

Introducción a la asignatura de Computación Avanzada

Grado en Física

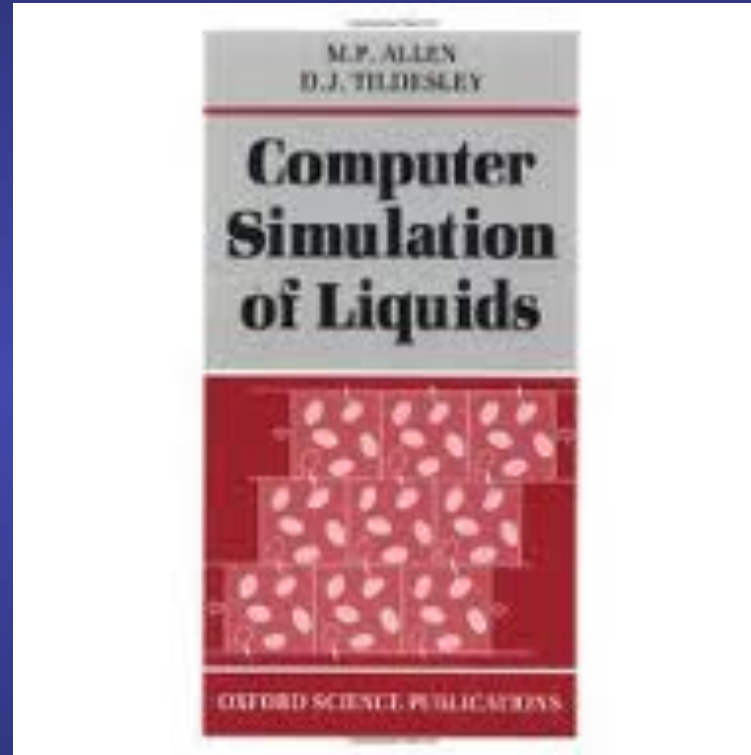
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Datos identificativos de la asignatura

1. DATOS IDENTIFICATIVOS DE LA ASIGNATURA	
Título/s	Grado en Física (Optativa)
Centro	Facultad de Ciencias
Módulo / materia	MATERIA COMPUTACIÓN AVANZADA MENCION FISICA APLICADA TODAS LAS OPTATIVAS MENCION FISICA FUNDAMENTAL TODAS LAS OPTATIVAS OPTATIVAS TRANSVERSALES G-FISICA
Código y denominación	G80 - Computación Avanzada
Créditos ECTS	6
Curso / Cuatrimestre	CUATRIMESTRAL (1)
Web	http://www.ctr.unican.es/asignaturas/Computacion_Avanzada_4_F/
Idioma de impartición	Inglés
Forma de impartición	Presencial

Bibliography:



**M. P. Allen and D. J. Tildesley
Computer Simulation of Liquids
Oxford Science Publications
ISBN 0 19 855645 4**

How to reach me

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In the web page, you can find:

- The program of the course
- Slides of the different lecture
- The code implementing the simulation of a liquid interacting via a Lennard-Jones potential

Office hours:

- At the end of each lecture
- At any moment, under request by e-mail

Physical problem to be solved during this course

Given a set of N classical particles (atoms or molecules)

whose microscopic state may be specified in terms of:

- positions \vec{q}_i
- momenta \vec{p}_i

Note that the classical description has to be adequate. If not we can not specify at the same time the coordinates and momenta of a given molecule

and whose Hamiltonian may be written as the sum of kinetic and potential energy functions of the set of coordinates and momenta of each molecule i

$$\vec{q} = (\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$$

$$\vec{p} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N)$$

$$\mathcal{H}(\vec{q}, \vec{p}) = \mathcal{K}(\vec{p}) + \mathcal{V}(\vec{q})$$

$$\mathcal{K}(\vec{p}) \equiv \text{kinetic energy}$$

$$\mathcal{V}(\vec{q}) \equiv \text{potential energy}$$

Solve numerically in the computer the equations of motion which governs the time evolution of the system and all its mechanical properties

Physical problem to be solved during this course

In particular, we will simulate numerically the evolution with time of N classical particles interacting via a two-body potential (the Lennard-Jones potential)

Why molecular dynamics?

Why Lennard-Jones potential?

Advantages

It allows to solve time dependent problems:

- Reactions
- Collisions
- Diffusion
- Growth
- Vibrations
- Fractures
- Radiation damage
- ...

Standard two-body effective pair potential

Well known parameters for many elements

Provides reasonable description of closed shells atoms (such as inert gases)

It is more parallelizable than other methods, such as Monte Carlo techniques

Disadvantages

More complex (differential equations)

Less adaptable

Ergodicity problems

It require forces

Note about the generalized coordinates

May be simply the set of cartesian coordinates \vec{r}_i of each atom or nucleus in the system

Sometimes it is more useful to treat the molecule as a rigid body.

In this case, \vec{q} will consist of:

- the Cartesian coordinates of the center of mass of each molecule
- together with a set of variables $\vec{\Omega}_i$ that specify the molecular orientation

In any case, \vec{p} stands for the appropriate set of conjugate momenta

Kinetic and potential energy functions

Usually the kinetic energy \mathcal{K} takes the form

$$\mathcal{K} = \sum_{i=1}^N \sum_{\alpha} \frac{p_{i\alpha}^2}{2m_i}$$

m_i molecular mass

α runs over the different (x, y, z) components of the momentum of the molecule

The potential energy \mathcal{V} contains the interesting information regarding intermolecular interactions

Potential energy function of an atomic system

Consider a system containing N atoms.

The potential energy may be divided into terms depending on the coordinates of individual, pairs, triplets, etc.

Expected to be small

$$\mathcal{V} = \sum_i v_1(\vec{r}_i) + \underbrace{\sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)}_{\text{Particle interactions}} + \dots$$

One body potential

$$v_1(\vec{r}_i)$$

One body potential
Represents the effect of an external field (including, for example, the contained walls)

Particle interactions

$$v_2(\vec{r}_i, \vec{r}_j)$$

Pair potential
Depends only on the magnitude of the pair separation

$$r_{ij} = |\vec{r}_i - \vec{r}_j|$$

The notation $\sum_i \sum_{j>i}$ indicates a summation over all distinct pairs i and j without containing any pair twice. The same care must be taken for triplets, etc.

$$v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)$$

Three particle potential
Significant at liquid densities. Rarely included in computer simulations (very time consuming on a computer)

The effective pair potential

The potential energy may be divided into terms depending on the coordinates of individual, pairs, triplets, etc.

$$\mathcal{V} = \sum_i v_1(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

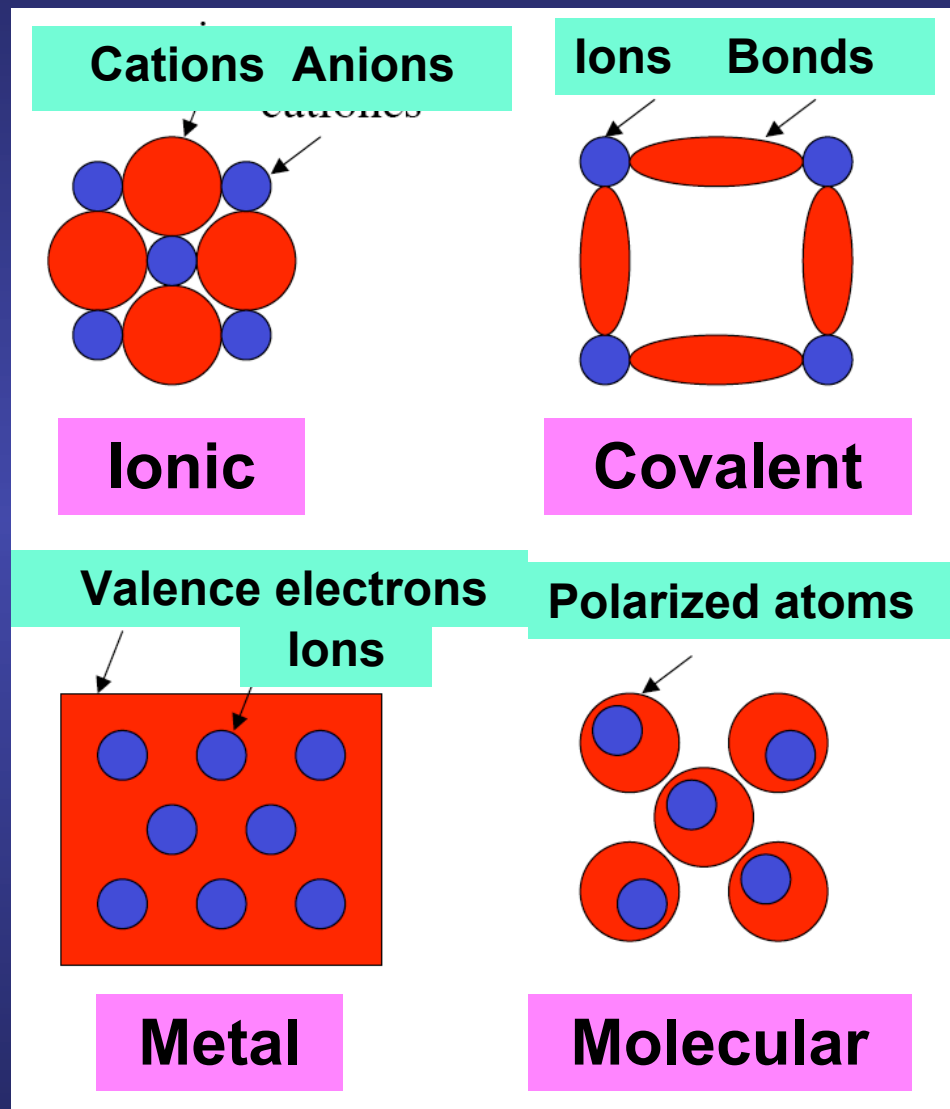
The pairwise approximation gives a remarkably good description because the **average three body effects can be partially included by defining an “effective” pair potential**

$$\mathcal{V} \approx \sum_i v_1(\vec{r}_i) + \sum_i \sum_{j>i} v_2^{\text{eff}}(r_{ij})$$

The pair potentials appearing in computer simulations are generally to be regarded as effective pair potentials of this kind, representing many-body effects

A consequence of this approximation is that the effective pair potential needed to reproduce experimental data may turn out to depend on the density, temperature, etc. while the true two-body potential does not.

Types of bonds



Types of simulations

What do we want regarding...?

The model:

- Realistic or more approximate

The energy:

- Prevalence of repulsion?
- Bonds are broken?

The scale:

- Atoms?
- Molecules?
- Continuum?

Example of ideal effective pair potentials

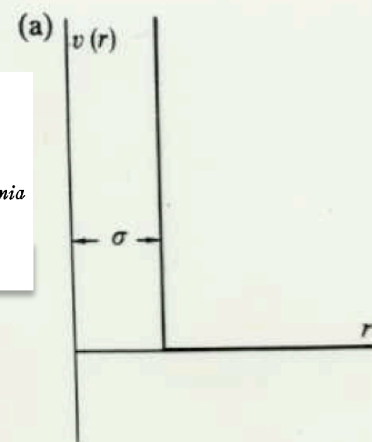
Hard-sphere potential

Phase Transition for a Hard Sphere System

B. J. ALDER AND T. E. WAINWRIGHT

University of California Radiation Laboratory, Livermore, California
(Received August 12, 1957)

J. Chem. Phys. **27**, 1208 (1957)



Discovery of non-trivial phase transitions,
not evident just looking the equations

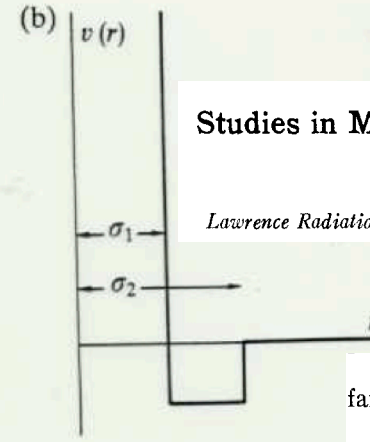
Square-well potential

Studies in Molecular Dynamics. I. General Method*

B. J. ALDER AND T. E. WAINWRIGHT

Lawrence Radiation Laboratory, University of California, Livermore, California

J. Chem. Phys. **31**, 459 (1959)



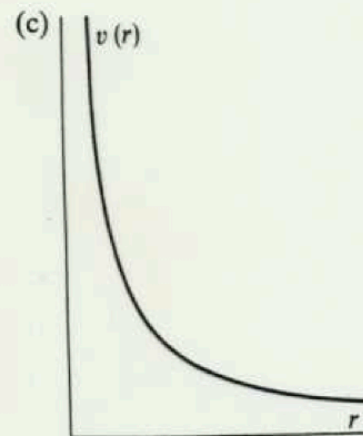
The most general interaction potential which has so far been used is the square-well potential, V ,

$$\begin{aligned} V &= \infty & r < \sigma_1 \\ V &= V_0 & \sigma_1 < r < \sigma_2 \\ V &= 0 & r > \sigma_2, \end{aligned}$$

Soft sphere potential ($\nu=1$)

$$v^{SS}(r) = \varepsilon \left(\frac{\sigma}{r} \right)^\nu = ar^{-\nu}$$

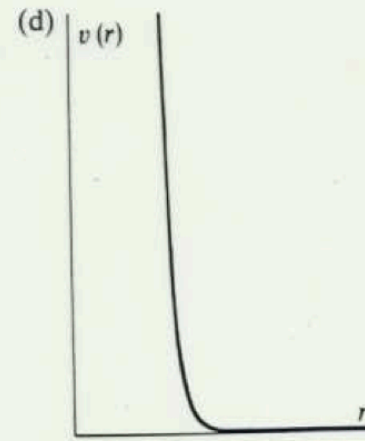
No attractive part



Soft sphere potential ($\nu=12$)

$$v^{SS}(r) = \varepsilon \left(\frac{\sigma}{r} \right)^\nu = ar^{-\nu}$$

The soft-sphere potential becomes progressively harder as ν increases



No attractive part

It is useful to divide realistic potentials in separate attractive and repulsive components

Attractive interaction

Van der Waals-London or fluctuating dipole interaction

Classical argument

C. Kittel

Introduction to Solid State Physics (3rd Edition)
John Wiley and sons

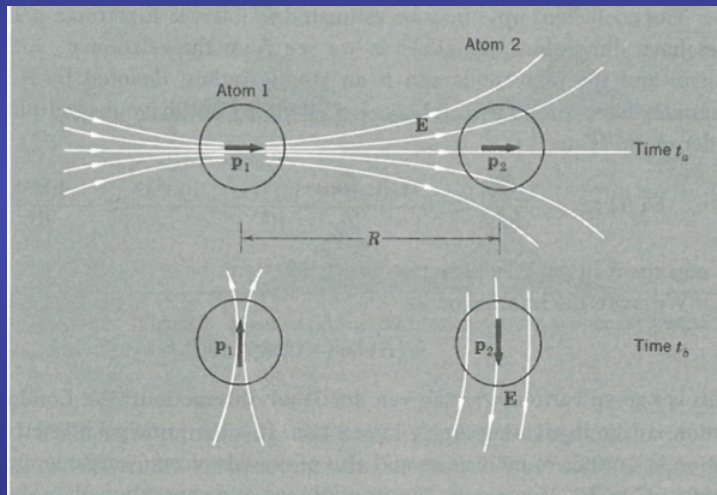


Figure 3 Origin of the van der Waals interaction, according to a classical argument. At one instant of time there is a dipole moment p_1 on atom 1. This produces an electric field E at atom 2, which acquires an induced dipole moment p_2 . Diagrams are shown for two times, t_a and t_b . The interaction is always attractive: the closer the atoms, the tighter the binding.

Electric field produced by dipole 1 on position 2

$$\vec{E}_{12} = \frac{1}{4\pi\epsilon_0} \frac{3(\vec{p}_1 \cdot \hat{r}_{12})\hat{r}_{12} - \vec{p}_1}{r_{12}^3}$$

Instantaneous dipole induced by this field on 2

$$\vec{p}_2 = \alpha_2 \vec{E}_{12} \propto \frac{1}{r_{12}^3}$$

Potential energy of the dipole moment

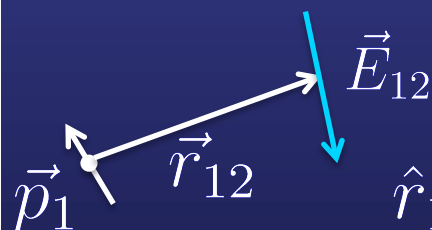
$$U_{12} = -\vec{p}_2 \cdot \vec{E}_{12} \propto -E_{12}^2 \propto -\frac{1}{r_{12}^6}$$

$$U(R) = -\frac{C}{R^6}$$

Always attractive

J. D. Jackson

Classical Electrodynamics (Chapter 4)
John Wiley and Sons



\hat{r}_{12} Is the unit vector directed from 1 to 2

It is useful to divide realistic potentials in separate attractive and repulsive components

Attractive interaction

Van der Waals-London or fluctuating dipole interaction

Quantum argument

Hamiltonian for a system of two interacting oscillators

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + \Delta\mathcal{H}_{12}$$

Where the perturbative term is the dipole-dipole interaction

$$\Delta\mathcal{H}_{12} = \frac{\vec{p}_1 \cdot \vec{p}_2 - 3(\vec{n} \cdot \vec{p}_1)(\vec{n} \cdot \vec{p}_2)}{r_{12}^3}$$

From first-order perturbation theory, we can compute the change in energy

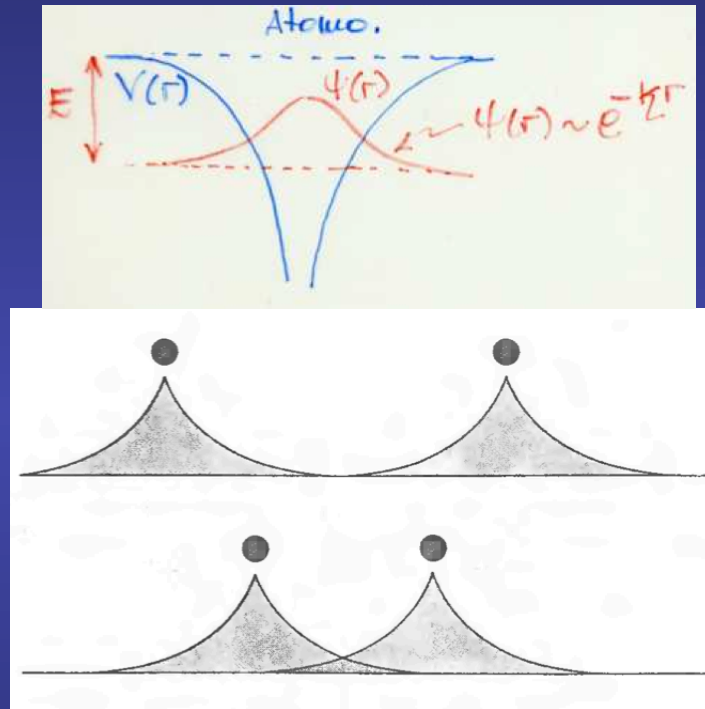
$$\Delta E \simeq \sum_n \frac{|\langle \psi_n | \Delta\mathcal{H}_{12} | \psi_0 \rangle|^2}{E_0 - E_n} \propto -\frac{1}{r_{12}^6}$$

C. Kittel

Introduction to Solid State Physics (3rd Edition)
John Wiley and sons

It is useful to divide realistic potentials in separate attractive and repulsive components

Repulsive interaction



$$\kappa = \frac{\sqrt{2mE}}{\hbar}$$

As the two atoms are brought together, their charge distribution gradually overlaps, changing the energy of the system. The overlap energy is repulsive due to the

Pauli exclusion principle:
No two electrons can have all their quantum numbers equal

When the charge of the two atoms overlap there is a tendency for electrons from atom B to occupy in part states of atom A already occupied by electrons of atom A and viceversa.

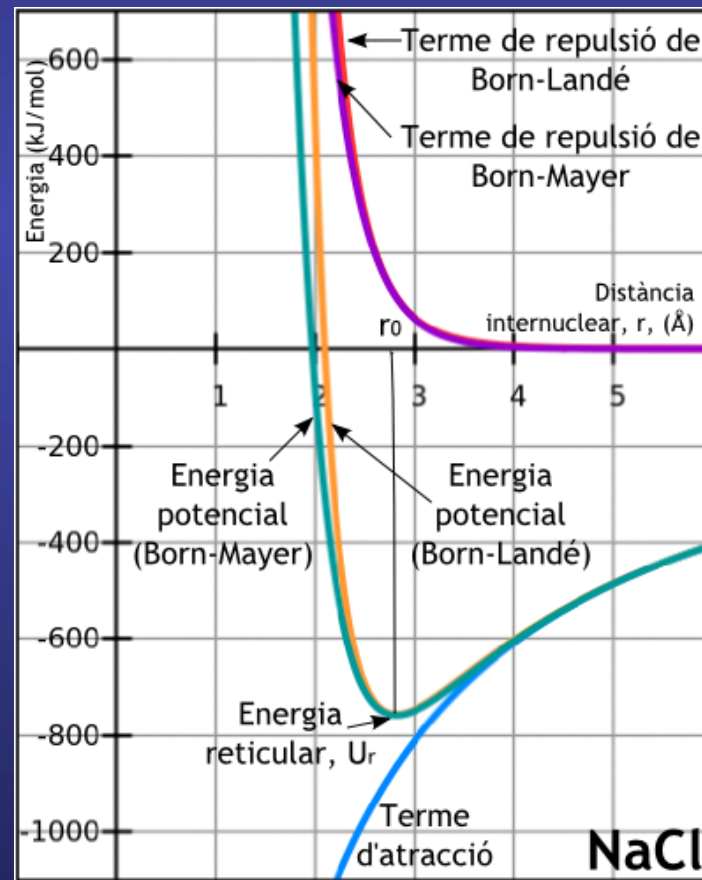
Electron distribution of atoms with closed shells can overlap only if accompanied by a partial promotion of electrons to higher unoccupied levels

Electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction

The repulsive interaction is exponential

Born-Mayer potential

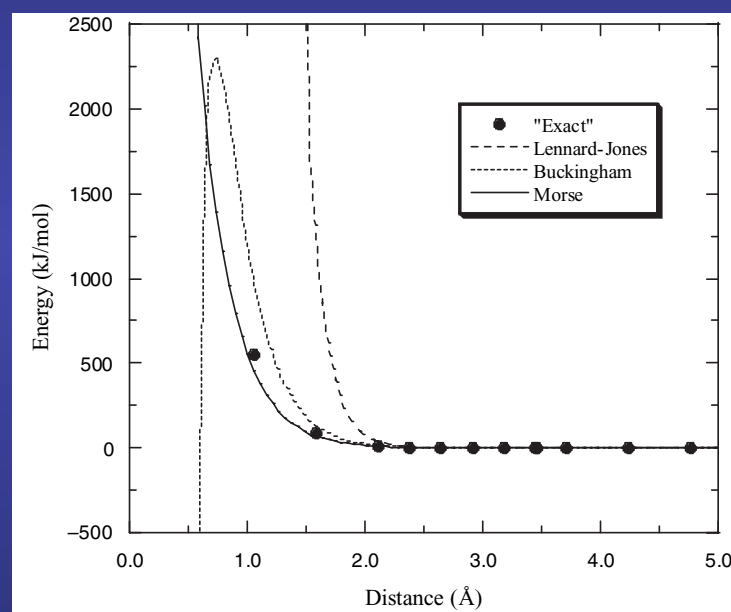
$$V(r) = Ae^{-\lambda r}$$



It is useful to divide realistic potentials in separate attractive and repulsive components

Buckingham potential

$$V(r) = Ae^{-\lambda r} - Cr^{-6}$$



F. Jensen
Introduction to Computational Chemistry
John Wiley and Sons

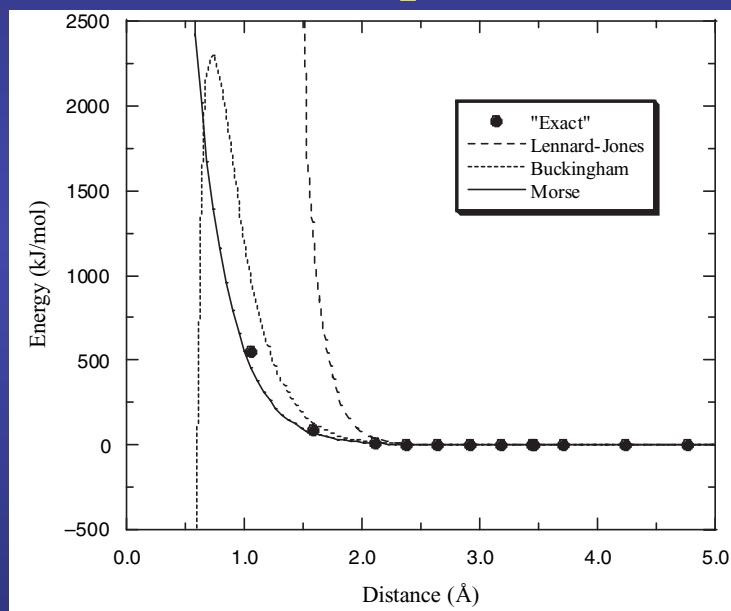
Because the exponential term converges to a constant as $r \rightarrow 0$, while the r^{-6} term diverges, the Buckingham potential “turns over” as r becomes small.

This may be problematic when dealing with a structure with very short interatomic distances

It is useful to divide realistic potentials in separate attractive and repulsive components

Lennard-Jones potential

$$v^{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



F. Jensen
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The repulsive term has no theoretical justification. It is used because it approximates the Pauli repulsion well, and is more convenient due to the relative computational efficiency of calculating r^{12} as the square of r^6 .

Comparison of effective two body potentials

Buckingham potential

$$V(r) = Ae^{-\lambda r} - Cr^{-6}$$

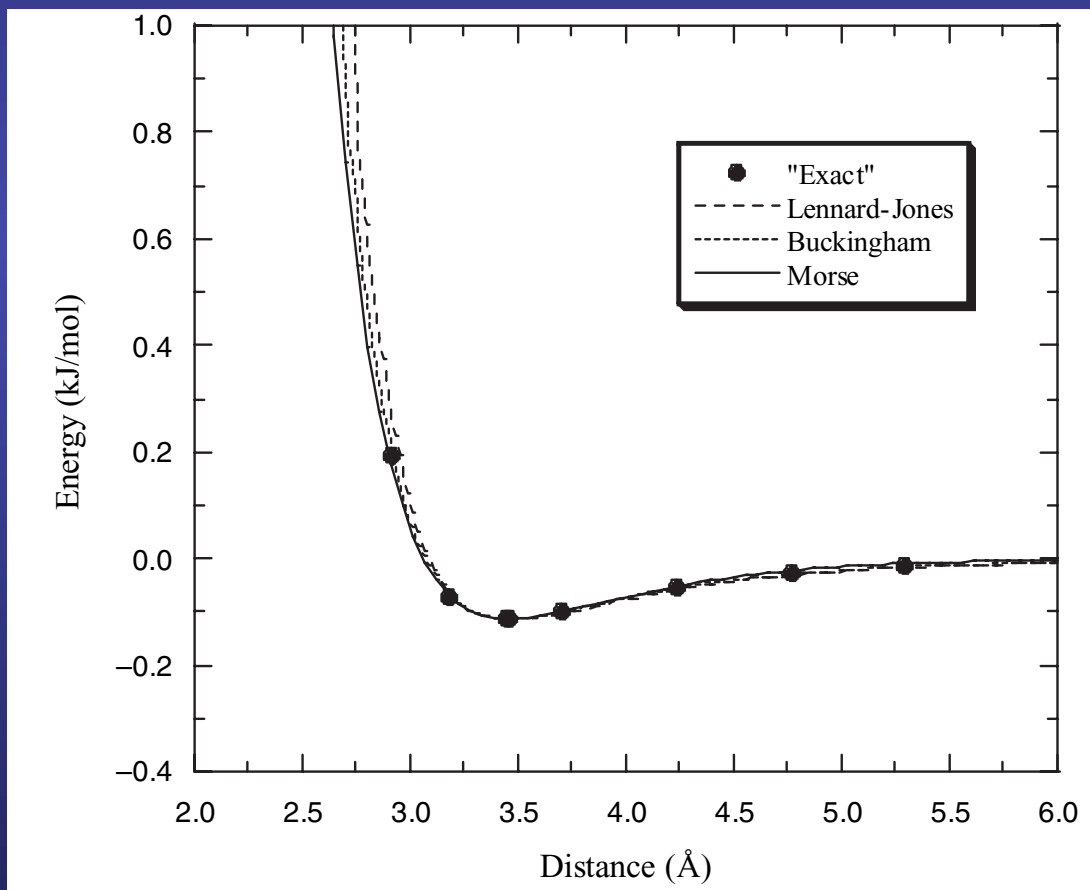
Lennard-Jones

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

Morse

$$V(r) = D_e \left(1 - e^{-\alpha(r-r_e)} \right)^2$$

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The Lennard-Jones potential

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

The well depth is often quoted as in units of temperature, $\frac{\varepsilon}{k_{\text{B}}}$, where k_{B} is the Boltzmann's constant

For instance, to simulate liquid Argon, reasonable values are:

$$\frac{\varepsilon}{k_{\text{B}}} \approx 120 \text{ K} \qquad \sigma \approx 0.34 \text{ nm}$$

We must emphasize that these are not the values which would apply to an isolated pair of argon atoms

The Lennard-Jones potential

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

The well depth is often quoted as in units of temperature, $\frac{\varepsilon}{k_{\text{B}}}$, where k_{B} is the Boltzmann's constant

Suitable energy and length parameters for interactions between pairs of identical atoms in different molecules

Table 1.1. Atom-atom interaction parameters

Atom	Source	$\varepsilon/k_{\text{B}}(\text{K})$	$\sigma(\text{nm})$
H	[Murad and Gubbins 1978]	8.6	0.281
He	[Maitland <i>et al.</i> 1981]	10.2	0.228
C	[Tildesley and Madden 1981]	51.2	0.335
N	[Cheung and Powles 1975]	37.3	0.331
O	[English and Venables 1974]	61.6	0.295
F	[Singer <i>et al.</i> 1977]	52.8	0.283
Ne	[Maitland <i>et al.</i> 1981]	47.0	0.272
S	[Tildesley and Madden, 1981]	183.0	0.352
Cl	[Singer <i>et al.</i> 1977]	173.5	0.335
Ar	[Maitland <i>et al.</i> 1981]	119.8	0.341
Br	[Singer <i>et al.</i> 1977]	257.2	0.354
Kr	[Maitland <i>et al.</i> 1981]	164.0	0.383

WARNING:

The parameters are not designed to be transferable: the C atom parameters in CS_2 are quite different from the values appropriate to a C in graphite

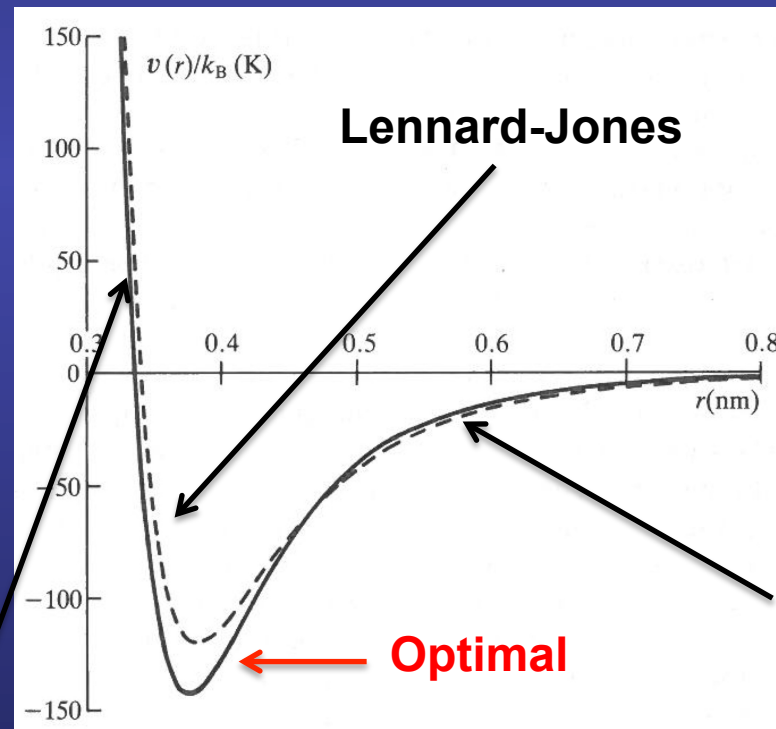
Interactions between unlike atoms in different molecules can be approximated by the **Lorentz-Berthelot mixing rules** (for instance, in CS_2)

$$\sigma_{CS} = \frac{1}{2} [\sigma_{CC} + \sigma_{SS}] \quad \varepsilon_{CS} = \sqrt{\varepsilon_{CC}\varepsilon_{SS}}$$

Is realistic the Lennard-Jones potential?

$$v^{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

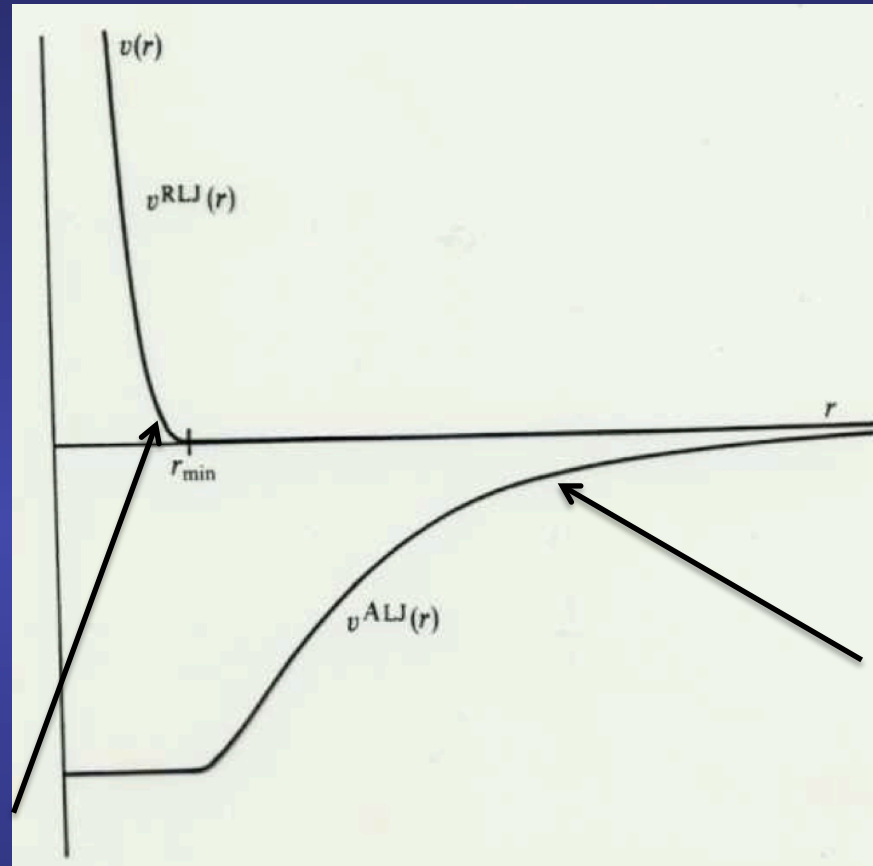
Dashed line: 12-6 effective Lennard-Jones potential for liquid Ar
Solid line: Bobetic-Barker-Maitland-Smith pair potential for liquid Ar
(derived after considering a large quantity of experimental data)



Steeply rising repulsive wall at short distances, due to non-bonded overlap between the electron clouds

Attractive tail at large separations, due to correlation between electron clouds surrounding the atoms. Responsible for cohesion in condensed phases

Separation of the Lennard-Jones potential into attractive and repulsive components



Steeply rising repulsive wall at short distances, due to non-bonded overlap between the electron clouds

Attractive tail at large separations, due to correlation between electron clouds surrounding the atoms. Responsible for cohesion in condensed phases

$$v^{RLJ}(r) = \begin{cases} v^{LJ}(r) + \varepsilon & r < r_{min} \\ 0 & r \geq r_{min} \end{cases}$$

$$v^{ALJ}(r) = \begin{cases} -\varepsilon & r < r_{min} \\ v^{LJ}(r) & r \geq r_{min} \end{cases}$$

Separation of the Lennard-Jones potential into attractive and repulsive components: energy scales

$$v^{\text{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$
$$= \epsilon \left[\left(\frac{r_0}{r} \right)^{12} - 2 \left(\frac{r_0}{r} \right)^6 \right]$$

$$r_0 = (2)^{1/6} \sigma \simeq 1.122\sigma$$

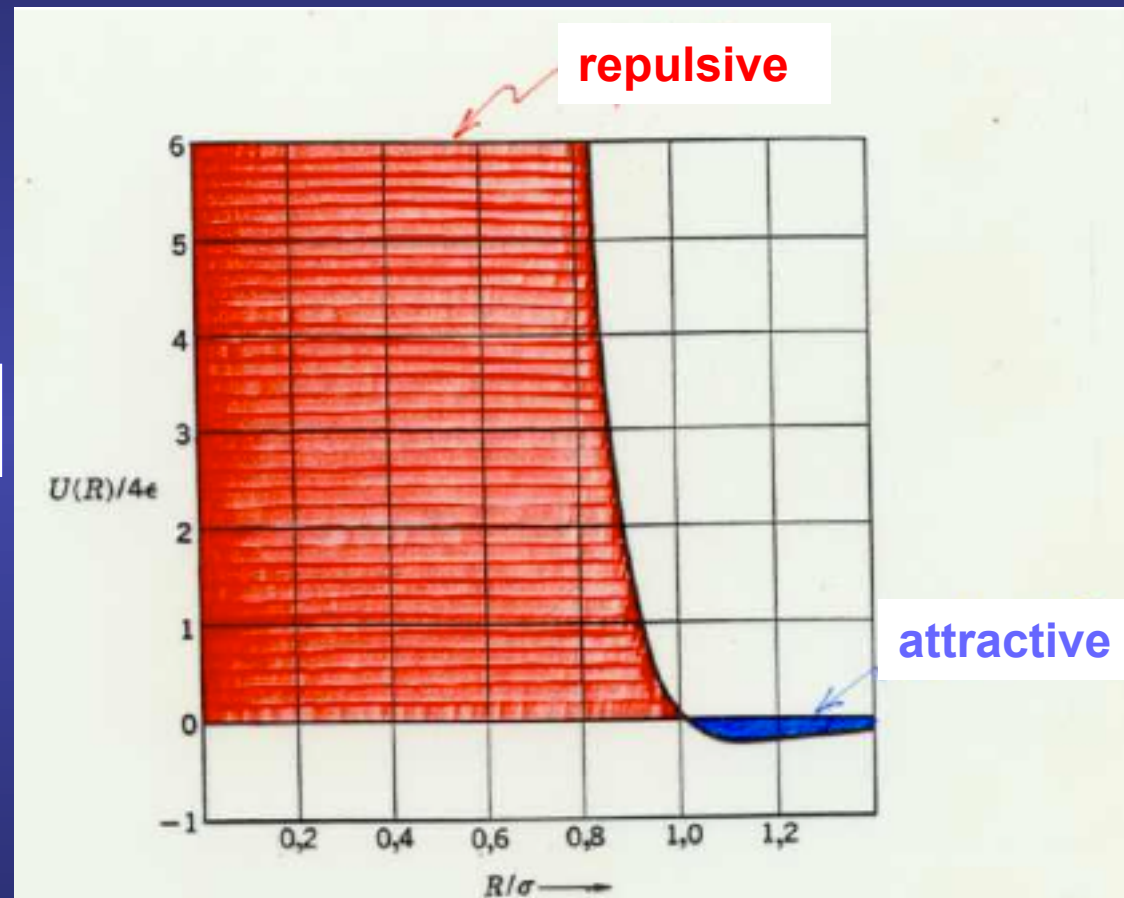


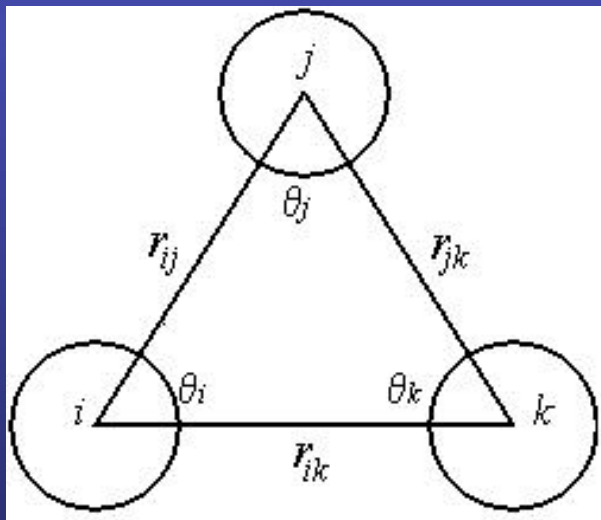
Figure 6 Form of the Lennard-Jones potential (10) which describes the interaction of two inert gas atoms. The minimum occurs at $R/\sigma = 2^{1/6} \cong 1.12$. Notice how steep the curve is inside the minimum, and how flat it is outside the minimum. The value of U at the minimum is $-\epsilon$, and $U = 0$ at $R = \sigma$.

Beyond the two body potential: the Axilrod-Teller potential

$$\mathcal{V} = \sum_i v_1(\vec{r}_i) + \sum_i \sum_{j>i} v_2(\vec{r}_i, \vec{r}_j) + \sum_i \sum_{j>i} \sum_{k>j>i} v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \dots$$

Axilrod-Teller potential:

Three body potential that results from a third-order perturbation correction to the attractive Van der Waals-London dispersion interactions



$$v_3(\vec{r}_i, \vec{r}_j, \vec{r}_k) = \nu \frac{1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k}{r_{ij}^3 r_{jk}^3 r_{ki}^3}$$

**For ions or charged particles, the long range
Coulomb interaction has to be added**

$$v^{zz}(r_{ij}) = \frac{z_i z_j}{4\pi\epsilon_0 r_{ij}}$$

**Where z_i, z_j are the charges of ions i and j ,
and ϵ_0 is the permittivity of free space**

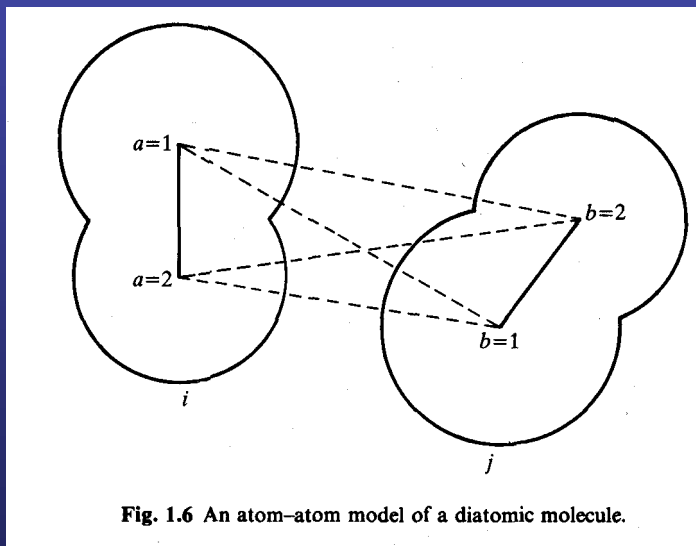
How to deal with molecular systems

Solution

Treat the molecule as a rigid or semi-rigid unit with fixed bond-lengths and, sometimes fixed bond and torsion angles

Justification

Bond vibrations are of very high frequency (difficult to handle in classical simulations), but of **low amplitude** (unimportant for many liquid properties)

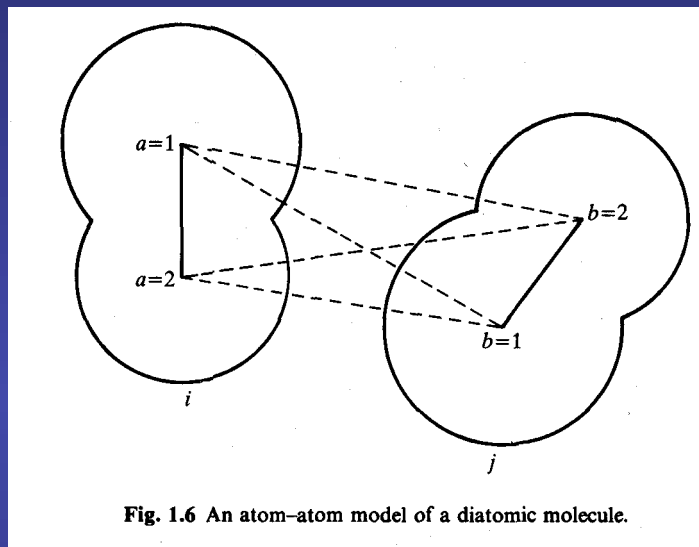


A diatomic molecule with a strongly binding interatomic potential energy surface can be simulated by a dum-bell with a rigid interatomic bond

Interaction between nuclei and electronic charge clouds of a pair of molecules

Complicated function if relative positions \vec{r}_i and \vec{r}_j and orientations $\vec{\Omega}_i$ and $\vec{\Omega}_j$

Interaction sites:
usually centered
more or less on the
position of the nuclei
in the real molecule



Simplified “atom-atom” or “site-site” approach

Pairwise contributions from distinct sites a in molecule i at position \vec{r}_{ia} ,
and site b in molecule j at position \vec{r}_{jb}

$$v(\vec{r}_{ij}, \vec{\Omega}_i, \vec{\Omega}_j) = \sum_a \sum_b v_{ab}(r_{ab})$$

Nitrogen, Fluorine,...
typically considered as
two Lennard-Jones
atoms separated by
fixed bond-lengths

Pair potential acting
between a and b

$$r_{ab} = |\vec{r}_{ia} - \vec{r}_{jb}|$$

Incorporate pole multipole moments at the center of charge to improve molecular charge distribution

Might be equal to the known (isolated molecule) variable

or

May be “effective” values chosen to give better description of the thermodynamic properties

Alternative

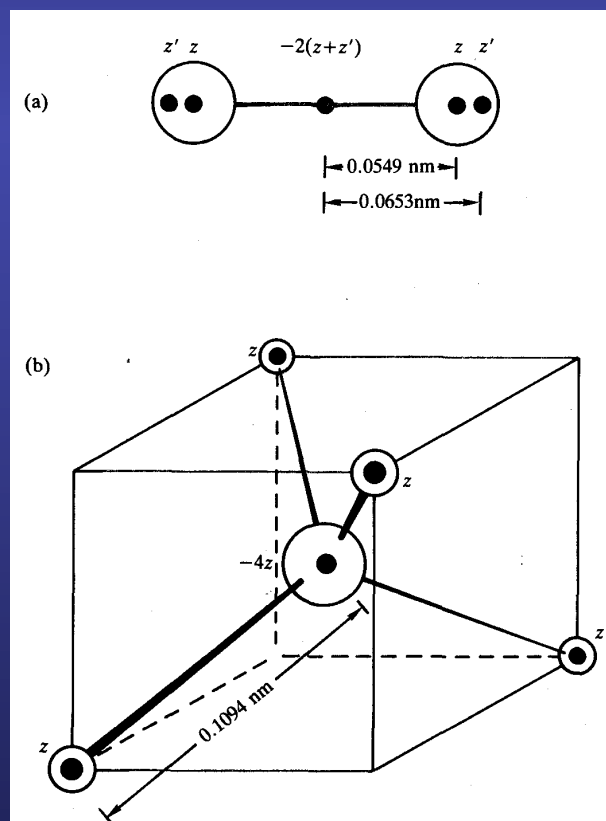
Use “partial charges” distributed in a “physically reasonable way” around the molecule to reproduce the known multipole moments

Electrostatic part of the interaction between **N₂ molecule** might be modelled using five partial charges placed along the axis

(first non-vanishing moment: quadrupole)

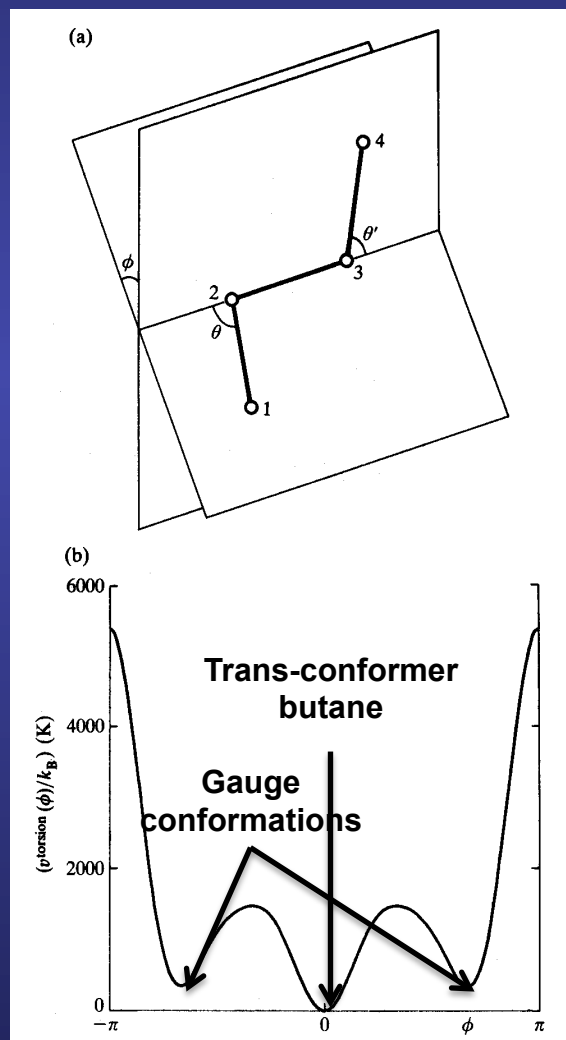
For **methane**, a tetrahedral arrangement of partial charges is appropriate

(first non-vanishing moment: octupole)



For large molecules, the complexity can be reduced by fixing some internal degrees of freedom

Model for butane:
 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$



Represent the molecule as a four-center molecule with **fixed bond-lengths** and **bond-bending angles** derived from known experimental data

Whole group of atoms (CH_3 and CH_2) are condensed into spherically symmetric effective “united atoms”

Interaction between such groups may be represented by Lennard-Jones potential with empirically chosen parameters

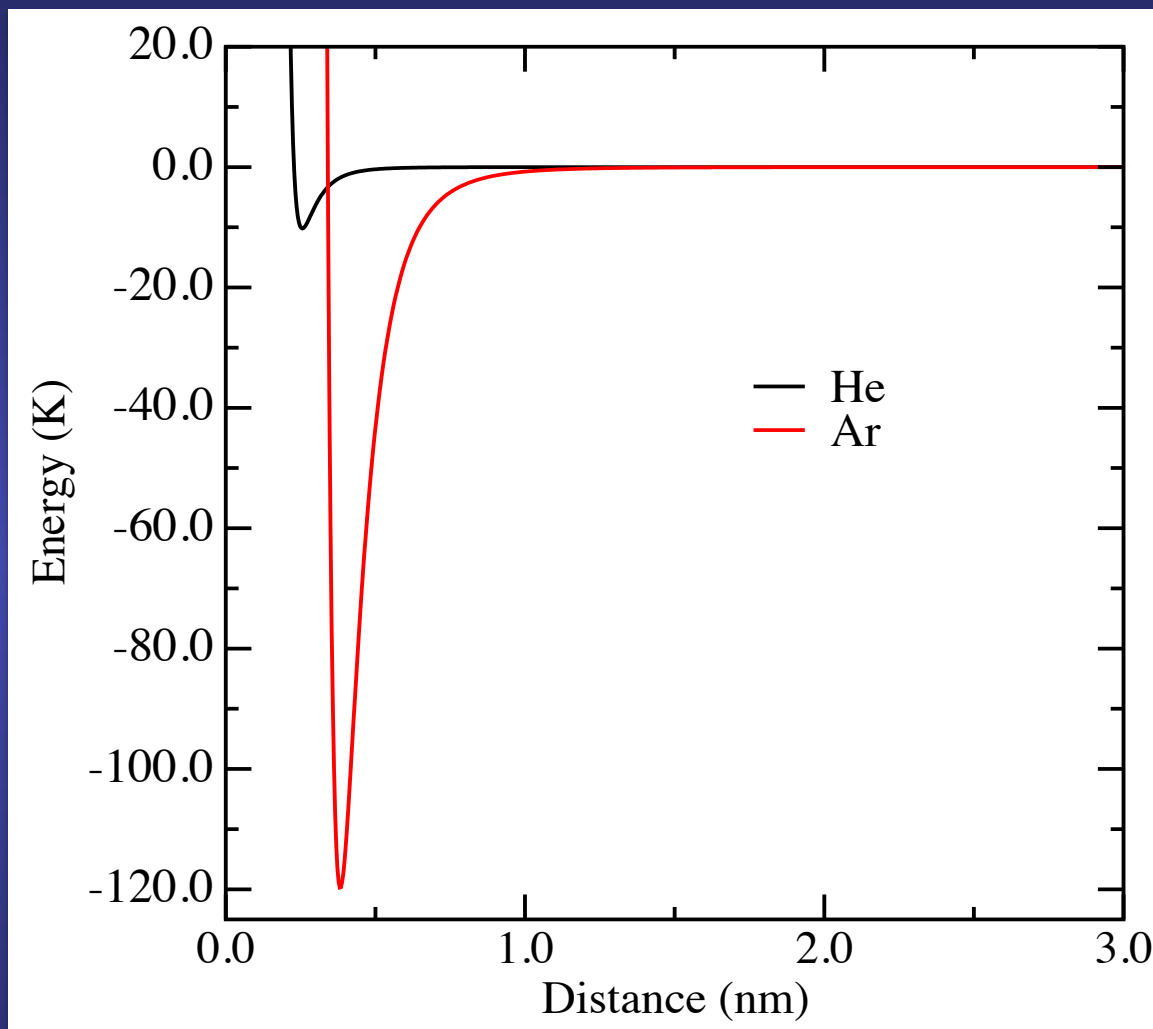
$\text{C}_1\text{-C}_2$, $\text{C}_2\text{-C}_3$, and $\text{C}_3\text{-C}_4$ bond lengths fixed

θ and θ' angles fixed (can be done by constraining the distances $\text{C}_1\text{-C}_3$ and $\text{C}_2\text{-C}_4$)

Just one internal degree of freedom is left unconstrained: the rotation about $\text{C}_2\text{-C}_3$ (the ϕ angle)

For each molecule, an extra term in the potential energy appears in the Hamiltonian $v_{\text{torsion}}(\phi)$

Reduced units



To know these critical points, should we perform two different simulations for essentially the same interatomic potential?

Lennard-Jones parameters:

- He:

$$\varepsilon/k_B = 10.2 \text{ K}$$

$$\sigma = 0.228 \text{ nm}$$

- Ar:

$$\varepsilon/k_B = 119.8 \text{ K}$$

$$\sigma = 0.341 \text{ nm}$$

The functional form is the same in both cases.

Only the parameters change

If the simulation for He predicts a phase transition at T_c^{He}

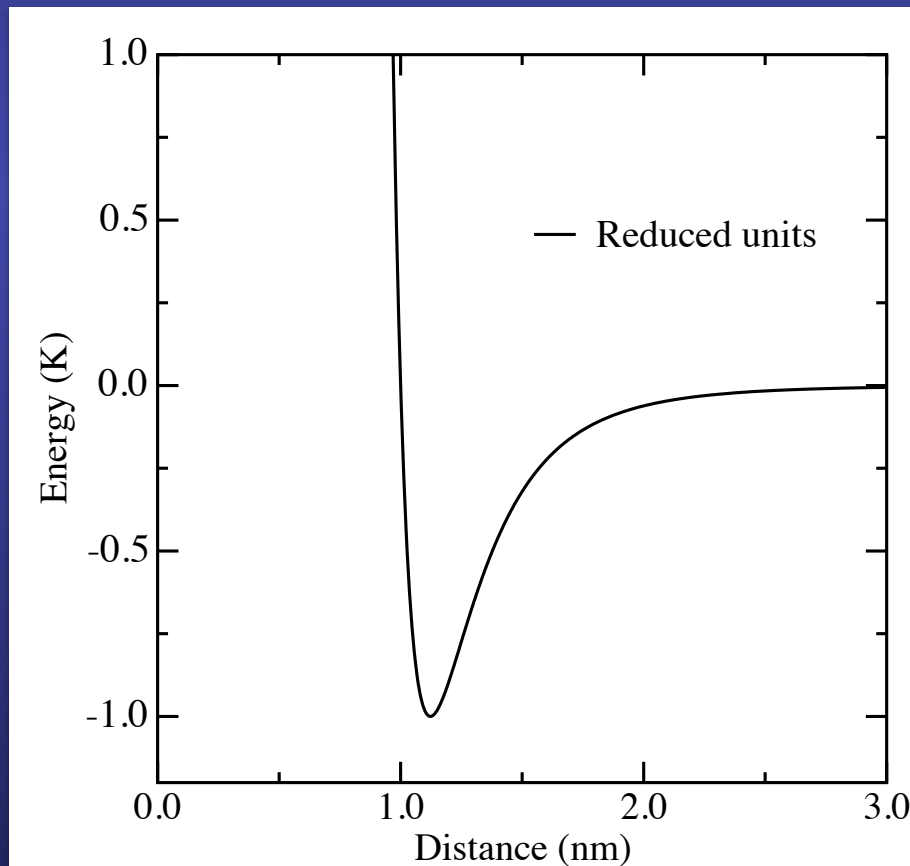
The same phase transition will occur for Ar, although at a different temperature T_c^{Ar}

The use of reduced units avoids the possible embarrassment of conducting essentially duplicate simulations

The interatomic potential is completely specified by two parameters: ϵ and σ

Take them as fundamental units for energy and length.

Units for other quantities (pressure, time, momentum,...) follow directly



density	$\rho^* = \rho\sigma^3$
temperature	$T^* = k_B T/\epsilon$
energy	$E^* = E/\epsilon$
pressure	$P^* = P\sigma^3/\epsilon$
time	$t^* = (\epsilon/m\sigma^2)^{1/2}t$
force	$\mathbf{f}^* = \mathbf{f}\sigma/\epsilon$
torque	$\boldsymbol{\tau}^* = \boldsymbol{\tau}/\epsilon$
surface tension	$\gamma^* = \gamma\sigma^2/\epsilon$

The molecular dynamic simulation is carried out only once.

The transformation from reduced to other units, will be done afterwards, taking into account the real values of ϵ and σ

Calculating the potential

```
C The potential energy will be stored in a variable V,  
C which is zeroed initially  
  V = 0.0  
  
C Outer loop begins  
DO 100 I = 1, N - 1  
  
C We assume that the coordinate vectors of our atoms  
C are stored in three FORTRAN arrays  
C RX(I), RY(I), and RZ(I),  
C with the particle index I  
C running from 1 to N (the number of particles)  
  
  RXI = RX(I)  
  RYI = RY(I)  
  RZI = RZ(I)  
  
C Inner loop begins.  
C We take care to count each pair only once  
DO 99 J = I + 1, N  
  
C Temporary variables RXI, RYI, RZI are used  
C not to make a large number of array references in the inner loop  
  RXIJ = RXI - RX(J)  
  RYIJ = RYI - RY(J)  
  RZIJ = RZI - RZ(J)  
  
  RIJSQ = RXIJ ** 2 + RYIJ ** 2 + RZIJ ** 2  
  
C For the Lennard-Jones potential, it is useful to  
C have precomputed the value of sigma^2,  
C which is stored in the variable SIGSQ  
  SR2 = SIGSQ / RIJSQ  
  SR6 = SR2 * SR2 * SR2  
  SR12 = SR6 ** 2  
  V = V + SR12 - SR6  
  
99 ENDDO  
  
100 ENDDO  
  
C The factor 4 x epsilon_0, which appears in every pair potential term,  
C is multiplied only once, at the very end, rather than many times  
C within the crucial inner loop.  
  
V = 4.0 * EPSLON * V
```

Ionic systems: the Born-Mayer potential

$$V_{ij}(r_{ij}) = A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Repulsive interaction between electronic clouds **Coulomb attraction**

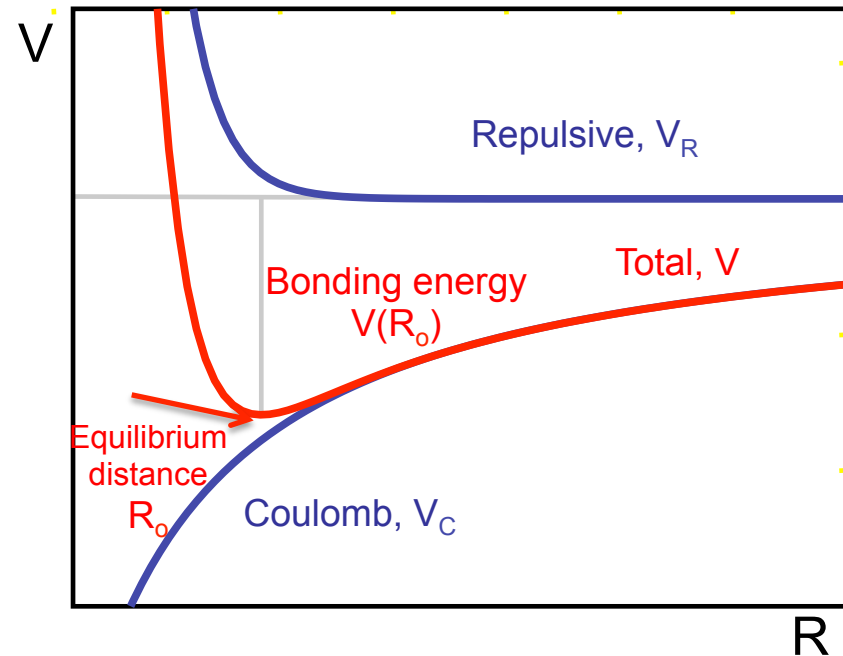
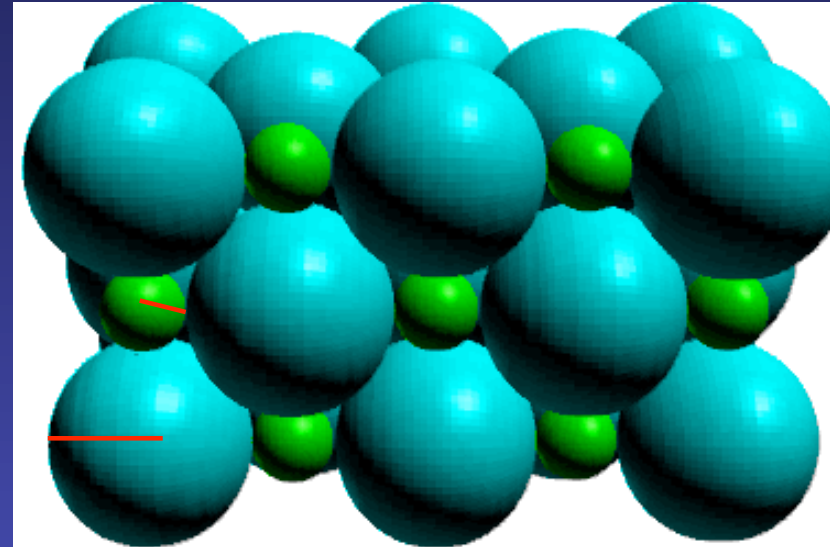
Ionic radii

$$A = A_0 \exp\left(\frac{R_i + R_j}{\rho}\right)$$

$$V_{ij}(r_{ij}) = A_0 \exp\left(-\frac{r_{ij} - R_i - R_j}{\rho}\right) - \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$

Two universal constants

$$A_0 = 0.103 \text{ eV} \qquad \rho = 0.345 \text{ \AA}$$



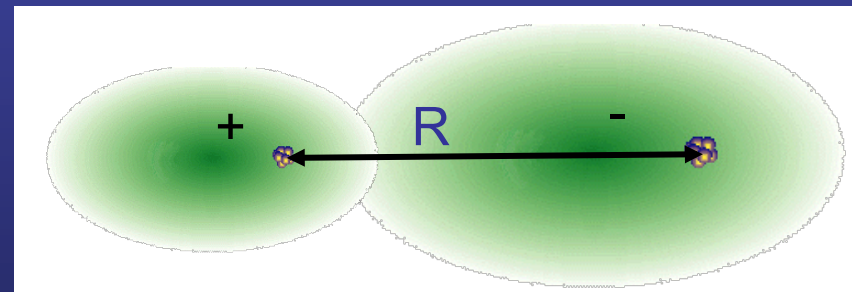
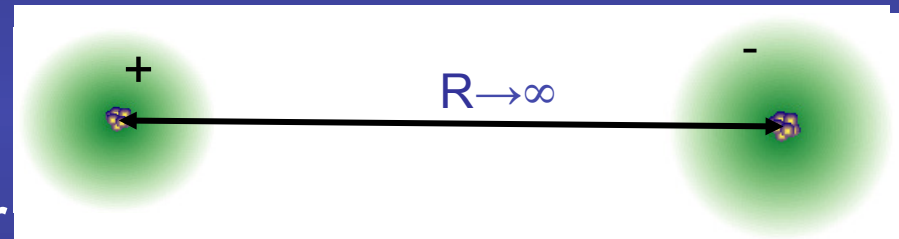
Ionic systems: the Born-Mayer potential.

Validity of the model

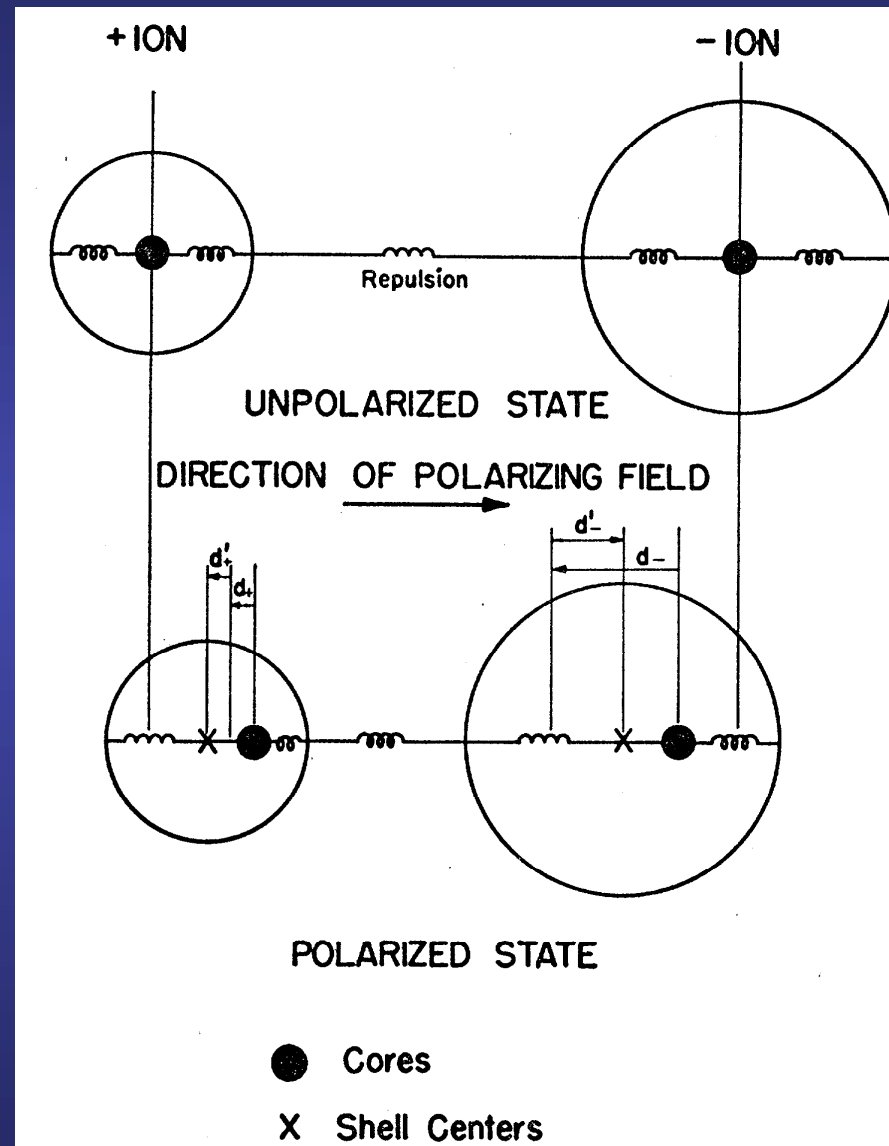
Model adequate only for **very ionic molecules**.

$V_{ij}(R_0)$ differs less than 10% from the experimental value for NaCl

- In this model, **ions** are considered **spherical**
- **Improvement**: consider possible deformations of their charge distributions (**polarizabilities**)
- With these extra polarizability terms, the errors in $V_{ij}(R_0)$ are smaller than 3%.



Shell model



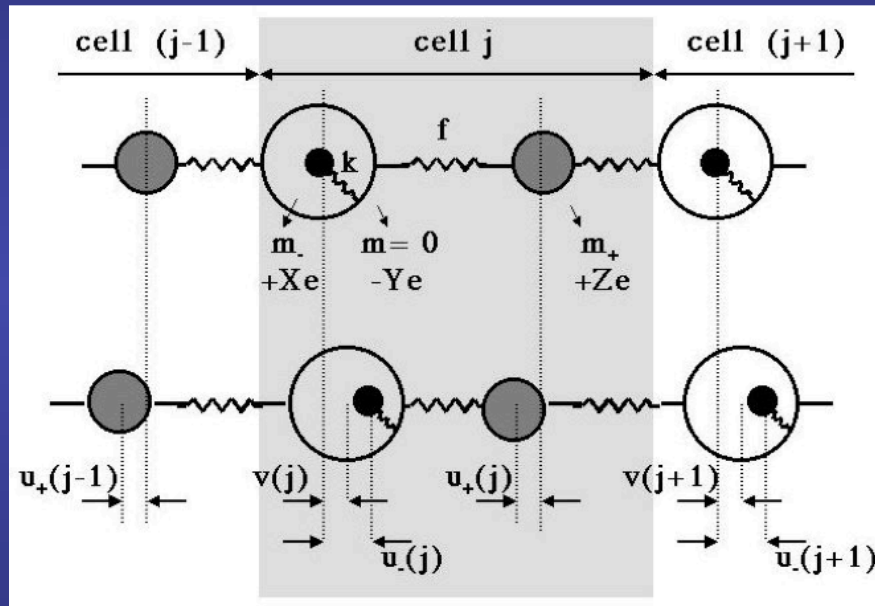
Shell model: linear chain

Courtesy of Ph. Ghosez,
Troisième Cycle de la Physique en Suisse
Romande

Each unit cell of lattice parameter a
contains two atoms:

One Cation of mass m_+ and static charge $+Z$

One Anion of mass m_- and static charge $-Z$



Anion:

Spherical atomic shell of negligible mass and
charge $-Y$ coupled to an ion core of charge $+X$
and mass m_-

Charge neutrality $X - Y = -Z$

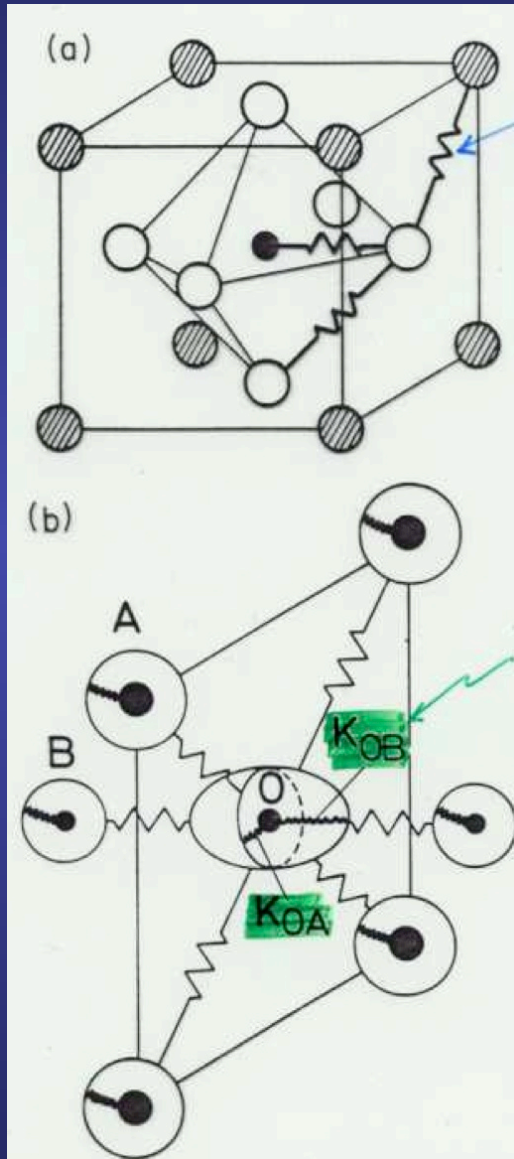
The **cation** is connected to the
anion through a string of force
constant f

The **anion core and shell** are
connected through a spring
of force constant k

For the j -th cell, the
relative displacements of
the cation, ion core and
ion-shell are respectively

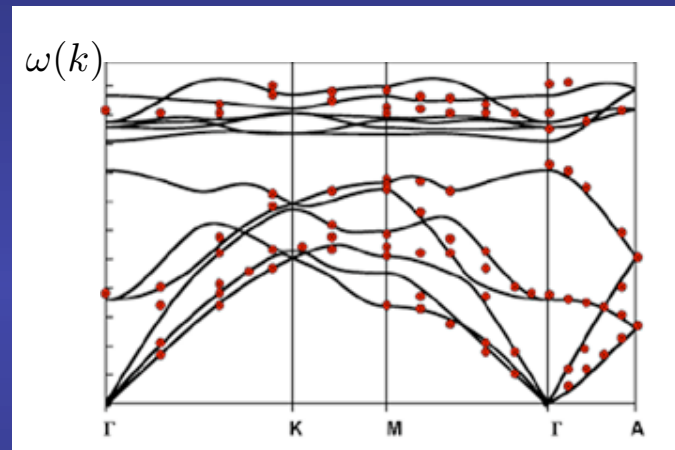
$$u_+(j), u_-(j), \text{ and } v(j)$$

Shell model



$$\frac{1}{2} f (r - r_0)^2$$

The first force constant allows to describe vibrations around an equilibrium position

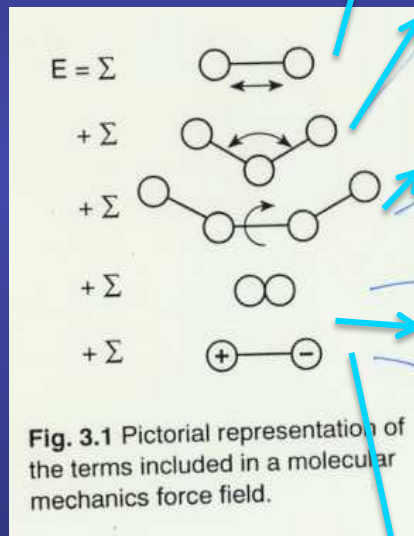


These parameters can be fitted to experiment

The second force constant, that accounts for the polarizability of the electronic cloud, acknowledges the internal structure of the atom

ABO3 perovskite

Covalent model without bond breaking



Bond stretching

Bond bending

Bond torsion

Van der Waals

Hydrogen bridge

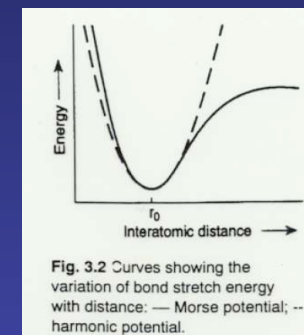
Electrostatic

$$E_l = \sum_b D_e [1 - \exp(-\alpha(l - l_0))] \quad \text{Morse potential}$$

$$E_l = \sum_b K_l (l - l_0)^2 \quad \text{Harmonic potential}$$

Morse potential

Harmonic potential



$$E_\theta = \sum K_\theta (\theta - \theta_0)^2$$

$$E_\phi = \sum_n V_n \cos(n\phi)$$

$$E_{\text{vdW}} = \sum_{i < j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

$$E_{\text{hb}} = \sum_{i < j} A_{ij} \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^{10} \right]$$

$$E_{\text{el}} = \sum_{i < j} \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}}$$