergence of $l(T=600)$ with the number of plane waves is similar to that displayed by $l(T=0)$. The convergent value for $T=600$ °K

overestimates the experimental one of about 1.5% .

Figure 1 shows also that the difference between the two values at zero and finite T , Δl , is strongly dependent on the value of NPW . Δl is indeed more than doubled when we pass from NPW = 380 to NPW = 2200. We must emphasize that we are observing variations on l of the order of milesimal part of $l(T=0)$. Therefore small errors on $l(T)$, lead to much larger error on Δl . In figure 4 we display the thermal expansion coefficient α determined via the slope of our interpolating straight line for $l(T)$. The variation of α with NPW is the same as that of Δl . The convergent value of α is about 2 times the experimental value measured for T larger than the Debye temperature (see table 3.2) .

Three main reasons can be responsible for the discrepancy of our result with experiment :

1) the use of only one special \vec{k} point in a cell of eight atoms.

As in the case of zero temperature results, the present ones are not expected to be at convergence to this respect.

2) The size of the MD cell.

Since our MD cell contains only 8 atoms, the error made in the computation of averages from eqs. (1.10, 1.11) is

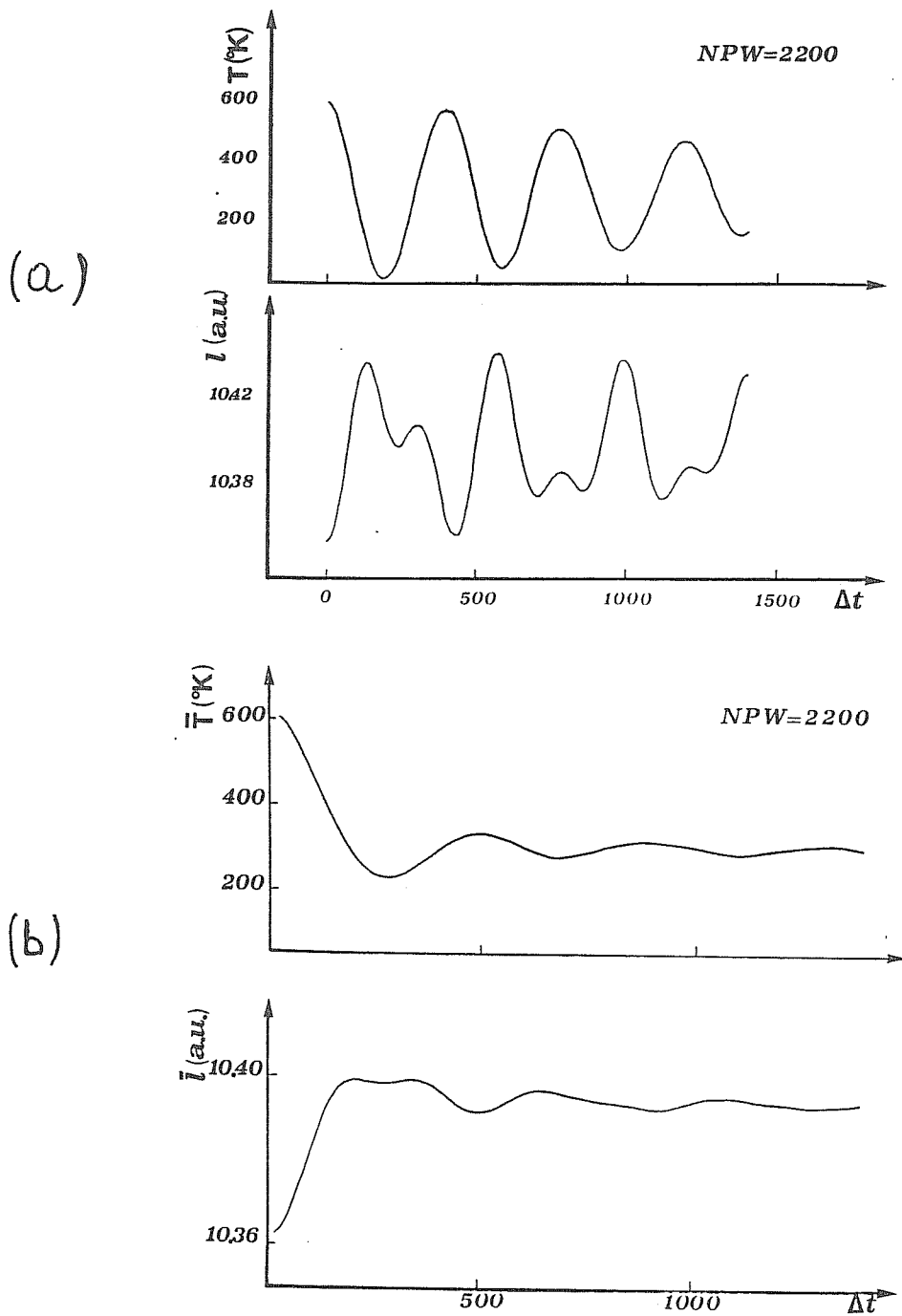


Fig. 3. Instantaneous (a) and average (b) values for the lattice parameter and the temperature, from a constant pressure MD run in which the temperature was initially raised to 600 K.

expected not to be negligible.

3) The disregard of the d nonlocal contribution to the pseudopotential. This effect can be reasonably supposed to be less significant than the first two.

We notice that as the size of the MD cell increases, the number of special \vec{k} points needed for accurate integrations over the Brillouin Zone decreases. Therefore an improvement on our calculated value for α should come from either an enlargement of the MD cell, with one \vec{k} point or from an increase of \vec{k} -points in a cell of eight atoms.

We may attempt an explanation of the large change which we obtain for α as the parameter NPW varies. The analysis of α computed from the Silicon phonon frequencies and the Grüneisen parameters obtained by G. B. Bachelet et. al. [24] can be useful to this respect. The method adopted in Ref.[24] combines the new MD-DF approach with the theory on quasi-harmonic lattice dynamics developed by De Lorenzi and Jacucci [25].

Table 3.4 shows the α values calculated by G. B. Bachelet et.al. at different fixed values of the conventional crystal cell volume. As in our case, this cell contains eight atoms. α is seen to be strongly dependent on the volume at which the calculation is performed. Its value is more

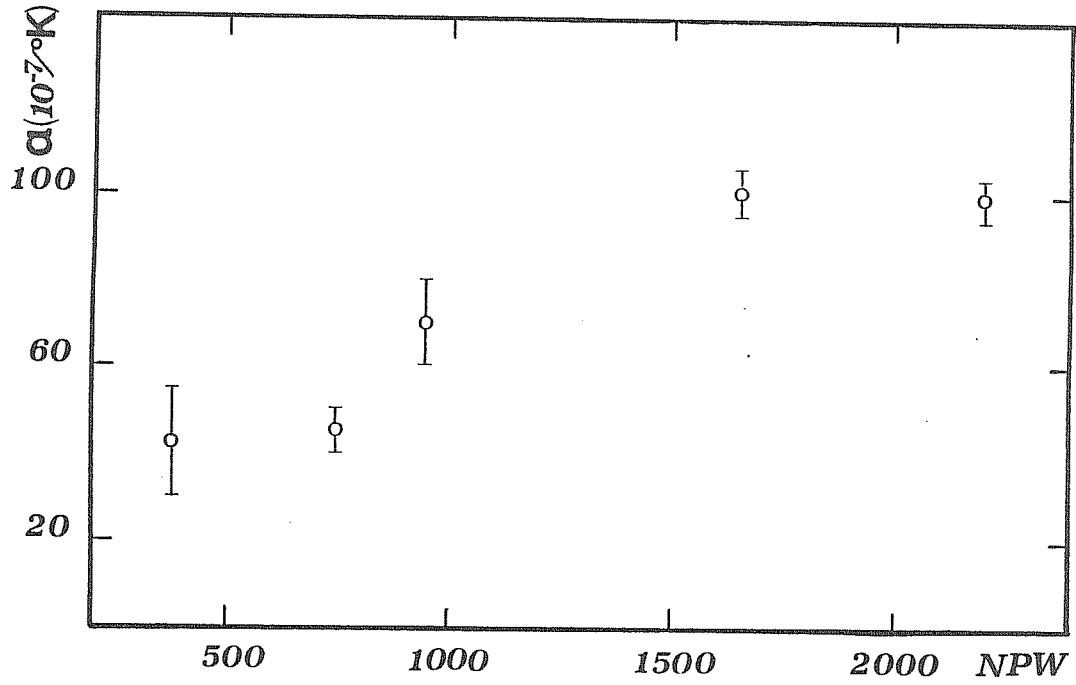


Fig. 4. Thermal expansion coefficient α as a function of the number of plane waves used in the calculation.

Table 3.4 : Thermal expansion coefficient α calculated for different values of the lattice constant (from ref. 24). The calculation is performed with EPW = 8.0 Ry .

LATTICE CONSTANT (a.u.)	THERMAL EXPANSION COEFFICIENT ($10^{-7}/^{\circ}\text{K}$)
10.263 ^(*)	48 ÷ 51
9.829 ^(†)	19 ÷ 20

(*) EXPERIMENTAL VALUE

(†) CALCULATED VALUE (Ref. 24)

than doubled when the experimental instead of the calculated lattice constant is used in its evaluation. This large vari-

ation is certainly also determined by the variation of the bulk modulus B with volume. This can be argued in the following way.

The dependence of B from the volume V can be determined by the Murnaghan's equation of state [26] :

$$E_{\text{Tot}}(V) = \frac{B_0 V}{B'_0} \left[\frac{(V_0/V)^{B'_0}}{B'_0 - 1} + 1 \right] + \text{const} \quad (3.1)$$

E_{Tot} indicates the total energy of the crystal; B_0 and B'_0 are respectively the bulk modulus and its pressure derivative calculated at the equilibrium volume V_0 . If the computed values of E_{Tot} are fitted to eq. (3.1) [14], B'_0 turns out to be 3.2. $B(V)$ can be calculated from the second volume derivative of eq. (3.1) and then used to establish the volume dependence of α (see eq. 1.16), under the hypothesis that the sum of Grüneisen parameters varies weakly with V . In this way, α turns out to be proportional to $V^{B'_0-1}$. Taking for B'_0 the value of 3.2,

$$\frac{\alpha(10.263)}{\alpha(9.829)} = 1.33$$

3.2. Results for the direct energy gap

In order to evaluate the variation of the direct energy gap of Silicon with the temperature, we have computed the electronic eigenvalues at the Γ point $\vec{k} = (0,0,0)$. The latter is included in our calculation for the total energy with a zero weighting factor. In our calculation, the Γ and the X points of the BZ are equivalent, since they differ by a reciprocal lattice vector of the chosen simple cubic supercell. Therefore the diagonalization of the Λ matrix (see eq. 1.4a) at $\vec{k} = (0,0,0)$ gives not only the electronic levels at Γ but also those at X.

We have first calculated the direct gap E_g at $T = 0$. To this end, we have optimized the total energy of Silicon via a steepest descent procedure, keeping fixed the crystal volume at its experimental value and the ions in the perfect crystal positions. The calculated energy levels at $T=0$ are reported in table 3.5. Our results compare well with those obtained by Yin and Cohen [14] within a conventional DF-LD approach.

We now turn to discuss our finite temperature results. The temperature derivative of the energy gap at constant pressure can be expressed as the sum of two terms :

$$\left(\frac{\partial E_g}{\partial T}\right)_P = \left(\frac{\partial E_g}{\partial T}\right)_V + \alpha \left(\frac{\partial E_g}{\partial \ln V}\right)_T \quad (3.2)$$

Table 3.5 : Electronic energy levels of Silicon at Γ and X, calculated using an energy cutoff of 14 Ry. The lattice parameter was fixed to the experimental value. The energies are measured from the top of the valence band (Γ'_{25}).

	$E_{th}^{(+)}$	$E_{expt.}^{(*)}$
Γ_1	-12.20	
X_1	-8.00	
X_4	-3.12	
Γ'_{25}	0.	
X_1^c	0.84	
Γ_{15}^c	2.61	3.40 (a)
Γ_{21}^c	3.06	4.18 (a)

(+) Calculated value

(*) Experimental value

(a) from Ref. [27]

The first term in the right-hand side of eq. (3.2) represents the "explicit" effect of the electron-phonon interaction, while the second term is related to rigid volume changes. The electron-phonon interaction induced by the thermal ionic motion, couples electronic states with different \vec{k} vectors, which are orthogonal in the equilibrium situation. The phonon frequencies in Silicon have at most values of 50 meV. Therefore the difference between the energy of the coupled electronic states will be correspondingly small. Due to the shapes of the Silicon energy bands in the neighborhood of $\vec{K} = (0,0,0)$, states having small energy differences are also separated by small \vec{k} vectors. Hence an accurate account of the electron-phonon interaction relies on the possibility of including very small phonon \vec{k} vectors in our calculation. This can be achieved only with a MD cell of much larger dimension than that we used. We have roughly estimated that an appropriate MD cell should be at least ten times larger than that adopted in the present calculation.

In principle, the MD-DF method allows to evaluate the electron-phonon effects on the energy gap variation with temperature. The practical calculation, however, is not feasible because the huge number of particles which should be considered is not manageable even by means of supercomputers.

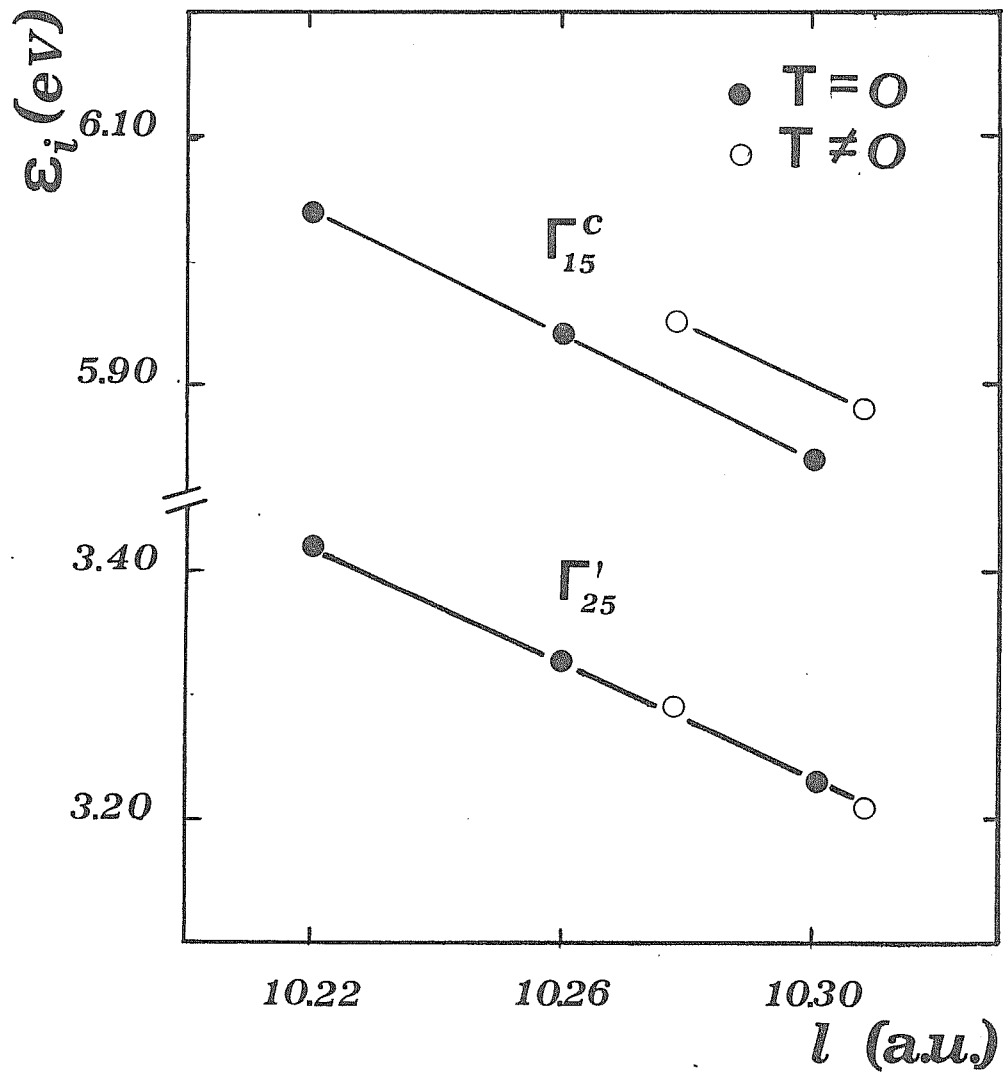


Fig. 5. Behaviour of the $\tilde{\epsilon}'_s$ and $\tilde{\epsilon}^c_s$ electronic levels of Silicon as functions of the lattice constant l . Both zero- and finite-temperature results are shown.

Therefore, our calculation is expected to account mainly for the implicit thermal expansion contribution to the temperature derivative of the energy gap. The latter contribution is the smallest of the two terms of eq. (3.2) : its measured value is -0.3×10^{-4} (eV / °K), against the measured value of -1.9×10^{-4} (eV / °K) for $\left(\frac{\partial E_g}{\partial T} \right)_V$. Our calculated value for $\left(\frac{\partial E_g}{\partial T} \right)_P$ is $+ 0.3 \times 10^{-4}$ (eV / °K). Though it has the same magnitude as the experimental datum, it has the wrong sign.

In order to investigate the reasons of our discrepancy with experiment, we have carried out a zero temperature calculation of $\left(\frac{\partial E_g}{\partial \ln V} \right)_T$. The so called deformation potentials $\left(\frac{\partial E}{\partial \ln V} \right)_T$ which we calculate are reported in table 3.6. As can be seen from this table, our result for $\left(\frac{\partial E_g}{\partial \ln V} \right)_T$ has the right sign .

In Fig. 5 we compare our results for the Γ'_{25} and Γ_{15}^c levels, as obtained from zero and finite temperature calculations. It is apparent that the main source of error in the sign of $\left(\frac{\partial E_g}{\partial T} \right)_P$ evaluated at finite temperature , is related to thermal effects on the Γ_{15}^c conduction level. The reasons why the effects of the temperature are more pronounced on this level than on the top of the valence band constitute an open question.

Table 3.6 : Deformation potentials for the electronic states of Silicon at Γ and X. Our calculated values are compared with other theoretical results and with the available experimental data.

	Present work	Ref. [28]	Expt.
Γ_1	-0.4	-1.0	
X_1	-3.8		
X_4	-4.7	-5.4	
Γ'_{25}	-8.1	-7.9	-8.6 (a) -4.6 (b)
X_1^c	-6.4	-5.5	
Γ_{15}^c	-8.6	-8.2	
Γ_{21}^c	-18.8	-20.3	

(a) From Ref. [29]

(b) From Ref. [30]

CONCLUSIONS

In this thesis work we have extended the original formulation of the Molecular Dynamic - Density Functional (MD-DF) approach, combining the latter with the constant pressure MD method due to Andersen.

We have tested this " ab initio " constant pressure MD method , in which the N-body potential is derived from DF theory , studying finite temperature properties for crystalline silicon : in particular we have studied the thermal expansion coefficient of silicon .

This property appears to be very sensitive to several parameters used in our calculation. Hence a careful analysis of how the thermal expansion coefficient depends on these parameters allows a broad test of the accuracy of our approach and of the possibility that it can be used in the future for the study of more complex physical situations, e.g. phase transitions .

A thorough analysis of the sensitivity of α from the parameters of the calculation should test its dependance on the following factors :

- 1) the number of plane waves (NPW) employed to describe the electronic states of the system;
- 2) the size of the MD cell;

3) the number of k -points used to integrate over the Brillouin Zone.

This thesis has been concerned with the first test, while the other two are part of our work in progress.

The convergence of the results for α with NPW has been found to be very slow. To achieve a convergent value, we had to employ a number of plane waves as high as 2200. The need for such high a NPW to correctly account for properties which depends on volume changes, restricts the possibility of using larger MD cells. This restriction is imposed by the exceedingly large computer memory required in calculations with large MD cells and large NPW.

In order to overcome this difficulty, one can think of introducing a correction to the total energy which allows to reproduce the convergent result by means of a reasonably small number of plane waves.

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