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Molecular dynamics using the tight-binding approximation: application to liquid silicon

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Abstract. We present molecular dynamical simulations of liquid silicon using the tight-binding approximation for electron-mediated interactions. Several structural and dynamical properties of liquid silicon are calculated and compared with the results of *ab initio* and classical molecular dynamics. The tight-binding model with parameters fitted to bulk crystalline properties is found to be very successful in characterizing the liquid state, which facilitates large-scale dynamical simulations.

1. Introduction

The proper physical description of the properties of liquid silicon (l-Si) is a great challenge and is also of substantial practical interest. Silicon melts at an unusually high temperature of 1680 K where the transition from a fourfold semiconducting crystal to a low-coordinated metallic liquid occurs. Upon melting the density of silicon increases by $\sim 10\%$ which indicates a transition to a more compact liquid state. However, the coordination number of l-Si (6.5) is much lower than those characteristic of typical closed-packed metallic liquids (12-14). Low coordination has been considered to be a signature of the existence of covalent bonds in the liquid. Experimentally l-Si is not easy to study due to the high melting temperature. Simple theoretical models also fail to describe the bonding characteristics of l-Si.

Classical molecular dynamics (MD) has been widely used to study materials at finite temperatures [1]. In conventional simulations the force laws between particles are determined from empirical potentials that have been fitted to reproduce some experimentally observed properties of the system. For closed-shell systems, such as rare-gases, a two-body potential may provide an adequate description of the system. However, for covalently bonded matter, such as most semiconductors, at least a three-body term is needed because of the persistence of directional bonds. A proper fitting of several parameters is tedious and does not guarantee that the same potential would describe the system well in various environments and in different phases [2-4]. It is also difficult to evaluate to what extent the results are biased by the choice of the model potential. Stillinger and Weber (SW) constructed a many-body potential for silicon which was fitted to apply to both the liquid and solid phases [2]. The SW potential has been the most exhaustively tested and used model potential for MD simulations of solid, liquid and amorphous Si.

Recently, a first principles approach to MD has become possible. Car and Parrinello (CP) extended MD to include electronic effects within the density functional framework

[5]. The CP method allows the interatomic forces to be calculated during the simulation from the electronic degrees of freedom. Because of the absence of empirical fitting, the results are very reliable, and, in principle, no transferability problems exist (on the condition of a proper choice of the pseudopotential). Unfortunately these calculations are computationally heavy, due to the explicitly included electronic effects, which limits the duration of the simulation and the size of the system. The CP method has been used, for example, for structural studies of Si clusters [6] and disordered Si [7]. Recently, Stich *et al* have successfully applied the CP method to liquid and amorphous Si [8, 9]. These results serve as a useful reference for testing the validity of more approximate methods.

The high computational cost of the first-principles calculations has motivated a simplified but still quantum mechanical approach to MD. In the tight-binding (TB) model the electronic effects are treated approximately, leaving the computational cost modest compared with the CP simulations. However, the TB model coupled with MD [10] has the advantage over classical potentials that the interatomic interactions are determined at the microscopic level so that electronic bonding enters in a natural way. As an empirical method, the TB approximation still has to tackle the problem of transferability. However, as we argue below, a TB model derived in the bulk environment can give very good results from clusters to the liquid state. Goodwin, Skinner and Pettifor have developed a modification to the TB model that increases the transferability of the parameters from the bulk [11]. We will show that their modification, quite successful for Si clusters, also works very well in a MD study of liquid Si. To evaluate the performance of the method and the parametrization several structural and dynamical properties of l-Si are calculated and the results are compared with those of *ab initio* [8, 9] and classical [2, 12] MD simulations. While this paper was being written, we became aware of similar recent work by Wang *et al* [13], who have applied a TB-MD model to defects in bulk Si. Their conclusions are parallel to those of ours.

The rest of the paper is organized as follows: In section 2 we describe the TB formalism and parameters suitable for MD simulations of l-Si. In section 3 the results of the simulation are given and analysed, and in section 4 we present the conclusions.

2. The tight-binding approximation

The tight-binding expression for the total energy is

$$E^{\text{tot}} = \sum_i E^i - \sum_{m \neq n} \phi(\mathbf{R}_n - \mathbf{R}_m). \quad (1)$$

The first term describes the quantum mechanical bonding energy obtained as a sum of the approximate electronic eigenstates E^i . The second term is the classical pair potential that depends on the distance $\mathbf{R}_n - \mathbf{R}_m$ from atom n to atom m .

The bonding energy is derived from a simplified description of the Hamiltonian. The electronic wavefunction is expanded in terms of a small set of localized and orthogonal basis functions ψ_ν

$$\Phi^i(\mathbf{r}) = \sum_{\nu n} C_{\nu n}^i \psi_\nu(\mathbf{r} - \mathbf{R}_n). \quad (2)$$

The basis functions are usually the occupied or partially occupied atomic orbitals of the free atom, e.g. a single s state and three p states for silicon.

The Hamiltonian matrix is defined as

$$H_{\nu\mu, nm} = \int \psi_\nu(\mathbf{r} - \mathbf{R}_n) H \psi_\mu(\mathbf{r} - \mathbf{R}_m) d^3r \quad (3)$$

where H is the single-particle Hamiltonian. Then the Schrödinger equation reads

$$\sum_{\nu\mu nm} H_{\nu\mu, nm} C_{\nu n}^i - E^i C_{\nu n}^i = 0 \quad (4)$$

from which one can derive the eigenvectors and the eigenvalues, either through exact diagonalization or using some iterative algorithm [10], and finally the band structure energy.

The simplification of the TB scheme can be achieved by considering the matrix elements $H_{\nu\mu, nm}$ as parameters. Thus the rigorous integrals in (3) are replaced with angle- and distance-dependent functions fitted to experiment or to first-principles theories. For silicon with the minimal basis set of four atomic orbitals this approximation produces a parametrized TB matrix the dimensions of which are $4N$, where N is the number of atoms considered. Low dimensions of the matrix are essential if it is diagonalized at each stage. The parameters of the pair potential in (1) are adjusted simultaneously with the TB matrix elements.

In a tight-binding formulation for silicon we use the parametrization reported by Harrison [14] with the modification provided by Goodwin *et al* [11]. Harrison's original TB parametrization was adjusted to reproduce the equilibrium properties of the Si diamond structure. Goodwin *et al* rescaled the parameters in order to increase transferability to environments that depart from the diamond lattice. They introduced a scaling function f that modifies the distance dependence of Harrison's Hamiltonian elements $H_\alpha(1)$ and the pair potential parameter $\phi(1)$

$$\begin{aligned} H_\alpha\left(\frac{r_0}{r}\right) &= H_\alpha(1) \left(\frac{f(r_0/r)}{f(1)}\right)^n \\ \phi\left(\frac{r_0}{r}\right) &= \phi(1) \left(\frac{f(r_0/r)}{f(1)}\right)^m \end{aligned} \quad (5)$$

where r is the distance between atoms, r_0 is the equilibrium nearest-neighbour distance of the diamond lattice and α denotes the interatomic bonding ($ss\sigma$, $sp\sigma$, $sp\pi$, $pp\pi$). $H_\alpha(1)$ and $\phi(1)$ refer to parameters for the diamond structure at equilibrium.

The scaling function f does not affect the fitting to the volume and the energy of the diamond at equilibrium but it is used to compensate for Harrison's overestimation of bond lengths in other structures. The form of f is a smoothed step function

$$f\left(\frac{r_0}{r}\right) = \frac{r_0}{r} \exp\left(-\frac{r}{r_c}\right)^{n_c} \quad (6)$$

where the values of r_c and n_c define the position and the sharpness of the step. The step is positioned between the first- and the second-nearest neighbours in the diamond lattice. The smoothness of the scaling factor is essential in a molecular

dynamical simulation of a liquid in order to avoid too abrupt changes in the forces between atoms that move continuously. Also, truncated parameters are sufficiently short-ranged so that all the non-zero interactions in the liquid can be calculated.

The final set of the parameters used is [11]

$$\begin{array}{ll}
 E_s = -6.173 \text{ eV} & E_p = 2.122 \text{ eV} \\
 \phi(1) = 3.4581 & \\
 H_{ss\sigma}(1) = -1.82 \text{ eV} & H_{sp\sigma}(1) = 1.96 \text{ eV} \\
 H_{pp\sigma}(1) = 3.06 \text{ eV} & H_{pp\pi}(1) = -0.87 \text{ eV} \\
 n = 2 & m = 4.54 \\
 r_c = 3.6 \text{ \AA} & n_c = 6.48.
 \end{array}$$

The coefficients $H_\alpha(1)$ [14] and the pair potential parameter $\phi(1)$ were taken from the fitting to diamond at equilibrium. The state energies E_s and E_p and the pair-potential exponent m were adjusted to give the best fit to the diamond FCC energy difference and to the diamond SC energy difference. The parameters of the scaling function n_c and r_c were adjusted to obtain the FCC bulk modulus and the equilibrium volume. The angular dependence of the parameters is calculated following Slater and Koster [15].

The scaling method of Goodwin *et al* essentially improves the agreement of the tight-binding results with *ab initio* results in structures other than diamond silicon. The transferability of the parameters was tested by performing MD simulations of small silicon clusters [11]. Here these parameters are used in a liquid simulation, which is another major deviation from the bulk crystalline environment where the fitting was done.

3. Molecular dynamics

The combined TB-MD has been introduced elsewhere [10], and the relevant dynamical equations are not repeated here. The MD simulation of the liquid silicon is performed with a 64-atom model system in a cubic cell of a side 10.86 Å which corresponds to the experimental density of 2.59 g cm⁻³. Periodic boundary conditions are imposed in all three space dimensions. Based on earlier investigations the use of only the Γ -point was considered satisfactory [8]. The initial configuration was a random-like state resulting from a previous 3 ps long simulation of the system at high temperature. The system is then followed at an average temperature of 1740 K for a total time of 10 ps. The integration time step is 10⁻¹⁵ s resulting in deviations in the total energy that were less than 0.5% of the variations in the potential energy. A fairly large integration time step (about 10 times longer than a typical CP step [8] and about the same order as that in classical simulations [12]) is possible because of the exact algorithm employed to diagonalize the 256 × 256 Hamiltonian matrix.

The structural properties of l-Si are characterized by the correlation functions. The radial pair correlation function $g(r)$ in figure 1 is proportional to the probability of finding an atom at the distance r , on the condition that there is one at the origin. Thus the position of the first peak indicates the average distance to the nearest neighbours,

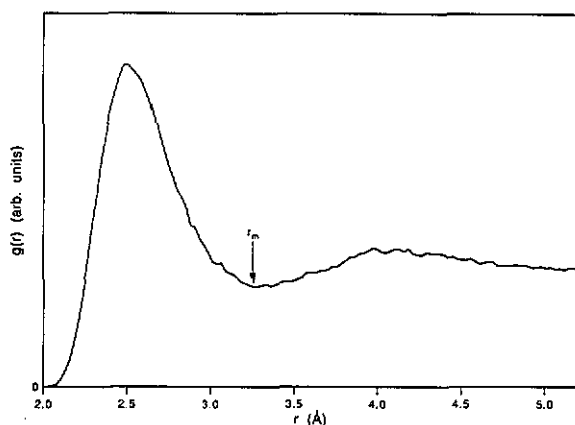


Figure 1. Pair correlation function $g(r)$ of l-Si from TB simulation. The radial distribution of the first nearest neighbours is centred at ~ 2.5 Å. The first minimum of $g(r)$ is the nearest-neighbour cut-off distance $r_m = 3.3$ Å. The coordination number $N = 6.4$ is calculated from (7).

and the second peak to the next-nearest neighbours. The disappearance of peaks at large distances indicates that there is no long-range order in the liquid. From figure 1, the average nearest-neighbour distance in l-Si is ~ 2.5 Å, which is similar to the CP result of ~ 2.46 Å [8] and to the experimental values of ~ 2.4 – 2.5 Å [16, 17]. The coordination number N is derived by integrating the pair correlation function up to the first minimum r_m

$$N = 4\pi\rho \int_0^{r_m} r^2 g(r) dr. \quad (7)$$

The coordination number of 6.4 from the function in figure 1, with $r_m = 3.3$ Å, is in agreement with the theoretical 6.5 from CP calculations [8] and with the experimental estimate of 6.4 [16, 17]. In classical simulations using the Stillinger-Weber (SW) potential the coordination numbers vary substantially (~ 8 in [2] and ~ 4.5 calculated from the distribution shown in table 1 based in [12]).

Table 1. Distribution of local coordinations $d(N)(\%)$ in l-Si. The results are from tight-binding (TB), *ab initio* (CP) and classical (SW) simulations.

| N | $d(N)_{TB}$ | $d(N)_{CP}$ | $d(N)_{SW}$ |
|-----|-------------|-------------|-------------|
| 3 | — | — | 2.3 |
| 4 | 6.4 | 4.6 | 29.4 |
| 5 | 19.5 | 18.0 | 47.7 |
| 6 | 30.8 | 33.3 | 18.5 |
| 7 | 26.3 | 30.3 | 2.1 |
| 8 | 13.0 | 13.3 | — |
| 9 | 3.9 | 2.7 | — |

Further characterization of the structure is given by the fraction of atoms with a given coordination number. In table 1 we compare our distribution of local coordinations with those calculated with the SW model [12] and the CP scheme [9]. Clearly, our

TB simulation succeeds in reproducing the CP distribution where sixfold and sevenfold coordinations are dominant.

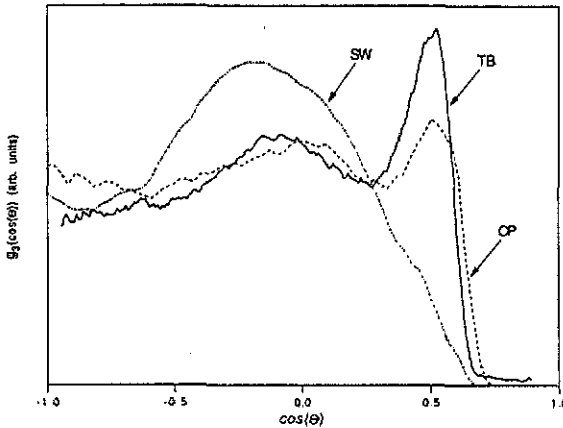


Figure 2. Bond-angle distribution $g_3(\theta, r_m)$ as a function of $\cos(\theta)$ where θ is the angle between an atom and its two nearest neighbours: full curve, TB simulation; dotted curve, *ab initio* result [8]; chain curve, classical MD [12]. Bond-angles at $\theta \sim 60^\circ$ and $\theta \sim 100^\circ$ are favoured in TB and *ab initio* distributions.

Triplet correlations are represented by the distribution of bond angles $g_3(\theta, r_m)$, where θ is an angle between a central atom and two of its neighbours at a distance less than r_m . Figure 2 shows a comparison between the TB, CP and SW results. The TB and CP curves show two maxima at favourable angles of $\theta \sim 60^\circ$ and $\theta \sim 100^\circ$ (actually $\theta \sim 90^\circ$ in the CP simulation [9]). The structure of the SW liquid is qualitatively very different indicating a single broad maximum close to the tetrahedral angle $\theta \sim 110^\circ$ [9, 12]. Thus the bonding properties are more accurately characterized by TB calculations with approximate electronic effects than by SW potential with an empirical three-body term.

To study the dynamics of l-Si the mean-square displacement and the velocity autocorrelation function are calculated. The mean-square displacement is derived from the displacement of the atom $R_I(t)$ in the time period t as

$$\langle R^2(t) \rangle = \left\langle \frac{1}{N} \sum_{I=1}^N |R_I(t+s) - R_I(s)|^2 \right\rangle_s \quad (8)$$

where s is a set of initial states and the brackets denote an average. We choose the states s randomly during the simulation in order to avoid unphysical correlations due to sampling at regular intervals. The mean-square displacement for l-Si as an average over 64 initial states is shown in figure 3. The atoms have travelled approximately 6 Å in 5 ps so that during the entire simulation the atoms have moved an average distance which is comparable with the size of the simulation cell. Thus a substantial part of the phase space is sampled. From the linear part of the curve one can obtain an estimate of the diffusion coefficient D

$$D = \lim_{t \rightarrow \infty} \frac{\langle R^2(t) \rangle}{6t}$$

We deduce a diffusion constant $D = 1.1 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ at 1740 K. This is smaller than the reported CP result $D = 2.2 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ at 1800 K [8] but close to the SW value of $D = 0.98 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ at 2010 K by Allen and Broughton [18]. Because of the temperature dependence the diffusion values from different simulations are not directly comparable. Experimental data for the self-diffusion of Si are not available.

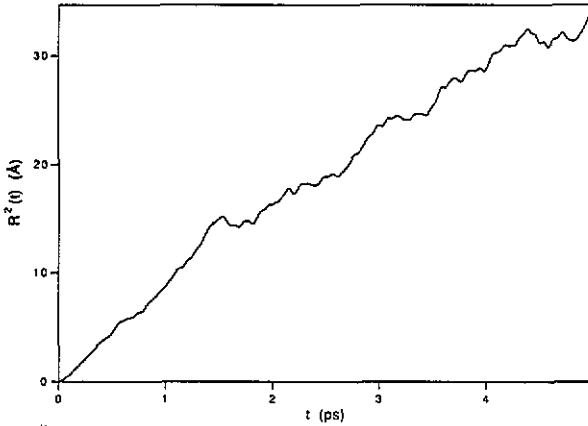


Figure 3. Time dependence of the mean-square displacement $R^2(t)$ in TB l-Si calculated from (8). The diffusion coefficient $D = 1.1 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ derivation is based on (9).

The velocity autocorrelation functions $Z(t)$ characterize the motion of atoms in the liquid. $Z(t)$ is also calculated as an average over the initial states s

$$Z(t) = \frac{\langle \mathbf{v}(t+s) \cdot \mathbf{v}(s) \rangle_s}{\langle \mathbf{v}(s) \cdot \mathbf{v}(s) \rangle_s}. \quad (10)$$

The TB velocity autocorrelation function is compared with the CP result [8] in figure 4. The oscillations of the functions indicate some regularity in the velocities, such as vibrations due to formation of covalent bonds between pairs of Si atoms. The $Z(t)$ of our simulation oscillates more pronouncedly than the CP velocity correlation. The negative values indicate a backscatter effect which is absent in the CP simulation. Thus backscattering diminishes diffusion in the TB liquid. By Fourier transforming the velocity autocorrelation function we obtain the phonon spectrum $Z(\omega)$

$$Z(\omega) = \frac{2}{\pi} \int_0^{\infty} Z(t) \cos(\omega t) dt. \quad (11)$$

The spectrum $Z(\omega)$ of our simulation is shown in figure 5 together with the CP [8] and the SW [12] results. The TB spectrum is intermediate between the CP curve, which has a small shoulder close to the optical frequency of covalent Si ($\sim 60 \text{ THz}$), and the SW spectrum, which exaggerates the crystalline properties. From the zero limit of the phonon spectrum we can determine the diffusion coefficient

$$D = \frac{k_b T}{M} \lim_{\omega \rightarrow 0} Z(\omega). \quad (12)$$

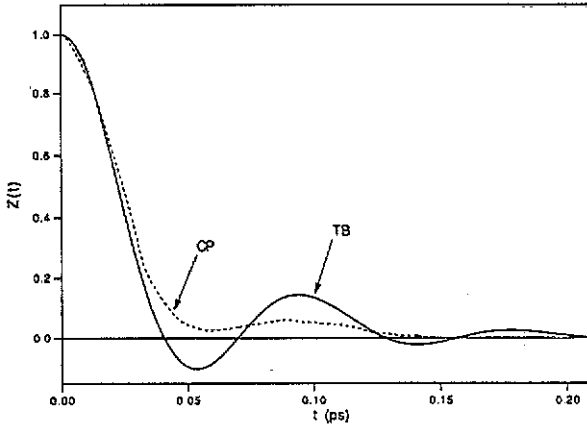


Figure 4. Velocity autocorrelation function $Z(t)$ as a function of time t from (10): full curve, TB method; dotted curve, *ab initio* simulation. Oscillations indicate the existence of some bonds in l-Si.

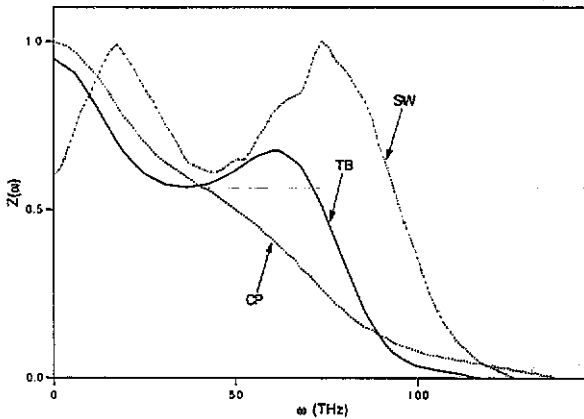


Figure 5. Phonon spectrum $Z(\omega)$ as a function of frequency ω based on (11): full curve, TB simulation; dotted curve, *ab initio* method [8]; chain curve, classical MD [12]. The TB result for the diffusion coefficient $D = 1.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ is derived from (12).

From (12) we obtain $D = 1.3 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ which is larger than the value estimated from the mean-square displacement but smaller than the CP result of $D \sim 2.0 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, also derived from (12) [8].

Finally, in figure 6 we show the density of the electronic energy eigenvalues $N(E)$ calculated as an average over the entire MD trajectory. The Fermi level is positioned at the origin. Clearly, l-Si shows metallic behaviour which is evident from the absence of the gap at the Fermi energy. The density of the Kohn-Sham eigenvalues calculated within the CP scheme is also displayed for comparison [8]. Qualitatively, the peaks at the negative energies indicate the presence of s, p and sp-hybridized states in the l-Si.

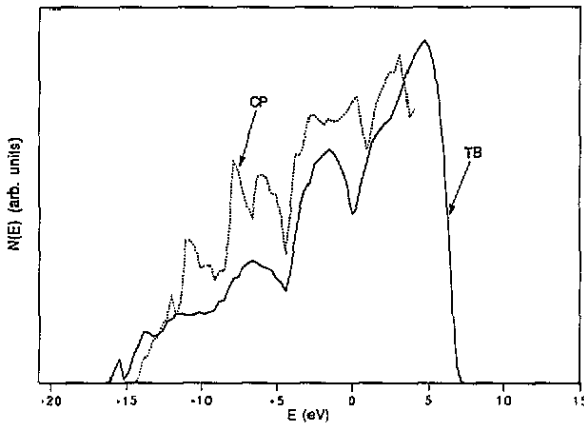


Figure 6. Density of the energy eigenvalues $N(E)$ as a function of energy E : full curve, TB curve; dotted curve, *ab initio* result [8]. The absence of the energy gap indicates that l-Si is metallic.

4. Conclusions

By performing molecular dynamical simulations of liquid silicon we have shown that the liquid state can be successfully studied within the TB approximation. The validity of the model clearly depends on the parameters used. The TB parametrization derived by Goodwin *et al* for the bulk environment and tested for clusters has been applied here to the other extreme of a liquid state. The properties of the TB liquid silicon, which depend sensitively on the short-range correlations, agree well with much more time-consuming *ab initio* results. Thus the simplified approach to the electronic bonding is seen to include the essential physics. This provides a means for efficiently simulating complex systems over long time sequences.

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