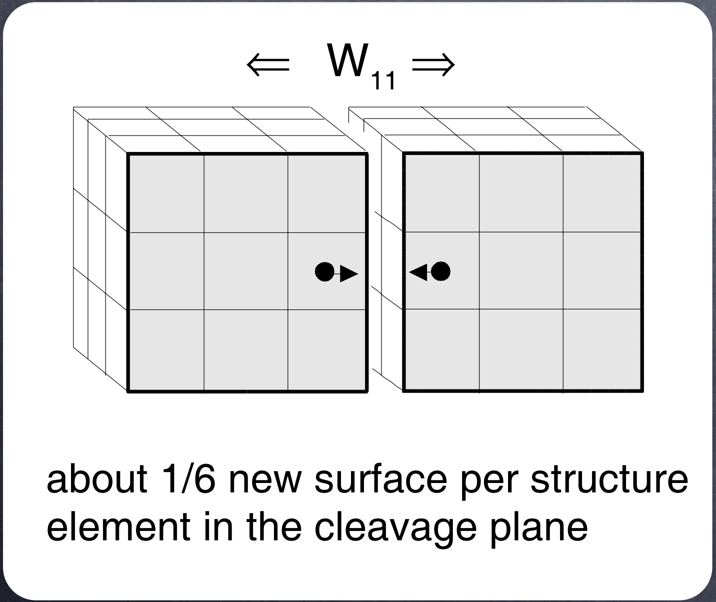
Surface Energy

The work W_{11} to bring two identical ideal surfaces in vacuum together is related to the surface energy γ_1 of the material:

$$W_{11} = -2\,\gamma_1 \qquad \text{(normalized to unit area!)}$$

W_{11} corresponds to to the work of cohesion in an ideal case and is normalized to the area of the surfaces. This work should be identical to separating a body into two halves. In reality the separation process is irreversible (due to energy dissipation), thus the separation / cohesion work is larger than the surface energy.

⇒ high surface energy ↔ strong cohesion → high boiling point...



about 1/6 new surface per structure element in the cleavage plane

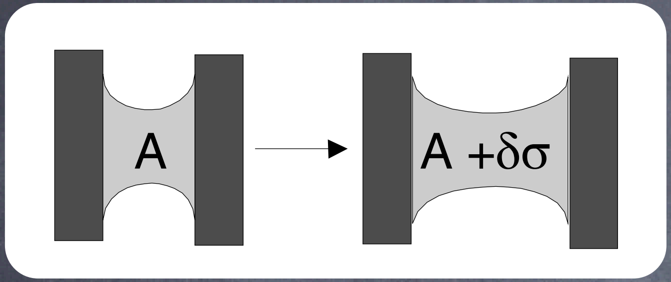
substrate material	surface energy γ (mJ m−2)
mica	4500
gold	~1000
PTFE	19
octadecane surface	28

⇒ high energy surfaces tend to reduce energy by adsorption of contaminants from environment !

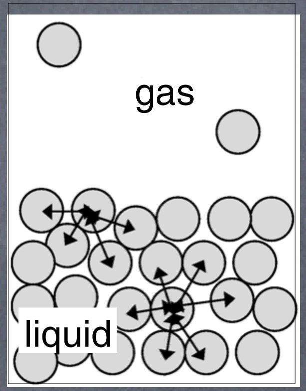
Surface Tension

Surface tension γ is defined by the infinitesimal work dw required to increase the surface by an infinitesimal area $d\sigma$:

$$dw = \gamma\ \delta\sigma$$

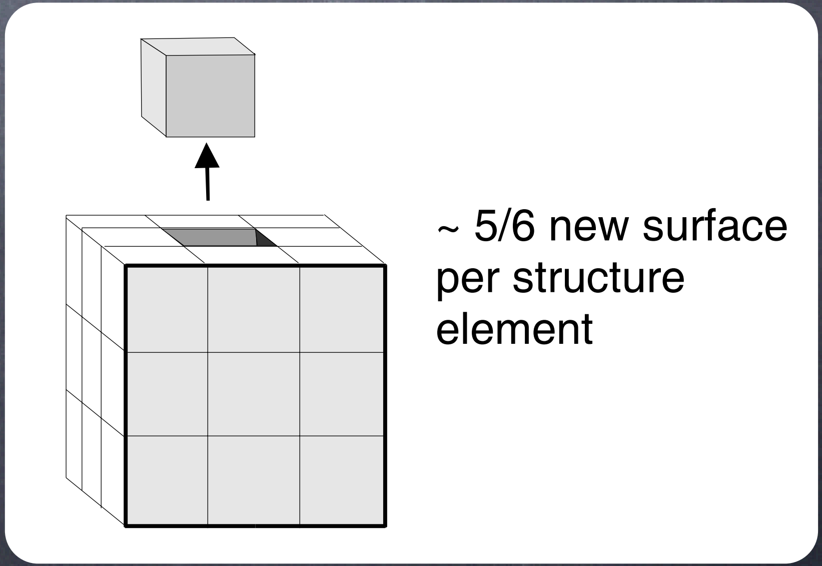


→ work has to be applied to increase surface, since liquids tend to minimize their surface (spherical droplet)
→ force balance



→ surface tension of liquids corresponds to surface energy of solids
→ surface tension / surface energy correlates to evaporation enthalpy ΔH_{vap}

material	γ (mN m^{-1})	ΔH_{vap} (kJ mol^{-1})
C_6H_6	28.8	30.8
MeOH	26.6	35.3
H_2O	72.7	40.7
Hg	472	59.3



~ 5/6 new surface per structure element

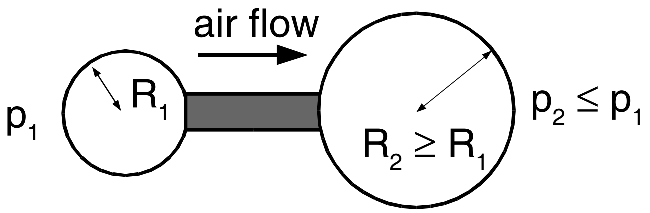
Measuring Surface Tension

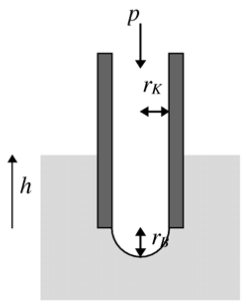
The Young–Laplace equation describes the pressure difference Δp between the inside and the outside of a curved object (bubble, droplet, cavity) with radius r_a and r_b ($r_a \perp r_b$, in symmetric geometry $r = r_a = r_b$) with respect to the surface tension γ :

$$\Delta p = \gamma \left(\frac{1}{r_a} + \frac{1}{r_b} \right)$$

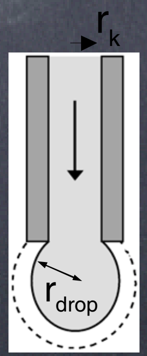
or in terms of internal pressure:

$$p_{in} = p_{out} + 2\gamma / r$$

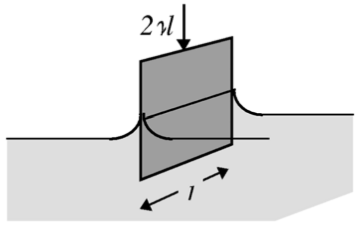




a) maximum bubble pressure method: a gas is pressed through a capillary with radius r_K till the cavity reaches $r_B = r_K$ → $\gamma = r_K \Delta p/2$ with $\Delta p = p_{bubble} - h \rho g$ (h: hydrostatic pressure, ρ: density of liquid, g: gravitational constant)



b) drop weight method: maximum drop size before release $m_{drop}\, g = 2\pi\, r_k\, \gamma$ with weight of drop m_{drop} ⇒ $4/3\, \pi\, r_{drop}\, \rho_{liq}\, g = 2\pi\, r_k\, \gamma$

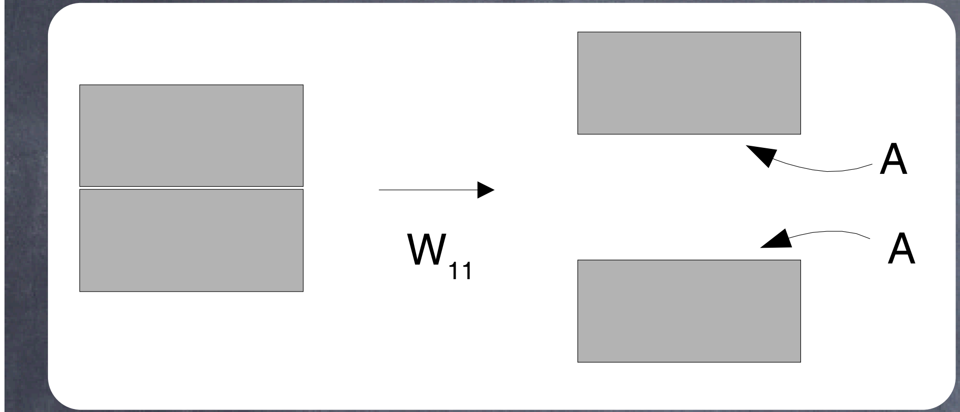


c) Wilhelmi plate method: force F (in addition to gravitational force) on a plate with width l partially immersed into a liquid $F = 2l\, \gamma$

Cohesion

Cohesion forces act within a condensed material (liquid, solid) to keep it together.

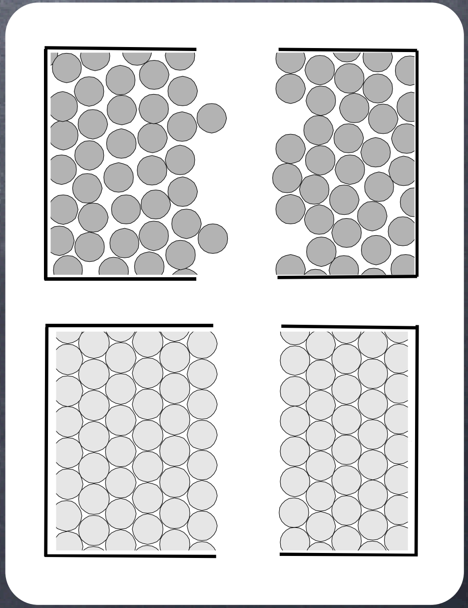
work of cohesion W_{11}: free energy change, or reversible work done, to cleave / separate a material from contact to infinity in vacuum



$$W_{11} = \overbrace{2\,A}^{\text{new cleavage area}}\,\underbrace{\gamma}_{\text{surface (free) energy}}$$

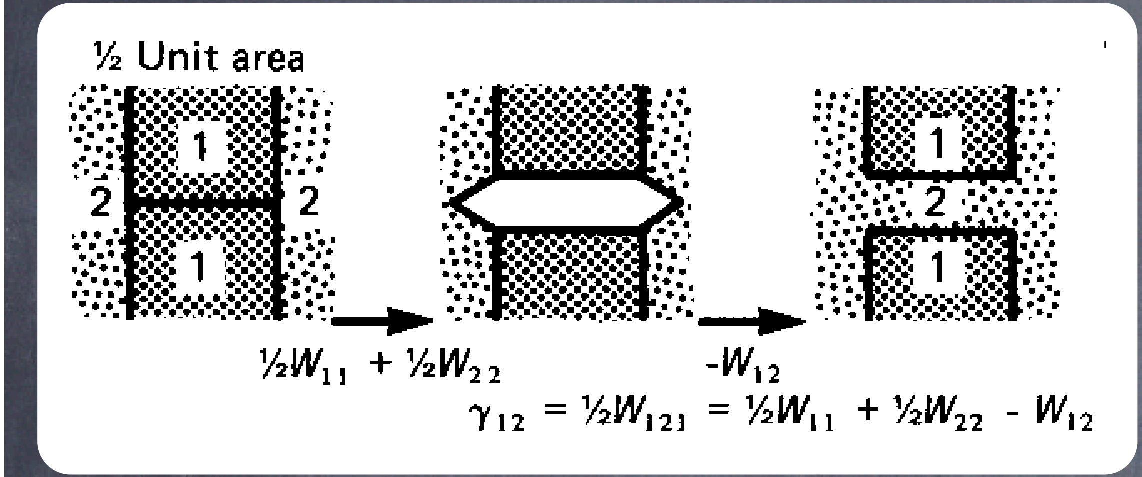
- cohesion in amorphous solids and liquids is isotropic:
  → random fracture plane (e.g. glass)

- cohesion in crystalline solids is anisotropic:
  → fracture along crystal planes (e.g. Si single crystal wafer)



Adhesion

The adhesion forces act between the surfaces of two different condensed bodies in contact.



$$\gamma_{12} = \overbrace{\gamma_1 + \gamma_2}^{\text{surface energies 1 and 2}} - \underset{\uparrow \atop \text{work of adhesion}}{W_{12}}$$

Dupré equation: total free energy change corresponds to interfacial energy γ_{12}

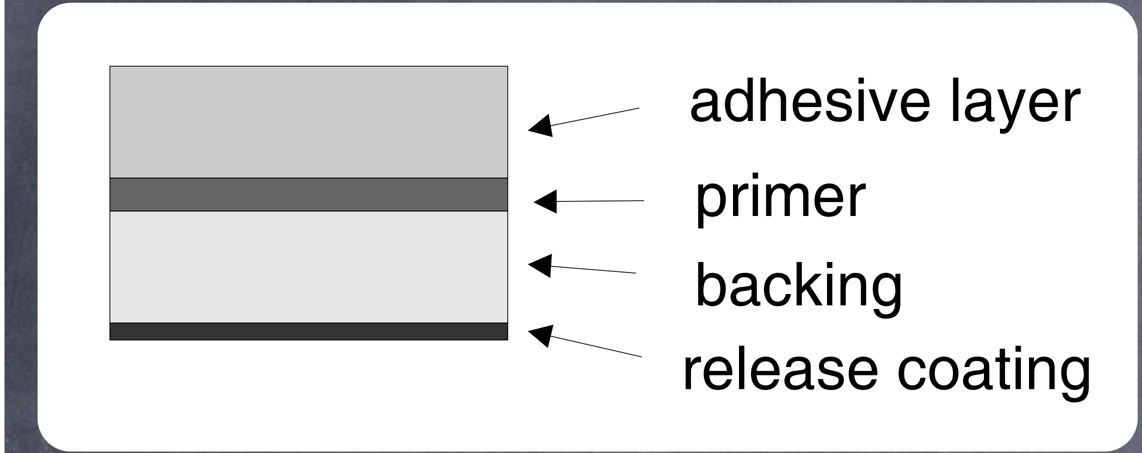
→ this process can be split into two hypothetical steps:

a) generate new surface for materials 1 and 2 in vacuum: $W = \gamma_1 + \gamma_2$ (normalized to unit area!)

b) bring two new surfaces into contact (work of adhesion): W_{12}

⇒ since all media attract each other (assuming neutral total charge) in vacuum: work of cohesion (W_{11}) and work of adhesion (W_{12}) are always positive (work is required to separate material)!

Practical Example: Adhesive Tape



tack: in adhesives tack describes the property to bond at moderate applied pressure (tack involves both, 1. bonding and 2. debonding step)

adhesion layer:
- base elastomer (rubber, polyacrylates, block copolymers), high M_w, low T_g (below RT)
- tackifiers (rosin, terpenes, hydrocarbon resins), low M_w (300–3000 g/mol), high T_g (> RT)

primer: increases adhesion (→ covalent bonding) of adhesive layer to backing (phenolic elastomer resins, corona–treatment, chlorinated polyolefins)

backing: supports adhesive layer, mechanical strength (paper, polypropylene)

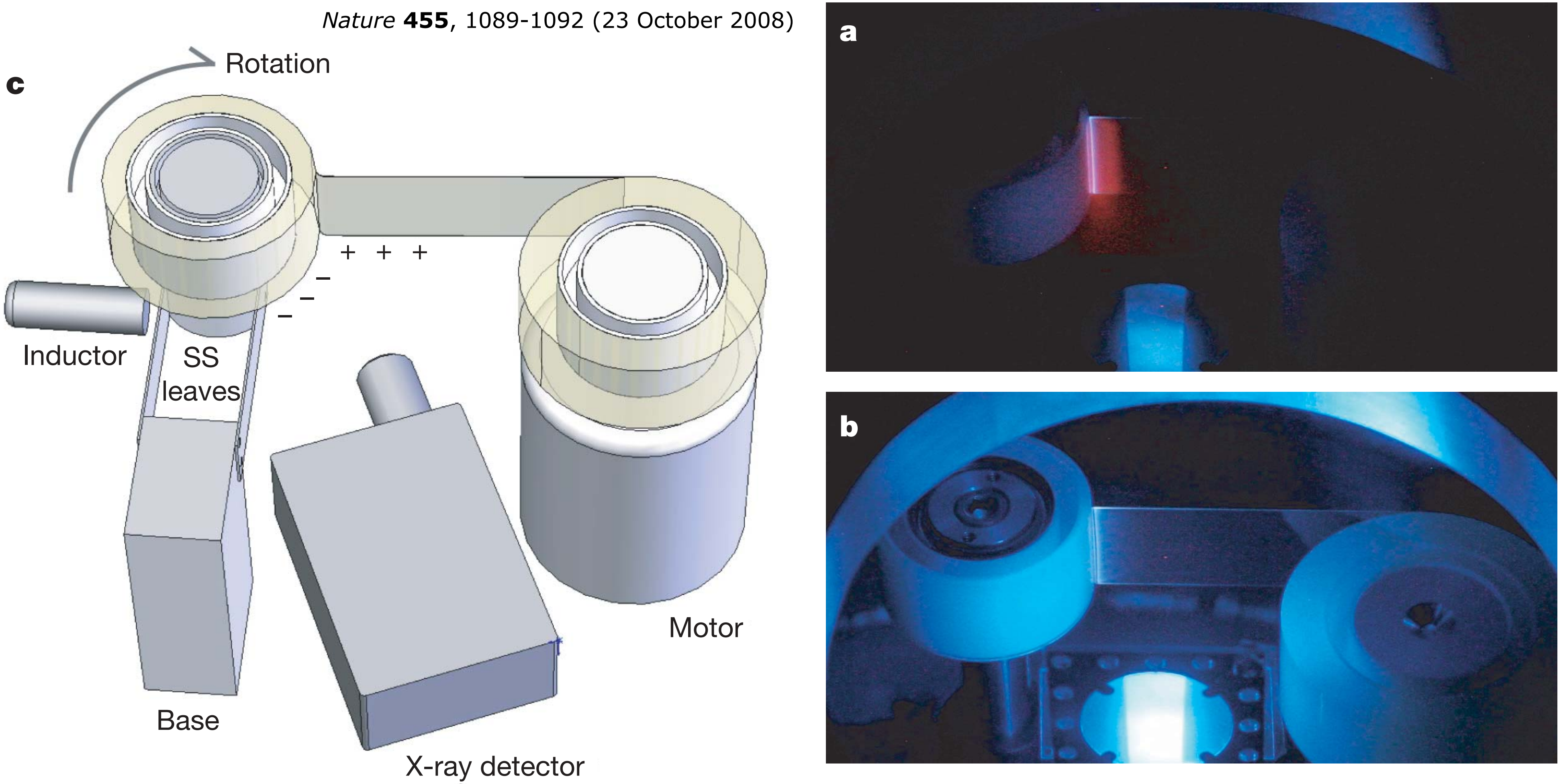
release coating: reduces adhesion of adhesive layer and allows release of rolled up tapes etc. (silicones, alkyds, stearyl derivatives of vinyl polymers)

physical parameters determining adhesion properties:

- tack: immediate "bond" formation upon contact with surface
- adhesion: force required to remove adhesive tape / "break bond" → depends on debonding process
- cohesion: internal mechanical strength that holds adhesive layer (and whole tape structure) together

Practical Example: Adhesive Tape

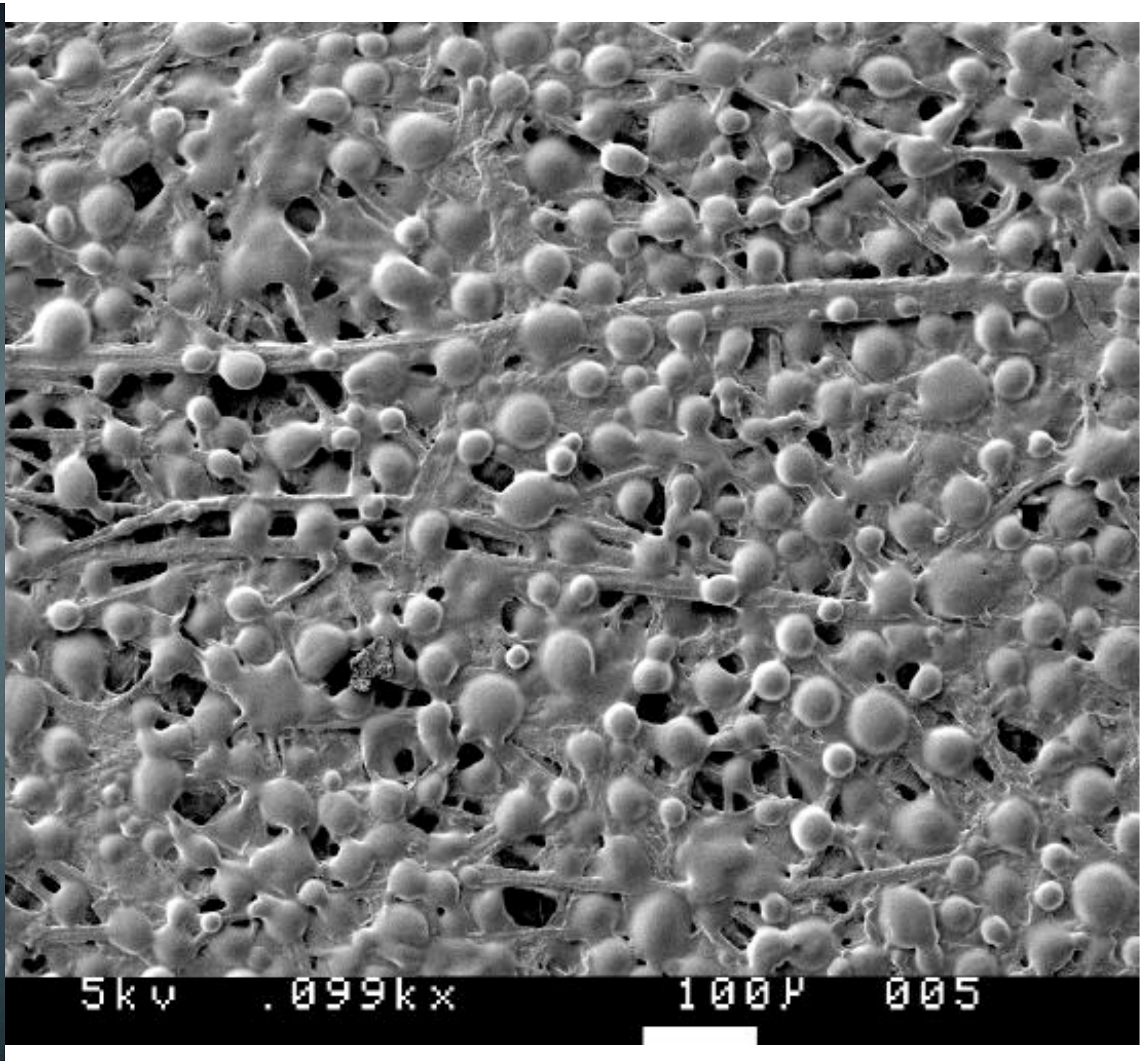
Nature **455**, 1089-1092 (23 October 2008)



Relative motion between two contacting surfaces can produce visible light, called triboluminescence: mechanical energy into electromagnetic radiation

peeling common adhesive tape in a moderate vacuum produces radio and visible emission.

Practical Example: Post-It



-> point contacts

Fundamental Interactions

In nuclear and high-energy physics 6 fundamental forces are recognized, which describe the structure of matter.

- the strong interaction - the weak interaction	-> act inside the nucleus, range < 10-5 nm ~ 1/10000 of the diameter of an atom
- the electromagnetic interaction	-> source of all intermolecular forces ! (Hellman-Feynman)
- gravitation	-> very long-range between macroscopic objects, negligible between molecules
- the super-strong interaction - the super-weak interaction	-> very particular forces only used in nuclear physics (don't bother...)

<u>Hellman-Feynman theorem</u>: "Once the spatial distribution of the electron clouds has been determined by solving the Schrödinger equation, the intermolecular forces may be calculated on the basis of straightforward classical electrostatics."

Pair Potentials

- van der Waals: deviation of behavior of real gases from ideal gas law (pV = nRT):

$$(p+\underbrace{\frac{a}{V^2}}_{})(\underbrace{V-b}_{})=RT$$

excluded volume of atoms / molecules

attractive intermolecular forces (→ van der Waals forces)

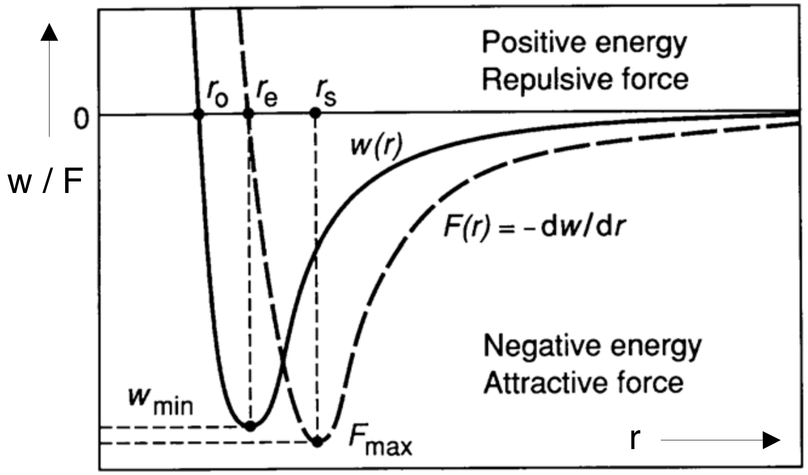
- Mie: general interaction "pair potential" to describe complex intermolecular interactions:

$$w(r)=-\underbrace{\frac{A}{r^n}}_{}+\underbrace{\frac{B}{r^m}}_{}$$

repulsive term

attractive term

- Lennard-Jones:



$$w(r)=-\underbrace{\frac{A}{r^6}}_{}+\underbrace{\frac{B}{r^{12}}}_{}$$

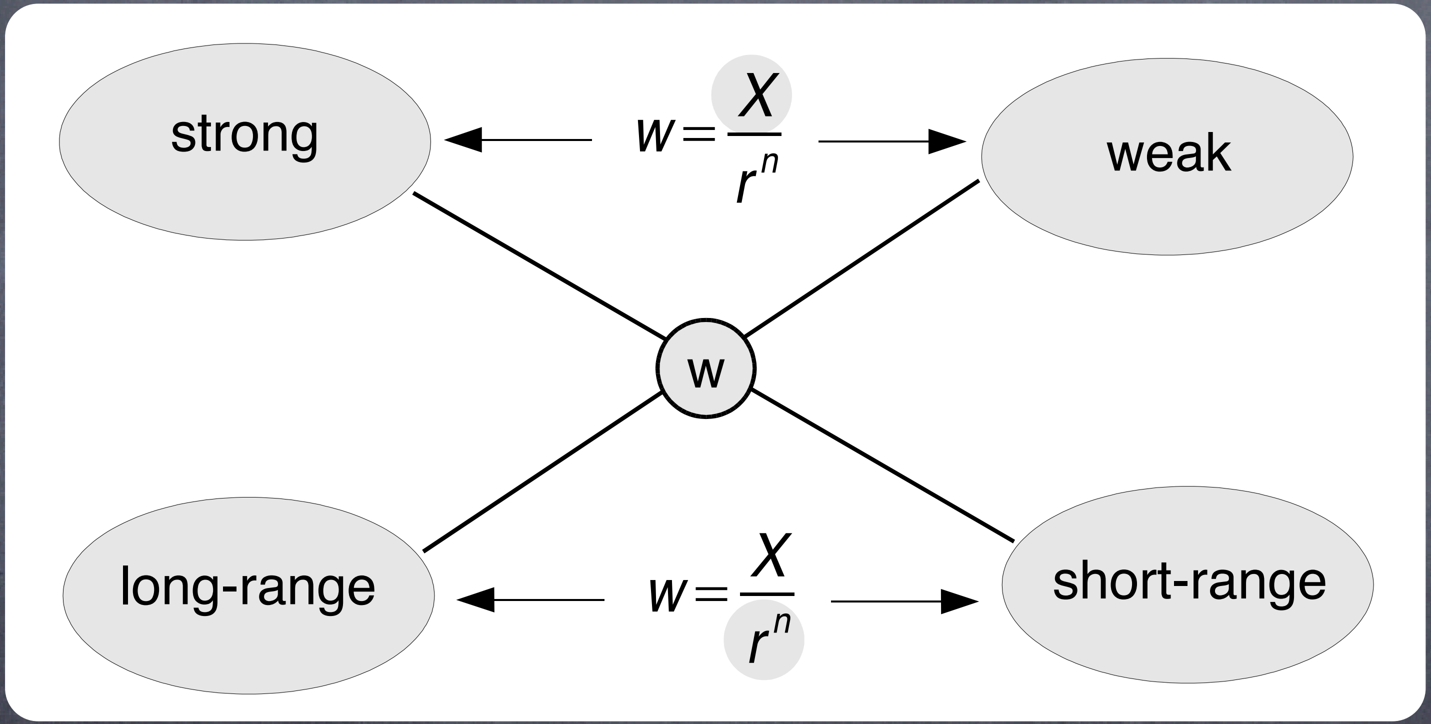
very short-range "hard sphere" repulsion

long-range attractive van der Waals interaction

Range and Strength of Forces

The interaction parameter X determines the strength of the interaction.

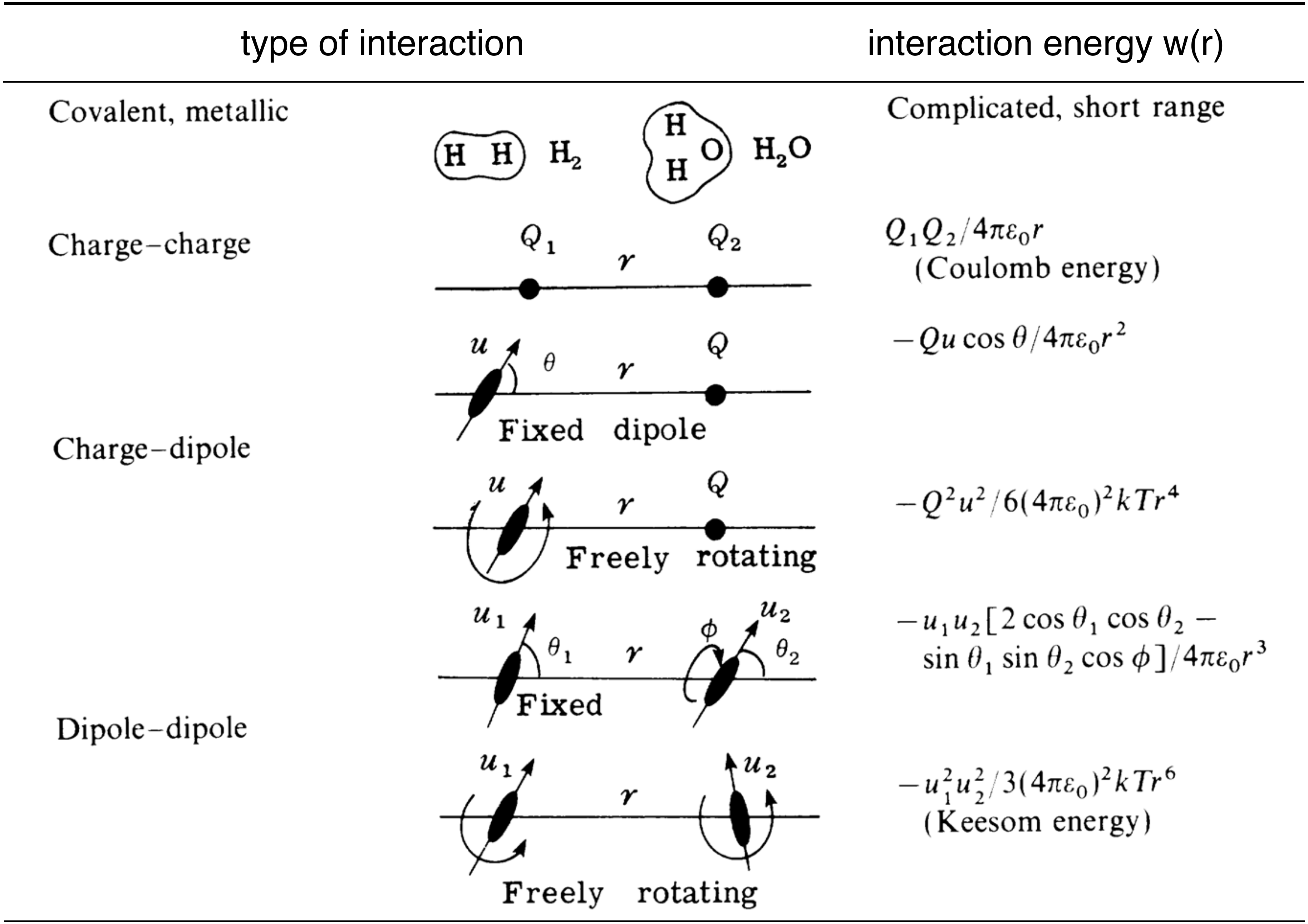
→ the larger X the stronger the interaction



The exponent in the distance variable r determines the range of the interaction.

→ the larger the exponent n the shorter the interaction range

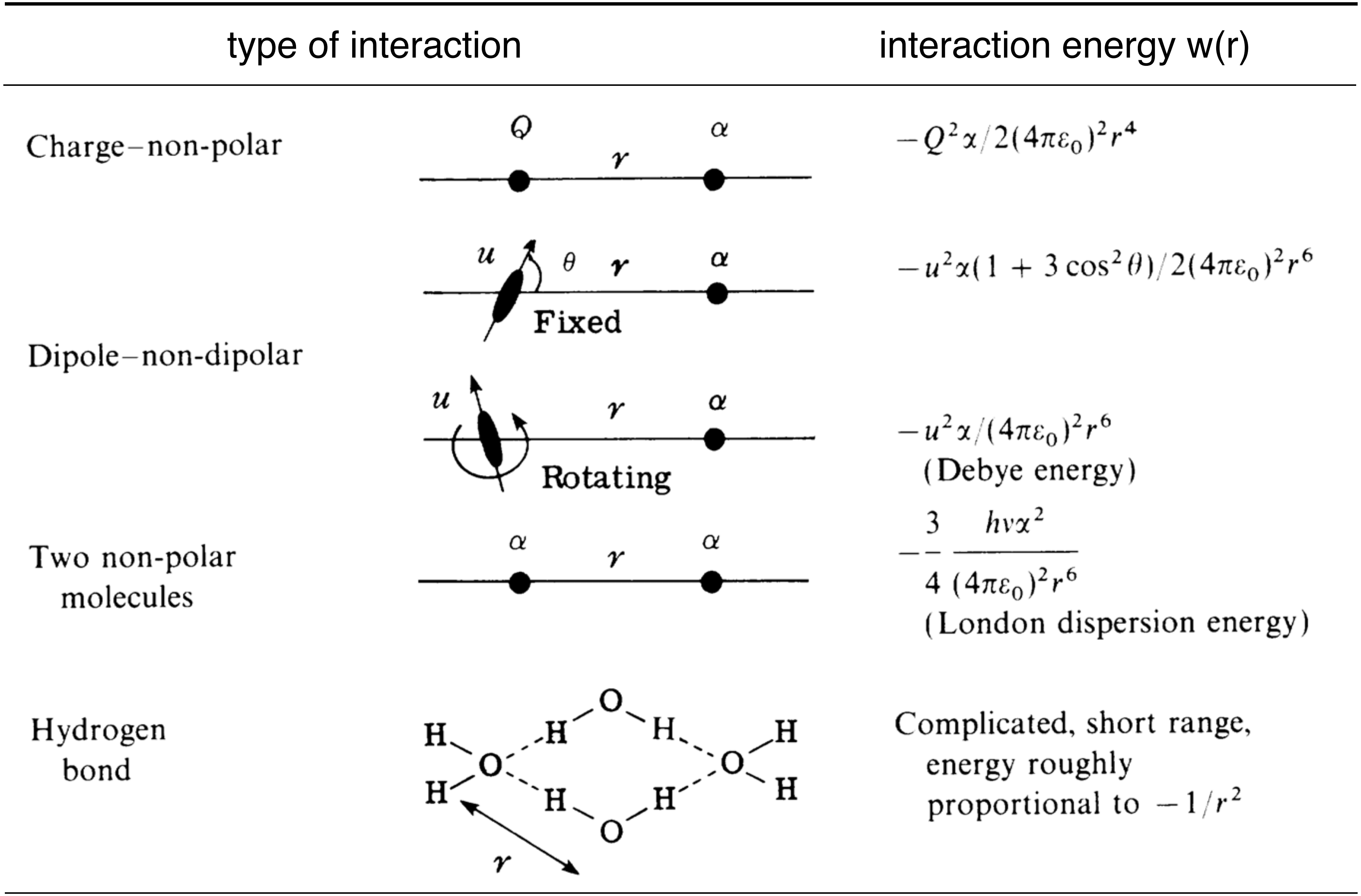
Type of Interactions 1



type of interaction		interaction energy w(r)
Covalent, metallic	H H H_2 H H O H_2O	Complicated, short range
Charge–charge	Q_1 r Q_2	$Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	u θ r Q Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	u r Q Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2kTr^4$
Dipole–dipole	u_1 θ_1 r ϕ u_2 θ_2 Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	u_1 r u_2 Freely rotating	$-u_1^2u_2^2/3(4\pi\varepsilon_0)^2kTr^6$ (Keesom energy)

J. Israelachvili; "Intermolecular and Surface Forces", Second Ed.; Academic Press Limited: London, **1995**, p. 28

Type of Interactions 2

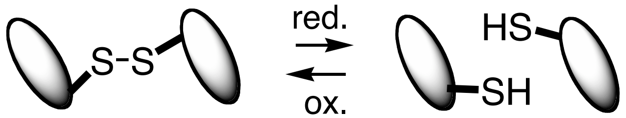


type of interaction	interaction energy w(r)
Charge–non-polar	$-Q^2\alpha/2(4\pi\varepsilon_0)^2r^4$
Dipole–non-dipolar	$-u^2\alpha(1+3\cos^2\theta)/2(4\pi\varepsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\varepsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules	$-\frac{3}{4}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond	Complicated, short range, energy roughly proportional to $-1/r^2$

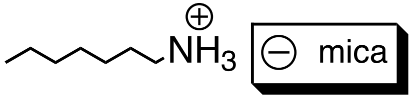
J. Israelachvili; "Intermolecular and Surface Forces", Second Ed.; Academic Press Limited: London, **1995**, p. 28

Intermolecular Interactions

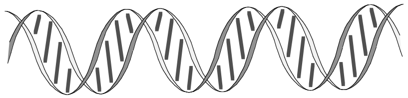
- **covalent**:
  e.g. disulfide bonds



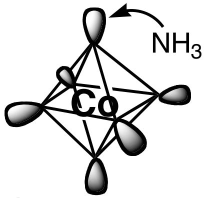
- **ionic**:
  e.g. ammonium salts on mica



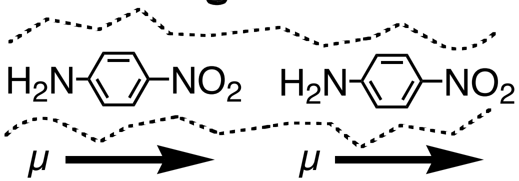
- **H-bonding**:
  e.g. DNA double helix



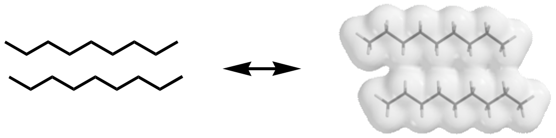
- **coordinative**:
  e.g. transition metal complexes



- **dipole-dipole**:
  e.g. nitroaniline in zeolite



- **dispersion**:
  e.g. alkyl chains



- **charge transfer (CT)**: e.g. intercalation of trinitrofluorenone into triphenylene columns
- **topological link**:
  - catenanes / rotaxanes
  - endohedral fullerene complexes
- **form anisotropy**:
  - liquid crystals
  - ordered colloidal dispersions

Chemical Bonds

Chemical bonds: strong bonds between atoms to form molecules and extended solids.
→ relates to cohesion within a covalent bonded material

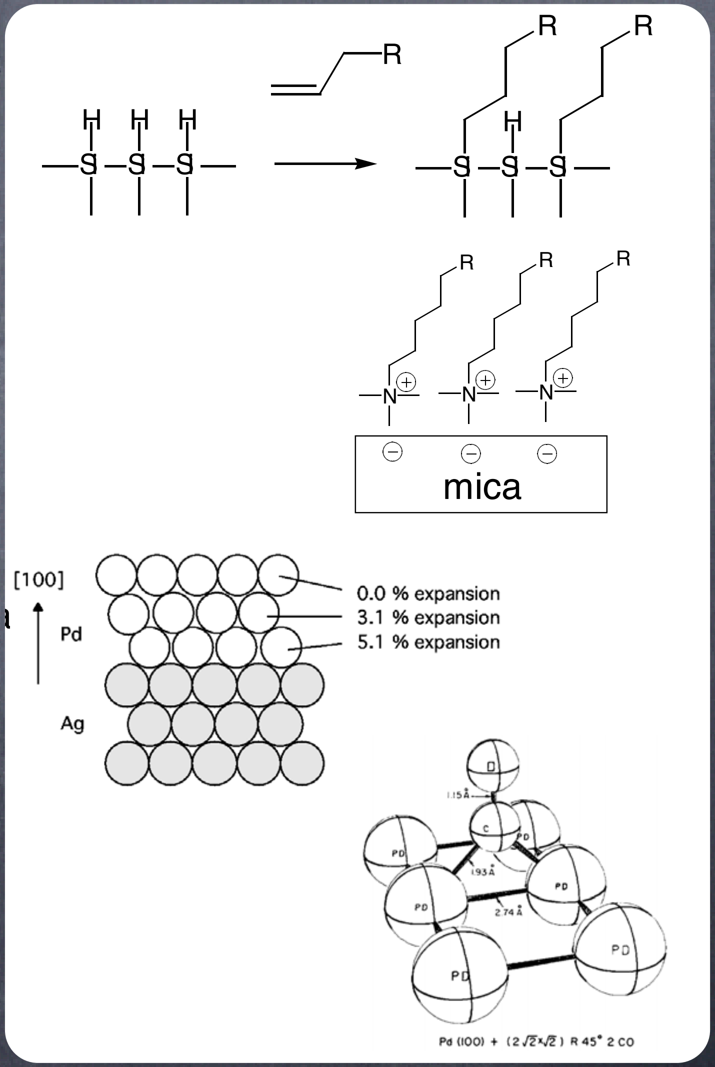
Examples in surface sciences:

-covalent surface bonds: hydrosilylation of hydrogen terminated silicon surface (radical, thermal, photochem., catalytic):

-ionic surface bonds: quaternary ammonium salts on mica:

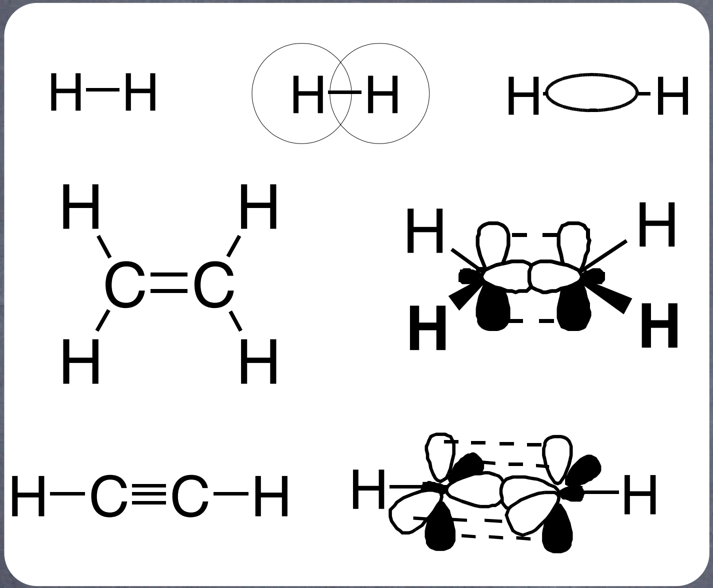
-metallic surface bonds: interface between two metal layers

-coordinative surface bonds: CO adsorbates on d-transition metal surfaces (somewhere between covalent and coordinative):



Covalent Bond

Sharing of valence electrons (in pairs) between two atoms (usually non-metals) leads to a covalent bond between these atoms → molecules



single bond: two s-orbitals overlap to form a σ-bond

double bond: two sp^2-orbitals overlap to form a σ-bond
two p-orbitals overlap to form a π-bond

triple bond: two sp-orbitals overlap to form a σ-bond
four p-orbitals overlap to form two π-bonds

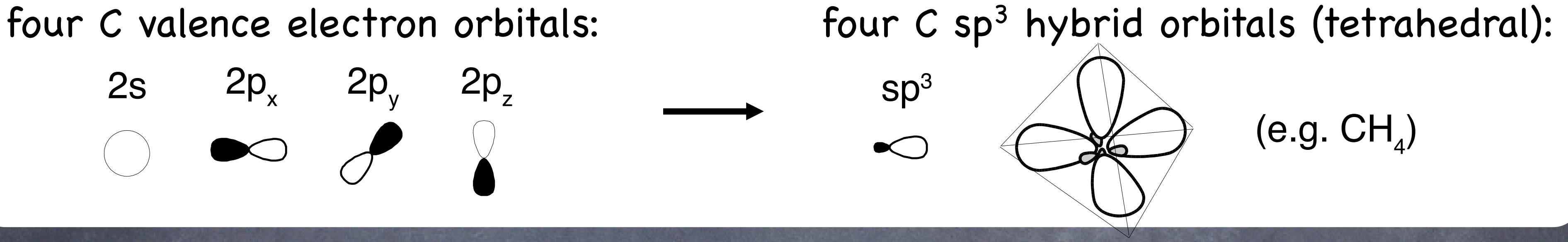
bond type	length (pm)	energy (kJ mol^{-1})
C–C	154	347-356
C=C	134	611-632
C≡C	120	833-837

→ equal distribution of bonding electrons between atoms leads to non-polar bond (H–H)
→ localization of bonding electron pair towards one atom (more electronegative) leads to polar bond ($H^{\delta+}$–$Cl^{\delta-}$) → extreme case: ionic bond

VB and MO theory

VB theory: In the valence bond (VB) theory resonance energy is gained by exchange of electrons between two atoms (orbital overlap). Bonding electrons are localized between two bonding atoms and are not distinguishable.

→ description of bonding geometries by hybrid orbitals:



four C valence electron orbitals:

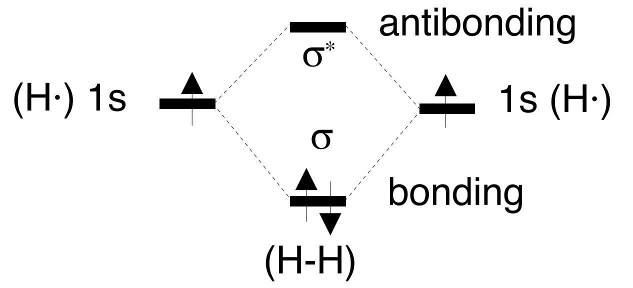
four C sp^3 hybrid orbitals (tetrahedral):

MO theory: In the molecular orbital (MO) theory bonding electrons are not localized between two atoms of a bond, but distributed in a group of molecular orbitals over the entire molecule.

→ quantum mechanical description by the Schrödinger equation: $H\,\psi_{MO} = E\,\psi_{MO}$

→ MO are generated by a linear combination of atomic orbitals (LCAO):

$\psi_{MO} = c_1\,\varphi_1 + c_2\,\varphi_2 + c_3\,\varphi_3 + \ldots + c_n\,\varphi_n$ → wave function of MO: ψ_{MO}; atomic orbital (AO): φ



→ MO theory is basis for computational treatment of molecular structure (semi-empirical, ab-initio)

→ frontier orbitals HOMO / LUMO

Ionic Bond

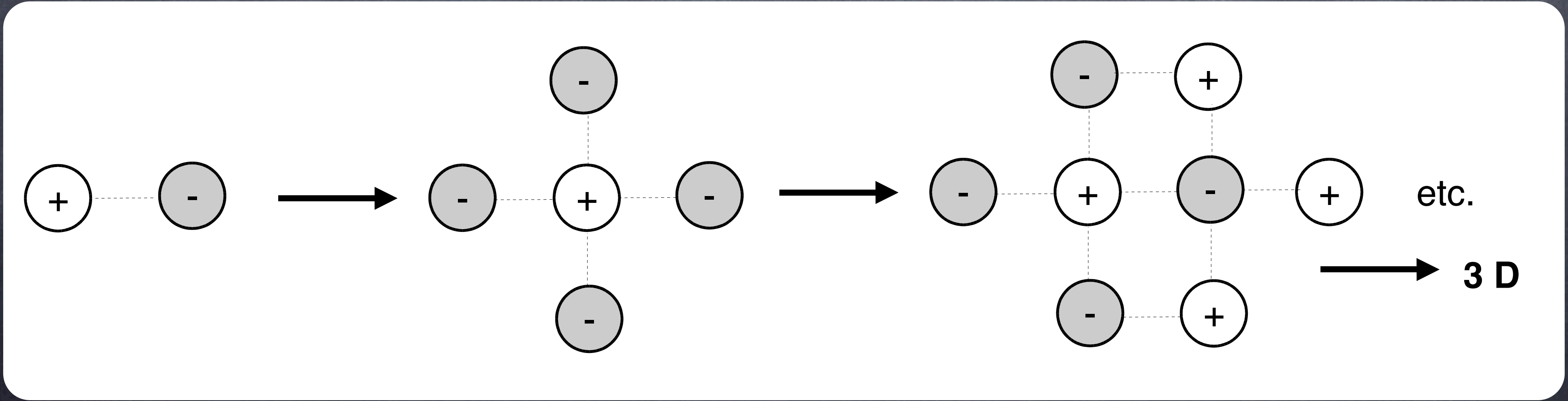
ionic bonds are formed by strong Coulomb interactions between two oppositely charged species (e.g. Na+Cl-)

→ the potential energy varies with the distance r between the two ions by 1/r (the force varies with $1/r^2$)

→ description by formal electron transfer from newly formed cation (usually metals) to newly formed anion (usually non-metals)

→ "simplest bond" / extreme case of polar bond

→ ionic bond is not localized / directed, but acts isotropically / radial-symmetrically around ions → leads to extended aggregation and ionic crystals with one cation being surrounded by many anions and vice versa

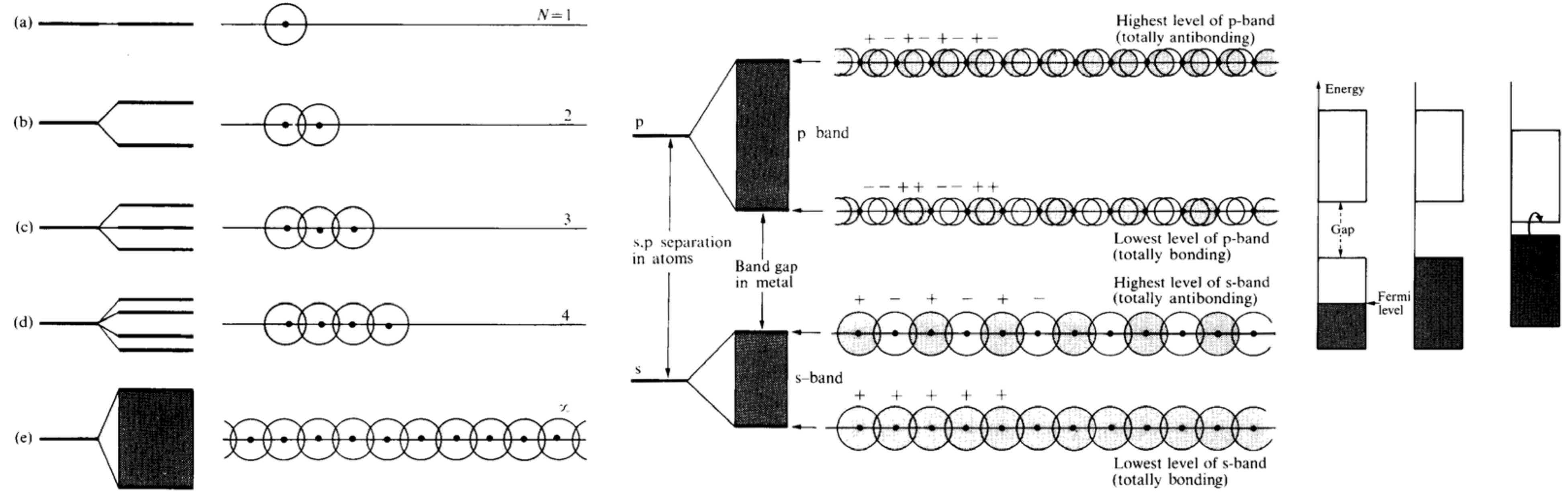


Metallic Bond

metallic bond: attractive interactions / bonds in metals are mediated by free moving valence electrons (electron sea) between positively charged atoms over entire sample

- electron sea: high electron mobility → good thermal and electrical conductivity
- metallic bond is weak (compared to covalent bond) → ductile metals

→ theoretical description of metallic bond by band theory:

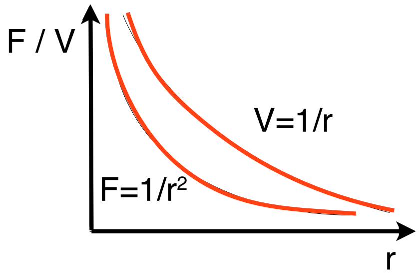


Electrostatic Interactions

The force F (Coulomb force) acting between two charges q_1 and q_2 separated by a distance r in vacuum (ε_0) depends on the separation by $1/r^2$.

$$q_1 \overset{r}{\longleftrightarrow} q_2 \qquad F = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} \xrightarrow[\text{with } \varepsilon_r]{\text{in medium}} F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

(relative permittivity, dielectric constant)



→ the electrostatic forces are additive: in a system of many charges the force on a single charge is obtained by summing all the interactions with the other charges

- electrical work w_e:
  potential energy V:

$$w_e \text{ or } V = -\int_{\infty}^{r} F\,dr = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_r r}$$

- electric potential:

$$\phi = \frac{q_2}{4\pi\varepsilon_0\varepsilon_r r} \longrightarrow w_e \text{ or } V = q_1\,\phi$$

- electric field strength:

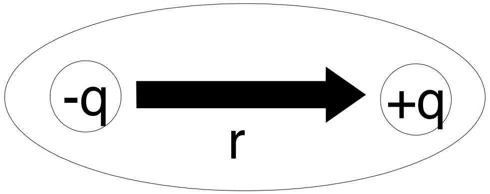
$$E = \frac{q_2}{4\pi\varepsilon_0\varepsilon_r r^2} \longrightarrow F = q_1\,E$$

van der Waals Interactions

Collection of attractive interactions between molecules based on dipole / dipole, dipole / induced-dipole, and induced-dipole / induced-dipole interaction (Keesom, Debye, London dispersion energies)

dipole moment μ : equal charge q separated at a fixed distance r

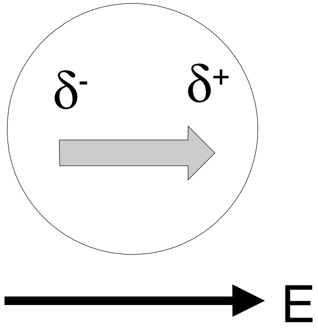
$\mu = q\, r$



unit: debye (D) = $3.336\ 10^{-30}$ C m

induced dipole μ_i: dipole induced in a polarizable molecule by electric field

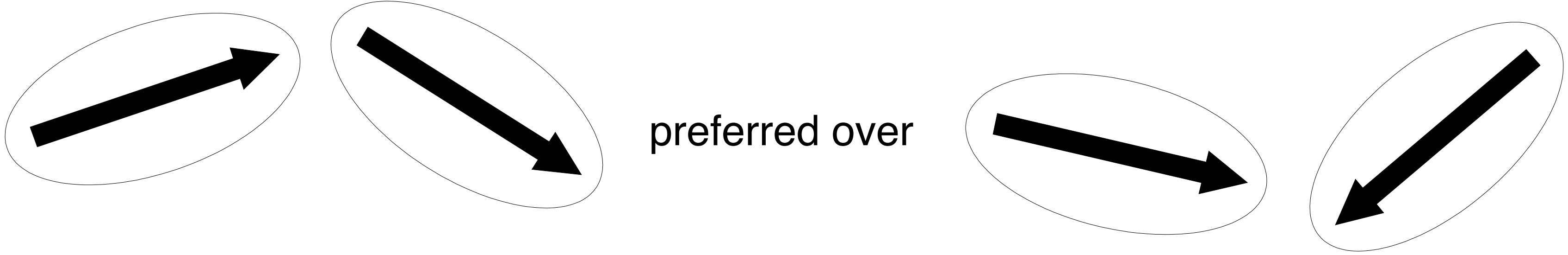
$\mu_i = \alpha\, E$



α : polarizability
E : electric field

Dipole / Dipole Interactions

Interaction of freely rotating dipoles (liquid) depends on the thermal energy (kT) and is referred to as Keesom energy (Boltzmann distribution of orientations).



preferred over

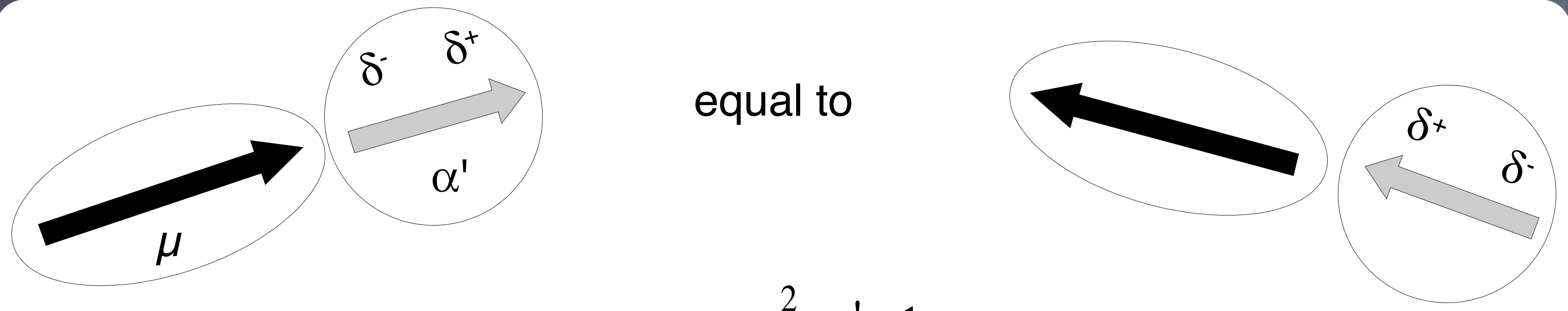
$$V = -\frac{2}{3kT}\left(\frac{\mu_1\mu_2}{4\pi\varepsilon_0}\right)^2\frac{1}{r^6}$$

At 25°C the average interaction energy for pairs of molecules with $\mu = 1$ D is about -1.4 kJ mol^{-1} when the separation is 0.3 nm.

The average molar kinetic energy at 25°C is $3/2\ RT = 3.7$ kJ mol^{-1}.

Dipole / Induced-Dipole Interactions

A dipole near a polarizable molecule induces a dipole (charge dislocation) in the neutral molecule leading to an attractive interaction, the corresponding potential energy is referred to as Debye energy.



$$V = -\frac{\mu^2 \alpha'}{4\pi\varepsilon_0}\frac{1}{r^6}$$

α' is the polarizability volume given by $\alpha' = \alpha / 4\pi\varepsilon_0$ (unit: cm^3)

The interaction energy is independent of the temperature because the induced dipole follows immediately the motion of the permanent dipole and is thus not affected by thermal motion, and it depends on $1/r^6$ (like the dipole / dipole interaction).
For a molecule with μ = 1 D (e.g. HCl) near a molecule with polarizability volume α' = 10-23 cm^3 (e.g. benzene) the average interaction energy is about -0.8 kJ mol-1 at a separation of 0.3 nm.

Induced-Dipole/Induced-Dipole IAs

Random fluctuations in a polarizable molecule lead to a temporary dipole which induces a corresponding dipole in a nearby molecule, leading to attractive dispersion interactions. The involved potential energy is called the London dispersion energy.

$$V = -\frac{3}{2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon_0)^2}\frac{1}{r^6}\frac{I_1 I_2}{I_1+I_2} = -\frac{3}{2}\frac{\alpha_1'\alpha_2'}{r^6}\frac{I_1 I_2}{I_1+I_2}$$

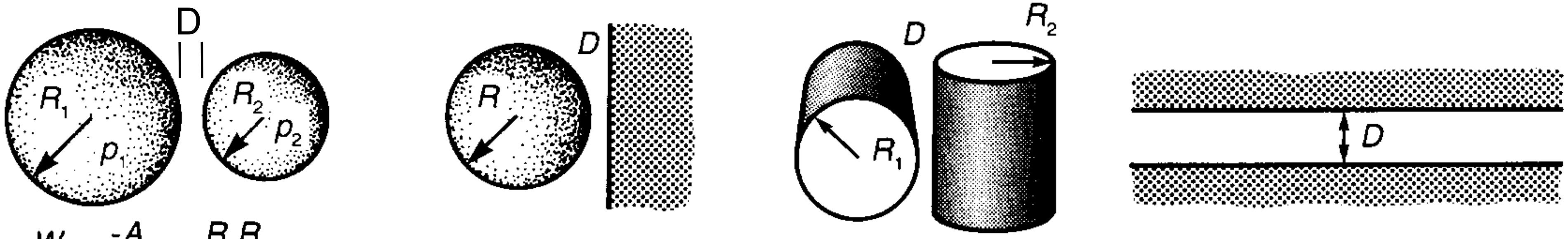
I_n is the ionization energy, with $I = h\nu$, ν is the electronic absorption frequency

In the case of two methane molecules with $\alpha' = 2.6 \cdot 10-24\ \mathrm{cm}^3$ and $I = 7$ eV the dispersion energy becomes -5 kJ mol^{-1} for a separation of 0.3 nm (comparable to the enthalpy of vaporization of methane ΔH_{vapor} = 8.2 kJ mol-1).

van der Waals Forces: Macroscopic

The van der Waals forces between two macroscopic bodies can be calculated (as approximation) by integrating over the molecular / atom-atom vdW pair potential ($w(r) = -C / r^6$) of all molecules / atoms in one body with all molecules / atoms in the other body.

→ interaction free energies are expressed in terms of the Hamaker constant:
$A = \pi 2 C \rho_1 \rho_2 \sim 10^{-19}$ J (in vacuum)
with $\rho_{1/2}$ being the atom density of body 1 / 2, C is the coefficient in the molecular / atom-atom pair potential



Two spheres
$W = \frac{-A}{6D} \frac{R_1 R_2}{(R_1 + R_2)}$

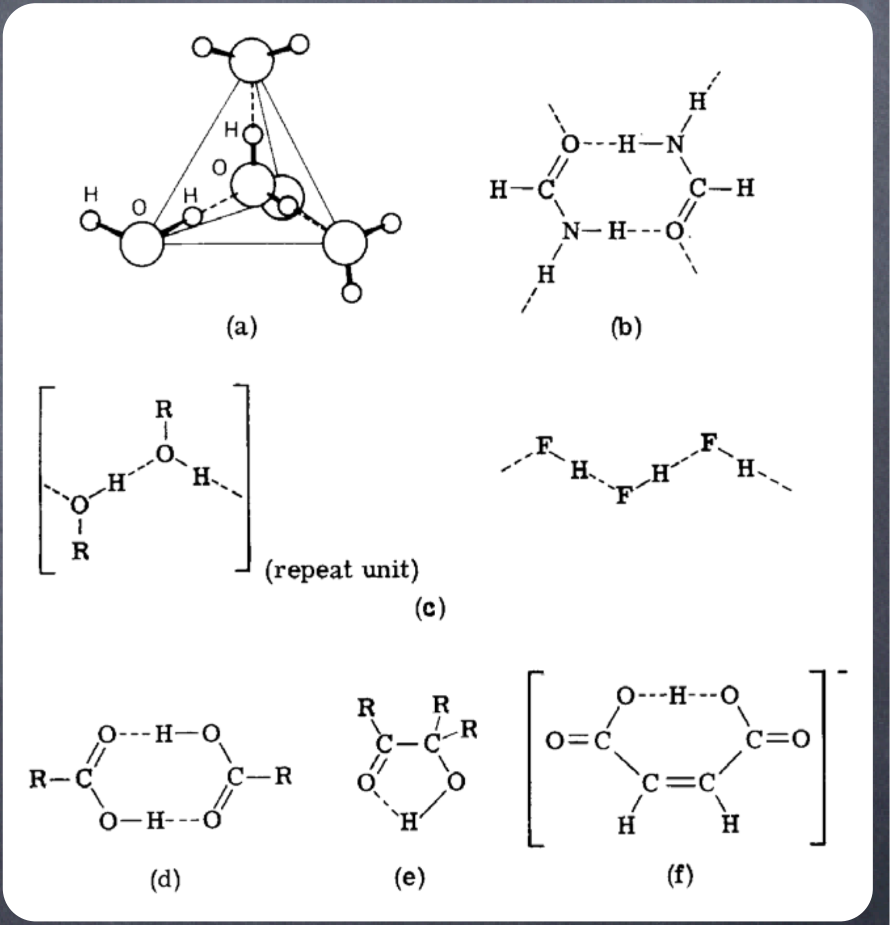
Sphere–surface
$W = -AR/6D$

Two crossed cylinders
$W = -A\sqrt{R_1 R_2}/6D$

Two surfaces
$W = -A/12\pi D^2$ per unit area

Hydrogen Bonding

highly polarized bond of hydrogen with heteroatom (e.g. $-X^{\delta-}-H^{\delta+}$, X = O, N, F) provides strong protonic character to hydrogen (proton donor) → H can interact with electron donating group / atom / electron lone pair (proton acceptor) ⇒ H-mediated "bond"



→ elongation of bond in H-donor

→ very short distance of H and electron donor (H-acceptor)
⇒ for H_2O: O-H = 0.10 nm, O…H = 0.176 nm,

theoretical vdW radius O/H = 0.26 nm

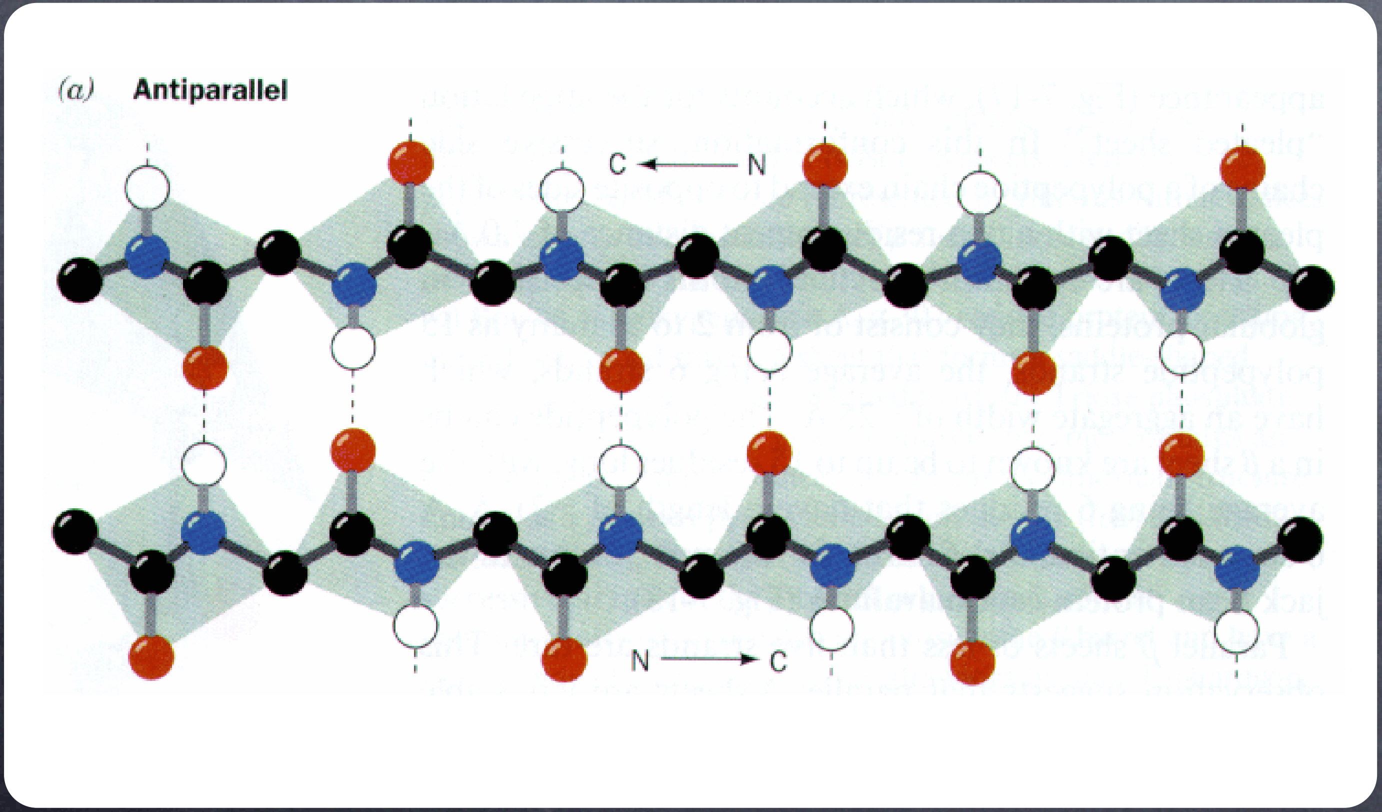
H-bonding in H_2O:
→ particular structure of ice
→ hydrophobic effect (restructuring of H-bonding network around hydrophobic solute is entropically unfavorable)

Hydrogen Bonding: Proteins

Hydrogen bonding of the amide groups via N-H...O=C leads to secondary and tertiary structures of proteins:

- α-helix (chiral, tubular structure)

- β-pleated sheet (extended flat structure)



Hydrogen Bonding: DNA

The base pairing in the DNA double helix is mediated by hydrogen bonding between the nucleic acid moieties:

- 2 H-bonds between adenine and thymine
- 3 H-bonds between guanine and cytosine