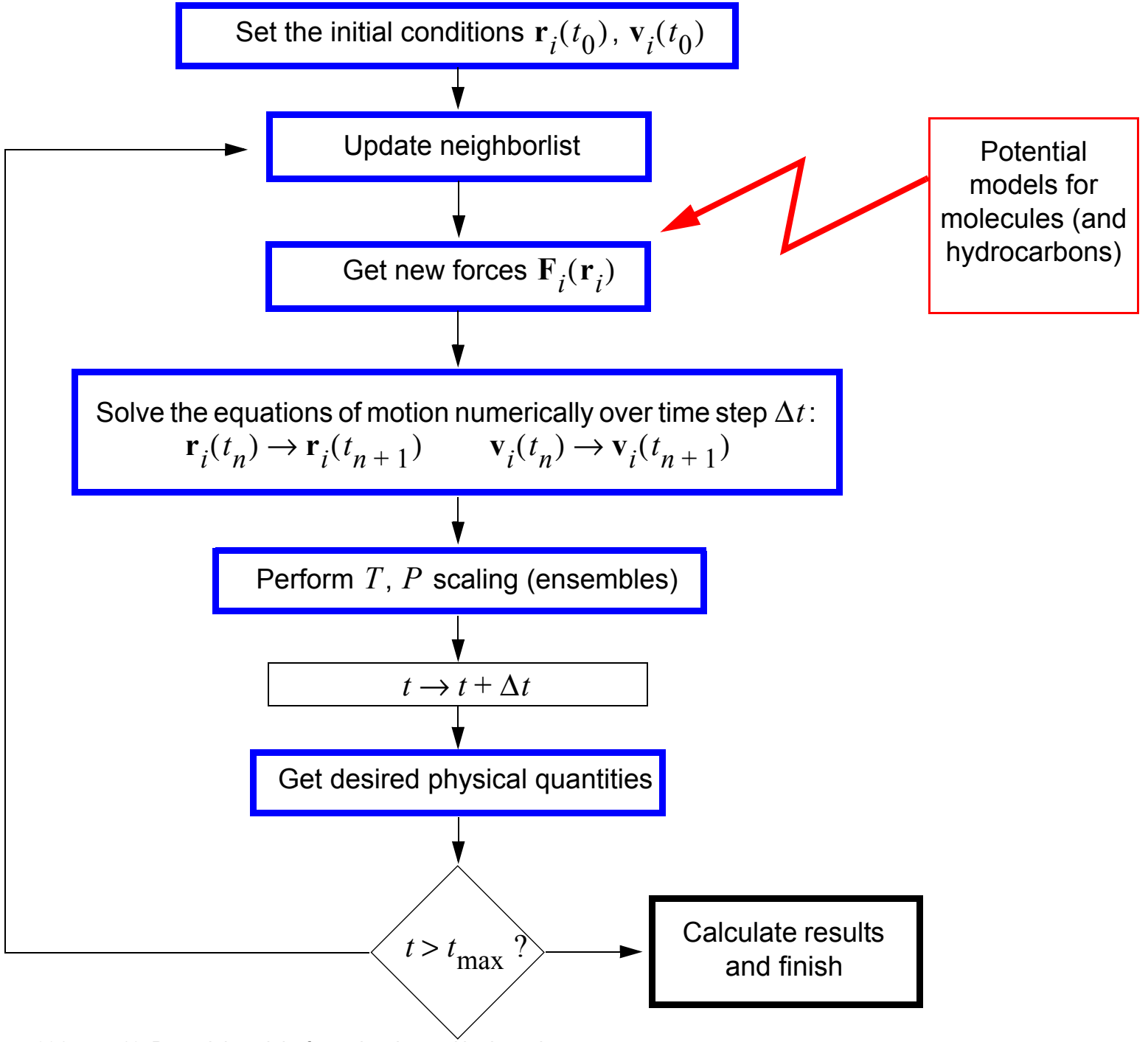

Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$
Update neighborlist
Get new forces $\mathbf{F}_i(\mathbf{r}_i)$
Potential models for molecules (and hydrocarbons)
Solve the equations of motion numerically over time step Δt:
$\mathbf{r}_i(t_n) \rightarrow \mathbf{r}_i(t_{n+1})$ $\mathbf{v}_i(t_n) \rightarrow \mathbf{v}_i(t_{n+1})$
Perform T, P scaling (ensembles)
$t \rightarrow t + \Delta t$
Get desired physical quantities
$t > t_{\max}$?
Calculate results and finish

Molecular interaction models

- Since molecules are bonded by covalent bonds, at least angular terms are needed,
  - In many cases many more complicated terms as well: e.g. carbon chains the difference between “single” and “double” bonds often is important $\Rightarrow$ at least a four-body term is needed.

- To describe complex molecules a large set of **force fields** have been developed.
  - **Molecular mechanics**: use of force fields, no reactions (i.e. bond breaking or creation)
  - Fixed neighbor topology (except for so called non-bonded interactions).

  - The total energy of a molecule can be given as

$$E = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{cross}} + E_{\text{nonbond}}$$

E_{bond}: energy change related to a change of bond length (V_2)

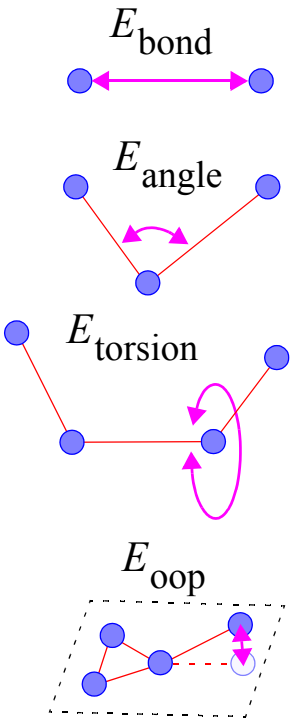
E_{angle}: energy change associated with a change in the bond angle,(V_3)

E_{torsion}: torsion, i.e. energy associated with the rotation between two parts of a molecule relative to each other (also termed dihedral)

E_{oop}: “out-of-plane” interactions, i.e. the energy change when one part of a molecule is out of the plane with another (keeps the molecule planar)

E_{cross}: cross terms between the other interaction terms

E_{nonbond}: interaction energies which are not associated with covalent bonding (e.g. ionic or van der Waals terms)



  - In the following we describe the terms, using notation more common in chemistry rather than the physics notation used earlier on the course.

Molecular interaction models

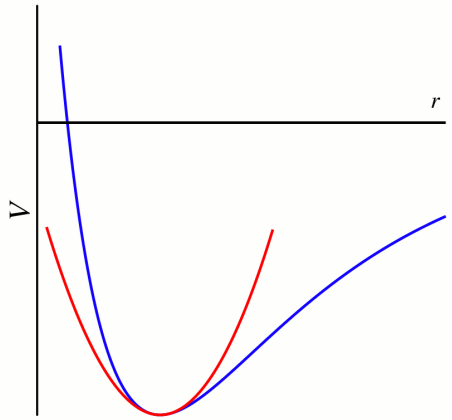
- **The term** E_{bond}
  - This term describes the energy change associated with the bond length. It is a simple pair potential, and could be e.g. a Morse or LJ potential.
    - At its simplest, it is purely harmonic, i.e.

$$E_{bond} = \sum_{bonds} \frac{1}{2} k_b (b - b_0)^2$$

      where b is the bond length.
    - If we write this term instead as

$$E_i = \sum_j \frac{1}{2} k (r_{ij} - r_0)^2$$

      we see that it is the same thing as the pair potentials dealt with earlier.
    - Can be good enough in problems where we are always close to equilibrium, since any smooth potential well can always be to the first order approximated by a harmonic well.
    - But harmonic potentials obviously can not describe large displacements of atoms or bond breaking reasonably.
    - In solids, the harmonic approximation corresponds to the elastic regime, i.e. the one where stress is directly proportional to the strain (Hooke's law).
      - A historical footnote is that Hooke presented the law already in the 1678 as "*Ut tensio, sic vis.*"[1] so it did not originally have to do much with interatomic potentials...



Molecular interaction models

- To improve on the bond model beyond the elastic regime, one can add higher-order terms to it, e.g.

$$E_{\text{bond}} = \sum_{\text{bonds}} K_2(b-b_0)^2 + K_3(b-b_0)^3 + K_4(b-b_0)^4$$

- Larger strain can be described, but not bond breaking: if here $b \to \infty$ thenalso $E \to \infty$ => bonds cannot break

- The familiar Morse potential

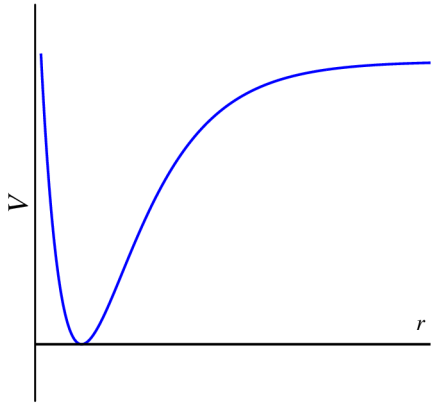
$$E_{\text{bond}} = \sum_{\text{bonds}} D_b \left\{ 1 - e^{-a(b-b_0)} \right\}^2 = \sum_{\text{bonds}} D_b \left\{ e^{-2a(b-b_0)} - 2e^{-a(b-b_0)} + 1 \right\}$$

is much used to describe bond energies.

This is shifted in E axis so that $E_{\text{bond}}(b_0) = 0$.

1. The Power of any spring is in the same proportion with the Tension thereof.

- It is good in that $E \rightarrow \text{constant}$ when $b \rightarrow \infty$ so it can describe bond breaking.
- But on the other hand it never goes fully to 0, which is not quite realistic either as in reality a covalent bond does break essentially completely at some interatomic distance.



Molecular interaction models

- **Angular terms** E_{angle}

  - The angular terms describe the energy change associated with two bonds forming an angle with each other. Most kinds of covalent bonds have some angle which is most favoured by them - for sp^3 hybridized bonds it is ~ 109^o, for sp^2 120^o and so on.

  - Like for bond lengths, the easiest way to describe bond angles is to use a harmonic term like

$$E_{\text{angle}} = \sum_{\text{angles}} \frac{1}{2} H_\theta (\theta - \theta_0)^2,$$

    where θ_0 is the equilibrium angle and H_θ a constant which describes the angular dependence well. This may work well up to 10^o or so, but for larger angles additional terms are needed.

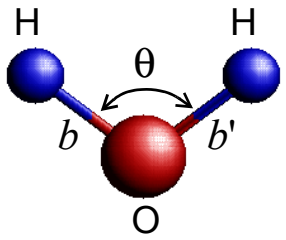
  - A typical means for improvement is, surprise surprise, third-order terms and so forth, for instance

$$E_{\text{angle}} = \sum_{\text{angles}} H_2 (\theta - \theta_0)^2 + H_3 (\theta - \theta_0)^3$$

  - An example: by taking the simplest possible bond length and angular terms, it is already possible to describe one water molecule to some extent:

$$E_{\text{H}_2\text{O}} = K_{\text{OH}} (b - b^0_{\text{OH}})^2 + K_{\text{OH}} (b' - b^0_{\text{OH}})^2 + K_{\text{HOH}} (\theta - \theta^0_{\text{HOH}})^2$$

    where b and b' are the lengths of the two bonds and θ the angle between them.

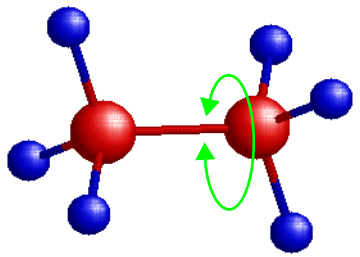


Molecular interaction models

- **Torsional terms** E_{torsion}

  - The bond and angular terms were already familiar from the potentials for solids. In the physics and chemistry of molecules there are many important effects which can not be described solely with these terms.

  - The most fundamental of these is probably torsion. By this, the rotations of one part of a molecule with respect to another is meant. A simple example is the rotation of two parts of the ethane molecule C_2H_6 around the central C-C carbon bond.



  - Torsional forces can be caused by e.g. dipole-dipole-interactions and bond conjugation.

  - If the angle between two parts is described by an angle ϕ, it is clear that the function f which describes the rotation should have the property $f(\phi) = f(\phi + 2\pi)$, because it is possible to do a full rotation around the central bond and return to the initial state. The trigonometric functions $\sin$ and $\cos$ of course fulfil this requirement, so it is natural to describe the torsional energy with a a few terms in a Fourier series

$$E_{\text{torsion}} = V_1(1 + \cos(\phi)) + V_2(1 + \cos(2\phi)) + V_3(1 + \cos(3\phi))$$

Molecular interaction models

- **Out-of-plane terms** E_{oop}
  - With the out-of-plane-terms one describes the energy which in (some cases) is associated with the displacement of atoms out of the plane in which they should be. This is relevant in some (parts of) molecules where atoms are known to lie all in the same plane. The functional form can be rather simple,

$$E_{\mathrm{oop}} = \sum_{\chi} H_{\chi} \chi^2$$

  where χ is the displacement out of the plane.

- **Cross terms** E_{cross}
  - The cross-terms are functions which contain several of the above-mentioned quantities. They could e.g. describe how a stretched bond has a weaker angular dependence than a normal one. Or they can describe the relations between two displacements, an angle and a torsion and so one.

- **Non-bonding terms** E_{nonbond}
  - With the non-bonding terms all effects which affect the energy of a molecule but are not covalent bonds are meant. These are e.g. van der Waals-terms, electrostatic Coulomb interactions and hydrogen bonds. For this terms one could thus further divide

$$E_{\mathrm{nonbond}} = E_{\mathrm{vdW}} + E_{\mathrm{Coulomb}} + E_{\mathrm{hbond}}$$

  - The van der Waals term is often a simple Lennard-Jones-potential, and E_{Coulomb} a Coulomb potential for some, usually fractional, charges q_i.

Molecular interaction models

- If all of the above are included except for hydrogen bonds, the total energy expression can for instance look like

$$V(R) = \underbrace{\sum_b D_b \left[1 - \exp(-a(b - b_0))\right]^2}_{E_{bond}} + \underbrace{\sum_\theta H_\theta (\theta - \theta_0)^2}_{E_{angle}} + \underbrace{\sum_\phi H_\phi \left[1 + s\cos(n\phi)\right]}_{E_{torsion}}$$

$$+ \underbrace{\sum_\chi H_\chi \chi^2}_{E_{oop}} + \underbrace{\sum_b \sum_{b'} F_{bb'} (b - b_0)(b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0)}_{E_{cross}}$$

$$+ \sum_b \sum_\theta F_{b\theta} (b - b_0)(\theta - \theta_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'\phi} (\theta - \theta_0)(\theta' - \theta'_0)\cos\phi$$

$$+ \sum_\chi \sum_{\chi'} F_{\chi\chi'} \chi\chi' + \sum_i \sum_{j>i} \left[\underbrace{\frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^6}}_{E_{vdW}} + \underbrace{\frac{q_i q_j}{r_{ij}}}_{E_{Coulomb}} \right]$$

- There are many popular force fields in the literature:
  AMBER, CHARMM, MM2, MM3, MM4, ...

- **GROMACS** is a GPL'ed MD code able to use various force fields.
  - Home page: **http://www.gromacs.org/**

Brenner potential

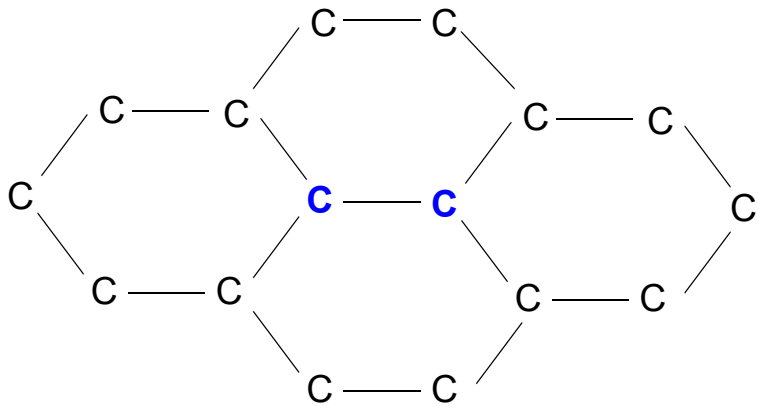
- The Brenner potential [D. W. Brenner, *Phys. Rev. B* **42** (1990) 9458] is a 'simple' potential for hydrocarbons, which is based on the Tersoff potential but developed further from this.

  - The ideas behind the potential 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.

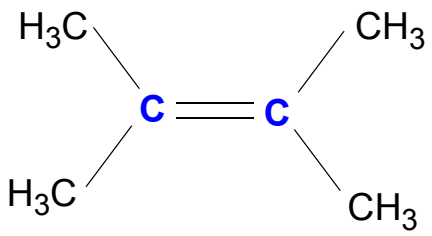
  - The issue here can be understood as follows. Consider first graphite:



  - 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.

Brenner potential

- Then consider the following molecule:



- Here there is a double bond between the two **C atoms marked in blue.** But the local neighbourhood of these two atoms is identical to the two **C atoms in blue** 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 V_{R} and V_{A} just like Tersoff. But the environment-dependence obtains additional parts.

Brenner potential

- $\bar{B}_{ij}$ is now:

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

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 $N_i^{(\mathrm{H})}$ are the number of H neighbours of one atom, $N_i^{(\mathrm{C})}$ the number of C neighbours of one atom, and $N_i^{(\mathrm{t})}$ the total number of neighbours. The number of neighbours is calculated by utilizing the normal Tersoff cutoff-function

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

Brenner potential

- The sums over f_{ij} thus gives an effective number of neighbours (coordination!):

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

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

- The values of $N_i^{(\mathrm{t})}$ 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 $N_i^{(\mathrm{t})} < 4$)

Brenner potential

- 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

$$x_{ik} = 3 \Rightarrow F(x_{ik}) = 0 \Rightarrow N_{ij}^{\mathrm{conj}} = 1 \, .$$

- If the bond on the other hand is conjugated, $N_{ij}^{\mathrm{conj}} \geq 2$.

- The remaining question is how to form the functions $F_{ij}(N_i^{(\mathrm{t})}, N_j^{(\mathrm{t})}, N_i^{\mathrm{conj}})$ and $H_{ij}(N_i^{(\mathrm{H})}, N_i^{(\mathrm{C})})$?
- 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.

Brenner potential

- 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 isobutane
$H_{CH}(1,2)$	−0.3321	CH bond energy in cyclohexane
$\frac{\partial H_{CH}(1,1)}{\partial C}$	−0.128 05	Centered difference
$\frac{\partial H_{CH}(2,0)}{\partial C}$	−0.076 55	Centered difference
$\frac{\partial H_{CH}(0,2)}{\partial H}$	−0.130 75	Centered difference
$\frac{\partial H_{CH}(1,1)}{\partial H}$	−0.0764	Centered difference

Brenner potential

- 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.

Brenner 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.

- 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.

Brenner potential

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]

Brenner potential

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]

Brenner potential

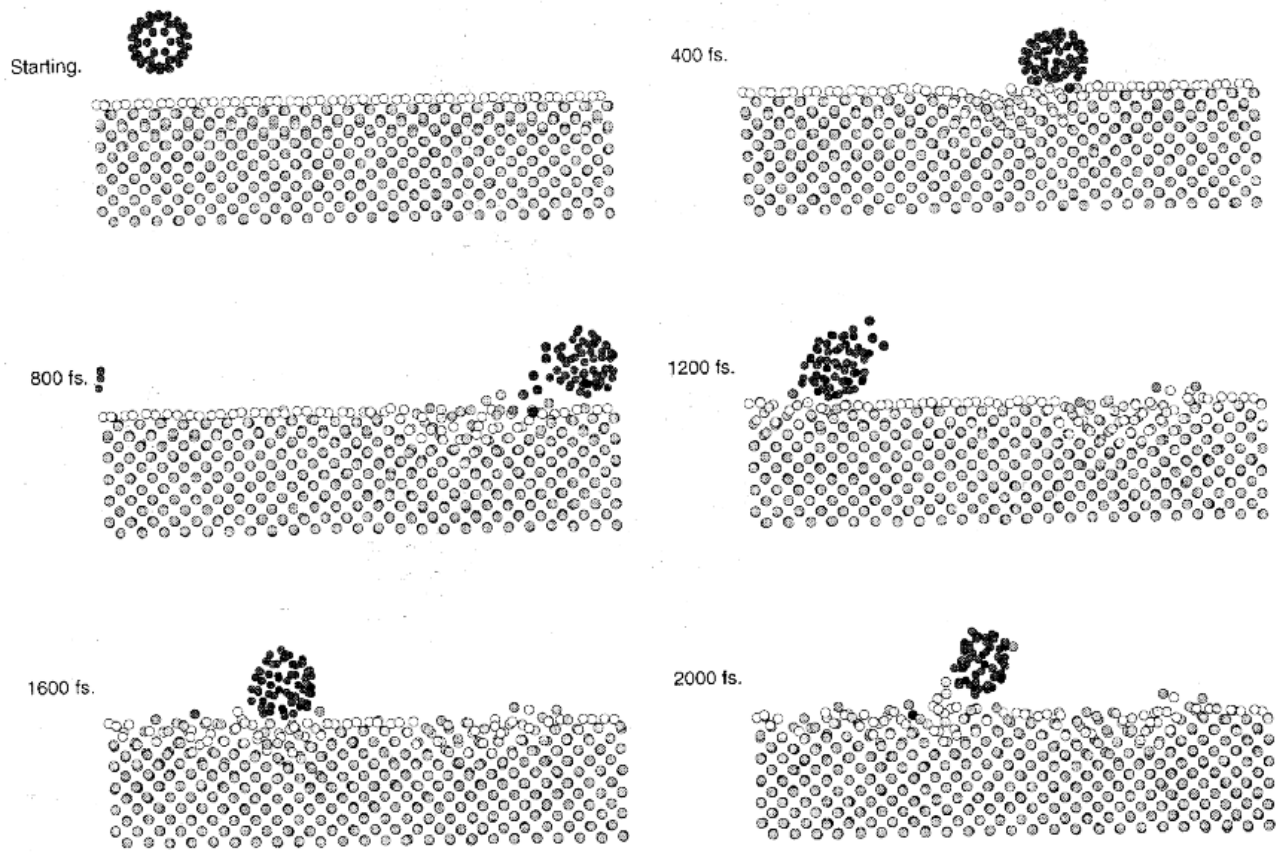
- Later Murty and Atwater [Phys. Rev. B 51 (1991) 4889] have made a Si-H version of the Brenner potential, and Beardmore and Smith [Phil. Mag. A 74 (1996) 1439] a combined C-Si-H-version.

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

Brenner potential

- Example application: Beardmore and Smith examined in their paper how a fullerene C_{60} hits an Si surface.
  - Case I: 250 eV C_{60} $\rightarrow$ virgin Si, incoming angle 80^o i.e. the fullerene forms bonds with the surface and rotates along it for a while (note the periodic boundary conditions).

Fig. 11

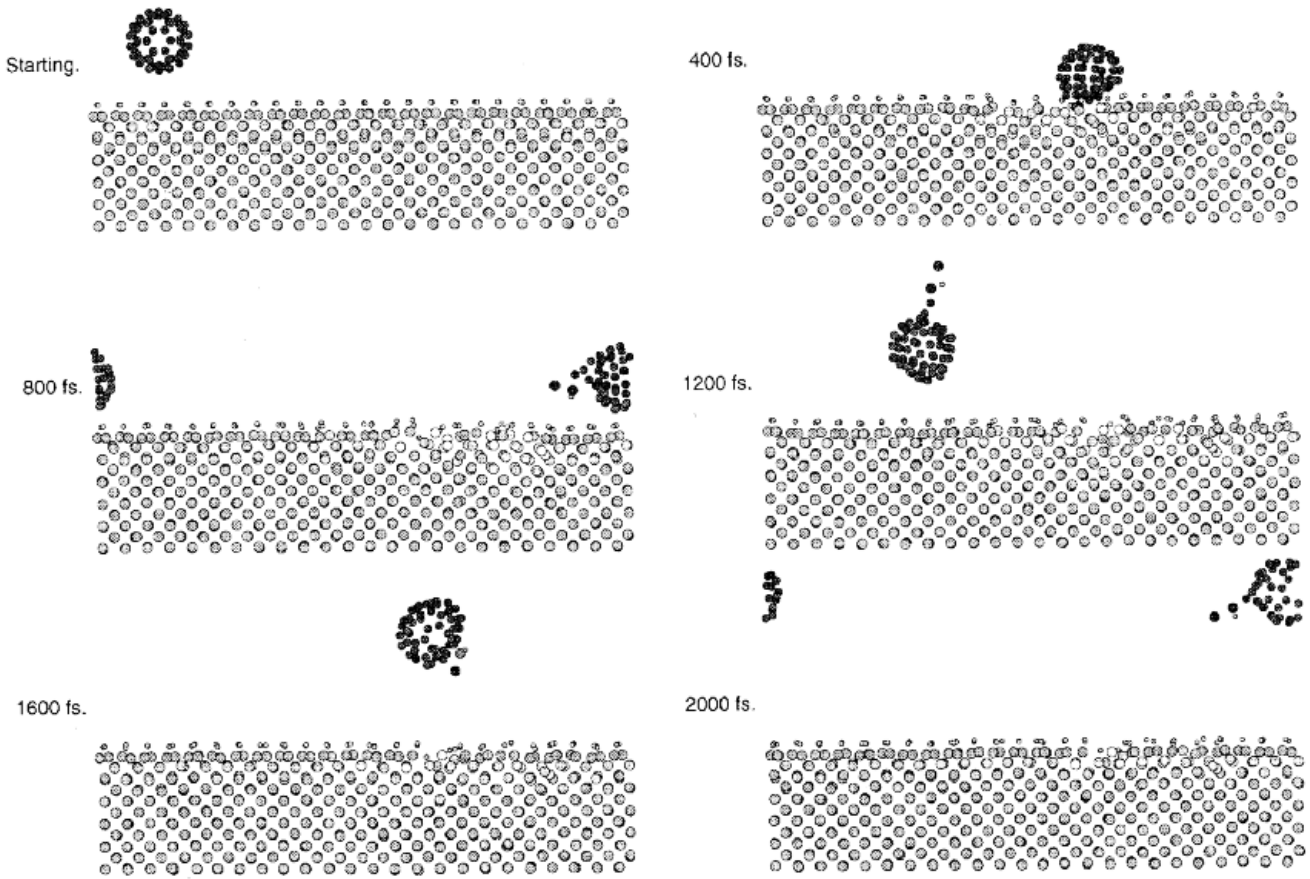


Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on bare Si{100} during a 2 ps simulation.

Brenner potential

- 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} $\rightarrow$ H-terminated Si, 80^{o}.

Fig. 12



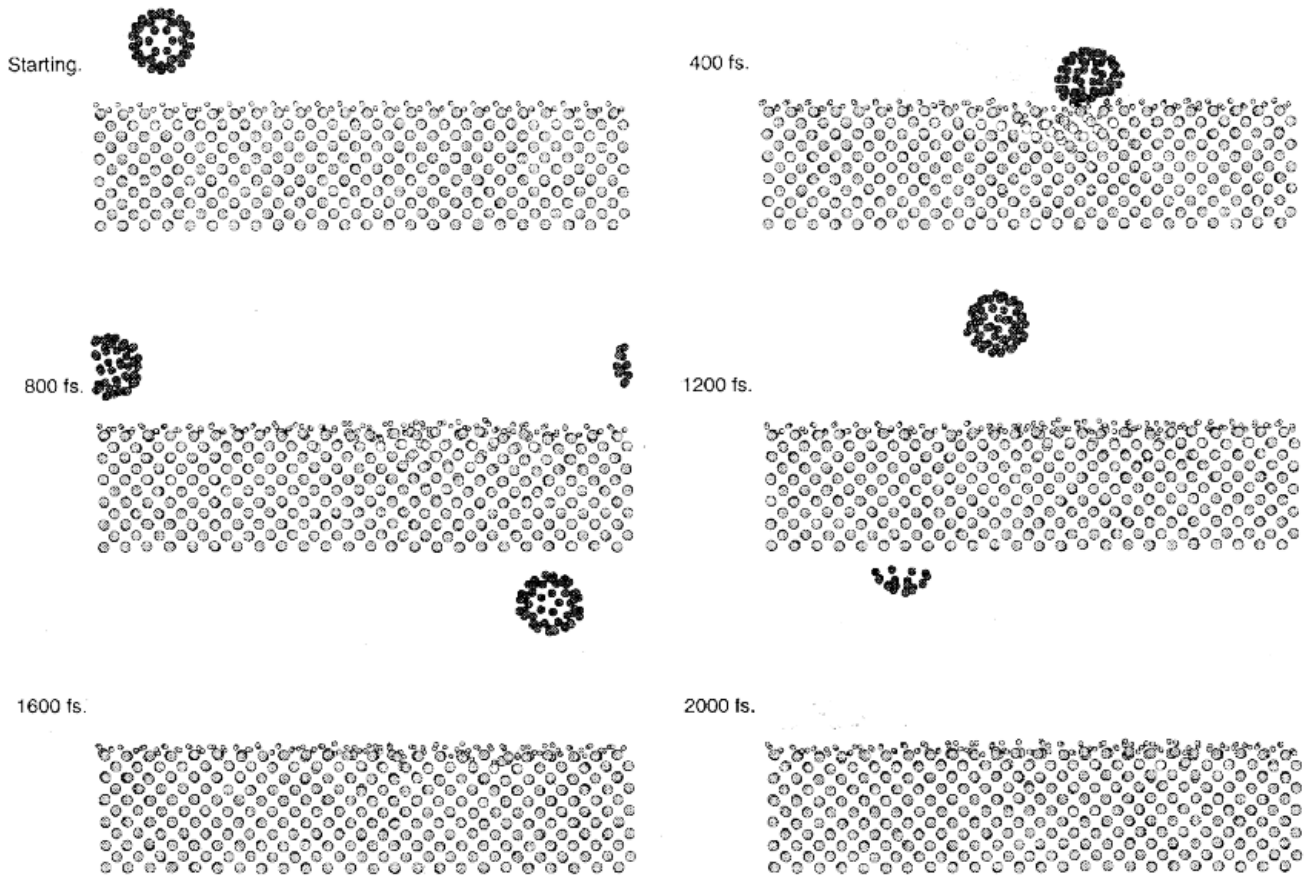
Atomic positions for a 250 eV C_{60} molecule incident at 80° to normal on 1 MLH Si{100} during a 2 ps simulation.

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.

Brenner potential

- Case III: 250 eV C_{60} → doubly H-terminated Si, 80°

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.

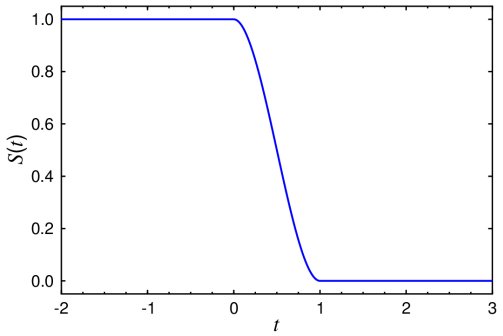
- So now the protective H layer is so thick that there are no C-Si bonds formed at all, and the fullerene bounces back intact.

Stuart potential

- Long range interactions are important also in graphite and in **multiwalled carbon nanotubes** (MWCNTs)

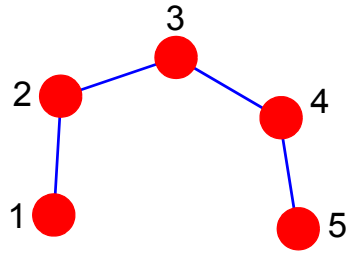
  - Stuart *et al.* [J. Chem. Phys. **112** (2000) 6472] used the Lennard-Jones potential to model the dispersion and intermolecular interaction:

$$V_{ij}^{\mathrm{LJ}}(r) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$



  - However, LJ should be switched off when molecules approach
    - Switching depends on interatomic distance [$S(t_r(r_{ij}))$], bond order [$S(t_b(b_{ij}))$], and connectivity [C_{ij}]:

Connectivity: no LJ interaction among 1,2,3,4, LJ possible between 1 and 5



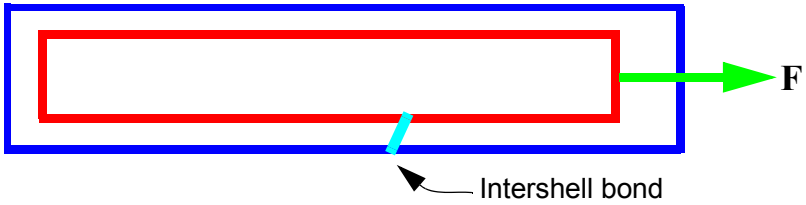
$$E_{\mathrm{b}} = \sum_i \sum_{j>i} [V_{\mathrm{R}}(r_{ij}) + \bar{B}_{ij} V_{\mathrm{A}}(r_{ij}) + E_{ij}^{\mathrm{LJ}}]$$

$$E_{ij}^{\mathrm{LJ}} = S(t_r(r_{ij}))S(t_b(b_{ij}))C_{ij}V_{ij}^{\mathrm{LJ}}(r_{ij}) + [1 - S(t_r(r_{ij}))]C_{ij}V_{ij}^{\mathrm{LJ}}(r_{ij})$$

- For C-C interaction $\sigma_{ij} = 3.40$ Å (graphite interlayer distance) $\Rightarrow$ large neighbor lists ($r_{\mathrm{cutoff}} \approx 11$ Å)!

Stuart potential

- Example: Load transfer between shells in MWCNTs [M. Huhtala *et al.*, *Phys. Rev. B* **70** (2004) 045404]



$$E = \varepsilon_i(\hat{n},\hat{m})\,\pi\tilde{d}(L-x) - A(\hat{n},\hat{m})\,\pi\tilde{d}(L-x)\cos\left[\frac{2\pi x}{\lambda(\hat{n},\hat{m})}\right].$$

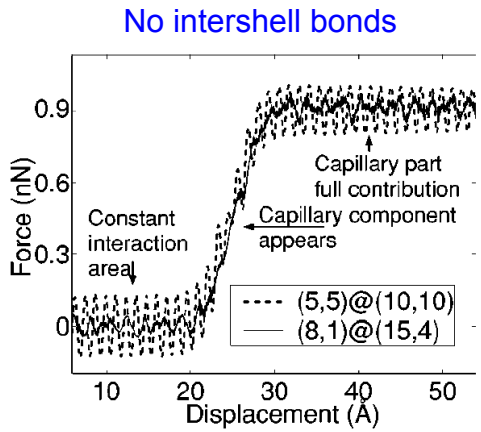


FIG. 1. Force vs displacement plotted for intact nanotube sliding. The displacement is measured from the point where the tube ends are even.

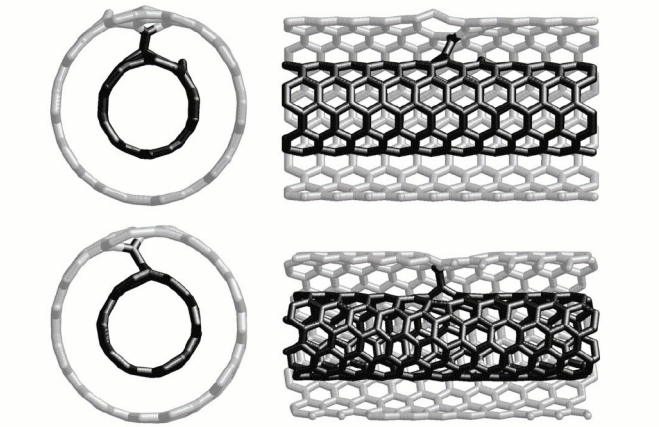


FIG. 2. Two views of a covalent intershell bond in tubes with different chiralities. Such bonds can be formed, for example, due to on-shell vacancies or intershell interstitials. The bonds shown are due to vacancy-pair reconstructions. As can be observed, the bond orientation is chirality dependent and there are several possible orientations in each particular tube.

Defect type	Force (nN)
Single vacancy	0.08—0.4
Two vacancies	6.4—7.8
Intershell interstitial	4.9—6.3
Intershell dimer	3.8—7.3