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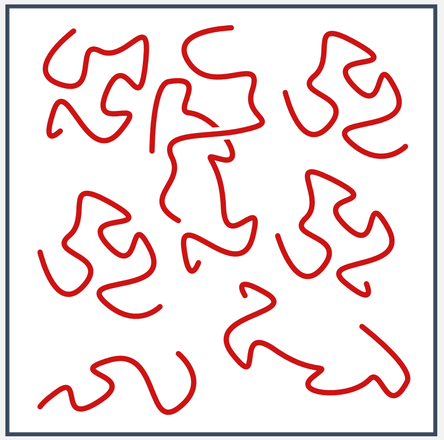
# 3 Structures of Polymers in the Condensed State

# Condensed States of Polymers

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

## viscous liquids

(solutions, polymer melts)



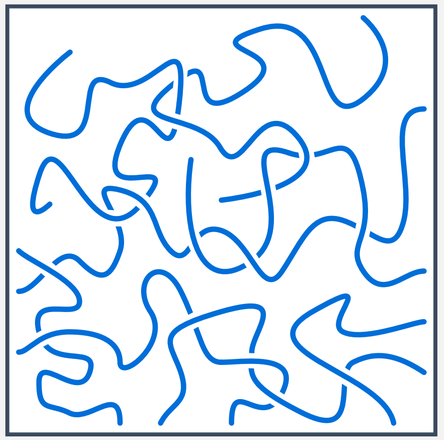
easy chain movement

silicones (PDMS):

$T_g$ = - 123 °C

$T_m$ = - 40 °C

## amorphous glasses

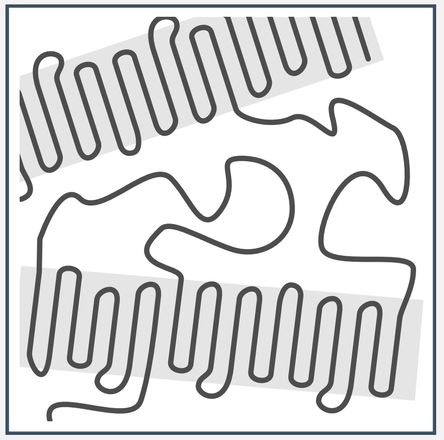


only local movement of chain segments

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

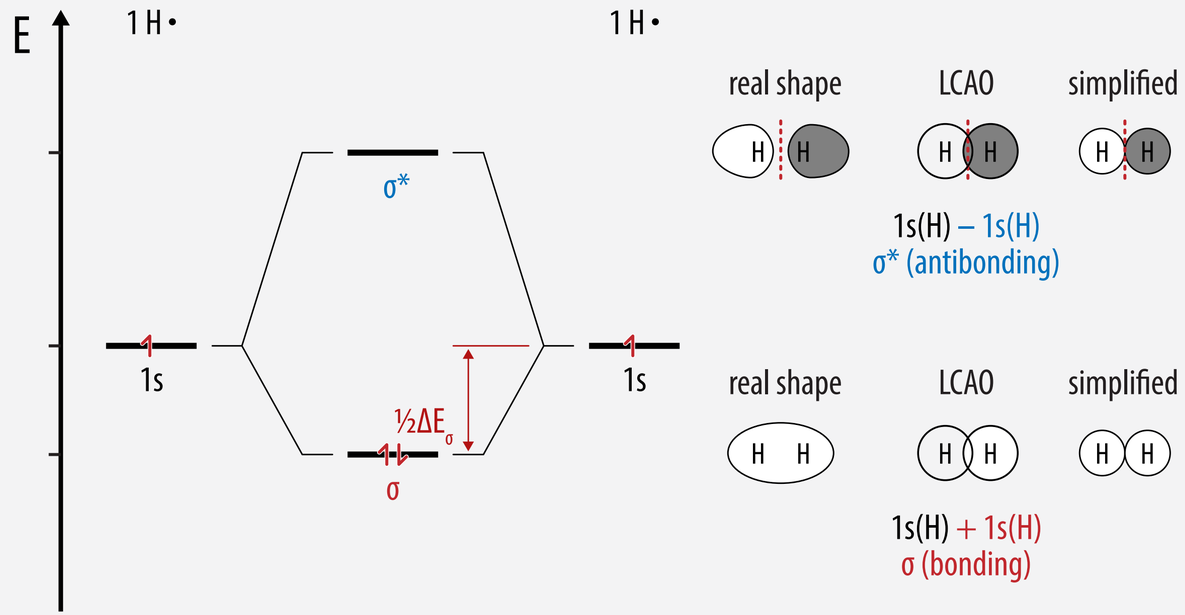
- **all polymers go through a glass transition! Some are glassy at operating temperature (Chapter 3.2)**

# 3.1
# The Cohesive Energy

# Covalent Bonds vs. Secondary Interactions

# Molecular Orbital Energy Diagrams

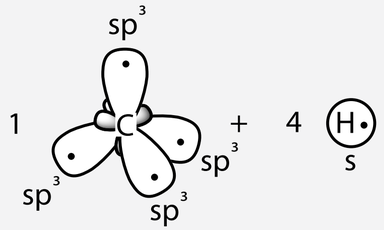
- schematic molecular orbital energy diagram for a symmetric diatomic molecule (such as $H_2$)

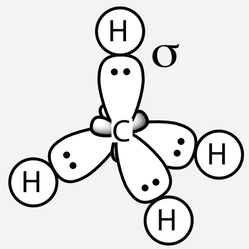


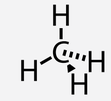

- **energy splitting increases with atomic orbital overlap**
- **number of orbitals preserved but sum of orbital energies (electron density) increases**
- **bond energy is stabilization of filled bonding orbital σ (due to electron delocalization)**
- **antibonding orbital σ* is energetically destabilized but remains empty**

# Formation of Carbon-Hydrogen Bonds

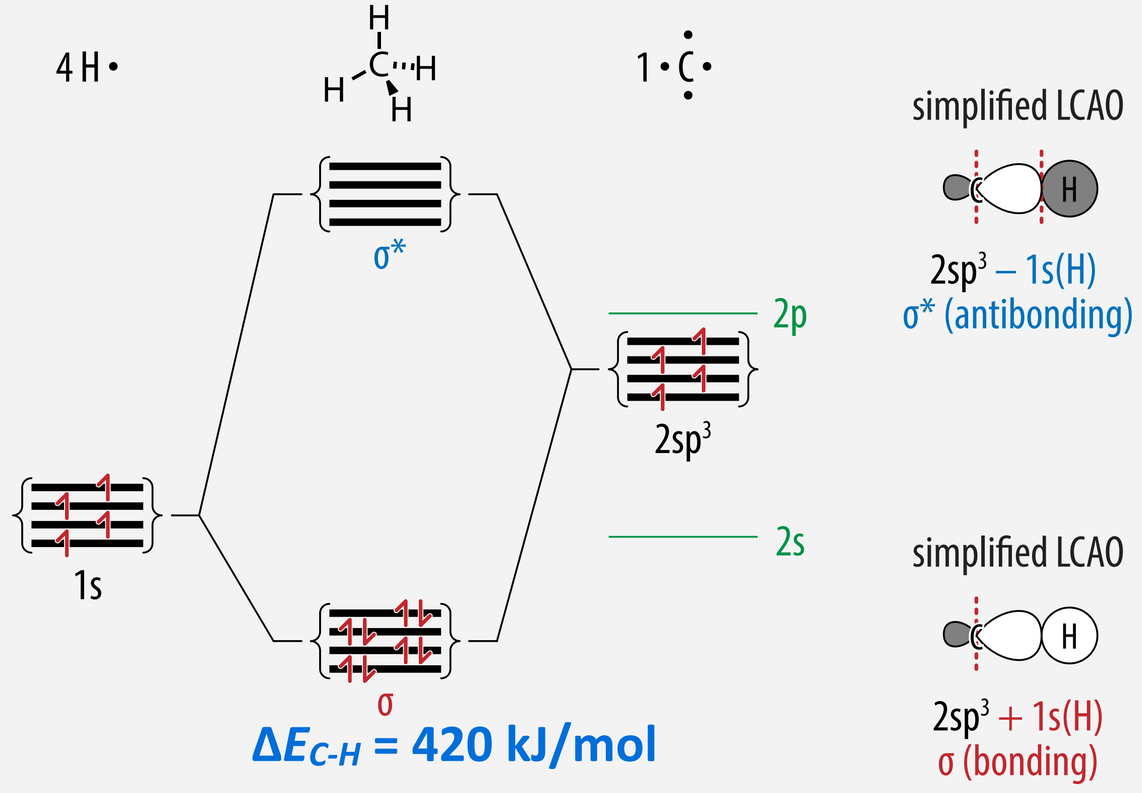
- covalent bonds can be described by linear combination of atomic or hybrid orbitals
- single bonds are σ-bonds (rotational symmetry) between sp3, sp2, sp, or s orbitals



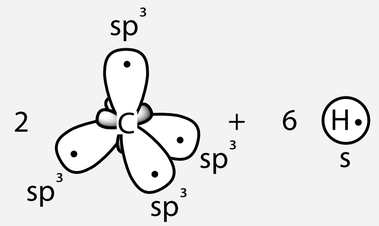

methane

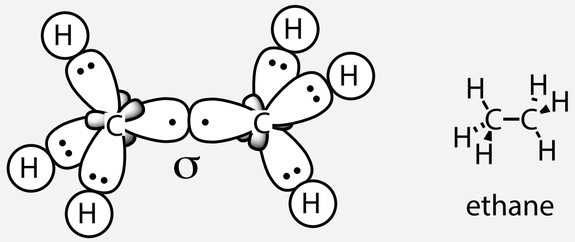



- **due to rotational symmetry of the σ-orbital, rotation is free without breaking the bond**

# Formation of Carbon-Carbon Single Bonds

- covalent bonds can be described by linear combination of atomic or hybrid orbitals

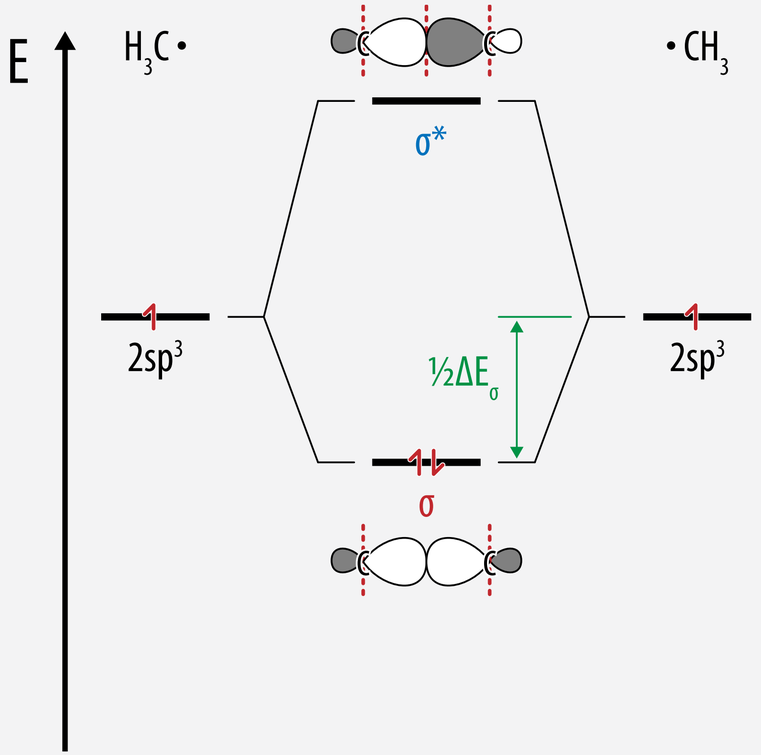






ethane

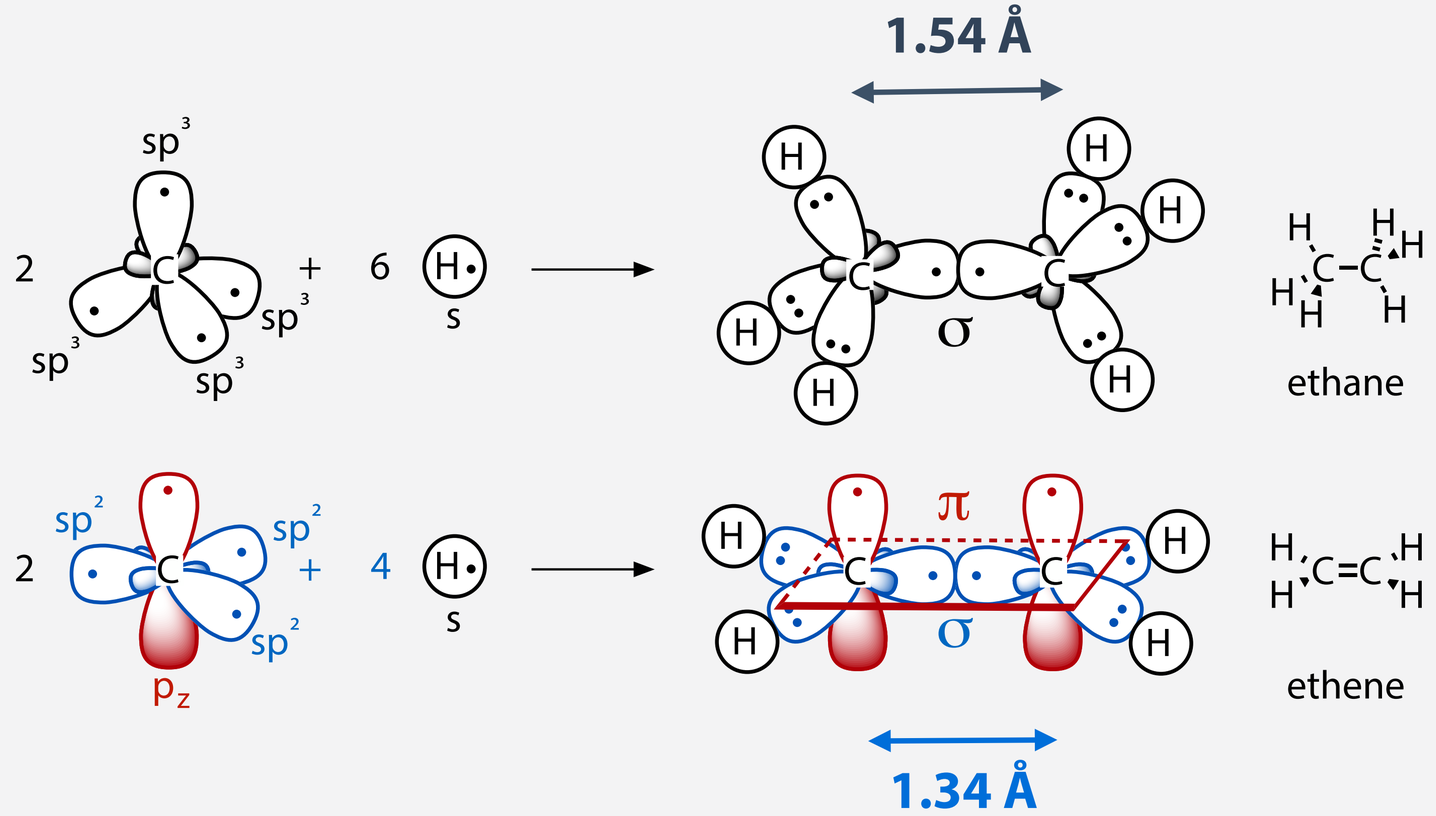



$\Delta E_{C\text{-}C}$ = 347 kJ/mol

- due to rotational symmetry of the σ-orbital, rotation is free without breaking the bond

# Formation of Carbon-Carbon Multiple Bonds

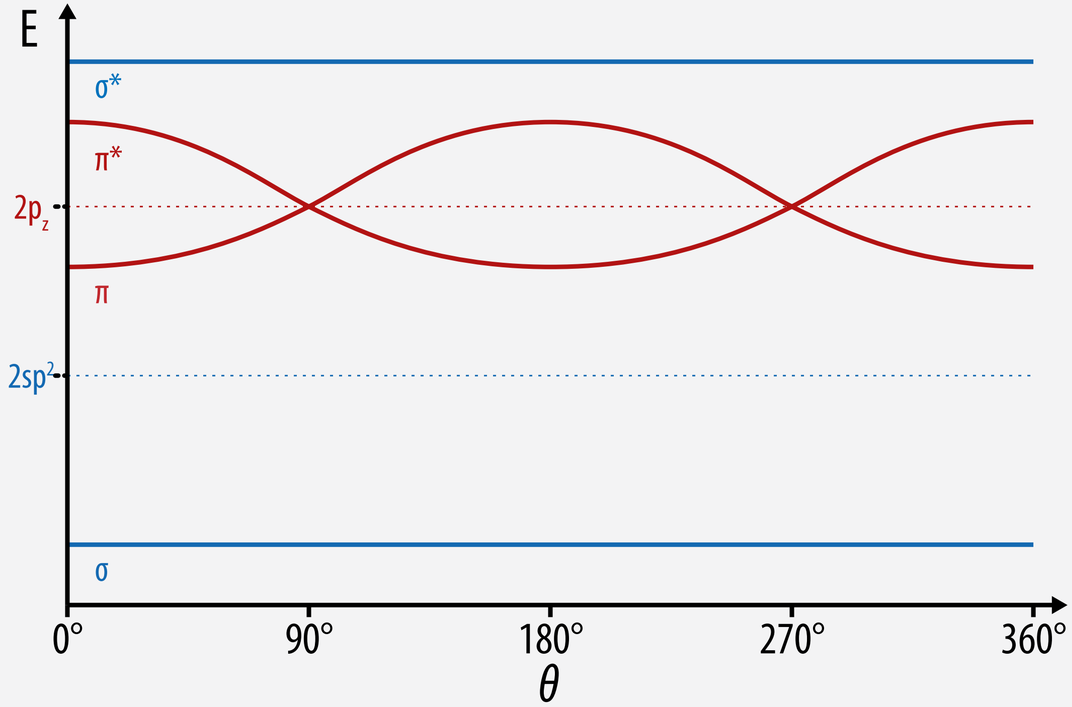
- π bonds between residual p orbitals, node plane along bond, therefore no rotational symmetry

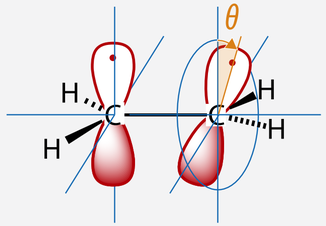


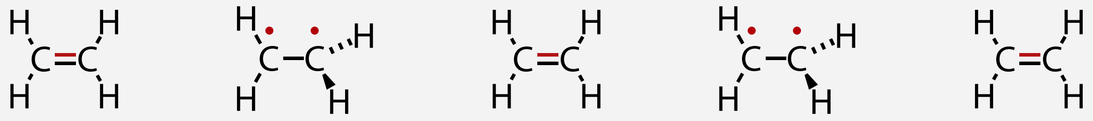

- rotation around π-bounds requires breaking them, but energetically too costly at room temperature

# Rotation Around a Double Bond

- σ bond has rotational symmetry relative to carbon.carbon bond axis, but π bond does not



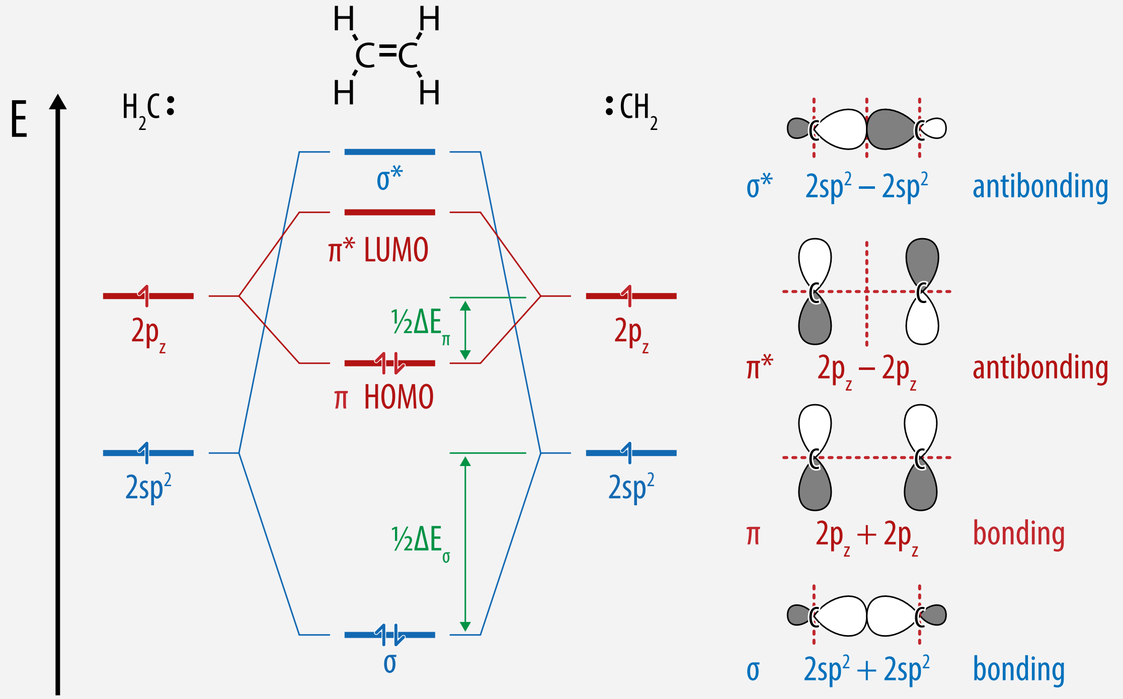



- **rotating π orbitals by 90° requires breaking the π bond (≈260 kJ/mol), disfavorable at r.t.**

# Molecular Orbital View of the Carbon-Carbon Double Bond

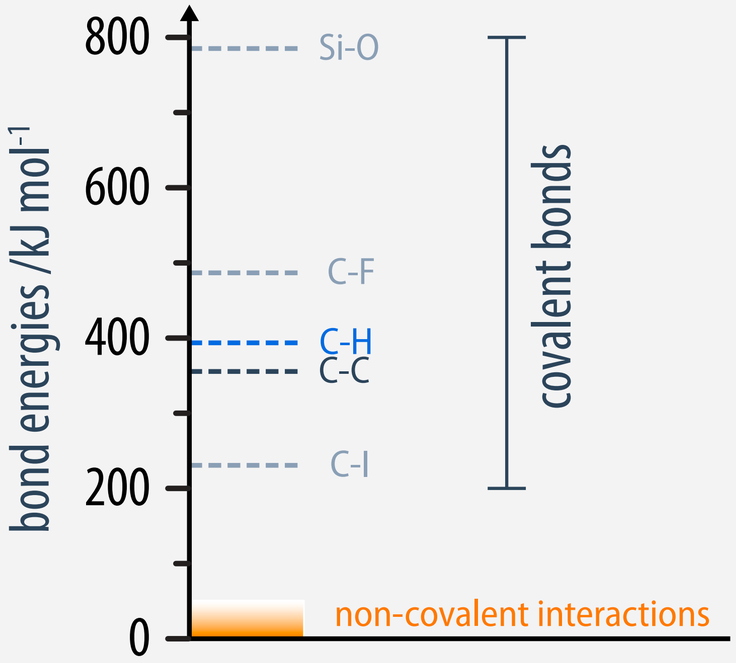
- simplified and schematic molecular orbital energy diagram of the ethene molecule

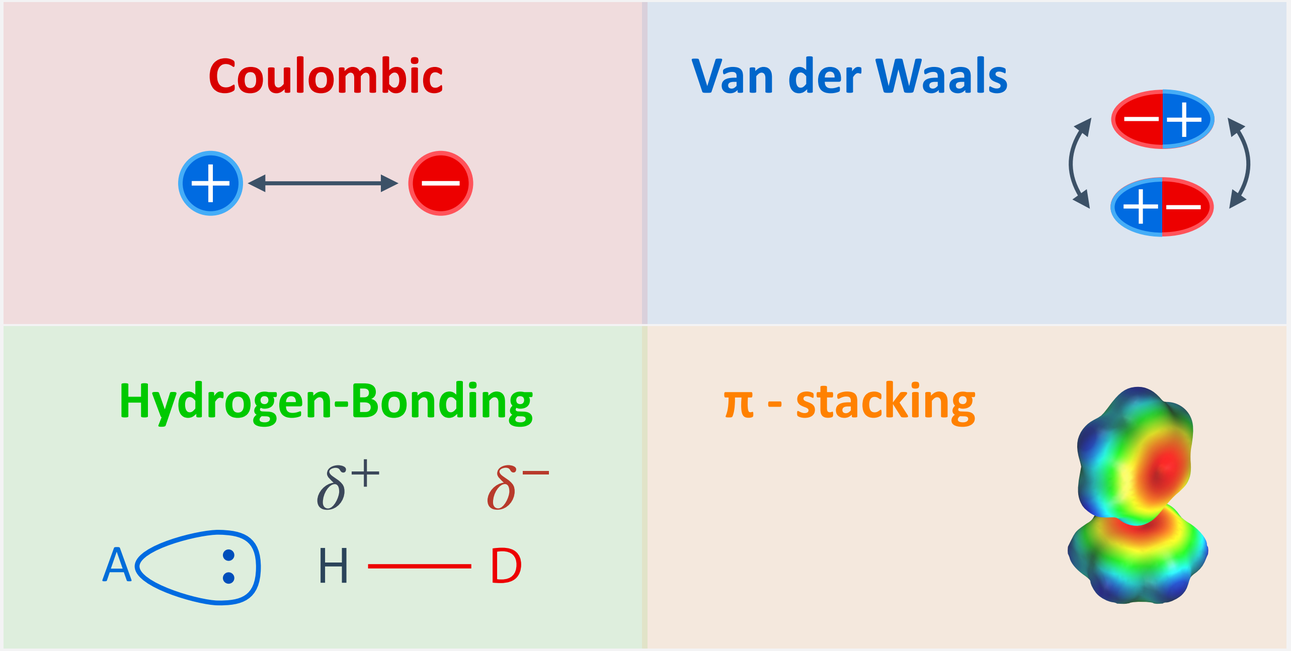



- **only orbitals of matching symmetry & orientation interact, $sp^2$ with $sp^2$, and $p_z$ with $p_z$**
- **distinct σ bond (from two $sp^2$) and π bond (from two $p_z$) with different energy, symmetry**
- **chemistry ruled by highest occupied, lowest unoccupied molecular orbitals (HOMO, LUMO)**
- **typically π HOMO and π* LUMO, located between σ and σ* because $p_z$ overlap much smaller**

# Non-Covalent Interactions

- non-covalent forces dictate polymer conformations and inter-chain interactions.




- individual non-covalent interactions are of transient nature (thermal energy at r.t.: 2.5 kJ/mol)
- collectively, they compete with or assist each other
- they hence determine geometry and strength of the molecular organisation in the condensed state

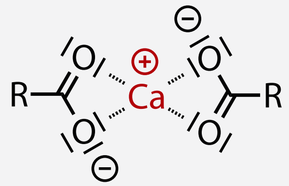
# Types of Attractive Non-Covalent Interactions

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

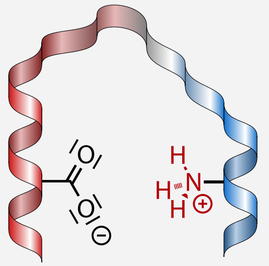
  strong (100 - 400 kJ/mol),

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

  not directional




salt bridges



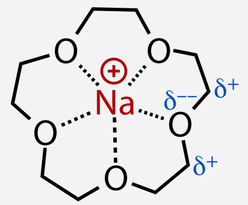
acid-base pairs
(in particular in proteins)

- **charge-dipole interactions**

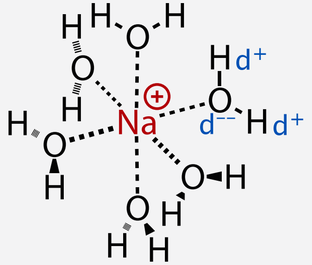
  moderately strong (50 - 200 kJ/mol),
  (stronger, when partially covalent (100 - 400 kJ/mol)

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

  depends on dipole orientation




cation-binding hosts




solvation

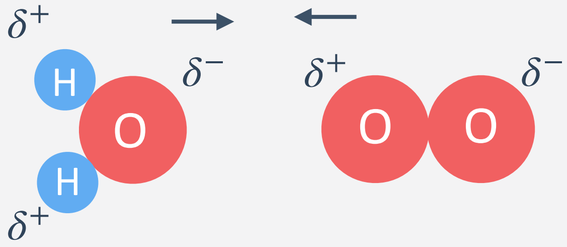
# Types of Attractive Non-Covalent Interactions

- **charge-induced dipole**

  relatively weak,

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

  depends on polarizability



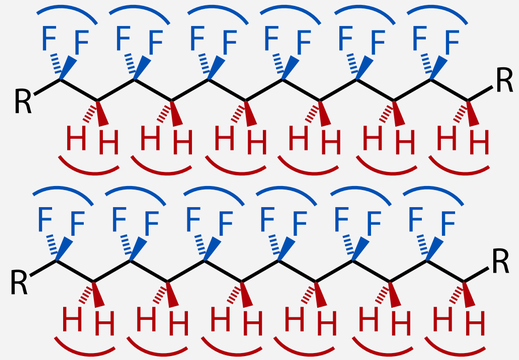

oxygen in water

- **dipole-dipole interactions**

  relatively weak (10 - 50 kJ/mol),

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

  depends on mutual orientation of dipole moments




poly(vinylidene difluoride) PVDF
polar order, dielectricity

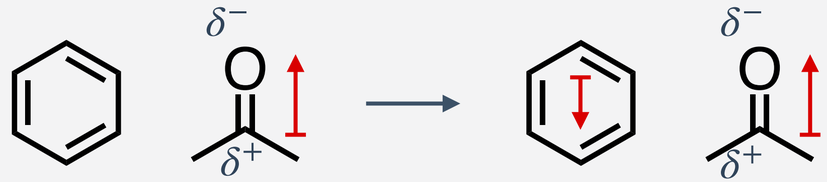
# Types of Attractive Non-Covalent Interactions

- **dipole-induced dipole**

  relatively weak (2 - 30 kJ/mol),

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

  depends on polarizability



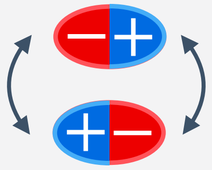

solubility of apolar compounds (benzene)
in polar solvents (acetone)

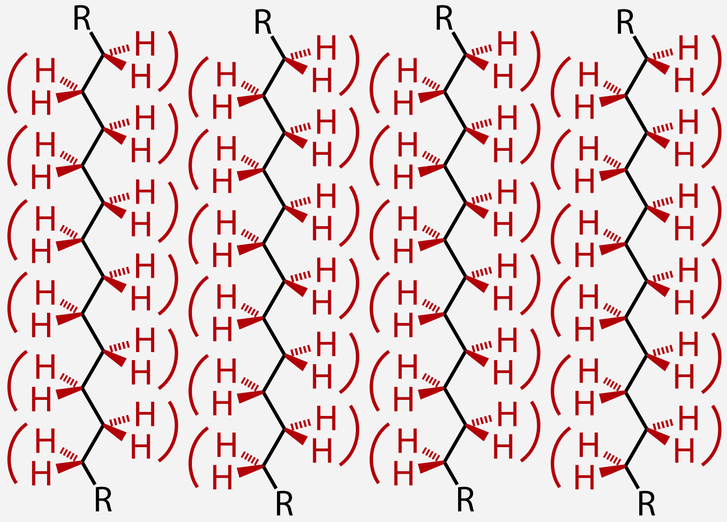
- **dispersion**

  weak (2 - 20 kJ/mol),

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

  mutual synchronisation of
  fluctuating, instantaneous dipoles



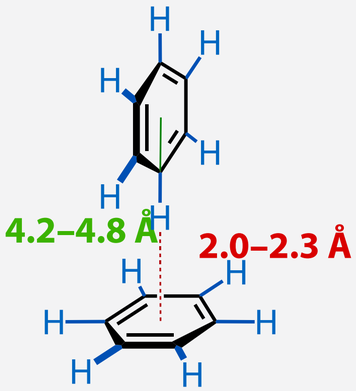


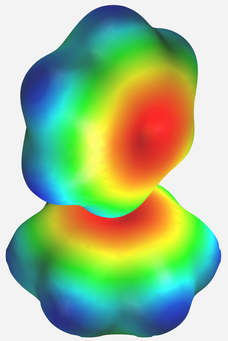

polyethylene (PE)

# Types of π–π Interactions

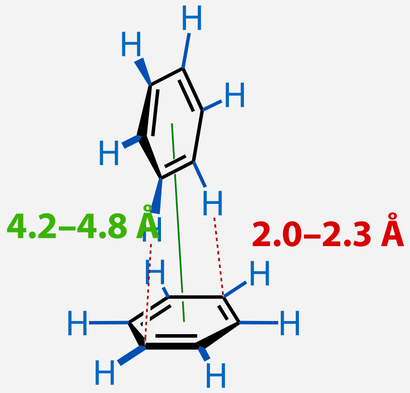
- **π–π interactions are weak (5–50 kJ/mol) and have a short range ($E \propto r^{-6}$)**

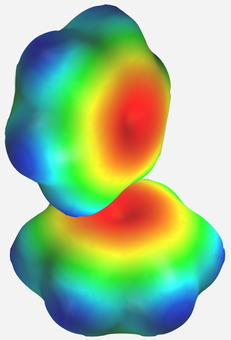
edge-to-face



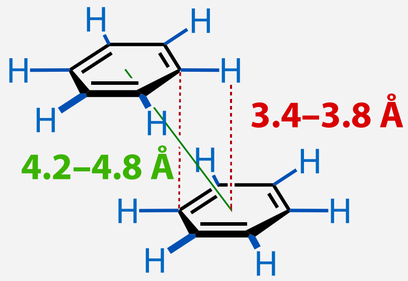



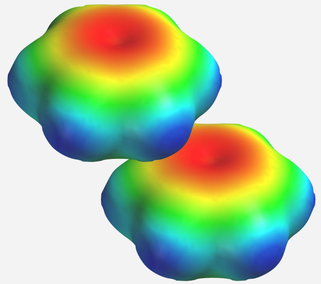
edge-to-face



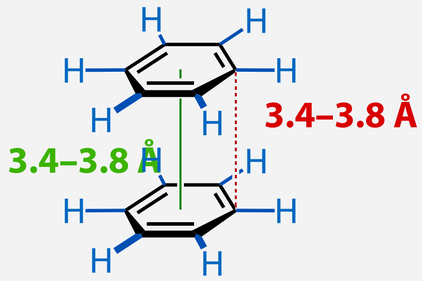



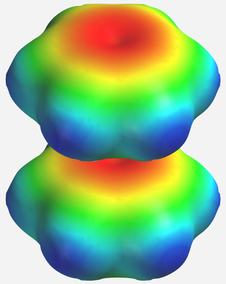
parallel-displaced



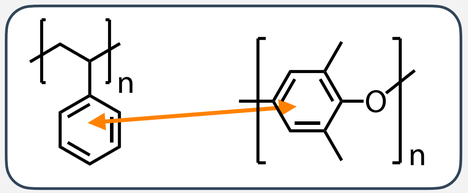



face-to-face



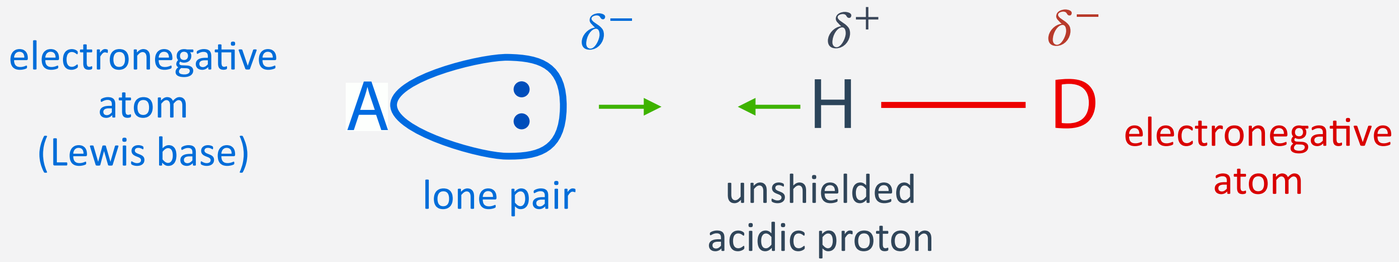



- **π–π interactions are a combination of dispersive with quadrupolar interactions**
- **π–π interactions account for the miscibility of some polymers (see Chapter 5)**



# Hydrogen-Bonding - Simplified Overview

- predominant electrostatic interaction of H atom and two more electronegative atoms (usually N and O)



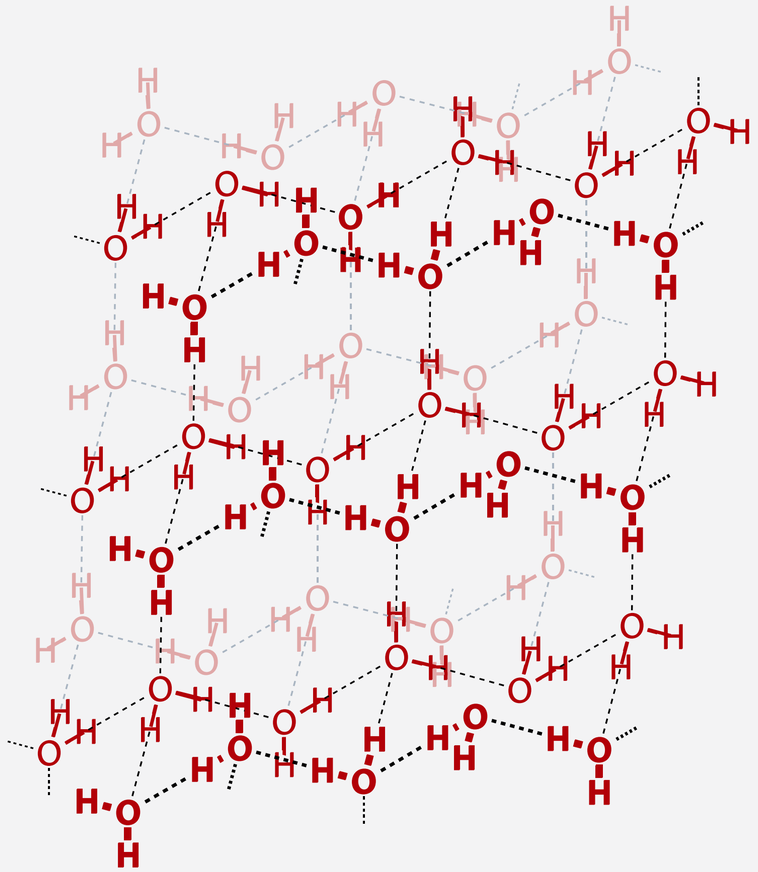

| | weak H-bonds | moderate H-bonds | strong H-bonds |
|---|---|---|---|
| **typical feature:** | the donor is often **C** | often neutral **D** and **A** | often charged **D** and **A** |
| **bond strength** | 2-20 kJ/mol | 20-60 kJ/mol | 60-170 kJ/mol |
| **D-H···A angle** | 90-150° | 130-180° | 170-180° |
| **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**

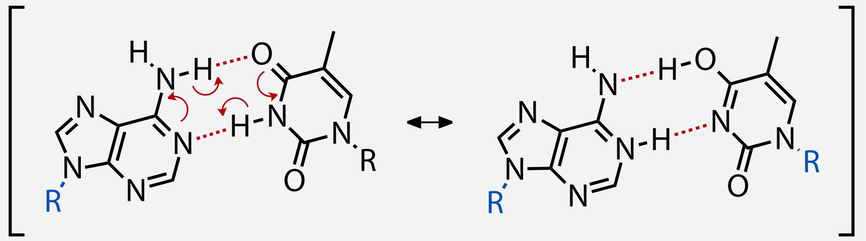
- **high directionality (often preferably linear geometry, D-H···A angle ≈ 180 °) and variable bond strengths**

# Hydrogen-Bonding in Biological Systems

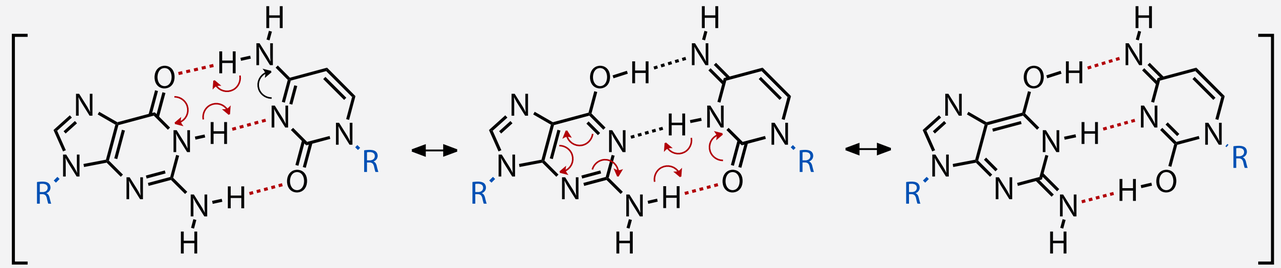
## structure of water



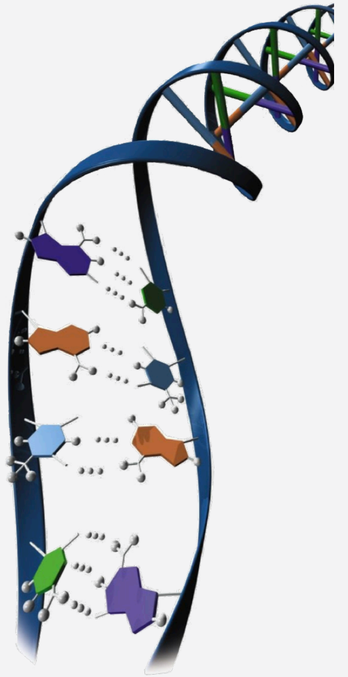
## DNA



adenine–thymine



guanine-cytosine

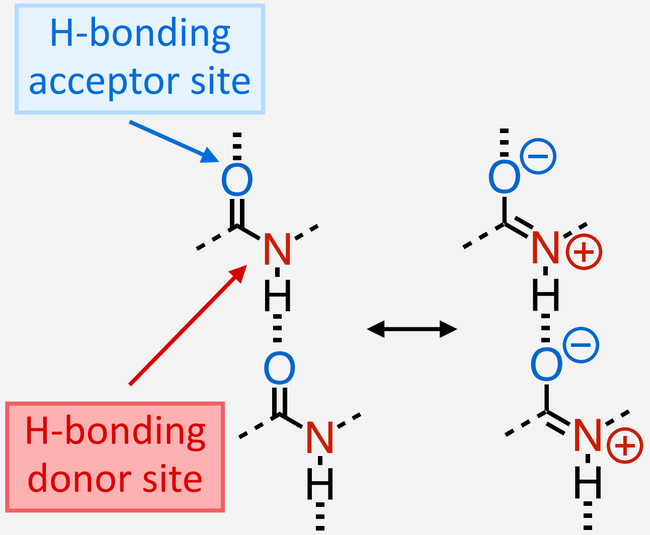


- complementary arrangements of hydrogen-bond acceptors/donors for selective binding

# Hydrogen-Bonding in Biological and Synthetic Polymers

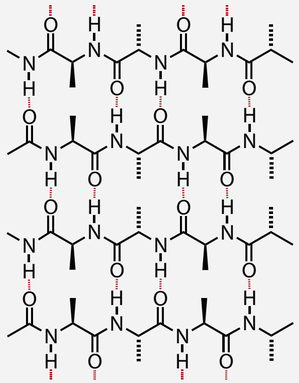
- amide groups: simultaneous hydrogen-bonding donor and acceptor

## amide group

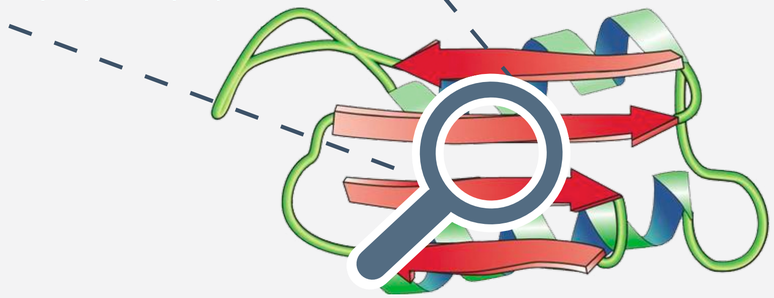



resonance-enhanced hydrogen bonding

## proteins

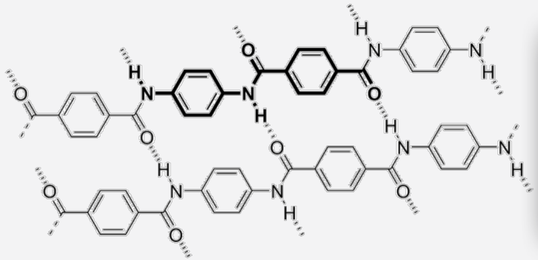


(anti)parallel β-sheet

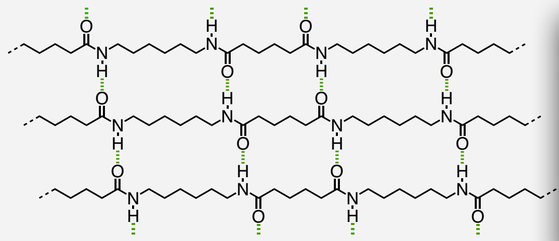


α-helices & β-sheets

## synthetic polymers



Kevlar



nylon

- **highly directional and attractive interactions between polymer segments**

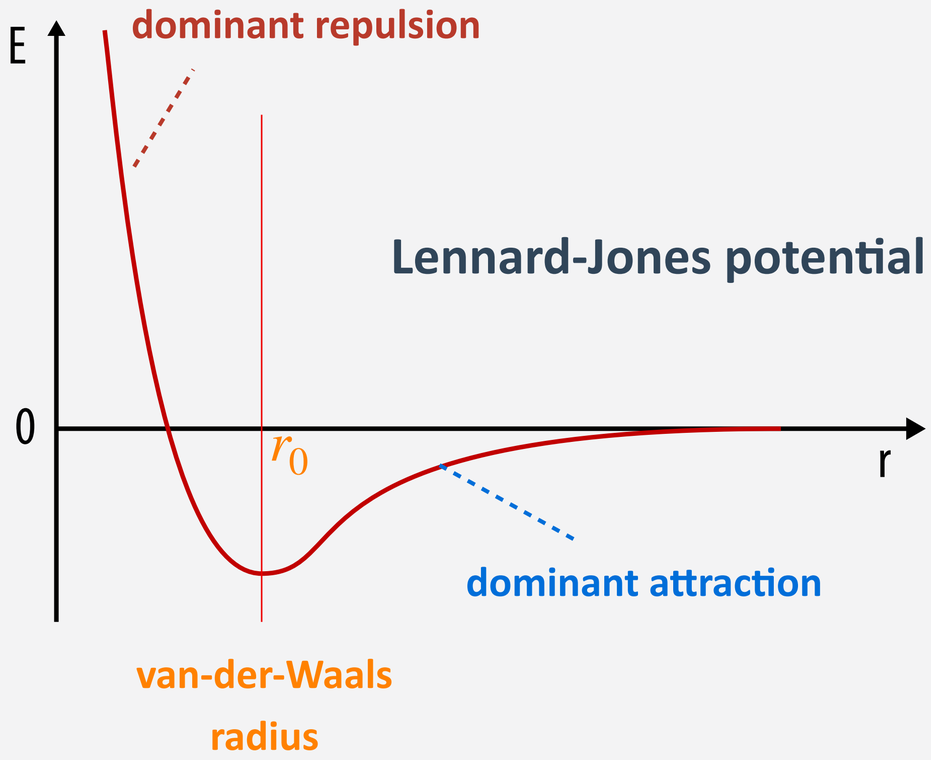
# van-der-Waals Interactions

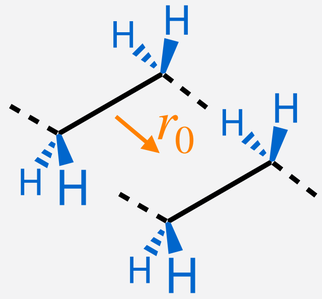
- **attractive dispersion and repulsion are combined by the Lennard-Jones potential.**
- at short distances, electrostatic repulsion between valence electrons (Pauli exclusion principle)
  (scales approximately with $r^{-12}$)

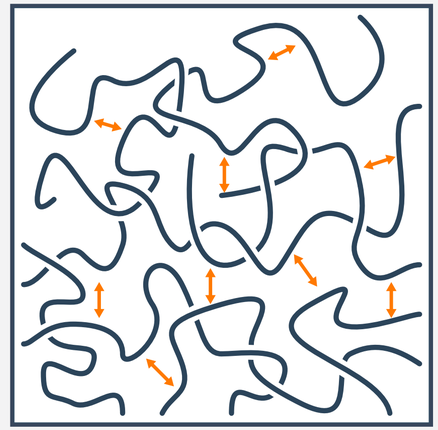
$$U = \boxed{-\frac{A}{r^6}} + \boxed{\frac{B}{r^{12}}}$$

**attractive van-der-Waals interactions**

**repulsive term**



- **in approximation, secondary interactions in PE are 10 kJ/mol per repeat unit**

# Cohesive Energy

- required energy (**cohesive energy**) for separation of molecules of a liquid or solid: $E_{coh} \approx \Delta H_{vap} - RT$

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

- **for polymers, only indirect measurements of $E_{coh}$, 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**

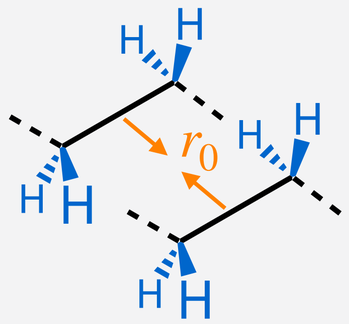
we will meet the compression modulus in **Chapter 4.1** again



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

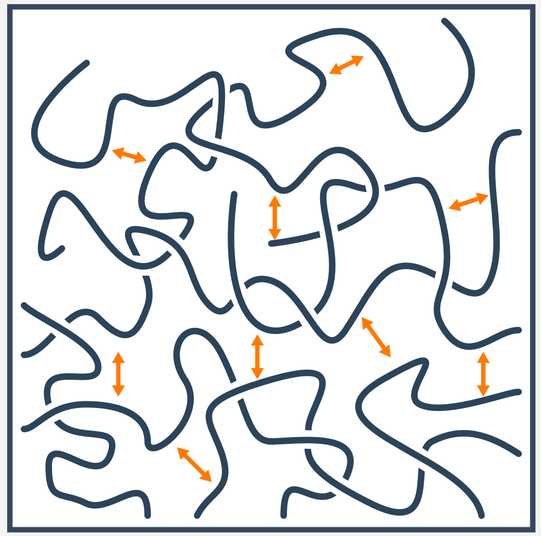
# Cohesive Energy of Polyethylene

- **for PE:** $E_{coh} \approx 10\ kJ/mol$ **per repeating unit**




$\Delta E \sim 10\ kJ/mol$

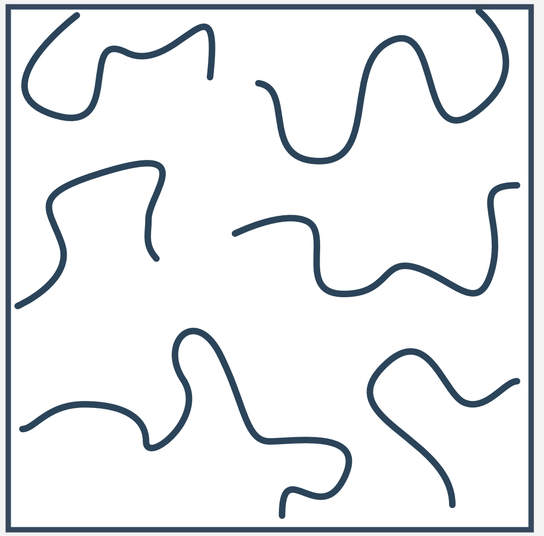
**bulk state**



**high cohesive energy**

$\Delta T$

**gas phase**



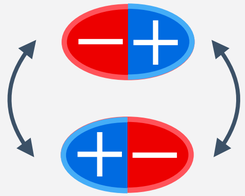
**does not exist for polymers**

- **… and a degree of polymerization of 100:** $E_{coh} \approx 1000\ kJ/mol$
- **no evaporation of a polymer by simple heat addition without bond breakage!**
- **bond breakage occurs before liquid-gas phase transition.**

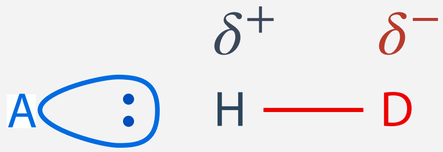
# Dominant Intermolecular Interactions in Polymers

- weak compared to covalent bonds of the polymer backbone; determine structure, facilitate processing

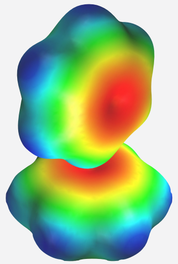
**dispersion**



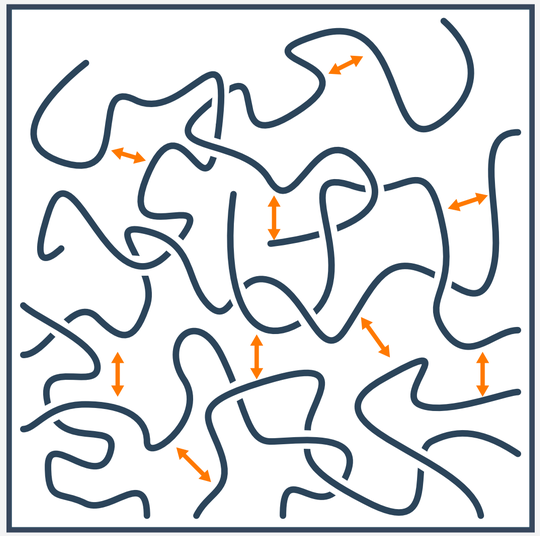
**H-bond**




**$\pi$-$\pi$ stacking**



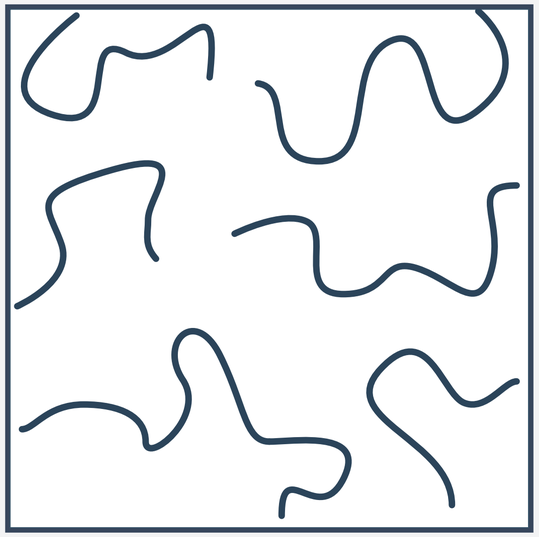
**bulk state**



**high cohesive energy**

$\Delta T$

**gas phase**



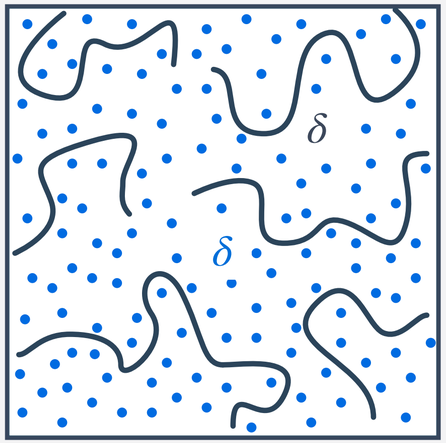
**does not exist for polymers**

# Solubility

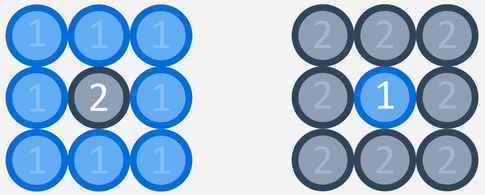
# Solubility Parameter

- **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, $\Delta H_{mix}$**




thought experiment:
mixing black 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**

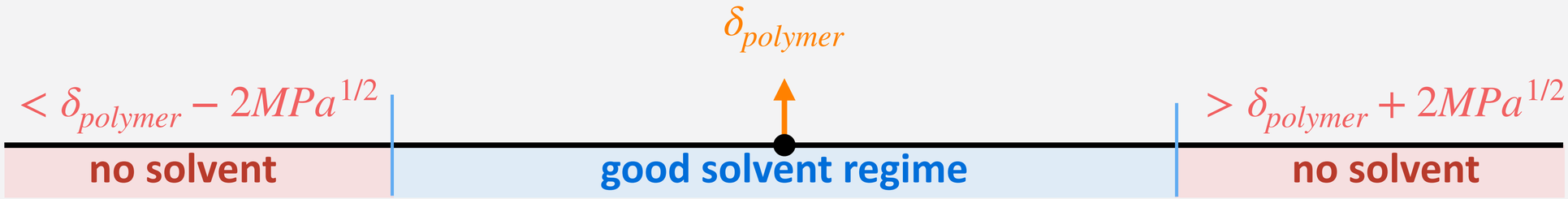
$$\delta = \sqrt{\frac{E_{coh}}{V_0}}$$

cohesive energy density

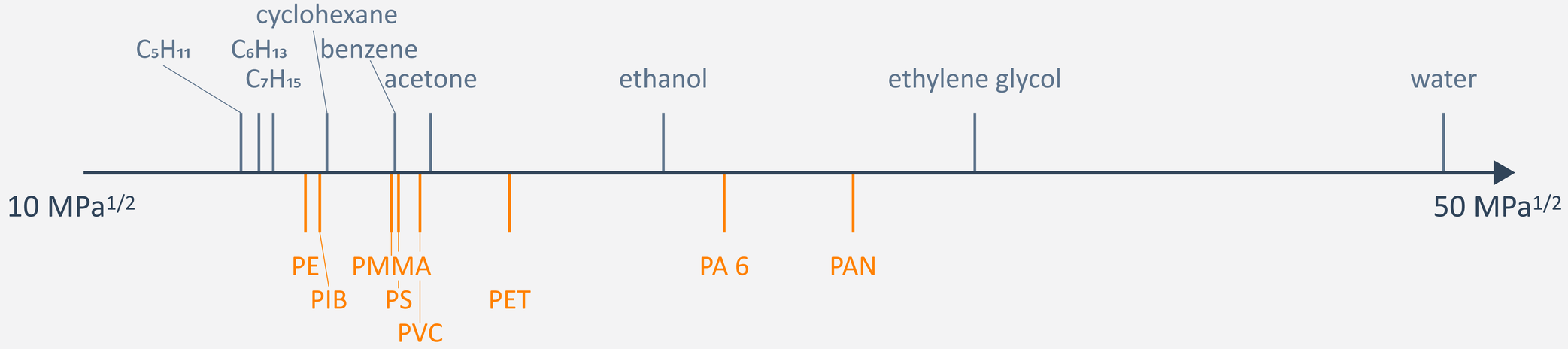
$V_0$ refers to monomer/repeating unit

# Hildebrand Solubility Parameter

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




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



# Measurement of the Hansen Solubility Parameter

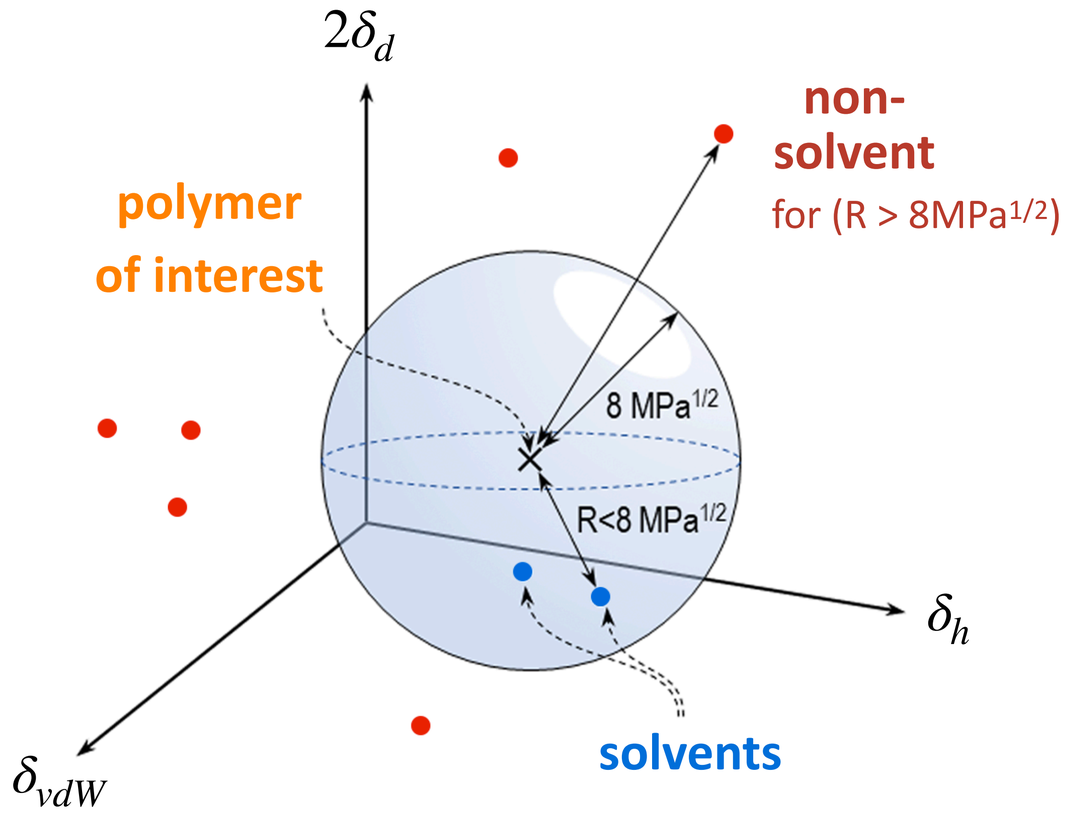
- **in practice, dissection of the contributions to the solubility parameter according to the Hansen model:**
  (including specific intermolecular interactions such as H-bonds)

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

$h$ : **hydrogen bonding**

$d$ : **dipolar interactions**

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




- **estimation of $\delta$ by comparing the effect of different solvents with known $\delta$-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:**

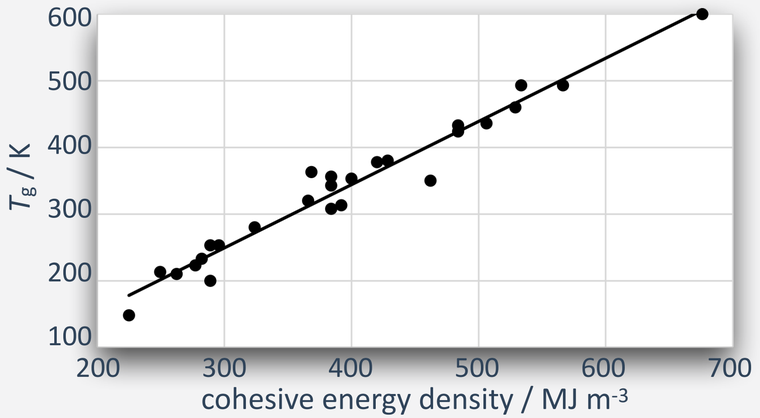
$$\delta^2_{PMMA} = \frac{E_{coh}}{V_0} \sim 533\ Jcm^{-3} \qquad K_{PMMA} = 4.3\ GPa \quad \text{(measured: } 5.1\ GPa\text{)}$$

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

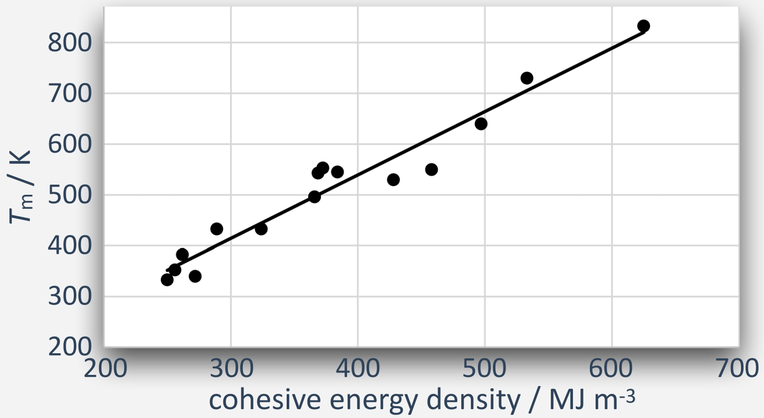
surface tension

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

glass transition temperature



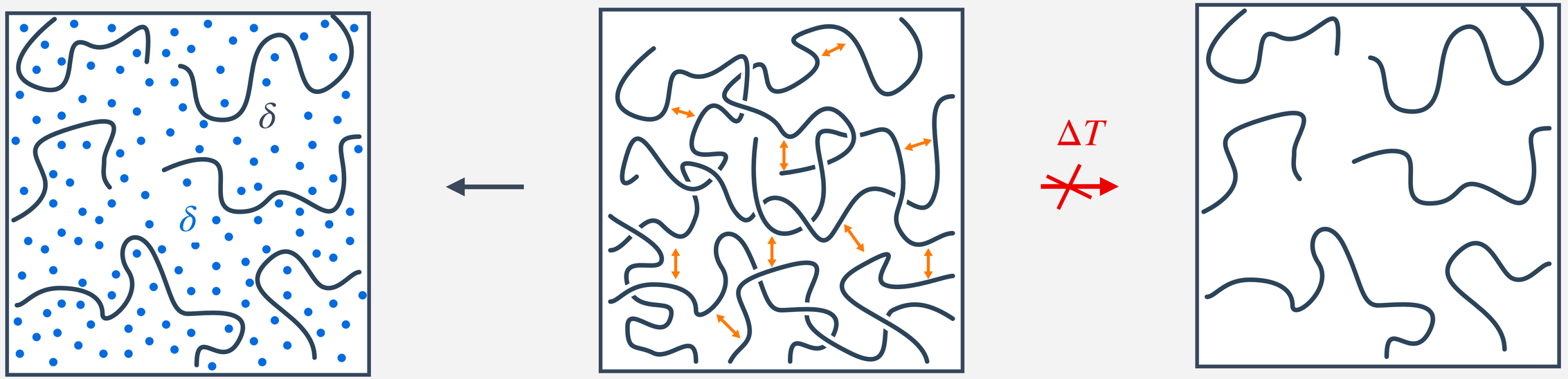

melting temperature



# 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**