ANNUAL LETTER REPORT BY O.F. SANKEY

P.I. FOR N00014-85-K-0442

Theory of electronic states and formations energies of defect complexes, interstitial defects, and crystal growth in semiconductors. Period covering Oct. 1988-Oct. 1989.

I. Introduction

The

We have successfully completed our first version of an ab-initio molecular dynamics computer code, which can simulate the motion of atoms at a surface and in the bulk of a semiconductor. We combine Newton's equation for the nuclei,

is combined

F = ma with the Schrodinger equation for the electrons, ~~$H\Psi=E\Psi$~~ Psi, to obtain a uniform picture of a covalent systems dynamical properties.

performed

~~In~~ this document, ~~we~~ will list some of the simulations that we have performed. These simulations should not be considered ~~as~~ being final, but we decided to try a variety of problems without going into extreme depth, so that we can better assess the strengths and weaknesses of the technique.

is developed with

We have developed a tight-binding method, ~~whose~~ tight-binding matrix elements ~~are~~ calculated entirely from first principles. No fitting to experiment of any quantities is needed or done. ~~We use~~ this tight-binding

will

Hamiltonian ~~to~~ calculate the electronic structure of the material. The electronic structure theory is based on the local density approximation (LDA), with no adjustable parameters. We have made a number of approximations which are detailed in Refs. 1, 2, and 3. The use of approximations is essential to having a method which is fast enough to be useful for simulation of medium and large size systems. Where possible, ~~we have compared~~ our results to experimental data and find agreement consistent with the LDA.

We calculate forces on the Si atoms by employing the Hellmann-Feynman theorem. As a consequence of our ab-initio tight binding approach, in conjunction with a careful optimization of computational techniques, we find that it is practically possible to perform molecular dynamics simulations in supercells containing up to a couple hundred atoms. We are working on dramatic generalizations and enhancements of the procedure, and expect to make rapid progress.

We close this section with a mention of some general features of the simulations we have performed. In each simulation we choose initial conditions so that the linear and angular momentum is zero, and the center of mass is stationary. Additionally, we will always use the convention that "temperature" T will refer to "kinetic temperature", that the value of T such that (3/2)kT = average kinetic energy per particle of the system.

The rest of this report gives brief examples of a variety of simulations.

II. Brief Examples of Simulations

For some simulations we have produced a plot of "kinetic temperature" T vs. time, where T satisfies the equation: average kinetic energy per particle = $(3/2)k_bT$. This type of plot illustrates the time dependence of the kinetic energy of the system. As we expect from classical equipartition, a system which starts from equilibrium at temperature 2T rapidly converts about half of that energy into potential energy. The temperature then fluctuates about T. Thus, for a system started with equilibrium geometry, we may confidently predict that the final average temperature will be quite close to half of the initial kinetic temperature we started with. Note that this comment is valid only for cases where we start from eqilibrium, however.

A second kind of plot we provide is what we term a "snapshot graph", which for planar motions gives the trajectories of each particle in the central supercell. For non-planar dynamics, we show a projection onto the xy plane.

Another plot which lends insight into the molecular dynamics is a graph of $\langle r^2(t) \rangle$, which illustrates how far an "average" atom deviates from its starting position at time t from where it began at t=0. Here <> is a configuration average over all particles in a cell.

We have in many cases performed a "dynamical quenching" of the system. By this we refer to a procedure designed to find a geometrical configuration with minimum potential energy. The minimum found may be a global minimum (as we will illustrate for small clusters of atoms), or a local minimum for a more complicated example, such as the dynamical quenching of a large number of atoms at a very high temperature. The method we found most effective was to quench the atomic velocities (i.e. set them to zero) near a peak of the temperature vs. time plot, then let the system evolve naturally until it reached the next maximum, quench again, and so on. This was found to be a very effective and accurate means of finding minimum energy configurations.

For some of our calculations we found it useful to calculate double time autocorrelation functions of two kinds. These are convenient because they probe the "memory" of the system. Roughly speaking, we may interpret small (in some appropriate sense) values of an autocorrelation function evaluated at two different times to mean that the dynamical variable from which we construct the correlation function is only weakly correlated, or entirely uncorrelated. We may think of this as a gauge of "information loss" with time evolution. Some specific functions we calculate:

1. A velocity-velocity autocorrelation function:

$$g(\tau) = \frac{\langle \vec{v}(\tau) \cdot \vec{v}(0) \rangle}{\langle \vec{v}(0) \cdot \vec{v}(0) \rangle} ,$$

where a cell average <> is taken of the dot product of atomic velocities at two times t_1 and t_2, and where $\tau = t_2 - t_1$. Since this function is invariant under translations of the temporal origin, we may take g to be a function only of τ.

2\. A position-position autocorrelation function:

$$G_x(\tau) = \langle \vec{u}(\tau) \cdot \vec{u}(0) \rangle ,$$

where τ is the same as for the previous equation. Here u is the departure from equilibrium. Function g_x obviously contains information about the "diffusive" properties of the molecular motion.

In either case, it is worthwhile to further consider the Fourier transforms of the correlation functions. The frequency domain version of g and g_x is clearly the natural function to work with if we are interested in a normal mode view of the motion. In this case, the frequency functions are interpreted as a spectral mode-density.

II-A Si Clusters.

The simplest class of problems susceptible to our techniques is the dynamics of small silicon clusters. Our technique does not require periodicity, so that reciprocal lattice vectors G are never used. This allows molecules, bulk systems, and surfaces to be handled all within the same framework.

For Si clusters we investigate vibrational modes, equilibrium ground state geometries, electronic states, high temperature phenomena, and collisions. The following simulations illustrate these.

Si_3 at room temperature

An Si_3 molecule is started at equilibrium with random planar velocities having an average energy of 600K. The center of mass is at rest and the molecule has no angular momentum. This constrains the motion to two dimensions.

Figure 1.

A snapshot of the simulation showing the positions of the three atoms in the Si_3 cluster over the time of the simulation. The motion is entirely in the plane. There are 2200 time steps each of 1.57 fs.

Figure 2.

The kinetic "temperature" as a function of time for the Si_3 simulation. The system starts at 600K, but the average over the whole simulation is close to 300K as expected from the equipartition theorem. Notice that the "temperature" of the molecule oscillates between 600K and 0K.

Si_3 at ~2500K

We now consider what happens to an Si_3 molecule at high temperature. A Si_3 molecule is started with random planar velocities having an initial average energy of 3000K. The atoms were not started from equilibrium; rather they were started from a right isosceles triangle with a bond length of 2.0 Å. The average temperature over the entire simulation is ~2500K. The center of mass is at rest and the molecule has no angular momentum. This constrains the motion to two dimensions. There were 3600 time steps, with each time step being 1.57 fs.

Figure 3.

A snapshot of the time evolution of the Si_3 simulation at ~2500K. The motion is entirely 2 dimensional, and is very far from harmonic.

Figure 4.

The temperature of the system as a function of time. The system started with an average kinetic energy of 3000K, but higher temperatures are seen since the system was not started from the equilibrium geometry.

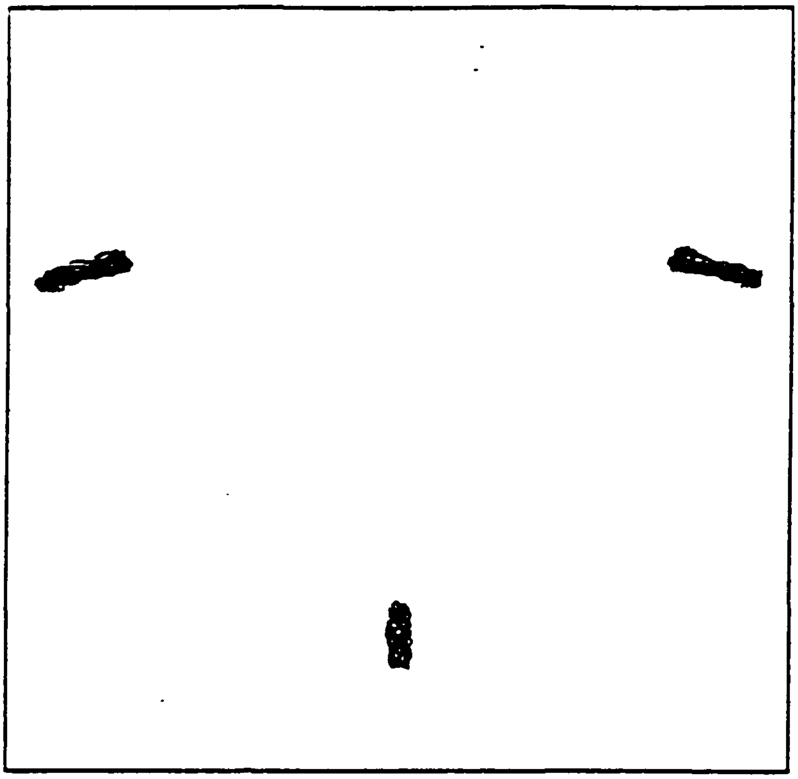


Fig. 1.

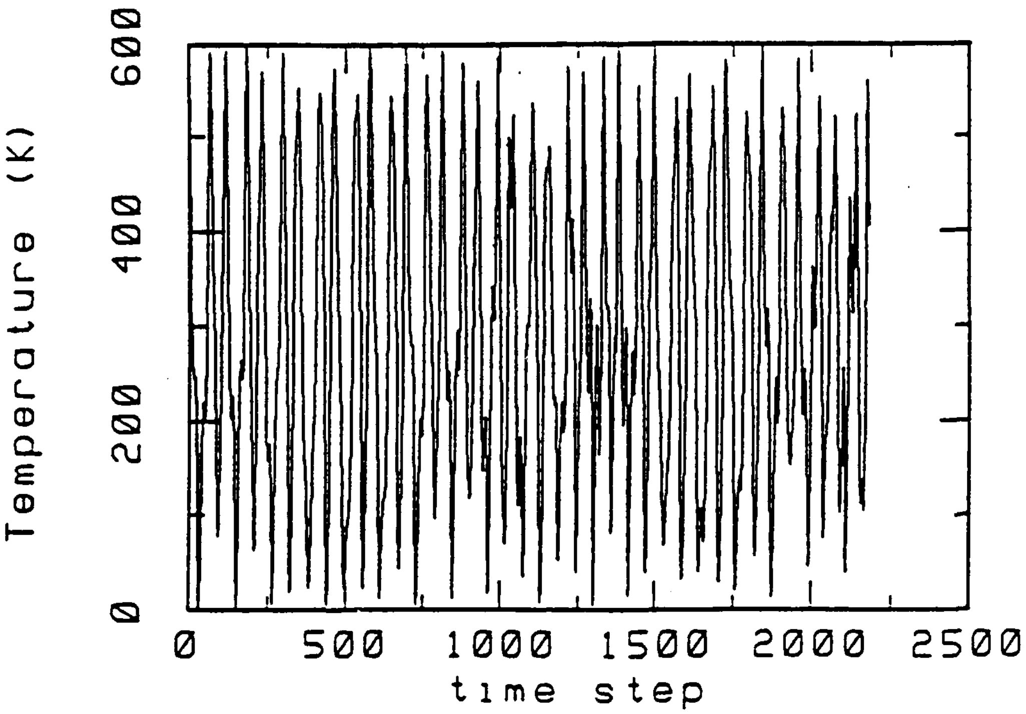

Temperature (K)
0
200
400
600
0
500
1000
1500
2000
2500
time step

Fig. 2.

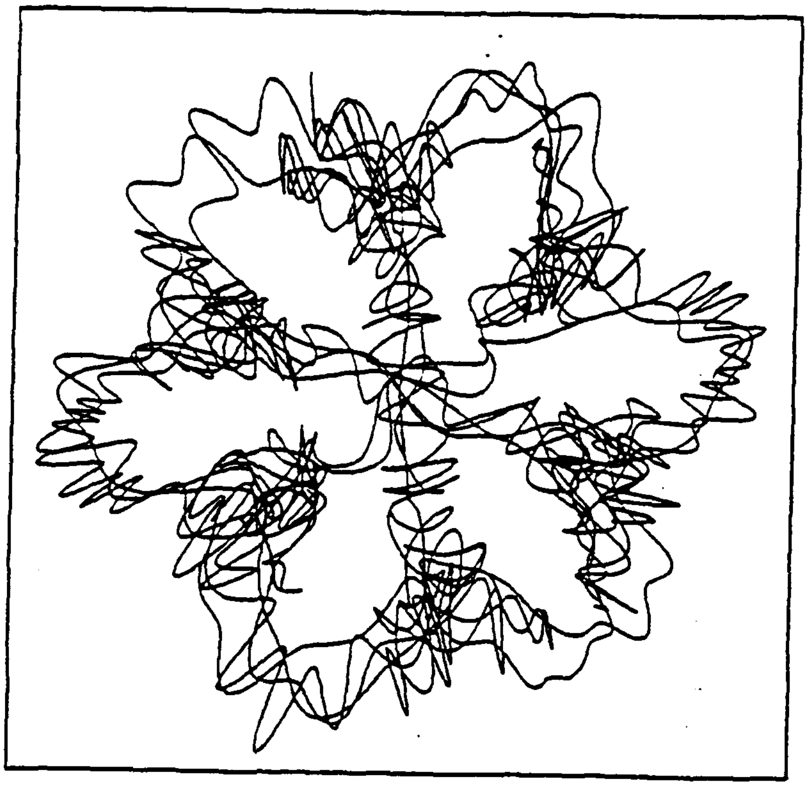


Fig. 3

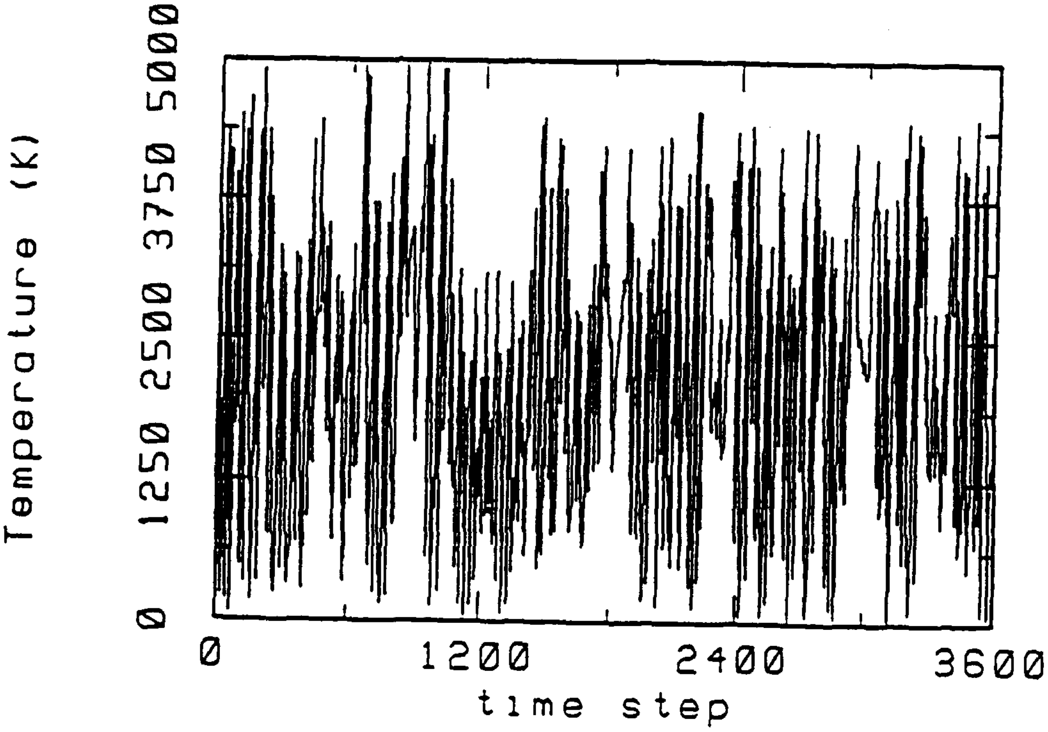

Temperature (K)
0
1250
2500
3750
5000
0
1200
2400
3600
time step

Fig. 4

Dynamical quenching of Si_3

A dynamical quenching was performed on an Si_3 molecule to find the ground state structure. The Si_3 molecule was started in a right triangle with sides of 1Å and 2Å. The atoms start very close together, and in fact the atoms would fly apart if they were not annealed. However, since it is quenched, the system relaxes rapidly to the equilibrium structure in ~100 time steps. The final geometry is that of an isosceles triangle.

Figure 5.

A snapshot of the dynamical quenching of the Si_3 molecule. The final positions are indicated by the "dots".

Figure 6.

The temperature as a function of time during the quench. We use the annealing procedure discussed in Section II.

Figure 7.

The final minimum energy geometry of the Si_3 molecule.

Figure 8.

The energy eigenvalues of the single particle LDA Hamiltonian, as a function of angle for the Si_3 molecule. The bond length is kept fixed at 2.189A. The Fermi energy shown in the figure separates occupied from unoccupied states. For the case of an equilateral triangle (60 degrees), the system has partially occupied levels, and is unstable.

Vibrational spectra of Si_3

Figure 9.

The spectrum of vibrational modes obtained from the ω-transform of the velocity-velocity autocorrelation function, $< v(\tau)v(0) >/< v(0)v(0) >$. The peaks occurred at normal mode frequencies, with broadening determined by the total elapsed time of the simulation. (In this figure, 3600 steps of 1.57 fs

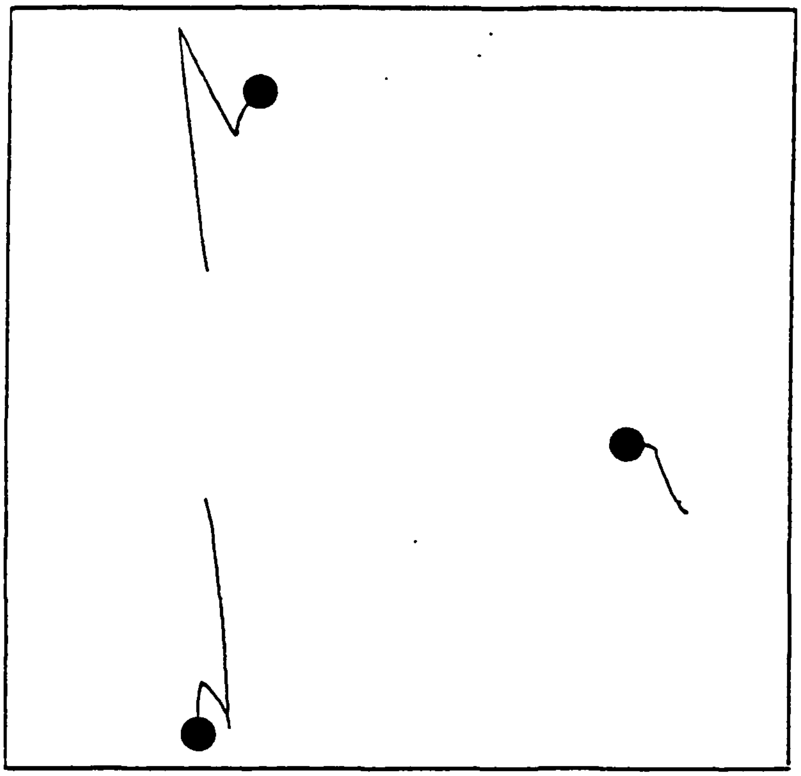


Fig. 5

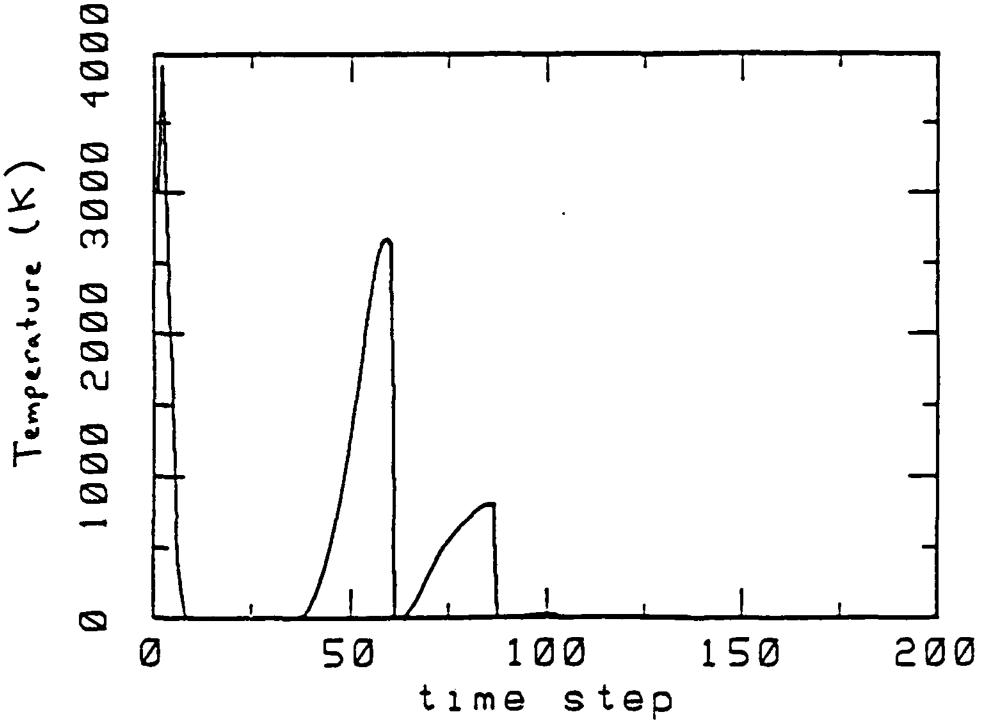


Fig. 6

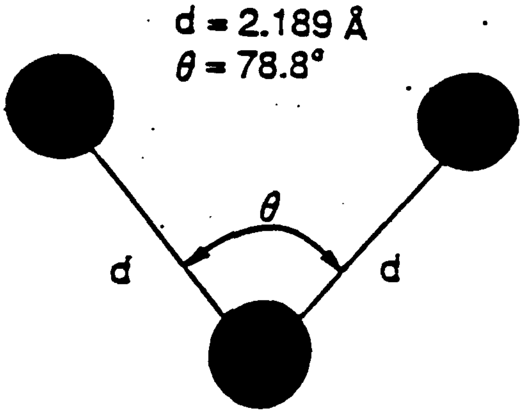

d = 2.189 Å
θ = 78.8°
θ
d
d

Fig. 7

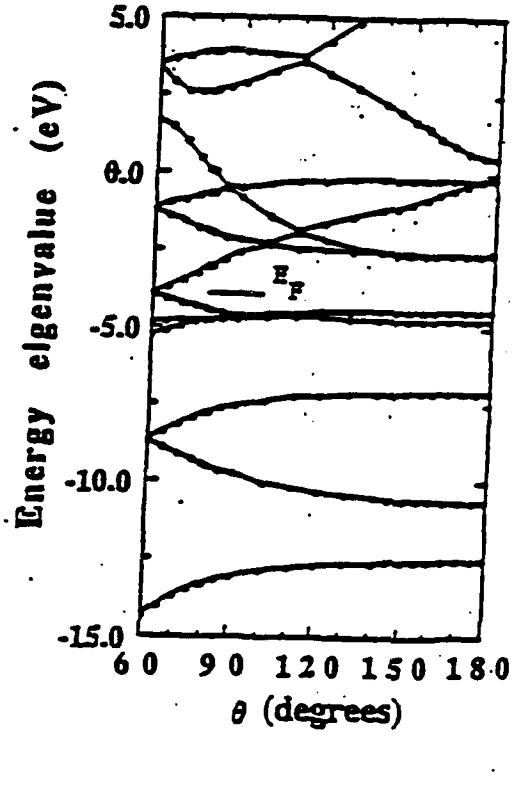

5.0
0.0
-5.0
-10.0
-15.0
Energy eigenvalue (eV)
E_F
60
90
120
150
180
θ (degrees)

Fig. 8

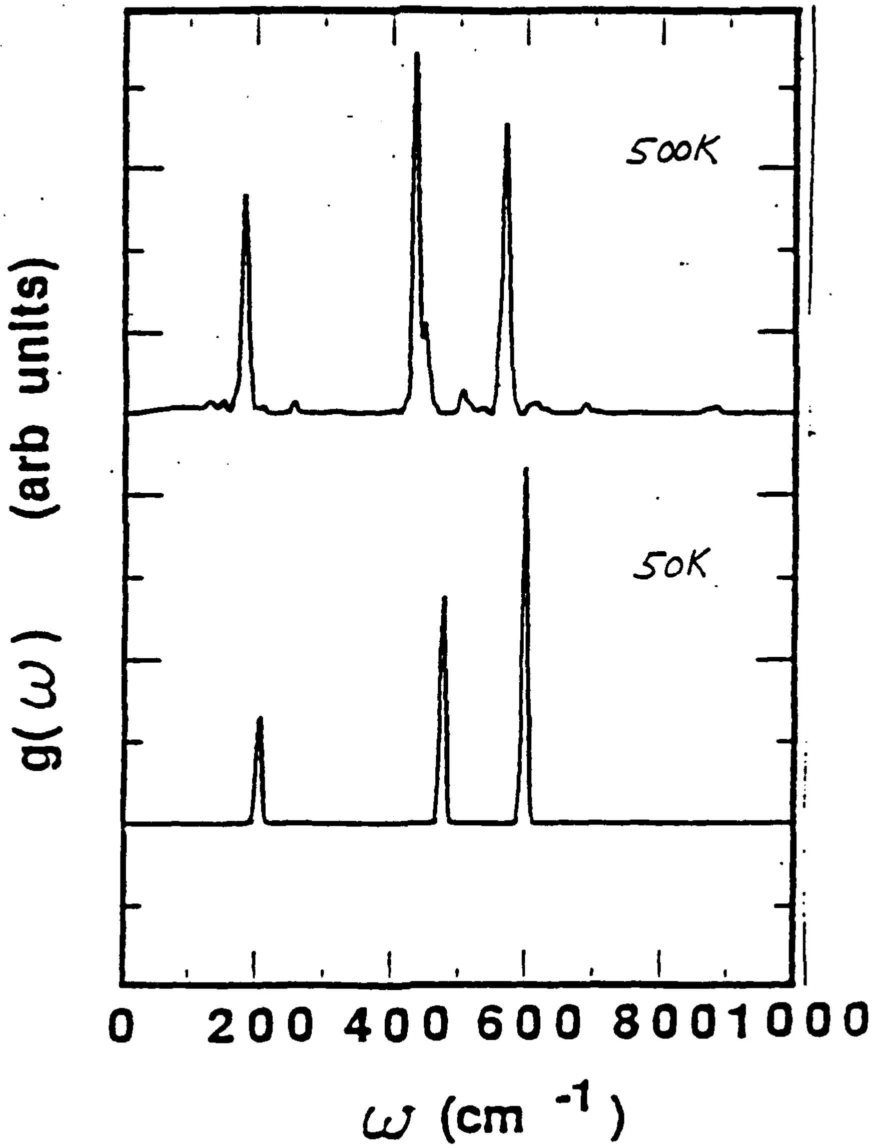


Fig. 9

were used). Two different average temperatures are shown. The simulation has no angular momentum or center of mass motion leaving the number of vibrational modes at 3n-6.

Figure 10.

We show for completeness the equilibrium structures determined through dynamical quenching for Si_4, Si_5, Si_6, and Si_7.

Collisions involving five Si atoms.

Our final simulation involving Si clusters involves the collision of two Si_2 molecules to form an Si^4 molecule.

The simulation begins with two Si_2 molecules coming together and colliding to form Si_4. The center of mass motion and total angular momentum are zero. When the two collide, a large energy of bonding is converted into kinetic energy and the newly created Si_4 molecule vibrates violently. The vibration continues for a time, and finally a dynamical is performed to bring the system to its equilibrium geometry.

Figure 11.

The snapshot of the time evolution of the collision between two Si_2 molecules to form a highly excited Si_4 molecule.

Figure 12.

The temperature as a function of time for the collision of two Si_2 molecules. The first 1000 time steps are free motion of non-interacting Si_2 molecules. At time step ~1000 the two molecules interact and the kinetic temperature rises substantially. The newly formed Si_4 molecule evolves naturally in time until about time step 2500 when the system is dynamical quenched equilibrium.

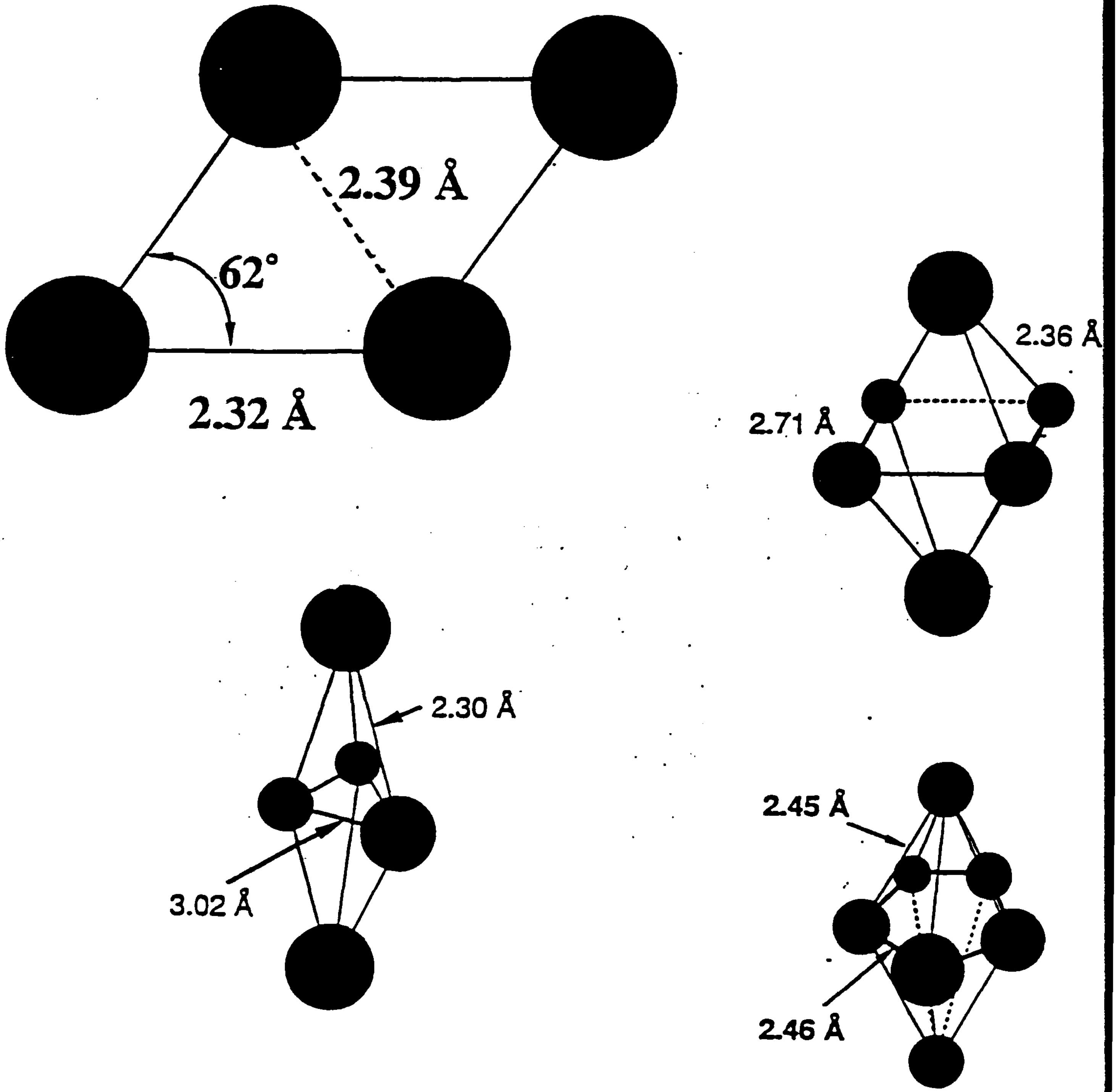


Fig. 10

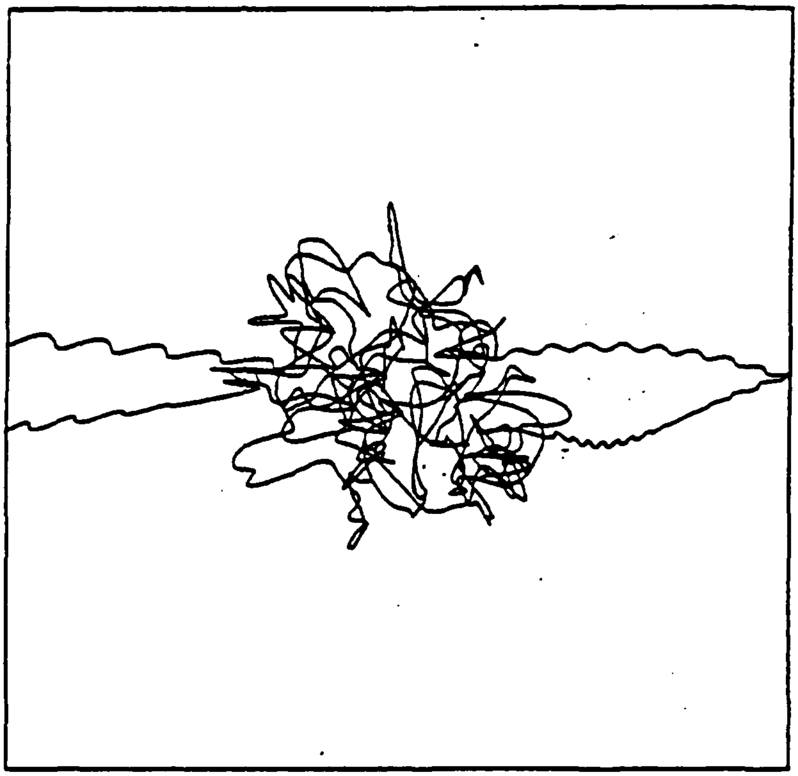


Fig. 11

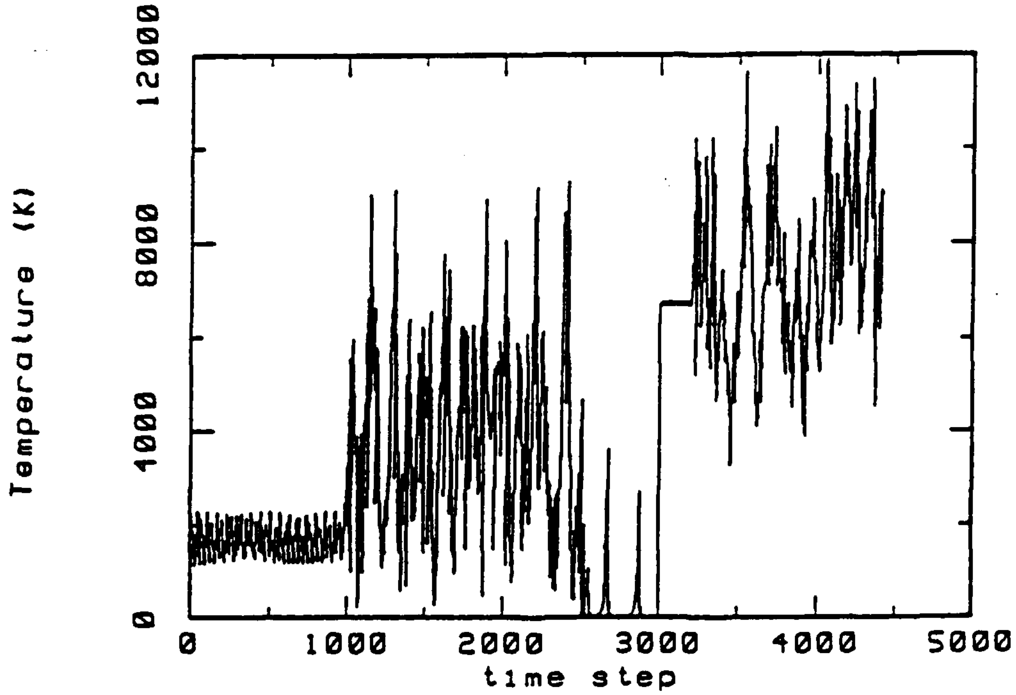

Temperature (K)
0
4000
8000
12000
0
1000
2000
3000
4000
5000
time step

Fig. 12

[100] phonons in bulk Si.

We now compute dynamically the phonon vibrational modes of bulk Si for phonons in the [100] direction. A supercell is used which contains 16 Si atoms. Eight special k points are used from the entire Brillouin zone in the computation of the total energy from which the forces are determined.

Figure 13.

(a) The [0 -1 1] plane in the diamond lattice, from which the supercell is constructed.

(b) The supercell geometry used to determine phonon modes with wavevector along X. The cell contains four segments of the type shown in (a). The larger atoms are shifted above the plane by $a/\sqrt{2}$, where a is the cubic lattice constant of the diamond lattice. There are 16 atoms in this cell (some edge atoms are in different cells), and the atoms in this cell can vibrate with phonon modes of wavevector 0/4, 1/4, 2/4, 3/4, and 4/4 of the X point in the Brillouin zone.

Simulation of all modes with k along [100].

This simulation shows bulk phonon modes of all polarizations with wavevector along [100]. The system is started from the equilibrium configuration, and the atoms are given random velocities with an initial temperature of 600K. This yields an average over the entire simulation of ~300K. The motion consists of a linear combination phonon of the five wavevectors (0, 0.2, 0.4, 0.6, 0.8, and 1.0 of $\frac{2\pi}{a}$ (100)), with all polarizations.

Figure 14.

A snapshot of the first few atoms in the supercell for the simulation with all modes present. Notice that for k along [100], the amplitude is much

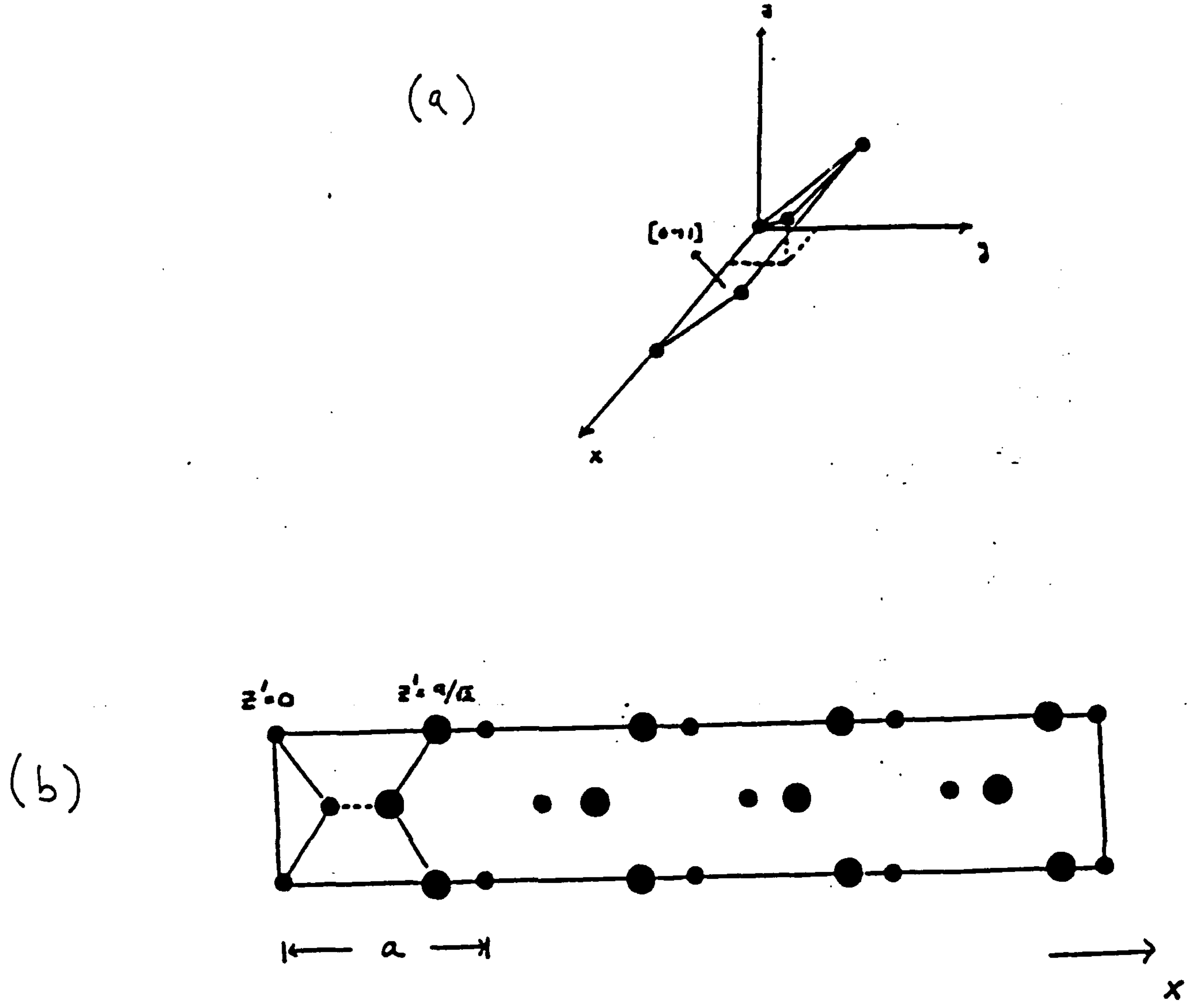


Fig-13

greater perpendicular to k, than parallel to k. This is due to the low-frequency transverse acoustic mode.

Figure 15.

The double fourier transform of the transverse velocity-velocity autocorrelation function, $g_n(t)$, where n is an index for particle n. The transform to ω-space was described in the introduction. The new feature of the double transform is the use of a spatial k transform with the atomic position of atom n. Thus $g_n(t)$ is transformed to $g(k,\omega)$. This function is plotted as a function of ω for the various values of k. Turning the figure on its side yields the more conventional ω vs. k dispersion relation.

Figure 16.

Conventional phonon dispersion relation calculated by computing the dynamical matrix using the frozen phonon technique in the supercell geometry describe above. The atoms are moved by small amounts statistically from equilibrium, and effective spring constants are determined. About 100 k vectors in the Brillouin zone are used to evaluate the electronic total energy. The theory is in close agreement with experiment.

Simulation of lattice relatation around Si vacancy.

We have simulated the lattice relaxation around a Si vacancy. We use a 32 atom BCC supercell geometry for the perfect crystal. Since one site is a vacancy, the atom at the origin is missing and there are actually only 31 atoms. The lattice constant chosen is 5.5Å, as this corresponds to the theoretical bulk minimum. Four special k-points are used. They are 0.285593(1,1,1), 0.285593(-1,-1,1), 0.285593(-1,1,-1), and 0.285593(1,-1,-1) in inverse Å units. These are the Monkhorst-Pack special points for the BCC lattice with lattice constant 5.5Å.

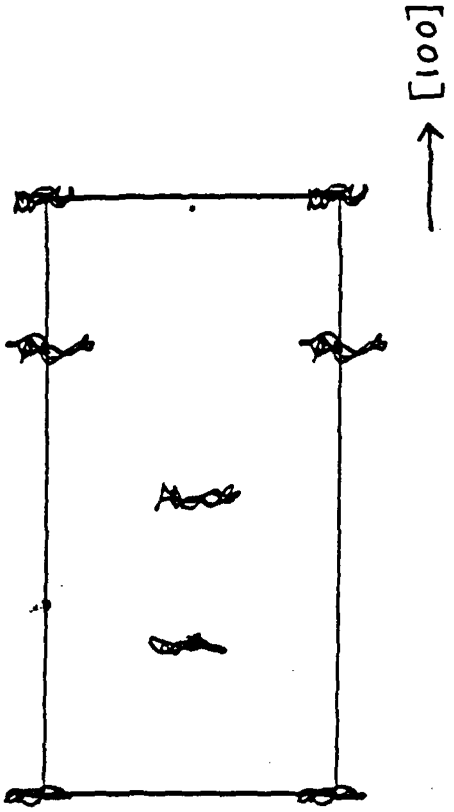

[100]

Fig. 14

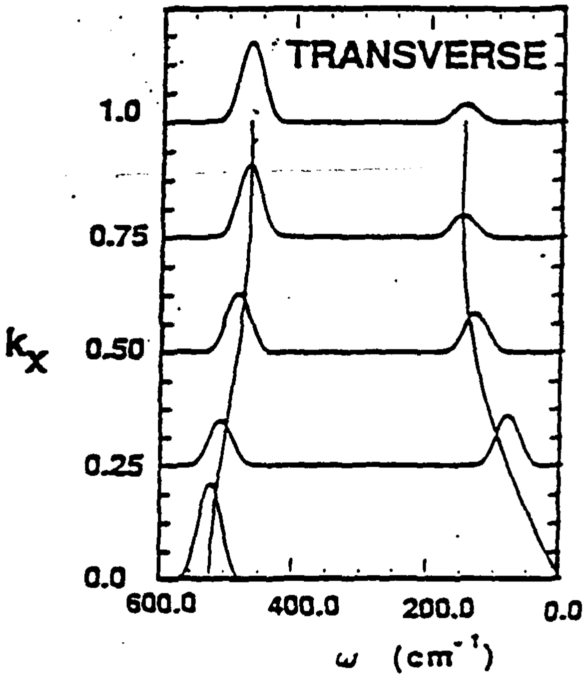

TRANSVERSE
k_x
1.0
0.75
0.50
0.25
0.0
600.0
400.0
200.0
0.0
ω (cm^{-1})

Fig. 15

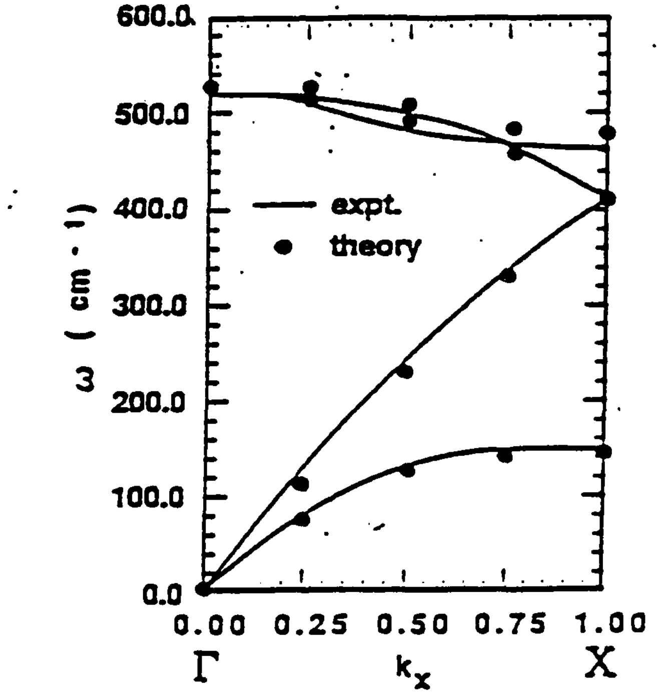

600.0
500.0
400.0
300.0
200.0
100.0
0.0
ω (cm⁻¹)
expt.
theory
0.00
0.25
0.50
0.75
1.00
Γ
k_x
X

Fig. 16

The simulation starts at the "ideal" positions, meaning the atoms are in the same position as if the vacancy were not there. We give the atoms random velocities with average temperature of 600K. Normally this would yield after some time an average velocity of 300K (room temperature). After 200 time steps (each of .206 fs), we begin to quench the system.

Figure 17.

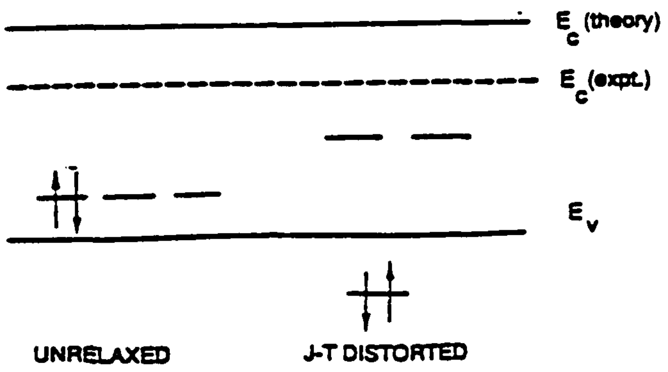
The electronic energy level spectrum in the band gap region for the vacancy. A triply degenerate level is found in the band gap which is occupied by two electrons. This corresponds to the situation at time $t=0$ (unrelaxed). Because the levels are degenerate and partially occupied, the system can undergo a Jahn-Teller distortion in which the symmetry is broken. The level structure at the end of the anneal is shown on the right. A single level is found at lower energy and is doubly occupied. A pair of doubly degenerate levels are found at higher energy are are unoccupied (for the case of the neutral vacancy).

Figure 18.

The final positions of the first nearest neighbors around the vacancy drawn to scale. The square shows the geometry of the "ideal" unrelaxed system, and the rectangle the geometry of the Jahn-Teller distorted system. The Jahn-Teller distortion is of tetragonal symmetry with the x and z displacements being equal, while the y displacement is different. The final tetragonal pattern could have been either x-, y-, or z-like. It came out y-like in this simulation, because there was no energy barrier from the configuration which existed when the annealing began at the 200th step.

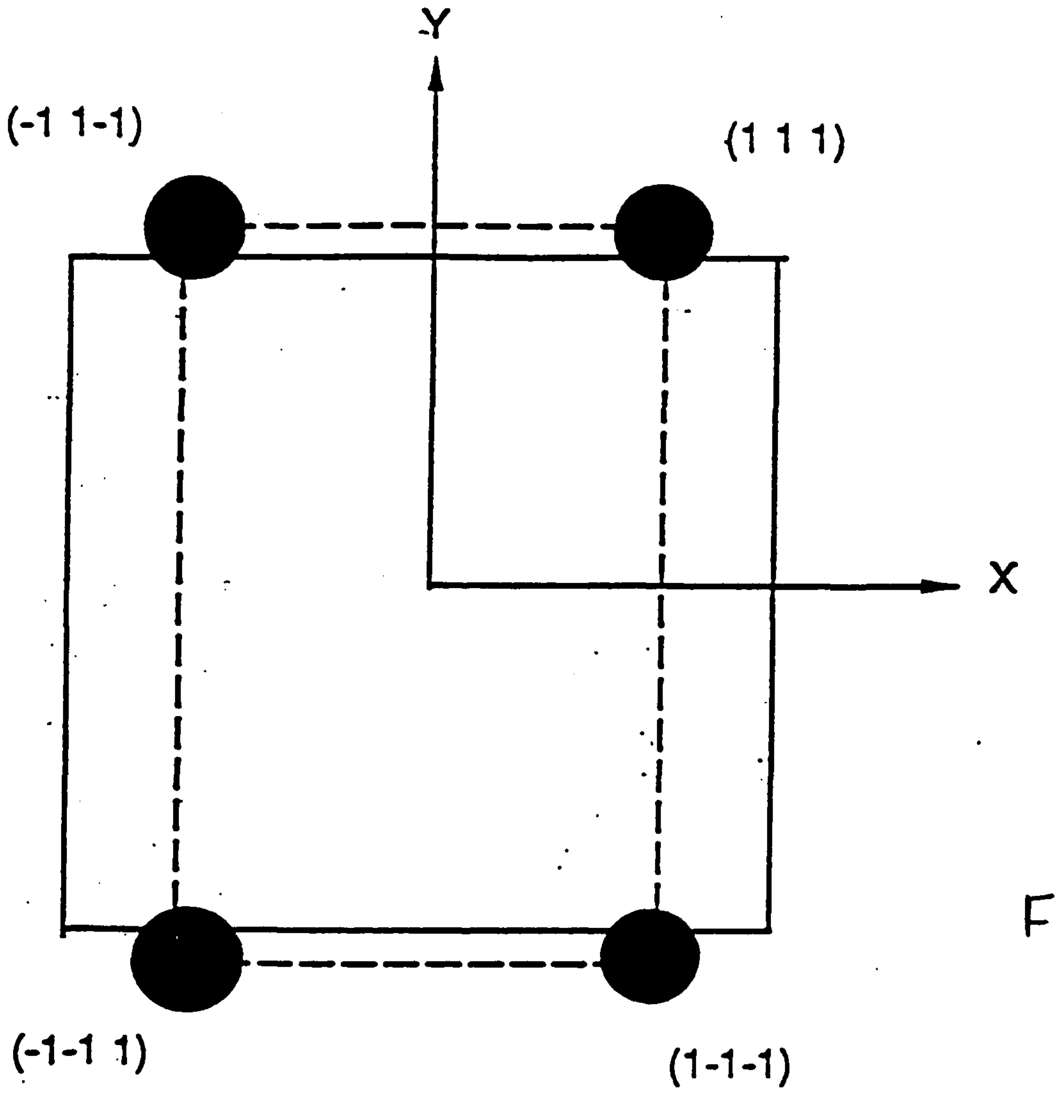
Free vibrations and simulated annealing of "liquid" Si at 1500K.

In this simulation, we start the particles at equilibrium, but with the very high average velocity of 3000K. This ought to yield (according to the



E_c (theory)
E_c (expt.)
E_v
UNRELAXED
J-T DISTORTED

Fig. 17



Y
X
(-1 1-1)
(1 1 1)
(-1-1 1)
(1-1-1)

Fig. 18

equipartition theorem) an average temperature near equilibrium of about 1500K. This is near the melting point of bulk Si (expt. 1683K). This high temperature stipulation was exploratory, so that only the k equal to zero wavevector is used as a "special" point to sum over the Brillouin zone. Four special points should be used for a more rigorous simulation.

The simulation is in two parts. In the first 500 times steps (2.09 fs each), the particles are allowed to move freely under the equations of motion. They can vibrate and/or diffuse. In the next 800 time steps the system is annealed by quenching the system by setting the velocities equal to zero on occasion.

Figure 19.

The snapshot of the first 500 time steps of the simulation where the atoms are moving freely. The geometry is the 32 atoms BCC geometry. One notices large excursions from the equilibrium positions, indicating diffusive motion and or melting.

Figure 20.

The average "temperature" as a function of time. At the first time step, the particles are started from equilibrium with an average velocity corresponding to a temperature of 3000K. Within a very few time steps, the kinetic energy is reduced by about a factor of 2, having been converted into potential energy. The average temperature over the whole simulation is 1400K, but large fluctuations are evident.

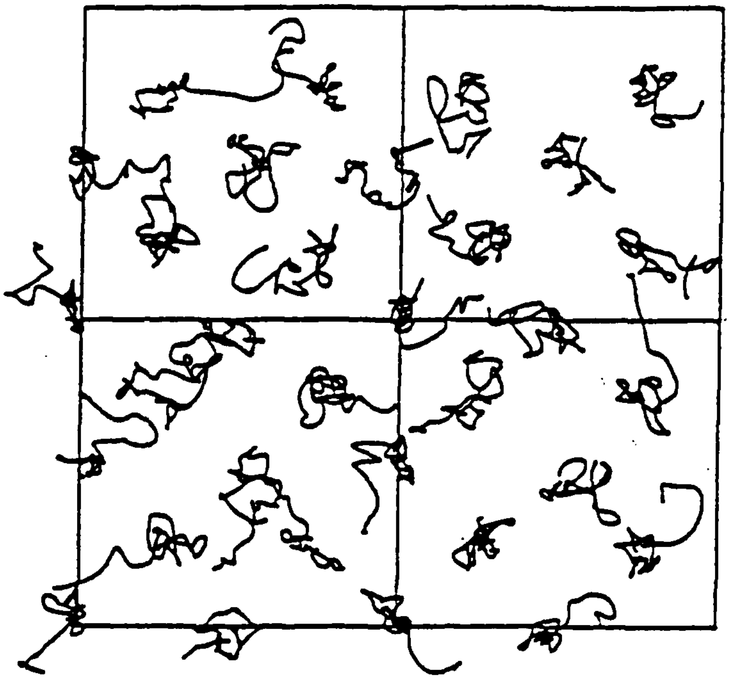


Fig. 19

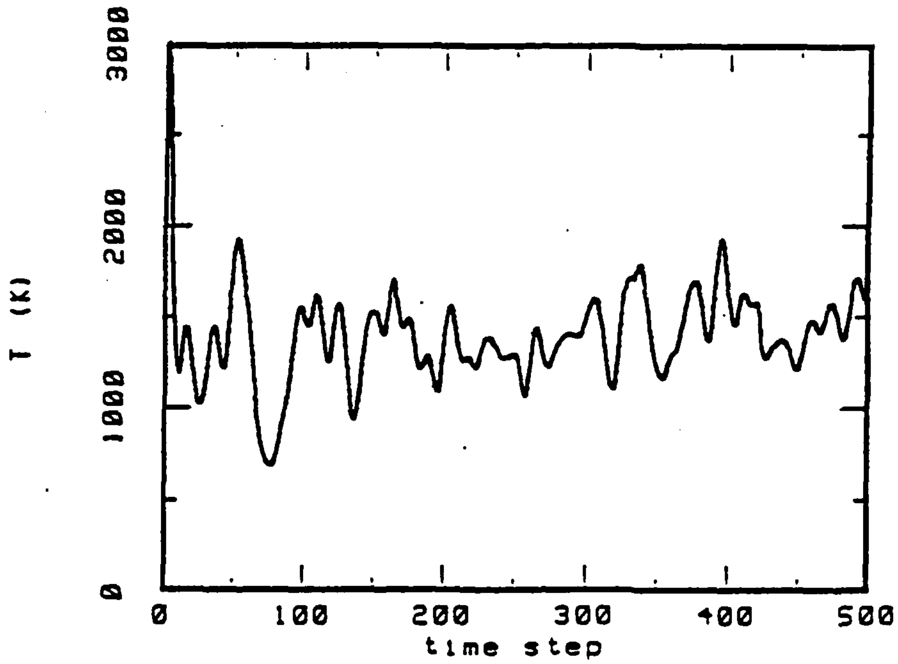


Fig 20

Summary

We have just illustrated a few applications of our newly developed quantum molecular dynamics method and computer code. The simulations reported here are our first and we anticipate large leaps are still possible. We believe our work is a major breakthrough in the area of quantum molecular dynamics.

References

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