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3

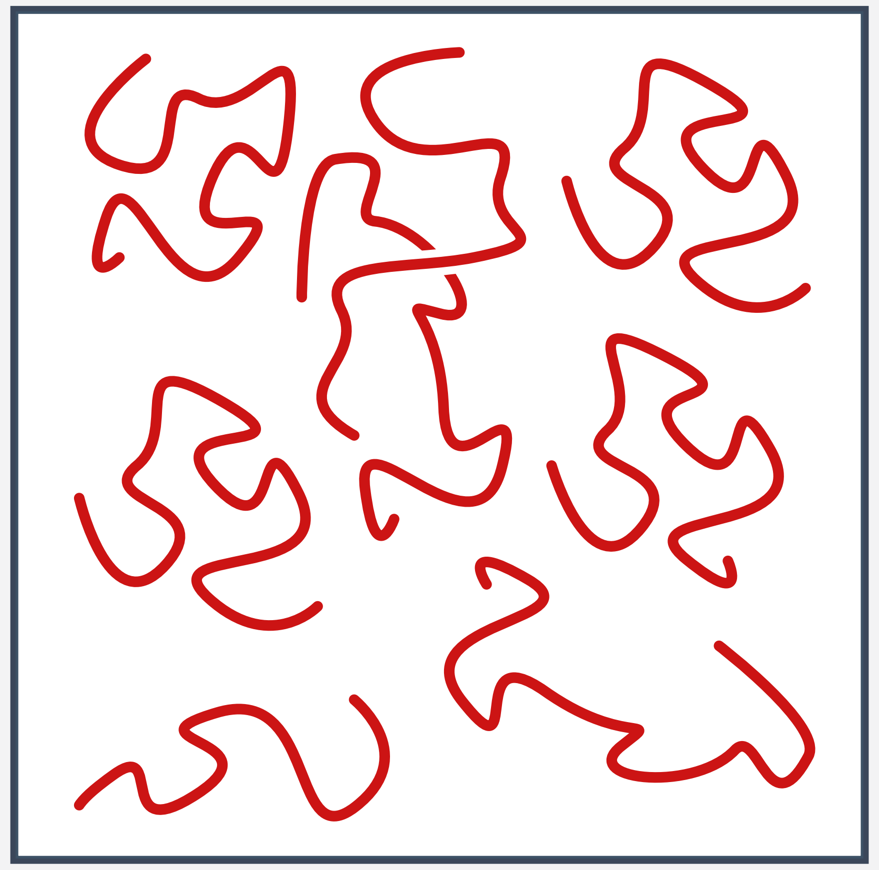
Structures of Polymers in the Condensed State

Condensed States of Polymers

- polymer phases determined by chemical constitution, processing history, external parameters (*T*, solution)

viscous liquids

(solutions, polymer melts)



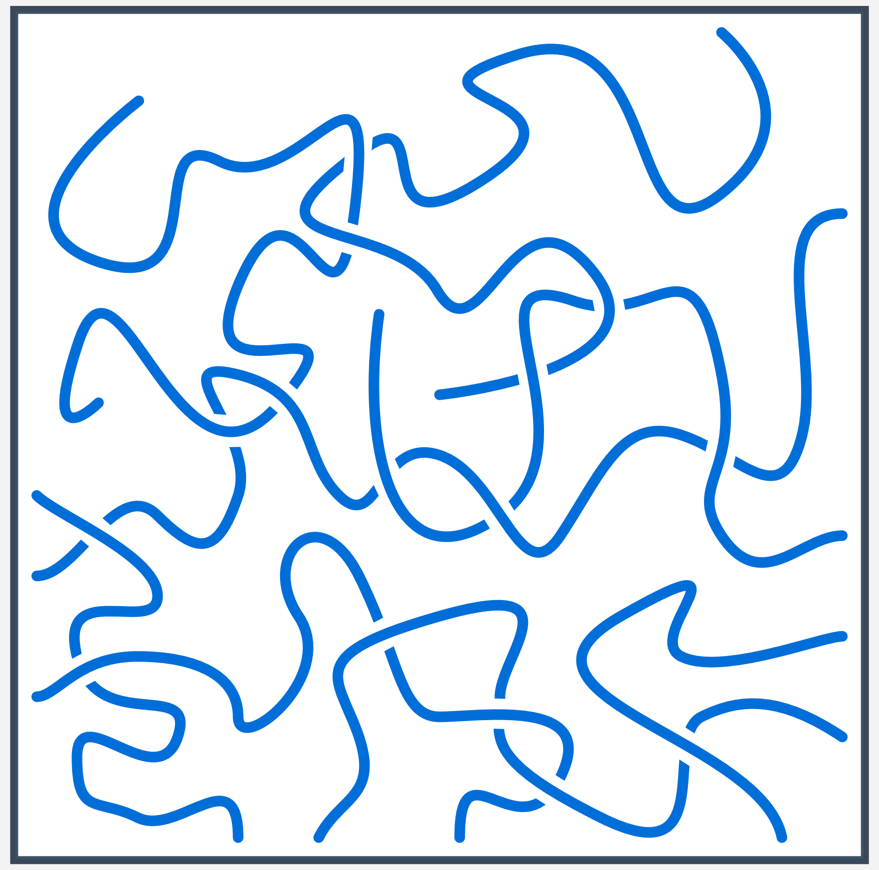
easy chain movement

silicones (PDMS):

T_g = - 123 °C

T_m = - 40 °C

amorphous glasses

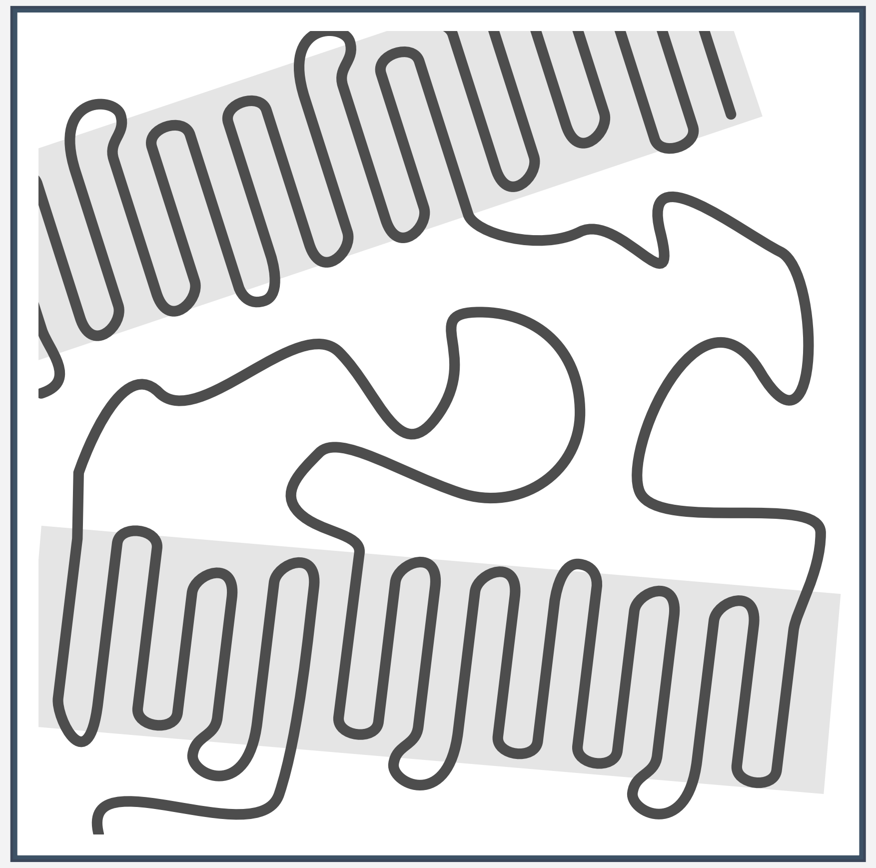


only local movement of chain segments

polystyrene:

T_g = 100 °C

semi-crystalline



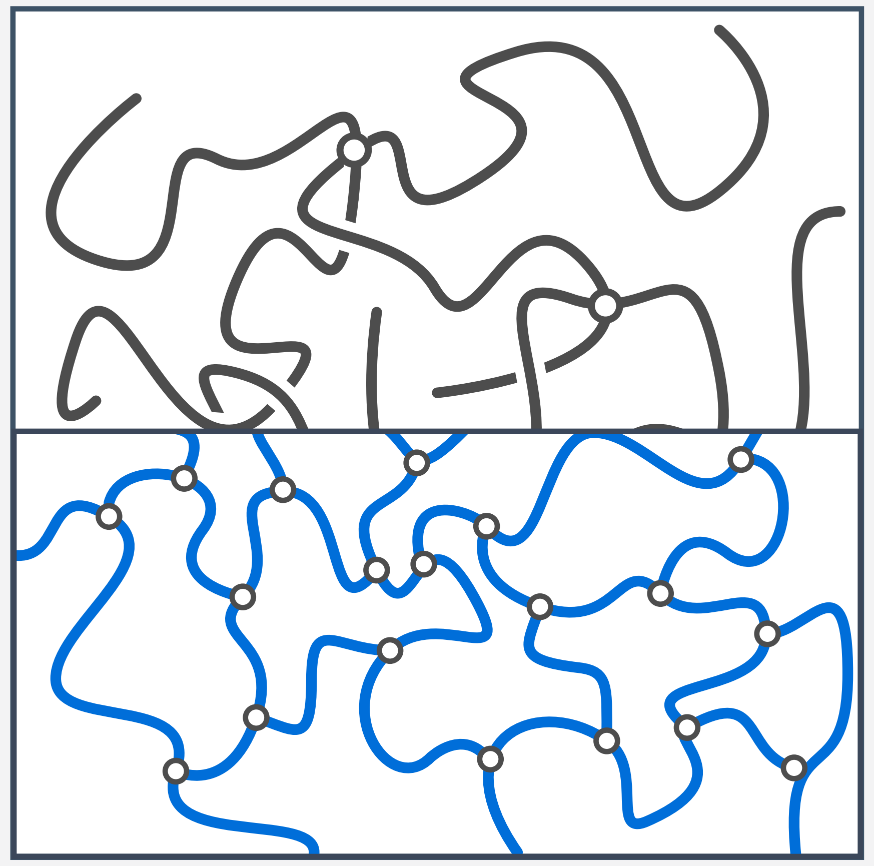
restricted chain movement by crystallization

nylon 6,6:

T_g = -50 °C

T_m = 265 °C

elastomers or thermosets



restricted chain movement by cross-links

polyisoprene:

T_g = -73 °C

- **all polymers show a glass transition;** **some are glassy at operating temperature (room temperature)**

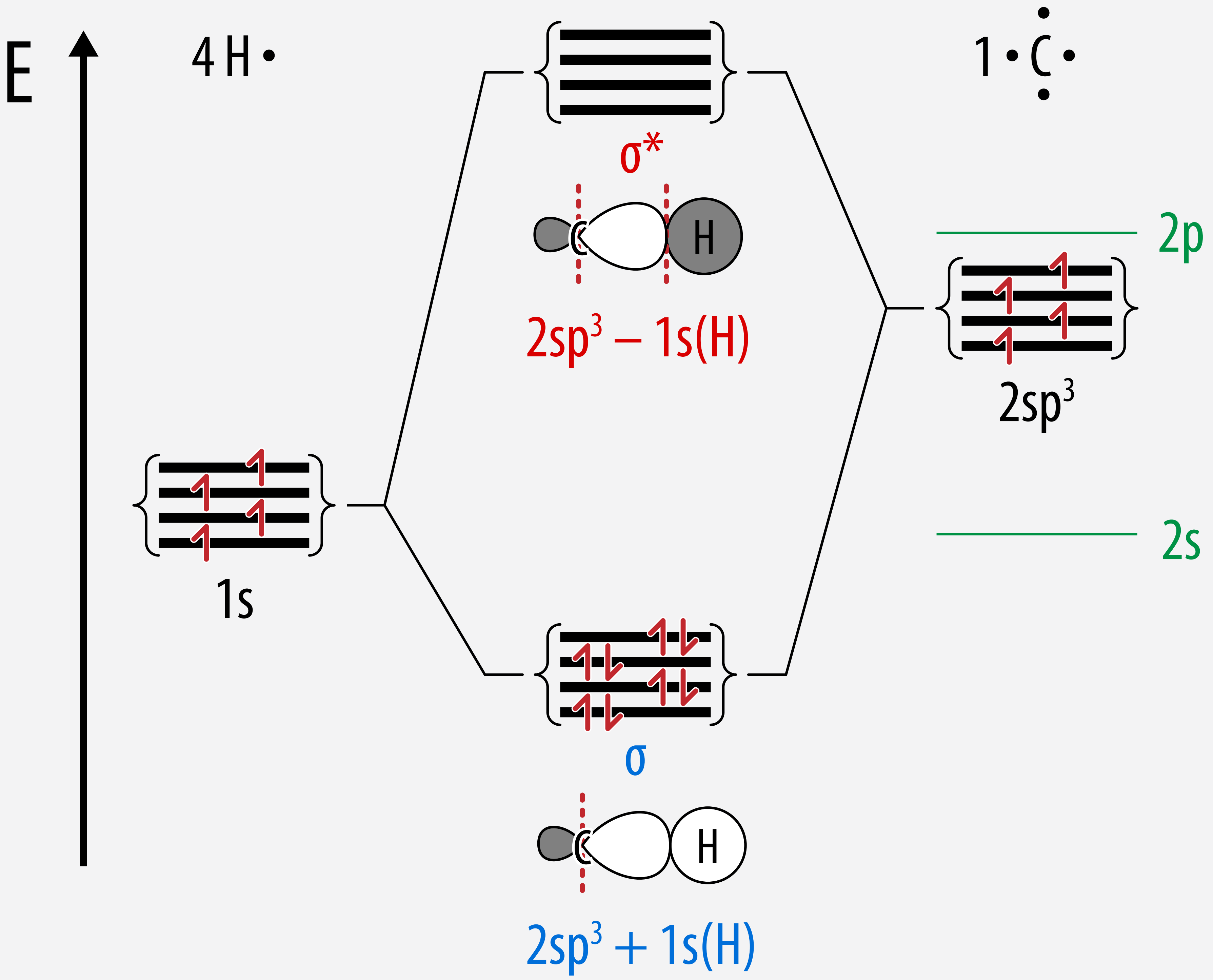
3.1

The Cohesive Energy

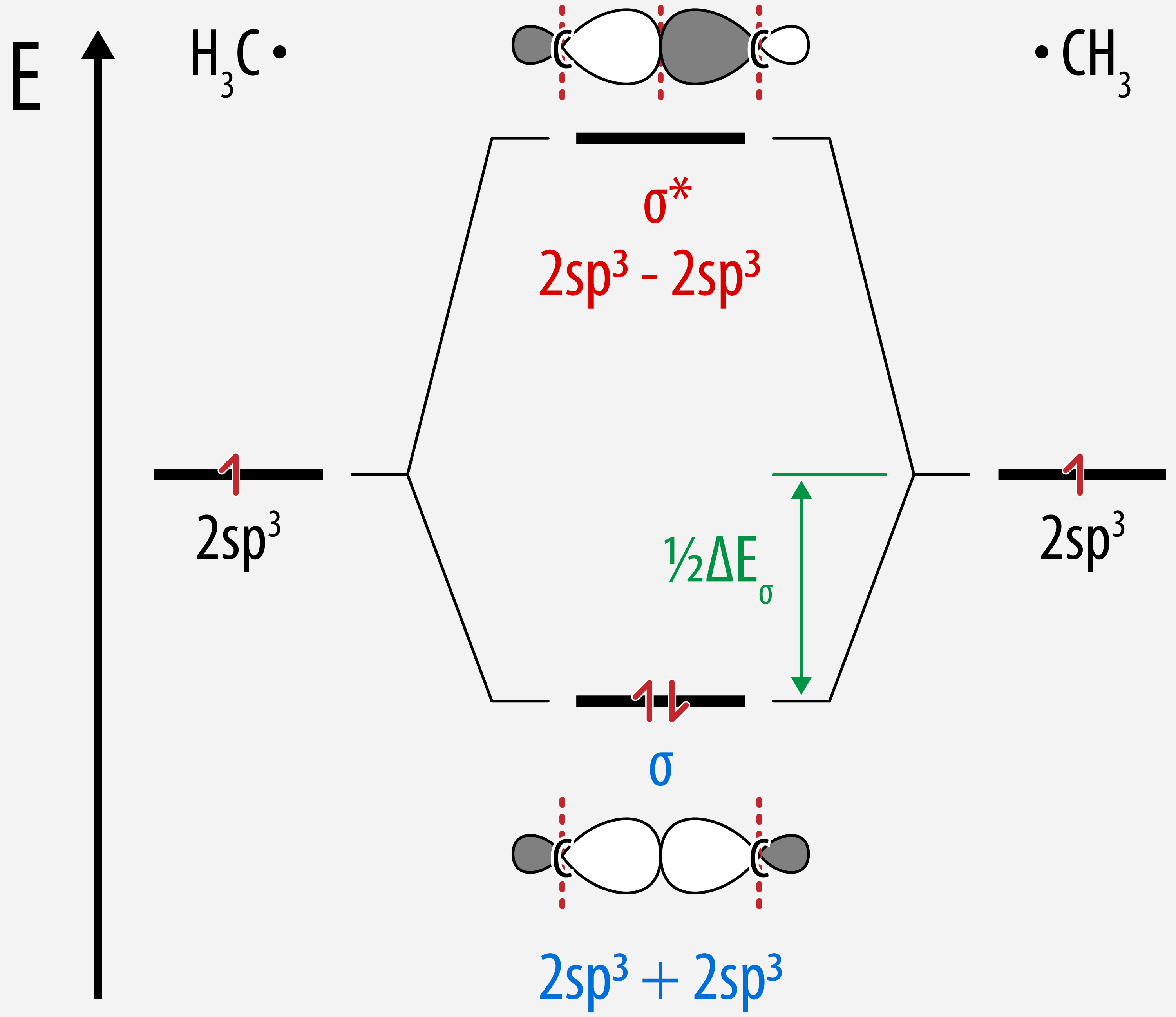
Covalent Bonds vs. Secondary Interactions

Covalent Bond Strengths

- molecular orbital diagrams for the C–H (example: methane) and C–C (example: ethane) bond:



$\Delta E_{C\text{-}H} \approx 420$ kJ/mol

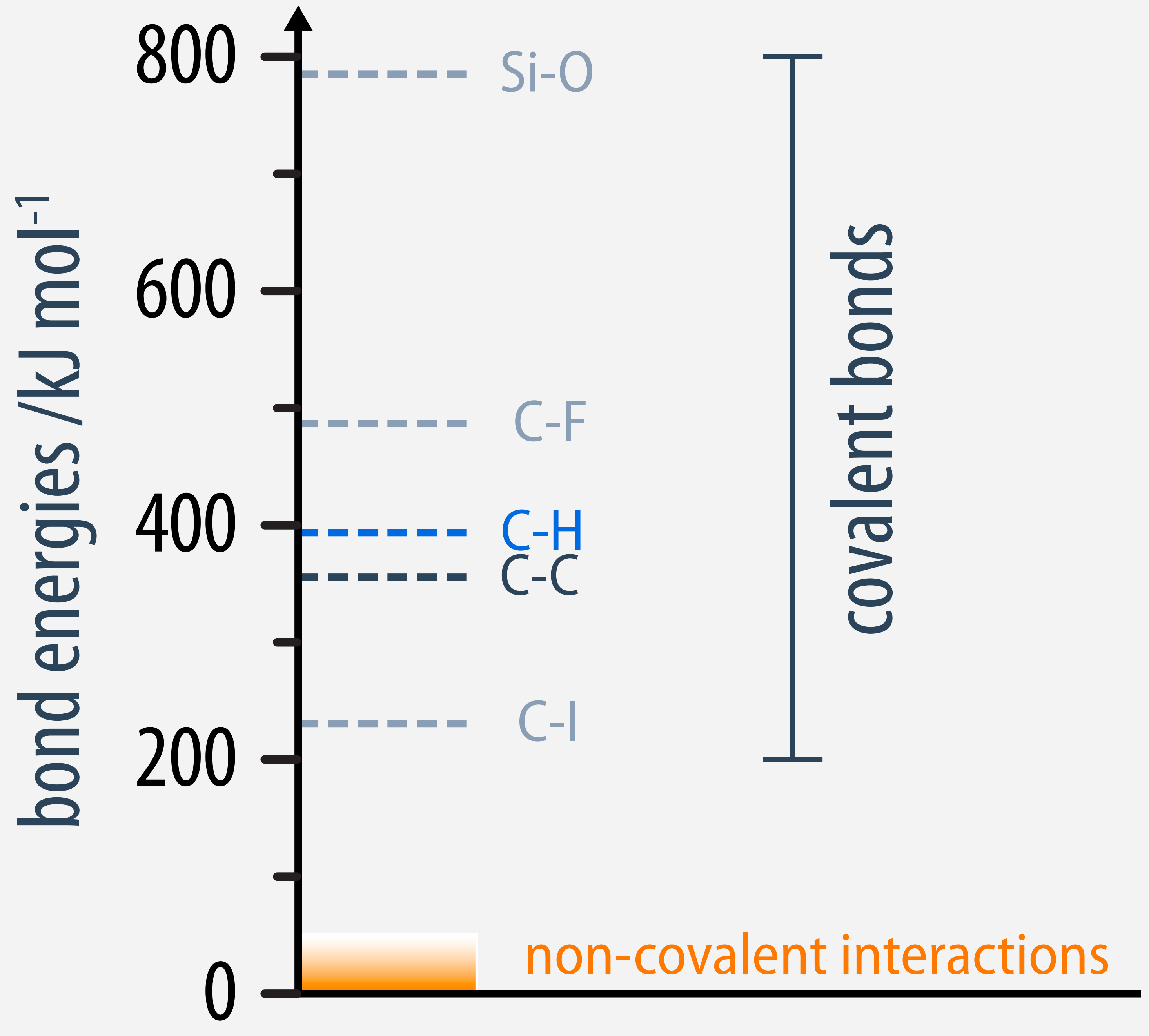


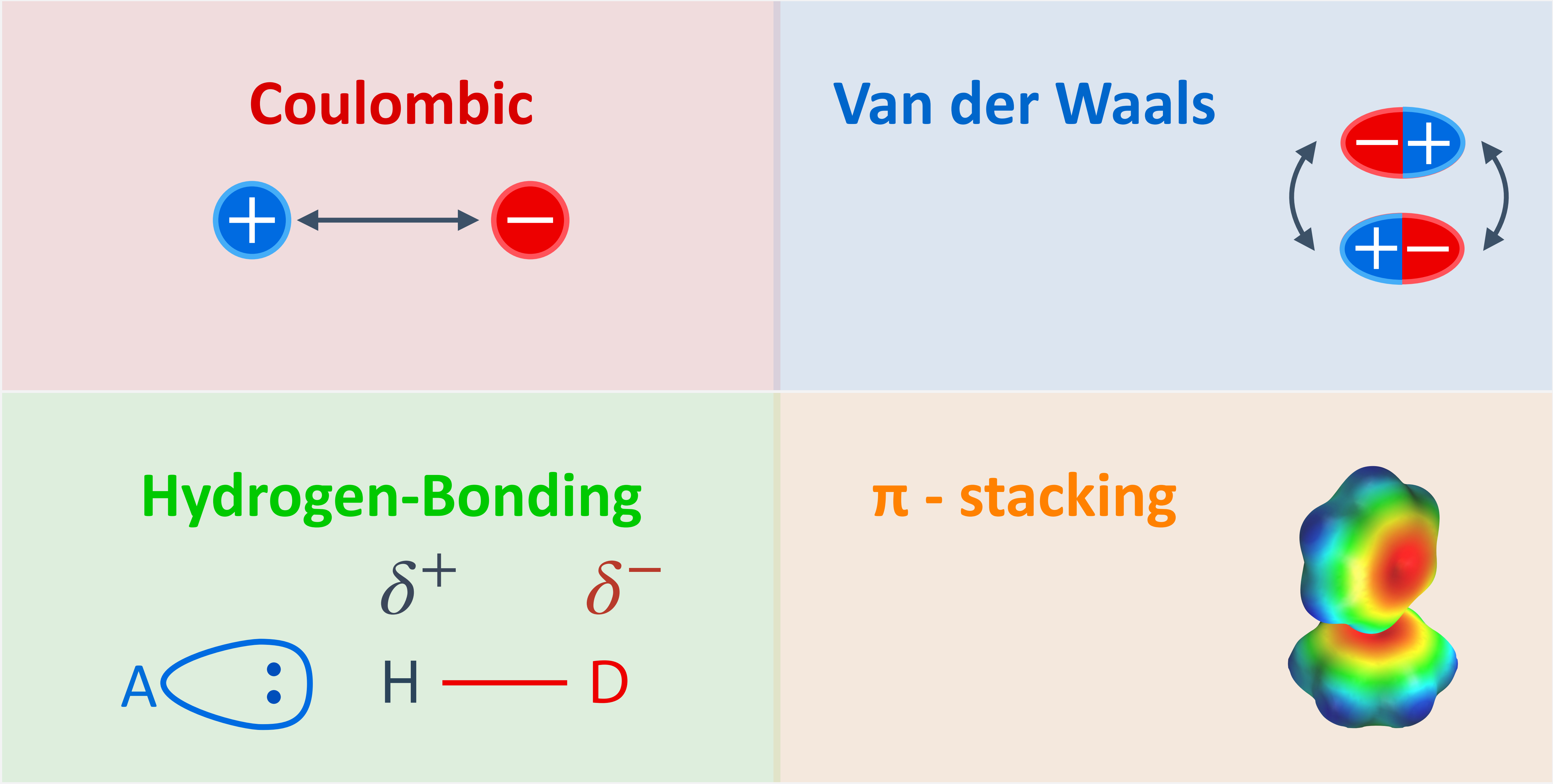
$\Delta E_{C\text{-}C} \approx 350$ kJ/mol

- **bond strength arises from stabilisation of filled σ-orbitals via direct overlap of atomic orbitals**

Non-Covalent Interactions

- non-covalent forces govern polymer conformations and inter-chain interactions





- **individual non-covalent interactions are weak (thermal energy at r.t.: ≈ 2.5 kJ/mol) and transient**
- **in combination, they can reinforce or counteract one another**
- **together, they dictate the geometry and stability of molecular organisation in the condensed phase**

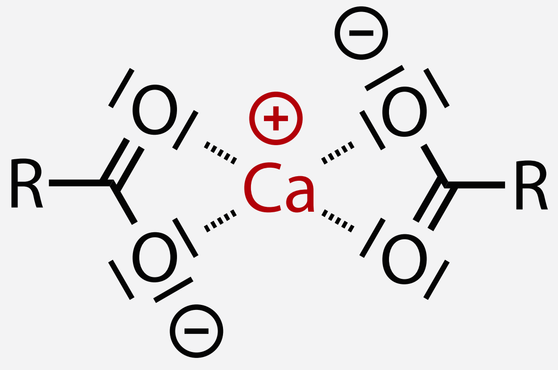
Types of Attractive Non-Covalent Interactions

- **Coulombic interactions (charge-charge)**

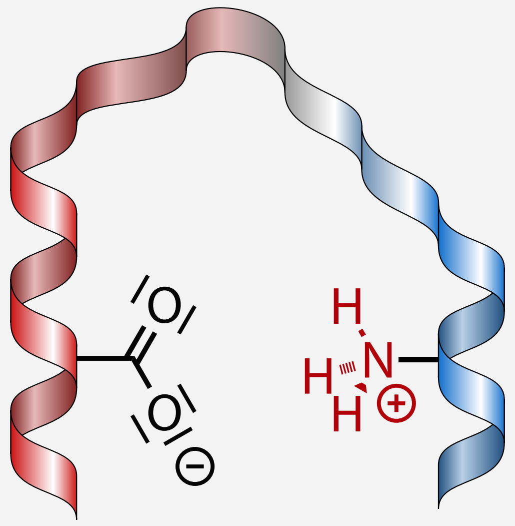
strong (100 - 400 kJ/mol),

longest range interaction ($E \propto r^{-1}$),

non-directional



salt bridges



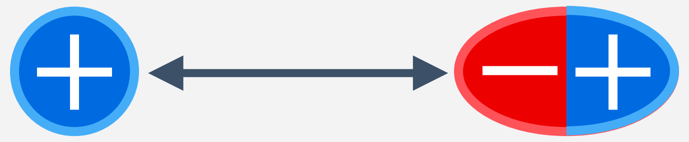
acid-base pairs
(in particular in proteins)

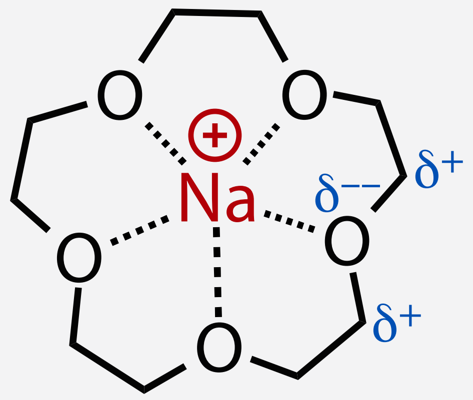
- **charge-dipole interactions**

moderately strong (50 - 200 kJ/mol),
(stronger, when partially covalent (100 - 400 kJ/mol)

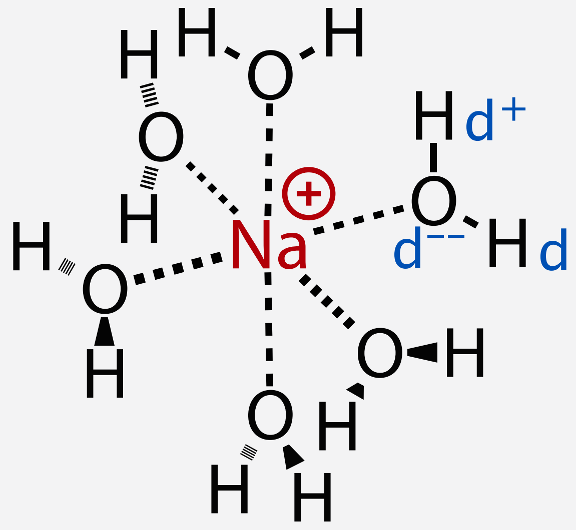
long range ($E \propto r^{-2}$),

depends on dipole orientation





cation-binding hosts



solvation

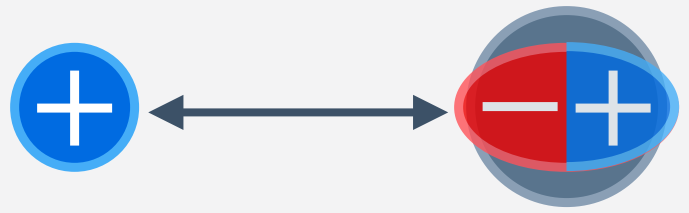
Types of Attractive Non-Covalent Interactions

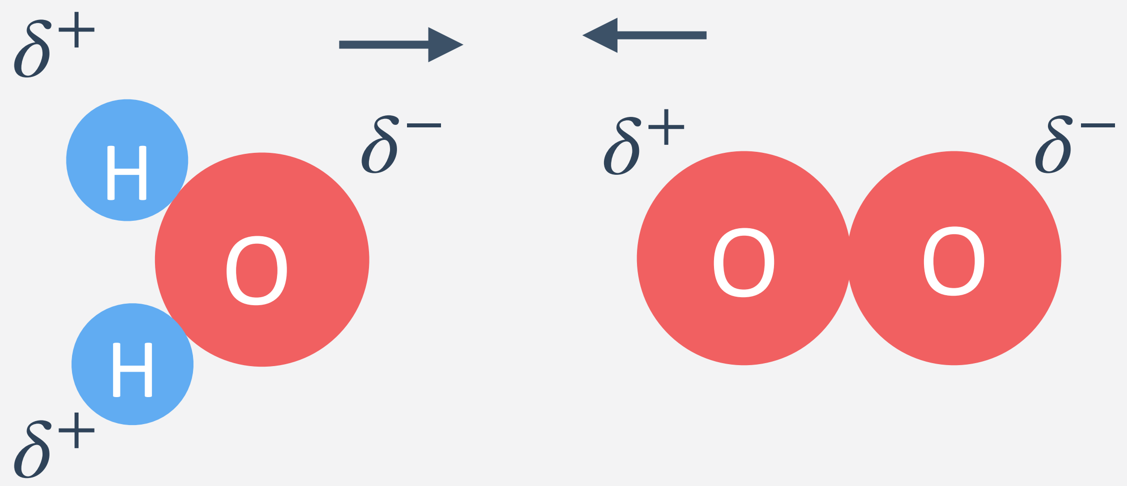
- **charge-induced dipole**

  relatively weak,

  moderate range force ($E \propto r^{-4}$),

  strength depends on polarizability





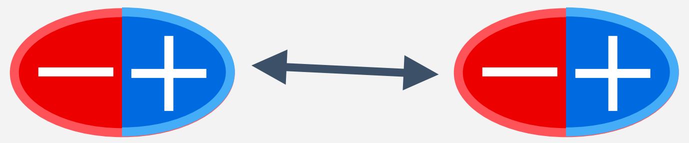
oxygen in water

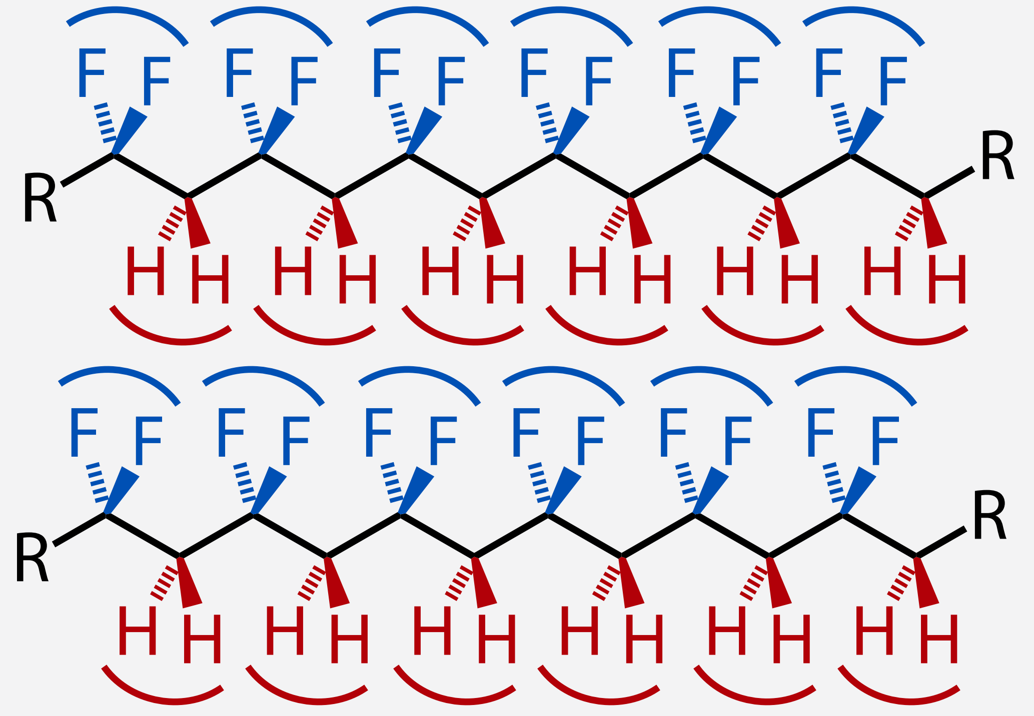
- **dipole-dipole interactions**

  weak (10 - 50 kJ/mol),

  short range ($E \propto r^{-3}$),

  strongly dependent on relative dipole orientation





poly(vinylidene difluoride) PVDF
polar order, dielectricity

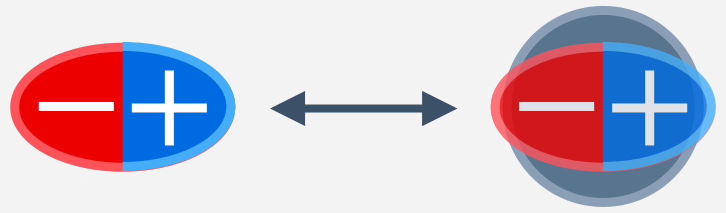
Types of Attractive Non-Covalent Interactions

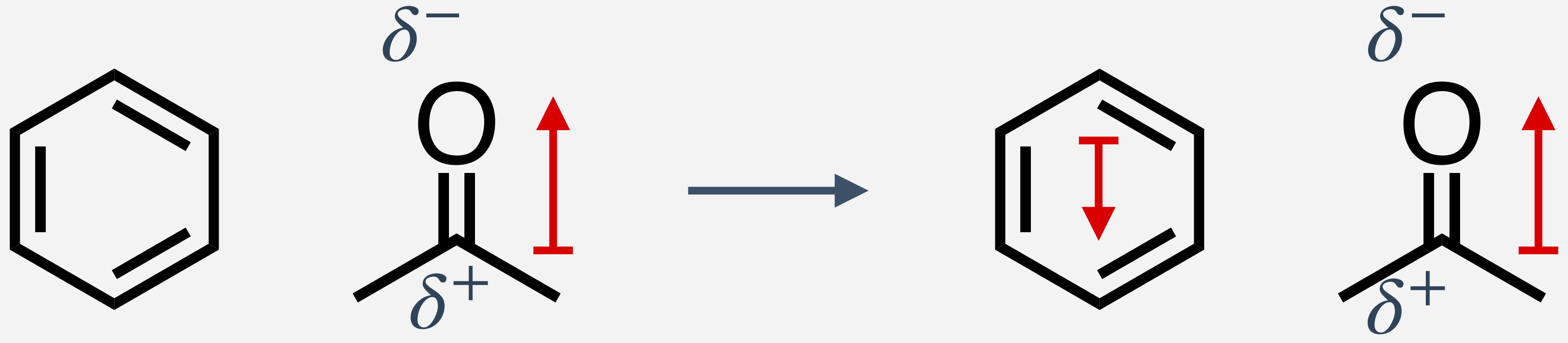
- **dipole-induced dipole**

  weak (2 - 30 kJ/mol),

  short ranged ($E \propto r^{-6}$),

  strength depends on polarizability





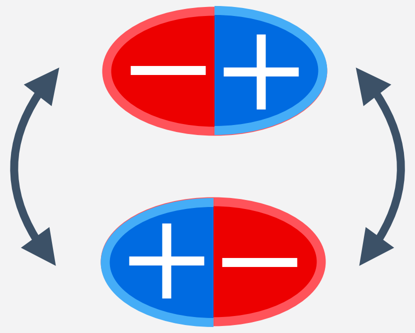
solubility of apolar compounds (benzene) in polar solvents (acetone)

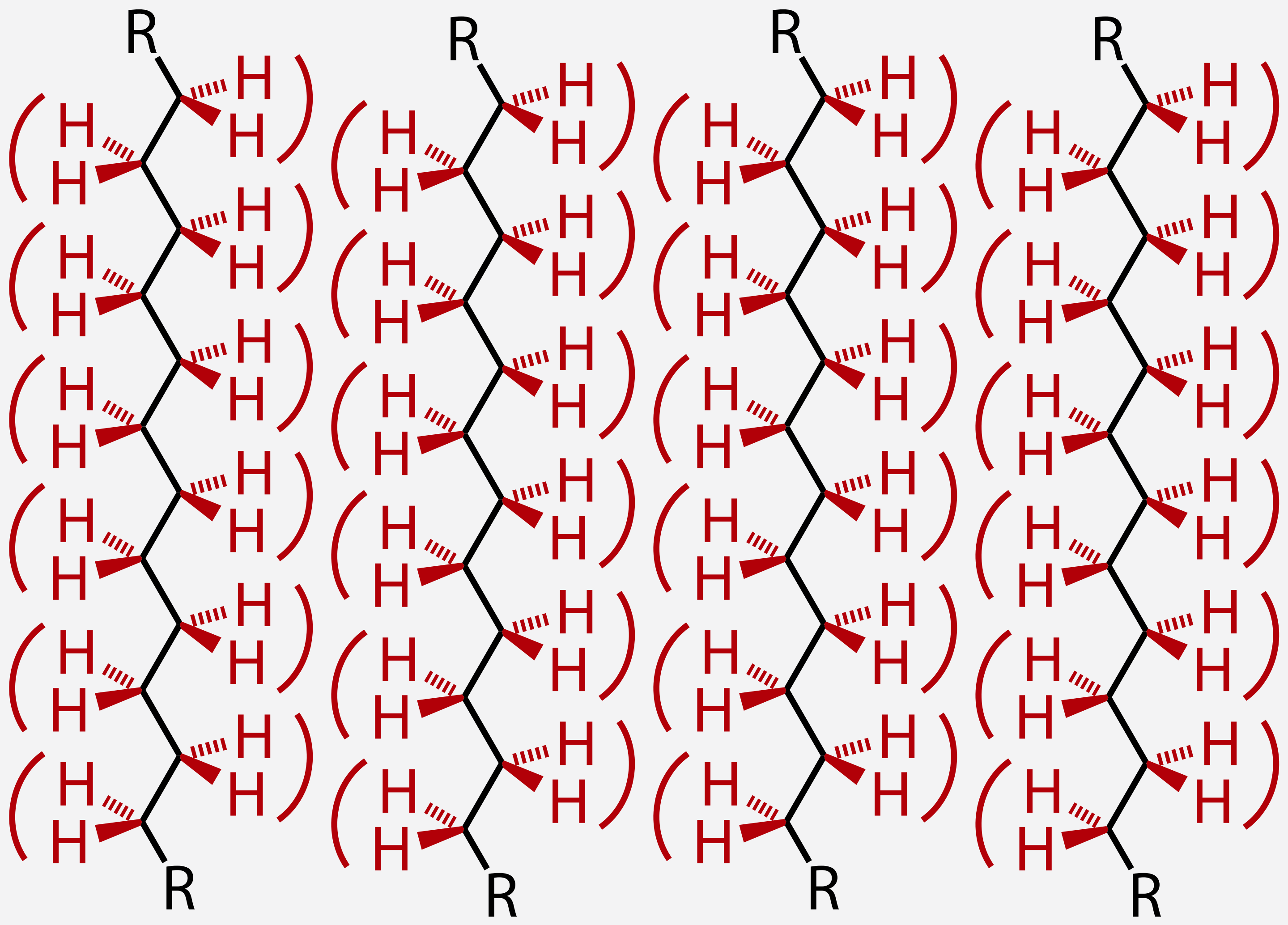
- **dispersion**

  weak (2 - 20 kJ/mol),

  short range ($E \propto r^{-6}$),

  arises from correlated fluctuations of instantaneous dipoles

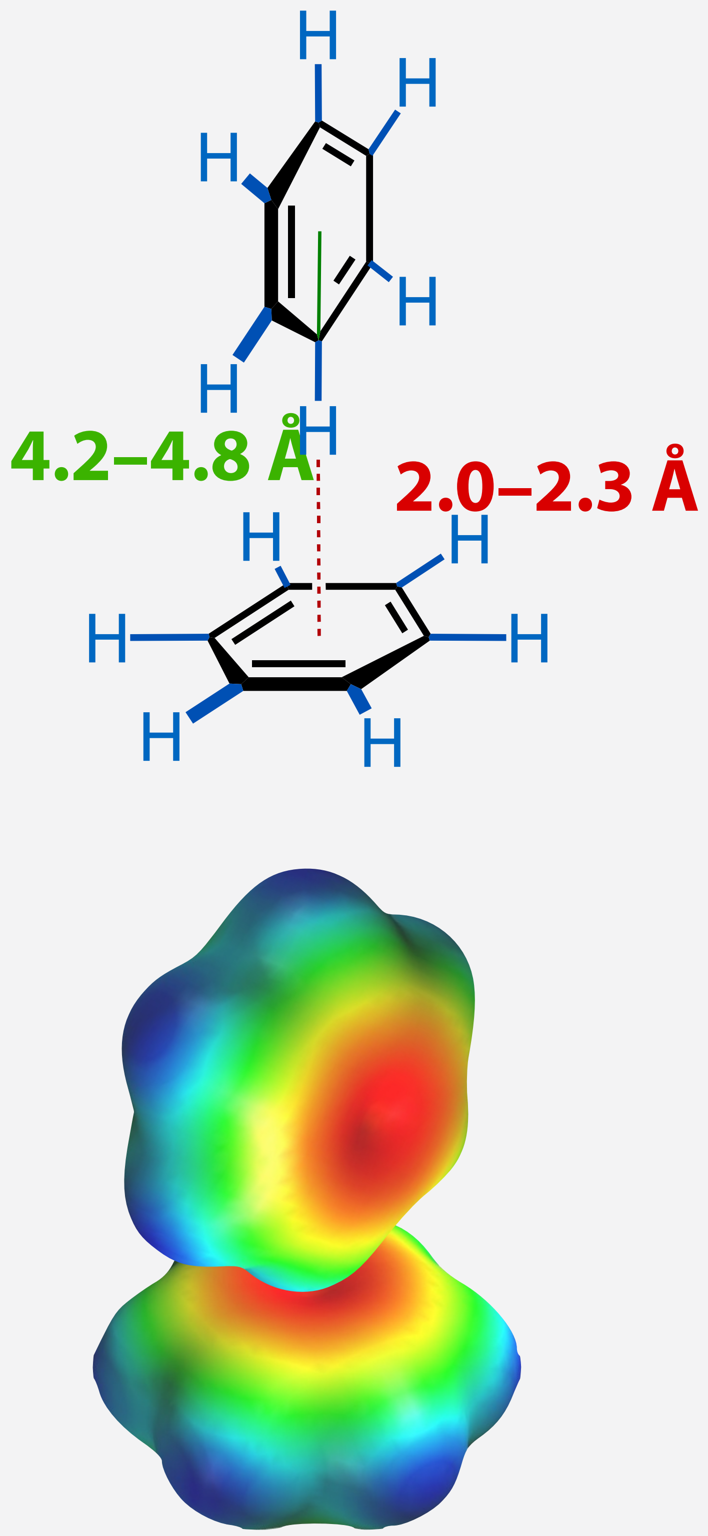


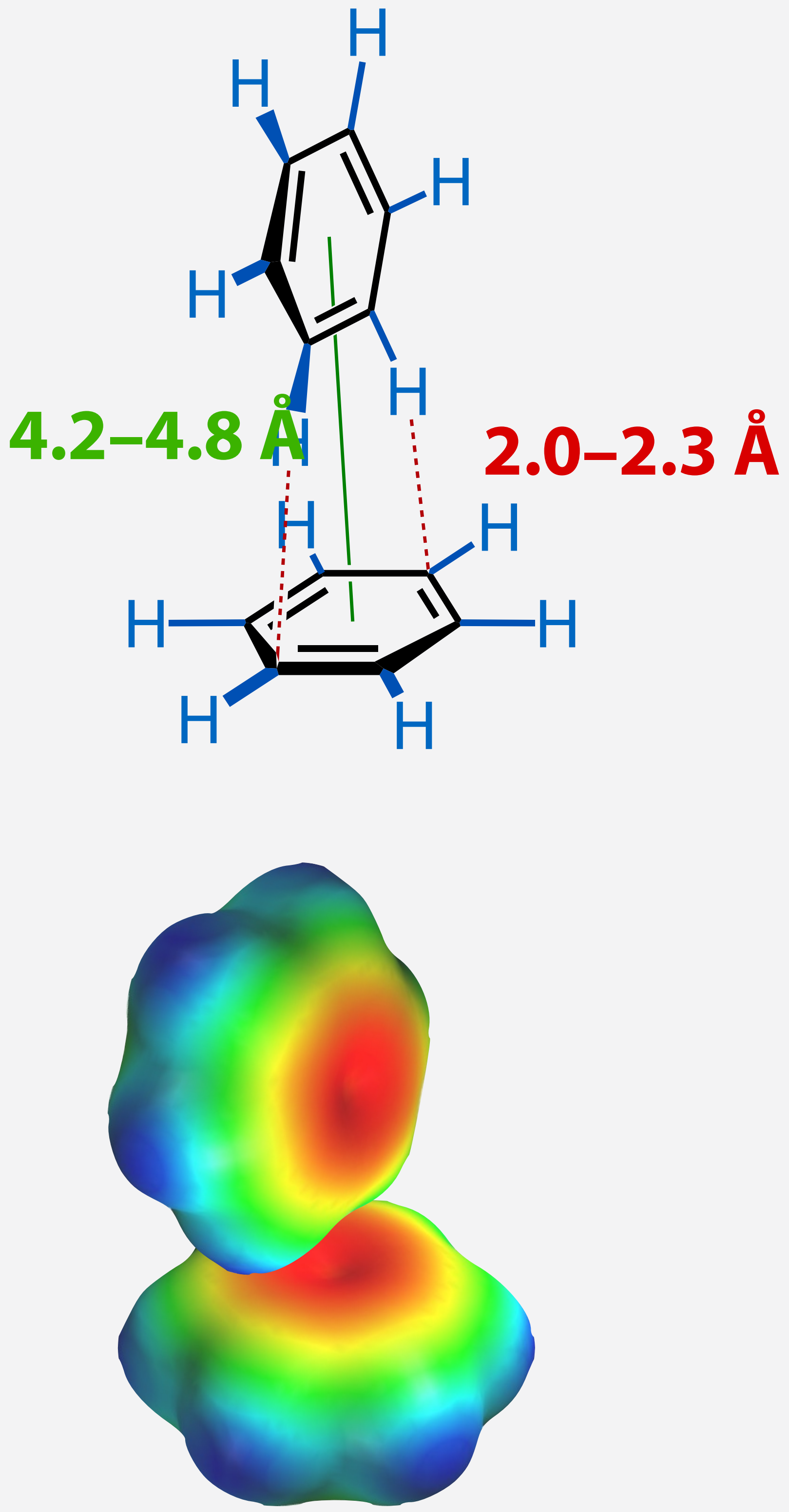


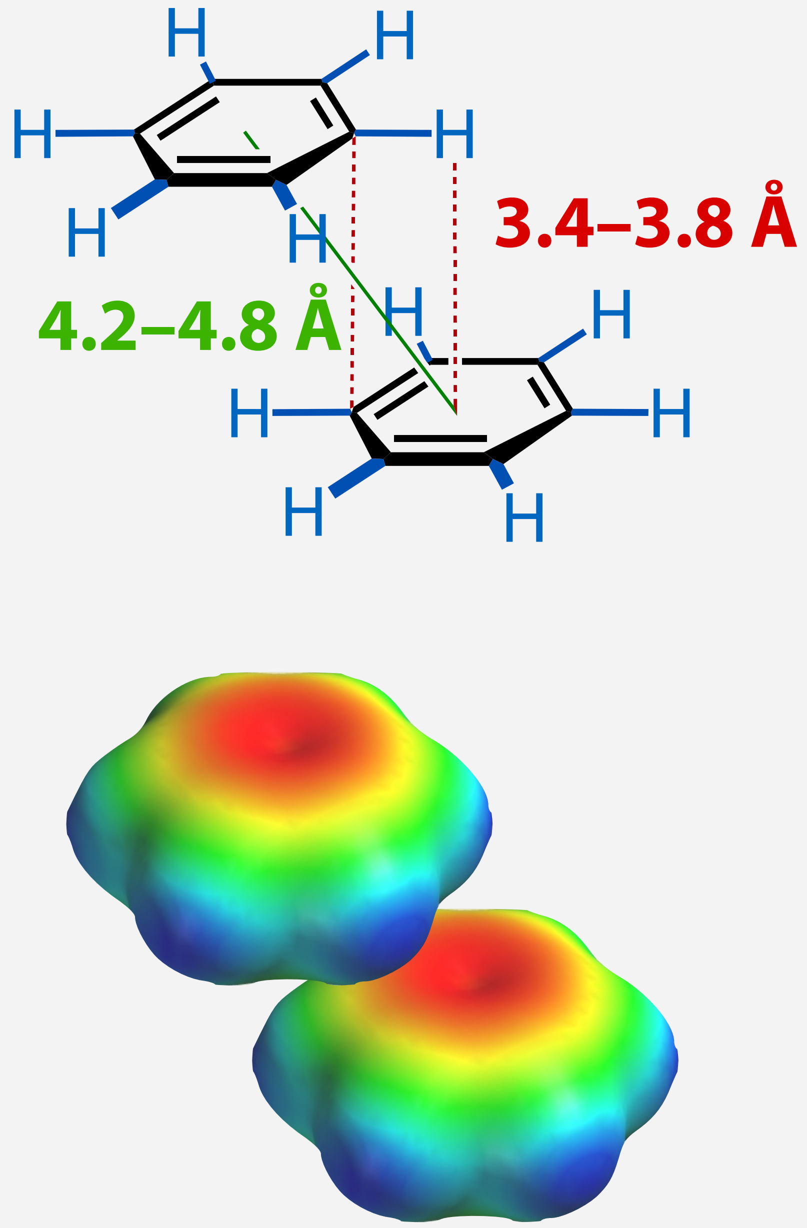
polyethylene (PE)

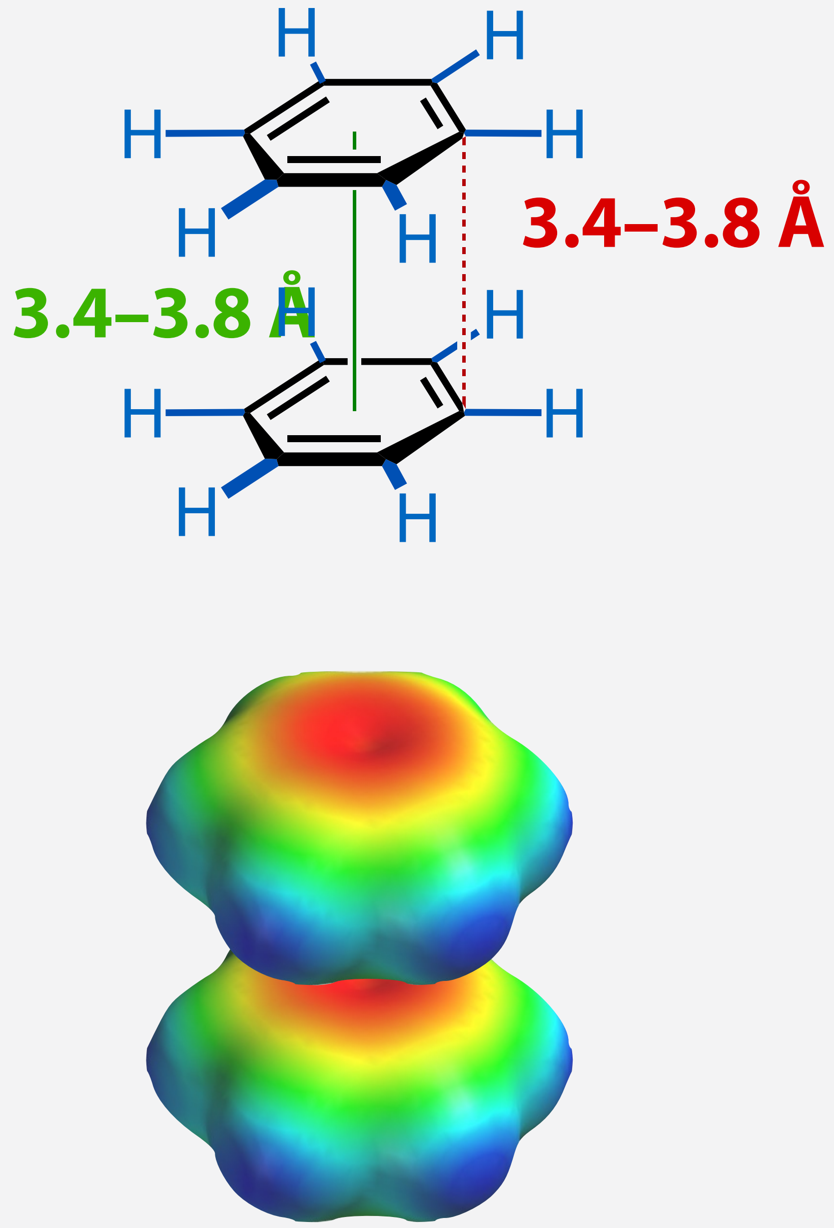
Types of π–π Interactions

- π–π interactions are weak (5–50 kJ/mol) and short-ranged ($E \propto r^{-6}$)

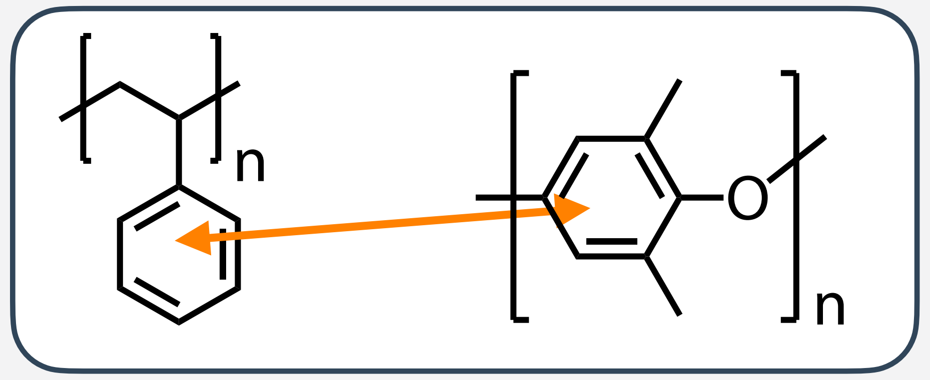

edge-to-face


edge-to-face


parallel-displaced

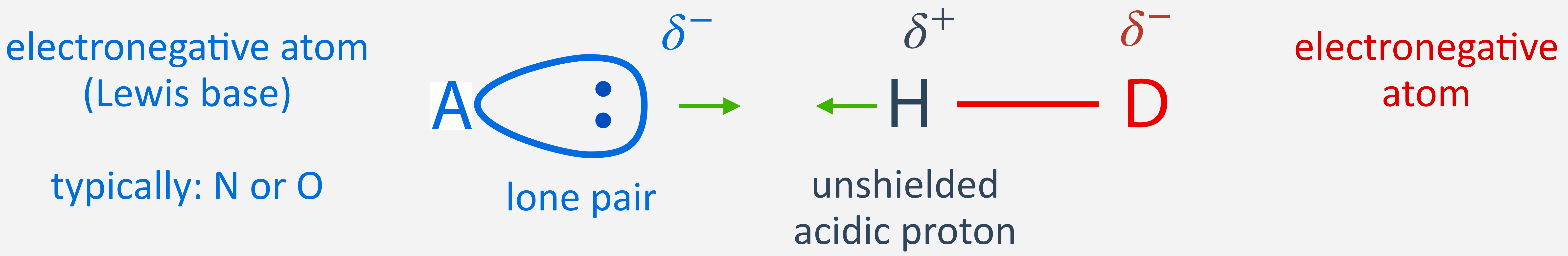

face-to-face

- arise from a combination of **dispersion** with **quadrupolar electrostatics**
- key role in the miscibility and organisation of aromatic polymers (see Chapter 5)



Hydrogen-Bonding - Simplified Overview

- specific attractive interaction between polarised D–H group and electronegative atom with lone pairs:



electronegative atom
(Lewis base)

typically: N or O

A

δ^-

lone pair

δ^+

H

unshielded
acidic proton

δ^-

D

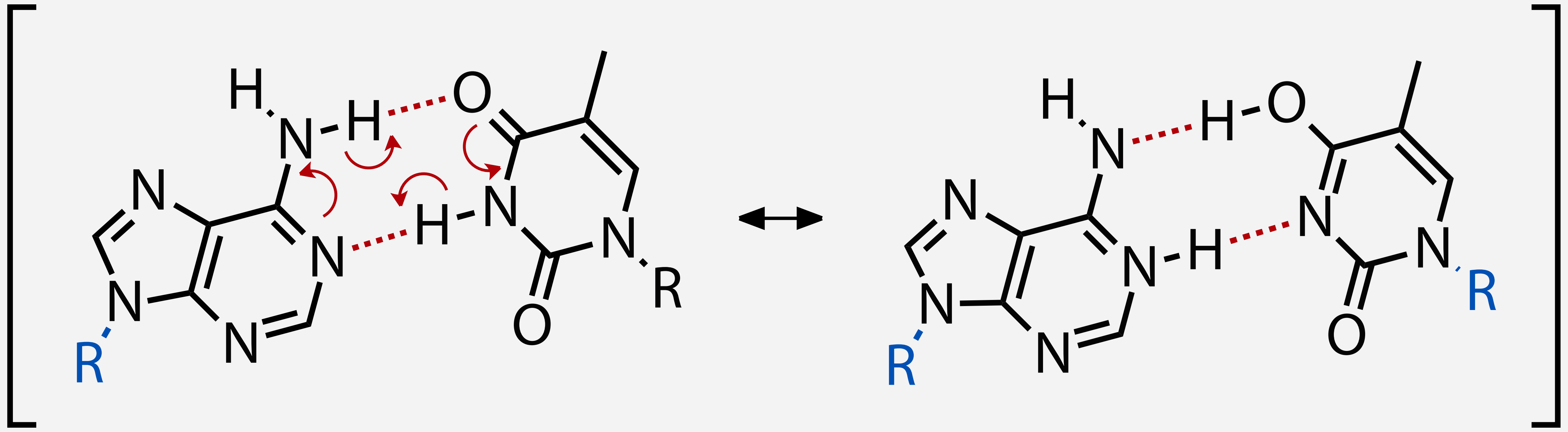
electronegative
atom

	weak H-bonds	moderate H-bonds	strong H-bonds
typical feature:	the donor is often **C**	often neutral **D** and **A**	often charged **D** and **A**
bond strength	2-20 kJ/mol	20-60 kJ/mol	60-170 kJ/mol
D–H···A angle	90-150°	130-180°	170-180°
H···A	2.2-3.2 Å	1.5-2.2 Å	1.2-1.5 Å
bond character	electrostatic	mostly electrostatic	covalent

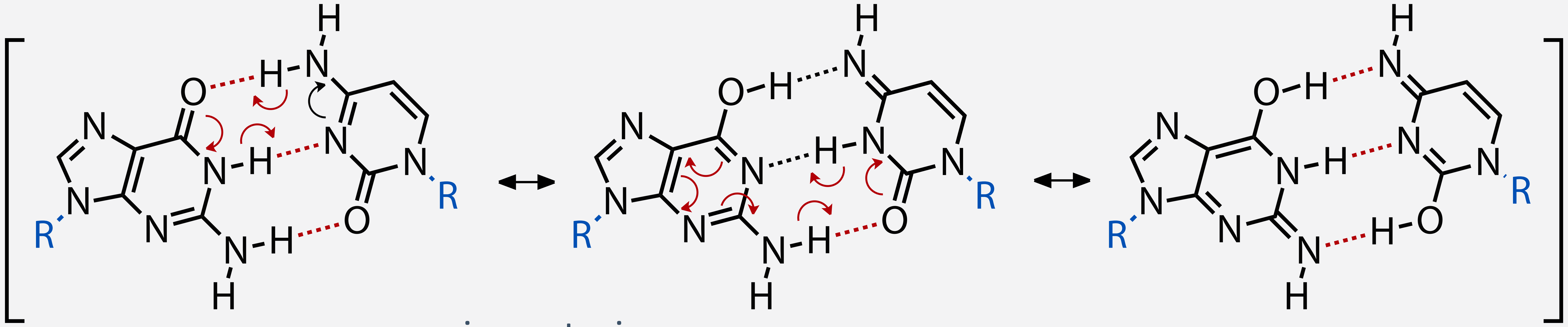
most relevant for polymer structure formation

- **strength & geometry vary with acceptor/donor type, from purely electrostatic to nearly covalent**

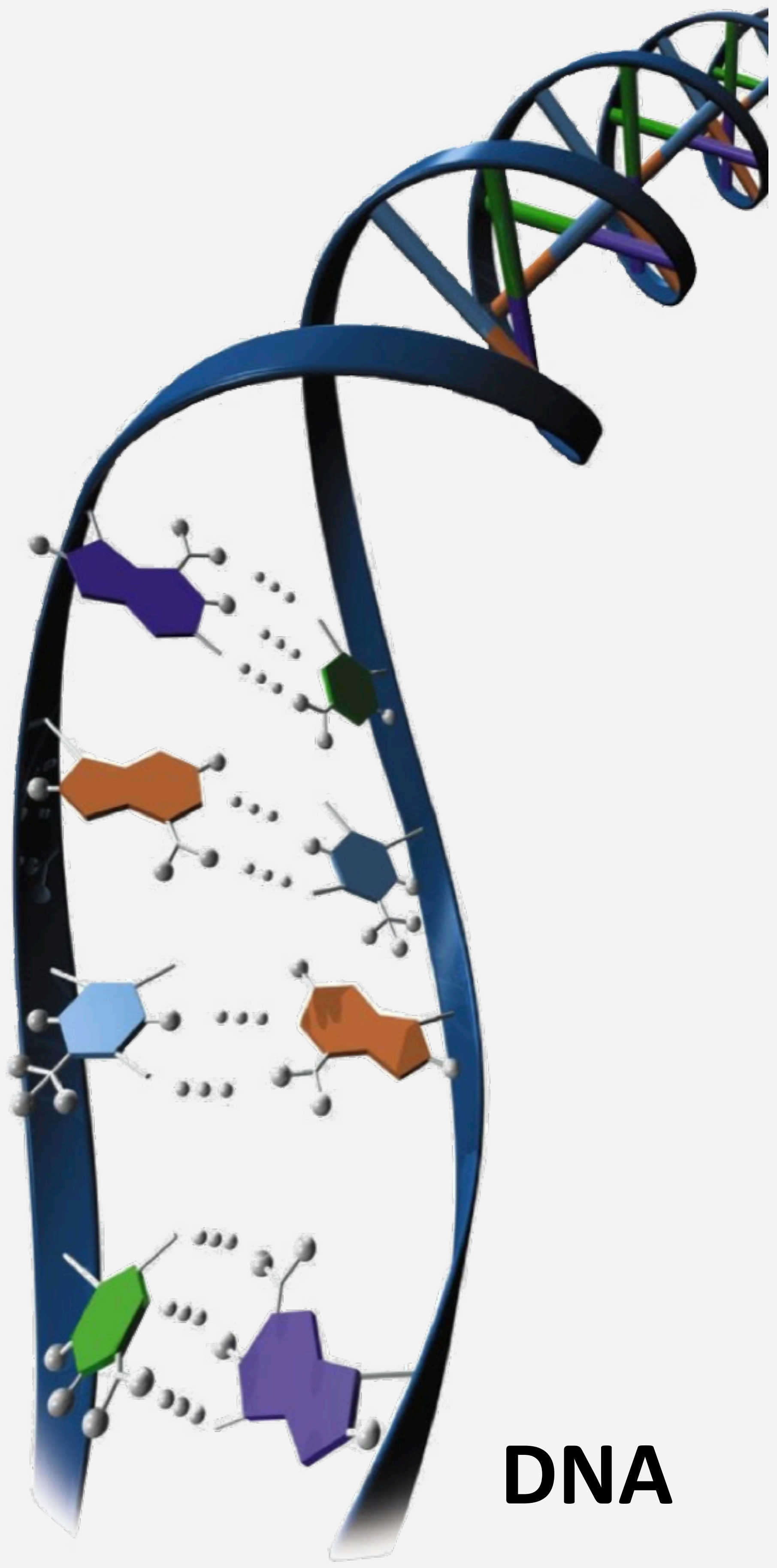
Hydrogen-Bonding in Biological Systems



adenine–thymine



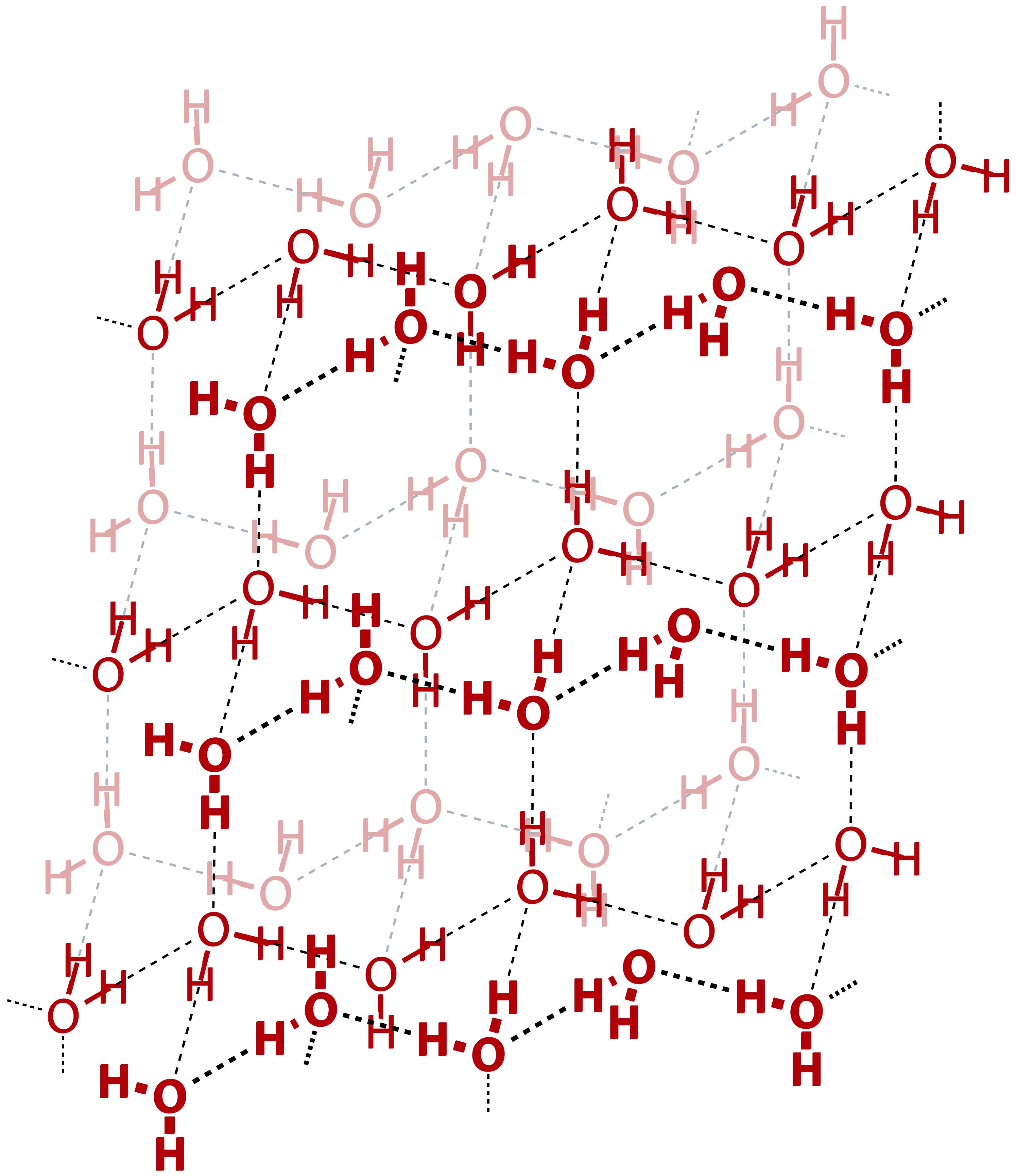
guanine-cytosine



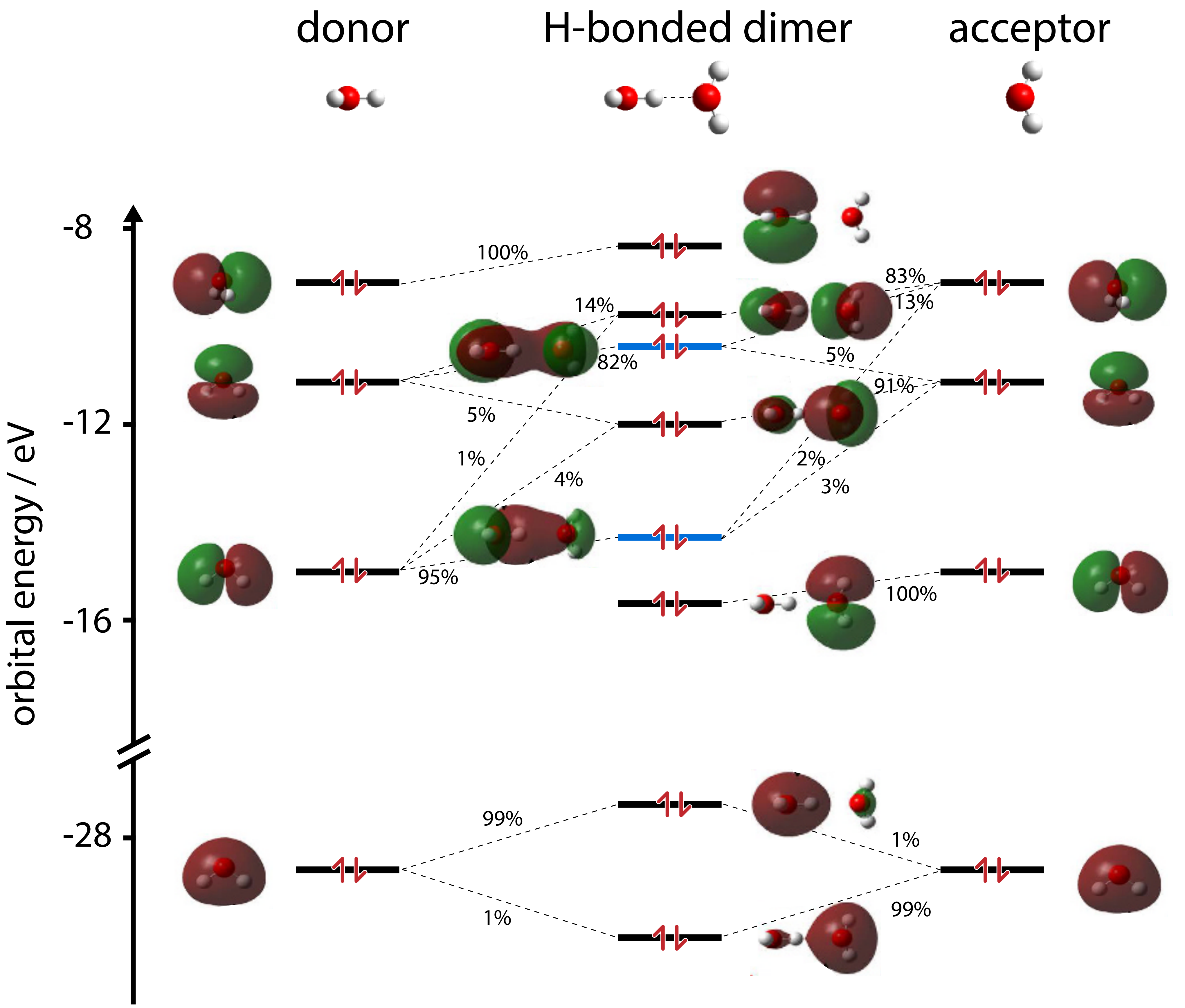
- **complementary arrangements of hydrogen-bond acceptors/donors enables selective recognition**

Directionality of the H-Bond

structure of water



molecular orbital diagram of the water dimer



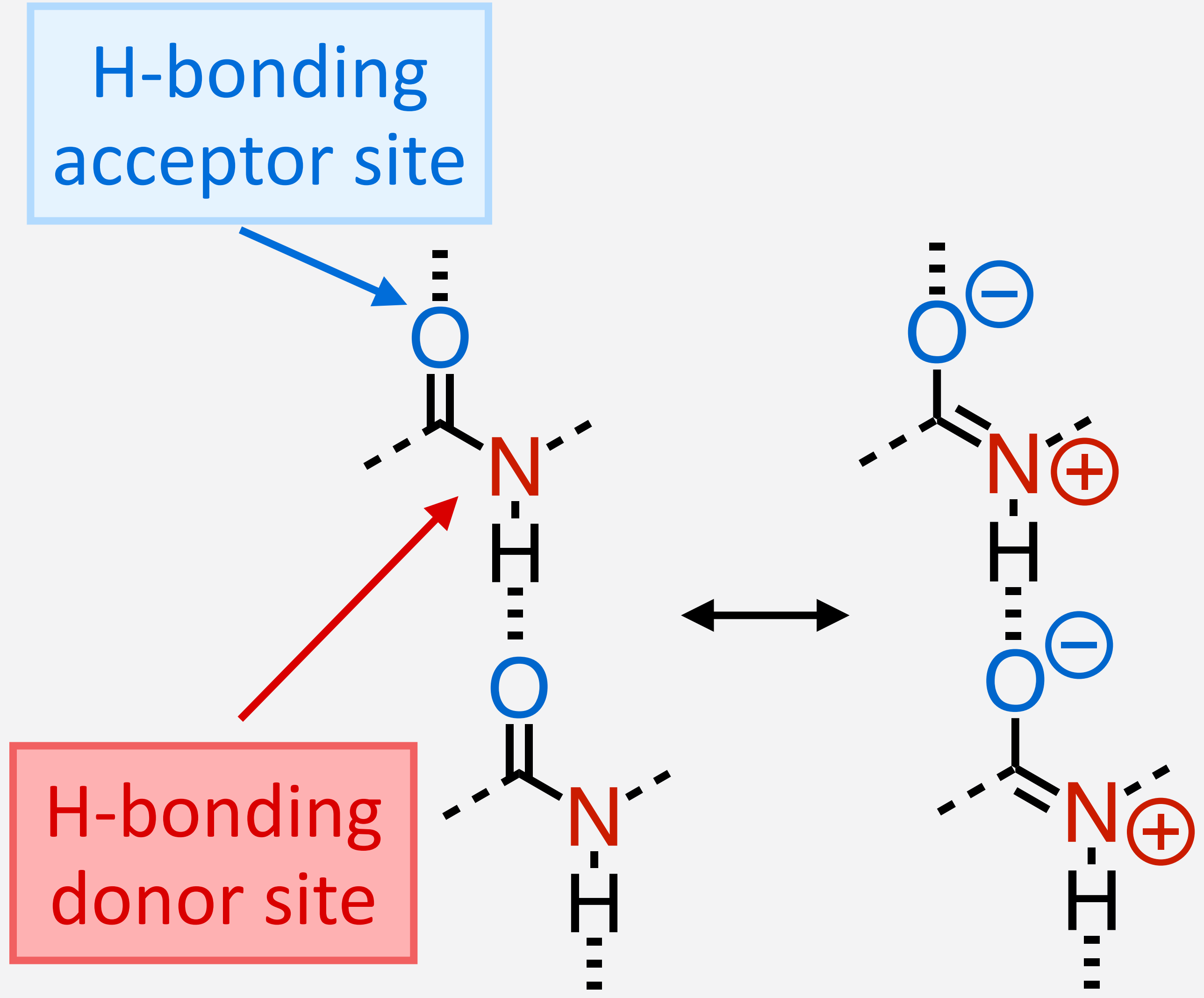
- **the partial covalent character from orbital overlap favors near-linear geometric arrangement**
- **stronger covalent contribution: ➞ more linear, highly directional H bond (D–H···A angle ≈ 180 °)**

Z. Wang, R.-Q. Zhang, *Sci. Reports* **2016**, *6*, 22099

Hydrogen-Bonding Based on Amide Groups

- amide groups: simultaneous hydrogen-bonding donors and acceptors, enabling infinite H-bond arrays

amide group

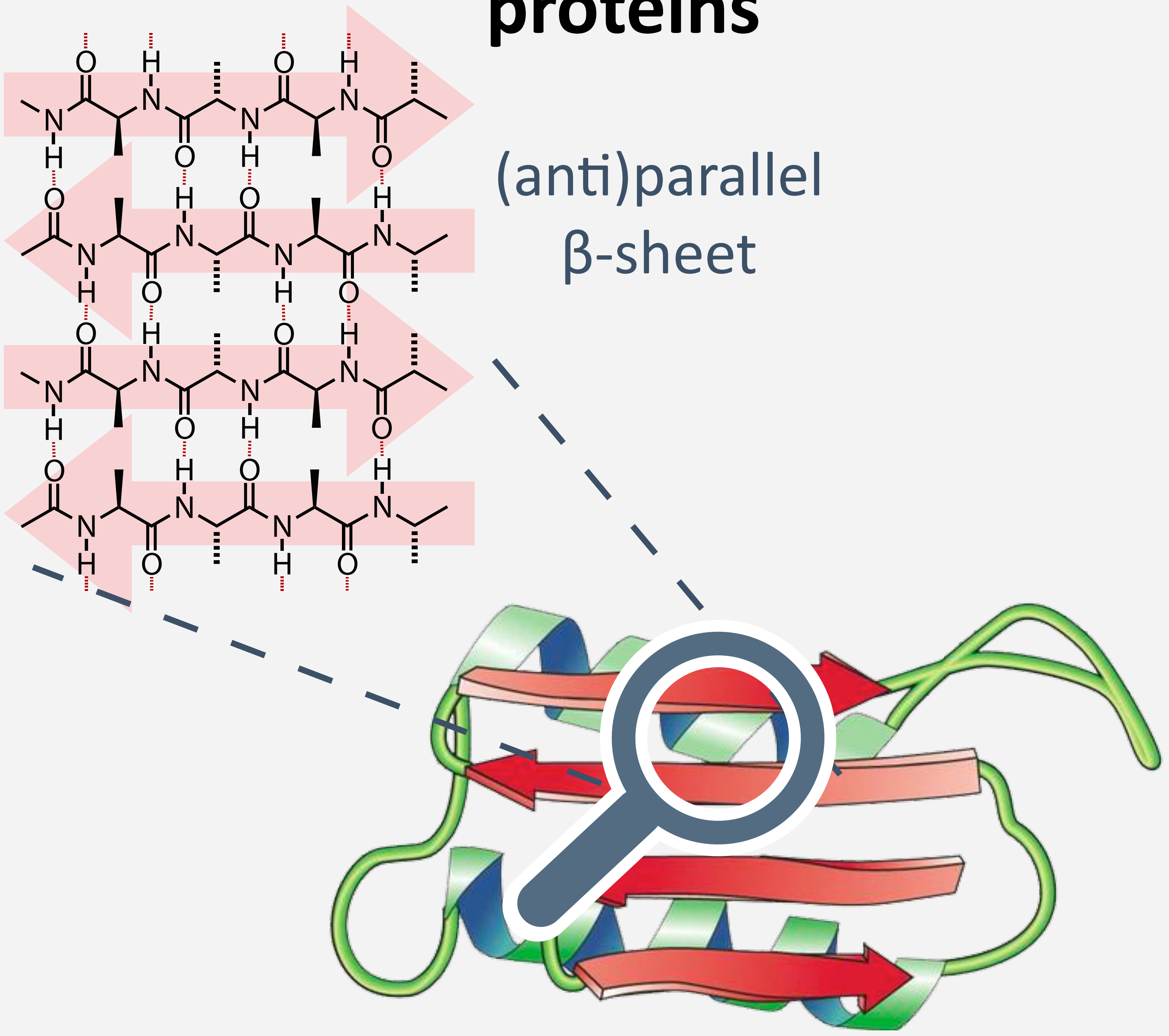


H-bonding acceptor site

H-bonding donor site

resonance-enhanced hydrogen bonding

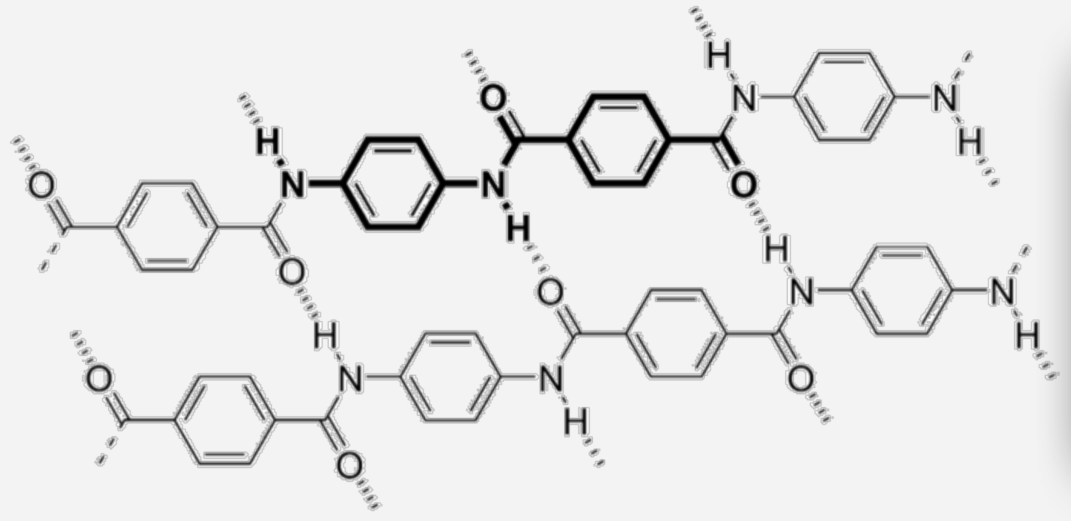
proteins



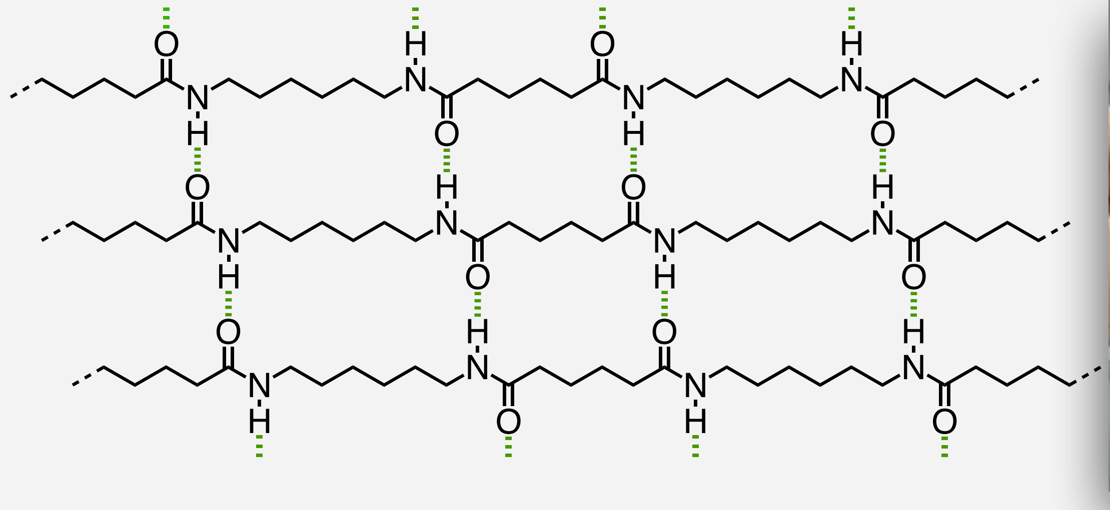
(anti)parallel β-sheet

α-helices & β-sheets

synthetic polymers



Kevlar



Nylon-6,6

- **highly directional, cooperative interactions stabilising protein structures & crystalline polymer segments**

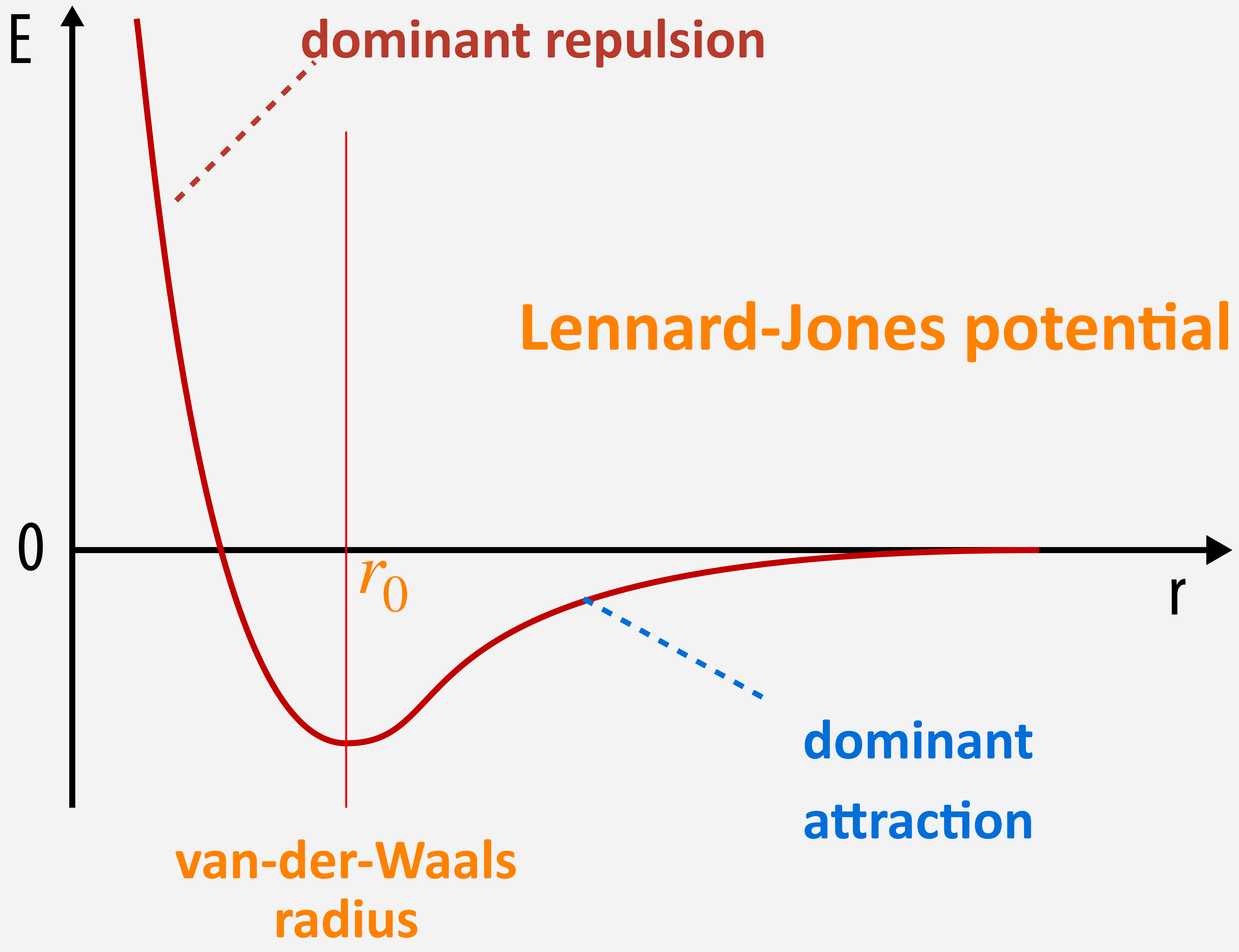
van-der-Waals Interactions

- **net interaction (balance of attraction and repulsion) described by the Lennard-Jones potential.**
- attraction: London dispersion ($\propto r^{-6}$)
- repulsion: Pauli exclusion of valence electrons ($\propto r^{-12}$)

$$U = \boxed{-\frac{A}{r^6}} + \boxed{\frac{B}{r^{12}}}$$

attractive van-der-Waals interactions

repulsive term



- **the Lennard-Jones minimum defines equilibrium distance and cohesive energy in molecular systems**

Cohesive Energy

- **cohesive energy** = energy required to separate molecules in a condensed phase: $E_{coh} \approx \Delta H_{vap} - RT$

at equilibrium: $$\frac{dU}{dr} = 6Ar^{-7} - 12Br^{-13} = 0 \longrightarrow r_0 = \sqrt[6]{\frac{2B}{A}} \longrightarrow E_{coh} = \frac{-A^2}{4B}$$

- **in polymers, E_{coh} is accessible only indirectly, e.g. via the compression modulus K:**

$$K = -V_0 \frac{\partial U}{\partial V^2}\Big|_{V=V_0} = \frac{8E_{coh}}{V_0}$$

(see exercise)

high compressibility

low compression modulus

low compressibility

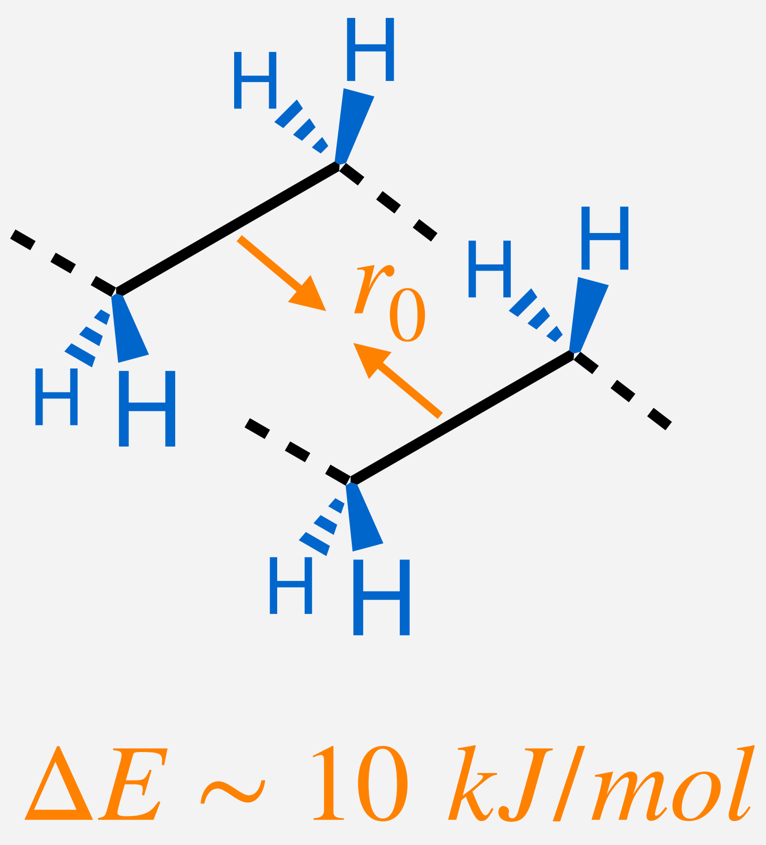
high compression modulus

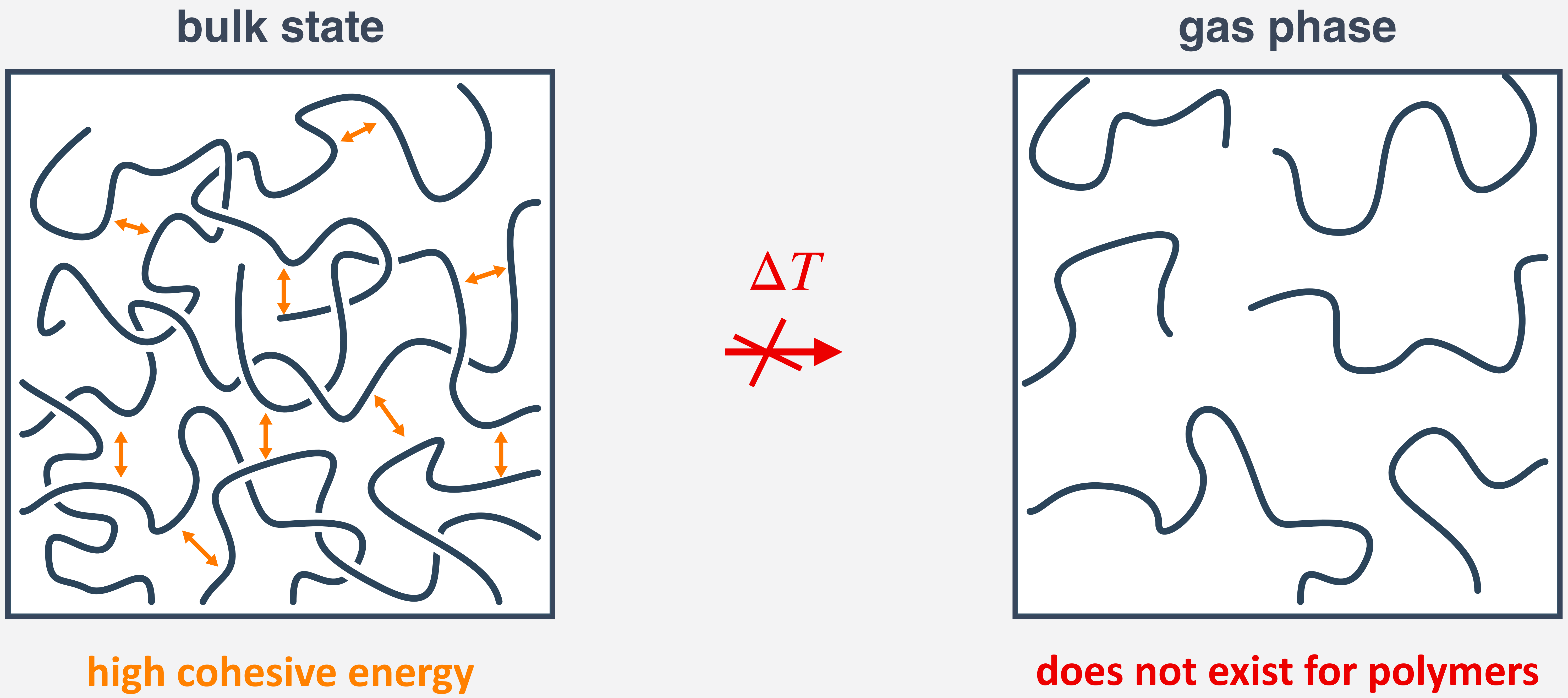
we will meet the compression modulus in **Chapter 4.1** again

E_{coh}, V_0 refer to monomer/repeating unit

Cohesive Energy of Polyethylene

- **cohesive energy of PE** $\approx 10\ \mathrm{kJ/mol}$ **per repeating unit**



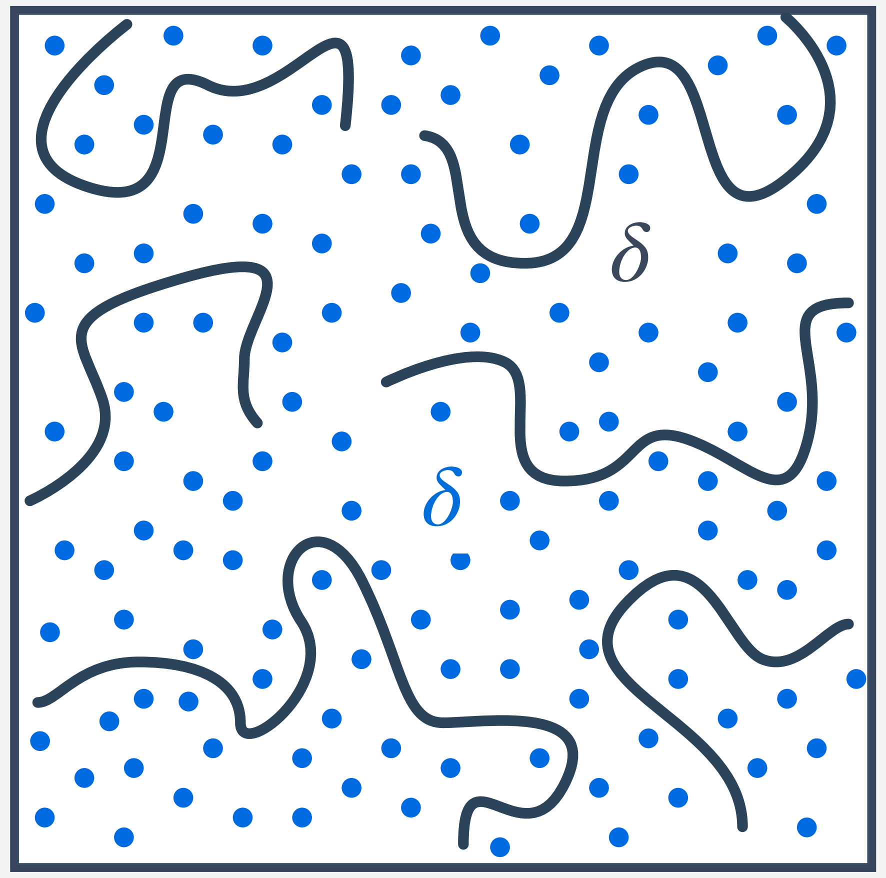


- **with a degree of polymerization of only 100:** $E_{\mathrm{coh}} \approx 1000\ \mathrm{kJ/mol}$
- **polymer cannot evaporate by simple heating: bond scission occurs before vaporisation**

compare the cohesive energy of a polymer with bond energies (Slide 116)!

Solubility

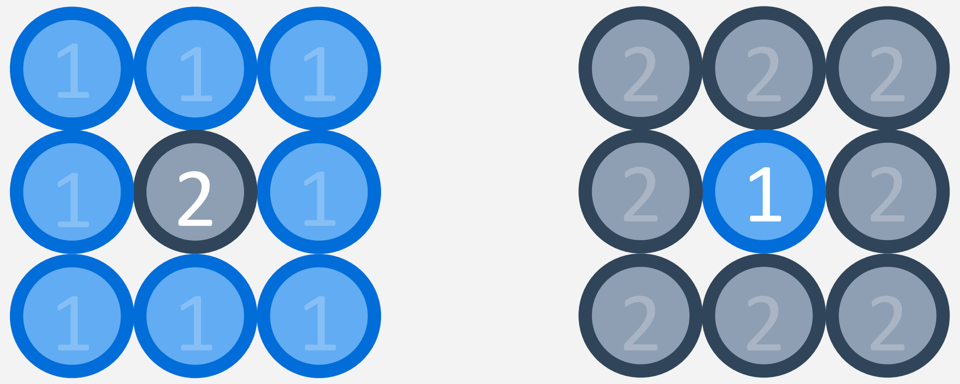
Solubility Parameter



- **mixing processes are typically driven by entropy, countervailed by enthalpy**
  (if not specific interactions such as hydrogen-bonding are considered)

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

- **the cohesive energy is then a measure for the solvation enthalpy, ΔH_{mix}**



thought experiment:
mixing blue and grey balls

$$\Delta H_{mix} = E_{coh}^{(1)} + E_{coh}^{(2)} - 2E_{coh}^{(12)}$$

$$\approx E_{coh}^{(1)} + E_{coh}^{(2)} - 2\sqrt{E_{coh}^{(1)}E_{coh}^{(2)}}$$

$$= (\sqrt{E_{coh}^{(1)}} - \sqrt{E_{coh}^{(2)}})^2 = V_0(\delta_1 - \delta_2)^2$$

solubility parameter

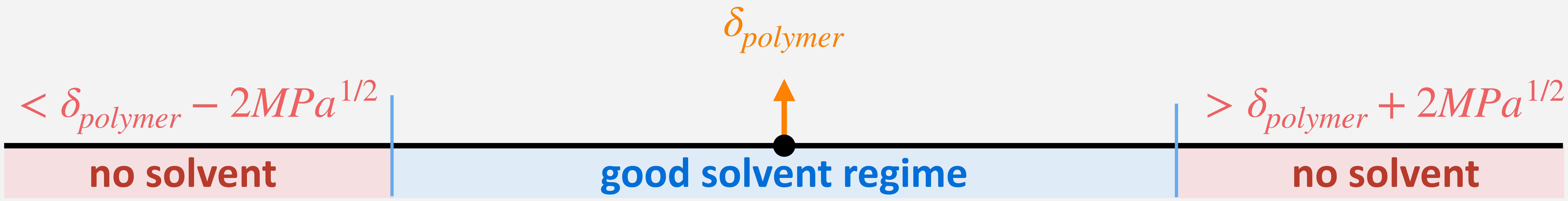
$$\delta = \sqrt{\frac{E_{coh}}{V_0}}$$

↑ cohesive energy density

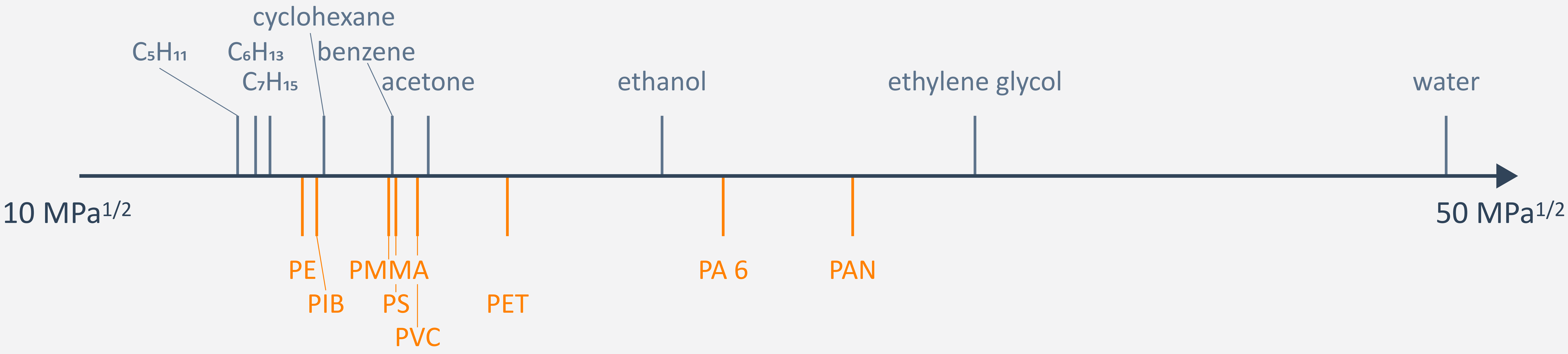
V_0 refers to monomer/repeating unit

Hildebrand Solubility Parameter

- **solubility is favoured, when $\delta_1 \sim \delta_2$ and ΔH_{mix} is consequently small.**



- hydrogen-bonding compounds show highest δ, followed by those with permanent dipols and those interacting only by dispersion forces:



Measurement of the Hansen Solubility Parameter

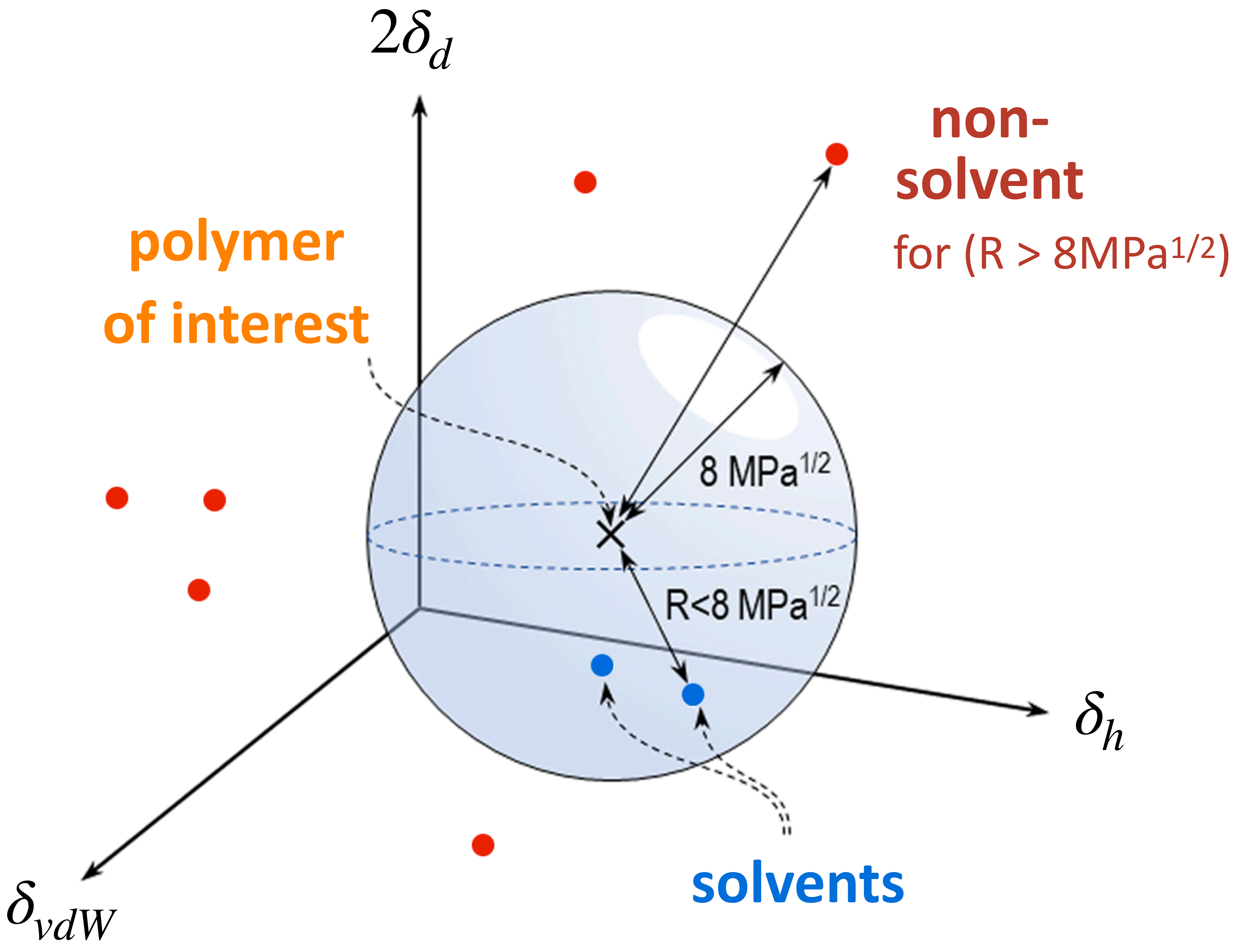
- **in practice, dissection of the contributions to the solubility parameter according to the Hansen model:**
  (including specific intermolecular interactions such as H-bonds)

$$\delta^2 = {\delta_h}^2 + {\delta_d}^2 + {\delta_{vdW}}^2$$

h **: hydrogen bonding**

d **: dipolar interactions**

vdW **: van-der-Waals interactions**



- **estimation of δ by comparing the effect of different solvents with known δ-terms**

Implications

- **polymer solubility is of great technological importance**

  examples: chemical synthesis, processing, gels (soft contact lenses), solvent removal, plasticisation, …

- **measurement of solubility parameter allows to determine the E_{coh} and parameters that depend on it:**

$$\delta^2_{PMMA} = \frac{E_{coh}}{V_0} \sim 533\ Jcm^{-3}$$

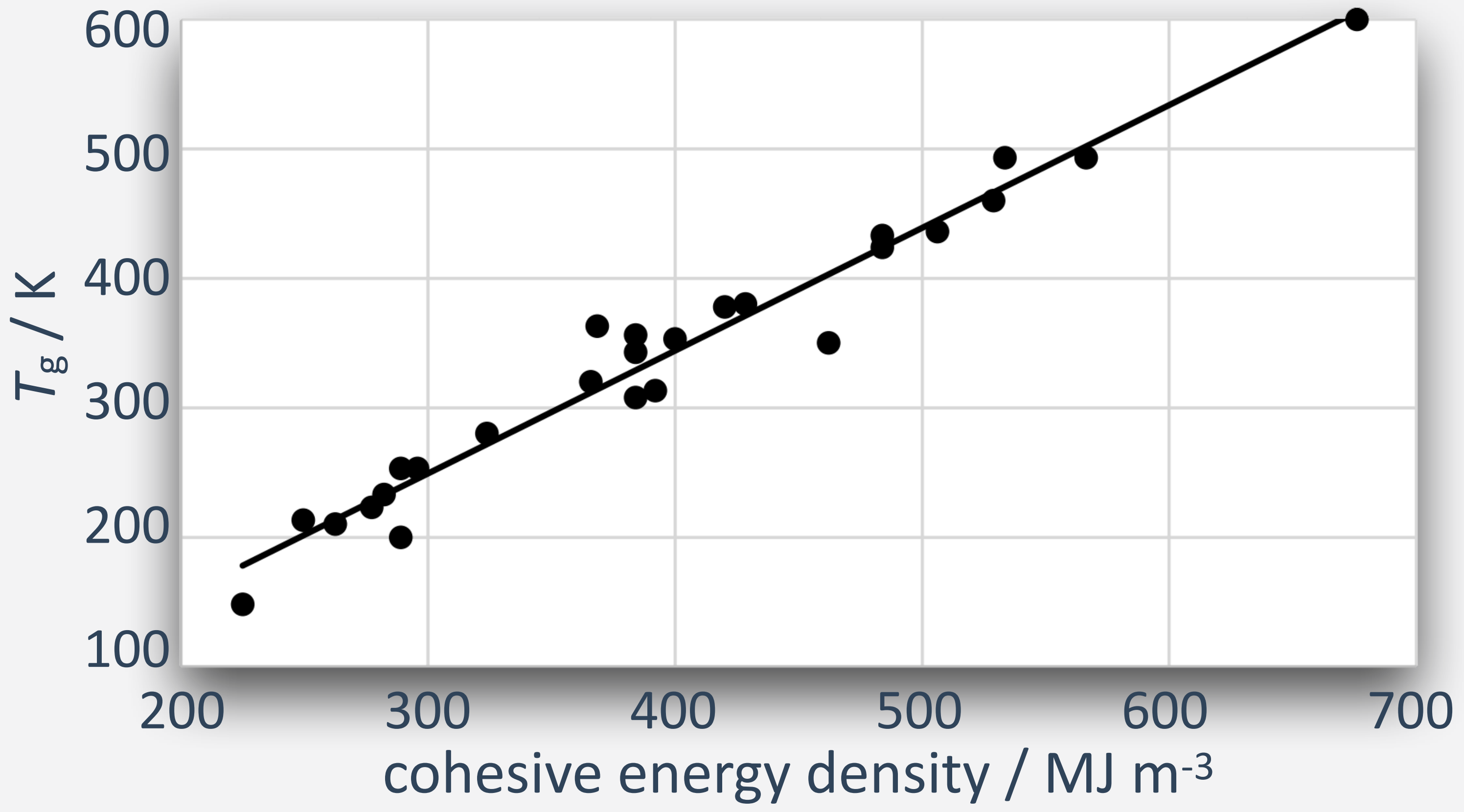
$$K_{PMMA} = 4.3\ GPa \quad \text{(measured: } 5.1\ GPa\text{)}$$

- **δ and E_{coh} further relate to surface energy, resistance to cavitation, sound propagation, T_g…**

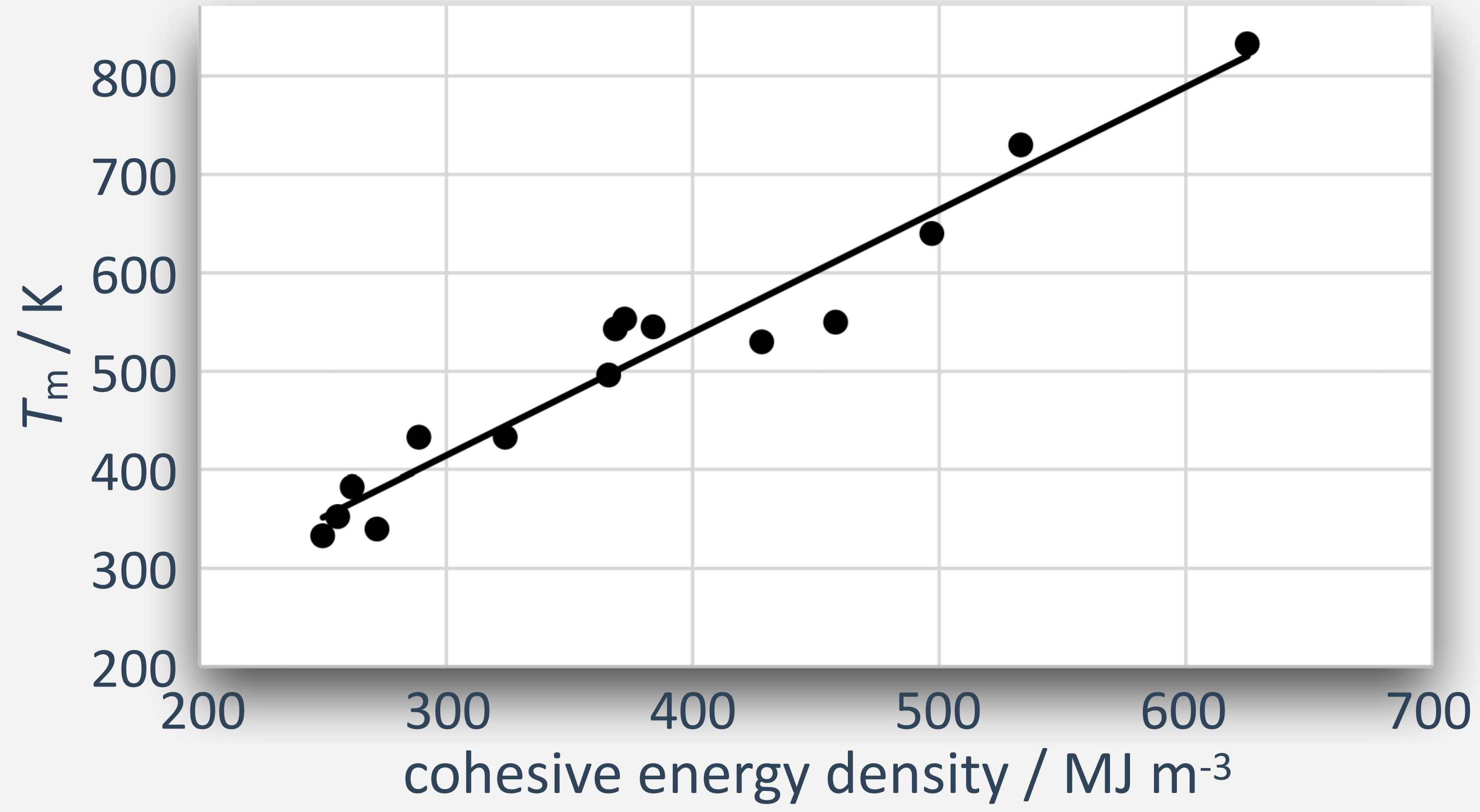
surface tension

$$\gamma = 0.75 \cdot {E_{coh}}^{2/3} = 0.75 \cdot \delta^{4/3} V^{2/3}$$

glass transition temperature



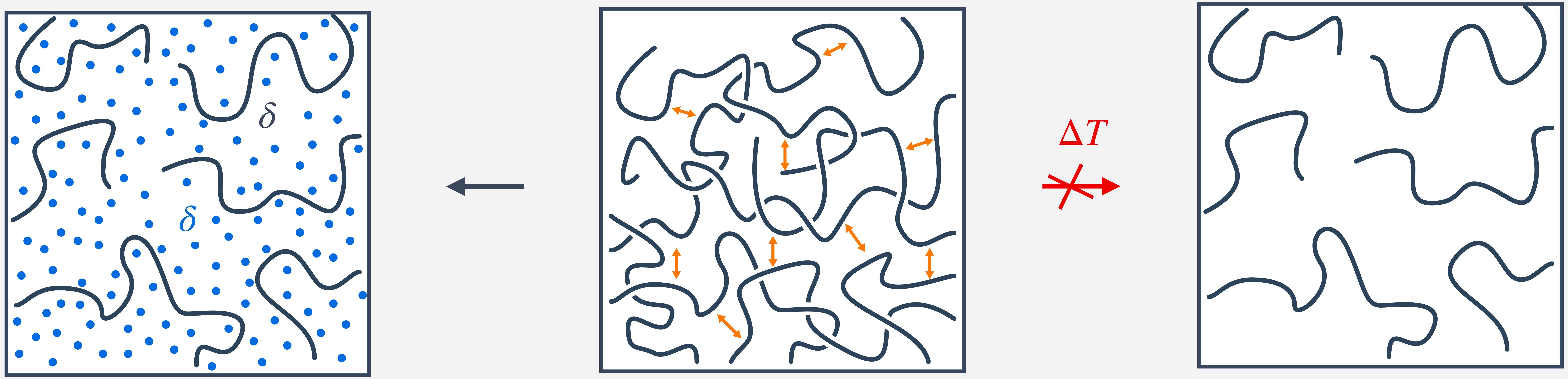
melting temperature



Measurement of Cohesive Energy via the Solubility Parameter

- covalent bond breakage prohibits entering the gas phase and E_{coh} measurement via heat of evaporation

solution **bulk state** **gas phase**



$$\delta = \sqrt{\frac{E_{coh}}{V_0}}$$

high cohesive energy

does not exist for polymers