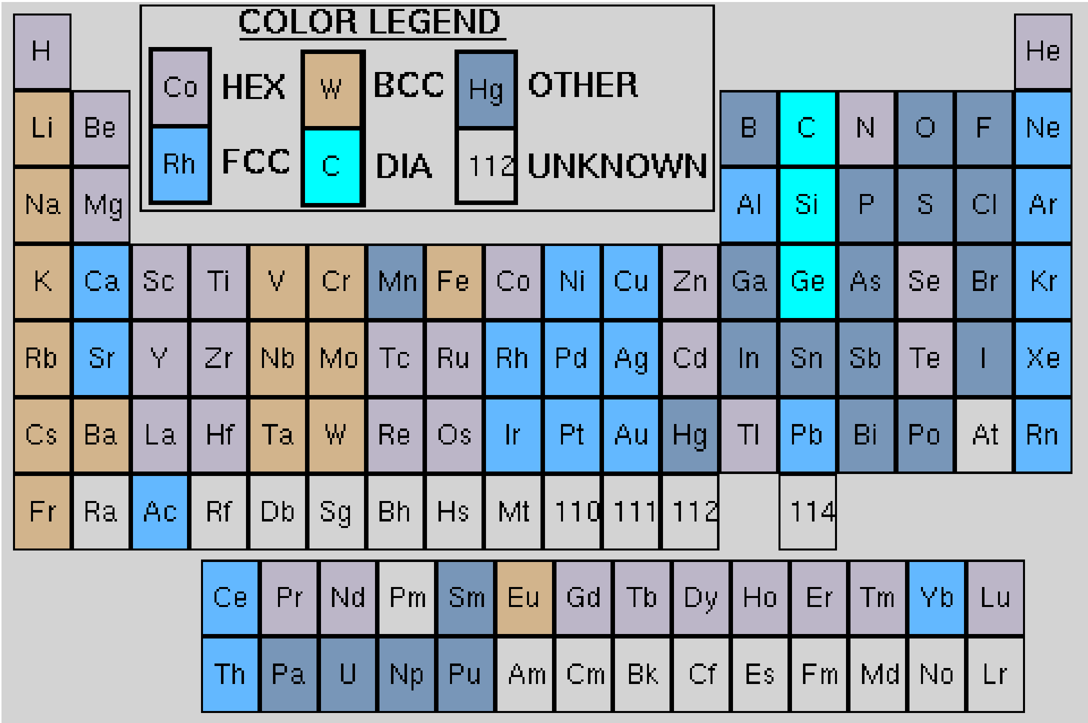
Diamond- and zincblende structure potentials

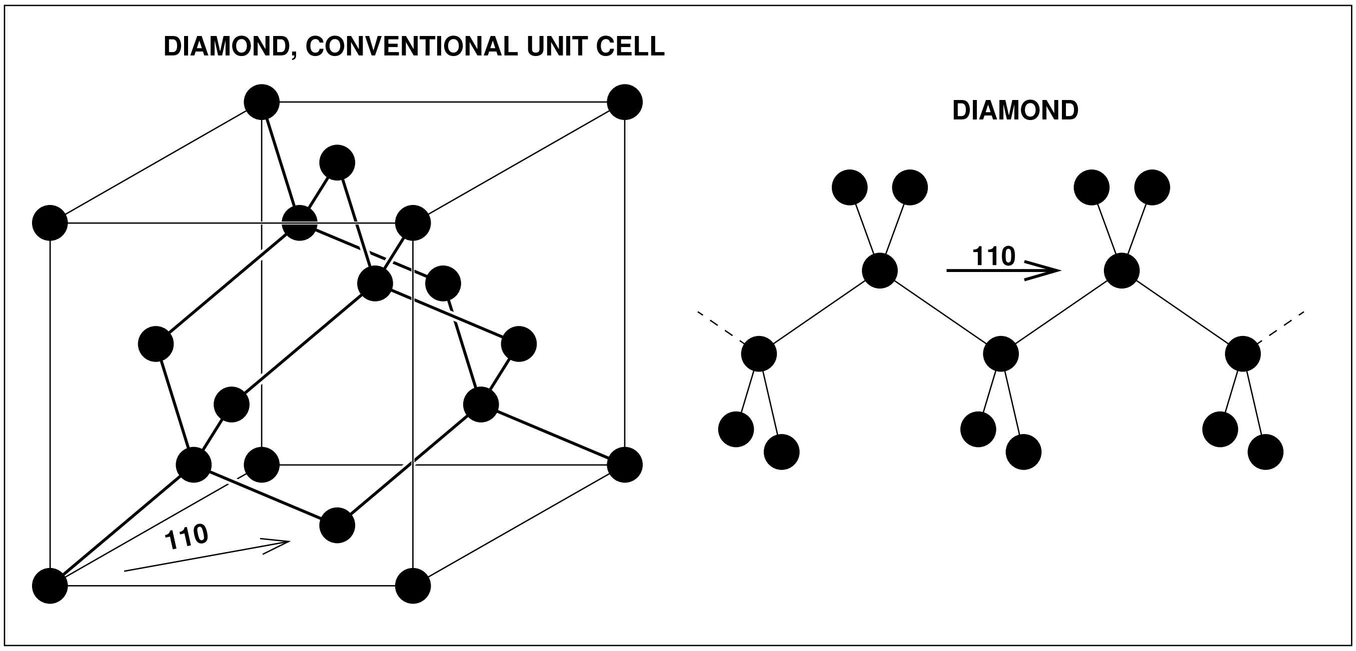
- Only three elements have the diamond (DIA) structure:



- However, since almost the whole semiconductor industry and micromechanical engineering industry is based on Si technology, the interest in studying diamond-structured semiconductors is immense.

- In addition, the most common compound semiconductors (GaAs, AlAs, InAs, etc.) have the zincblende structure, which is essentially the same as diamond except that there are 2 atom types. This further increases the interest in describing this crystal structure.

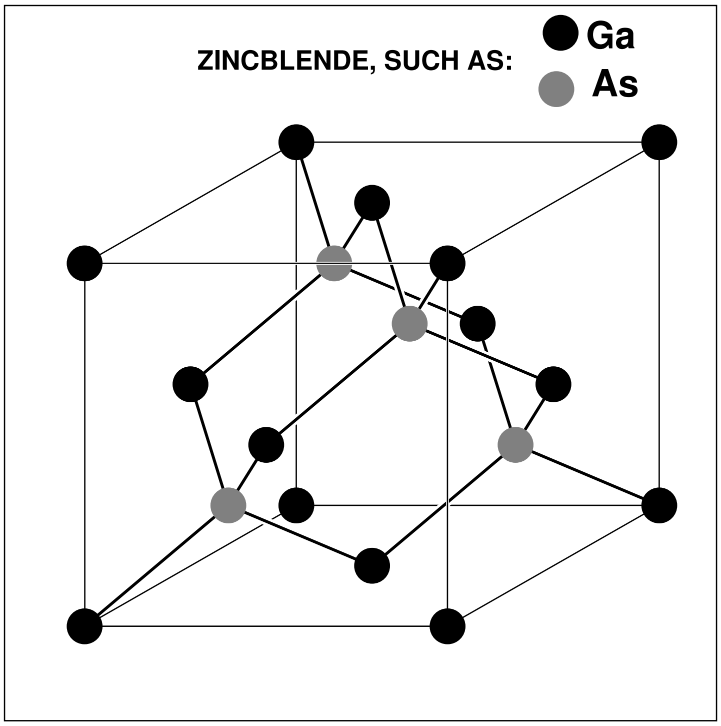
- The diamond structure is (2 ways of looking at the same thing)



The structure is essentially two FCC structures inside each other which have been displaced by (a/4,a/4,a/4) from each other, where a is the side length of the conventional unit cube. The unit cell has 8 atoms, 4 in both FCC sublattices (note that the atoms on the sides and corners are divided into several cells).

In terms of bonding the crucial feature is that every atom has exactly 4 neighbours. The bonds are covalent or predominantly covalent, and the nearest neighbours are distributed such that if one atom is in the middle of a regular tetrahedron, the 4 neighbours are the corners of this tetrahedron. The angle between any two bonds of the same atom becomes $\cos^{-1}(-1/3) \approx 109.47^{\circ}$. Chemically this corresponds to the sp^3 hybridization of electrons.

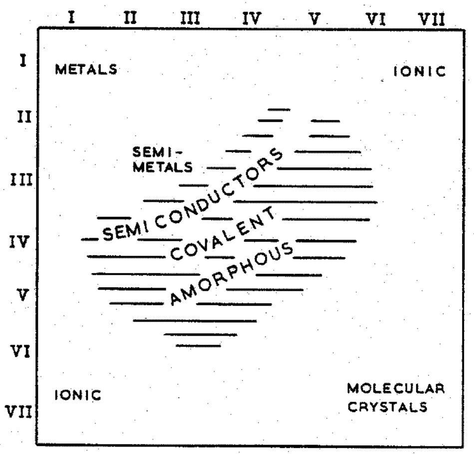
- The zincblende structure is the same except that one FCC sublattice has atoms of one type, the other of the other type. One unit cell thus has 4 atoms of type A and 4 of type B.



Covalent bonds

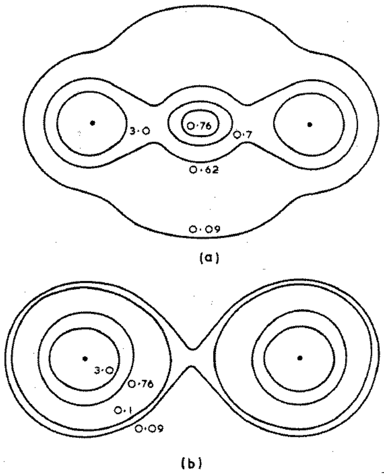
- In a covalent bonds atoms share electrons and thus in some sense achieve a filled electron shell.

- In solids covalent bonds typically form between elements which have a similar outer electron structure.

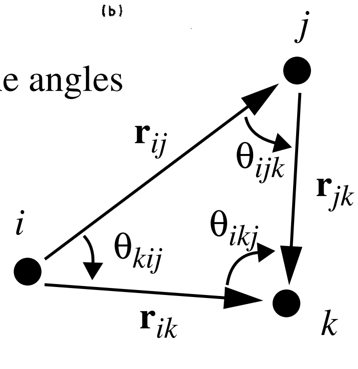


- Some elements: C, Si, Ge, S, Se, Te
- III-V-componds (GaAs, InP, ...)
- II-VI-compounds (ZnSe, CdTe, ...)
- various compounds such as SiC
- molecular crystals (e.g. oxygen where the basic element is the O_2 molecule, H_2O etc. etc.)

- The electrons extend to the space between the atoms. As an example on the right the electron structure of the Si_2 dimer is compared to the superposition of the density of two Si atoms:



- Because of the nature of the hybridization of the electron orbitals, the covalent bonds typically have a strong directional dependence, with some preferred angles between the bonds. For instance, the energy of three atoms will depend not only on the distances $\mathbf{r}_{ij}$, $\mathbf{r}_{ik}$ and $\mathbf{r}_{jk}$ but also on the angles between them θ_{kij}, θ_{ijk} and θ_{ikj}:



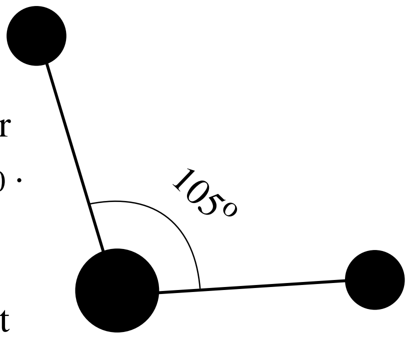
- Si has 4 outer electrons, and these can form 4 bonds with sp^3 hybridization, i.e. the angle of 109.47° .

- From this directional dependence, it also follows that the crystal (or amorphous) structure of covalent solids is often fairly open. The number of nearest neighbours is usually only 2-4, whereas it is 12 close-packed structure. Hence the packing fraction (a measure of the relative atomic density) in diamond is only 0.34, whereas it in FCC is 0.74, a difference of more than a factor of 2!

Dealing with covalent bonding: explicit angles vs. bond order

- Before we proceed with semiconductors, let us think quite generally about the angular properties of covalent bonds.

- Since we know for any given covalently bonded material that there is one or a few angles between the bonds which give a minimum in the energy, one can immediately see a **purely geometrically motivated** way of constructing a potential: simply put in an explicit angular term which gives a minimum at the equilibrium angle θ_0 .



- For instance, consider a single water molecule H_2O. We know that the angle between the two O-H bonds is about 105^o. Thus if one wants to construct an interatomic potential to describe water, one could get the structure right simply by including an explicit
angular energy term of the form

$$E_{\text{angular}} = K_\theta (\theta - 105°)^2$$

into the potential. I will call potentials with these kinds of terms "**explicit angular**" potentials (this is my own term).

- Some thought reveals an obvious problem, though. This kind of a potential term always gives a minimum at only one angle, and nowhere else. However, any knowledge of physics or chemistry reveals that this is not realistic. For instance, consider the carbon allotropes graphite and diamond. In one the angle between bonds is 120^o, in the other 109.47^o. The energy difference between the two phases is vanishingly small. An explicit angular potential can not possibly describe carbon in both allotropes correctly.

- Thus although it is easy to construct explicit angular potentials for a known geometry, they do not have a fundamental physical motivation.

- An alternative, physically motivated approach to construct potentials for covalent systems is through the concept of "**bond order**" (this is a well-established and widely used term, as opposed to "explicit angular").

- By bond order one means is that the strength of a single chemical bond is affected by the chemical neighbourhood: the more neighbours an atom has, the weaker are the bonds which are formed to these atoms. This can be described in potentials of the form

$$V = V_{\text{repulsive}}(r_{ij}) + b_{ijk} V_{\text{attractive}}(r_{ij})$$

  by constructing an environment-dependent term b_{ijk} which weakens the pair interaction when the number of neighbours (**coordination number**) Z of an atom is increased.
  - For simplicity we here deal with cases where only bonds to nearest-neighbour atoms are considered.

- This idea is well motivated qualitatively from basic chemistry: if an atom has N outer electrons, these can form (with other atoms of the same type in a symmetric configuration):
  - a single (dimer) bond with N pairs of electrons
  - two bonds with N/2 pairs of electrons
  - three bonds with N/3 pairs of electrons

  and so forth

- Since for every larger number of bonds one bond has less pairs of electrons, it is quite natural that the strength of a single bond tends to decrease.

- However, the strength of the bond is not directly proportional to the number of electron pairs in it, and the behaviour of the energy/bond may vary quite a lot from one material to another.

- If the energy/bond decreases very rapidly with the coordination number, the most stable form of the atom is a dimer. If, on the other hand, the dependence is weak, the material wants to maximize its coordination number and will end up in a close-packed configuration.
  - In the limiting case of b_{ijk} = constant we get a pure pair potential.

- We can thus think that the strength of bond is a monotonously decreasing function of the coordination number. The equilibrium structure is determined by the balance between the number of bonds and the single bond strength, since the total energy is the product of the two.

- This formalism allows us to adjust how many numbers of neighbours an atom "wants to have". This now gives a physical motivation to the preferred angles between bonds: if e.g. the ideal coordination is 4, and the bonds are arranged symmetrically about an atom, one automatically gets the tetrahedral bonding configuration with an angle of 109.47° between the bonds.

- The great advantage here is that now the angle needs not be fixed, because it is perfectly possible to construct potentials which give the same energy for 2 different configurations. Thus one can (and as we shall se people have) constructed potentials which e.g. give local energy minima of equal depth for both the graphite and diamond configurations, thus solving the carbon problem!

- Based on pseudopotential theory Abell [Phys. Rev. B 31 (1985) 6184] has argued that the term b_{ijk} should be of the form

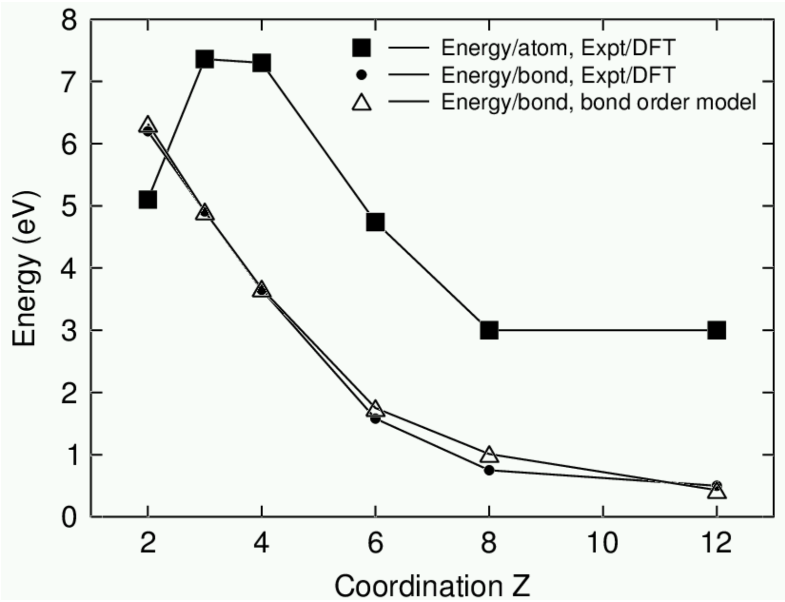
$$b_{ijk} \propto Z^{-\delta}$$

where Z is the coordination number and δ some number. More specifically, in the so called second-moment approximation of tight binding one obtains

$$b_{ijk} \propto Z^{-\frac{1}{2}} = \frac{1}{\sqrt{Z}}$$

- Let us make all this concrete with an example: carbon. The table below shows the energy/bond and energy/atom for a number of different coordinations of carbon. The values for Z=2, 3 and 4 are from experiment and the values for the hypothetical phases Z>4 from a DFT calculation which also reproduces the experimental values well [Furthmüller et al, Phys. Rev. B 50 (1994) 15606; data compiled in Albe, Phys. Rev. B 65, 195124].

Z	Phase	Energy/atom (eV)	Energy/bond (eV)	Energy/bond bond order model
2	dimer	3.10	6.20	6.32
3	graphite	7.36	4.91	4.91
4	diamond	7.30	3.65	3.67
6	simple cubic	4.74	1.58	1.75
8	BCC	3.00	0.75	1.01
12	FCC	3.00	0.50	0.43



- The last column shows a fit to the data obtained with a bond order model of the $1/(\sqrt{Z})$ form. As you can see, a quite good fit is obtained for all phases, and especially the most important ones are described very well.

- Note also that the bond order model correctly predicts that graphite and diamond are almost equal in energy.

- The generality of this approach was shown by Brenner, who proved that this form is mathematically equivalent with the EAM formalism (after suitable transformations), and specifically that if δ = -1/2 one can obtain exactly the Finnis-Sinclair / Cleri-Rosato-like metal potentials!

Classical Si potentials

[One important source: Balamane, Phys. Rev. B 46 (1992) 2250]

- Because of the directional dependence of the bonds, all decent Si potentials have some sort of an angular dependence, and hence they are at least 3-body potentials.

- Some potentials have an explicit 3-body form, i.e. the potential has the shape:

$$V = \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k)$$

  These potentials are called by Balamane *cluster-potentials.* They typically also are *explicit angular* potentials.

  In other potentials the angular dependence is hidden in the 2-body part so that there is no explicit V_3 part. These are called by Balamane *cluster functionals.*

- The philosophy of the cluster functionals is similar to the EMT/EAM potentials: calculate a pair potential, but let its strength be affected by the environment. A common formulation is

$$V = V_{\text{repulsive}}(r_{ij}) + b_{ijk} V_{\text{attractive}}(r_{ij})$$

  which is the same as for *bond-order* potentials. Here the attractive and repulsive parts themselves are pure pair potentials, but there is a coefficient b_{ijk} which has an environment-dependence. The main difference to EAM is that although they can be cast in the form above, in them b_{ijk} has no angular dependence, whereas in the Si potential there must be one.

- Hence in the Si potentials there also has to be a three-body loop $\sum_{i,j,k} (\boldsymbol{r}_{ij}, \boldsymbol{r}_{ik})$ which gives the angles.

Efficiency of semiconductor vs. metal potentials

- Assume the number of atoms is N and the average number of neighbours per atom is M
- A pair potential and an EAM potential is then $O(NM)$
- A three-body potential is $O(NM^2)$
-
- So it would appear like the Si potentials are a factor of M slower than EAM potentials.

- But this is most of the time not true in reality. This is because for covalent bonding, long-range interactions are weak compared to the nearest neighbour-ones, so it is often enough to only include nearest-neighbour interactions. So for Si $M = 4$. But in metals long-range interactions are important (e.g. for surface properties and to get the difference between the FCC and HCP phases right), so often $M \sim 50$ in metals.

- Because $4^2 < 50$ the Si potentials with three-body terms may in fact be faster than EAM potentials without one!

- But there are additional funny effects. For some Si potentials the cutoff is set so that in the crystalline phase $M = 4$, but it increases strongly in a disordered (amorphous or liquid) phase. So the speed of the potential may be strongly affected by what phase of a material is simulated!

The Stillinger-Weber-potential

- Stillinger and Weber [*Phys. Rev. B*, **31** (1985) 5262] (**SW**) developed a potential, which describes fairly well both crystalline and liquid silicon - they in fact constructed it to give the melting temperature right. The potential has become quite popular over the years because it turned out to describe well several properties which it was not really designed to describe originally (such as point defect energies).

- The potential is an explicit angular potential, and has the form

$$V = \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k)$$

$$,V_2(r_{ij}) = \varepsilon f_2(r_{ij}/\sigma)$$

$$V_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \varepsilon f_3(\mathbf{r}_i/\sigma, \mathbf{r}_j/\sigma, \mathbf{r}_k/\sigma) \quad .$$

where V_2 is the pair potential and V_3 the three-body part. The f_i are

$$f_2(r) = \begin{cases} A(Br^{-p} - 1)\exp[(r-a)^{-1}], & r < a \\ 0, & r \geq a \end{cases}$$

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \quad ,$$

where θ_{jik} is the angle, which the vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$ make at the atom i and the function h is

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda\exp[\gamma(r_{ij} - a)^{-1} + \gamma(r_{ik} - a)^{-1}]\left(\cos\theta_{jik} + \frac{1}{3}\right)^2 \quad .$$

- The constants A, B, p, a, λ and γ are all positive and were determined by demanding that the diamond structure is the most stable one and that the melting point, cohesive energy and lattice parameter are about right.

- According to rumours the potential was also fit to the elastic constants (which are reproduced fairly well), although the authors never stated this in the paper!

- The actual parameter values are

$$\begin{aligned} \sigma &= 2.0951\text{Å}, & \varepsilon &= 2.1672\text{eV}, \\ A &= 7.0496, & B &= 0.60222, \\ p &= 4, & a &= 1.80, \\ \lambda &= 21.0 \quad \text{and} & \gamma &= 1.20 \quad . \end{aligned}$$

- The melting point was fit to be almost exactly right with a rather dirty trick: the authors modified the cohesive energy to get the melting point close to the right value of 1685 K. The cohesive energy of the potential is 4.334 eV, when the right value is 4.63 eV. So this is a 7% mismatch. If this is corrected by direct scaling, the melting point will go wrong.

- The authors examined the structure of molten Si by comparing the maxima and minima of the structure factor $S(k)$ to measured values:

	MD	measured
1. maximum	2.53	2.80
1. minimum	3.25	3.25
2. maximum	5.35	5.75
3. maximum	8.16	8.50
4. maximum	10.60	11.20

- The potential describes fairly well melting and liquid Si. However, it is important to realize that the angle between bonds is ‘forced’ to the ideal tetrahedral angle with the cosine term $(\cos\theta_{jik} - 1/3)^2$. This is not a good feature, because of the reasons given above for “explicit angular” potentials.

The EDIP potential

- The EDIP-potential is fairly similar to the SW one, but it has been derived from an *ab initio*-calculated database of the cohesive properties of Si both in the diamond and graphite phases.

The potential is:

$$E_i = \sum_{j\neq i} V_2(R_{ij}, Z_i) + \sum_{j\neq i} \sum_{k\neq i, k>j} V_3(\vec{R}_{ij}, \vec{R}_{ik}, Z_i), \quad (1)$$

$$Z_i = \sum_{m\neq i} f(R_{im}) \qquad (2)$$

$$f(r) = \begin{cases} 1 & \text{if } r < c \\ \exp\left(\frac{\alpha}{1-x^{-3}}\right) & \text{if } c < r < a \\ 0 & \text{if } r > a \end{cases} \qquad (3)$$

$$V_2(r, Z) = A\left[\left(\frac{B}{r}\right)^{\rho} - p(Z)\right] \exp\left(\frac{\sigma}{r-a}\right) \qquad (4)$$

$$p(Z) = \mathrm{e}^{-\beta Z^2} \qquad (5)$$

$$V_3(\vec{R}_{ij}, \vec{R}_{ik}, Z_i) = g(R_{ij}) g(R_{ik}) h(l_{ijk}, Z_i) \qquad (6)$$

$$l_{ijk} \;=\; \cos\theta_{ijk} \;=\; \vec{R}_{ij} \cdot \vec{R}_{ik}/R_{ij}R_{ik}$$

$$g(r) = \exp\left(\frac{\gamma}{r-a}\right) \qquad (7)$$

$$h(l, Z) = H\left(\frac{l+\tau(Z)}{w(Z)}\right) \qquad (8)$$

$$h(l, Z) = \lambda\left[\left(1 - e^{-Q(Z)(l+\tau(Z))^2}\right) + \eta Q(Z)(l+\tau(Z))^2\right] \qquad (9)$$

$$w(Z)^{-2} = Q(Z) = Q_0 e^{-\mu Z}$$

(jos joku on sitä mieltä että tuo näyttää kuin suoraan kopioidulta Juston julkaisusta, onnittelut hyväst havaintokyvystä !)

So the main difference to SW is the environment-dependence in the form of the effective coordination number Z, which modifies the terms.

((n.b. Justo, Bazant & co published this potential twice: first the functional form [Bazant *et al.,* Phys. Rev. B 56 (1997) 8542)] without parameters, then the parameters [Justo *et al.* Phys. Rev. B 58 (1998) 2539]. This is of course one way to get additional length to your publication list...))

- The potential is available in the web
  http://www-math.mit.edu/~bazant/EDIP/
  including Fortran and C codes by which it can be evaluated efficiently.

- The parameter-values are:

TABLE I. Values of the parameters that define the potential, obtained from a simulated annealing fit to the database described in the text.

$A = 7.9821730$ eV	$B = 1.5075463$ Å	$\rho = 1.2085196$
$a = 3.1213820$ Å	$c = 2.5609104$ Å	$\sigma = 0.5774108$ Å
$\lambda = 1.4533108$ eV	$\gamma = 1.1247945$ Å	$\eta = 0.2523244$
$Q_0 = 312.1341346$	$\mu = 0.6966326$	$\beta = 0.0070975$
$\alpha = 3.1083847$		

- As required in a good fit, a large number of other properties have also been tested in the potential, the most important of which is that the diamond structure is the minimum of several common crystal structures (see table on right).

  But note that EDIP does overestimate the energy of many other phases fairly much compared to DFT.

TABLE II. Energy and lattice parameters for high symmetry structures. Here we consider the ground-state diamond cubic (DC), face centered cubic (FCC), body centered cubic (BCC), simple cubic (SC) and hexagonal close-packed (HCP) crystals. For DC, the cohesive energy per atom E_c^{DC} is given in eV, while for the other crystals the difference of the cohesive energy E_c from the ground state DC crystal, $\Delta E = E_c - E_c^{DC}$, is given. All lattice constants a_o are for the conventional unit cells in Å. For the hexagonal crystals we also give the c/a ratios. We also compute the lattice constant and binding energy of an isolated hexagonal plane (HEX). For this comparison we use the SW potential with the rescaled cohesive energy for the ground state, as described in Ref.[2].

		DFT/LDA	EDIP	SW	T2	T3
DC	E	-4.65	-4.650	-4.63	-4.63	-4.63
	a_o	5.43	5.430	5.431	5.431	5.432
SC	ΔE	0.348	0.532	0.293	0.343	0.318
	a_o	2.528	2.503	2.612	2.501	2.544
BCC	ΔE	0.525	1.594	0.300	0.644	0.432
	a_o	3.088	3.243	3.245	3.126	3.084
FCC	ΔE	0.566	1.840	0.423	0.548	0.761
	a_o	3.885	4.081	4.147	3.861	3.897
HCP	ΔE	0.552	0.933	0.321	0.551	0.761
	a_o	2.735	2.564	3.647	2.730	2.756
	c/a	1.633	2.130	0.884	1.633	1.633
HEX	ΔE	0.774	0.640	1.268		
	a_o	3.861	4.018	4.104		

- Among the best properties of the EDIP potential is that it reproduces the elastic constants very well, gives both good point defect, stacking fault and dislocation properties, and describes amorphous Si well. Also the melting point is described well, the potential predicts 1550   50 K [Nord*et al,* PRB 65 (2002) 165329], quite close to the experimental value of 1685 K.

  For example the radial distribution function of amorphous Si compared to experiments is reproduced fairly well:

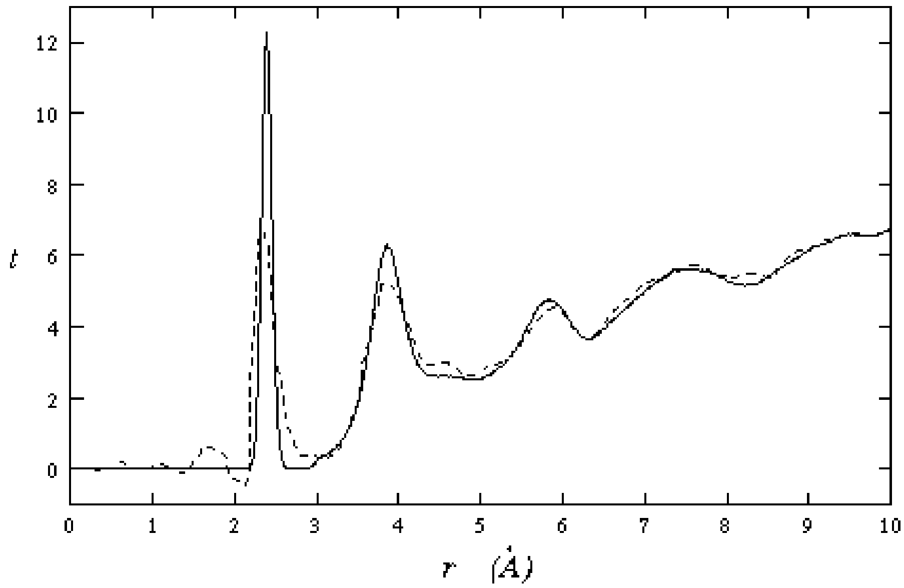


FIG. 11. Radial distribution function $t(r) = 4\pi\rho r g(r)$ for the amorphous phase at room temperature and zero pressure using our model, compared with the results of neutron scattering experiments on pure evaporated-beam-deposited a-Si thin films by Kugler *et. al.*[68].

- The EDIP potential clearly is one of the best Si potentials available now, most tests of its properties have been quite favourable to it.

- Another new Si potential is [Lenosky et. al, “Highly Optimized Empirical Potential Model of Silicon”, Modelling and Simulation in Materials Science and Engineering **8** (2000) 825]. This is a combination of EAM and SW models, which gives truly excellent fits to a large number of elastic constants, different structures and defect properties. However, it contains some questionable features (such as a negative electron density for some distances r) so its transferability outside the parameter database to which it has been originally fit is questionable.

Tersoff potential

- The Tersoff potential [first good Si fit in *Phys. Rev. B* **38** (1988) 9902] is a cluster-functional and bond order potential which has an environment dependence and no absolute minimum at the tetrahedral angle. Tersoff based his potential on the ideas presented by Abell a few years earlier. The Tersoff or more appropriately **Tersoff-Abell formalism** is probably the most widely used bond order potential formalism and has become the basis or inspiration for a huge number of potentials developed since then.

  Tersoff-like potentials are pure bond order potential motivated by the approach presented a few pages back in these notes, i.e. of the form:

$$V = V_{\text{repulsive}}(r_{ij}) + b_{ijk}V_{\text{attractive}}(r_{ij})$$

- The original Tersoff potential has the following form. The total energy is

$$E = \frac{1}{2}\sum_{i \neq j} V_{ij} \quad ,$$

  where

$$V_{ij} = f_{\mathrm{C}}(r_{ij})[a_{ij}f_{\mathrm{R}}(r_{ij}) + b_{ij}f_{\mathrm{A}}(r_{ij})] \quad ,$$

  repulsive part $\quad f_{\mathrm{R}}(r) = Ae^{-\lambda_1 r} \quad ,$

  attractive part $\quad f_{\mathrm{A}}(r) = -Be^{-\lambda_2 r} \quad ,$

  potential cutoff function

$$f_{\mathrm{C}}(r) = \begin{cases} 1, & r \leq R - D \\ \frac{1}{2} - \frac{1}{2}\sin\left(\frac{\pi}{2}\frac{(r-R)}{D}\right), & R - D < r < R + D \\ 0, & r \geq R + D \end{cases} \quad ,$$

  and

$$b_{ij} = (1+\beta^n \zeta_{ij}^n)^{-1/2n} \quad ,$$

$$\zeta_{ij} = \sum_{k \neq i,\, j} f_C(r_{ik}) g(\theta_{jik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \quad ,$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2} \quad ,$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n} \text{ and}$$

$$\eta_{ij} = \sum_{k \neq i,\, j} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3] \quad .$$

- Here, as above, the distance between atoms i and j is r_{ij} and the angle between bonds ij and ik is θ_{jik} .

- Inspection of the terms shows that there is an angular dependence, but because is embedded inside the b_{ij} term, it does not give a fixed minimum angle between bonds. The relation to the bond order potential basic formalism is as follows: if $n = 1$, $c = 0$, $\beta = 1$ and $\lambda_3 = 0$ we get the "pure" bond order potential with

$$b_{ij} \propto Z^{-\frac{1}{2}} = \frac{1}{\sqrt{Z}}$$

- Tersoff could not find a parameter set $\{A, B, \lambda_1, \lambda_2, \alpha, \beta, n, c, d, h, \lambda_3, R, D\}$ which would describe well both the reconstructed Si surfaces and its elastic properties. Because of this he gave two parametrizations: Si C, which describes well elastic properties, and Si B, which gives good surface properties. Tersoff's Si A is the original potential which proved to be unstable. Si(B) is also known as Tersoff 2 and Si(C) as Tersoff 3.

	Si(B)	Si(C)
A (eV)	3264.7	1830.8
B (eV)	95.373	471.18
λ_1 (Å^{-1})	3.2394	2.4799

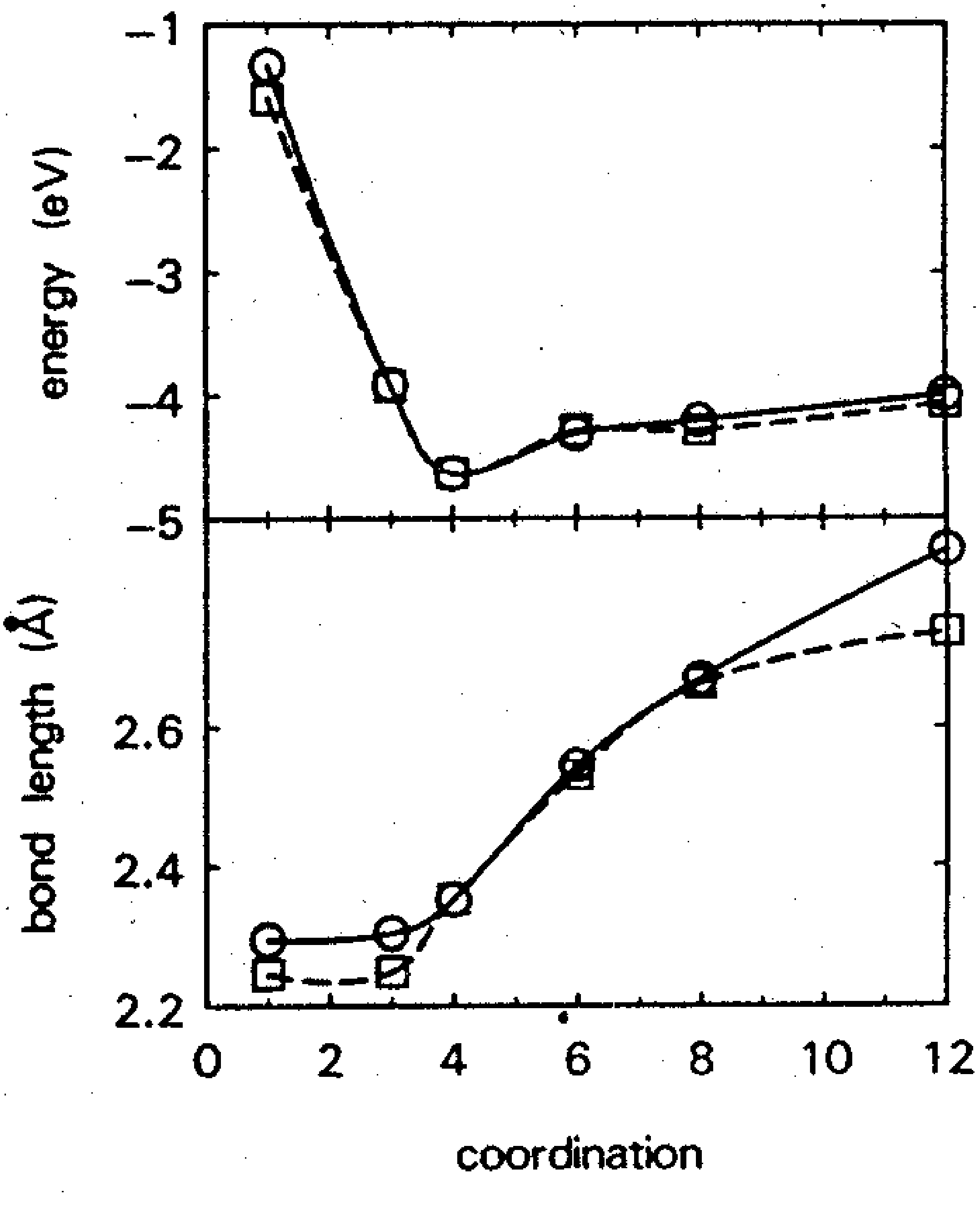
	Si(B)	Si(C)
λ_2 (Å^{-1})	1.3258	1.3722
α	0.0	0.0
β	0.33675	1.0999×10^{-6}
n	22.956	0.78734
c	4.8381	1.0039×10^{5}
d	2.0417	16.218
h	0.0	-0.59826
λ_3 (Å^{-1})	1.3258	1.7322
R (Å)	3.0	2.85
D (Å)	0.2	0.15

The parameter λ_3 is an interesting case: it does not affect the equilibrium properties at all, only properties far from equilibrium. Tersoff himself said it can be set to 0, and this is often done. However, in far-from-equilibrium studies it has proven to be best to include λ_3.

- Note also that since $\alpha = 0$, the two last equations in the potential form are meaningless (give exactly 1). Although Tersoff have these two equations, I am not aware of any case where they would actually have been used.

- Below is a comparison of the energies and bond lengths obtained with Tersoff for different coordination numbers compared to experimental and *ab initio*-calculations.

- Why should anyone care about e.g. 12-fold coordinated Si, which obviously does not exist in nature? The thing is, although some coordination numbers may not exist in the ground state, they may still be present e.g. in defects, surfaces and metastable molecules.

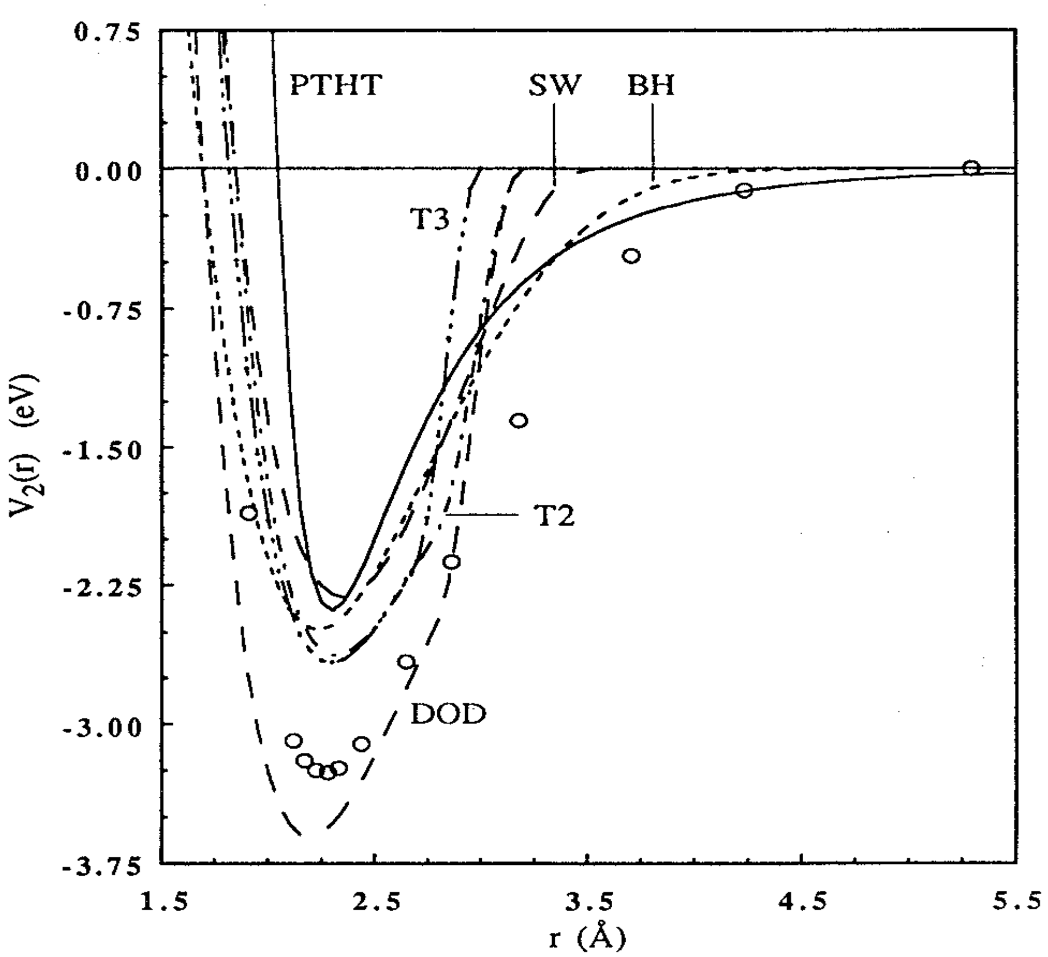


−1
−2
−3
−4
−5
energy (eV)
2.6
2.4
2.2
bond length (Å)
0
2
4
6
8
10
12
coordination

- Balamane & co have done an extensive comparison of Si potentials, looking e.g. at bulk, surface, defect and small molecule properties. [H. Balamane, T. Halicioglu, W. A. Tiller, *Phys. Rev. B* **46** (1992) 2250.]. Unfortunately EDIP was not part of this comparison.

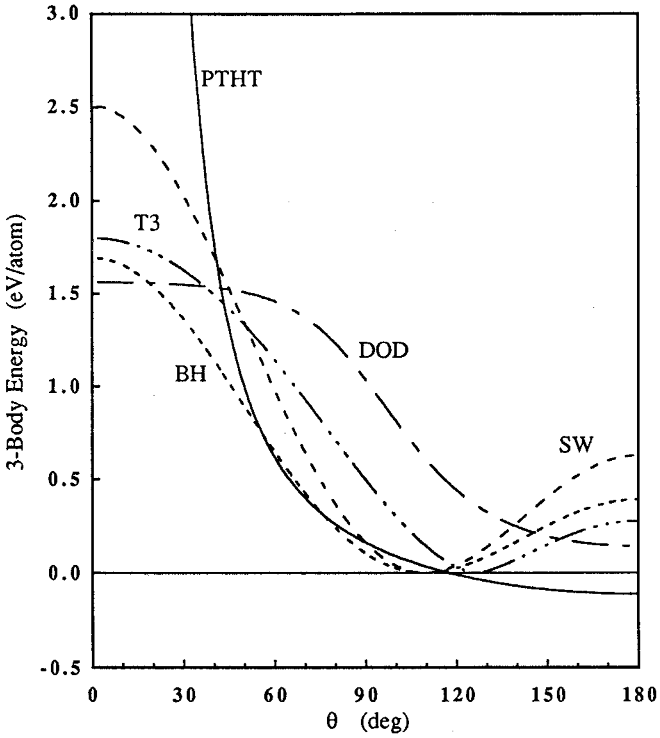
- Included were the SW, and Tersoff potentials Si(B) [T2] and Si(C) [T3]. Also included were the Biswas-Hamann potential (BH) [PRL 55 (1985) 2001, PRB 34 (1986) 895.], the Tersoff-like Dodson potential [DOD; *Phys. Rev. B* **35** (1987) 2795.] and the potential by Pearson *et al.* (PTHT; *Cryst. Growth.* **70** (1984) 33.].

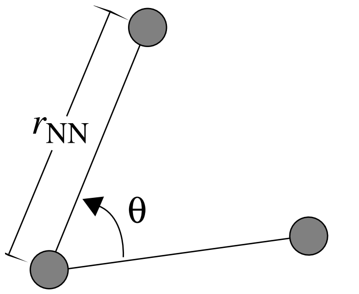
- Below is the pair term of the potentials $V_2(r)$. The spheres are *ab initio* results.



We see that except for DOD the potentials are fairly similar. BH and PTPH have a long range compared to the others.

- Here is the energy of three Si atoms/atom:

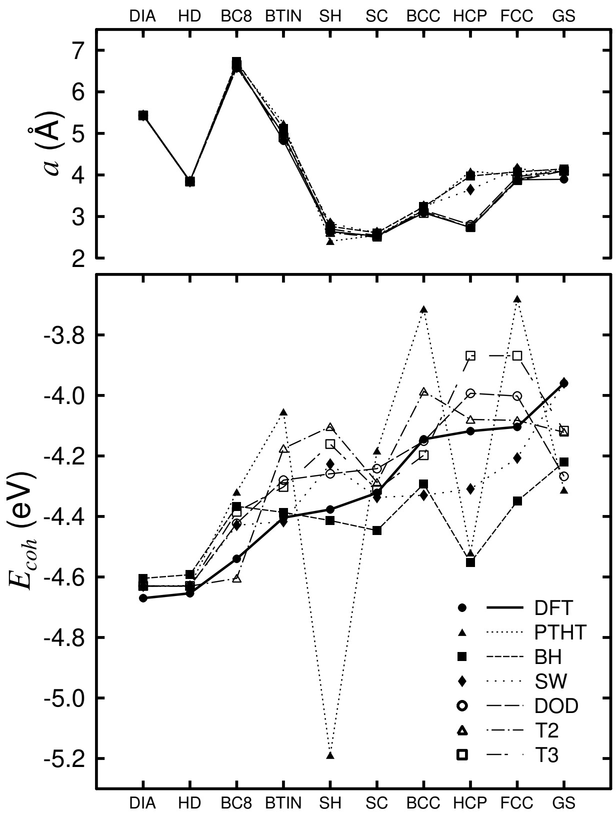




Note that the energy becomes fairly large for small angles for all the potentials.

- In the adjacent picture the cohesive energies of different structures are shown, compared to DFT calculations. Note that PTHT predicts that the simple hexagonal structure is the most stable one(!).

DIA=diamond
HD=hexagonal diamond
BC8=bc-8
BTIN=β–tin
SH=hexagonal
SC=cubic
BCC=body-centered cubic
HCP=hexagonal close-packed
FCC=face-centered cubic
GS=graphite



- And below are the elastic properties of the potentials

	experi ment	PTHT	BH	SW	DOD	T2	T3
B	0.99	2.788	1.692	1.083	0.884	0.98	0.98
B'	4.2	7.82	5.66	2.93	4.27	4.58	4.30
c_{11}	1.67	2.969	2.042	1.616	1.206	1.217	1.425
c_{12}	0.65	2.697	1.517	0.816	0.722	0.858	0.754
c_{44}	0.81	0.446	0.451	0.603	0.659	0.103	0.690
c_{44}^0	1.11	2.190	1.049	1.172	3.475	0.923	1.188
ζ	0.74	1.03	0.74	0.63	1.06	0.83	0.67
$\nu_{TA}(X)$	4.4	4.5	5.6	6.7		2.7	9
$\nu_{TO}(X)$	13.9	19.3	14.5	15.9		15.3	16
$\nu_{LOA}(X)$	12.3	13.8	12.2	13.1		11.7	12
$\nu_{LTO}(\Gamma)$	15.3	18.3	16	18.1		16.5	16

$$[B], [c_{ij}] = \text{Mbar}, [\nu] = \text{THz}, B' = \frac{dB}{dP} .$$

We see that T3 and SW give good elastic properties. Lattice vibrations are described well by the BH potential.

- And here are a bunch of energies for lattice defects.

	DFT	PTHT	BH	SW	DOD	T2	T3
V	3-4	0.77	2.12	2.82	2.57	2.81	3.70
	4.5	2.50	3.83	4.63	3.23	2.83	4.10
		38.5	-25.7	-24	14.7	1	10.5
V_S	4.19	2.83	2.30	3.36	4.17	1.40	3.50
	5.01	4.53	4.72	6.00	8.12	4.15	10.5
	-9.5	-15.9	-12.5	-11.8	-14.5	-14.9	-8.8
I_T	5-6	0.63	1.56	5.25	3.03	5.03	3.45
		1.91	4.57	12.21	5.00	5.85	6.92
		3.8	8	9	9.1	7.3	10.5
I_H	4-5	0.84	2.89	6.95	2.61	3.67	4.61
		5.32	9.31	17.10	5.1 1	5.39	8.22
		7.4	11.5	14.7	7.3	7.6	10.2
I_B	4-5	1.92	2.54	5.99	4.39	2.84	5.86
I_S		1.47	3.30	3.66*	3.49	2.32	4.70

V = vacancy V_S =split vacancy

I_T =tetrahedral interstitial I_H =hexagonal interstitial

I_B =bond-centered interstitial I_S =split interstitial.

The first number is the energy of the ground state, the second the energy of the ideal (non-relaxed) structure, and the third gives the radial relaxation of the nearest neighbours in percent (negative value inwards, positive outwards).

* Note that Balamane have an error here, this is my own determination.

- The table tells predominantly that the short-range potentials (SW, DOD, T2, T3) describe defects best. SW is good in that it predicts that the simple vacancy and split interstitial are the ground state defects, which agrees with ab initio results for uncharged defects.

- Finally a table of the properties of the Si (100) surface:

	DFT	PTHT	BH	SW	DOD	T2	T3
				1×1			
γ	2.5	1.805	2.080	2.315	1.779	2.015	2.126
σ_{xx}	2.535	1.176	1.421	0	0	0	0
σ_{yy}	0.855	2.363	1.683	0	0.145	0.625	-0.236
				1×1 relaxed			
$\Delta\gamma$	-0.03	-0.077	-0.027	0	-0.085	-0.004	-0.037
σ_{xx}		-0.427	0.848	0	0.515	0.023	0.076
σ_{yy}		-2.176	0.273	0	-2.775	0.080	-1.693
Δ	-5.1	-7.0	-5.5	0	-10.2	-2.3	-7.2
				2×1			
$\Delta\gamma$	-0.93	-0.690	-0.709	-0.899	-0.714	-1.258	-0.759
σ_{xx}	0.693	-0.808	0.669	1.167	-0.094	0.703	0.367
σ_{yy}	-1.945	-1.731	0.008	-0.051	-1.709	0.190	-1.236
Δ	-24.4	-23.3	-13.3	-8.3	-22.9	-14.6	-15.6
				c2×2			
$\Delta\gamma$		-0.839	-0.703	-0.824	-0.720	-1.143	-0.753
σ_{xx}		-1.356	0.898	1.691	0.274	1.517	0.865
σ_{yy}		-1.419	0.851	0.574	-0.866	0.567	-0.344

γ=surface energy (eV), $\Delta\gamma$=change in surface energy from 1x1,
σ_{ii}=surface tension tensor (x in the direction of the dimer bond and y in the direction of the dimer row),
Δ= Distance change between 1. and 2. layer (%).

- The conclusions of the authors are that no potential is clearly superior. Different potentials describe different properties well.

  SW, **T3** and to some extent **DOD** are good for elastic properties

  T3, SW, DOD, T2 and **BH** give fairly good values for the point defects, to the extent this is possible to judge considering that the experimental values are not known very well either!

  The (100) surface is described best by **BH, SW** and **T3**. No potential describes the complicated reconstructions of the (111) surface.

- **EDIP** was not part of this comparison, but it is clear it would be among the best at least for the elastic and defect properties.

MEAM models

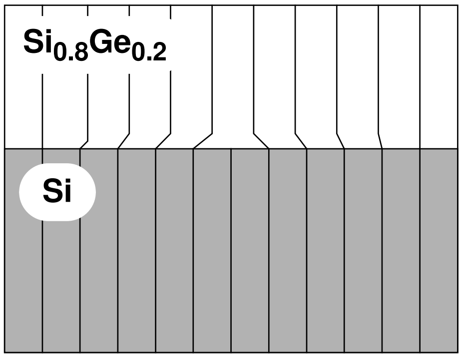
- There also exist so called MEAM (modified EAM) models for Si. This is basically EAM to which an angular term has been added. Baskes has developed some models, but is apparently not quite satisfied with them, at least the last time I heard about this (sometime in 2000).

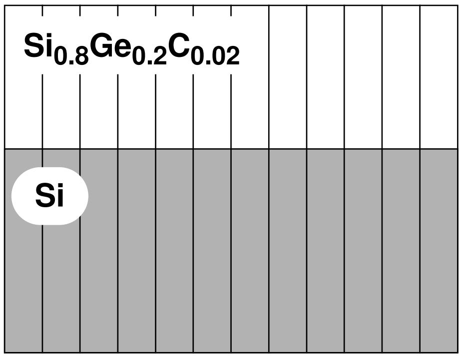
Potentials for SiGeC alloys

- The alloys of Si are something of a hot topic now (~ 2002). Silicon carbide is interesting both for its mechanical hardness as well as its possibilities in high-voltage or high-current electronics. Silicon-germanium compounds ($Si_{1-x}Ge_x$) again are very interesting because by adding some 20 % Ge to Si one can get the electron mobility (and hence integrated circuit speed) about as high as in GaAs, about twice the value in Si. But because the device is still based on Si, one does not have to change to the more complicated GaAs manufacturing technology.

  In $Si_{1-x}Ge_x$-compounds there is, however, the problem that their lattice constant does not match that of Si (on top of which the SiGe is grown). The latest promising word is then $Si_{1-x-y}Ge_xC_y$ where x ~ 0.2 and y ~ x/10. That is, only a few years ago someone realized that by adding a little bit of carbon one can get a perfect lattice match to Si.

  For instance because of this it is interesting to have models for SiGe-, SiGeC and SiC-compounds.





- The Stillinger-Weber potential has two Ge-parametrizations [Ding and Andersen, Phys. Rev. B **34** (1986) 6987 and Wang and Stroud, Phys. Rev. B **38** (1988) 1384]. Out of these, the Ding and Andersen potential has: σ=2.181 Å and ε = 1.93 eV; the other parameters are identical to Si. Wang-Stroud is like Ding-Andersen except that λ = 31.

  One can construct a SiGe compound potential simply by taking the geometric average of the Si and Ge parameters:

$$\sigma_{SiGe} = \sqrt{\sigma_{Si}\sigma_{Ge}}$$
$$\varepsilon_{SiGe} = \sqrt{\varepsilon_{Si}\varepsilon_{Ge}}$$
$$\lambda_{SiGe} = \sqrt{\lambda_{Si}\lambda_{Ge}}$$

- There is also actually a SW-parametrization for C [Pailthorpe and Mahon, Thin Solid Films **192/193** (1990) 34], but this should normally not be used - since SW has a minimum for sp^3 bonding, but carbon also can be favourably in the triply bonded graphite sp^2 configuration, with bond angles of 120 , the SW parametrization is of very limited usability.

  But in describing the lattice compensation of $Si_{1-x-y}Ge_xC_y$ for y ~ 0.01 the combination of the three SW potentials actually does correctly reproduce the good lattice match to Si.

- Tersoff has also developed potentials for SiC and SiGe [PRB 39 (1989) 5566.]. The formalism is almost the same as for his Si potential:

$$E = \frac{1}{2}\sum_{i \neq j} V_{ij} \quad , \quad V_{ij} = f_{\mathrm{C}}(r_{ij})[f_{\mathrm{R}}(r_{ij}) + b_{ij} f_{\mathrm{A}}(r_{ij})] \quad ,$$

$$f_{\mathrm{R}}(r_{ij}) = A_{ij} e^{-\lambda_{ij} r_{ij}} \quad , \quad f_{\mathrm{A}}(r_{ij}) = -B_{ij} e^{-\mu_{ij} r_{ij}} \quad ,$$

$$f_{\mathrm{C}}(r_{ij}) = \begin{cases} 1, & r_{ij} \leq R_{ij} \\ \frac{1}{2} + \frac{1}{2}\cos\pi\left(\frac{r_{ij} - R_{ij}}{S_{ij} - R_{ij}}\right), & R_{ij} < r_{ij} < S_{ij} \\ 0, & r \geq S_{ij} \end{cases} \quad ,$$

$$b_{ij} = \chi_{ij}(1 + \beta_i^{n_i} \zeta_{ij}^{n_i})^{-1/2n_i} \quad , \quad \zeta_{ij} = \sum_{k \neq i,\, j} f_{\mathrm{C}}(r_{ik}) \omega_{ik} g(\theta_{ijk}) \quad ,$$

$$g(\theta_{ijk}) = 1 + \left(\frac{c_i}{d_i}\right)^2 - \left(\frac{c_i}{d_i^2 + (h_i - \cos\theta_{ijk})}\right)^2$$

Here the indices *ij* on the parameters denote the atom types. The mixed parameters λ_{ij}, μ_{ij}, A_{ij}, B_{ij}, R_{ij}, S_{ij} are obtained by interpolation from the elemental parameters:

$$\lambda_{ij} = \frac{\lambda_i + \lambda_j}{2} \quad , \quad \mu_{ij} = \frac{\mu_i + \mu_j}{2} \quad ,$$

$$A_{ij} = \sqrt{A_i A_j} \quad , \quad B_{ij} = \sqrt{B_i B_j} \quad ,$$

$$R_{ij} = \sqrt{R_i R_j} \quad , \quad S_{ij} = \sqrt{S_i S_j} \quad .$$

- A new parameter is χ by which the mixed potential can be finetuned. Tersoff set $\chi_{ii} = 1$ and $\chi_{ij} = \chi_{ji}$, so there is only one free parameter for the mixed interactions, all the others are determined from the elemental parameters. Moreover, ω_{ik} could be used to finetune the mixed interactions but Tersoff set $\omega_{ik} = 1$

- The parameter values for C, Si and Ge were obtained from a fit to the properties of different structures, and the finetuning parameters χ were obtained from the cohesive energies of SiC and (hypothetical) zinc-blende SiGe. The Si parameters are just Si(C) without λ_3.

	C	Si	Ge
A (eV)	1393.6	1830.8	1769
B (eV)	346.7	471.18	419.23
λ (Å)	3.4879	2.4799	2.4451
μ (Å)	2.2119	1.7322	1.7047
β	1.5724×10^{-7}	1.1000×10^{-6}	9.0166×10^{-7}
n	0.72751	0.7873	0.75627
c	3.8049×10^{4}	1.0039×10^{5}	1.0643×10^{5}
d	4.384	16.217	15.652
h	-0.57058	-0.59825	-0.43884
R (Å)	1.8	2.7	2.8
S (Å)	2.1	3.0	3.1
$\chi_{\text{C-Si}} = 0.9776$ $\quad\chi_{\text{Si-Ge}} = 1.00061$			

- The potential gives the following properties for SiC:

	Tersoff	Experiment
a (Å)	4.32	4.36
B (Mbar)	2.2	2.2
c_{11} (Mbar)	4.2	3.6
c_{12} (Mbar)	1.2	1.5
c_{44} (Mbar)	2.6	1.5

- Tersoff also calculated the energies for a few stoichiometric defects (eV):

	Tersoff	DFT
$V_{\mathrm{Si}} + V_{\mathrm{C}}$	7.4	12.7
$\mathrm{C_{Si}} + \mathrm{Si_C}$	7.2	8.4
$\mathrm{Si}_{T\mathrm{C}} + \mathrm{C}_{T\mathrm{Si}}$	22.6	23.3
$\mathrm{Si}_{T\mathrm{Si}} + \mathrm{C}_{T\mathrm{C}}$	23.2	26.0
$\mathrm{C}_{T\mathrm{C}} - \mathrm{C}_{T\mathrm{Si}}$	3.0	2.4

  Here V_{Si} is the Si vacancy, $\mathrm{C_{Si}}$ is a carbon atom on an Si site, and $\mathrm{C}_{T\mathrm{Si}}$ a C atom on a tetrahedral site, surrounded by C atoms.

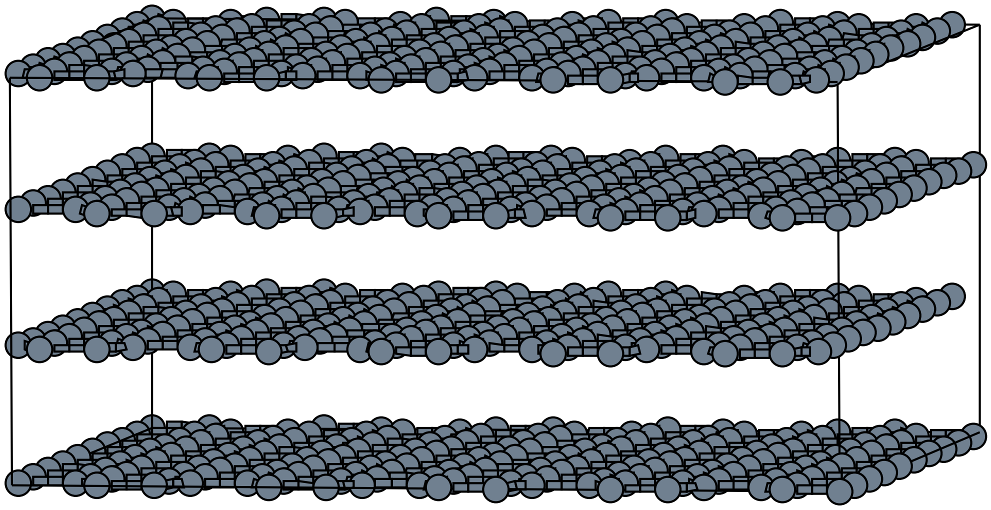
- The potential predicts the properties of SiC fairly well, especially considering that the potentials has only one parameter which is really fit to the properties of the compound (χ). And even this parameter is fairly close to 1. Only the shear modulus c_{44} and the formation energies of vacancies are pretty bad.

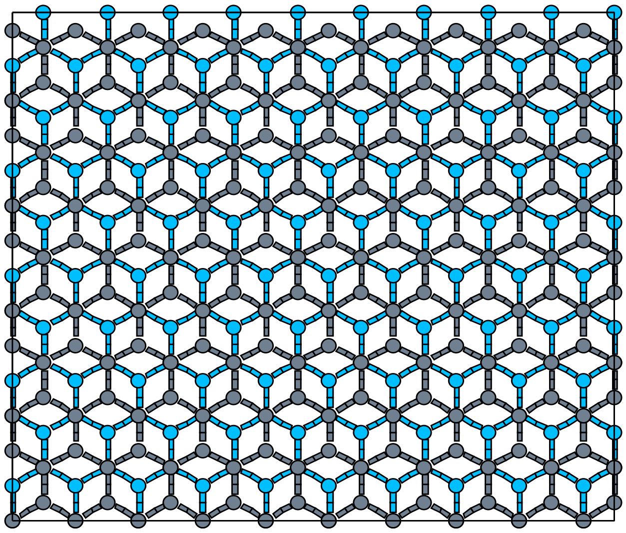
- One problem here is that in reality SiC is partly ionic in its bonding, which is not accounted for at all in the Tersoff potentials. One potential where this is taken into account is [Shimojo, Phys. Rev. Lett. **84** (2000) 3338] but this potential uses explicit angles so it is also problematic

- Nowadays also a wealth of reparametrizations exist for the Tersoff formalism SiC potential - it seems almost every group working on SiC has made their own parametrization...

C potentials

- Constructing a potential for elemental C is complicated (as noted above) because it has two structures which are practically identical in energy: diamond and graphite. Both have a cohesive energy of about 7.4 eV. The structure of graphite is:





(side view and top view):

As noted above, this situation clearly can not be described with an explicit angle potential, but a bond order potential like Tersoff can handle this.

- The Tersoff parametrization for C does, however, describe both bonding types well [Tersoff, Phys. Rev. Lett. **61** (1988) 2879], and is clearly the most used C potential in the materials physics community.

- But it describes the graphite-to-diamond potential poorly. But simply by increasing the parameter S in the potential to 2.46 Å[Nordlund *et al.*, Phys. Rev. Lett. **77** (1996) 699] one can make this transition much better described:

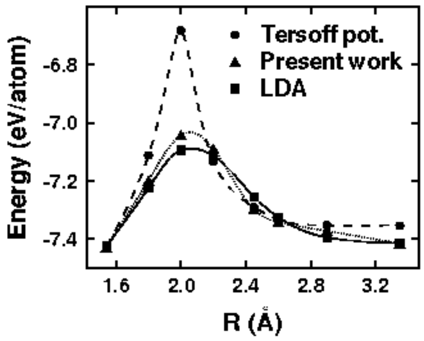


FIG. 2. Total energy per atom of the diamond to rhombohedral graphite transformation as a function of the interlayer distance R parameter. The squares show the energy given by *ab initio* calculations in Ref. [22], the circles the result of the original Tersoff potential, and the triangles the result of our potential. The lines are drawn to guide the eye.

Increasing the cutoff has also proved to be useful for simulating growth.

- But there is a significant problem with the Tersoff C potential: because of its short cutoff, it does not describe the interaction between graphite layers at all. The Chelikowsky carbon potential [Phys. Rev. B **45** (1992) 20] *is claimed to* describe this interaction, but in fact it does not (the student who made the potential had messed up the units in a figure by a factor of 2).

- There are two good solutions I know of to this.
  - Nordlund *et al.* have made an extension to the Tersoff potential which does describe the interaction between graphite layers well [Phys. Rev. Lett. **77** (1996) 699]. However, the additional terms are very weak except precisely for configurations very close to the flat graphite layers, and do not have a deep physical motivation

  - A more general formulation which includes Lennard-Jones-like long-range potentials for many carbon bonding types (including polymers) by Stuart et al [J. Chem. Phys. 112 (2000) 6472].

- Later on in the course we will see how organic molecules can be described.

Ge-potentials

- As we saw above, pure Ge has two almost identical SW-parametrizations, and the Tersoff parametrization, which are all fairly good in the crystalline phase.

- But they all severely overestimate the melting point of Ge, giving about 2500 - 3000 K when the experimental value is 1210 K.

- Nordlund *et al.* tried to solve this in the same way as Stillinger and Weber obtained the right melting point for Si, i.e. decreasing the cohesive energy [Phys. Rev. B **57** (1998) 7556]. By decreasing the cohesive energy in the SW potential by 18 % (i.e. setting $\varepsilon = 1.56$ eV) we obtained a melting point 1230 ± 50 K, and at the same time the threshold displacement energy and mixing coefficient (important in ion irradiation physics) obtained reasonable values.

  But it is clear that this kind of solution is problematic.

Potentials for compound semiconductors

- Compound semiconductors are an interesting alternative to Si in some applications, especially opto-electronics.

- A Keating-type potential [Schabel and Martins, Phys. Rev. B **43** (1991) 11873] has been designed which can describe a large variety of semiconductors when the atoms are close to the ideal sites, but the model is absolutely terrible when the atoms are farther because it has a a harmonic ("r^2")-potential well.

- For GaAs there is the Smith potential, based on the Tersoff formalism [Nucl. Instr. Meth. Phys. Res. B **67** (1992) 335], which uses all the normal Tersoff parameters for Ga-Ga, Ga-As and As-As separately, except that $\lambda_3 = 0$. But this potential has a vanishingly small angular term, and hence all shear moduli are almost exactly 0.

  Sayed started from the Smith parametrizations, but fitted anew the Ga-As-interactions, and constructed an AlAs-potential. The GaAs potential is terrible because the zincblende-structure is not its ground state! However, by setting $\lambda_3 = 0$ it becomes fairly decent.

  Ashu made a potential for InAs following Sayed's approach, but this potential even has the wrong lattice spacing! However, Janne Nord has later made a reparametrization which describes InAs stably [Nordlund *et al.,* Comput. Mater. Sci. **18** (2000) 283].

- There also exist a tight-binding-based Tersoff-like parametrization by Conrad *et al,* [Phys. Rev. B **58** (1998) 4538] but this potential is terrible far from the ground state, it collapses into a state with at least a factor of 2 lower energy than the correct zincblende structure.

- The most recent approach is a modified Tersoff-like parametrization which gives the correct ground states for Ga, As and GaAs, as well as good melting properties for all three [Albe *et al.*, Phys. Rev. B. 66, 035205 (2002)]. The only major problem is As-rich surfaces and defects.

- We have also made a potential for GaN in this formalism [to be published].

Bond order potentials for metals and compounds

- As noted in the description of bond-order potentials above, they are actually equivalent to the basic EAM form. Hence nothing actually prevents from constructing metals potentials from a bond order, e.g. Tersoff-like form.

- We and Karsten Albe have done this, so far for Pt, Ni and W, obtaining potentials which are at least as good as the common EAM-like potentials for the same metals.

- The Pt and Ni potentials were constructed together with a fit to the metal-carbon compound. Again we obtained a quite decent potential, showing that the bond order concept carries further even to complex compounds. The PtC part is published in [Albe *et al.*, Phys. Rev. B 65, 195124 (2002)].