Molecular Simulation Research Projects

Intermolecular Interactions

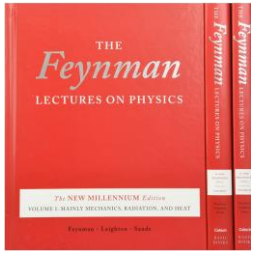
& Intramolecular

Prof Tina Düren, Dr Matthew Lennox, and Dr Carmelo Herdes

Richard Feynman, Lectures in Physics

Richard P. Feynman
Theoretical physicist

When taking over the introductory course in physics in 1961 at Caltech.



One Sentence to Be Passed on to the Next Generation

One-hour video, click here

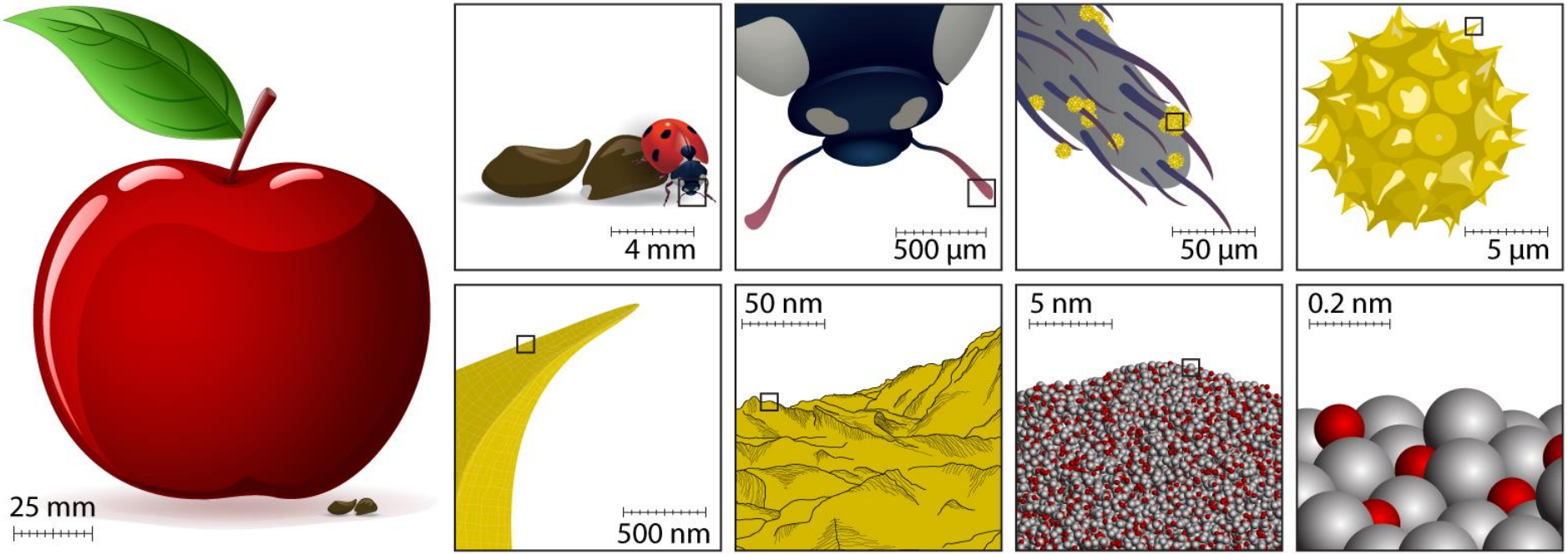
"I believe it is the atomic hypothesis *(or the atomic fact, or whatever you wish to call it)…*

…In that one sentence, you will see, there is an enormous amount of information about the world, if just a little ***imagination and thinking*** *are applied."*

…this is what this course is about!

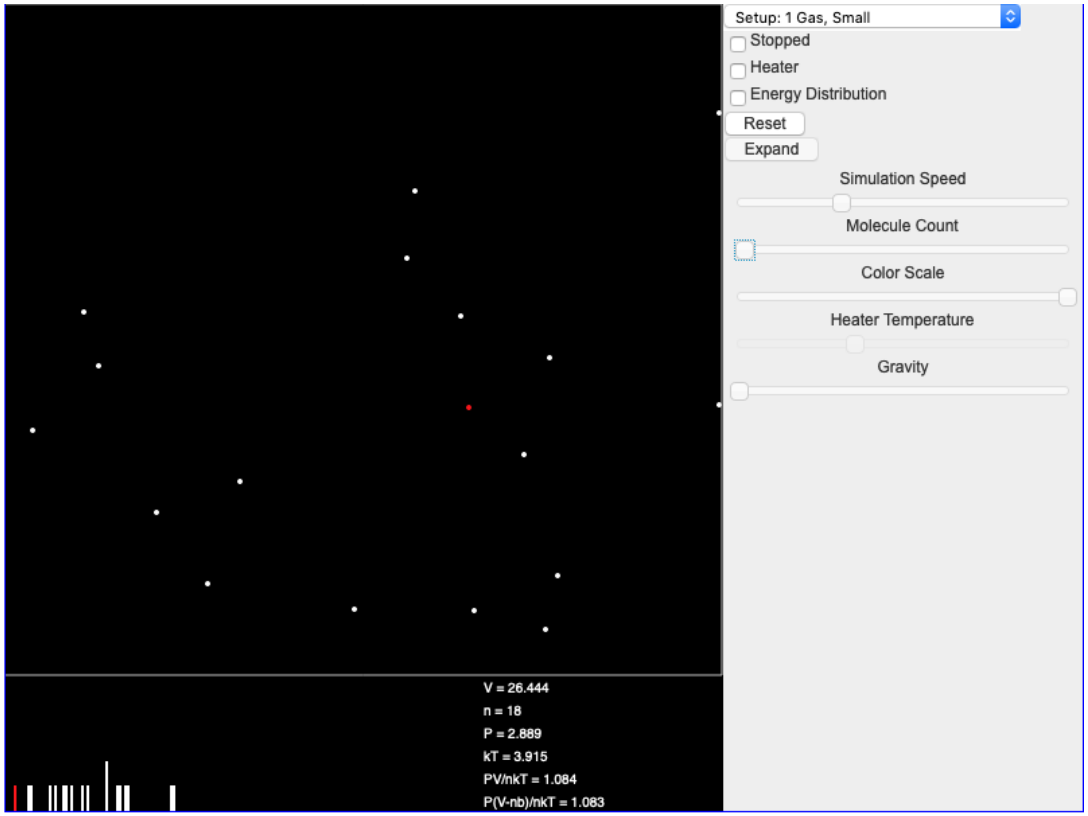
Adjusting the focus

We will look at the world from an atomistic perspective



From: http://atomsinmotion.com/book/chapter1/atoms
Website contains some really nice explanations.

Ideal gas model – no interaction



$$PV = nKT$$

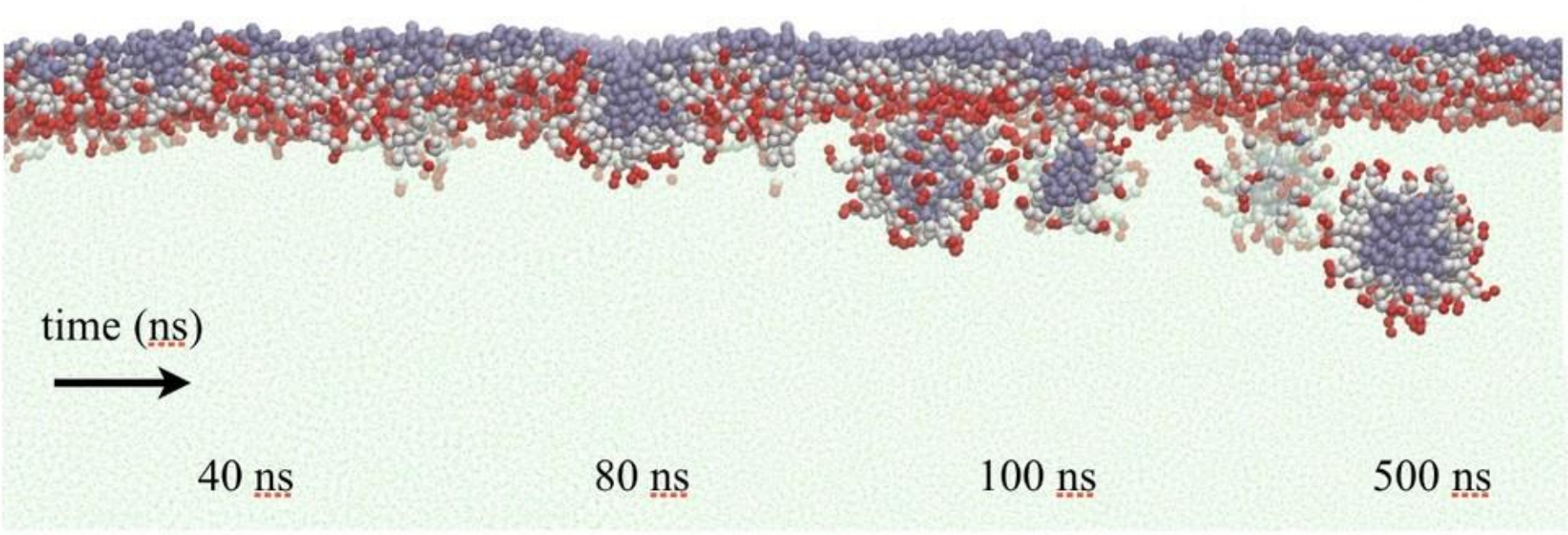
1. Point particles - no volume.
2. These particles move in random directions.
3. These particles do not interact with each other or the surroundings.

http://www.falstad.com/gas/

This simulation corresponds to a hard-sphere potential which is similar to an ideal gas.

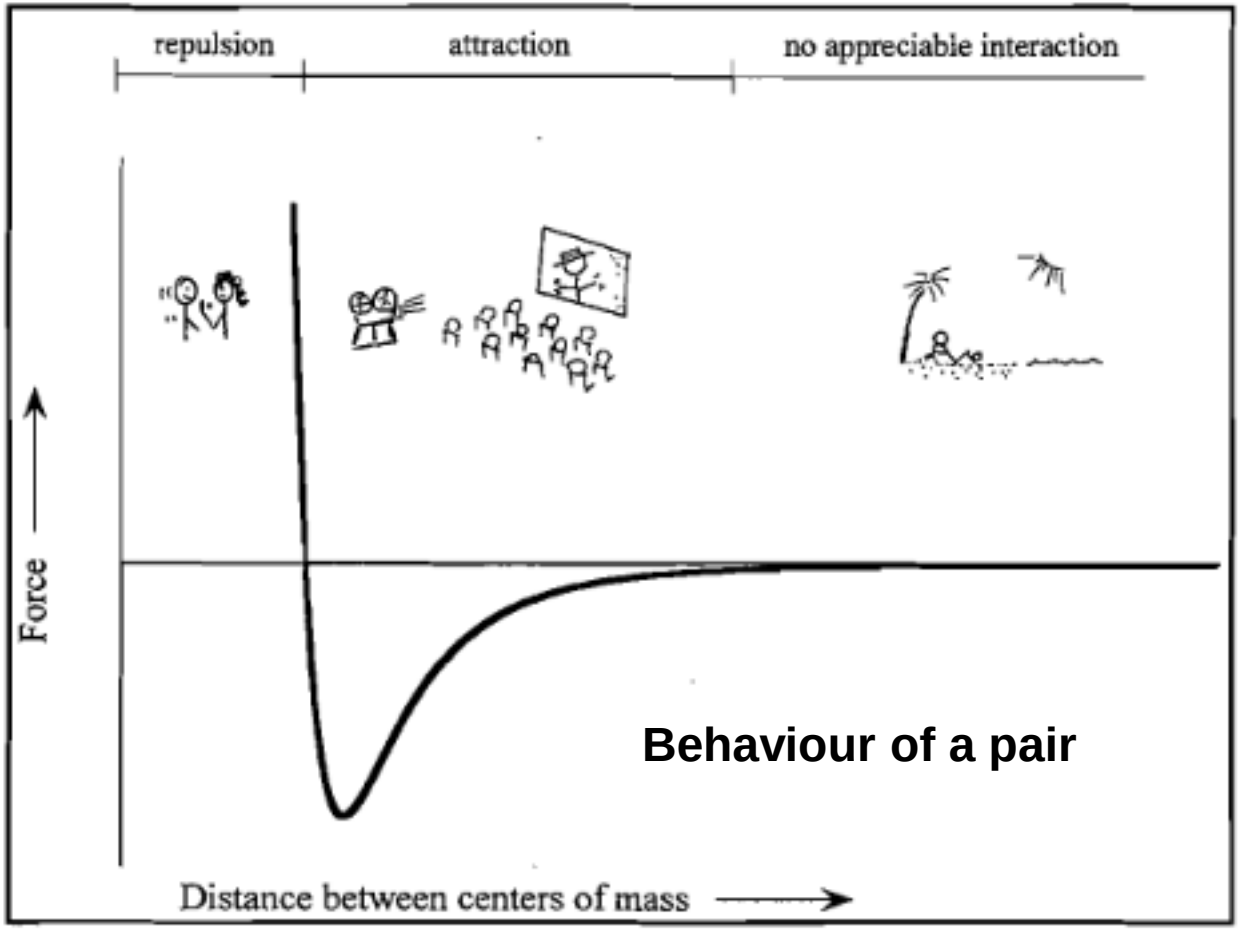
In nature molecules do interact …

Coarse-grained molecular dynamic simulation of surfactants /water/air interface

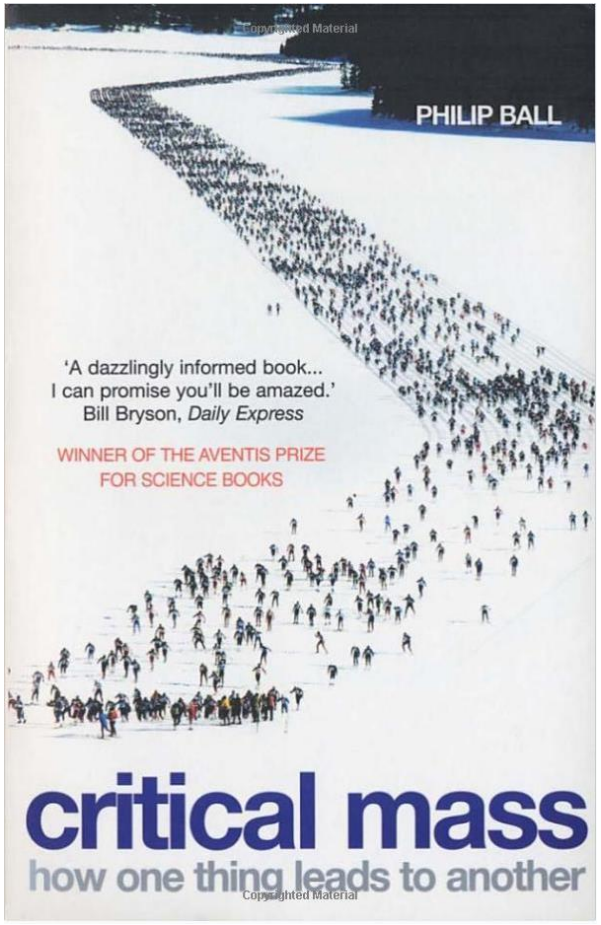


Click here for a more details about this simulation

Humans do interact …



Behaviour of a pair

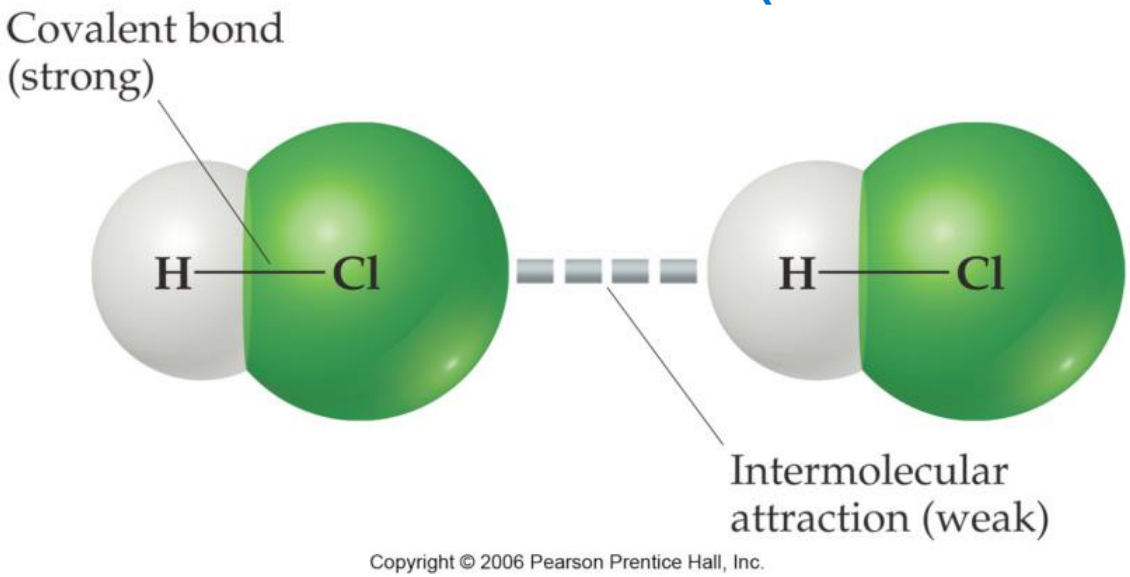


Behaviour of the collective

E.A. Müller, HUMAN SOCIETIES A Curious Application of Thermodynamics, 1998 Chemical Engineering Education 32(3):230

How to compute the energy of a system

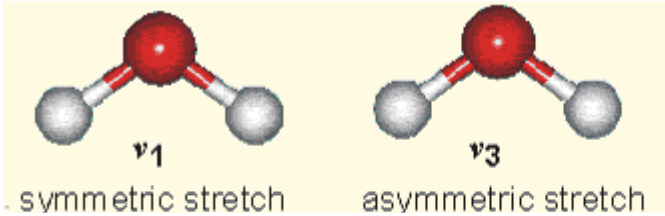
$$U_{potential} = \underbrace{U_{stretching} + U_{bending} + U_{torsion}}_{\text{Intramolecular interactions (bonded interactions)}} + \underbrace{U_{\text{van der Waals}} + U_{\text{electrostatic}}}_{\text{Intermolecular interactions (non-bonded interactions)}}$$



- U = energy. We are after the minimization of U!
- Chemical bonds are intramolecular interactions ranging from 150–1100 kJ/mol.
- Attractive and repulsive forces are intermolecular interactions ranging from 1–50 kJ/mol.

Intramolecular interactions: Bond stretching

- Often represented by simple harmonic potential



http://www1.lsbu.ac.uk/water/vibrat.html

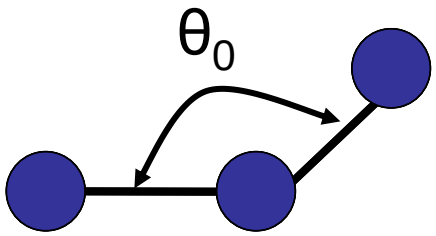
$$u_{stretch}\left(r_{ij}\right) = \frac{k_b}{2}\left(r_{ij} - r_0\right)^2$$

- Plays a big role e.g. for Infrared (or vibrational) spectroscopy of use to identify chemical substances.

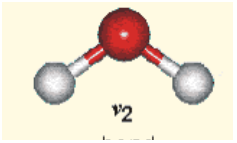
- Not on the time scale of phenomena that we are interested in (VLE, LLE, adsorption, diffusion).

Intramolecular interactions: Molecule bending

- Represented by harmonic function around equilibrium angle θ_0



$$u_{bend}\left(\theta_{ijk}\right) = \frac{k_\theta}{2}\left(\theta_{ijk} - \theta_0\right)^2$$

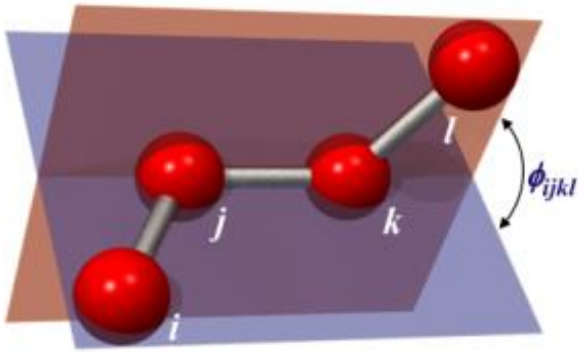


- Force constant is significantly smaller than for bond stretching.
- Bond bending is taken into account for flexible molecules with three or more (pseudo) atoms

Intramolecular interactions: Torsion

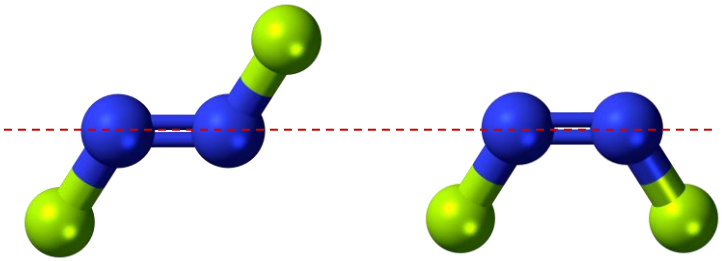
- Depends on the **dihedral angle** Φ made by the two planes incorporating the first and last three atoms involved in the torsion

$$u_{tors}\left(\phi_{ijkl}\right) = \frac{k_\phi}{2}\left(1+\cos 3\phi_{ijkl}\right)$$



Proper dihedral

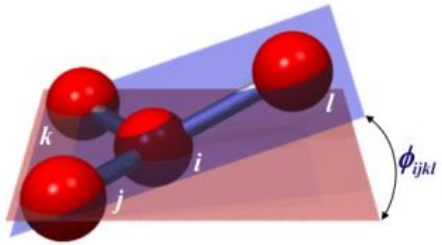
- Torsional motions are generally hundreds of times less stiff than bond stretching motions.



Trans Cis

- Needs to be taken into account for flexible molecules consisting of more than four (pseudo)atoms

Improper dihedral



Intermolecular distance

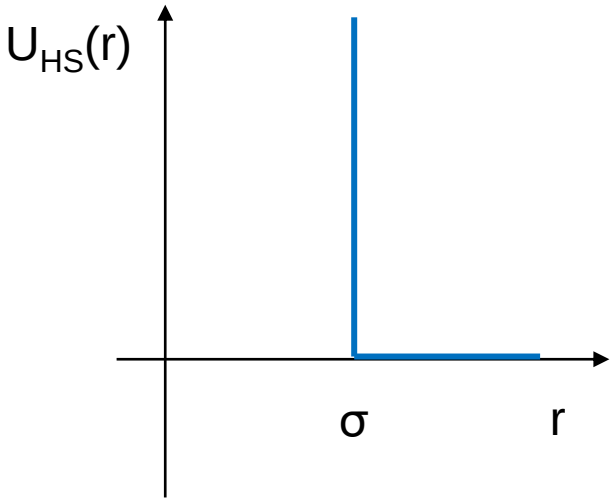
- The total potential energy is a function of the positions of all molecules of the system.
- It can be written as an infinite sum of two-body, three-body, etc. potentials.

$$U = \underbrace{\sum_{i<j} u(r_i, r_j)}_{\text{Potential between two molecules i and j}} + \underbrace{\sum_{i<j<k} \Delta u_{ijk}(r_i, r_j, r_k)}_{\text{Accounts for distortion of the pair potential due to the presence of the third molecule k.}} + \ldots$$

0

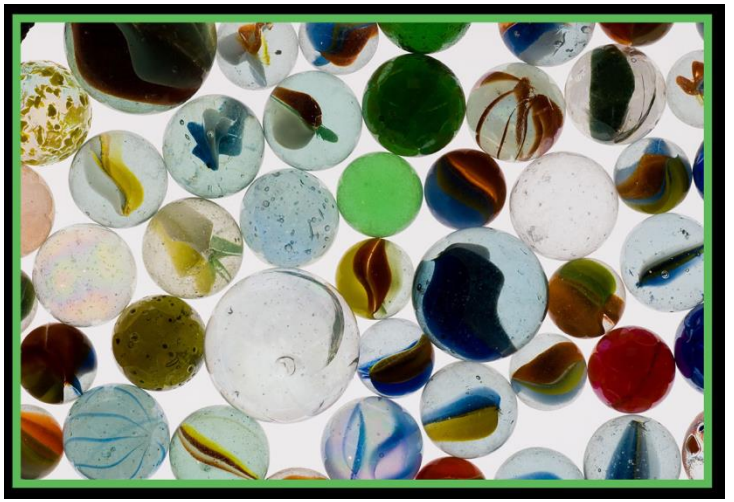
- Three-body and higher-body interactions are mostly ignored.

Hard sphere potential



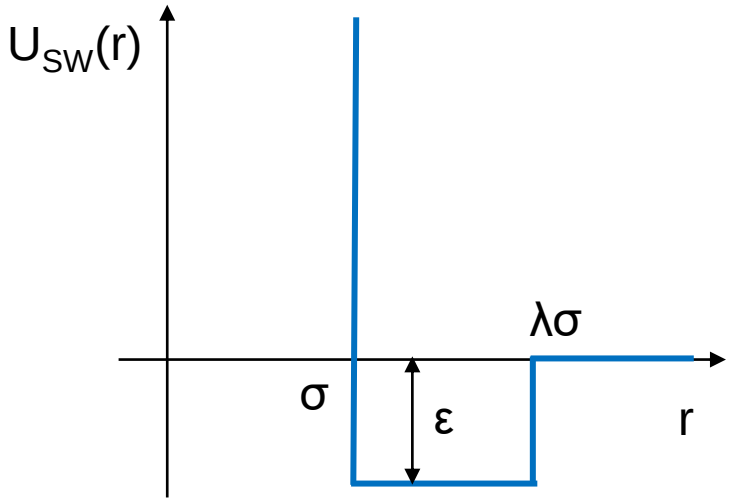
$$U_{HS} = \begin{cases} \infty & r \le \sigma \\ 0 & r > \sigma \end{cases}$$

- Simplest pair potential
- Takes volume exclusion into account (molecules can't come closer than their hard sphere diameter)
- Describes only repulsion, no attraction



http://stickly-foto.com/pages/murmeln.htm

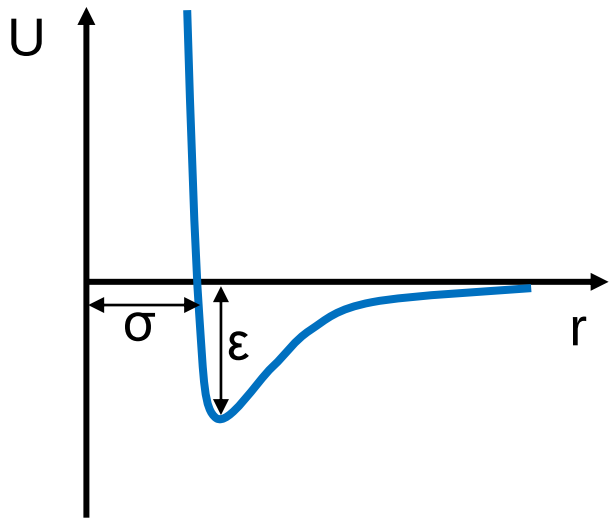
Square well potential



$$U_{SW} = \begin{cases} \infty & r \le \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & \lambda\sigma < r \end{cases}$$

- Somewhat more realistic
- Contains a region of attraction as well as the repulsive hard core.
- Although the square-well potential and the hard sphere potential are very simple they can provide valuable physical insight when used in molecular simulation.

Lennard Jones potential



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

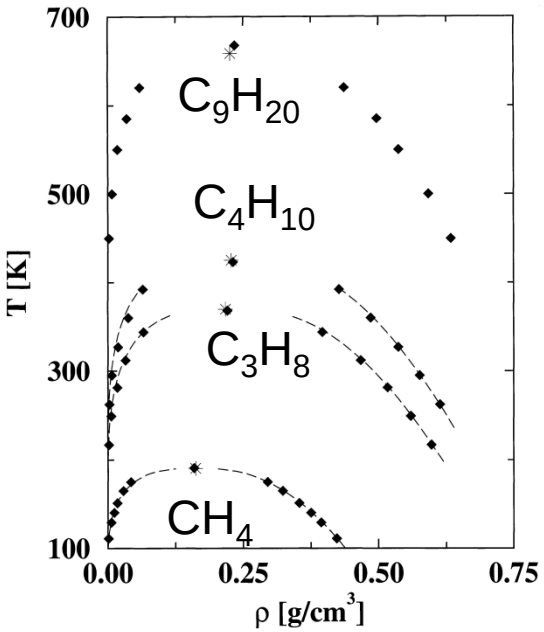
- Very realistic representation of intermolecular interaction.
- Attractive term: $1/r^6$
- Repulsive term: $1/r^{12}$

LJ parameters are fitted to exp. data

- Second virial coefficient

$$B_2(T) = -2\pi \int_0^\infty \left[\exp\left(-\frac{U(r)}{kT} \right) - 1 \right] r^2 dr$$

- Viscosity data
- Vapour Liquid Equilibria



* Exp critical point

\- Exp vapour liquid coexistence curve

◆ Simulation results

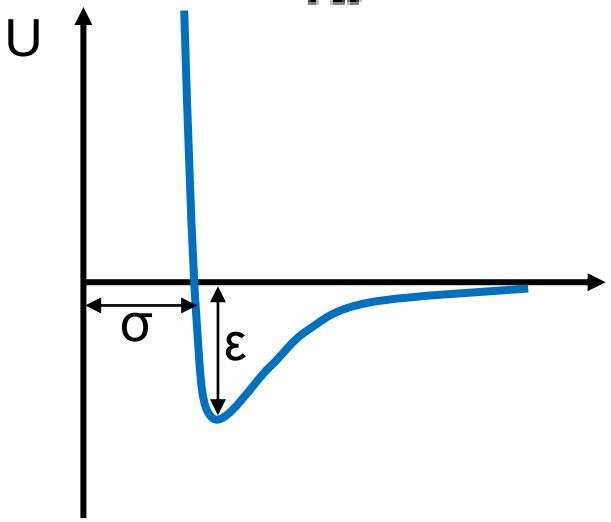
J. Phys. Chem. B, 1998, 102 (14), pp 2569–2577

Different values for LJ parameters exist

TABLE 1

Values of LJ parameters for Ar, Kr, CH_4 and N_2 from the second virial coefficient (a) and from the viscosity (b) taken from the literature.

System	σ (Å)	ϵ/k (K)	
Ar	3.504	117.7	(a)
	3.336	141.2	(a)
	3.400	122.0	(a)
	3.405	119.8	(a)
	3.465	116.0	(b)
	3.418	124.0	(b)
	3.542	93.3	(b)



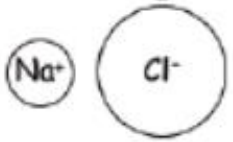
Molecular Engineering 6: 319-325, 1996.

- Always check how LJ parameters were derived and if they are appropriate for the application

Electrostatic interactions

Very strong
&
long range

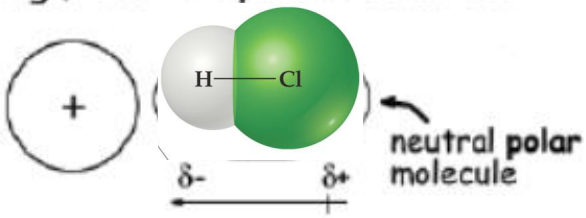
ion-ion:
opposite charges attract



$$u(R) \sim \frac{q_1 q_2}{R}$$

Strong
&
short range

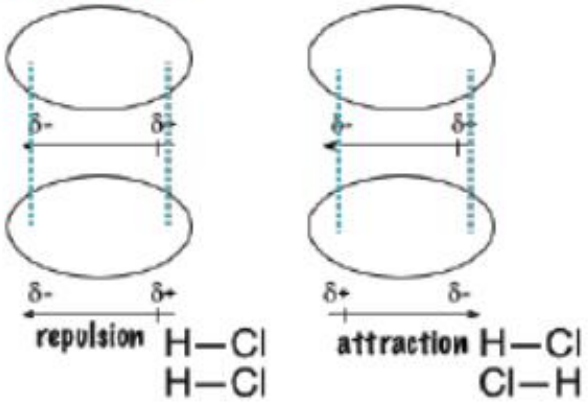
ion-dipole:
e.g., ions in aqueous solution



$$u(R) \sim \frac{q_1 \mu}{R^2}$$

Moderately strong
&
short range

dipole-dipole

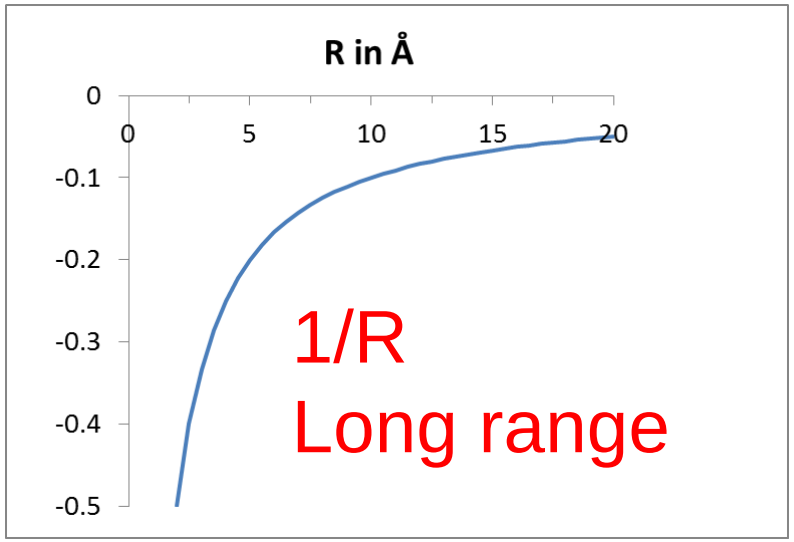


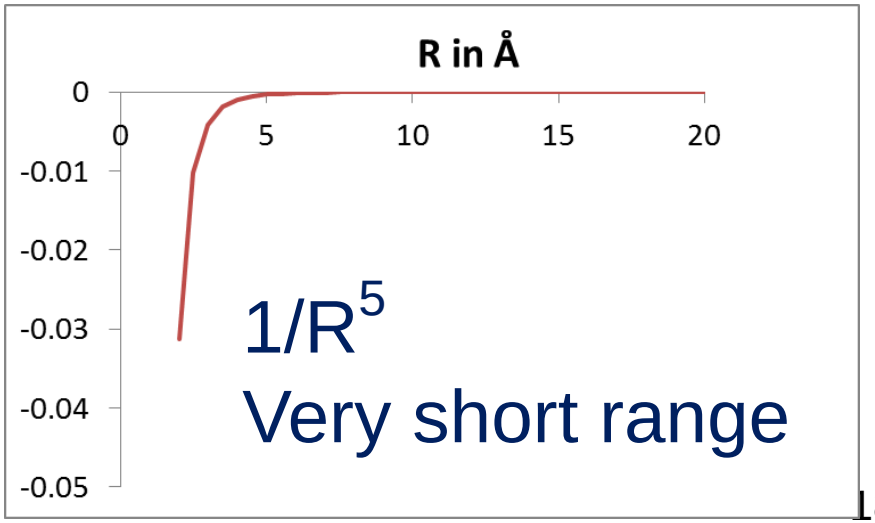
$$u(R) \sim \frac{\mu^4}{R^3}$$

q: charge on ion, μ: dipole moment

Dependence of multipole interactions on the distance between two particles

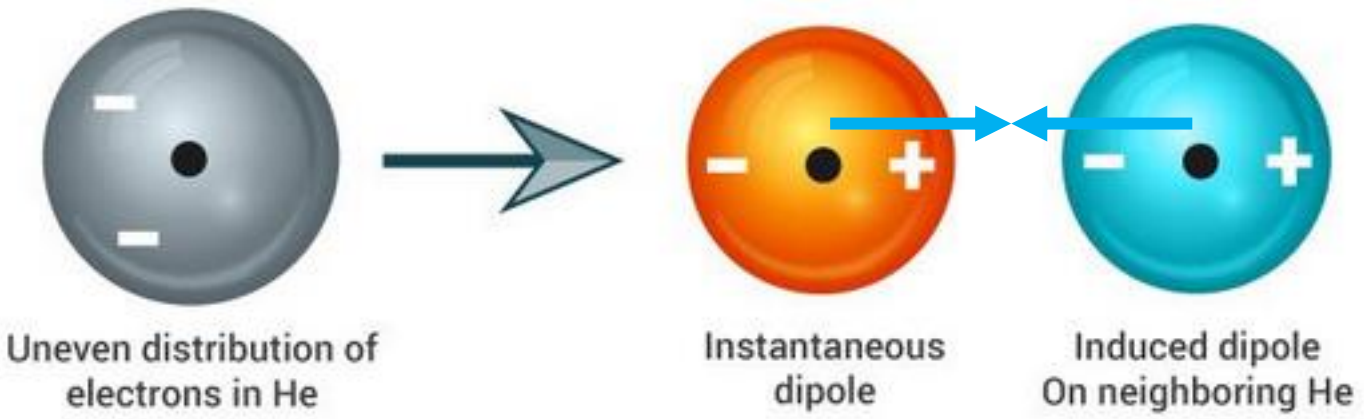
ELECTRIC	Monopole	Dipole	Quadrupole	Octupole	Hexadecapole
Monopole	1/R	$1/R^2$	$1/R^3$	$1/R^4$	$1/R^5$
Dipole	$1/R^2$	$1/R^3$	$1/R^4$	$1/R^5$	**$1/R^6$**
Quadrupole	$1/R^3$	$1/R^4$	$1/R^5$	**$1/R^6$**	$1/R^7$
Octupole	$1/R^4$	$1/R^5$	**$1/R^6$**	$1/R^7$	$1/R^8$
Hexadecapole	$1/R^5$	**$1/R^6$**	$1/R^7$	$1/R^8$	$1/R^9$



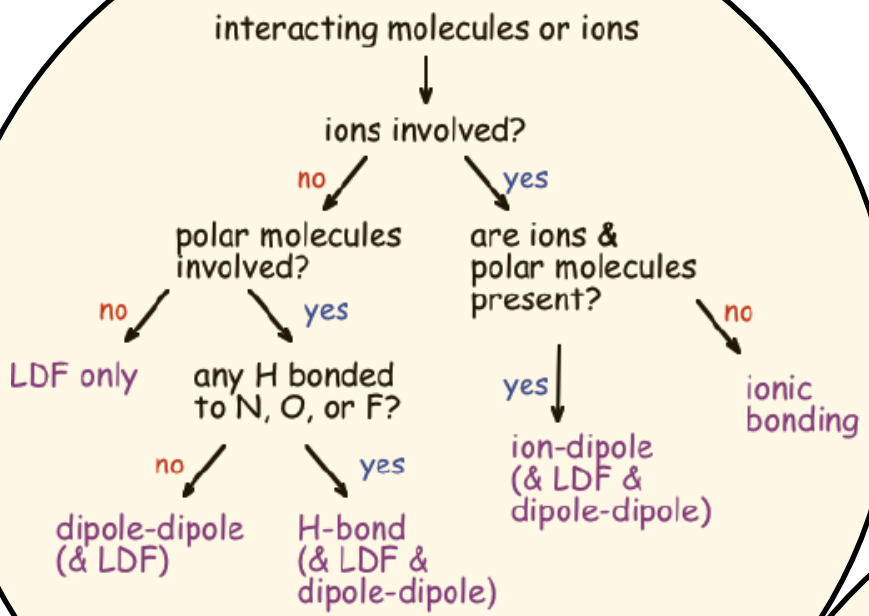


London Dispersion forces

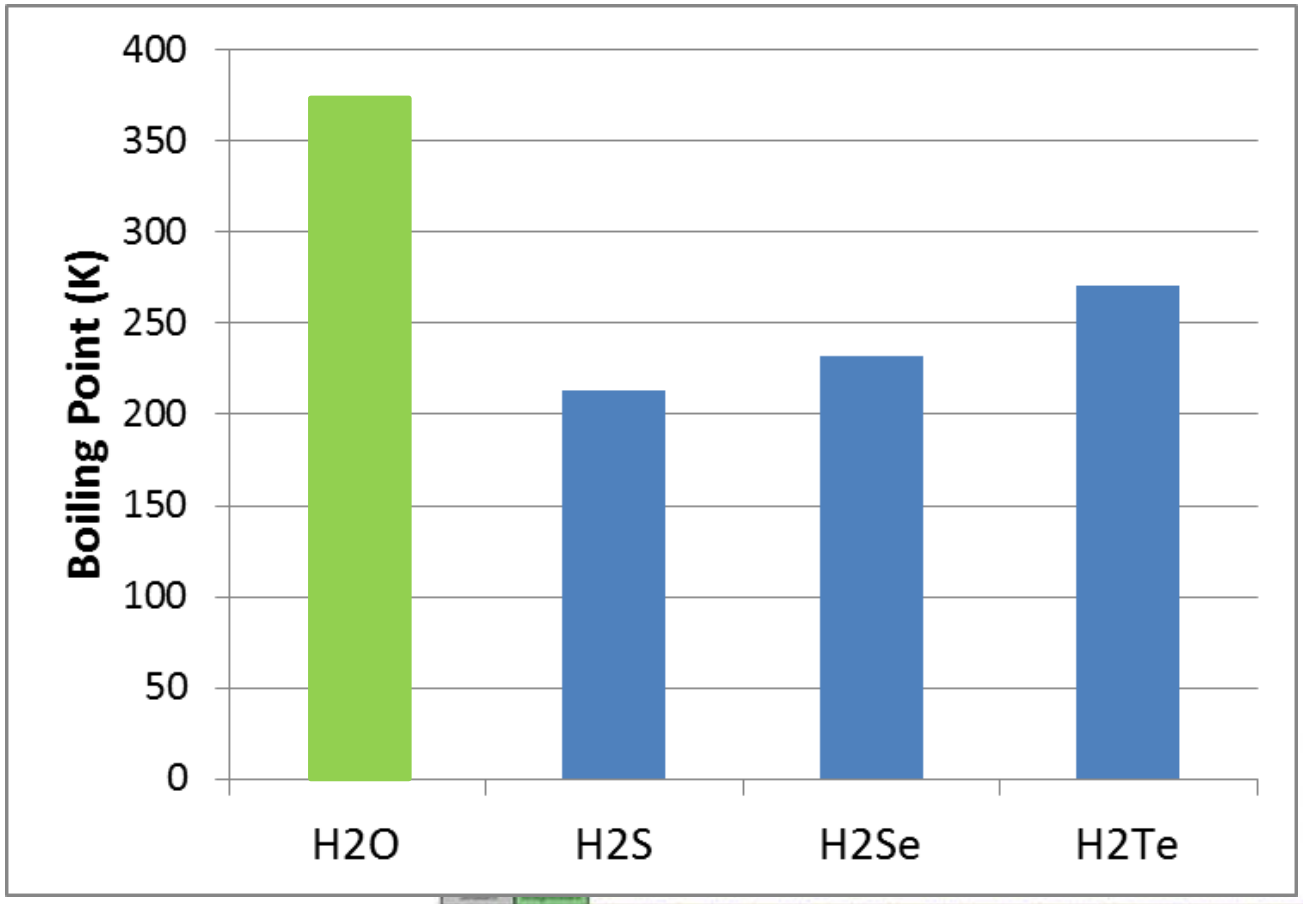
- Part of the van der Waals forces (vdW), i.e., depend on the distance.
- Present in all molecules; temporary partial charges give temporary polarity.
- Weak interactions (0.05 - 2 kJ/mol) and their strength increases with the polarizability (the squishiness of the electron cloud)

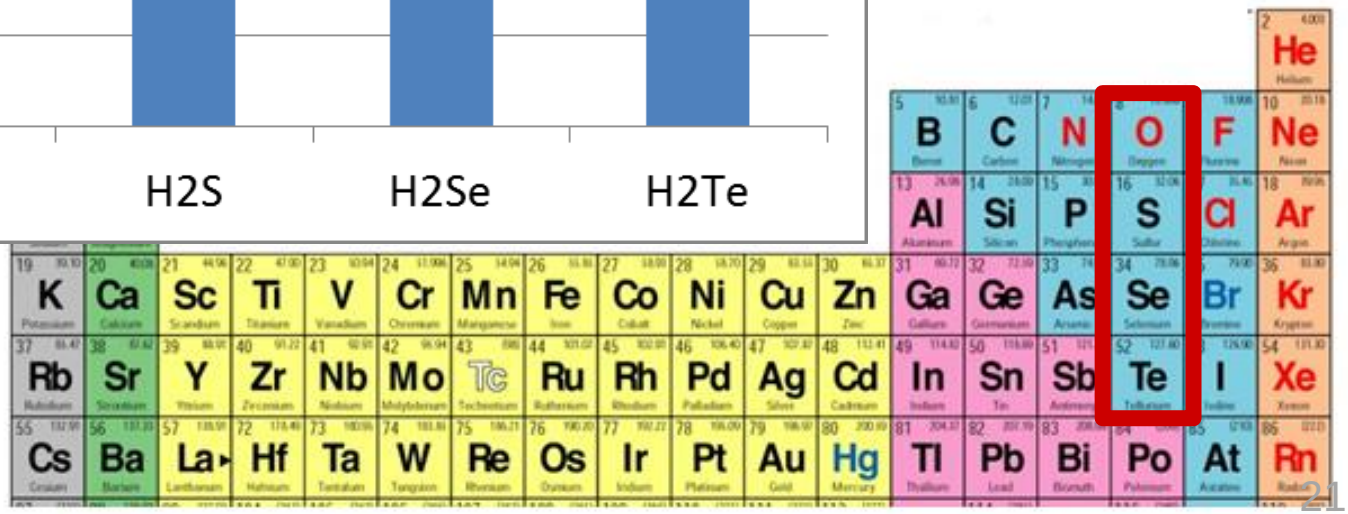


What intermolecular forces are present?

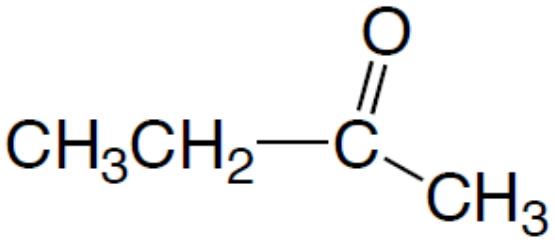
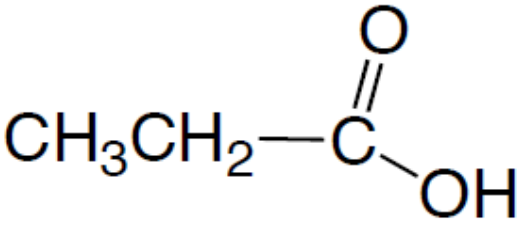


Boiling point – measure for intermolecular interaction

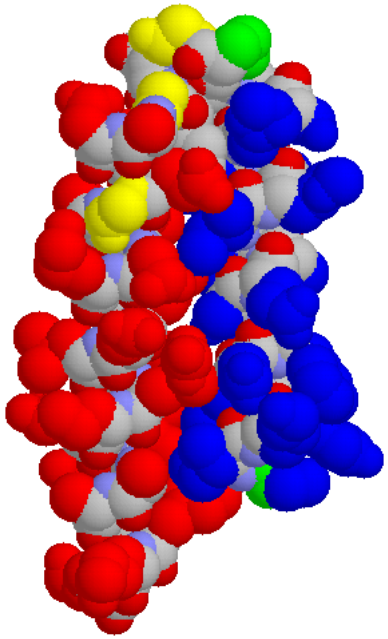




Boiling point – measure for intermolecular interaction

Molecule	BP (°C)	Structure	MW (g/mol)
Pentane	36	$CH_3CH_2CH_2CH_2—CH_3$	72
Diethyl ether	34	$CH_3CH_2—O—CH_2CH_3$	74
Butanone	80		72
Propanoic acid	141		74

vdW and electrostatic interactions



http://www.chembio.uoguelph.ca/educmat/phy456/456lec02.htm

- Responsible for protein folding and enzymatic recognition, i.e., sustaining live as you know it!

…this interactions drive life in the universe!

References

- Ken A. Dill, Sarina Bromberg “Molecular Driving Forces”, Garland Science, 2nd Ed. 2011