Molecular interaction models 1. Reactive models

- To describe atomic interactions in molecules more complex than a dimer, a pair potential is not enough. Since molecules are bonded by covalent bonds, at least angular terms are needed, and in many cases many more complicated terms as well. For instance, in carbon chains the difference between “single” and “double” bonds often is important, and for this at least a four-body term is needed.

- In materials physics, people are often interested in phase transitions or other phenomena where the chemical bonds may break. This means that the interatomic potential model have to be able to handle bond breaking. Since phase transitions often involve chemical reactions, models which can handle bond breaking are called **reactive** interatomic potentials. Furthermore, to be fully transferable the models should be able to also describe all the phases of the material in a single parametrization.

- The opposite is models which deal with systems where covalent bonds never break. This category of potentials is called **molecular mechanics force fields,** and is dealt with later.

- That an interatomic potential is reactive means at a minimum that the energy of a bond goes smoothly to zero when the bond length goes to infinity. All the interatomic potentials dealt with so far on this course are reactive.

- A hugely important set of molecules are of course the organic ones, i.e. those based on carbon. So having **reactive** interatomic potentials for carbon-based molecules is of course of great interest. Nevertheless, there do not exist many such models. In fact, here is an exhaustive list of all reactive transferable potentials for organic materials:

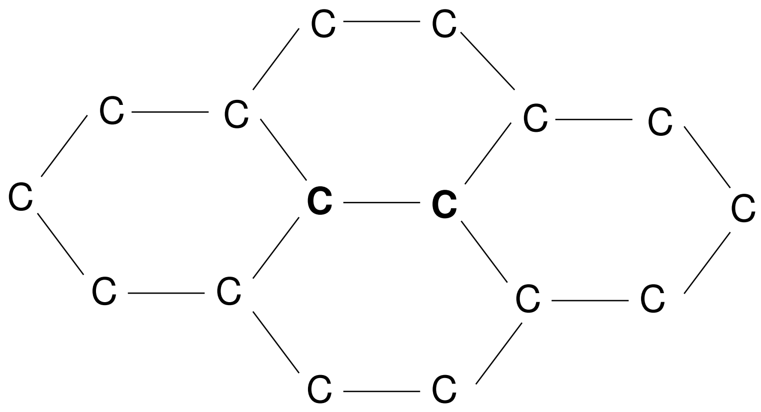
    - The **Brenner** reactive bond-order potential (**REBO**) for C, H and simple hydrocarbon molecules.
        - In addition, there is the further development of this called AIREBO model which can also handle long-range interactions between molecules

- Since this is the only one, we describe it in some detail.

Brenner potential

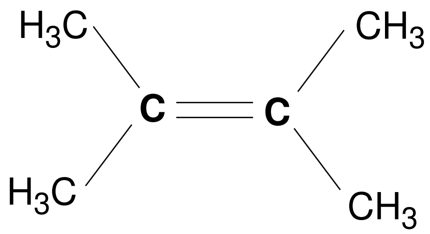
- The Brenner potential [D. W. Brenner, Phys. Rev. B 42 (1990) 9458] is a potential for hydrocarbons, which is based on the Tersoff potential but developed further from this. We describe it here in some detail because the ideas behind show how information on chemical bonding can be added in a well-motivated way to a classical potential. The Brenner potential is also attractive in that it can describe chemical reactions, which the potentials with harmonic terms can not.

  The basic Tersoff potential contains a bonding term E_{bond} and an angular term E_{angle}. But these can not describe alone e.g. conjugated bonds. The issue here can be understood as follows. Consider first graphite:

  Here all the carbons have an identical local neighbourhood. Because carbon has 4 outer electrons, but only three bonds, every bond has 1 1/3 electrons.

  The consider the following molecule:

  Here there is a double bond between the two **C atoms marked in bold.** But the local neighbourhood of these two atoms is identical to the two **C atoms in bold** in graphite. Because the Tersoff potential only accounts for the nearest neighbours, it describes the middle bond here in the same way as the bonds in graphite, although in reality there is a clear difference in bond character, strength and length.

- To improve on problems like this, Brenner added terms which depend on the chemical environment into the Tersoff potential.
- Brenner starts with the Tersoff potential

$$E_b=\sum_i \sum_{j(>i)} [V_R(r_{ij})-\bar{B}_{ij}V_A(r_{ij})]$$

and defines the repulsive and attractive parts just V_R and V_A just like Tersoff. But the environment-dependence obtains additional parts. $\overline{B}_{ij}$ is now:

$$\bar{B}_{ij}=(B_{ij}+B_{ji})/2+F_{ij}(N_i^{(t)},N_j^{(t)},N_{ij}^{\mathrm{conj}})$$

where

$$B_{ij}=\left[1+\sum_{k(\neq i,j)} G_i(\theta_{ijk})f_{ik}(r_{ik})e^{\alpha_{ijk}[(r_{ij}-R_{ij}^{(e)})-(r_{ik}-R_{ik}^{(e)})]}+H_{ij}(N_i^{(\mathrm{H})},N_i^{(\mathrm{C})})\right]^{-\delta_i}$$

The first part is almost as Tersoff's formulation (except no power of three in the exponential), but the H_{ij} and F_{ij} are new. Here $N_{\mathrm{i}}^{(\mathrm{H})}$ are the number of H neighbours of one atom, $N_{\mathrm{i}}^{(\mathrm{C})}$ the number of C neighbours of one atom, and $N_{\mathrm{i}}^{(\mathrm{t})}$ the total number of neighbours. The number of neighbours is calculated by utilizing the normal Tersoff cutoff-function

$$f_{ij}(r)=\begin{cases} 1, & r<R_{ij}^{(1)} \\ \left[1+\cos\left[\dfrac{\pi(r-R_{ij}^{(1)})}{(R_{ij}^{(2)}-R_{ij}^{(1)})}\right]\right]\Big/2, & R_{ij}^{(1)}<r<R_{ij}^{(2)} \\ 0, & r>R_{ij}^{(2)}\ . \end{cases}$$

which is 1 at normal bond lengths. The sums over f_{ij} thus gives an effective number of neighbours:

$$N_i^{(\mathrm{H})} = \sum_{j(=\text{hydrogen})} f_{ij}(r_{ij})$$

$$N_i^{(\mathrm{C})} = \sum_{j(=\text{carbon})} f_{ij}(r_{ij})$$

$$N_i^{(t)} = N_i^{(\mathrm{H})} + N_i^{(\mathrm{C})}$$

The values of $N_i^{(t)}$ can be used to deduce whether some C atom is part of a conjugated system. If any C atom has even one neighbour which does not have 4 neighbours, it is interpreted as conjugated. (because all quantities are continuous, the precise requirement is in fact $N_i^{(t)} < 4$)

The continuous quantity N_{ij}^{conj} which describes whether a bond ij is conjugated is calculated as

$$N_{ij}^{\mathrm{conj}} = 1 + \sum_{\text{carbons } k(\neq i,j)} f_{ik}(r_{ik}) F(x_{ik}) + \sum_{\text{carbons } l(\neq i,j)} f_{jl}(r_{jl}) F(x_{jl})$$

where

$$F(x_{ik}) = \begin{cases} 1, & x_{ik} \leq 2 \\ \{1 + \cos[\pi(x_{ik} - 2)]\}/2, & 2 < x_{ik} < 3 \\ 0, & x_{ik} \geq 3 \end{cases}$$

and

$$x_{ik} = N_k^{\mathrm{tot}} - f_{ik}(r_{ik})$$

So if one carbon atom has exactly 4 bonds we get

$x_{ik} = 3$ => $F(x_{ik}) = 0$ => $N_{ij}^{conj} = 1$

If the bond on the other hand is conjugated, N_{ij}^{conj} >=2.

The remaining question is how to form the functions $F_{ij}\,(N_i^{(t)}, N_j^{(t)}, N_{ij}^{conj})$ and $H_{ij}(N_i^{(H)}, N_i^{(C)})$? Brenner does this simply by fitting into a large set of experimental data. As many as possible of the values for integer indices are set to some values directly derived from experiments, and thereafter spline interpolation is used to interpolate values smoothly for non-integer arguments.

For instance, the values for integer arguments determined in version 1 of the potential for the function *H* are:

$H_{CC}(1,1)$	−0.0175	CC bond energy in benzene
$H_{CC}(2,0)$	−0.0070	CC double bond in ethylene
$H_{CC}(3,0)$	0.0119	CC single bond in ethane
$H_{CC}(1,2)$	0.0115	CC single bond in isobutane
$H_{CC}(2,1)$	0.0118	CC single bond in cyclohexane
$H_{CH}(1,0)$	−0.0760	Atomization energy of CH_2
$H_{CH}(2,0)$	−0.2163	Atomization energy of CH_3
$H_{CH}(3,0)$	−0.3375	Atomization energy of methane
$H_{CH}(0,1)$	−0.1792	CH bond energy in acetylene
$H_{CH}(0,2)$	−0.2407	CH bond energy in benzene
$H_{CH}(1,1)$	−0.2477	CH bond energy in ethylene
$H_{CH}(2,1)$	−0.3320	CH bond energy in ethane
$H_{CH}(0,3)$	−0.3323	Tertiary-HC bond energy in isobutar
$H_{CH}(1,2)$	−0.3321	CH bond energy in cyclohexane
$\dfrac{\partial H_{CH}(1,1)}{\partial C}$	−0.128 05	Centered difference
$\dfrac{\partial H_{CH}(2,0)}{\partial C}$	−0.076 55	Centered difference
$\dfrac{\partial H_{CH}(0,2)}{\partial H}$	−0.130 75	Centered difference
$\dfrac{\partial H_{CH}(1,1)}{\partial H}$	−0.0764	Centered difference

and for function F:

$F(1,1,1)$	0.1511	CC triple bond in acetylene
$F(2,2,1)$	0.075	Average energy of bonds in $(CH_3)_2C{=}C(CH_3)$ and $(CH_3)HC{=}CH(CH_3)$ equal double bond
$F(1,2,1)$	0.0126	Atomization energy of $HC{=}CH_2$
$F(1,3,1),F(1,3,2)$	−0.1130	Single bond in H_3C—CH
$F(0,3,1),F(0,3,2)$	−0.1220	Single bond in H_3C—C
$F(0,2,2)$	−0.0445	Conjugated double bond in $C{=}CH(CH_2)$
$F(0,2,1)$	0.0320	Double bond in $C{=}CH_2$
$F(0,1,1)$	0.1100	Atomization energy of C_2H
$F(1,1,2)$	0.0074	Atomization energy of CH_2CCH
$\frac{\partial F(3,1,1)}{\partial i}$	−0.1160	Centered difference
$\frac{\partial F(3,2,1)}{\partial i}$	−0.132 05	Centered difference
$\frac{\partial F(3,1,2)}{\partial i}$	−0.0610	Centered difference
$\frac{\partial F(2,3,2)}{\partial i}$	0.022 25	Centered difference
$\frac{\partial F(2,4,2)}{\partial i}$	−0.037 75	Centered difference
$\frac{\partial F(3,4,2)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,4,1)}{\partial i}$	0.0565	Centered difference
$\frac{\partial F(3,2,2)}{\partial i}$	−0.1065	Centered difference

In addition, Brenner also presented another parametrization of his potential.

- Crucial here are not the exact values, but the principle used: that as many parameters as possible are set to well-defined experimental quantities. Also the H values are largely derived from experimental data:

Hydrogen	$R_{HH}^{(e)}$	0.74144 Å	Gas-phase diatomic
	$D_{HH}^{(e)}$	4.7509 eV	Gas-phase diatomic
	β_{HH}	1.9436 Å^{-1}	Gas-phase diatomic
	S_{HH}	2.3432	Barrier for reaction (19)
	δ_{HH}	0.804 69	Set equal to carbon value
	α_{HHH}	3.0	Remove spurious wells from (19)
	G_{HH}	4.0	Barrier for reaction (19)
	$R_{HH}^{(1)}$	1.1 Å	Near-neighbor interactions
	$R_{HH}^{(2)}$	1.7 Å	Near-neighbor interactions

- Also the parameters for pure carbon were refitted by Brenner.

- (n. b. spline interpolation is a way to do interpolation almost as efficiently but much more accurately than using linear interpolation. See e.g. Press *et al.*, Numerical Recipes in C/Fortran90)

- Brenner tested his potential by calculating atomization energies for a large group of simple hydrocarbons. The results are listed on the next page.

  The potential was also shown to describe well the reconstructed and H-terminated diamond 111 surface and molecules chemisorbed on the surface.

TABLE IV. Atomization energies for various hydrocarbon molecules. Experimental values were derived from heats of formation using energies of 7.3768 eV for carbon and 2.375 eV for hydrogen.

	Molecule	Potential I (eV)	Potential II (eV)	Experimental value (eV)
Alkanes	methane	17.6	17.6	17.6[a]
	ethane	29.7	29.7	29.7[a]
	propane	42.0	42.0	42.0[a]
	n-butane	54.3	54.3	54.3[a]
	i-butane	54.3	54.3	54.4[a]
	n-pentane	66.5	66.5	66.6[a]
	isopentane	66.5	66.5	66.6[a]
	neopentane	66.8	66.8	66.7[a]
	cyclopropane	35.5	35.0	35.8[a]
	cyclobutane	48.7	48.5	48.2[a]
	cyclopentane	61.4	61.3	61.4[a]
	cyclohexane	73.6	73.6	73.6[a]
Alkenes	ethylene	23.6	23.6	23.6[a]
	propene	36.2	36.2	36.0[a]
	1-butene	48.5	48.5	48.5[b]
	cis-butene	48.8	48.9	48.6[b]
	isobutene	48.4	48.4	48.7[b]
	$(CH_3)_2C{=}C(CH_3)_2$	73.2	73.3	73.4[b]
	cyclopropene	28.2	27.3	28.8[b]
	cyclobutene	42.4	42.0	42.4[b]
	cyclopentene	55.7	55.7	55.6[b]
	1,4-pentadiene	55.0	55.0	54.8[b]
	$CH_2{=}CHCH{=}CH_2$	41.8	41.9	42.6[b]
	$CH_3CH{=}C{=}CH_2$	40.4	40.5	42.1[b]
	$H_2C{=}C{=}CH_2$	27.8	27.9	29.6[b]
Alkynes	acetylene	17.1	17.1	17.1[a]
	propyne	29.4	29.4	29.7[b]
	1-butyne	41.7	41.7	42.0[b]
	2-butyne	41.7	41.7	42.2[b]
Aromatics	benzene	57.5	57.5	57.5[a]
	toulene	69.6	69.6	70.1[b]
	1,4-dimethylbenzene	81.8	81.8	82.6[b]
	ethylbenzene	81.9	81.9	82.5[b]
	ethenylbenzene	76.2	76.2	76.5[b]
	ethynylbenzene	69.8	69.8	69.9[b]
	naphthalene	91.4	91.4	91.2[b]
Radicals	CH_2	7.8	7.8	7.8[c]
	CH_3	12.7	12.7	12.7[d]
	$H_3C_2H_2$	25.7	25.7	25.5[b]
	H_2C_2H	18.9	18.9	18.9[e]
	C_2H	12.2	12.2	12.2[f]
	CH_2CCH	24.5	24.5	25.8[b]
	n-C_3H_7	37.9	38.0	37.8[e]
	i-C_3H_7	38.3	38.3	38.0[e]
	t-C_4H_9	50.5	50.5	50.5[e]
	phenyl	52.7	52.7	52.7[e]

[a]From heat of formation at 0 K (from Ref. 41).
[b]From heat of formation at 300 K [from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. J. Heron, J. Chem. Ref. Data 6, Suppl. 1, I-774 (1977)].
[c]Calculated from Ref. 46.
[d]Calculated from Ref. 45.
[e]From heat of formation at 300 K (from Ref. 52).
[f]From heat of formation at 0 K [from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. J. Heron, J. Chem. Ref. Data 6, Suppl. 1, I-774 (1977)].

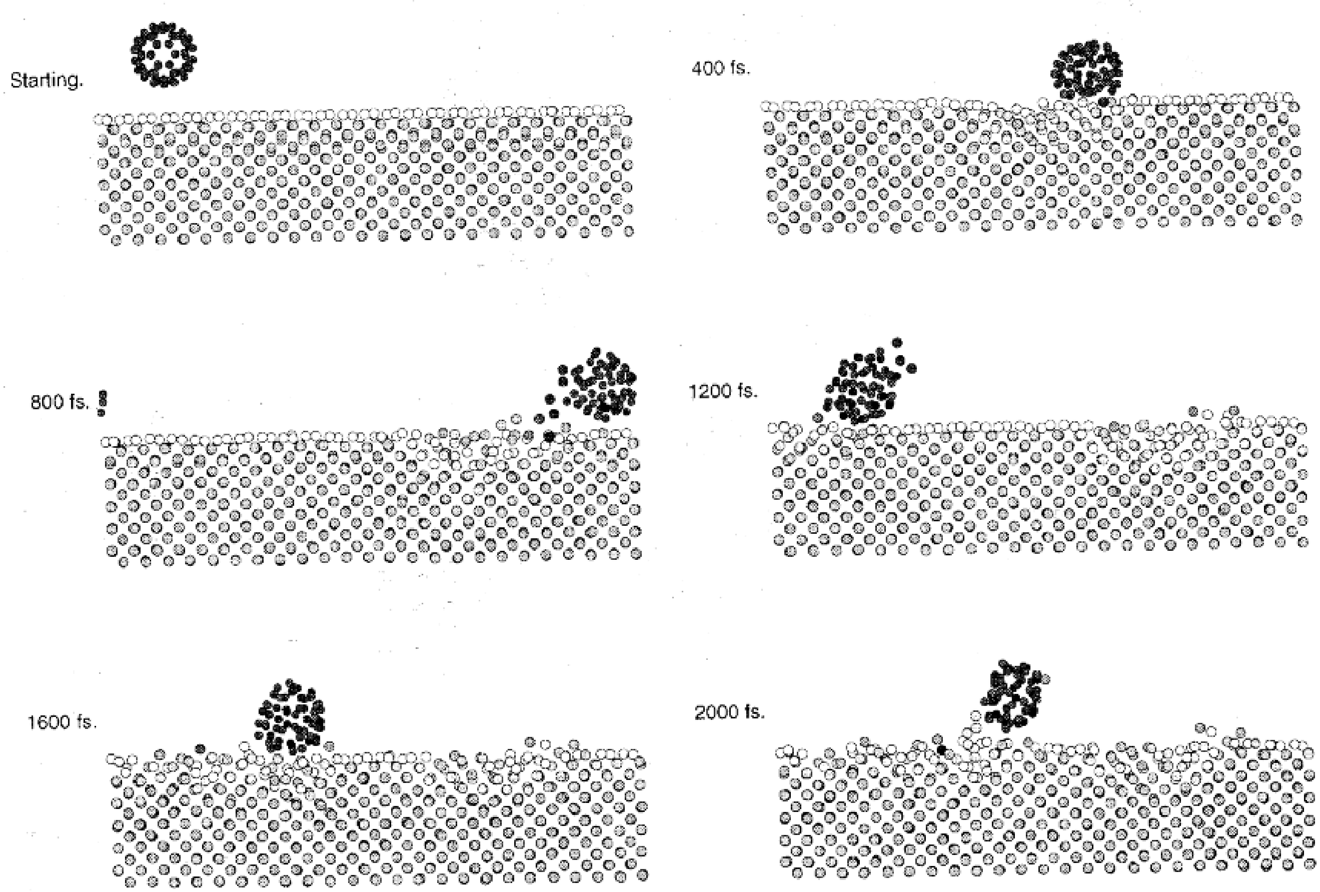
- Later Murty and Atwater [Phys. Rev. B **51** (1991) 4889] have made a Si-H version of the Brenner potential, and Beardmore and Smith [Phil. Mag. A **74** (1996) 1439] a combined C-Si-H-version.

- Brenner himself has later added a torsional term to the potential, and at least two groups have added long-range interactions into it: [Stuart *et al.,* J. Chem. Phys. **112** (2000) 6472] and [Che *et al.*, Theor. Chem. Acc. **102** (1999) 346].

- Example application: Beardmore and Smith examined in their paper how a fullerene C_{60} hits an Si surface.

  Case I: 250 eV C_{60} -> virgin Si, incoming angle 80^o

Fig. 11



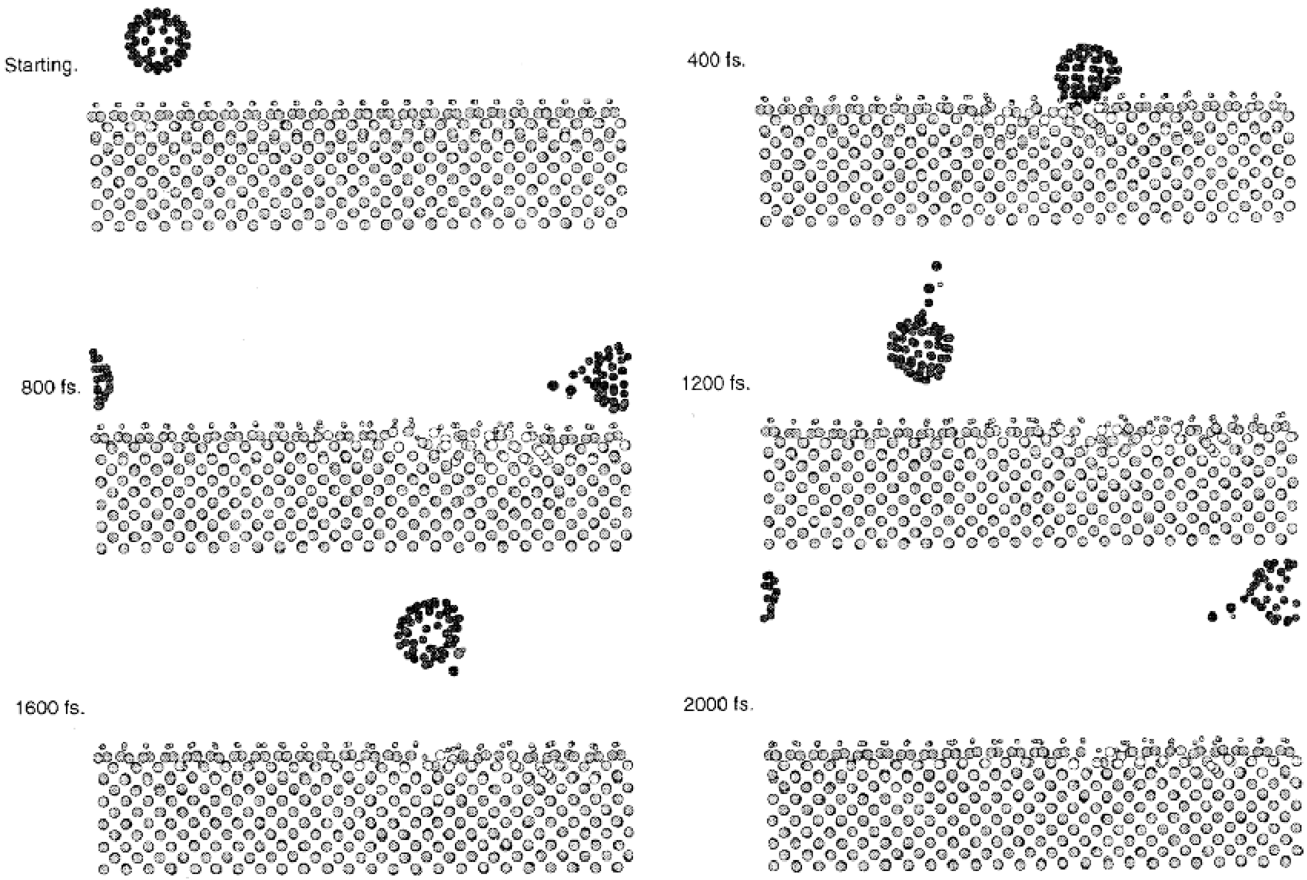
Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on bare Si{100} during a 2 ps simulation.

i.e. the fullerene forms bonds with the surface and rotates along it for a while (note the periodic boundary conditions).

But if the Si-surface is H-terminated (all dangling bonds are filled with a H) the behaviour changes:

Case II: 250 eV C_{60} -> H-terminated Si, 80^{o}

Fig. 12

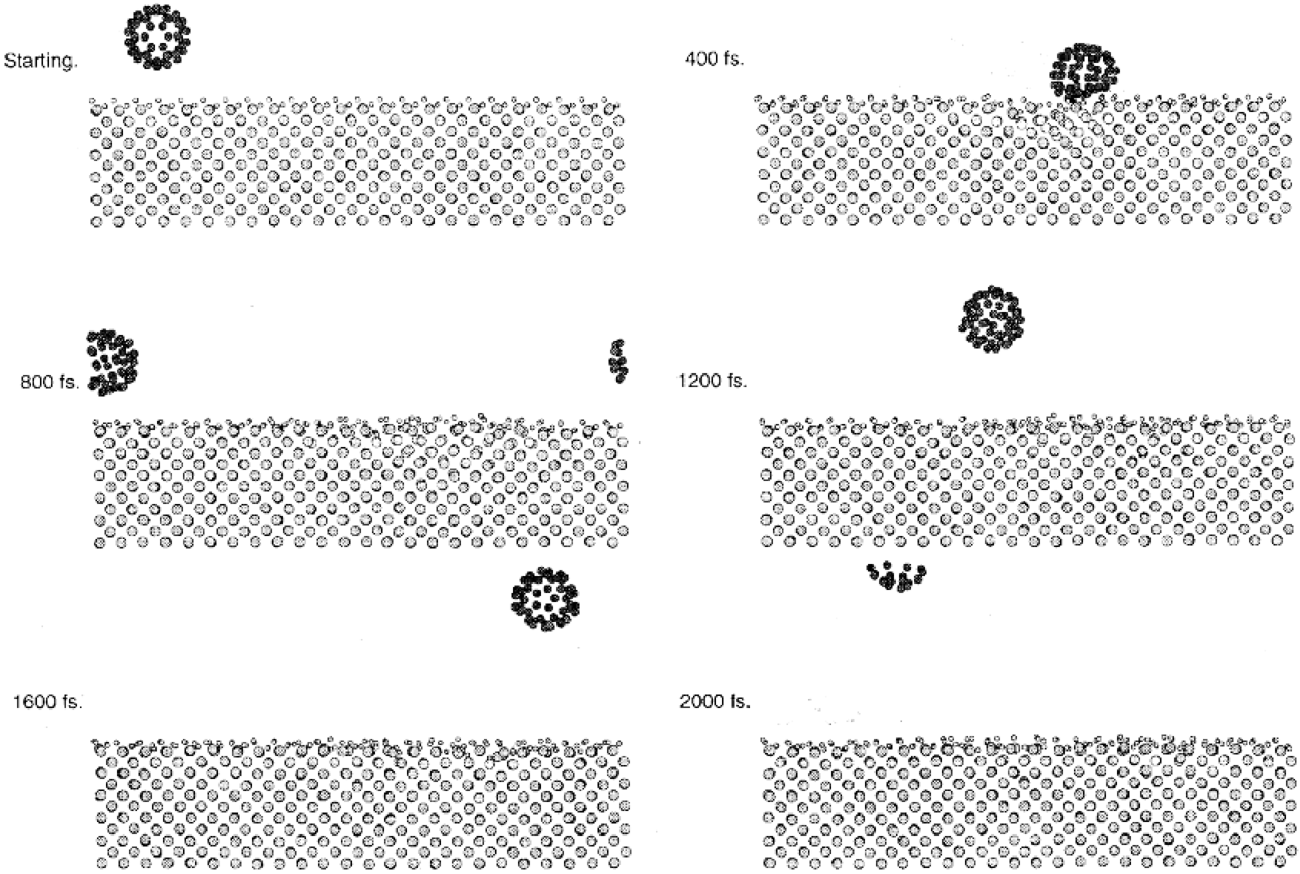


Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on 1 MLH Si{100} during a 2 ps simulation.

So the H protects the surface such that only a couple of bonds are formed with the surface, and the fullerene bounces back almost impact, having only taken up one Si atom.

Case III: 250 eV C_{60} -> doubly H-terminated Si, 80^{o}

Fig. 13



Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on 2 MLH Si{100} during a 2 ps simulation.

So now the protective H layer is so thick that there are no C-Si bonds formed at all, and the fullerene bounces back intact.