Calculating the forces between atoms

- The forces between atoms can be calculated in many different ways

- In this lecture we describe how one calculates forces from classical potentials. We describe primarily pair potentials, but many-body potentials are a fairly straightforward extension. Getting forces from quantum mechanical models requires a good knowledge of them, and is not dealt with on this course.

- A classical potential can be written in the form:

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

- V is the total potential energy of an N atom system. In principle all sums loop from 1 to N, in practice calculating them can often be much reduced

- V_1 is the single particle potential, which describes external forces, which could e.g. be an electric field. In systems with no external forces $V_1 = 0$.

- V_2 is a **pair potential** which only depends on the distance between atoms r_{ij}
  - if there were a direct dependence on the *vectors* $\boldsymbol{r}_i$, $\boldsymbol{r}_j$ => the potential would depend on the choice of the origin

- V_3 is a **three-body potential** which may have an angular dependence. To preserve the independence on the atom indices, the potential has to depend only on three variables, i.e. $V_3 = V_3(r_{ij}, r_{ik}, \theta_{ijk})$.

- Four-body potentials, and even five-body terms, do exist especially in chemical and biological applications. On this course we only briefly mention such terms, and focus on the V_2 and V_3 which are 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 an 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

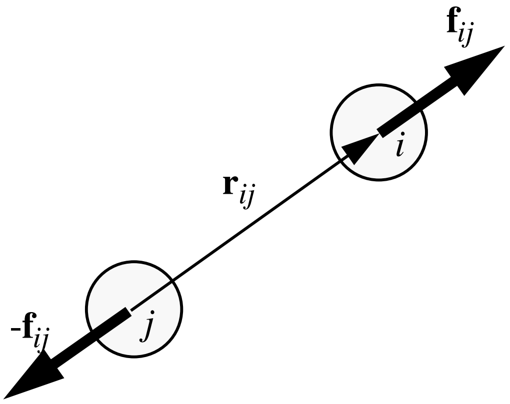
Force calculation for pair potentials

- Say we have a pure pair potential $V(r_{ij})$.
  The force acting on atom i from atom j is

  $$\mathbf{f}_{ij} = -\nabla_{\mathbf{r}_i} V(r_{ij}) = -\nabla_{\mathbf{r}_{ij}} V(r_{ij})$$

  $$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

  ergo: $$\mathbf{f}_{ij} = -\left[\frac{dV}{dr}\right]_{r = r_{ij}} \times \frac{\mathbf{r}_{ij}}{r_{ij}}$$



- Note that to be precise ∇ operates on the position $\mathbf{r}_i$ of atom i. For pair potentials this does not make any difference, but for many-body potentials it does.

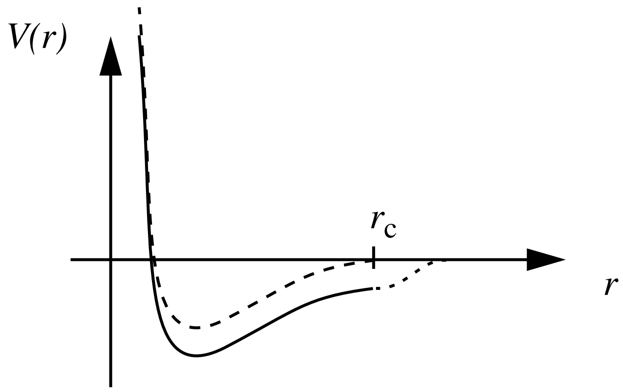
- Most potentials have a cut-off radius r_c. Atom pairs with $r_{ij} > r_c$ do not interact. Usually $r_c \approx$ a few Å .

- In case the potential extends to infinity, an analytical correction can be made to the energy, and other quantities of interest (calculated assuming the material is continuous, or with a lattice sum). So it could look like:

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

  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.

- This also means that the potential may have a discontinuity at r_c, which may lead to unphysical jumps in energy. The easy way to overcome this is to take the potential to zero in an interval $[r_c, r_c + \Delta r]$ so that at least the potential and the force are continuous (2:nd order polynomial). Or better yet, using a sine function one can get all derivatives to be continuous except at the interval limits. Or the potential may



simply be displaced, as the zero point of V is arbitrary with respect to the force derivation- but this changes the value of V_{TOT} which may be a problem.

- 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 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 ...
            dVdr = ...dV/dr of potential energy ...
            a = dVdr/m ! Unit transformations may be needed
            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
```

- 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 ...
            dVdr = ...dV/dr of potential energy ...
            a = dVdr/m ! Plus unit transformations !
            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
```

- 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 one may need to add a factor of 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 included).

A straightforward solution:

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

(either in constructing the neighbour list or forces) reduces the calculation time to one half. But for some many-body potentials this does not work.

- In addition to this, one has to notice that *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).

- Finally, note that the sign conventions in defining r_{ij} in the literature may vary.

- One practical way of checking whether all signs and factors of 1/2 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.

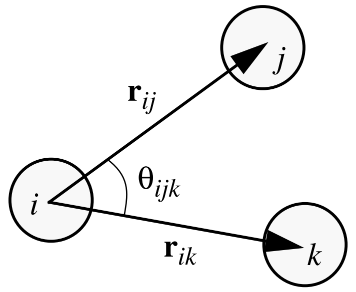
- Another good test: numerical derivation of V, already a 3-point approximation can easily be made accurate to 6-8 digits

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 $n\boldsymbol{F}_i$ 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

In this case one can utilize the following equalities:

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

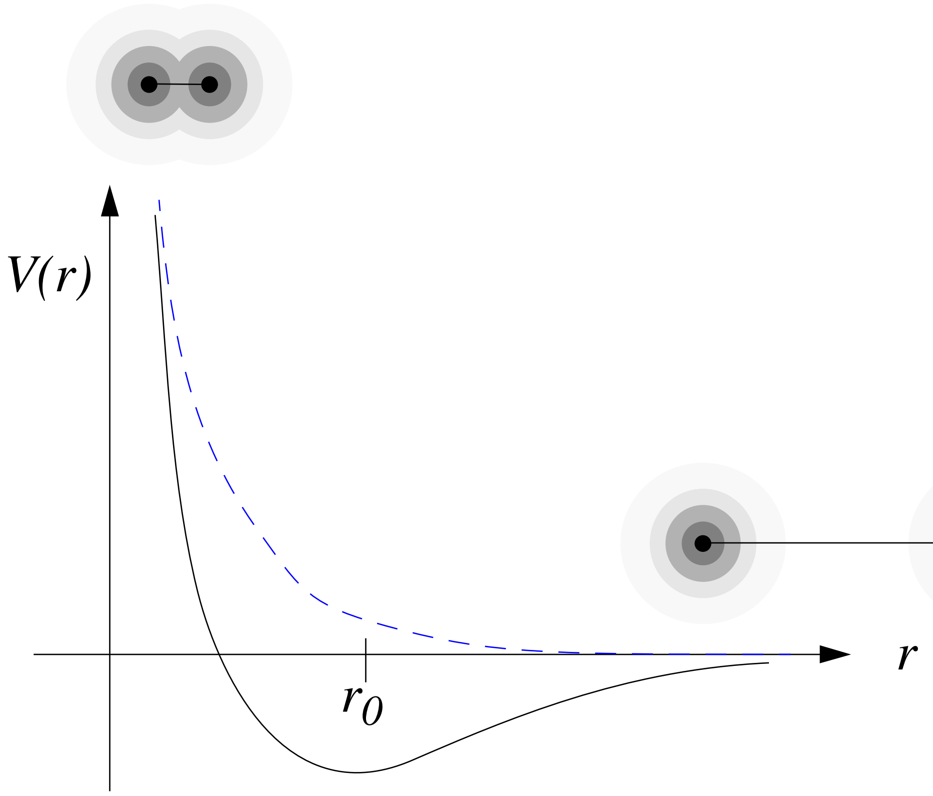
$$\nabla_i\cos\theta_{ijk} = \nabla_i\left(\frac{\boldsymbol{r}_{ij}\cdot\boldsymbol{r}_{ik}}{r_{ij}r_{ik}}\right) = \ldots\ldots = \left[\frac{\cos\theta_{ijk}}{r_{ij}^2} - \frac{1}{r_{ij}r_{ik}}\right]\boldsymbol{r}_{ij} - \left[\frac{\cos\theta_{ijk}}{r_{ik}^2} - \frac{1}{r_{ij}r_{ik}}\right]\boldsymbol{r}_{ik}$$

that is, the explicit cos-terms can be removed altogether, which is computationally efficient.

- 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 origin of interactions

Qualitatively a two-atom interaction looks like the following (most of you are certainly familiar with the shape from previous courses):



- 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, metallic ‘bonding’ or a covalent bond (due to pairing of valence electrons)
- But the potential between two atoms may also be purely repulsive (blue, dashed curve).

- A few examples

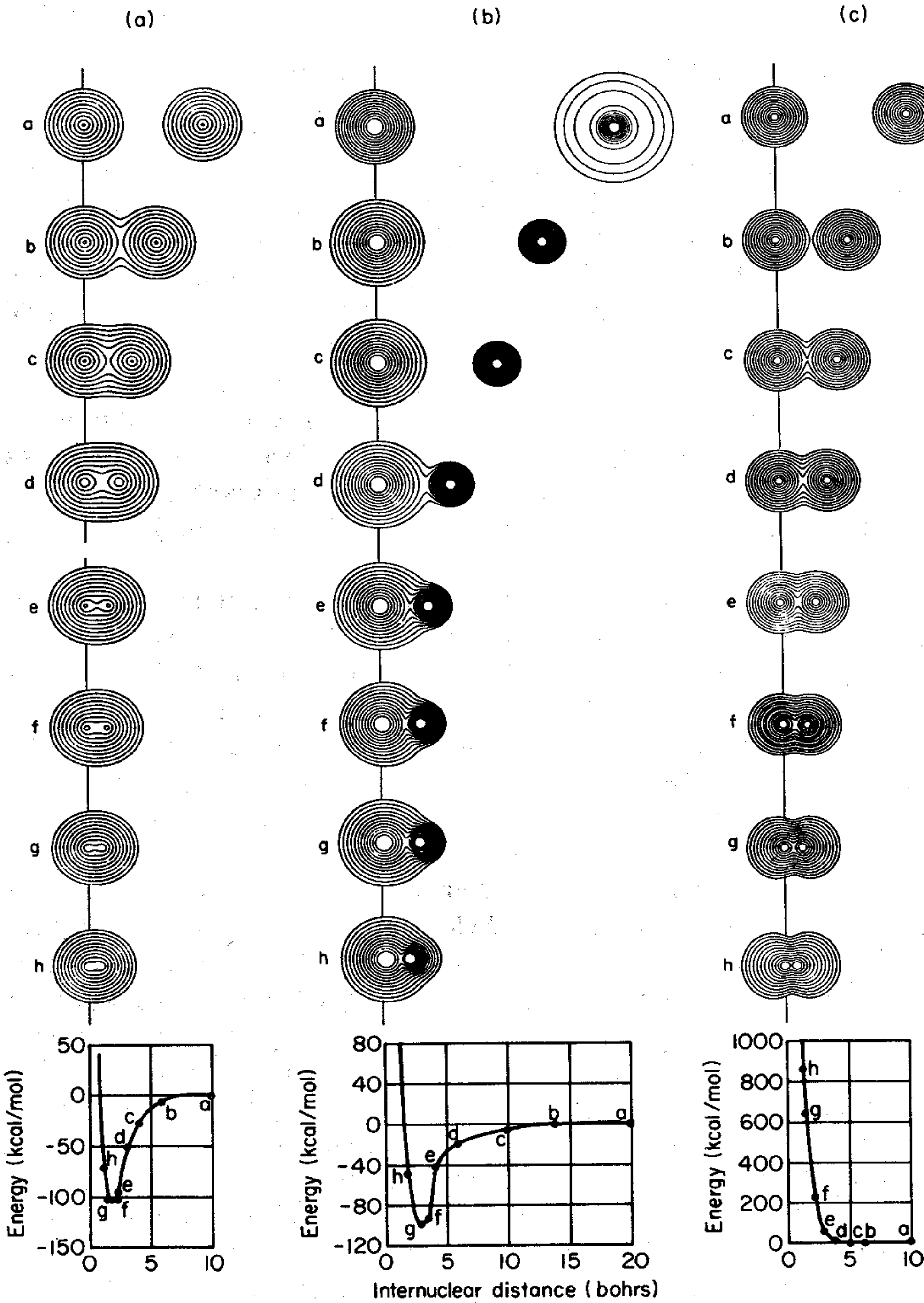


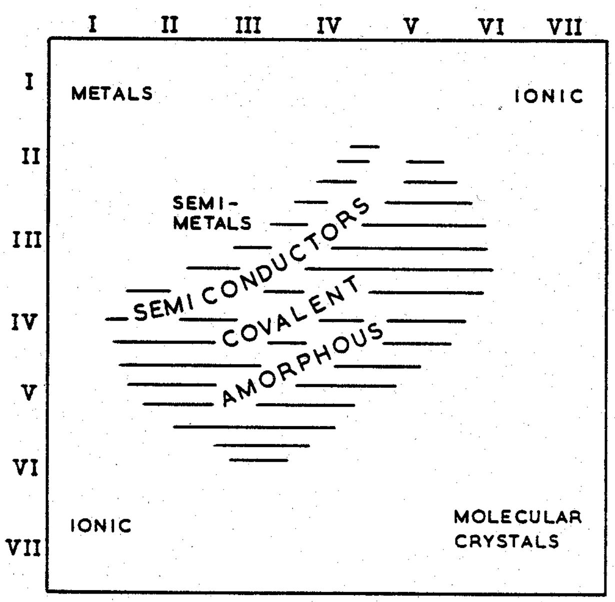
Fig. 1.2. **Electron density distribution contours generated by computer solution of the Schrödinger equation for interactions in three atomic systems (a) H_2, (b) LiF, and (c) He_2. At the bottom is plotted the potential energy of interaction at the different stages of the process a–h. The separation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

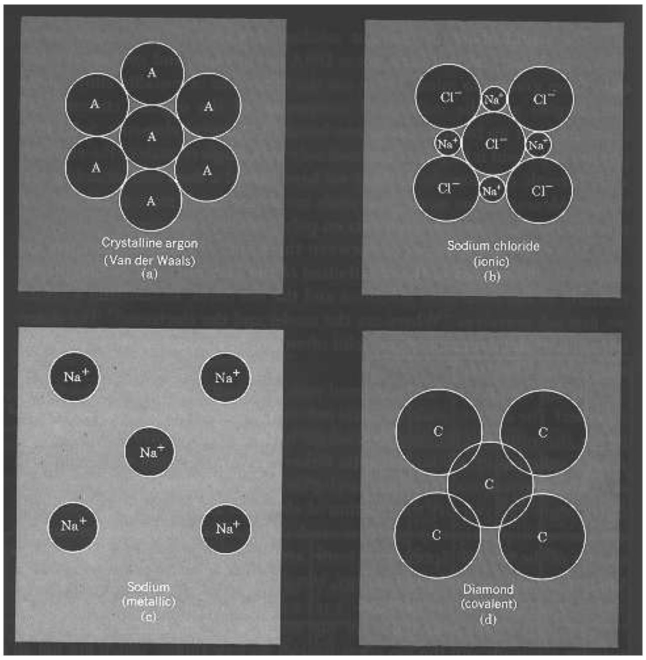
1 bohr = 0.53 Å

- Overview of bonding expected in different cases, and illustration of electron distributions

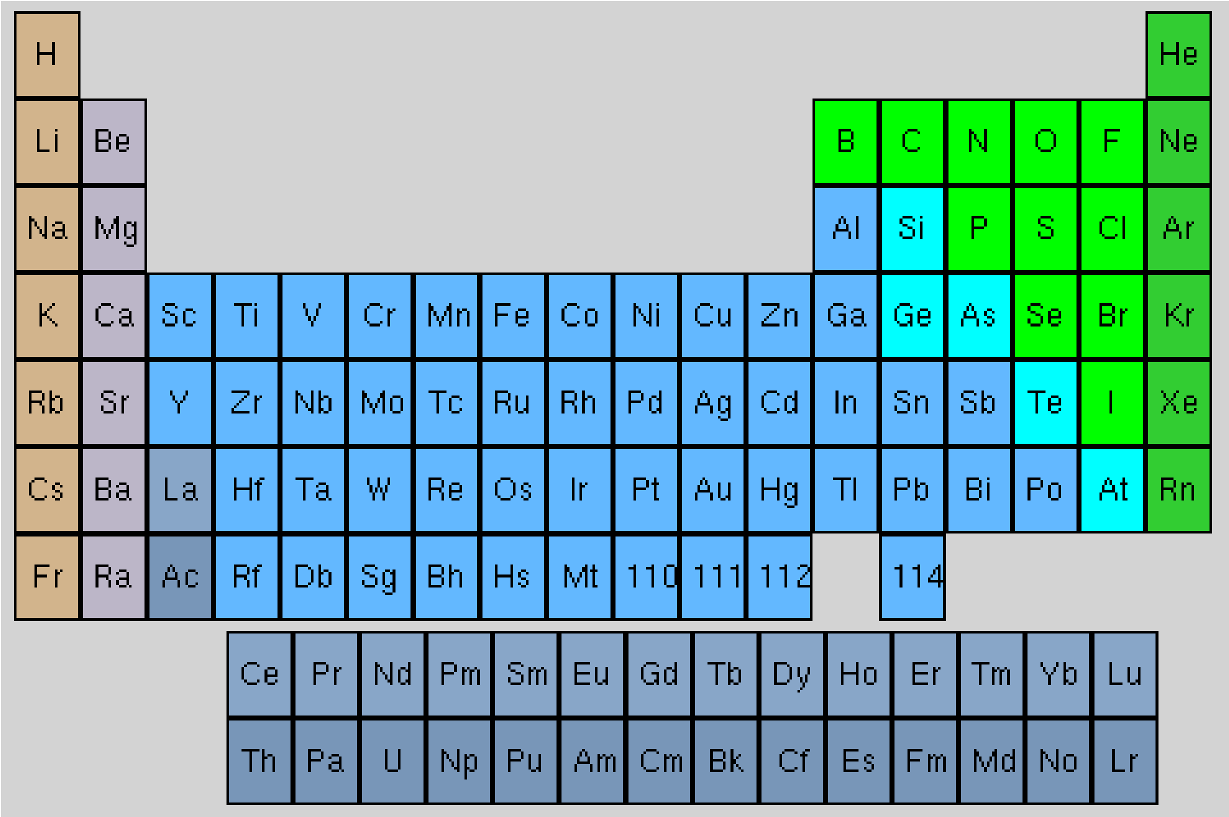
Period	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB		VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble gases
1	1 **H** 1.008																	2 **He** 4.003
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
3	11 **Na** 22.990	12 **Mg** 24.305											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:

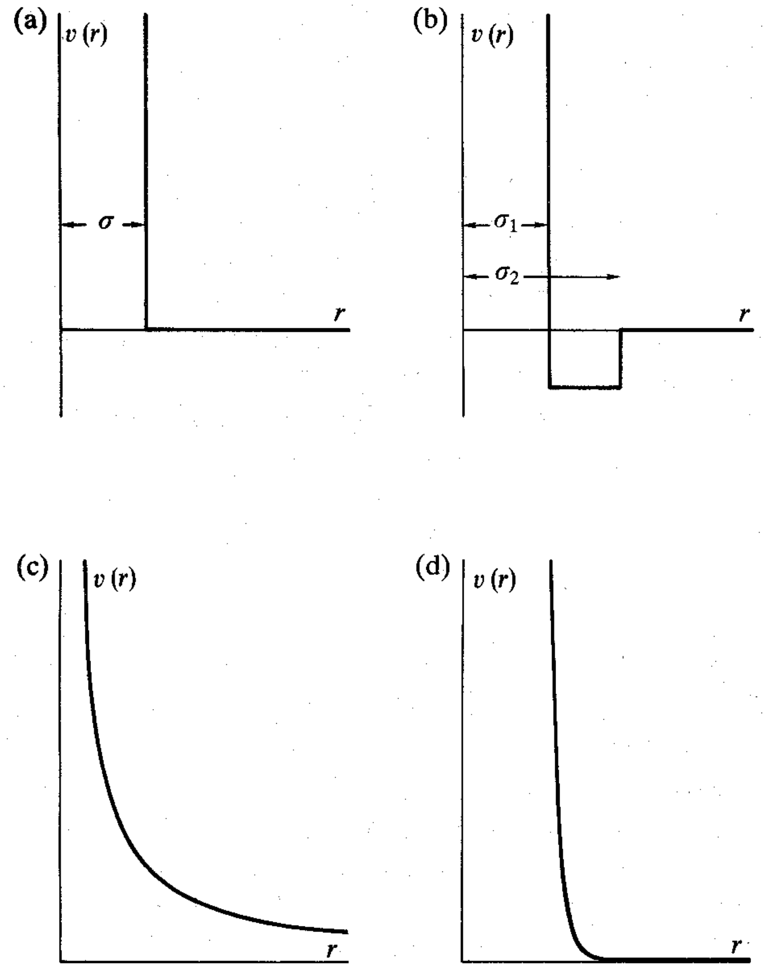


Fig. 1.4 Idealized pair potentials. (a) The hard-sphere potential; (b) The square-well potential; (c) The soft-sphere potential with repulsion parameter $\nu = 1$; (d) The soft-sphere potential with repulsion parameter $\nu = 12$.

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

- 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!

- square well: $$V^{SW}(r) = \begin{cases} \infty, & r < \sigma_1 \\ -\varepsilon, & \sigma_1 \leq r < \sigma_2 \\ 0, & r \geq \sigma_2 \end{cases}$$

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

“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 classically by considering how two charged spheres induce dipole-dipole interactions into each other, or quantum mechanically as the interactions between two oscillators [Kittel, Introduction to Solid State Physics, 7th edition, s. 62]. It is also known as the Van der Waals or London interaction.

- The repulsive term $1/r^{12}$ does not have a true physical motivation, other than that the exponent must be larger than 6 to get a potential well. The main reason for often using 12 is that 2•6 = 12 and hence it can be evaluated very efficiently.

- Also other exponents are nowadays used. The notation for any two exponents A and B is LJ (A-B) potential. So above we have the LJ (12-6) 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_{min} = -3.1 meV for Ne.

- LJ (12-6) potentials have proven to be amazingly good for noble gases (filled electron shells => almost always neutral) close to equilibrium. But they are obviously terrible for very small r (r <~ 1 Å) since the true interaction is ~ 1/r exp(-r) and not $1/r^{12}$

- 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 from one simulation can be transferred to different systems with straightforward scaling.

For instance for the Lennard-Jones-potential:

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

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

- other units:

$$t^* = t/[(m\sigma^2)/\varepsilon]^{1/2} \qquad \rho^* = \rho\sigma^3$$

$$T^* = k_B T/\varepsilon \qquad P^* = P\sigma^3/\varepsilon$$

$$\mathbf{f}^* = \mathbf{f}\sigma/\varepsilon \qquad v^* = v/[\varepsilon/m]^{1/2}$$

- 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. Although efficient programming is still important, saving time is nowadays seldom *that* critical, and using reduced units everywhere in a code can make it a major pain in the ~~as.~~ neck to remember how to get back to real units. Moreover, for a complex potential the only place where much time is spent is in the force calculation subroutine. So in my opinion it is seldom worth using reduced units except possibly inside the force calculation routine.

The 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. Does not have any real physical motivation behind it, but the Schrödinger equation happens to have an analytical solution for this functional form. Also, it is efficient to evaluate, in the form above only one exponential function needs to be evaluated. And the repulsive part is way much better than in LJ potentials

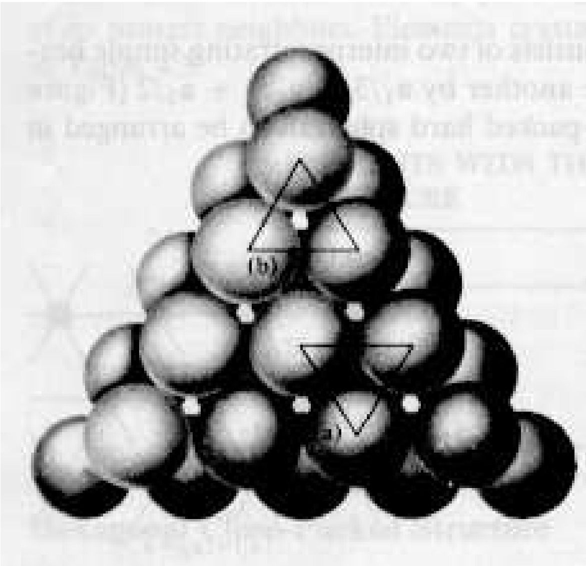
- A fit for many metals [Girifalco and Weizer, Phys. Rev. **114** (1959) 687]

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

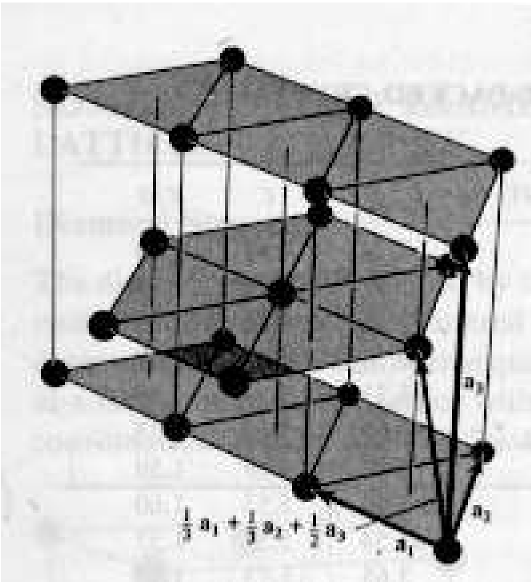
- Works decently, for being a pair potential.

- An ordinary pair potential inadvertently has a close-packed structure as the ground state (usually either “face-centered cubic”, FCC or “hexagonal close packed”, HCP). These structures get their name since they are the tightest way one can pack hard spheres in three dimensions.

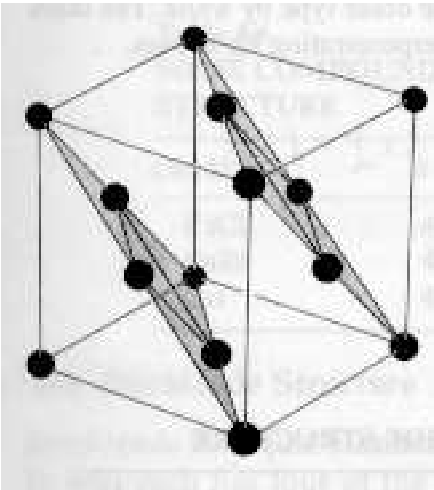
  [For details see e.g. Ashcroft-Mermin, chapter 4.]



HCP



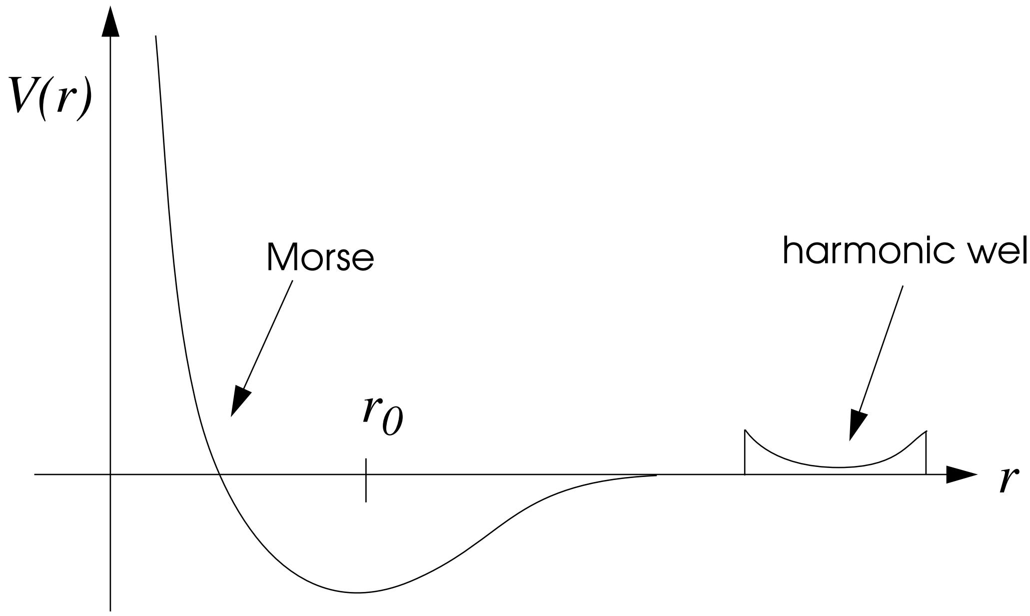
FCC



- 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:

  - The diamond lattice is an open structure, with only 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 positions

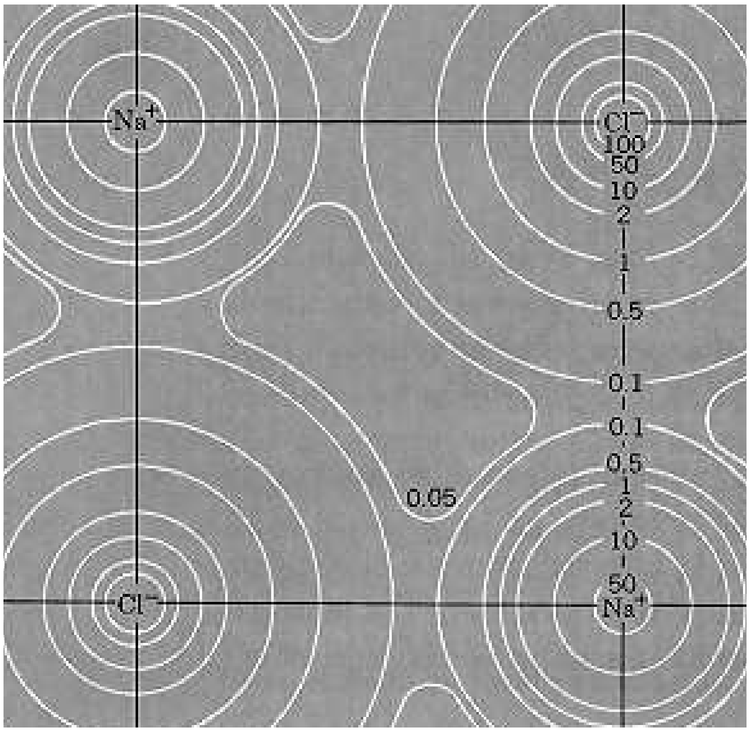
  - But what happens when atoms leave the harmonic well due to e.g. a high temperature: they will of course drop to the Morse potential well, so fcc structures will be created in the cell.

  - 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...

Ionic compounds

- An ionic compound consists of 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

    - One of the extreme examples: NaCl:



    - the bonding is something like 99% ionic

- 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.

- Ionic pair potentials typically contain a short-range (SR) term and the Coulomb interaction between ions:

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

- The short-range potential contains a description of the repulsive force between electrons packed closely together. Sometimes it can also contain an attractive van der Waals-interaction describing short-range attractive forces

- Most common forms for the short range potential:

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

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

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

- $1/r^6$-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.

- A (parenthetical) note on the use of the term van der Waals interaction. The term originally has meant the weak interaction between what can be understood as electrical dipoles. However, nowadays the term is very widely used to signify any interaction between atoms which is much weaker than covalent, metallic or ionic bonding, regardless of the origin of this weak interaction.

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.

- Two main approaches of constructing a potential exist:

  P1. Derivation of both the functional form and parameters purely from so called *ab initio* (quantum mechanical) electronic structure calculations

  ((Clarification of terms: *ab initio* is latin and means literally ~ "out of nothing", although most often it is translated as *first principles*. In physics this is used to denote calculations which are based only on well-known physical laws with no free fitting parameters. In condensed matter physics, it is used almost exclusively to mean quantum mechanical electronic structure calculations, i.e. Hartree-Fock or density-functional theory (DFT) calculations. Purists, though, tend to say DFT is not truly *ab initio))*

  P2. Fit of a potential with some generic motivation to empirical data, and when that is not available, to *ab initio* data

  Although the previous approach is better motivated physically, in practice the latter approach, or a combination of the two, actually 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 (the definition of "well" can vary a lot, but in condensed matter physics usually 5-20 % accuracy 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.

- Regarding fitting the parameters in a potential of type P2, 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. For instance, some Si bulk potentials predict that the Si dimer is non-bonding, which is utterly wrong. 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.

- Here I am rather partial: I am involved in a collaboration with Prof. Karsten Albe (TU Darmstadt) where we use a potential of type P2 and a fitting method of type 2 to develop potentials for complex materials. So far Karsten and/or my group has developed potentials for the systems BN, GaAs, GaN, PtC and NiC, as well as all the pure elements in this list. Although our approach does not give perfect potentials (which is impossible of course), the resulting potentials usually are much more transferable than most in the literature.

  - If interested in this approach, see K. Albe, K. Nordlund, and R. S. Averback, Phys. Rev. B 65, 195124 (2002), and references therein.

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

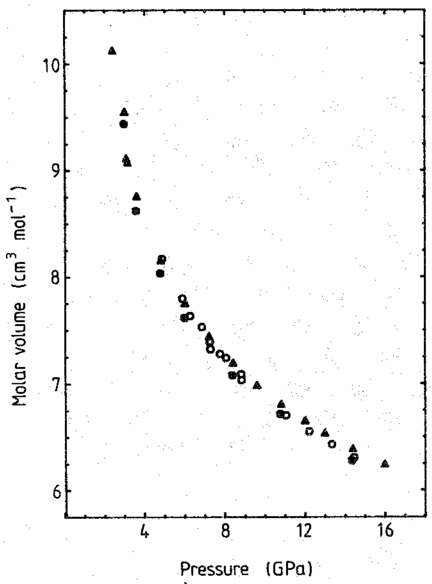


Figure 5. Pressure–volume isotherms of Ne at 293 K. ○, experimental data (after [19]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (Siska *et al* [21]).

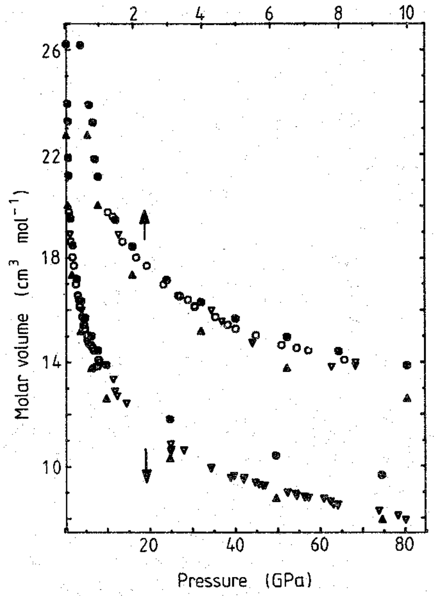


Figure 6. Pressure-volume isotherms of Ar at 293 K. The upper isotherm is in the pressure region 0 to 10 GPa and the lower one in the region 0 to 80 GPa. ○, experiment (after [19]); ▽, experiment (after [20]); ●, CPMD (Lennard-Jones 6–12); ▲, CPMD (exp–6 [20]).

- 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 electronic properties and may or may not be relevant depending on what kind of materials and properties are studied.

- **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.

  - 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...

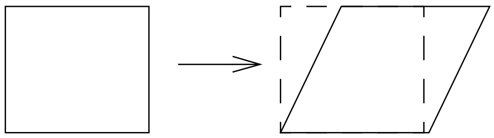
  - A good way to test the minimum energy: start from random atom positions, and quench the cell slowly enough so that it crystallizes. If the structure is the correct one, it probably is indeed the ground state. Unfortunately doing this may take forever.

    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}

- **Cohesive energy** (E_{coh} = energy difference between free atoms and the solid):

  = the minimum potential energy in the solid (except for sign difference)

  - Often easy to get right exactly



- **Elastic constants** $c_{\rho\sigma}$

  - Related to structural changes in the material

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

  and to the external stress (pressure) σ:

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

  (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

  $$e_{ii} = \frac{\partial u_i}{\partial x_i} \ ; \ e_{ij} = \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}$$

  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 $c_{44} = c_{xyxy}$.

  [Kittel, “Introduction to solid state physics”, 7th edition, ch. 3.]

  - 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 *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] = Voter	ref. [14] = Foi
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^f_{vac} (eV)	0.66 (d)	0.69	0.63	0.62
E^m_{vac} (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
$(1/a)(da/dT)(10^{-5}\,K^{-1})$	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.

- This is probably the best potential for Al, but even in this one, problems have been reported recently for certain surface properties.

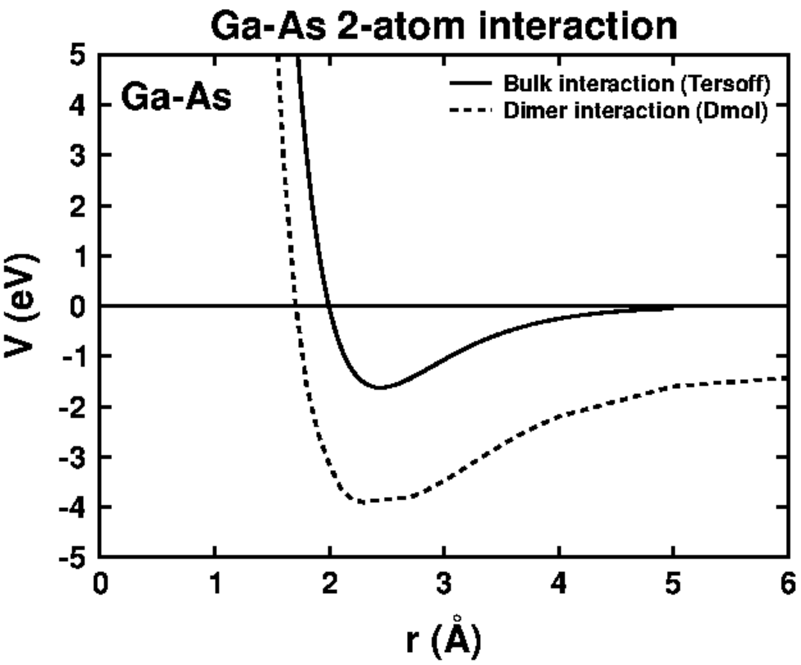
Weaknesses of pair potentials

- 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 [J. Moriarty, 1998, private communication].

- 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.

  - For instance the Ga-As interaction:



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

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.

- Also, vacancy formation energies are often completely wrong in pair potentials.

- 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

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