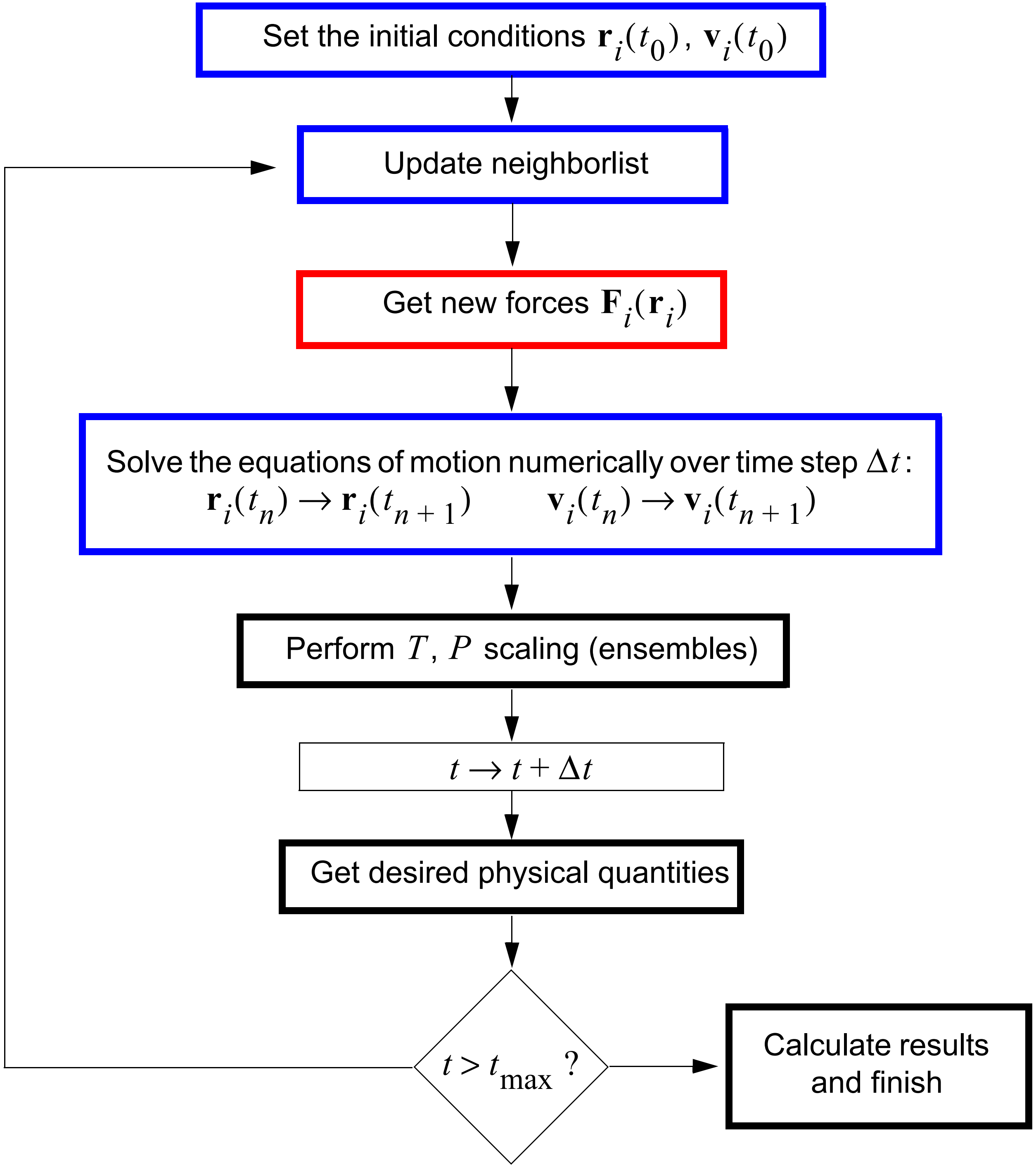


Set the initial conditions $\mathbf{r}_i(t_0)$, $\mathbf{v}_i(t_0)$

Update neighborlist

Get new forces $\mathbf{F}_i(\mathbf{r}_i)$

Solve the equations of motion numerically over time step Δt:

$$\mathbf{r}_i(t_n) \to \mathbf{r}_i(t_{n+1}) \qquad \mathbf{v}_i(t_n) \to \mathbf{v}_i(t_{n+1})$$

Perform T, P scaling (ensembles)

$t \to t + \Delta t$

Get desired physical quantities

$t > t_{\max}$?

Calculate results and finish

Calculating the forces between atoms

- The forces between atoms can be calculated in many different ways
  - This lecture:
    - classical potentials.
    - pair potentials, many-body potentials
  - Quantum mechanics
- A classical potential can be written in the form:

$$V = \sum_{i} V_1(\boldsymbol{r}_i) + \sum_{i,j} V_2(\boldsymbol{r}_i, \boldsymbol{r}_j) + \sum_{i,j,k} V_3(\boldsymbol{r}_i, \boldsymbol{r}_j, \boldsymbol{r}_k) + \dots$$

  - V is the total potential energy of an N atom system.
  - In principle all sums loop from 1 to N
  - V_1: **single particle potential**: external forces
  - V_2: **pair potential** which only depends on the distance between atoms r_{ij}
    - direct dependence on the *vectors* $\mathbf{r}_i$, $\mathbf{r}_j$ => dependence on the choice of the origin
  - V_3: **three-body potential** which may have an angular dependence
    - depends only on three variables, i.e. $V_3 = V_3(r_{ij}, r_{ik}, \theta_{ijk})$
  - **Four-body potentials**, even five-body terms: chemical and biological applications

Calculating the forces between atoms

- V_2 and V_3 enough to describe the basic mechanical and structural properties of most elements and simple compounds
- In order that things would not be too straightforward, in many cases a environment-dependence (i.e. implicit three-body term) is embedded into the two-body term V_2. We will give examples on these later.
- All terms which are not pure single particle or pair potentials are called **many-body** terms.

Calculating the forces between atoms

- Classification of empirical interatomic potentials [A. E. Carlsson, *Solid State Physics: Advances in Research and Applications*, **43** (1990) 1]
  - Pair Potential $V = \sum_{i,j} V_P(r_{ij})$
  - Pair Functional Potential $V = \sum_{i} V_{PF}(\rho_i)$, $\rho_i = \sum_{j \neq i} f(r_{ij})$

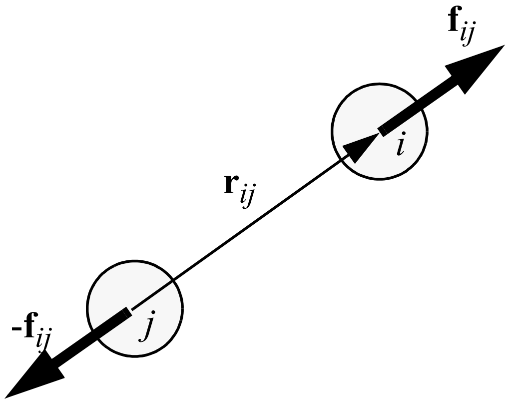
If $f(r) = ar$
$\Rightarrow$ back to pair potential

  - Cluster Potential $V = \sum_{i \neq j \neq k} V_{CP}(r_{ij}, r_{ik}, r_{jk})$

Only clusters of three atoms here

  - Cluster Functional Potential $V = \sum_{i} V_{CF}(\rho_i)$, $\rho_i = \sum_{\substack{j,k \\ i \neq j \neq k}} g(r_{ij}, r_{ik}, r_{jk})$
  - Real potentials often combinations of these: e.g. EAM for metals $V = \sum_{i} V_{PF}(\rho_i) + \sum_{i,j} V_P(r_{ij})$

Force calculation for pair potentials



- Pure pair potential $V(r_{ij})$. The force acting on atom i from atom j

$$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij}) = -\left[\frac{\partial V}{\partial x_{ij}}\hat{\mathbf{x}} + \frac{\partial V}{\partial y_{ij}}\hat{\mathbf{y}} + \frac{\partial V}{\partial z_{ij}}\hat{\mathbf{z}}\right],$$

($\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, $\hat{\mathbf{z}}$ unit vectors)

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j, \quad x_{ij} = x_i - x_j \text{ etc., } \frac{\partial V}{\partial x_{ij}} = \frac{\mathrm{d}V}{\mathrm{d}r}\frac{\partial r_{ij}}{\partial x_{ij}}, \quad \frac{\partial r_{ij}}{\partial x_{ij}} = \frac{x_{ij}}{r_{ij}}$$

$$\Rightarrow \quad \mathbf{f}_{ij} = -\left[\frac{\mathrm{d}V}{\mathrm{d}r}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$

- To be precise ∇ operates on the position $\mathbf{r}_i$ of atom i. (Makes a difference for many-body potentials.)
- Cut-off radius r_c: atom pairs with $r_{ij} > r_\mathrm{c}$ do not interact, $r_\mathrm{c} \approx \text{a few Å}$.

Force calculation for pair potentials

- In case the potential extends to infinity, an analytical correction can be made to the energy, and other quantities of interest:

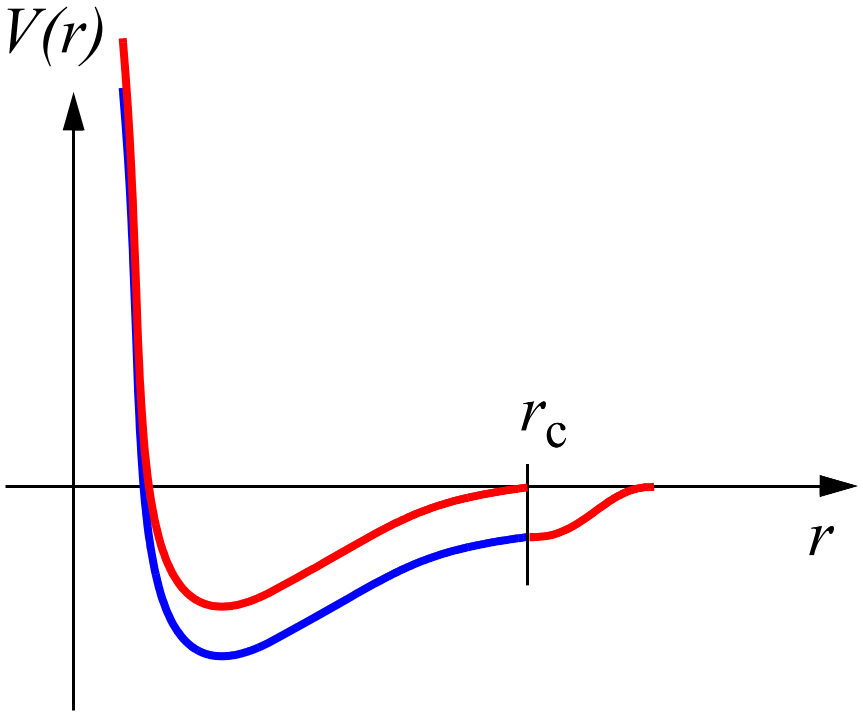
$$V_{\text{tot}} = V_2 + V_{\text{corr}} = E_c + 2\pi N\rho \int_{r_c}^{\infty} r^2 V(r) dr$$

where ρ is the atom density of the system.

  - This obviously assumes that when $r > r_c$ the atom density is constant everywhere, and thus does not work when for example a surface is present.

Force calculation for pair potentials

- Discontinuity at r_c $\Rightarrow$ jumps in energy
  - Solution: take the potential to zero in $[r_c, r_c + \Delta r]$
    - potential and the force are continuous (3^{rd} order polynomial) or
    - displace the potential, as the zero point of V is arbitrary but this changes the value of V_tot
  - Many modern potentials are in fact defined so that they have a well-defined cutoff r_c where V and at least the first derivative are $\equiv 0$.



Force calculation for pair potentials

- Example: cut-off of Lennard-Jones potential

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

- Shift and tilt the potential: $V(r)$ and $V'(r)$ continuous at r_{c}:

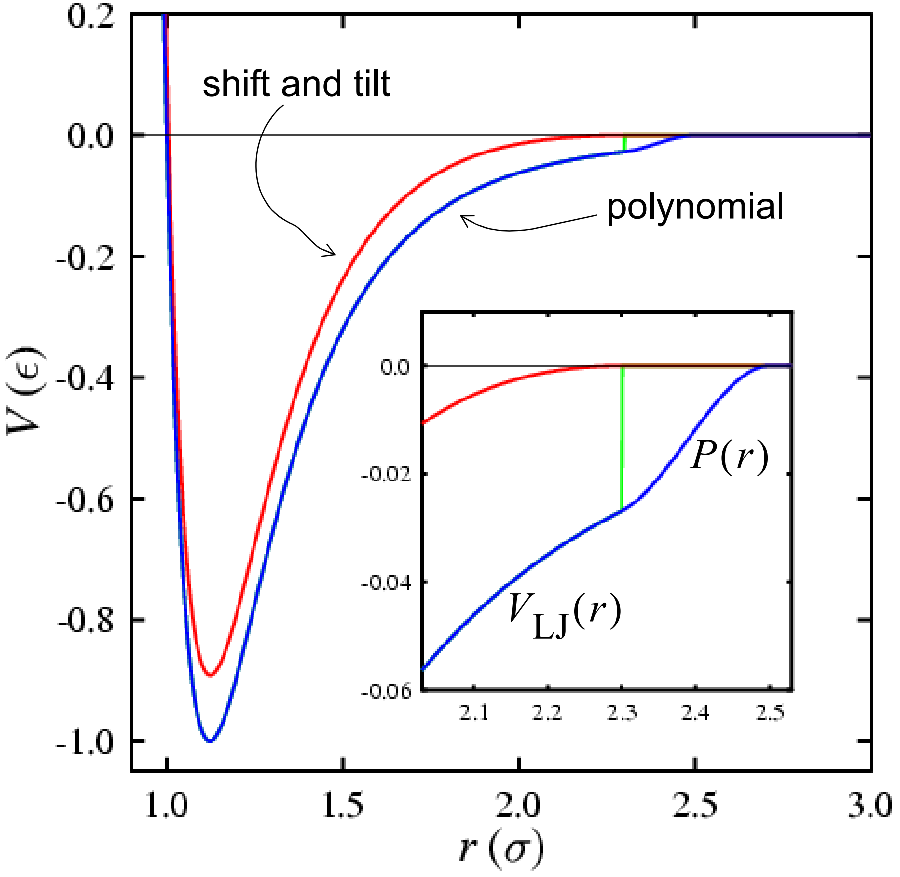
$$V(r) = V_{\mathrm{LJ}}(r) - (r - r_{\mathrm{c}})V'_{\mathrm{LJ}}(r_{\mathrm{c}}) - V_{\mathrm{LJ}}(r_{\mathrm{c}})$$

  - Problem: may change the potential at smaller r values

- Fit a polynomial $P(r) = ar^3 + br^2 + cr + d$ from $[r_{\mathrm{c}}, r_{\mathrm{c}} + \Delta r_{\mathrm{c}}]$:

$$\begin{cases} P(r_{\mathrm{c}}) = V_{\mathrm{LJ}}(r_{\mathrm{c}}) \\ P'(r_{\mathrm{c}}) = V'_{\mathrm{LJ}}(r_{\mathrm{c}}) \\ P(r_{\mathrm{c}} + \Delta r_{\mathrm{c}}) = 0 \\ P'(r_{\mathrm{c}} + \Delta r_{\mathrm{c}}) = 0 \end{cases}$$

$r_{\mathrm{c}} = 2.3\ \text{Å} \quad \Delta r_{\mathrm{c}} = 0.2\ \text{Å}$

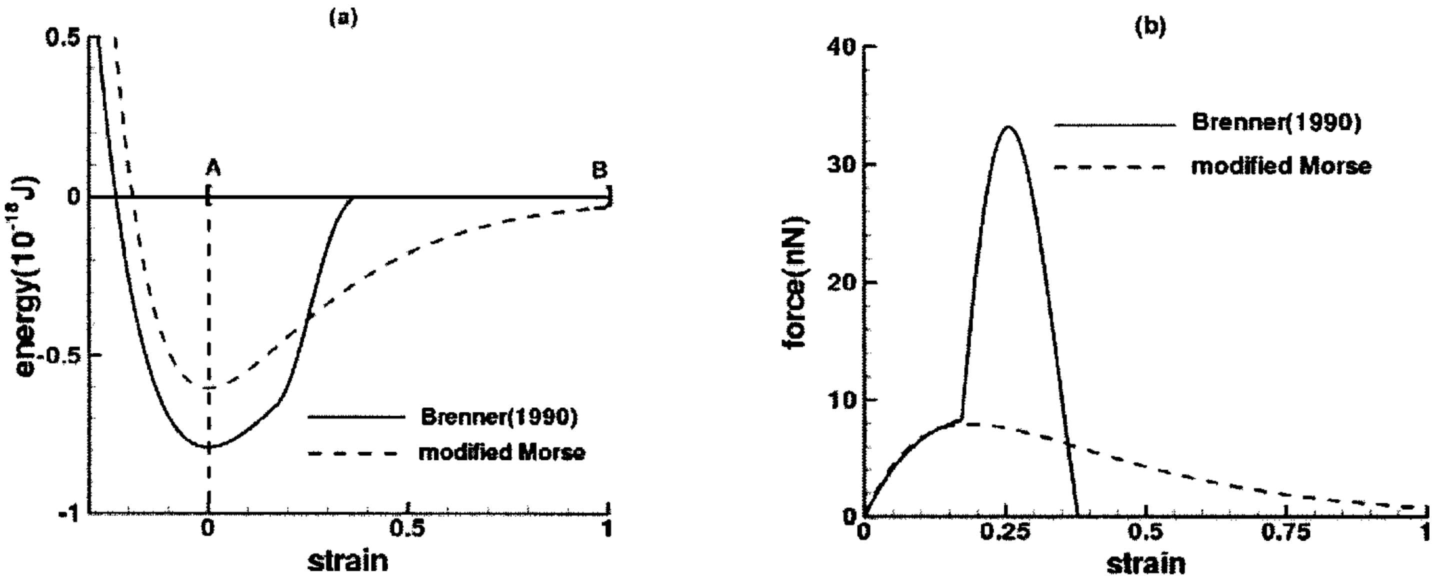


Force calculation for pair potentials

- Problem: high forces may result (see below)
- Brenner potential for carbon (Well, this is not a pair potential):

- Potential quickly to zero; doesn't look too bad

- However: huge forces; effect seen in fracture simulations
  (see also M. Sammalkorpi *et al.*, *Phys. Rev. B* **70** (2004) 245416.)



potential

force

T. Belytschko *et al.*, *Phys. Rev. B* **65** (2002) 235430.

Force calculation for pair potentials

- Force calculation without periodic boundaries or neighbour list:

```
do i=1,N
   do j=1,N
    if (i==j) cycle
    rijx = rx(j)-rx(i)
    rijy = ry(j)-ry(i)
    rijz = rz(j)-rz(i)
    rijsq = rijx**2+rijy**2+rijz**2
    rij = sqrt(rijsq)
    if (rij < rcut) then
      V = (Potential energy per atom)/2
      dVdr = ...derivative of potential energy with respect to its only argument r...
      a = -dVdr/m/2.0 ! Unit transformations may be needed. Note the factor 1/2!!
      ax(i) = ax(i)-rijx/rij*a ! The application on both
      ax(j) = ax(j)+rijx/rij*a ! i and j ensures that
      ay(i) = ay(i)-rijy/rij*a ! Newton’s third law is
      ay(j) = ay(j)+rijy/rij*a ! fulfilled
      az(i) = az(i)-rijz/rij*a
      az(j) = az(j)+rijz/rij*a
    endif
  enddo
enddo
```

Force calculation for pair potentials

- Use of Verlet neighbour list (cf. lecture 3):

```
startofineighbourlist=1
do i=1,N
  nneighboursi=neighbourlist(startofineighbourlist)
  do jj=1,nneighboursi
    j=neighbourlist(startofineighbourlist+jj)
    rijx = rx(j)-rx(i)
    rijy = ry(j)-ry(i)
    rijz = rz(j)-rz(i)
    rijsq = rijx**2+rijy**2+rijz**2
    rij = sqrt(rijsq)
    if (rij < rcut) then
      V = (Potential energy per atom)/2
      dVdr = ...derivative of potential energy with respect to its only argument r...
      a = -dVdr/m/2.0 ! Plus unit transformations ! Note the factor 1/2!!
      ax(i) = ax(i)-rijx/rij*a
      ax(j) = ax(j)+rijx/rij*a
      ay(i) = ay(i)-rijy/rij*a
      ay(j) = ay(j)+rijy/rij*a
      az(i) = az(i)-rijz/rij*a
      az(j) = az(j)+rijz/rij*a
    endif
  enddo
  startofineighbourlist=startofineighbourlist+nneighboursi+1
enddo
```

Force calculation for pair potentials

- Note that in the sum above every interaction is counted twice:

```
do i=1,N
   do j=1,N
        if (i==j) cycle
        ...
```

  - That is, e.g. interaction 1-3 is counted both as 1-3 and 3-1. Hence the factor 1/2 in front of the potential energy summation and forces (this actually depends on the exact definition of the potentials, some already have a factor of 1/2 in front).

- A straightforward solution:

```
do i=1,N-1
   do j=i+1,N
        ...
```

  (either in constructing the neighbour list or forces) reduces the calculation time to one half.

  - *For some many-body potentials this does not work.*

- $V(r)$ often is defined to give the total energy for a *pair* of atoms. When one wants the potential energy per *atom* one thus may have to include one more factor of 1/2. But this additional factor is not needed in the force calculation since the force always affects both atoms (Newton’s III law).

- Note that the sign conventions in defining r_{ij} in the literature may vary.

Force calculation for pair potentials

- One practical way of checking that you have correctly derived the forces from the potential energy and that all signs and factors of ½ are OK in you potential implementation:
  1. Calculate E_{pot} at 0 K and compare with an analytical prediction for some simple system, e.g. a dimer or perfect lattice.
  2. Simulate a two-atom system starting from a very small distance, so that E_{pot} is very large, much larger than the equilibrium energy per atom (say 10000 eV). When you run the simulation with a very small time step the atoms should explode outwards from each other so that the final E_{kin}/atom is the same as the original E_{pot}/atom. If you are uncertain what a 'very small' time step is, keep decreasing it until the answer doesn't change.

  3. Another good test: numerical derivation of potential energy:

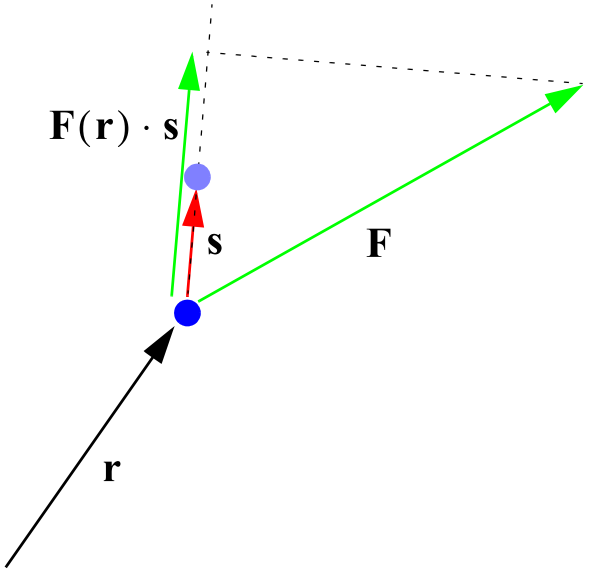
Move one atom in direction $\hat{\mathbf{s}}$ amount Δs.

Directional derivative of the potential (assume $|\hat{\mathbf{s}}| = 1$):

$$\frac{\partial V(\mathbf{r})}{\partial \hat{\mathbf{s}}} = \lim_{h \to 0} \frac{V(\mathbf{r} + h\hat{\mathbf{s}}) - V(\mathbf{r})}{h} = \nabla V(\mathbf{r}) \cdot \hat{\mathbf{s}} = -\mathbf{F}(\mathbf{r}) \cdot \hat{\mathbf{s}}$$

Computed from potential energy as $\Delta V / \Delta s$

Computed from forces as $F_x s_x + F_y s_y + F_z s_z$



Force calculation for a three-body potential

- For a pure pair potential for an interaction between atoms i and j $V_{ij} = V_{ji}$ because $V(r_{ij}) = V(r_{ji})$ and hence also $\nabla_i V_{ij} = \nabla_i V_{ji}$ as described above. This symmetry simplifies the force calculation.

- For a three-body potential things get trickier because V_{ij} may not = V_{ji}. To get the force $\mathbf{F}_i$ acting on an atom i one instead has to calculate

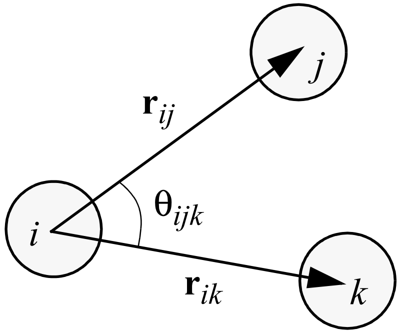
$$\boldsymbol{F}_i = -\nabla_i\left[\sum_j (V_{ij} + V_{ji}) + \sum_j\sum_k V_{jki}\right] = -\left[\sum_j (\nabla_i V_{ij} + \nabla_i V_{ji}) + \sum_j\sum_k \nabla_i V_{jki}\right]$$

- Many practical three-body potentials have been written such that

$$V_3(r_{ij}, r_{ik}, \theta_{ijk}) = V_3(r_{ij}, r_{ik}, \cos\theta_{ijk})$$

i.e. all angular information is in a cosine term.

Force calculation for a three-body potential



- In this case one can utilize the following equalities:

$$\cos\theta_{ijk} = \frac{\boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{ik}}{r_{ij} r_{ik}}$$

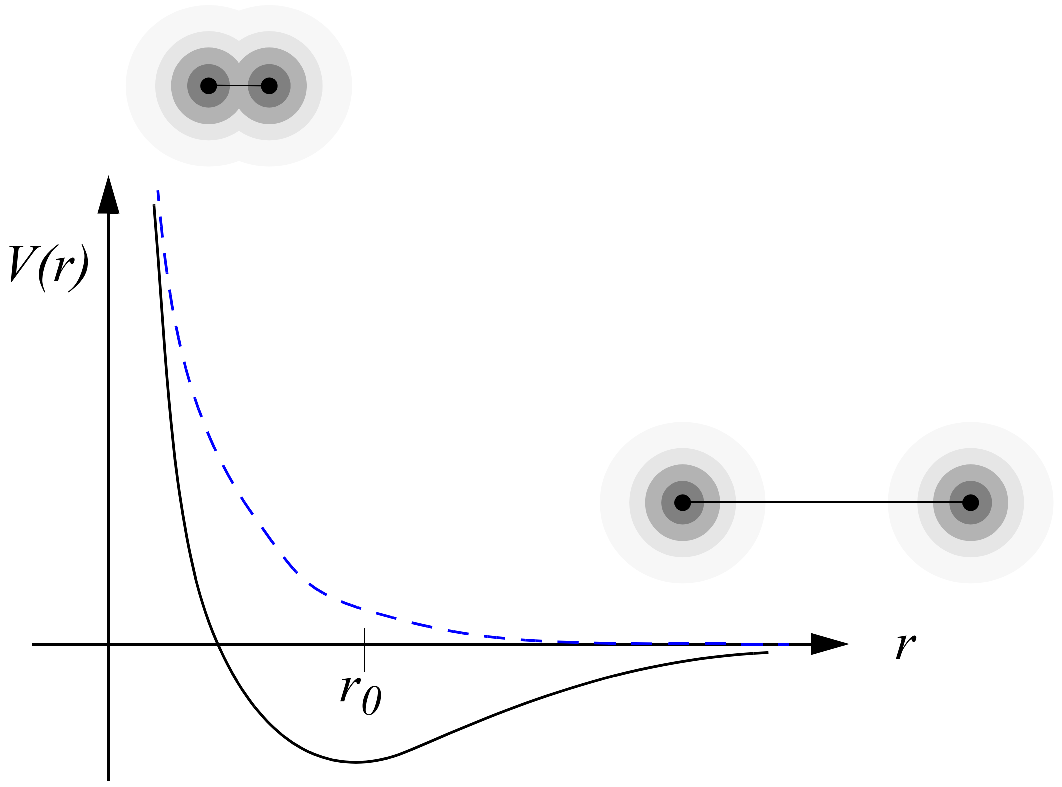
$$\nabla_i \cos\theta_{ijk} = \nabla_i \left(\frac{\boldsymbol{r}_{ij} \cdot \boldsymbol{r}_{ik}}{r_{ij} r_{ik}} \right) = \ldots\ldots = \left[\frac{\cos\theta_{ijk}}{r_{ij}^2} - \frac{1}{r_{ij} r_{ik}} \right] \boldsymbol{r}_{ij} + \left[\frac{\cos\theta_{ijk}}{r_{ik}^2} - \frac{1}{r_{ij} r_{ik}} \right] \boldsymbol{r}_{ik}$$

that is, no need to evaluate cos function.

- In many-body potentials there are often symmetries which can be used to reduce the number of operations needed in the force calculation even more.

The physical/chemical origin of interactions

- Qualitatively a two-atom interaction looks like the following:



- The minimum, i.e. equilibrium distance, is r_0.
- At small separations there is a strong repulsion. Just below r_0 this derives primarily from the Pauli rule preventing electrons being in states with the same quantum numbers, and from the electron-electron repulsion, whereas when the nuclei are very close to each other, the Coulombic repulsion between the nuclei dominates completely.
- At larger distances there may be an attraction, which can have different reasons: van der Waals attraction, Coulomb attraction, a covalent bond, (due to pairing of valence electrons) or metallic bonding
- Potential may also be purely repulsive

- A few examples (1 bohr = 0.53 Å)

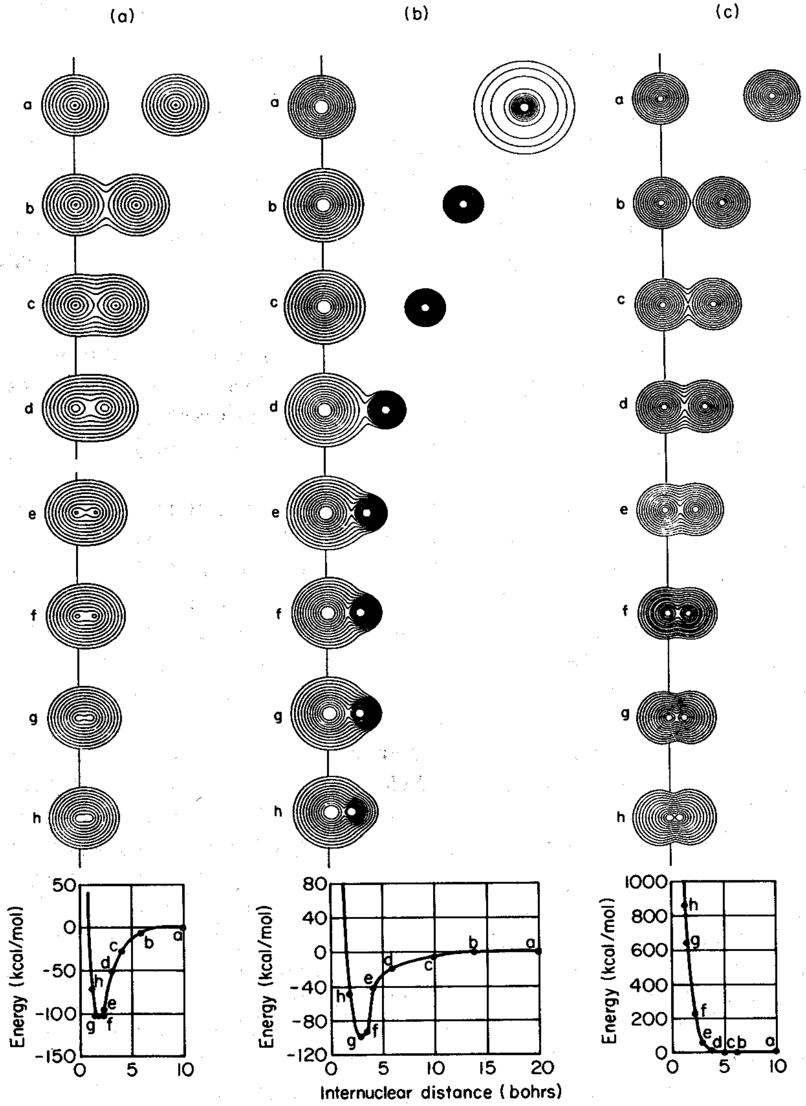
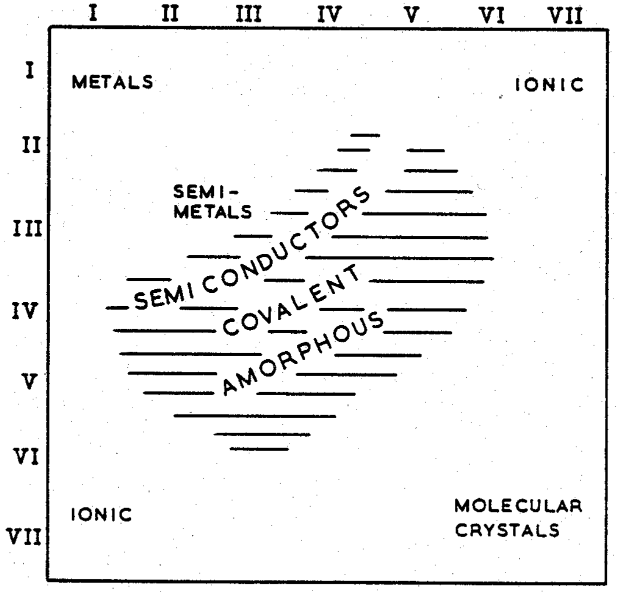
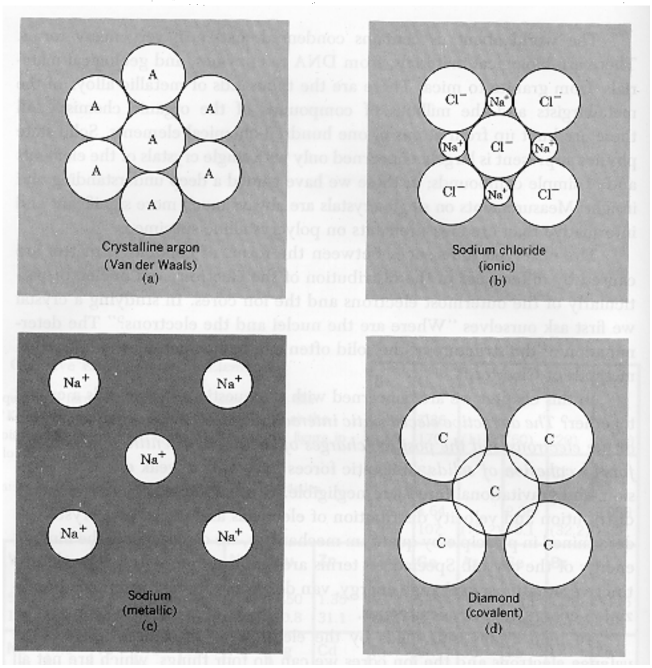
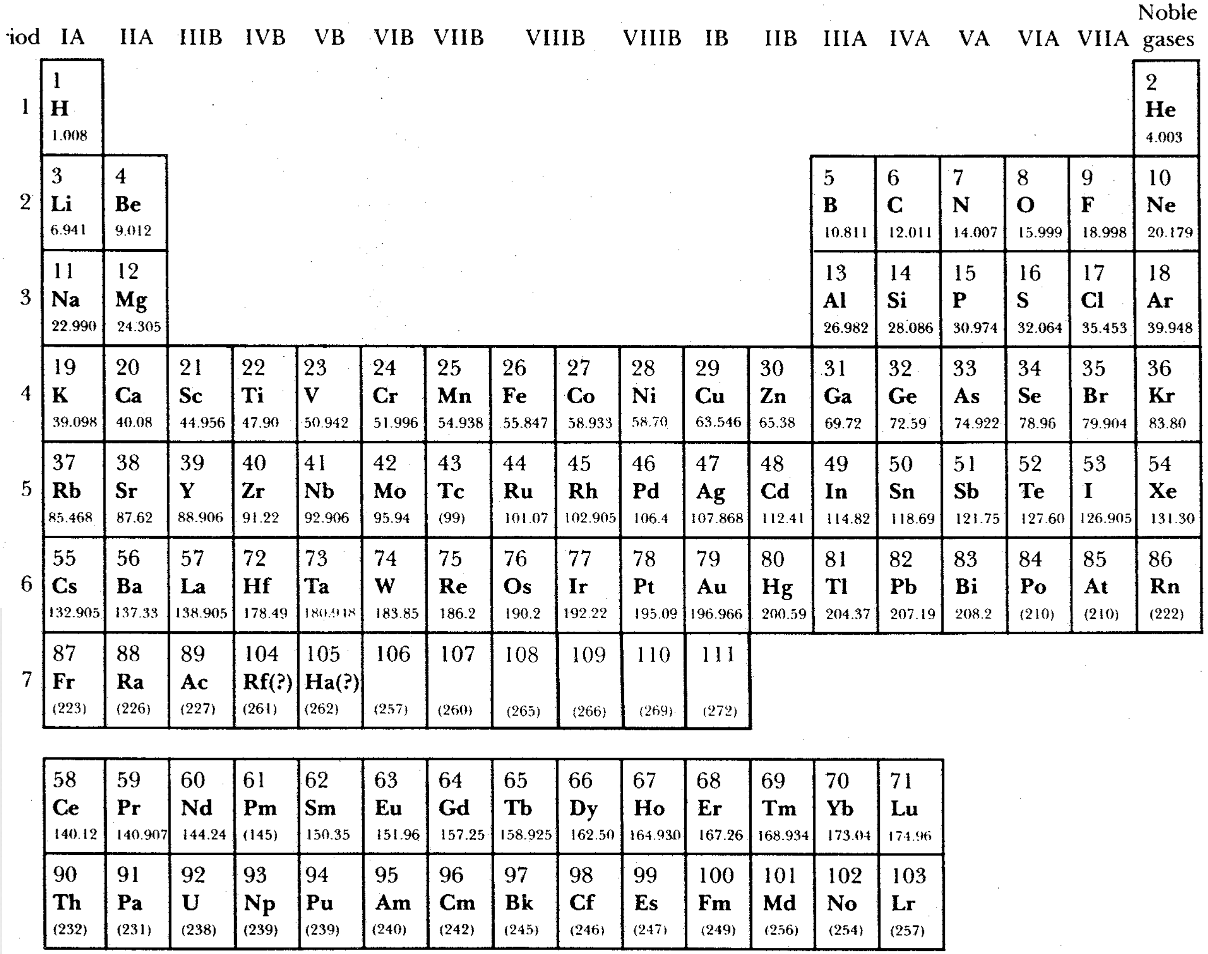


Fig. 1.2. Electron density distribution contours generated by computer solution of the Schrödinger equation for interactions in three atomic systems (a) H_2, (b) LiF, and (c) He_2. At the bottom is plotted the potential energy of interaction at the different stages of the process a–h. The separation is in atomic units. (After Wahl [3].)

- Overview of bonding expected in different cases, and illustration of electron distributions [Kittel, Introduction to Solid State physics]



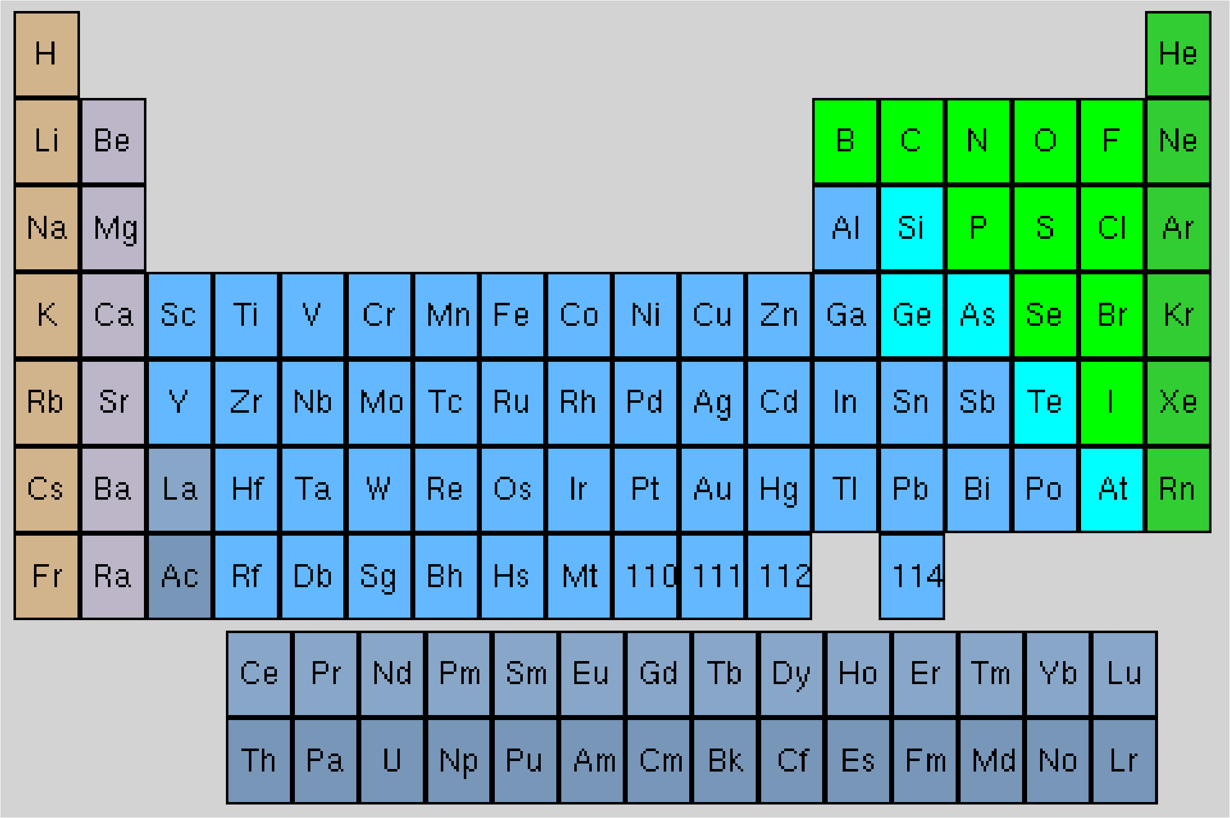




iod	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.064	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.08	21 **Sc** 44.956	22 **Ti** 47.90	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.70	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.922	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.80
5	37 **Rb** 85.468	38 **Sr** 87.62	39 **Y** 88.906	40 **Zr** 91.22	41 **Nb** 92.906	42 **Mo** 95.94	43 **Tc** (99)	44 **Ru** 101.07	45 **Rh** 102.905	46 **Pd** 106.4	47 **Ag** 107.868	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.69	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.905	54 **Xe** 131.30
6	55 **Cs** 132.905	56 **Ba** 137.33	57 **La** 138.905	72 **Hf** 178.49	73 **Ta** 180.918	74 **W** 183.85	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.966	80 **Hg** 200.59	81 **Tl** 204.37	82 **Pb** 207.19	83 **Bi** 208.2	84 **Po** (210)	85 **At** (210)	86 **Rn** (222)
7	87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf(?)** (261)	105 **Ha(?)** (262)	106 (257)	107 (260)	108 (265)	109 (266)	110 (269)	111 (272)							

58 **Ce** 140.12	59 **Pr** 140.907	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.35	63 **Eu** 151.96	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.50	67 **Ho** 164.930	68 **Er** 167.26	69 **Tm** 168.934	70 **Yb** 173.04	71 **Lu** 174.96
90 **Th** (232)	91 **Pa** (231)	92 **U** (238)	93 **Np** (239)	94 **Pu** (239)	95 **Am** (240)	96 **Cm** (242)	97 **Bk** (245)	98 **Cf** (246)	99 **Es** (247)	100 **Fm** (249)	101 **Md** (256)	102 **No** (254)	103 **Lr** (257)

- So for the pure elements we get the familiar division:



Idealized potentials for theoretical and qualitative studies

- Hard sphere: $V^{\mathrm{HS}}(r) = \begin{cases} \infty, & r < \sigma \\ 0, & r \ge \sigma \end{cases}$

- First MD simulations were carried out with this potential.

- The equations of motion reduce to calculating where the next collision occurs: true billiard ball physics
  - Applications in packing problems

- Square well:

$$V^{\mathrm{SW}}(r) = \begin{cases} \infty, & r < \sigma_1 \\ -\varepsilon, & \sigma_1 \le r < \sigma_2 \\ 0, & r \ge \sigma_2 \end{cases}$$

- soft sphere: $V^{\mathrm{SS}}(r) = \varepsilon\left[\frac{\sigma}{r}\right]^{\nu}$

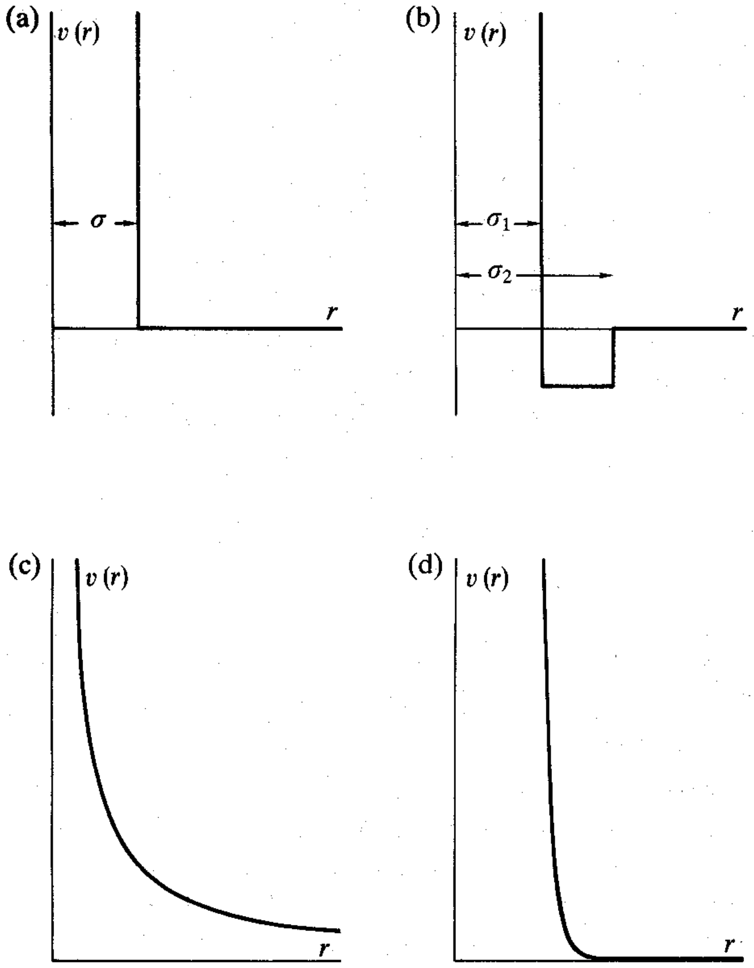


Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential; (b) The square-well potential; (c) The soft-sphere potential with repulsion parameter $\nu = 1$; (d) The soft-sphere potential with repulsion parameter $\nu = 12$.

Source: Allen-Tildesley

“Realistic” pair potentials

- Lennard-Jones (LJ)

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

  - The attractive $1/r^6$ - term can be derived from the dipole-dipole interaction, or as the interactions between two oscillators (QM) [Kittel, *Introduction to Solid State Physics*, 7th edition, p. 62]. It is also known as the Van der Waals or London interaction.
  - The repulsive term $1/r^{12}$ chosen for convenience.
  - Also other exponents used; notation for any two exponents A and B is LJ (A-B) potential.
  - ε and σ are usually chosen by fitting into experimental data. σ gives the equilibrium distance ε the cohesive energy.
  - A few Lennard-Jones-parameters for gases [Ashcroft-Mermin s. 398]:

	Ne	Ar	Kr	Xe
ε (eV)	0.0031	0.0104	0.0140	0.0200
σ (Å)	2.74	3.40	3.65	3.98

  - Very weak interaction: e.g. $V_{\text{min}} = -3.1\ \text{meV}$ for Ne.
  - LJ (12-6) potentials have proven to be good for noble gases (filled electron shells $\Rightarrow$ almost always neutral) close to equilibrium. But they are obviously terrible for very small r ($r \le 1$ Å) since the true interaction is about e^{-r}/r and not $1/r^{12}$.

“Realistic” pair potentials

- LJ potentials have been, and are used a lot, for instance in molecular modelling, in many cases even in systems where there is no physical motivation to using the LJ functional form. But if the fit is good for some purpose, using it may still be justified as long as the limitations are kept in mind.

- Reduced units

  - If a potential only has a couple of parameters, evaluating it can be really efficient in reduced units

  - Also, in reduced units the results are always the same, so the results can be transferred to different systems with straightforward scaling.

  - For instance for the Lennard-Jones-potential:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$ [or any $V(r) = \varepsilon f(r/\sigma)$)]

$\Rightarrow$ Natural length unit = σ
natural energy unit = ε

$$\Rightarrow V^{*}(x) = 4[x^{-12} - x^{-6}]$$

“Realistic” pair potentials

- other units:

$$t^* = t/[(m\sigma^2)/\varepsilon]^{1/2}$$

$$\rho^* = \rho\sigma^3$$

$$T^* = k_B T/\varepsilon$$

$$P^* = P\sigma^3/\varepsilon$$

$$\mathbf{f}^* = \mathbf{f}\sigma/\varepsilon$$

$$v^* = v/[\varepsilon/m]^{1/2}$$

- Reduced units were very popular when one had to save CPU time in every single multiplication, and when potentials were still as simple as LJ.

“Realistic” pair potentials

- Morse potential

  - Simple metals (sp-metals, e.g. Na, Mg, Al; and metals with the fcc- or hcp-structure), are at least to some extent describable with a pair potential

  - A popular choice: the Morse potential [P. M. Morse, *Phys. Rev.* **34** (1930) 57.]:

$$V(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$$

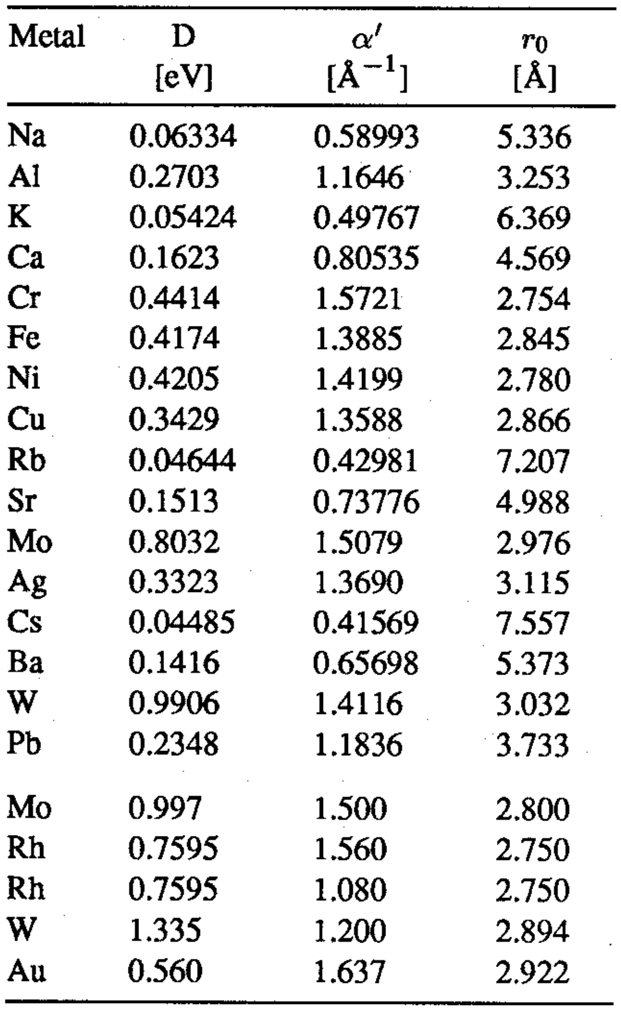
  - Designed originally to describe vibrations in molecules.
    - The Schrödinger equation happens to have an analytical solution for this functional form.

  - Efficient to evaluate, in the form above only one exponential function needs to be evaluated.

  - Decays faster at large r than Lennard-Jones: less problems with cut-off.

  - A fit for many metals [Girifalco and Weizer, *Phys. Rev.* **114** (1959) 687.]

  - Works decently for being a pair potential.

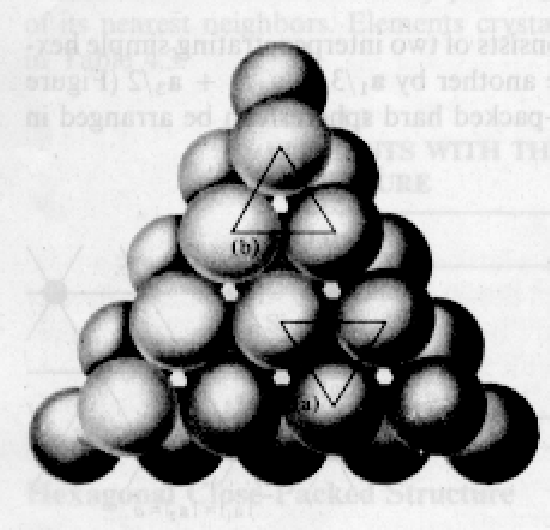


Metal	D [eV]	α' [Å^{-1}]	r_0 [Å]
Na	0.06334	0.58993	5.336
Al	0.2703	1.1646	3.253
K	0.05424	0.49767	6.369
Ca	0.1623	0.80535	4.569
Cr	0.4414	1.5721	2.754
Fe	0.4174	1.3885	2.845
Ni	0.4205	1.4199	2.780
Cu	0.3429	1.3588	2.866
Rb	0.04644	0.42981	7.207
Sr	0.1513	0.73776	4.988
Mo	0.8032	1.5079	2.976
Ag	0.3323	1.3690	3.115
Cs	0.04485	0.41569	7.557
Ba	0.1416	0.65698	5.373
W	0.9906	1.4116	3.032
Pb	0.2348	1.1836	3.733
Mo	0.997	1.500	2.800
Rh	0.7595	1.560	2.750
Rh	0.7595	1.080	2.750
W	1.335	1.200	2.894
Au	0.560	1.637	2.922

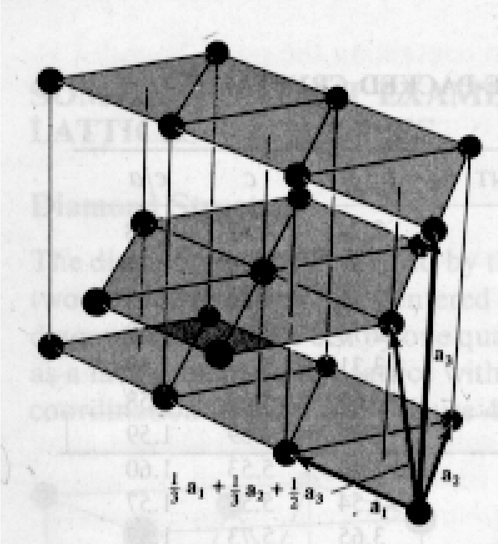
Girifalco and Weizer, *Phys. Rev.* **114** (1959) 687.

“Realistic” pair potentials

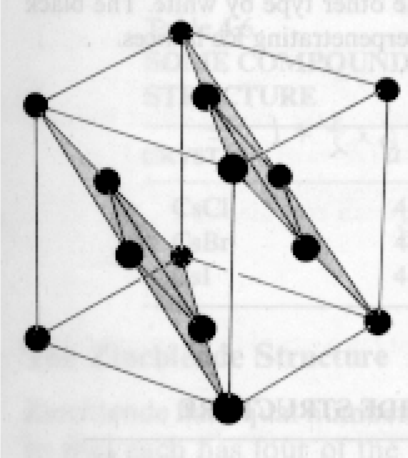
- An ordinary pair potential has a close-packed structure as the ground state. (usually either “face-centered cubic”, FCC or “hexagonal close packed”, HCP).



HCP

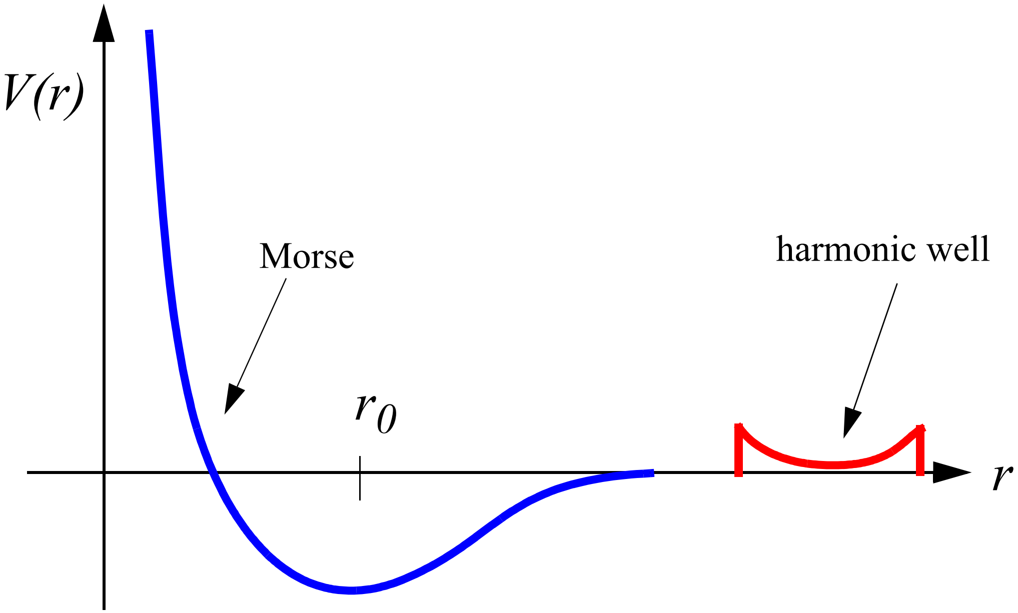


FCC



“Realistic” pair potentials

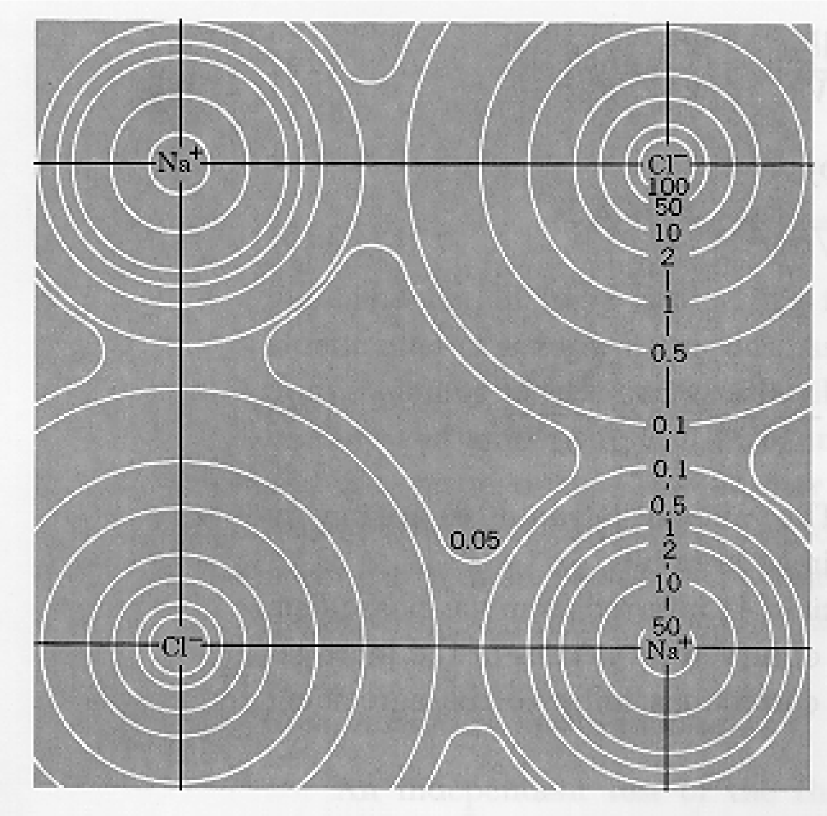
- A pair potential can thus not describe well elements with other structures than FCC or HCP. But this doesn’t mean people haven’t tried:
  - Diamond lattice: open structure, four nearest neighbours, very far from close packed.
  - Still, it is actually possible to make diamond stable locally with a pair potential, but this will become rather pathological (Mazzone potential for Si, [*Phys. Stat. Sol (b)* **165** (1991) 395.]):



  - Does actually work close to perfect lattice.
  - But what happens when atoms leave the harmonic well due to e.g. a high temperature?
    - System will collapse to close-packed structure => applicability of potential extremely limited
  - Unfortunately this is not uncommon regarding interatomic potentials: one has to be very critical of any new potential! Even well-respected physicists have presented potentials which have some very pathological features...

“Realistic” pair potentials

- Ionic compounds
  - Different ions, between which the electron density is very small. The ions have filled electron shells, and are thus unlikely to change their electron configuration
  - An extreme examples: NaCl:
  - A pair potential approximation works quite well, and potentials abound in the literature, as there is much experimental data available for the alkali halides which can be used in potential fitting.
  - Potentials typically contain a short-range (SR) term and the Coulomb interaction:



$$V(r_{ij}) = V_{\mathrm{SR}}(r_{ij}) + \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 r_{ij}};\ z_i \text{ = ion charges}$$

- V_{SR}: repulsive force between electrons packed closely together and an attractive van der Waals (vdW) interaction

“Realistic” pair potentials

- Most common forms for the short range potential:

Buckingham: $V_{\mathrm{SR}}(r) = Ae^{-r/\rho} - \frac{C}{r^6}$

Born-Huggins-Mayer: $V_{\mathrm{SR}}(r) = Ae^{-B(r-\sigma)} - \frac{C}{r^6} - \frac{D}{r^8}$

Morse: $V_{\mathrm{SR}}(r) = De^{-2\alpha(r-r_0)} - 2De^{-\alpha(r-r_0)}$

- $1/r^6$-term comes from the dipole-dipole interaction (again)

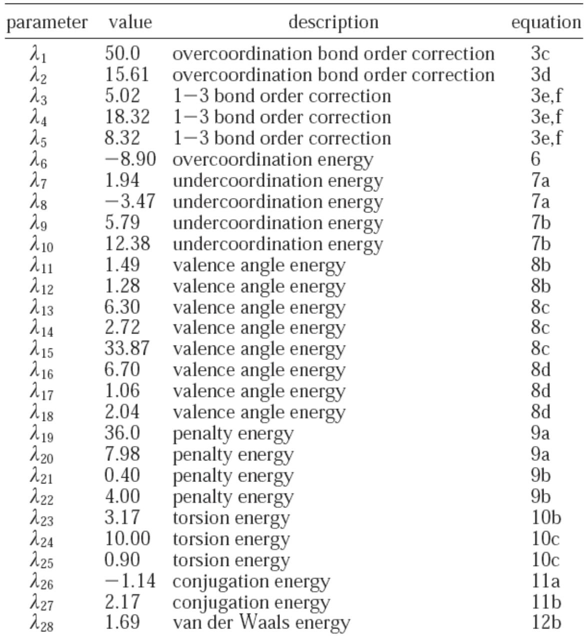
- The repulsion is usually significant only for nearest neighbours, and the vdW interaction for next-nearest neighbours. Frequently for instance in oxides the only interaction assumed between cations is their Coulombic repulsion.

Fitting of potential parameters

- In almost all classical potentials there is a number of free parameters, e.g. in Lennard-Jones 2 (ε and σ), Morse 3 (D, α, r_0) etc.
  - An extreme example: the ReaxFF model for hydrocarbons:
    A.C.T. van Duin *et al.*, *J. Chem. Phys. A* **105** (2001) 9396.

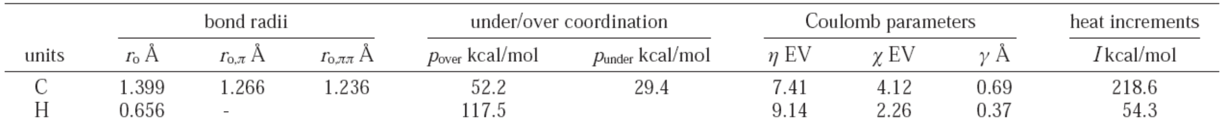
$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

TABLE 1: General Parameters



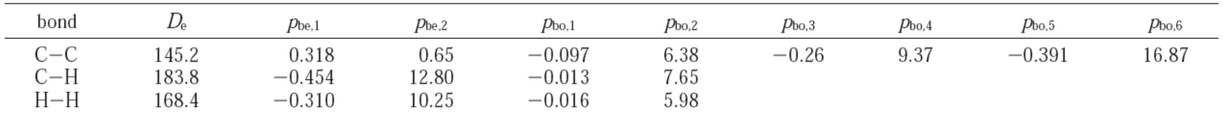
parameter	value	description	equation
λ_1	50.0	overcoordination bond order correction	3c
λ_2	15.61	overcoordination bond order correction	3d
λ_3	5.02	1−3 bond order correction	3e,f
λ_4	18.32	1−3 bond order correction	3e,f
λ_5	8.32	1−3 bond order correction	3e,f
λ_6	−8.90	overcoordination energy	6
λ_7	1.94	undercoordination energy	7a
λ_8	−3.47	undercoordination energy	7a
λ_9	5.79	undercoordination energy	7b
λ_{10}	12.38	undercoordination energy	7b
λ_{11}	1.49	valence angle energy	8b
λ_{12}	1.28	valence angle energy	8b
λ_{13}	6.30	valence angle energy	8c
λ_{14}	2.72	valence angle energy	8c
λ_{15}	33.87	valence angle energy	8c
λ_{16}	6.70	valence angle energy	8d
λ_{17}	1.06	valence angle energy	8d
λ_{18}	2.04	valence angle energy	8d
λ_{19}	36.0	penalty energy	9a
λ_{20}	7.98	penalty energy	9a
λ_{21}	0.40	penalty energy	9b
λ_{22}	4.00	penalty energy	9b
λ_{23}	3.17	torsion energy	10b
λ_{24}	10.00	torsion energy	10c
λ_{25}	0.90	torsion energy	10c
λ_{26}	−1.14	conjugation energy	11a
λ_{27}	2.17	conjugation energy	11b
λ_{28}	1.69	van der Waals energy	12b

TABLE 2: Atom Parameters As Used in Equations 2, 6, 7, 12, 13, and 14[a]



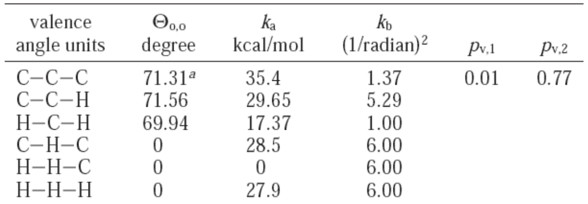
	bond radii			under/over coordination		Coulomb parameters			heat increments
units	r_o Å	$r_{o,\pi}$ Å	$r_{o,\pi\pi}$ Å	p_{over} kcal/mol	p_{under} kcal/mol	η EV	χ EV	γ Å	I kcal/mol
C	1.399	1.266	1.236	52.2	29.4	7.41	4.12	0.69	218.6
H	0.656	-		117.5		9.14	2.26	0.37	54.3

TABLE 4: Bond Parameters (D_e in kcal/mol) As Used in Equations 2 and 3



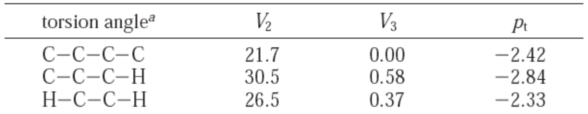
bond	D_e	$p_{\text{be},1}$	$p_{\text{be},2}$	$p_{\text{bo},1}$	$p_{\text{bo},2}$	$p_{\text{bo},3}$	$p_{\text{bo},4}$	$p_{\text{bo},5}$	$p_{\text{bo},6}$
C−C	145.2	0.318	0.65	−0.097	6.38	−0.26	9.37	−0.391	16.87
C−H	183.8	−0.454	12.80	−0.013	7.65				
H−H	168.4	−0.310	10.25	−0.016	5.98				

TABLE 5: Valence Angle Parameters As Used in Equations 8a−d



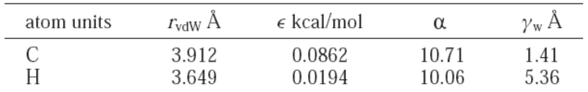
valence angle units	$\Theta_{o,o}$ degree	k_a kcal/mol	k_b (1/radian)^2	$p_{v,1}$	$p_{v,2}$
C−C−C	71.31[a]	35.4	1.37	0.01	0.77
C−C−H	71.56	29.65	5.29		
H−C−H	69.94	17.37	1.00		
C−H−C	0	28.5	6.00		
H−H−C	0	0	6.00		
H−H−H	0	27.9	6.00		

TABLE 6: Torsion and Conjugation Parameters (V_2 and V_3 in kcal/mol) As Used in Equations 10a−c



torsion angle[a]	V_2	V_3	p_t
C−C−C−C	21.7	0.00	−2.42
C−C−C−H	30.5	0.58	−2.84
H−C−C−H	26.5	0.37	−2.33

TABLE 3: van der Waals Parameters Used in Equation 12[a]



atom units	r_{vdW} Å	ϵ kcal/mol	α	γ_w Å
C	3.912	0.0862	10.71	1.41
H	3.649	0.0194	10.06	5.36

Fitting of potential parameters

- Two main approaches to develop a potential exist:

    1. Derivation from so called *ab initio* (quantum mechanical) calculations

    2. Fit to empirical and/or *ab initio* data

  - Although the previous approach is better motivated physically, in practice the latter approach, or a combination of the two, often works better.

- A good classical potential is one which with a small number of free parameters can describe a wide range of properties well (usually 5-20 % accuracy in condensed matter physics is considered to be "well", since experiments seldom are much more accurate than this).

- A related concept is that a good potential should be **transferable**, which means that it should be able to describe properties of other states of the material than those it was originally fitted to.

Fitting of potential parameters

- Regarding fitting the parameters in a potential of type 2, there are two opposite extreme approaches:

   1. ***“Blind fitting” :*** choose a functional form and a set of data to which the parameters are fit. Then use some fitting routine to obtain a best fit to all the data.

   2. ***“Parameter choice by hand”:*** use reliable experimental or *ab initio* data of crucial data to set as many potential parameters as possible exactly, then fit only the remaining (if any) parameters. For instance, the equilibrium separation, binding energy and vibration frequency for a dimer can be used to fix all the 3 Morse potential parameters.

- A pure approach 1 is dangerous in that quantities which are outside the original parameter set may obtain completely pathological values.
  - Example: some Si bulk potentials predict that the Si dimer is non-bonding.

- Also, if some potential parameter happens to be insensitive to all quantities in the data set, the fit may give ridiculously small or large values for it, which may cause trouble elsewhere.

- To obtain transferable potentials, approach 2 is thus usually to be preferred. On the other hand, if optimal precision in a limited set of systems (say, elastic properties of a perfect bulk crystal) is desirable, approach 1 may still be the better way to go.

- Most authors use approaches somewhere between 1 and 2.

Fitting of potential parameters

- A functional form can sometimes be derived from experimental equations of state $P(V)$. Example: solid Ne and Ar:

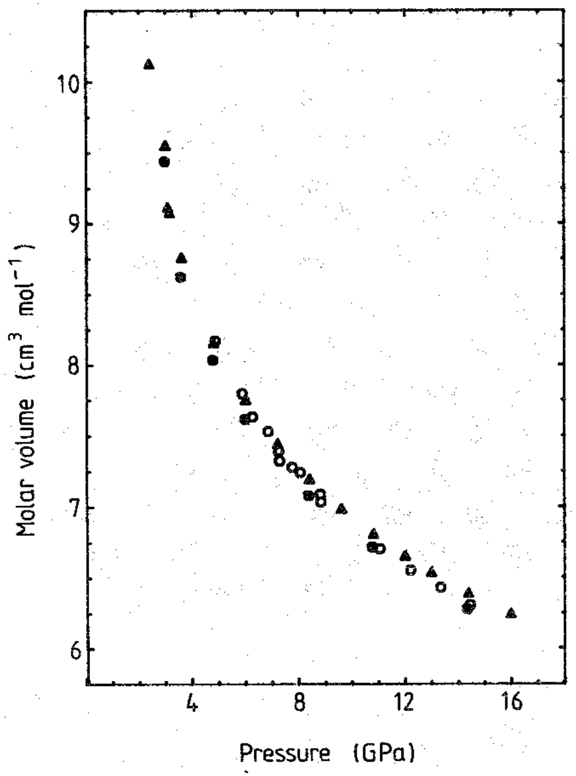


Figure 5. Pressure–volume isotherms of Ne at 293 K. ○, experimental data (after [19]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (Siska *et al* [21]).

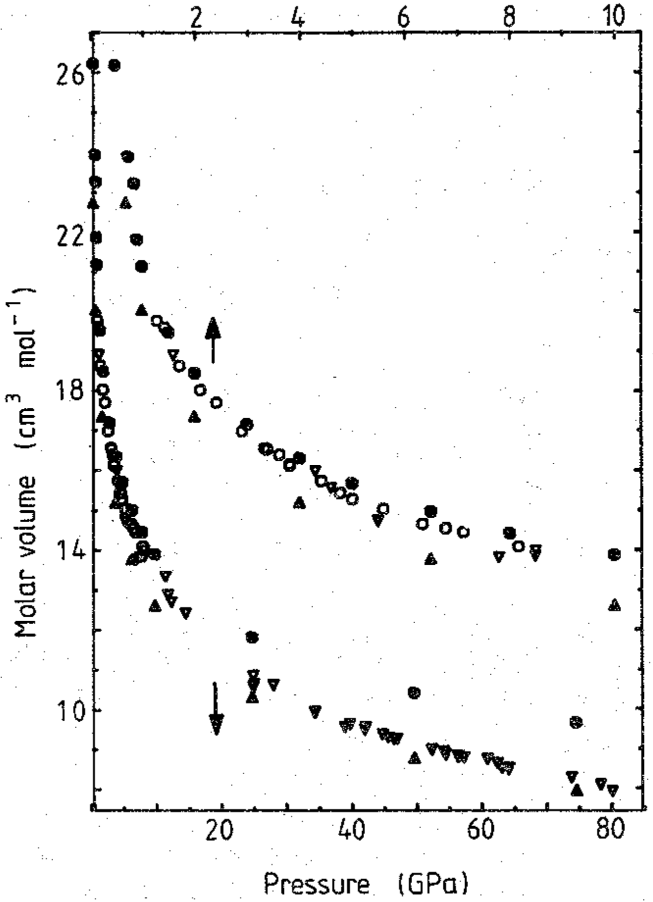
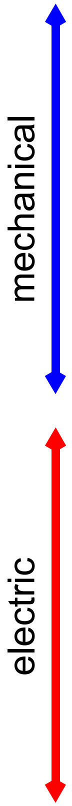


Figure 6. Pressure-volume isotherms of Ar at 293 K. The upper isotherm is in the pressure region 0 to 10 GPa and the lower one in the region 0 to 80 GPa. ○, experiment (after [19]); ▽, experiment (after [20]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (exp–6 [20]).

Fitting of potential parameters

- Here is a short list of macroscopic, physical, properties which can and often are used to derive or fit interatomic potentials:



Physical property	Atom-level property
Crystal structure	Balance of atomic forces.
Cohesive energy	Potential energy at the equilibrium atom positions
Elastic constants $c_{\rho\sigma}$	Long-wavelength acoustic vibrations Elastic distortions of unit cell.
Equation of state $P(V)$	Compression or expansion of material
Neutron scattering	Phonon $\omega(\mathbf{k})$ in the Brillouin zone.
Dielectric constant ε_∞	Electronic polarizability
Dielectric constant ε_0	Polarizarization of electrons and lattice; long-wavelength optical vibration modes;
Infrared absorption	Long-wavelength vibrations with a dipole moment.
Raman scattering	Long-wavelength vibrations which change the polarizability.

- Out of these, the first five depend purely on the mechanical properties of the material, and are relevant to almost all solids. The latter four involve electric properties and may or may not be relevant depending on what kind of materials and properties are studied.

Fitting of potential parameters

- **Crystal structure**:
  - The equilibrium crystal structure should be stable if one wants to describe any process where large atom displacements may occur (melting, surfaces, deposition, etc. etc.).
  - In equilibrium the force acting on every atom in the unit cell i should vanish:

$$\sum_j \mathbf{f}_{ij} = 0$$

  - Here the potential is only tested at a few r_{ij} values. (The smaller the crystal symmetry, the more values.)
  - Any potential has a minimum potential energy configuration, or many configurations with the same energy.
  - Example: Tersoff potential for Si [J. Tersoff, *Phys. Rev. B* **38** (1988) 9902.]

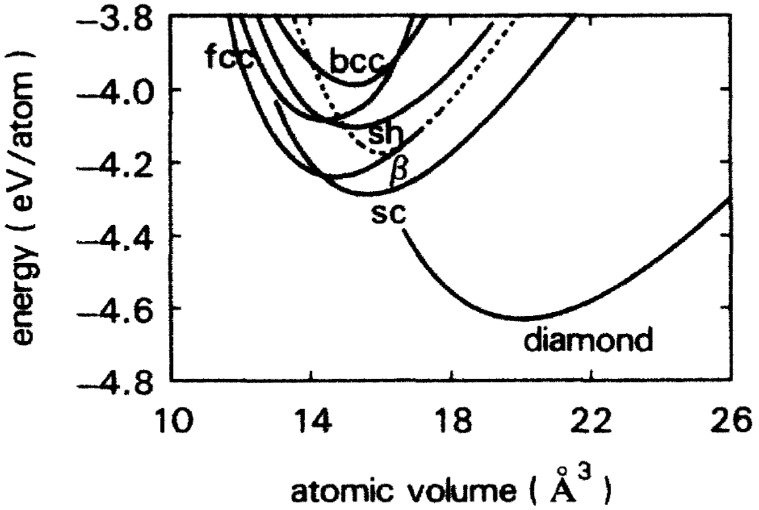


FIG. 3. Calculated cohesive energy vs volume per atom of silicon in the diamond, simple cubic (sc), β-tin (β), simple hexagonal (sh), bcc, and fcc structures. For β-tin, the dotted curve shows the result of the potential as given in Table I, while the solid curve results from taking $R=2.75$ Å and $D=0.1$ Å, as discussed in text.

Fitting of potential parameters

- Local stability is easy to achieve in a classical potential. But global stability (that is, that the real crystal structure is indeed the global minimum of the potential) may be surprisingly difficult.

- Even well-known authors make mistakes. For instance, the first Si potential of Tersoff [Tersoff, *Phys. Rev. Lett.* **56** (1986) 632.] was well motivated, well derived, and published in the best journal in physics. But the formation energy of the vacancy turned out to be negative, which means it did not have the right ground state structure...

- A good way to test the minimum energy: start from random atom positions, and quench the cell slowly enough so that it crystallizes. If the structure is the correct one, it probably is indeed the ground state. Unfortunately doing this may take forever.

- Another test: simulate a liquid and solid in equilibrium at the melting point, and check that the solid remains stable and the liquid recrystallizes to the same structure on slight cooling below T_{melt}.

Fitting of potential parameters

- **Cohesive energy** (E_{coh} = energy difference between free atoms and the solid):
  - Directly related to the potential minimum energy level
  - Often easy to get right exactly.

- **Elastic constants**[1] $c_{\rho\sigma}$
  - Related to deformation in the material

$$\mathbf{R}(\mathbf{r}) = \mathbf{r}' - \mathbf{r} = u_1(\mathbf{r})\hat{\mathbf{x}} + u_2(\mathbf{r})\hat{\mathbf{y}} + u_3(\mathbf{r})\hat{\mathbf{z}}$$

  and to the external stress (pressure) σ:

$$\sigma_\rho = \sum_\sigma c_{\rho\sigma} e_\sigma$$

  - Voigt notation for ρ- and σ-indexing: $xx \to 1$, $yy \to 2$, $zz \to 3$, $yz \to 4$, $zx \to 5$, $xy \to 6$
  - Here the strain (crystal distortion) components e_{ij} are

$$e_{ii} = \frac{\partial u_i}{\partial x_i} \quad ; \quad e_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

---

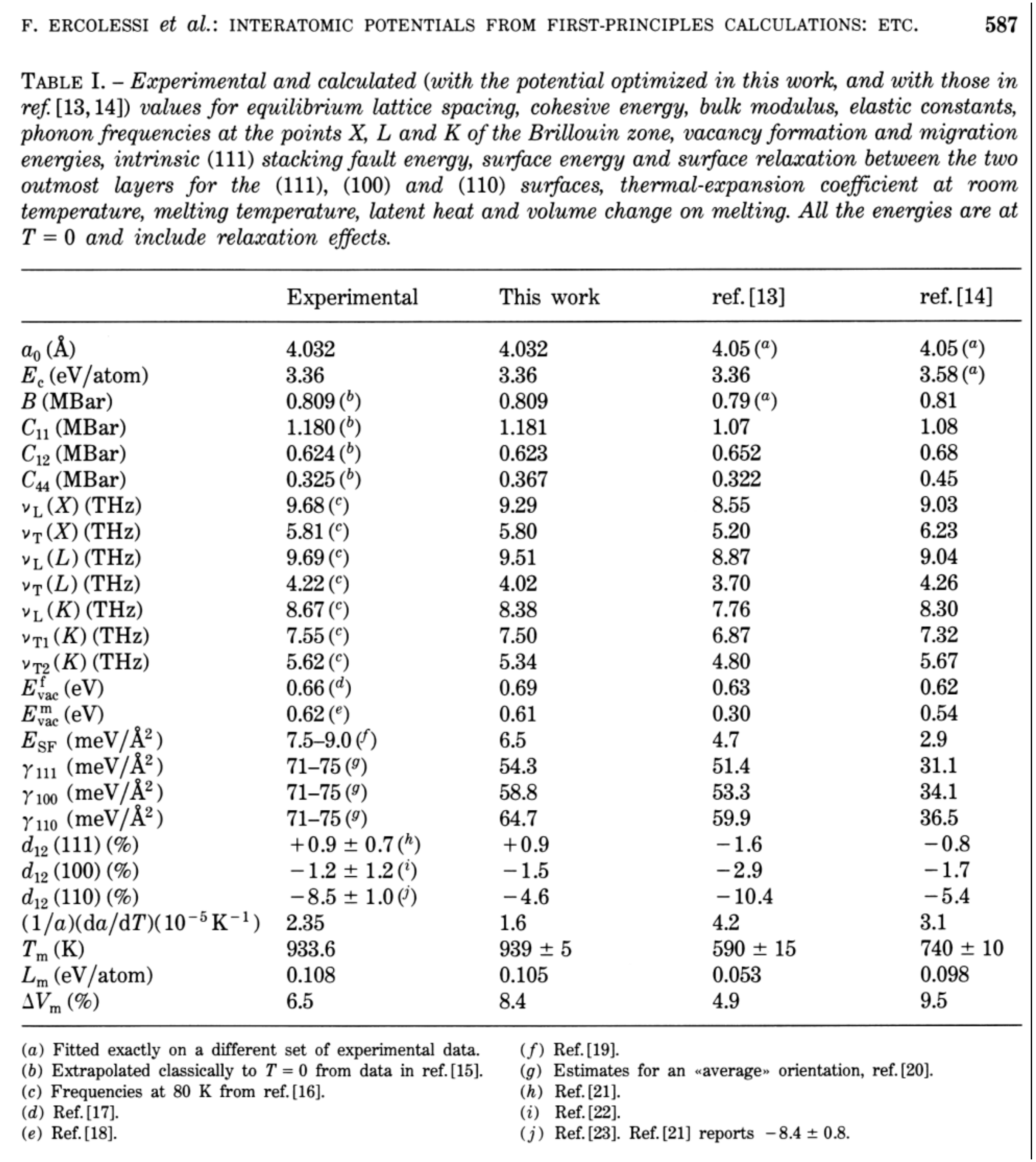
[1] See e.g. Kittel, *Introduction to solid state physics*, 7th edition, ch. 3.

Fitting of potential parameters

- The stress component σ_{ij} is the force which acts on the plane with the normal x_j in the direction x_i
- In principle there are 36 stress and strain components, but their number reduces to much smaller numbers in practice.
- For instance in a cubic crystal there are only three independent elastic constants $c_{11} = c_{xxxx}$, $c_{12} = c_{xxyy}$ and $c_{44} = c_{xyxy}$.

- Particularly important if there are deformations (compression, shear, melting) in the simulations. Also related to defect properties and the melting point ⇒ if we get the elastic constants about right we are already on a good way to a good potential.

- An example of an (unusually) good fit: F. Ercolessi, J. B. Adams, *Europhys. Lett.* 26 (1994) 583.



F. ERCOLESSI *et al.*: INTERATOMIC POTENTIALS FROM FIRST-PRINCIPLES CALCULATIONS: ETC. **587**

TABLE I. – *Experimental and calculated (with the potential optimized in this work, and with those in ref.* [13, 14]) *values for equilibrium lattice spacing, cohesive energy, bulk modulus, elastic constants, phonon frequencies at the points X, L and K of the Brillouin zone, vacancy formation and migration energies, intrinsic* (111) *stacking fault energy, surface energy and surface relaxation between the two outmost layers for the* (111), (100) *and* (110) *surfaces, thermal-expansion coefficient at room temperature, melting temperature, latent heat and volume change on melting. All the energies are at* $T = 0$ *and include relaxation effects.*

	Experimental	This work	ref. [13]	ref. [14]
a_0 (Å)	4.032	4.032	4.05 (a)	4.05 (a)
E_c (eV/atom)	3.36	3.36	3.36	3.58 (a)
B (MBar)	0.809 (b)	0.809	0.79 (a)	0.81
C_{11} (MBar)	1.180 (b)	1.181	1.07	1.08
C_{12} (MBar)	0.624 (b)	0.623	0.652	0.68
C_{44} (MBar)	0.325 (b)	0.367	0.322	0.45
$\nu_L(X)$ (THz)	9.68 (c)	9.29	8.55	9.03
$\nu_T(X)$ (THz)	5.81 (c)	5.80	5.20	6.23
$\nu_L(L)$ (THz)	9.69 (c)	9.51	8.87	9.04
$\nu_T(L)$ (THz)	4.22 (c)	4.02	3.70	4.26
$\nu_L(K)$ (THz)	8.67 (c)	8.38	7.76	8.30
$\nu_{T1}(K)$ (THz)	7.55 (c)	7.50	6.87	7.32
$\nu_{T2}(K)$ (THz)	5.62 (c)	5.34	4.80	5.67
E_{vac}^{f} (eV)	0.66 (d)	0.69	0.63	0.62
E_{vac}^{m} (eV)	0.62 (e)	0.61	0.30	0.54
E_{SF} (meV/Å^2)	7.5–9.0 (f)	6.5	4.7	2.9
γ_{111} (meV/Å^2)	71–75 (g)	54.3	51.4	31.1
γ_{100} (meV/Å^2)	71–75 (g)	58.8	53.3	34.1
γ_{110} (meV/Å^2)	71–75 (g)	64.7	59.9	36.5
d_{12} (111) (%)	$+0.9 \pm 0.7$ (h)	$+0.9$	-1.6	-0.8
d_{12} (100) (%)	-1.2 ± 1.2 (i)	-1.5	-2.9	-1.7
d_{12} (110) (%)	-8.5 ± 1.0 (j)	-4.6	-10.4	-5.4
$(1/a)(\mathrm{d}a/\mathrm{d}T)(10^{-5}\,\mathrm{K}^{-1})$	2.35	1.6	4.2	3.1
T_m (K)	933.6	939 ± 5	590 ± 15	740 ± 10
L_m (eV/atom)	0.108	0.105	0.053	0.098
ΔV_m (%)	6.5	8.4	4.9	9.5

(*a*) Fitted exactly on a different set of experimental data.
(*b*) Extrapolated classically to $T = 0$ from data in ref. [15].
(*c*) Frequencies at 80 K from ref. [16].
(*d*) Ref. [17].
(*e*) Ref. [18].
(*f*) Ref. [19].
(*g*) Estimates for an «average» orientation, ref. [20].
(*h*) Ref. [21].
(*i*) Ref. [22].
(*j*) Ref. [23]. Ref. [21] reports -8.4 ± 0.8.

Weaknesses of pair potentials

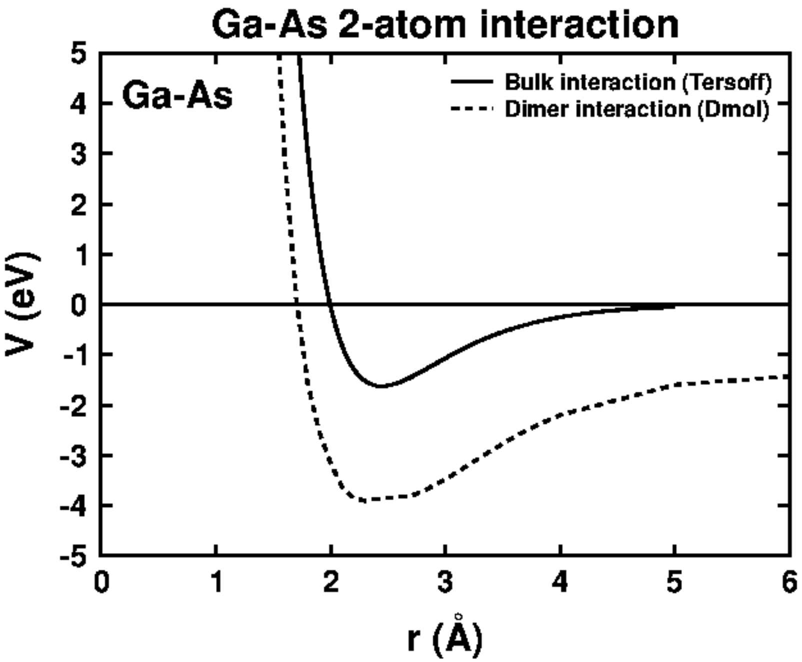
- A pair potential can never describe well the directional properties of covalent bonds. For instance in the diamond/zincblende structure (C, Si, Ge, α-Sn, many compound semiconductors) the ideal angle between bonds = 109.47^o . Similarly, in almost all molecules the directional properties of covalent bonds is of crucial importance.

- Also longer-range angular dependence is completely neglected. For instance in the structure of polymers torsional terms are important. Also, recent calculations of BCC metals have shown that 4-particle interactions are about 50 % of the bond.

- Pair potentials also do not account for the environmental dependence. They predict that the strength of the two-atom bond is as strong in a dimer as inside a material, which almost never is true.

Weaknesses of pair potentials

- For instance the Ga-As interaction:



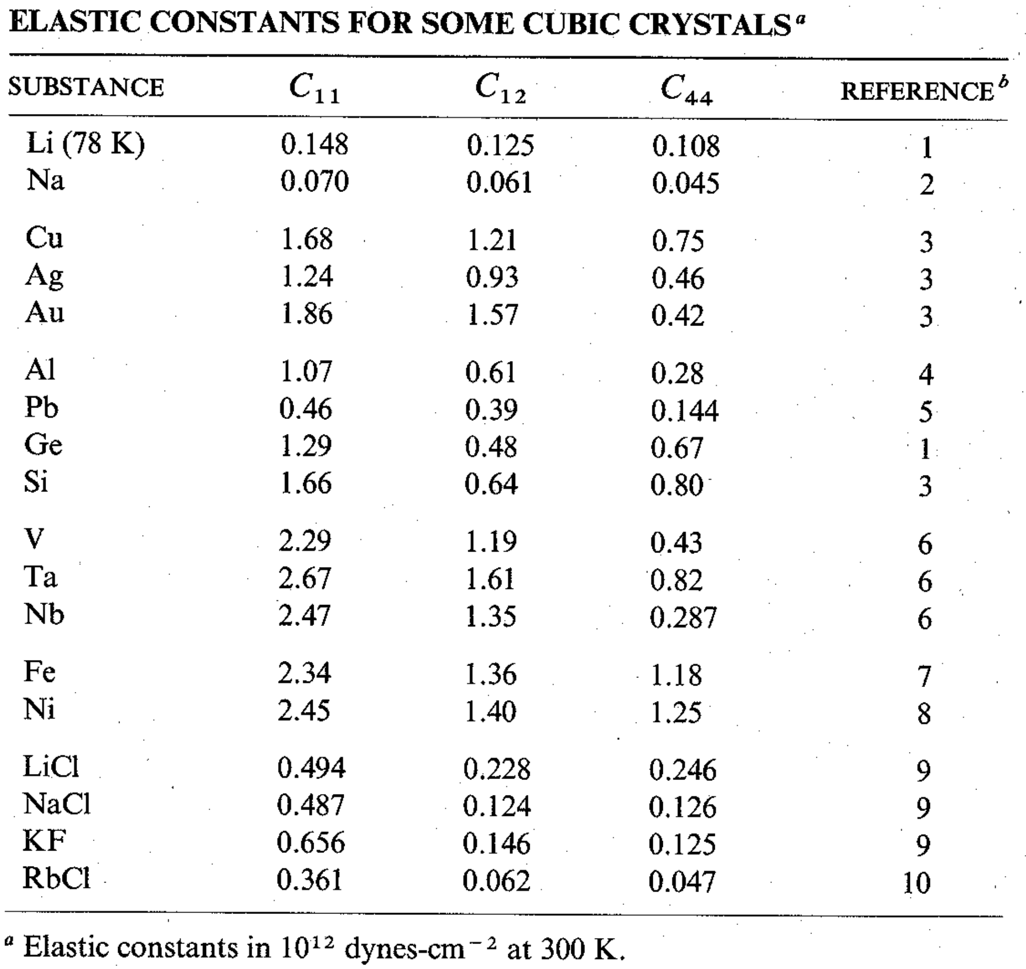
Weaknesses of pair potentials

- Moreover, a pair potential always predicts that the elastic constants $c_{12} = c_{44}$ for cubic crystals. but in reality:

- Also, vacancy formation energies are often completely wrong in pair potentials (see below).

- Pair potentials also usually give bad surface properties.

- *Summa summarum:* the pair potential approximation:
  - may work well close to equilibrium structure in many materials
  - is good for noble gases
  - is rather good for ionic compounds such as alkali halides
  - is rather bad for FCC and HCP metals
  - is terrible for covalently bonded materials



ELASTIC CONSTANTS FOR SOME CUBIC CRYSTALS[a]

SUBSTANCE	C_{11}	C_{12}	C_{44}	REFERENCE[b]
Li (78 K)	0.148	0.125	0.108	1
Na	0.070	0.061	0.045	2
Cu	1.68	1.21	0.75	3
Ag	1.24	0.93	0.46	3
Au	1.86	1.57	0.42	3
Al	1.07	0.61	0.28	4
Pb	0.46	0.39	0.144	5
Ge	1.29	0.48	0.67	1
Si	1.66	0.64	0.80	3
V	2.29	1.19	0.43	6
Ta	2.67	1.61	0.82	6
Nb	2.47	1.35	0.287	6
Fe	2.34	1.36	1.18	7
Ni	2.45	1.40	1.25	8
LiCl	0.494	0.228	0.246	9
NaCl	0.487	0.124	0.126	9
KF	0.656	0.146	0.125	9
RbCl	0.361	0.062	0.047	10

[a] Elastic constants in 10^{12} dynes-cm^{-2} at 300 K.

Source: Ashcroft-Mermin

- But for all these groups much better, and only slightly slower, models exist. These will be described later on this course.

Weaknesses of pair potentials

- Simple estimate of vacancy formation energy using pair potentials:

$$E_{\text{vac}}^{\text{f}} = E_{\text{tot}}(\text{vacancy}, N) - E_{\text{tot}}(\text{perfect}, N)$$

  - nearest neighbor pair potential, energy/bond= $V(r_{\text{nn}}) \equiv \phi$
  - no relaxation
  - fcc structure ⇒ 12 neighbors

$$E_{\text{tot}}(\text{vacancy}, N) = \frac{1}{2}[(N-12)12\phi + 12(12-1)\phi] = 6(N-1)\phi$$

$$E_{\text{tot}}(\text{perfect}, N) = \frac{1}{2}N12\phi = 6N\phi$$

$$\Rightarrow E_{\text{vac}}^{\text{f}} = -6\phi = -E_{\text{coh}}$$

  - However, ab initio calculations[1]:

Element	$\lvert E_{\text{coh}}\rvert$ (eV)	$E_{\text{vac}}^{\text{f}}$ (eV)
V	5.31	2.1 ± 0.2
Nb	7.57	2.6 ± 0.3
W	8.90	4.0 ± 0.2

  - Relaxation: only minor effect (far less than 1 eV).

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[1] A. E. Carlsson, *Solid State Physics: Advances in Research and Applications,* **43** (1990) 1.