

Molecular Dynamics of Covalent Crystals

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Abstract. A molecular mechanics-like two and three body potential is implemented in the ITAP molecular dynamics program *IMD*¹. First results on the simulation of covalent crystals are presented.

1 Introduction

Many predominantly covalent bonded crystals are composed of atoms which are simultaneously bonded to a given number of other atoms. The covalent character of the nearest atom-atom interactions gives rise to a particular crystal symmetry. Atoms with sp^3 hybridization like carbon and silicon exhibit a tetrahedral configuration with four nearest neighbours, while sp^2 hybrids of carbon and nitrogen may form trigonal planar arrangements with three atoms bonded to the center atom. For example, the tetrahedral coordination is found in diamond, cubic close packed silicon, and wurtzite or zinc blende structure of silicon carbide.

It is of increasing interest to material science to investigate the microscopic structure of such covalent systems, including a variety of crystal defects like vacancies, interfaces and grain boundaries. Among others, computer simulations of covalent crystals based on atomistic models might help to gain insight into the correlations of microscopic and macroscopic properties. However, in order to calculate reliable thermodynamical and mechanical properties by molecular dynamic methods adequate large systems should be explored. In turn, efficient software codes in combination with fast computer equipment are required for large scale simulations. We use the *IMD* package, which is a molecular dynamics software designed for risc workstations as well as for massively parallel computer architectures [1,2].

We are interested in the simulation of the atomistic structure of covalent materials, especially of interfaces. At first, a potential function based on a molecular mechanics approach is developed and the code for it is implemented in the *IMD* program. In the present report, the basic features of the model and first molecular dynamics results on the bulk structures of several tetrahedral and model systems are presented.

¹ See HLRS project: ITAP Molecular Dynamics (IMD)

2 Basic concept on the simulation of covalent crystals

2.1 Covalent crystals

The bond strengths and mutual bond orientations are the most typical atomistic features of covalent materials, like for example diamond, silicon carbide and silicon nitride. In order to describe covalent bonds a pair interaction potential is applied. The potential depth is related to the dissociation energy and the equilibrium distance characterizes the bond length. It is interesting to note, when comparing the pair interactions of the van der Waals type and of the covalent bond the latter is about ten to hundred times stronger than the former. Therefore, the van der Waals interaction may be neglected in a first approximation. (This assumption is not valid for molecular crystals.)

Although the strength and the form of the pair interaction significantly influences the material characteristics it cannot describe the anisotropy of the material. Therefore, another potential term must be taken into account. Essentially, the hybridization of the atom gives rise to preferred bond directions. The bonds i - j and i - k at atom i form the so-called valence angle. Depending of the hybridization of atom i typical values of the valence angle appear. In case of silicon and carbon, each with sp^3 hybridization, the angle is 109.47° , while for sp^2 carbon the angle is 120° . Any deviation from the equilibrium angle costs energy and should be described by an adequate potential which depends on the positions of the atoms involved, i.e. a three body function must be defined.

Higher order terms like torsion, inversion or cross functions are of less importance to the bulk properties [3]. Therefore, it is a well-established approach in atomistic simulations of covalent crystals that the pair interaction term and the three body potential may well characterize the structure and energetics of the system under investigation [4].

2.2 The model

In order to simulate covalently bonded systems a suitable force field ansatz must be chosen. The structure and energetics of the systems under investigation are essentially determined by the functional form and the parameters of the force field applied [5]. In the present study the potential used is based to some extent on the universal force field approach [6]. The force field parameters are estimated by general rules from a set of fundamental (atomic) parameters. The atomic parameters are based only on the element, its hybridization and its connectivity [6].

In the following, we focus on a force field approach which is capable to describe tetrahedral systems. However, the application of the model on trigonal planar and other systems is straightforward [6].

First, the analytical potential functions are discussed. The total potential energy is

$$E_{POT} = \sum_{i,j} V_{ij} + \sum_{i,j,k} V_{ijk}. \quad (1)$$

The pair interaction V_{ij} describes the bond between two atoms, while the three body potential V_{ijk} characterizes the direction of the bonds of an atom. The pair interaction of covalent bonds is written in the usual form of a Morse potential while for the valence angle function a fourier expansion is chosen

$$V_{ij} = D_{ij}(e^{-\alpha_{ij}(r_{ij}-r_{ij}^o)} - 1)^2 \quad (2)$$

$$V_{ijk} = k_{ijk} \sum_{n=p}^m C_n \cos(n\Theta_{ijk}) f(r_{ij}) f(r_{ik}). \quad (3)$$

The distance r_{ij} and the angle Θ_{ijk} are the actual values calculated during the simulation.

The parameters involved are given as follows. The equilibrium distance r_{ij}^o is assumed to be the sum of the atom type covalent radii: $r_{ij}^o = r_i + r_j$. In case of C and Si these radii are 0.77 and 1.17 Å, respectively. The dissociation energy D_{ij} is the geometric mean of D_i and D_j (C: 101, Si: 80 kcal/mol), and α_{ij} is calculated from D_{ij} and the force constant k_{ij}

$$\alpha_{ij} = \sqrt{k_{ij}/2D_{ij}}. \quad (4)$$

Considering the fourier term, the parameters p and m and in turn the expansion coefficients C_n depend on the hybridization of the atoms. In case of sp^3 hybrids like carbon and silicon the parameters are $p = 0$ and $m = 2$, and the coefficients C_n are given by

$$C_2 = 1/(4 \sin^2 \Theta^o) \quad , \quad C_1 = -4C_2 \cos \Theta^o \quad , \quad C_0 = C_2(2 \cos^2 \Theta^o + 1), \quad (5)$$

with the equilibrium angle $\Theta^o = 109.47^\circ$.

The function $f(r)$ is defined such that it is equal to one in case of the equilibrium distance r^o (1-2 interaction) and zero in case of the 1-3 equilibrium distance. In-between a smooth function is chosen, like for example a normalized cosine or error function.

The force constants k_{ij} and k_{ijk} are given by a generalization of Badger's rule [7]. The procedure to calculate the force constants is described in detail in reference [6]. It is noteworthy, that again solely atom based parameters are used. The force constants k_{ij} are 695, 462 and 275 kcal/mol/Å² for C-C, C-Si, and Si-Si, respectively. However, in case of silicon the force constant k_{ij} leads to unstable bulk structures because of quite strong 1-3 interactions. Therefore, α is set equal to five (this approximation will be refined soon). In case of k_{ijk} the force constants of atom i are, at present, assumed to be independent of the other atoms involved: 215 and 84 kcal/mol/deg² for C and Si, respectively.

2.3 Upgrading IMD

Using a force field approach in conjunction with well-known molecular mechanics and molecular dynamics methods enables one to analyse the phase space of the atomistic system under investigation [8]. At ITAP the *IMD* software package is developed for molecular dynamics simulation of large scale systems [1]. A detailed description of the actual procedures available in *IMD* is presented elsewhere [1,2]. In the following, a short description on the new modul is given in which the three body interaction energy is calculated.

So far, *IMD* considers pair interactions only. Now, the code is extended in order to take preferred bond orientations into account. This requires merely another loop over the particles. The calculation is performed such that first the pair interaction of the particles in one cell [2] is computed, meanwhile, the coordinates of the nearest neighbours are saved. Then, while still in the same cell, the neighbour list is used in a second loop to determine the valence angle energy. Fortunately, the three body term could be implemented in *IMD* in a straightforward way. The valence angle function is calculated analytically, while the pair functions (here: V_{ij} and $f(r_{ij})$) are tabulated in the *IMD* program as usual: for each type of atom-atom interaction the potential is listed as a function of the distance.

3 Recent Results

Comparing the computational time of the two and three body interaction code and of the 'classical' pair interaction program one finds, that the new code is less than about two times slower than the classical one. This is expected, because of the additional loop over the particles and of the analytical calculation of the three body force. Due to the implementation strategy the MPI timing remains similar to runs with the classical code. However, the memory access for the neighbour list update slightly slows down the efficiency.

In the following, first results on the simulation of covalent and model systems are presented.

Covalent crystals

The program, and in turn the force field, is tested by investigating the stability of given bulk structures. Therefore, the geometries of diamond, cubic close packed silicon and silicon carbide in zinc blende structure are calculated. Up to $N = 262144$ atoms and 64 cpus are used by molecular dynamics simulations. The microconvergence method and microcanonical ensemble as well as canonical ensemble (*NVT*) techniques are applied to equilibrate the systems. The calculations are performed using periodic boundary conditions as well as open boundaries. The calculations show that the system under investigation remains stable and the calculated geometries are independent on

the simulation method. The results are in good agreement with experimental data (Table 1).

		UFF	IMD	exp
C	C-C	1.57	1.55	1.54
	-C-	109	109	109
Si	Si-Si	2.23	2.33	2.35
	-Si-	110	109	109
SiC	Si-C	1.89	1.86 *	1.87
	-Si-	110	109	109
	-C-	110	109	109

Table 1. Geometries of some selected tetrahedral crystals (Distances in Å and angles in deg). The results of the *IMD* simulations are compared with calculations using the universal force field (UFF) [6] and with experimental datas [9]. (* The covalent radius of Si is chosen $r_{Si} = 1.10$ Å.)

In another test, the diamond structure is investigated again. However, the initial configuration is modified significantly. The atoms are displaced randomly: $\mathbf{x} \rightarrow \mathbf{x} + \boldsymbol{\lambda}$, with $\boldsymbol{\lambda}$ a three dimensional random number $\lambda \in [-0.15, 0.15]$, leading to a maximum displacement of $|\boldsymbol{\lambda}| = 0.5$ Å. After the system is equilibrated by molecular dynamics simulations the diamond structure is recreated.

Covalent interface

The (100) interface of SiC/CSi is analysed by molecular dynamics simulations using the microcanonical ensemble technique. The initial structure is generated as follows. First, the SiC zinc blende structure is chosen. Then, in one half of the simulation box the particle types are interchanged (Si \rightarrow C; C \rightarrow Si) leading to an SiC/CSi interface. Periodic boundary conditions as well as open boundaries are applied. The number of particles in the box is $N = 162432$, 10^4 steps and 64 processors are chosen. The molecular dynamics run took 59 cpu hours.

The simulations show that the crystal remains stable during the molecular dynamics run (Figure 1). However, the carbon atoms in the interface region are displaced from the initial positions to form strong C-C bonds of optimum length. This way, defects appear in the interface layer.

Model system

In order to investigate the influence of the bond strength on the material characteristics a two dimensional binary model system is considered. The total potential energy is given by the Lennard-Jones potential. Here, the

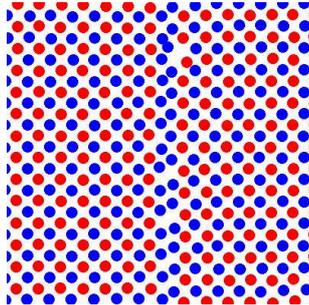


Fig. 1. Detail of the SiC/CSi (100) interface (C: blue; Si: red).

three body interaction is not applied, because of the primary focus on the strength of the pair interaction.

$$E_{POT} = \sum_{ij} \epsilon_{ij} [(r_{ij}^o/r_{ij})^{12} - 2(r_{ij}^o/r_{ij})^6]. \quad (6)$$

The equilibrium distance r_{ij}^o is set to unity for each particle type, A and B . On the contrary, the potential depths ϵ_{ij} are varied: The interaction strength B - B is chosen twice the one for A - A , and the unlike bond strength A - B is given by the arithmetic mean $(A + B)/2$. The initial structure represents an interface of two blocks, each of particles with similar type. Periodic boundary conditions are applied and a temperature significantly below the melting point is chosen. Then, the simulation box is elongated in x direction step by step. At each step a molecular dynamics run is performed using the Anderson thermostat to equilibrate the system. Usually, $46 * 10^3$ particles are used on 64 processors. In case of the strong interaction simulation the equilibration of one elongation step took about 28 hours of cpu time on T3E.

As expected, in case of weak interactions ($\epsilon_{AA} = 1$) the elongation of the particle box does not lead to any significant change of the crystal structure; this is valid until the system melts. However, for increasing interaction strength the material gets harder. In the latter case, the elongation of the box eventually results in a crack in the block of particles with stronger pair interaction (Figure 2).

4 Outlook

Our aim is to apply the *IMD* program on problems concerning the atomistic structure of precursor derived covalent ceramics, like silicon carbide and silicon nitride [10]. In particular, the technological production process yields covalent interfaces, too. For example, SiC/SiC and SiC/Si₃N₄ interfaces occur. The material behavior of the ceramics depends strongly on the interfaces

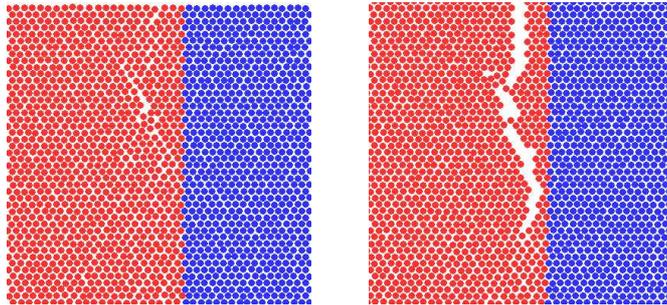


Fig. 2. Detail of the two dimensional interface of a binary system (A : blue; B : red; $\epsilon_{AA} = 10$). **Left:** Snapshot at the beginning of the fracture (3.25% elongation). **Right:** Snapshot of the crack (3.375% elongation). Interestingly, the fracture occurs inside the harder material, while the softer material as well as the interface remain undestroyed.

and, therefore, the knowledge of the atomistic structure is of special interest to material science.

The HLRS project started late 1998. So far, first steps in establishing the model and transferring the program code to massively parallel computers have been performed. The next steps will be to refine the pair potential approach and the memory allocation procedure for the nearest neighbour list. After that, the covalent crystals and interfaces are investigated in detail.

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