IV. Chemische binding

atomen: de bouwstenen van materie

Intermoleculaire krachten

- ***micro***scopische eigenschappen: bindingslengten en -hoeken, bindingsorde (BO), elektronendistributie, polariteit
  - gelokaliseerd e-model: molecule = som discrete bindingen
    - verdeling valentie-e en BO: Lewistheorie + resonantie
    - ruimtelijke structuur (bindingshoeken): VSEPR-theorie
    - orbitalen gebruikt voor binding: valentiebindingstheorie (VB)
  - MOT: molecule is geheel van kernen en elektronen
    - ruimtelijke structuur + e-configuratie + polariteit
  - VB+MOT: molecule = som discrete bindingen (VB) + gedeloka-liseerde elektronen (MOT)
- ***macro***scopische eigenschappen: smeltpunt, kookpunt, viscositeit, oppervlaktespanning
  - **intermoleculaire krachten: dispersie (vdW), ion-dipool, dipool-dipool, H-brugbinding**

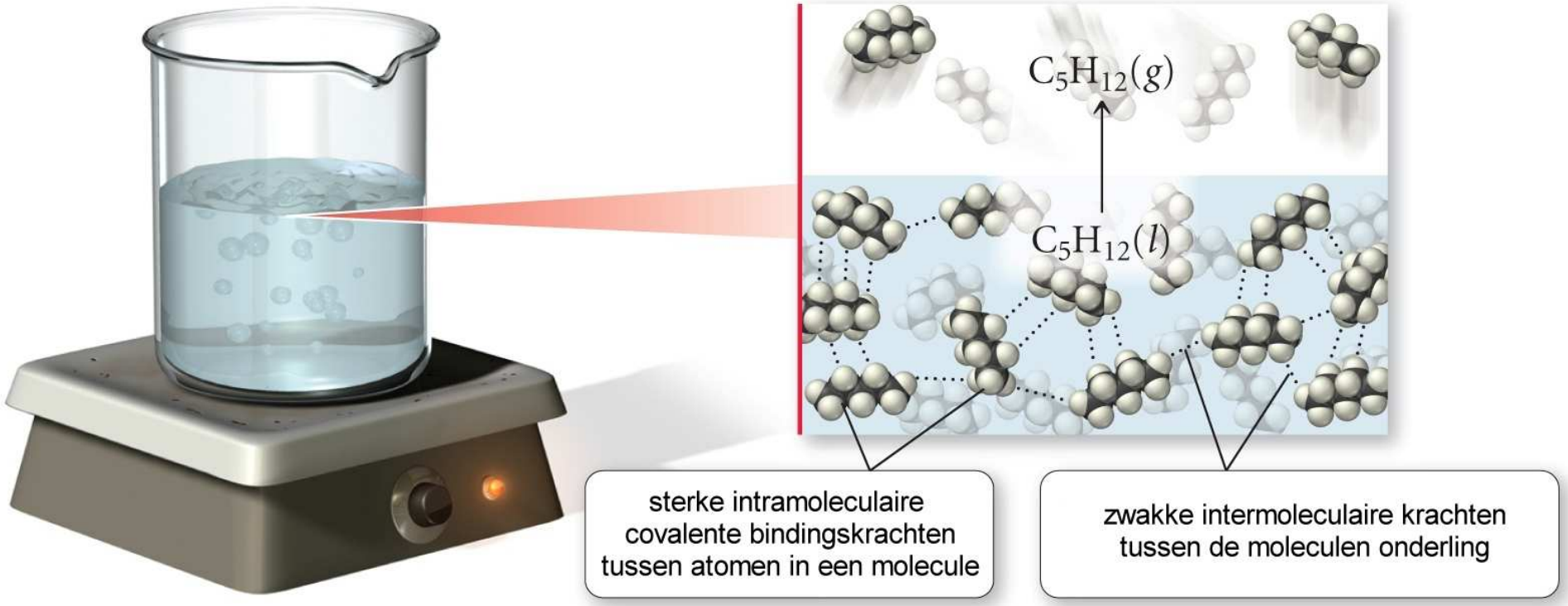
- smeltpunt
- kookpunt
- oplosbaarheid

vloeistoffen:

- oppervlaktespanning
- druppelvorming
- bevochtigen oppervlak
- capillaire werking
- viscositeit

intermoleculaire krachten: zwakke interacties tussen moleculen in een macroscopisch staal van de verbinding

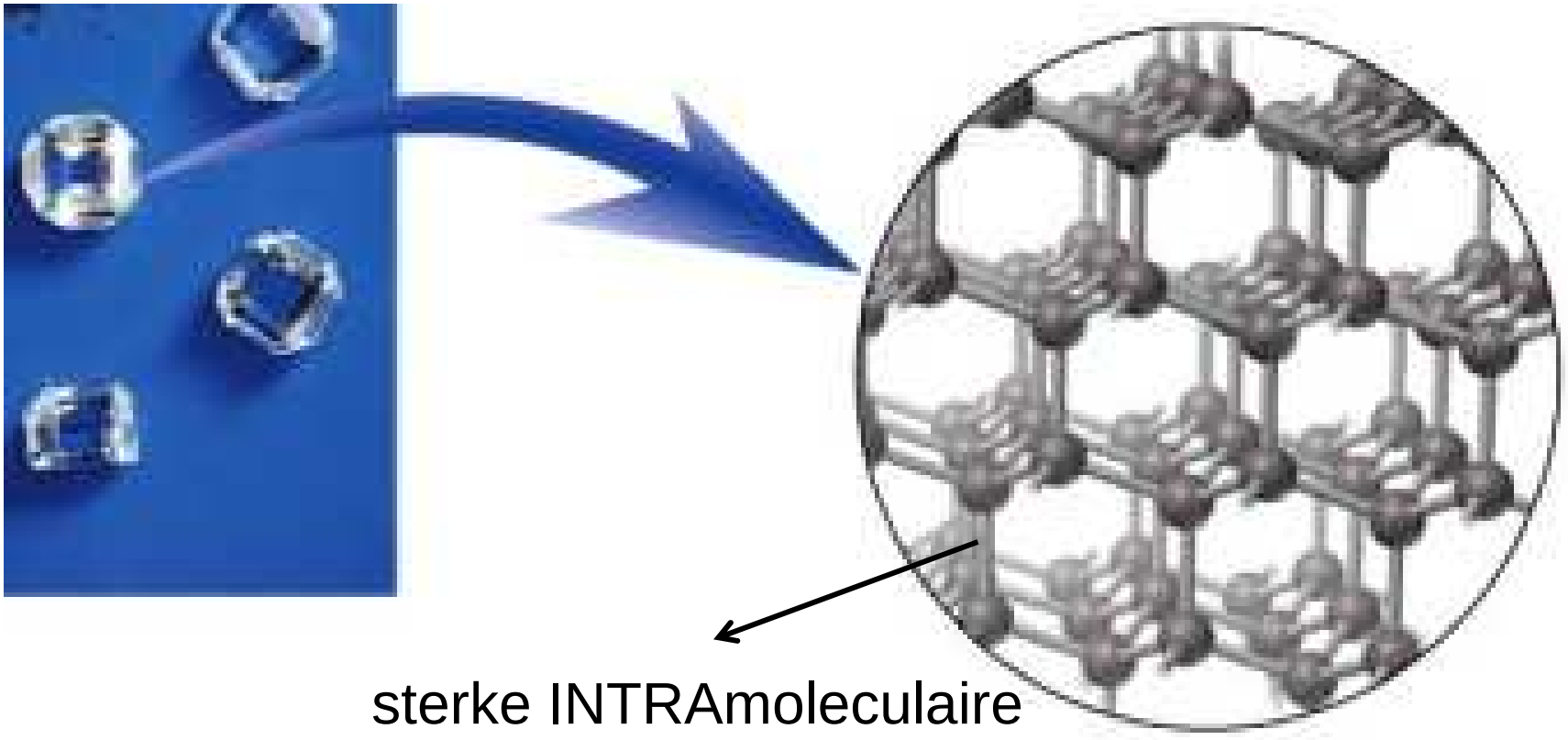
intramoleculaire krachten: sterke covalente interacties tussen atomen in één molecule



Kookpunt pentaan (C_5H_{12}) = 36°C

$\Rightarrow$ breken *INTER*moleculaire krachten

$\Rightarrow$ vereist energie $\Rightarrow$ endotherm

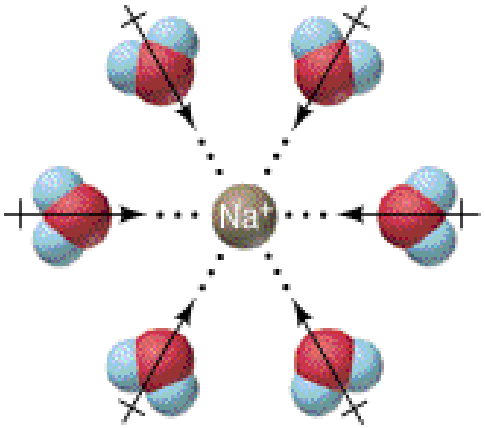


sterke INTRAmoleculaire krachten

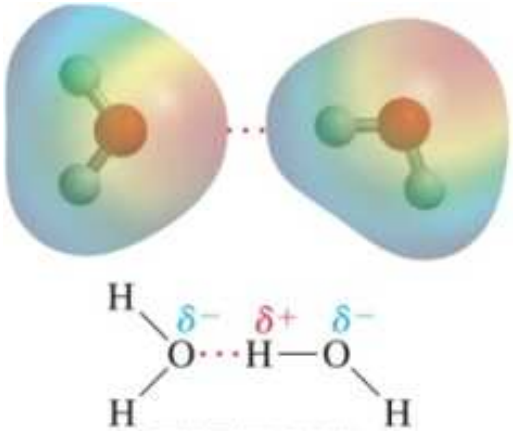
Smeltpunt diamant = 3550 ℃

Types intermoleculaire krachten

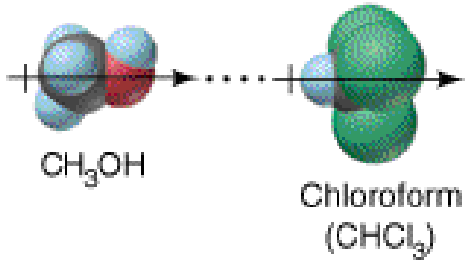
Intermoleculaire krachten



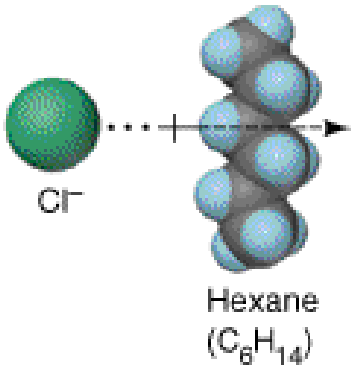
Ion-dipole



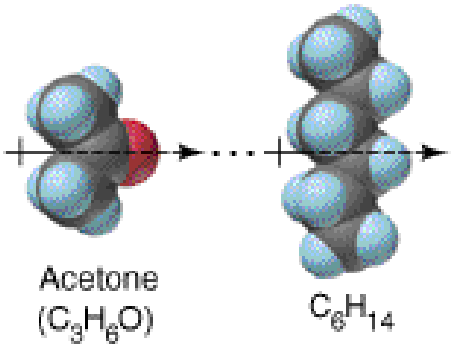
H bond



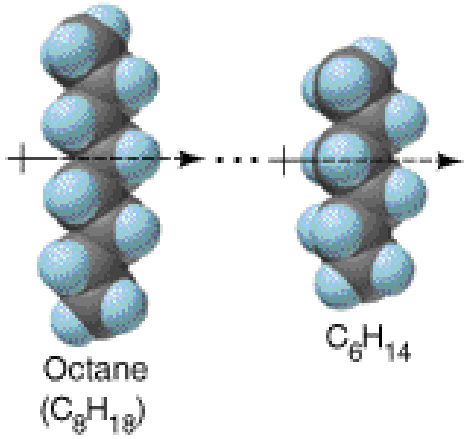
Dipole-dipole



Ion-induced dipole



Dipole-induced dipole



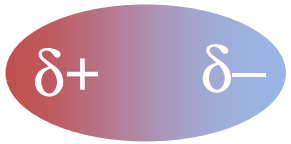
Dispersion

interactie	basis van de interactie	energie (kJ/mol)	voorbeeld
INTRAmoleculair			
ionair	kation + anion	400 - 4000	NaCl
covalent	gedeeld e-paar	150 - 1100	H-H
metallisch*	kation + gedelokaliseerde elektronen	75 - 1000	Fe
INTERmoleculair			
ion-dipool	ionaire lading + dipoollading	40 - 600	Na^{+} --- $^{\delta-}OH_2$
dipool-dipool	dipoollading + dipoollading	5 - 25	I-Cl---I-Cl
dispersie	polarizeerbare elektronenwolken	0.05 - 40	F-F---F-F
H-brugbinding	dipoollading op H-O,F,N + dipoollading op O,F,N-H	10 - 40	$HO\text{-}H^{\delta+}$---$^{\delta-}OH_2$

inTRAmoleculaire krachten >> inTERmoleculaire krachten

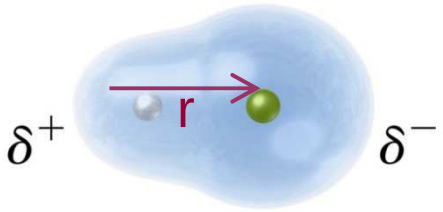
Permanente dipolen

$$\mu = |\delta| \times r$$



•<u>di-atomaire molecule</u>: moleculair dipoolmoment μ = bindingsdipool

$|\delta^+| = |\delta^-|$



HF

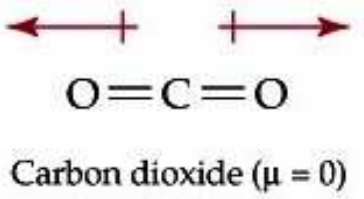
bindingsdipool

vector: grootte ~ ΔEN, richting: $\delta^+ \rightarrow \delta^-$

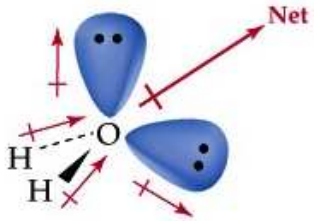
δ: fractie van 1.6×10^{-19}C

δA-B < δA=B

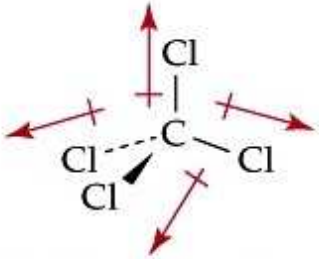
•<u>poly-atomaire molecule</u>: ***moleculair*** dipoolmoment μ = vectorsom van de bindingsdipolen = f(moleculaire geometrie)



Carbon dioxide (μ = 0)

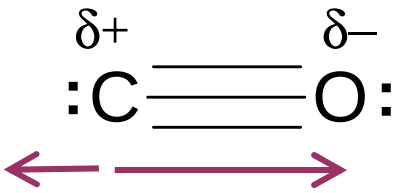


Water (μ = 1.85 D)

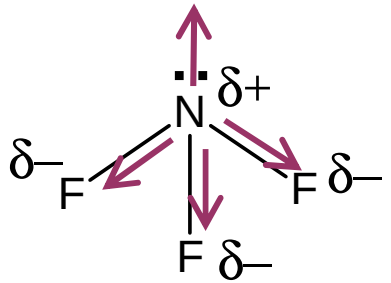


Tetrachloromethane (μ = 0)

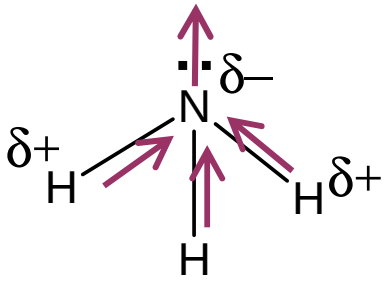
verbinding	μ (D)	verbinding	μ (D)
HF	1.83	NH_3	1.47
HCl	1.11	PH_3	0.58
HBr	0.83	AsH_3	0.20
HI	0.45	SbH_3	0.12
CO	0.11	NF_3	0.24
NO	0.16	BF_3	0
ClF	0.89	CH_4	0
H_2O	1.85		



μ = 0.11



μ = 0.24

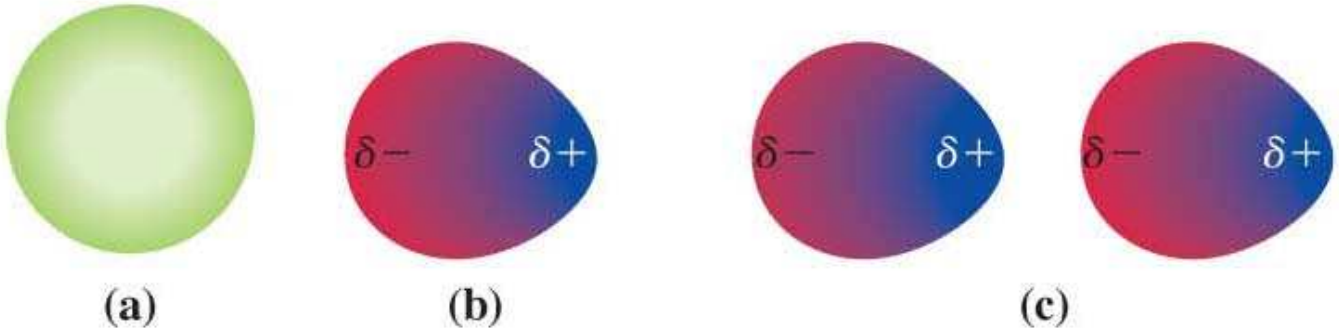


μ = 1.47

polaire moleculen:

dipoolmoment = ***permanente*** vervorming elektronenwolk

Instantane en geïnduceerde dipolen



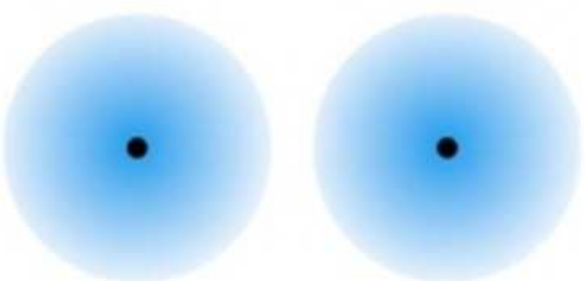
▲ FIGURE 12-2
Instantaneous and induced dipoles
(a) In the *normal condition*, a nonpolar molecule has a symmetrical charge distribution. **(b)** In the *instantaneous condition*, a displacement of the electronic charge produces an instantaneous dipole with a charge separation represented as $\delta+$ and $\delta-$. **(c)** In an *induced dipole*, the instantaneous dipole on the left induces a charge separation in the molecule on the right. The result is an instantaneous dipole–induced dipole attraction.

Dispersiekrachten

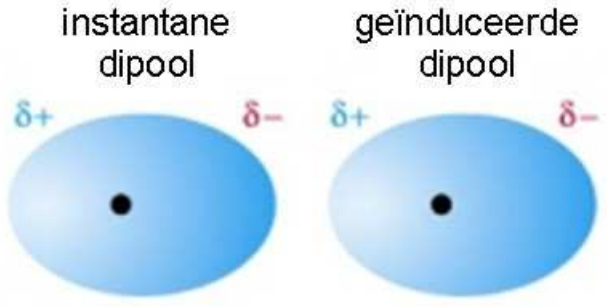
geïnduceerde dipool-geïnduceerde dipoolkrachten

van der Waalsinteractie; London-van der Waalskrachten

interactie tussen polarizeerbare elektronenwolken



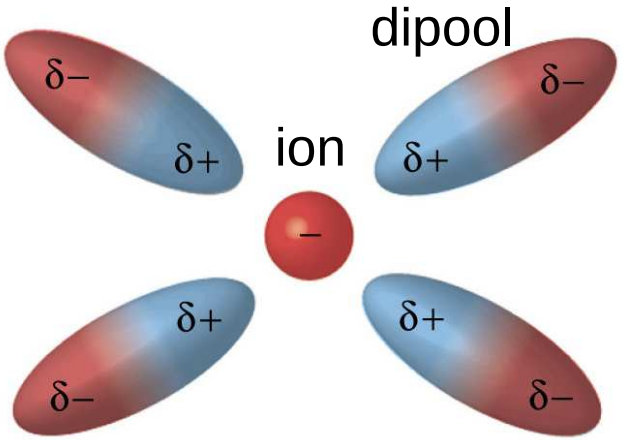
niet-polaire atomen of moleculen

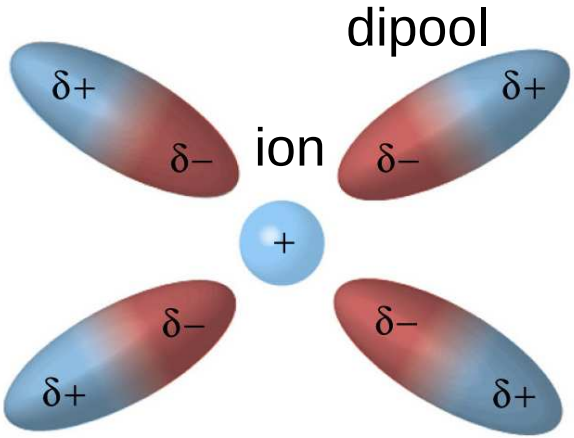


correlatie van de elektronenbeweging van de twee atomen of moleculen wanneer ze in mekaars nabijheid komen

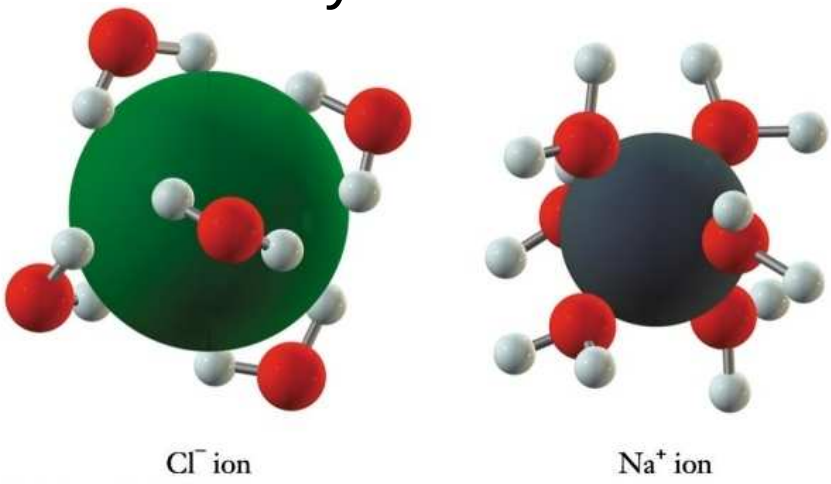
polarizeerbaarheid: ***tijdelijke*** vervormbaarheid elektronenwolk

Ion-dipoolkrachten

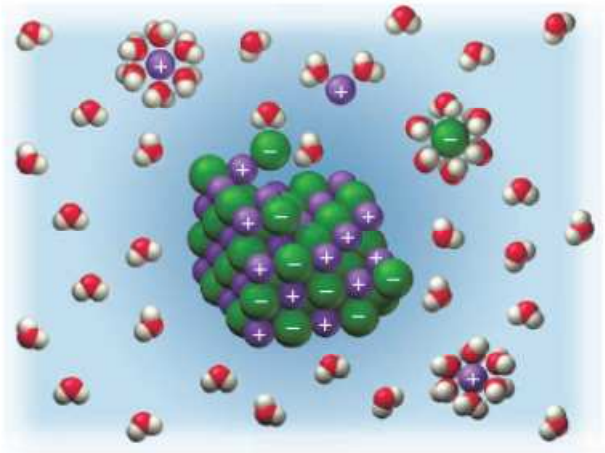




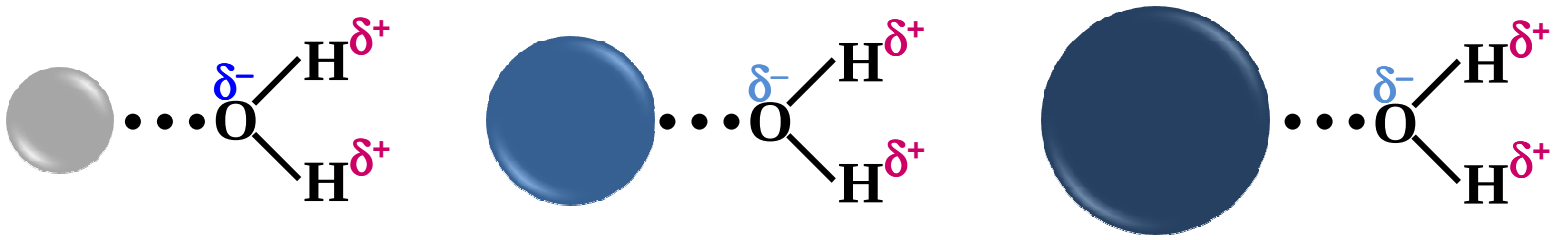
hydratatie



oplosbaarheid ionaire verbindingen in water



$$E_p \propto -\frac{|q| \times \mu}{r^2}$$

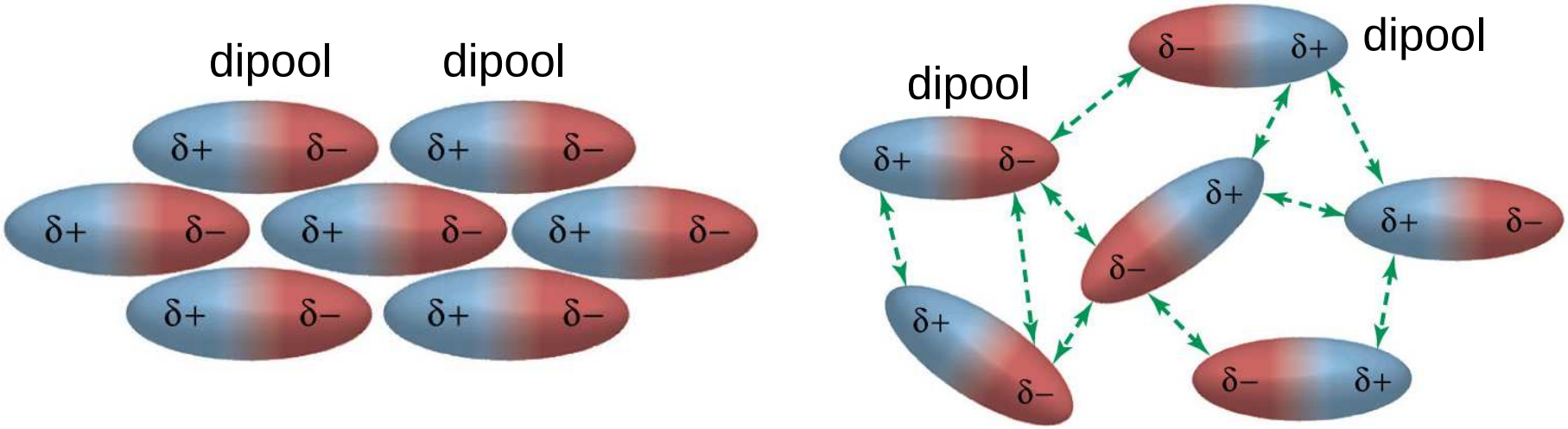


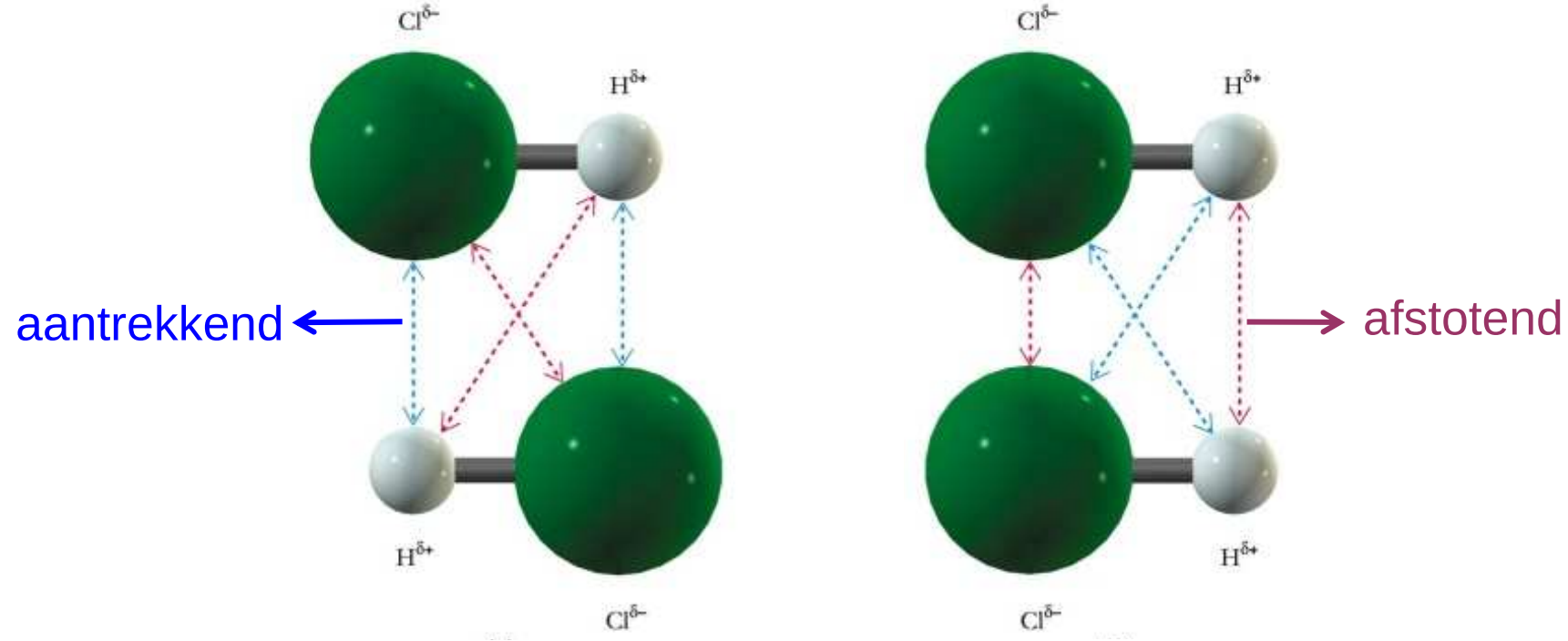
Mg^{2+} Na^{+} Cs^{+}

E_p: –1922 kJ/mol –405 kJ/mol –263 kJ/mol

- interactie hangt af van:
  - lading ion q: lading ↑ ⇒ sterkere interactie
  - dipoolmoment μ:
    dipoolmoment ↑ (partiële lading δ↑) ⇒ sterkere interactie
  - afstand ion-dipoollading:
    grootte ion ↑ ⇒ zwakkere interactie

Dipool-dipoolkrachten

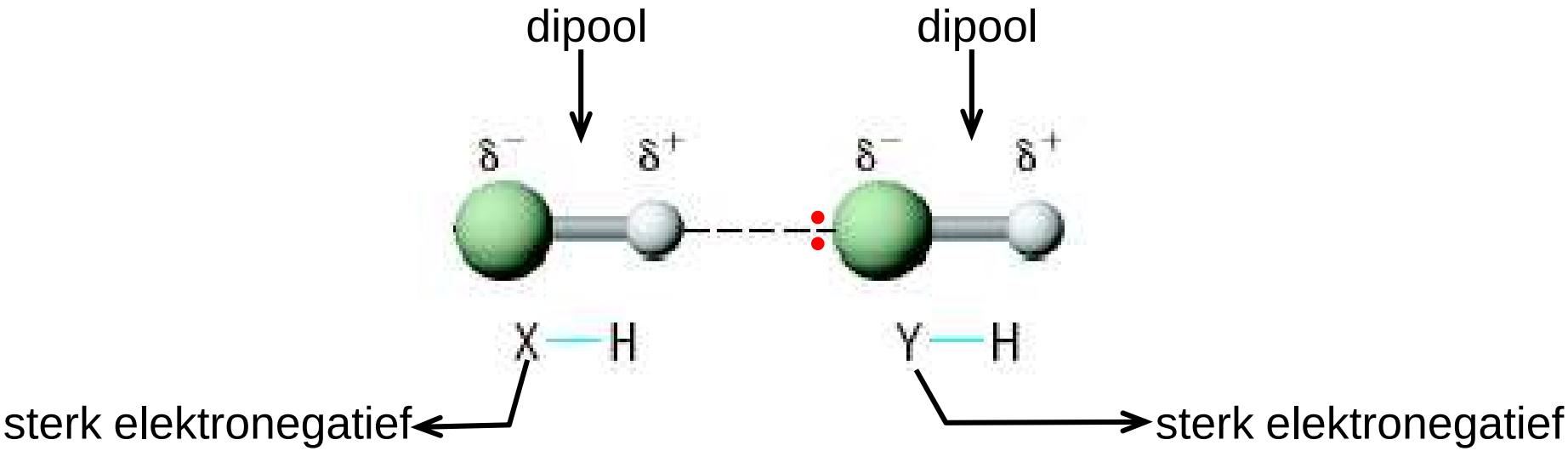




aantrekkend ← → afstotend

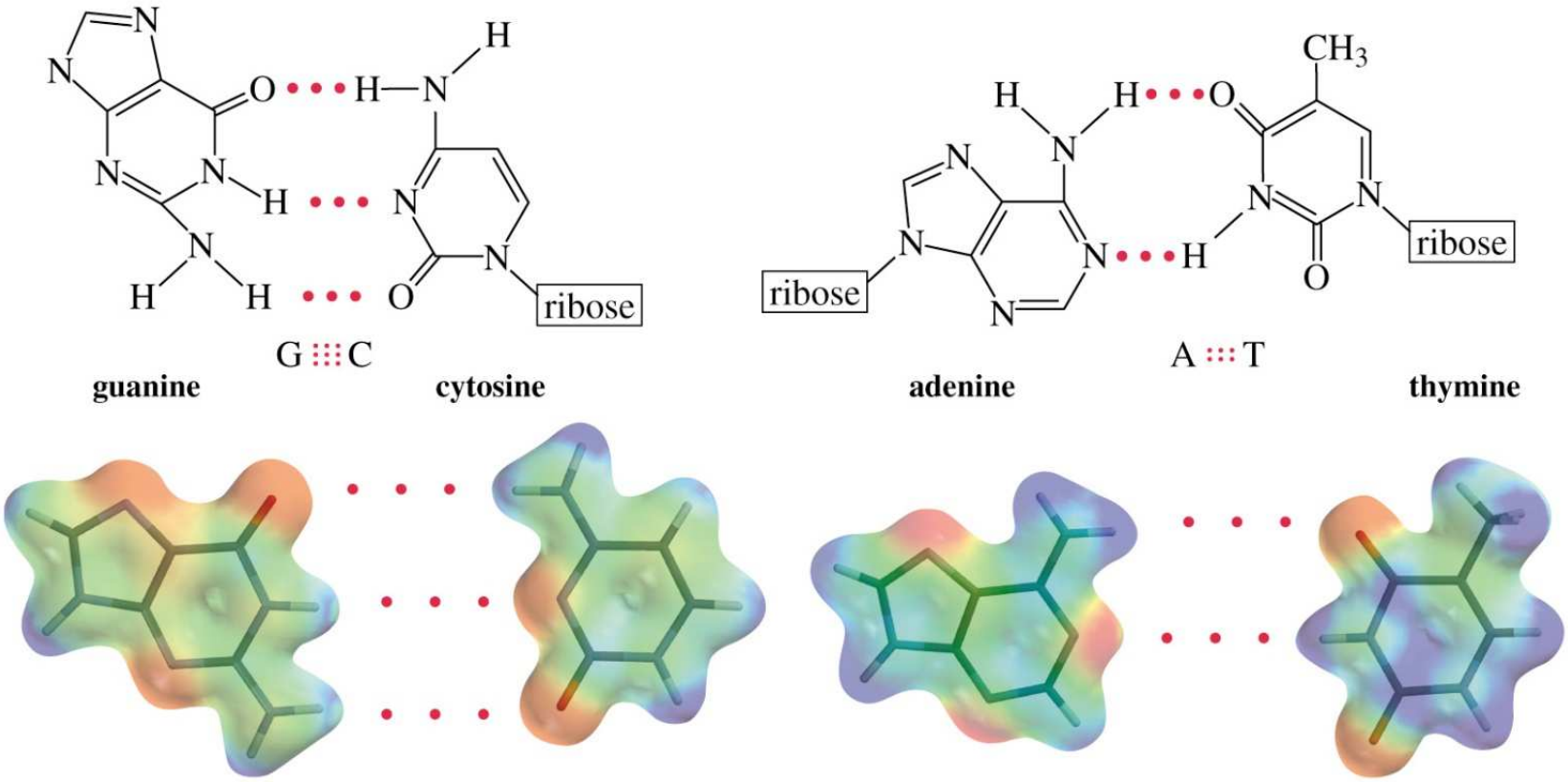
in vloeistof en vaste stof: energetisch meest gunstige schikking dipolen

H-brugbinding



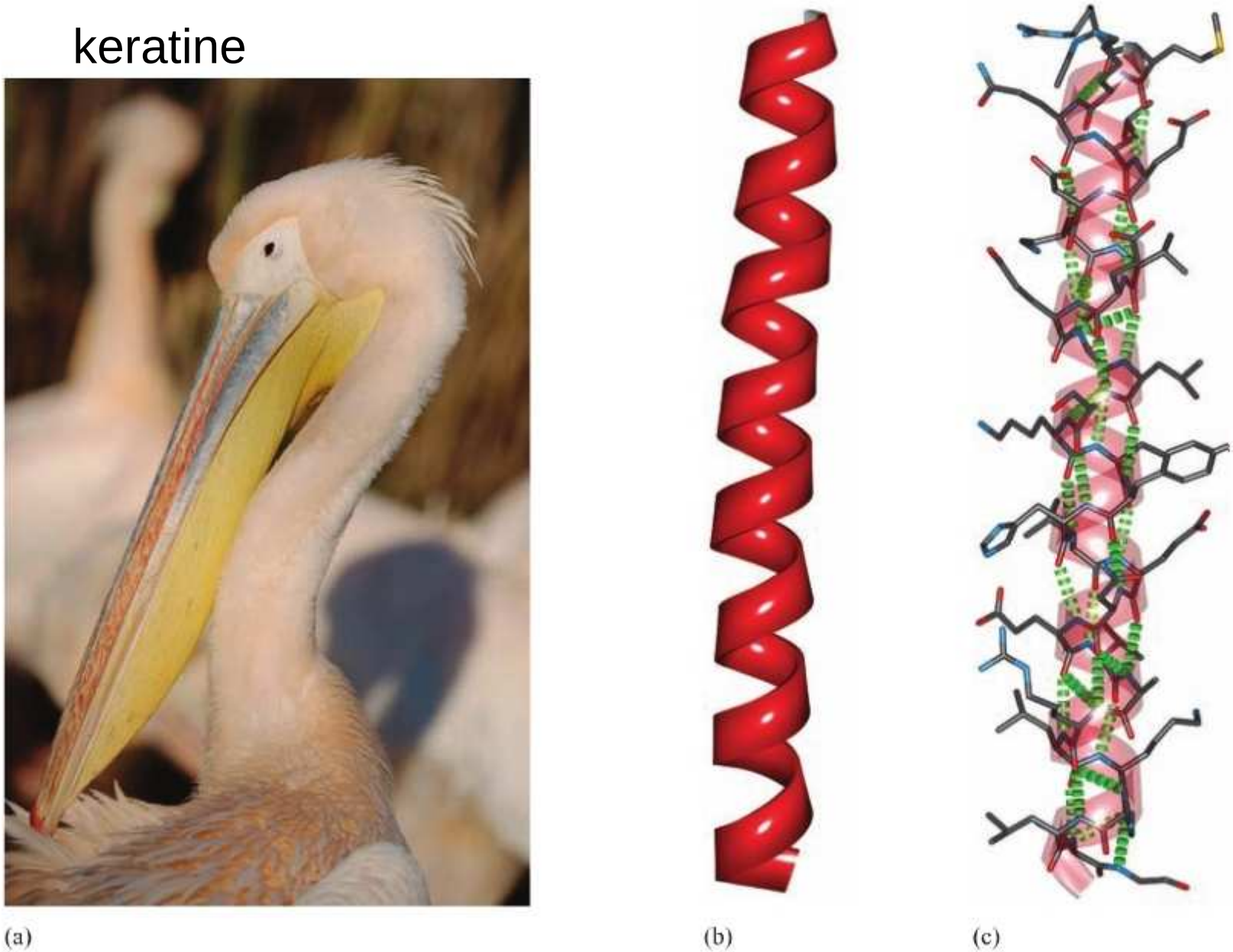
types H-brugbinding [X-H…:Y]		
N–H…:N–	O–H…:N–	F–H…:N–
N–H…:O–	O–H…:O–	F–H…:O–
N–H…:F–	O–H…:F–	F–H…:F–

sterkte H-brugbinding: H…:F > H…:O > H…:N



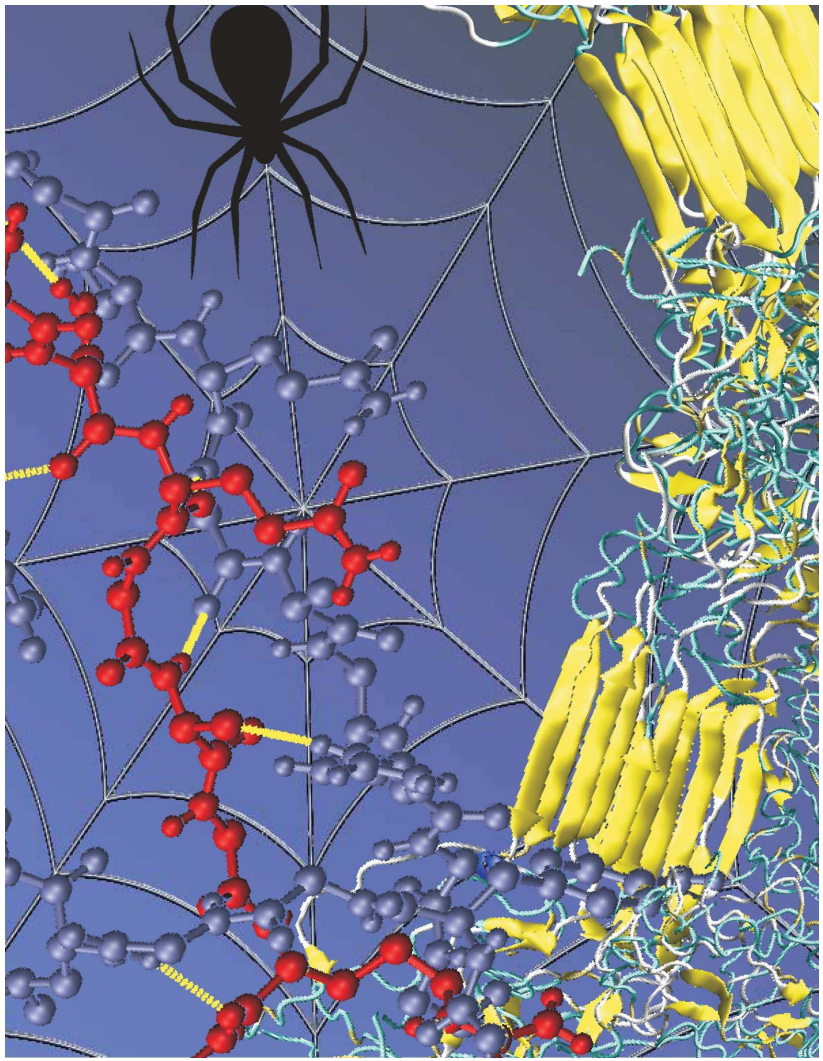
baseparing in DNA

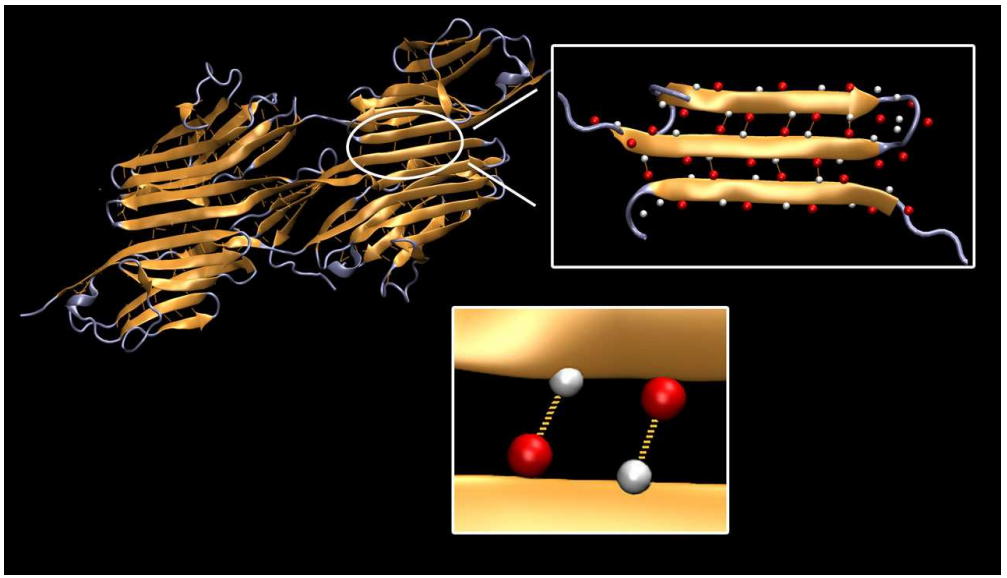
keratine



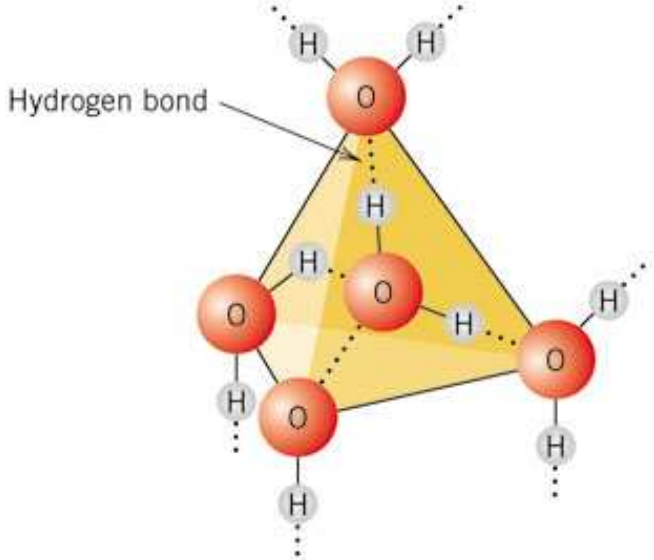
(a) (b) (c)

Fig. 35.24 (a) Keratin is the main component of the beak of the pelican (*Pelecanus onocrotalus*), and all other birds. (b) α-Helical secondary structure is characteristic of keratins. (c) The –C=O···N–H– hydrogen bonds (shown in green) between peptide units, four amino acid residues apart, are the main interactions that stabilize the α-helical conformation.

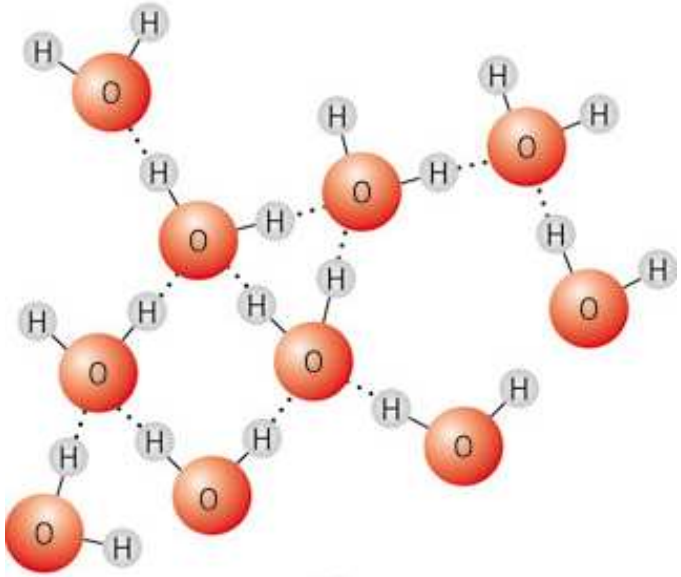




The strength of a biological material such as spider silk lies in the specific geometric configuration of structural proteins, which have small clusters of weak hydrogen bonds that work together to resist force and dissipate energy. This structure is as strong as steel, even though the "glue" of hydrogen bonds that hold spider silk together at the molecular level is 100 to 1,000 times weaker than steel's metallic bonds or Kevlar's covalent bonds.

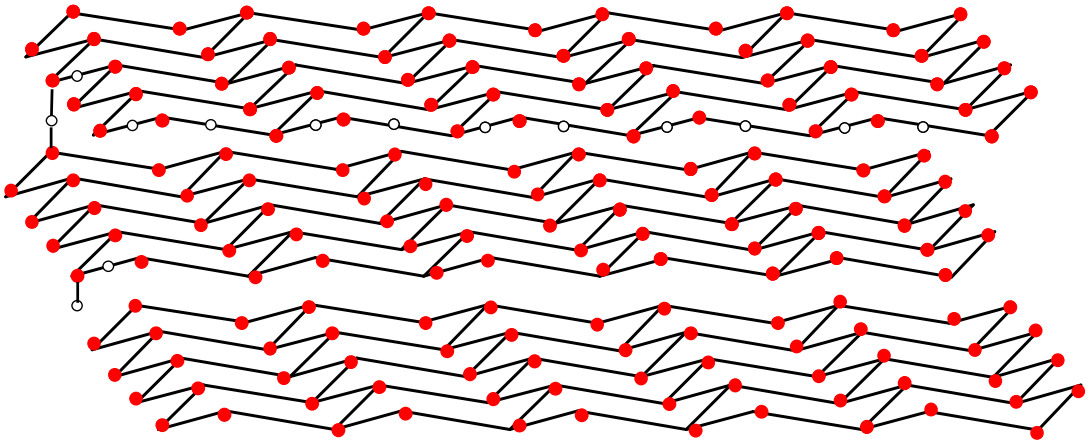


(a) ijs

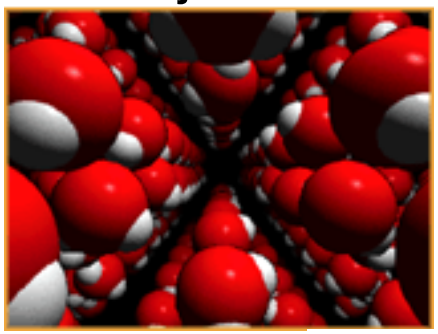


(b) vloeibaar water

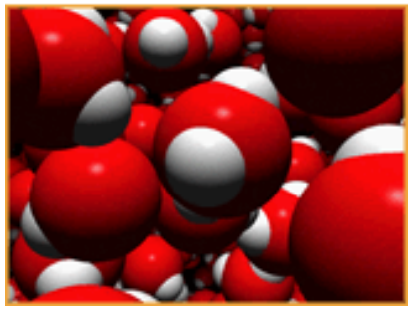
Volume ijs > volume water



ijs



water



Ijs: een open netwerk waarin de watermoleculen op hun plaats gehouden worden door H-brugbindingen. Als ijs smelt breken sommige van de H-bruggen en gaat de geordende structuur verloren. In de vloeistof bewegen de moleculen door en over elkaar heen en “stapelen” de moleculen minder uniform maar wel dichter op elkaar.

De openheid van het 3D netwerk in ijs is groter dan dit in water; vandaar dat de dichtheid van ijs kleiner is dan de dichtheid van water. Het volume van 1 g ijs is dus groter dan het volume van 1 g water.

Invloed intermoleculaire krachten op kookpunt en smeltpunt

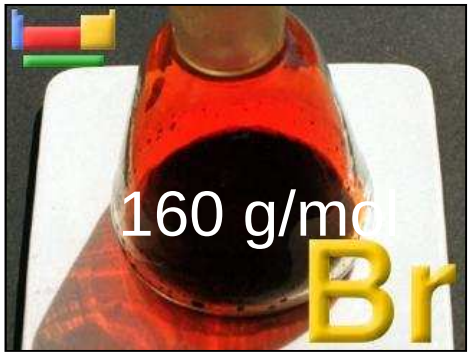
Invloed dispersiekrachten

polarizeerbaarheid e-wolk: f(grootte atoom/molecule) = f (MM)

Compound	Polarizability,* 10^{-25} cm^3	Molar Mass, amu	Boiling Point, K
H_2	7.90	2.0158	20.35
O_2	16.0	31.9988	90.19
N_2	17.6	28.0134	77.35
CH_4	26.0	16.04	109.15
C_2H_6	44.7	30.07	184.55
Cl_2	46.1	70.906	238.25
C_3H_8	62.9	44.11	231.05
CCl_4	105	153.81	349.95

*Sometimes polarizability is referred to as *polarizability volume*. Note that the units of polarizability given above have the units of volume. That provides a measure of the atomic or molecular volume.

•polarizeerbaarheid e-wolk: f(grootte atoom/molecule) = f (MM)



Cl_2: gas Br_2: vloeistof I_2: vaste stof

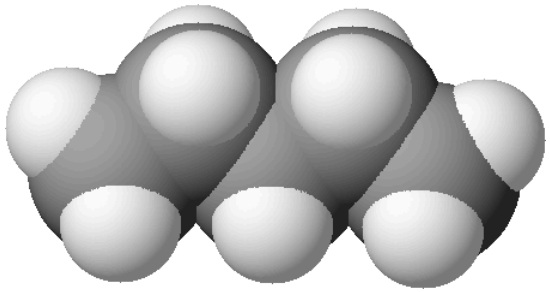
kookpunt:	–33℃	+59℃	+184℃

bindingse-paren: Cl-Cl (n = 3) < Br-Br (n = 4) < I-I (n = 5)

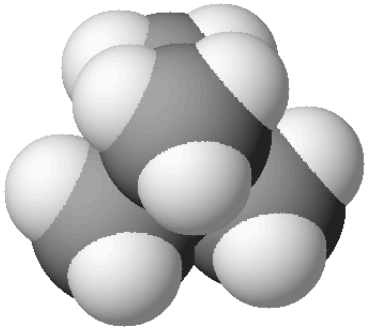
vrije e-paren: Cl (EN = 3; n = 3) < Br (EN = 2.8; n = 4) < I (EN = 2.5; n = 5)

toename kookpunt: ~ 1.2℃/g

•vorm molecule ⇒ contactoppervlak



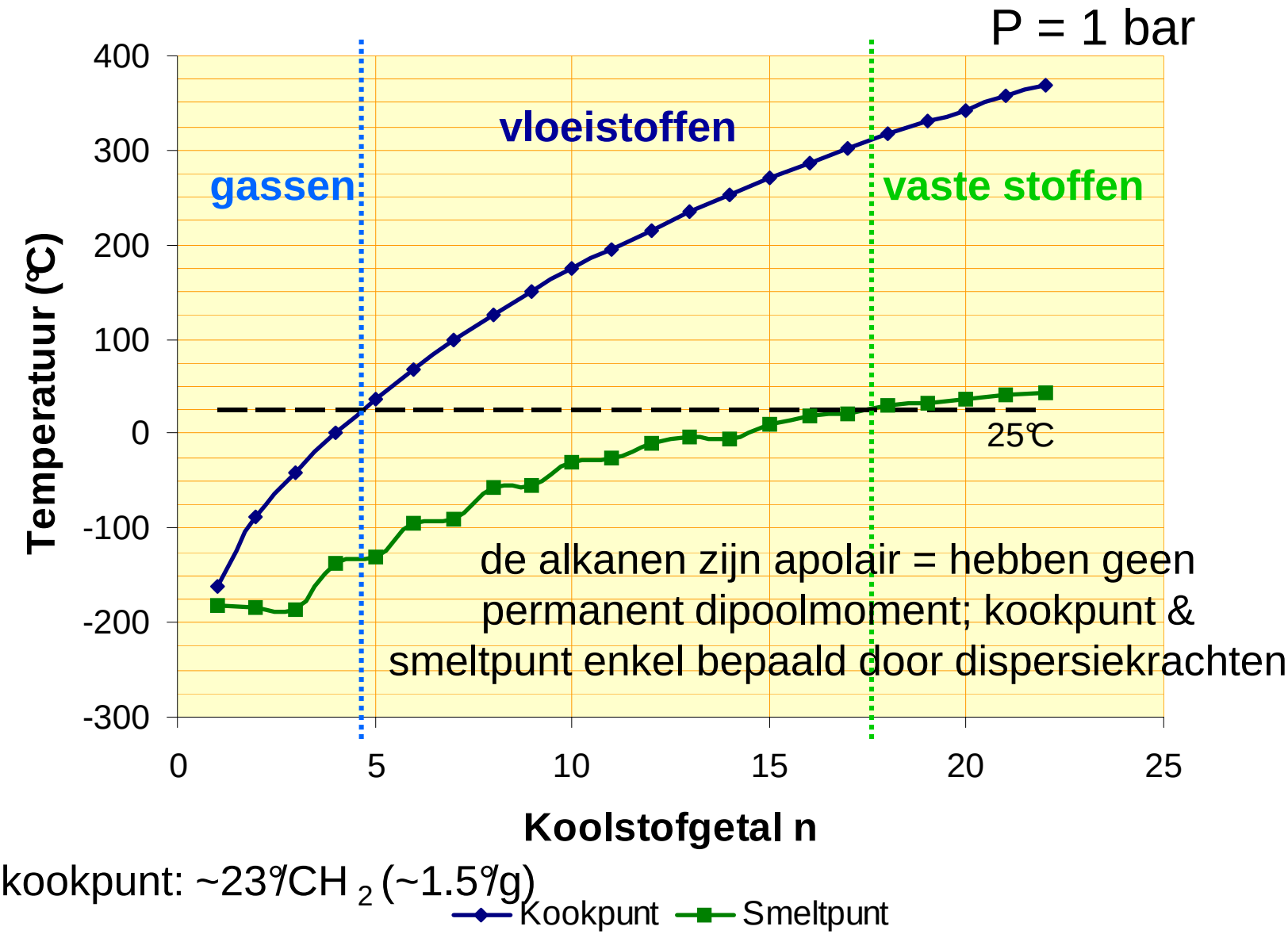
n-pentaan (kpt: 36℃)



2,2-diMe-propaan (kpt: 9.7℃)

kookpunt & smeltpunt n-alkanen ↑ met aantal C-atomen

dispersiekrachten nemen toe naarmate molecule meer elektronen bevat



toename kookpunt: ~23℃CH_2 (~1.5℃g)

- invloed op kookpunt
  - edelgassen: toename kookpunt: ~1°C/g

    He: -269°C; 4 g/mol Xe: ~ -33°C; 222 g/mol

    - Z_{eff} is groot $\Rightarrow$ elektronen sterk aan de kern gebonden

      He: n = 2; Rn: n = 6
    - klein contactoppervlak
  - alkanen: toename kookpunt: ~23°/CH_2 (~1.5°/g)

Vuistregel:

- kookpunt neemt toe met ~1° tot 1.5°/g

  invloed op kookpunt: f(polarizeerbaarheid elektronen)

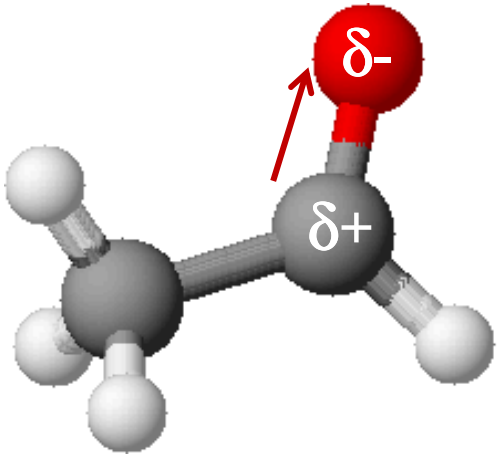
  polarizeerbaarheid: bindingse < vrije e-paren

  f(EN en n vrije e-paren)

  contactoppervlak belangrijk bij ≈MM!!

Invloed dipool-dipoolkrachten

N_2	NO	O_2
$\mu = 0$ (nonpolar) mol. mass = 28 u bp = 77.34 K	$\mu = 0.153$ D (polar) mol. mass = 30 u bp = 121.39 K	$\mu = 0$ (nonpolar) mol. mass = 32 u bp = 90.19 K

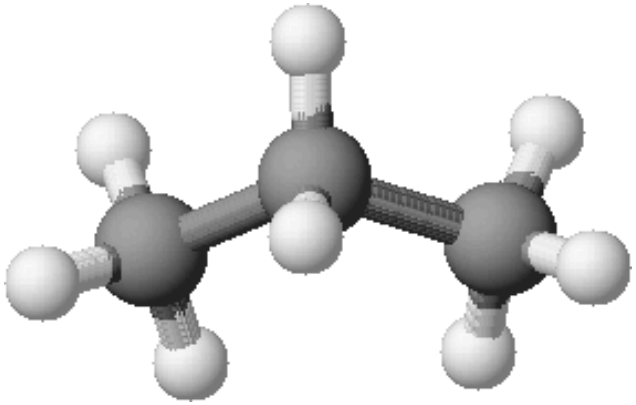


acetaldehyde

kookpunt = 21°C

MM: 44 g/mol

$\Delta EN_{C=O} = 1$



propaan

kookpunt = –42°C

MM: 44 g/mol

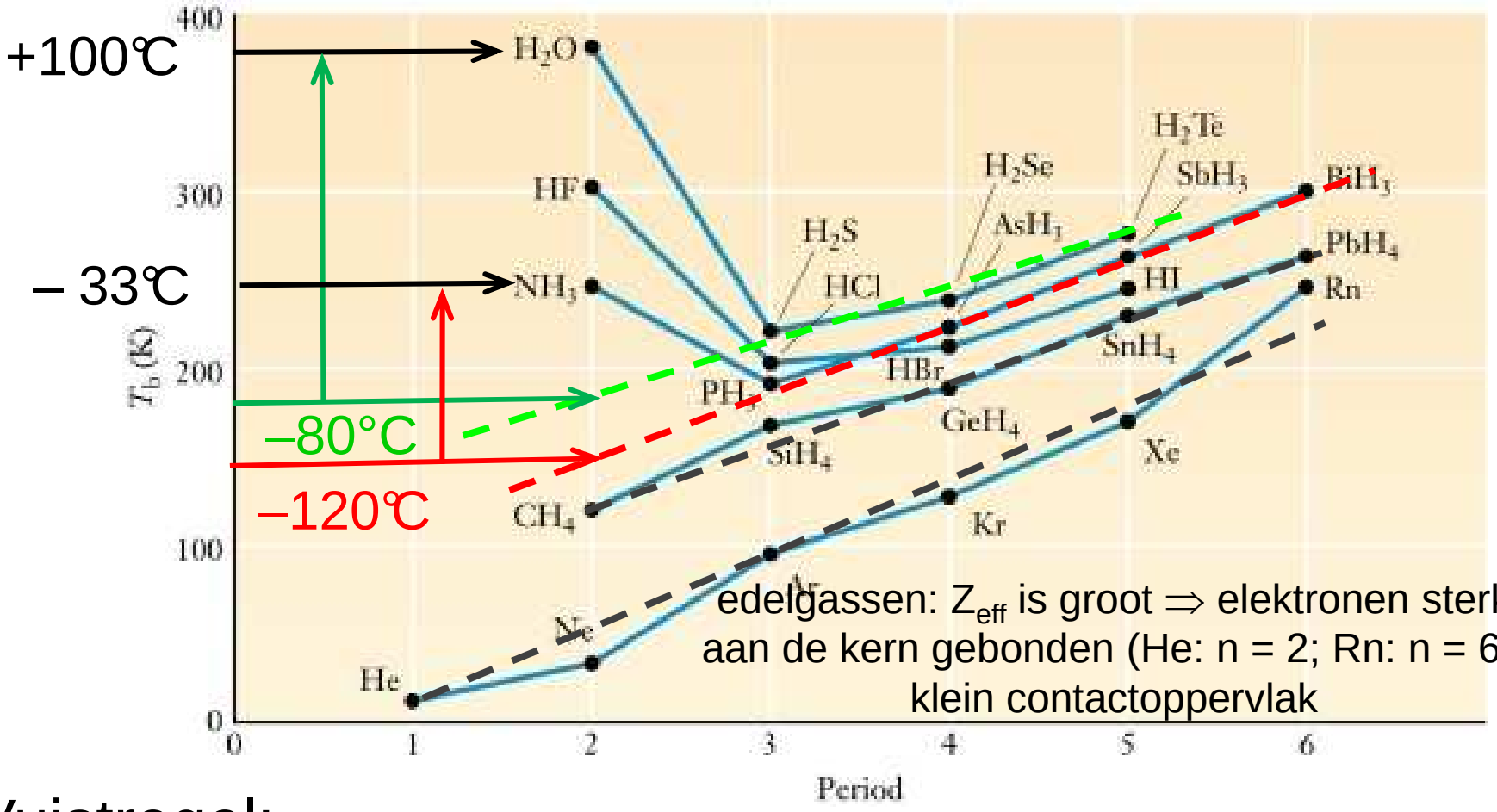
Vuistregel:

- kookpunt neemt toe met ~40° tot 60°;

  invloed op kookpunt: f(grootte μ) = f(ΔEN en geometrie)

  δA-B < δA=B

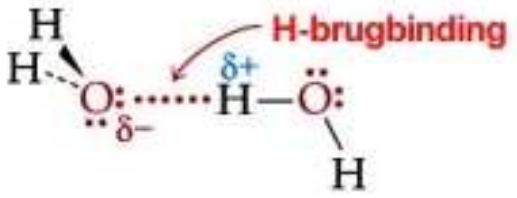
Invloed H-brugbinding

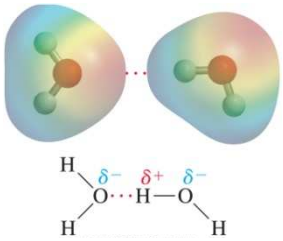


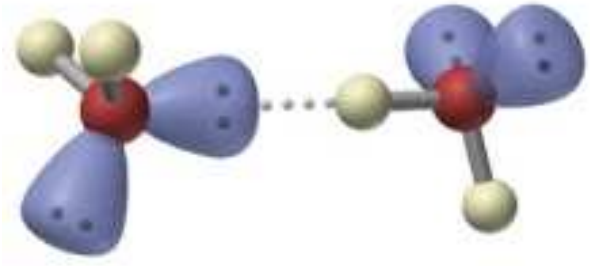
Vuistregel:

kookpunt neemt toe met ~90℃ voor NH_3

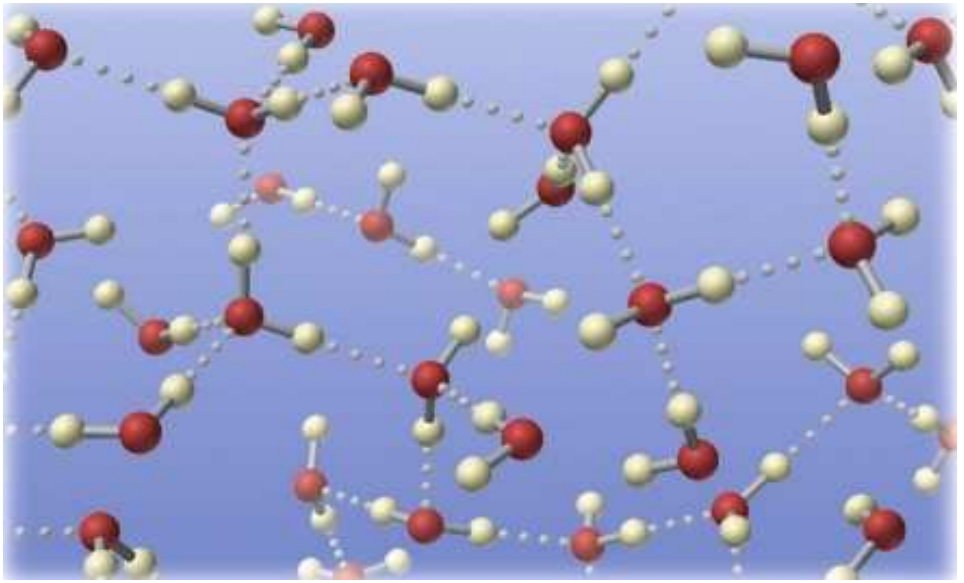
kookpunt neemt toe met ~180℃ voor H_2O



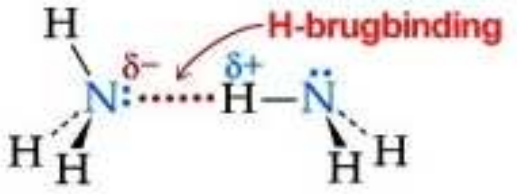


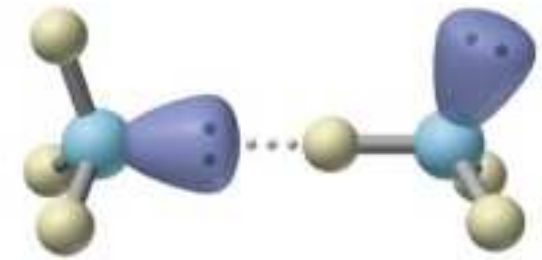


kookpunt: 100℃

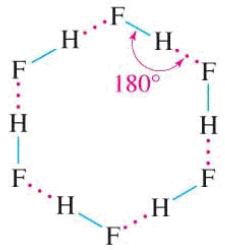


3D netwerk van H-brugbindingen tussen watermoleculen

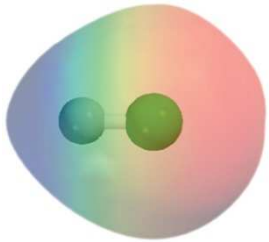




kookpunt: –33 ℃

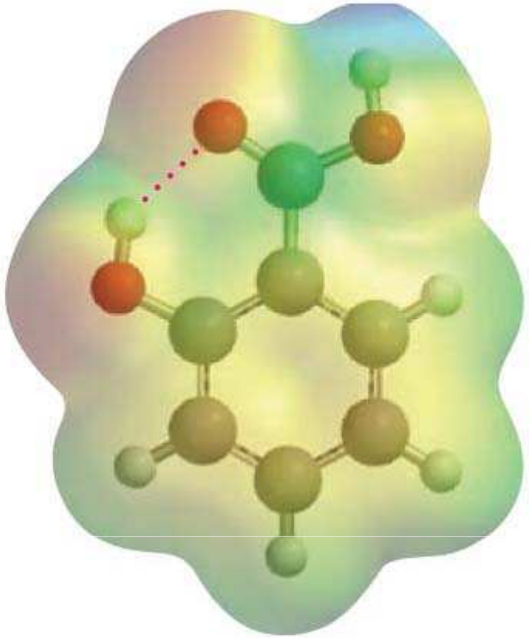


▲ FIGURE 12-6
Hydrogen bonding in gaseous hydrogen fluoride
In gaseous hydrogen fluoride, many of the HF molecules are associated into cyclic $(HF)_6$ structures of the type pictured here. Each H atom is bonded to one F atom by a single covalent bond (—) and to another F atom through a hydrogen bond (···).

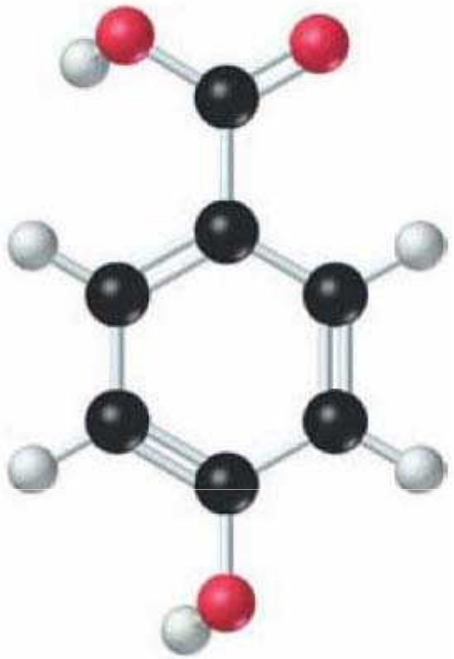


kookpunt: 20 ℃

*intra*moleculaire H-brugvorming



▲ Electrostatic potential map of salicylic acid showing intramolecular hydrogen bonding. The double bond character of certain bonds are not shown in the ball-and-stick model.



▲ There is no intramolecular hydrogen bonding in *para*-hydroxybenzoic acid.

o-hydroxybenzoëzuur: mp = 160℃

m-hydroxybenzoëzuur: mp = 201℃

p-hydroxybenzoëzuur: mp = 215℃

vuistregels grootte-ordes vergelijking kookpunt	
dispersie	kookpunt neemt toe met ~1°tot 1.5℅g; polarizeerbaarheid: bindingse < vrije e-paren f(EN en n vrije e-paren) contactoppervlak belangrijk bij ≈MM!!
dipoolmoment	kookpunt neemt toe met ~40° tot 60°; f = (grootte μ) = f(ΔEN en geometrie) δA-B < δA=B
H-brugbinding	kookpunt neemt toe met: ~90℃ voor NH_3 ~180℃ voor H_2O

	dispersie	dipool-dipool	H-brug
CCl_4	MM: 154 4 × 3 vrije e-paren op Cl (n = 3; EN = 3.15)	4 LW: tetraedrisch 4 bindingen CCl: ΔEN = 0.55 $\mu CCl_4 = 0$	geen
NH_3	MM: 17 1 vrij e-paar op N (n = 2; EN = 3.0)	4 LW: tetraedrisch 3 bd + 1 vrij e p trigonaal pyramidaal NH: ΔEN = 0.9 $\mu NH_3 > 0$ (groot)	H … :N
	CCl_4 >>>>>> NH_3	NH_3 >> CCl_4	NH_3 >> CCl_4
intermoleculaire krachten		$CCl_4 > NH_3$	

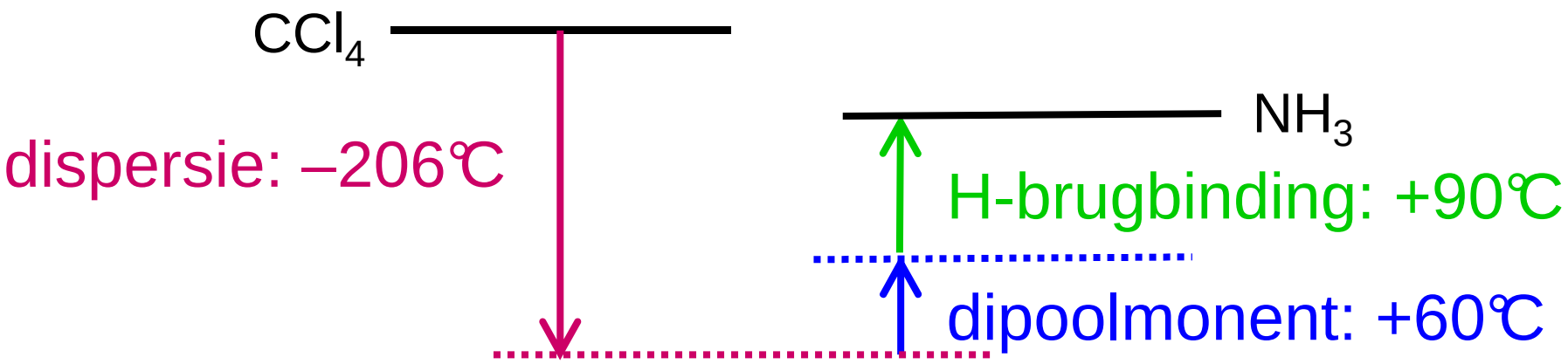
kookpunt NH_3 ≈

kookpunt CCl_4 – verschil in dispersiebijdrage + verschil in dipool-dipoolbijdrage + bijdrage H-brug

kookpunt NH_3 ≈

kookpunt CCl_4 – (1.5℃/g × 137 g) + (60℃ – 0℃) + 90°C =
kookpunt CCl_4 – 56℃

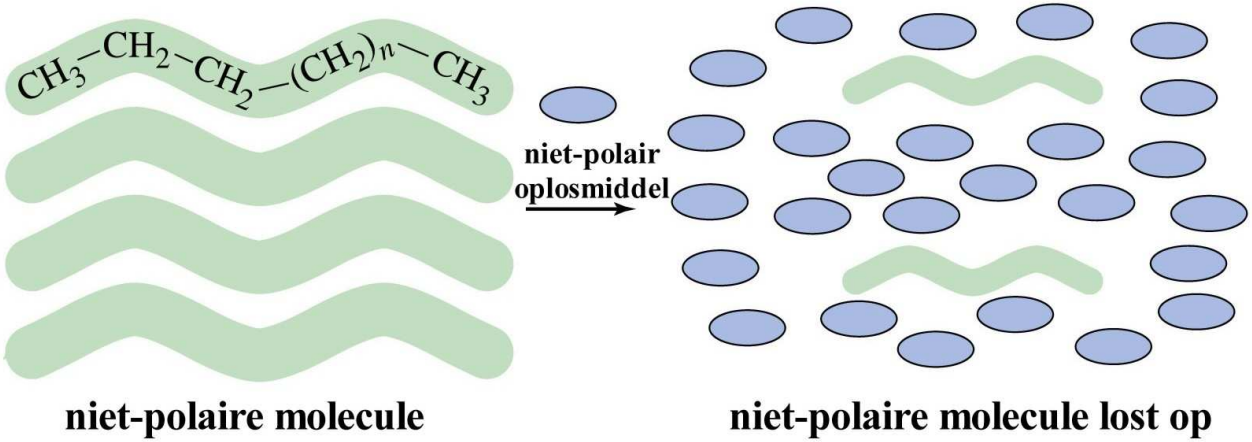
⇒ kookpunt ammoniak < kookpunt CCl_4

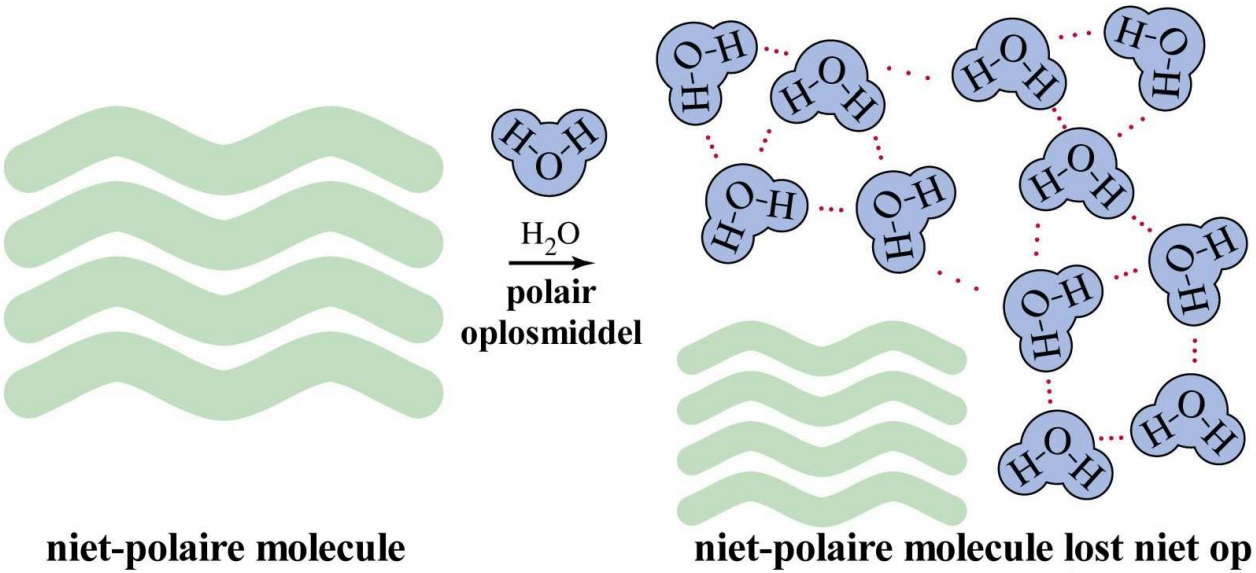


(g/mol)	kook-punt (℃)	(g/mol)	kook-punt (℃)	(g/mol)	kook-punt (℃)
He (4)	-269	H_2 (2)	-253	CH_3CH_3 (30)	-89
Ne (20)	-246	N_2 (28)	-196	$CH_3CH_2CH_3$(44)	-42
Ar (40)	-186	O_2 (32)	-183	CH_3OCH_3 (46)	-24
Kr (83.8)	-153	H_2O (18)	+100	CH_3COH (44)	+21
Xe (131.3)	-108	H_2S (34)	-60	n-C_5H_{12} (72)	+36
		NH_3 (17)	-33	1-penteen (70)	+30
		CO_2 (44)	-78	i-C_5H_{12} (72)	+30
HF (20)	+20	SO_2 (64)	-10	2,3-diMe-butaan	+10
HCl (36.5)	-85	CH_4 (16)	-162	n-C_6H_{14} (86)	+68
HBr (80.9)	-67	CF_4 (88)	-129	C_6H_6 (78)	+80
HI (127.9)	-35	CCl_4(154)	+77		

zie hfdst 6; pi-elektronen van benzeen zijn uitzonderlijk mobiel

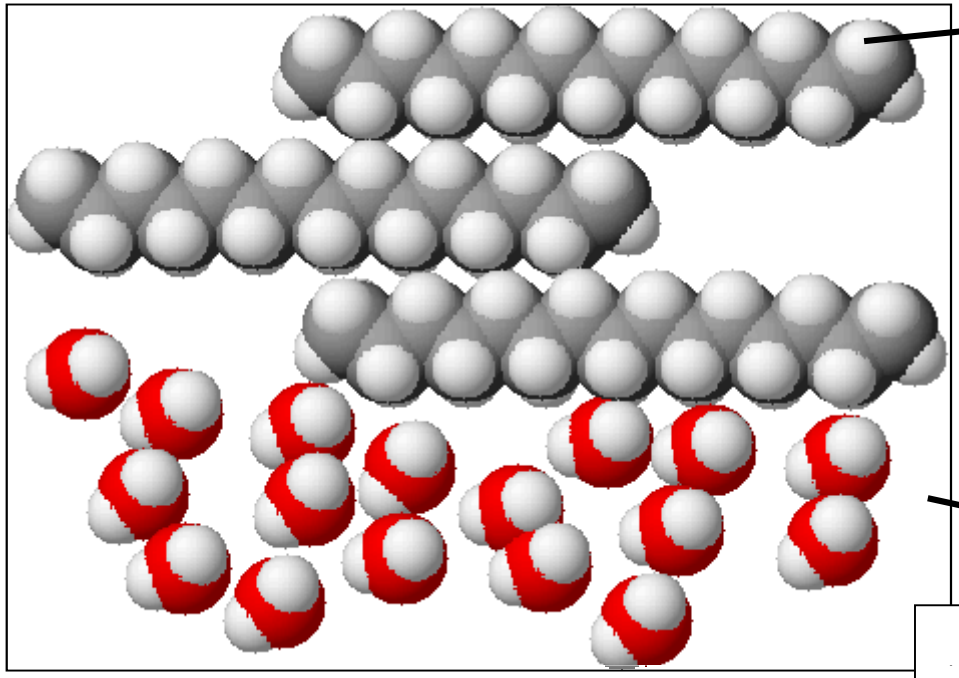
Invloed intermoleculaire krachten op oplosbaarheid





polaire molecule lost op in polair oplosmiddel

niet-polaire molecule lost op in niet-polair oplosmiddel

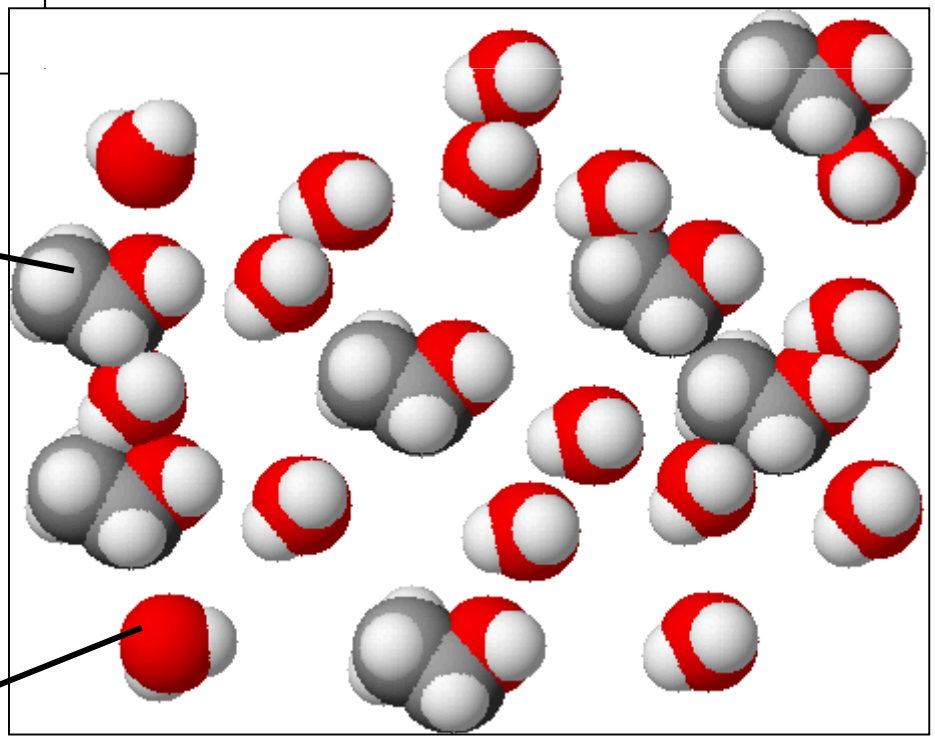


motorolie: KWS is ***a***polair

interacties:

KWS-water <<< water-water en KWS-KWS

water: polair



ethanol: polair

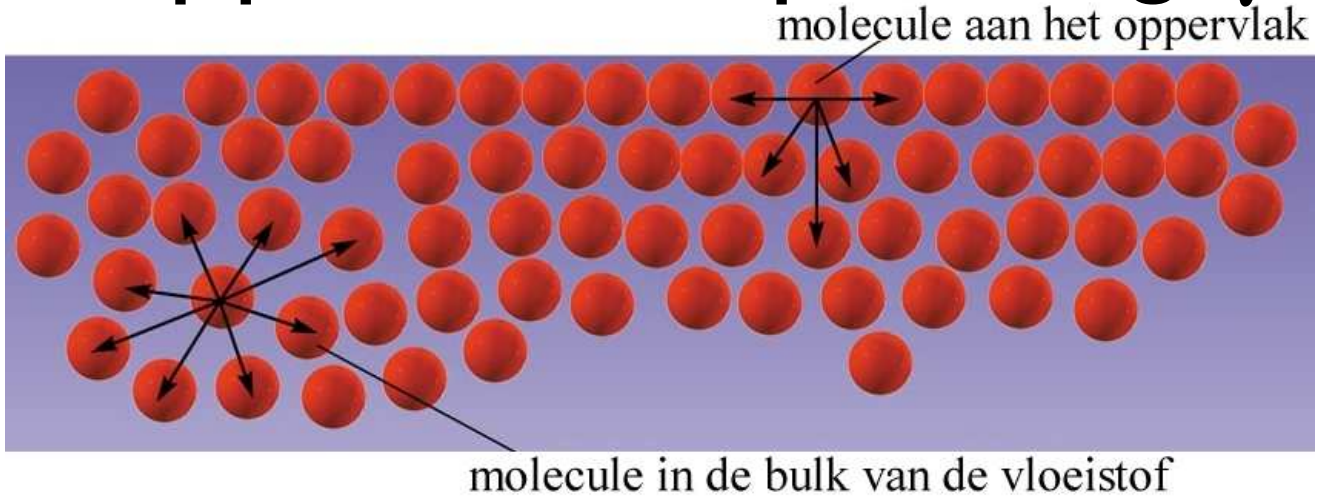
interacties:

ethanol-water ≅ water-water en ethanol-ethanol

water: polair

Eigenschappen van vloeistoffen

Oppervlaktespanning γ

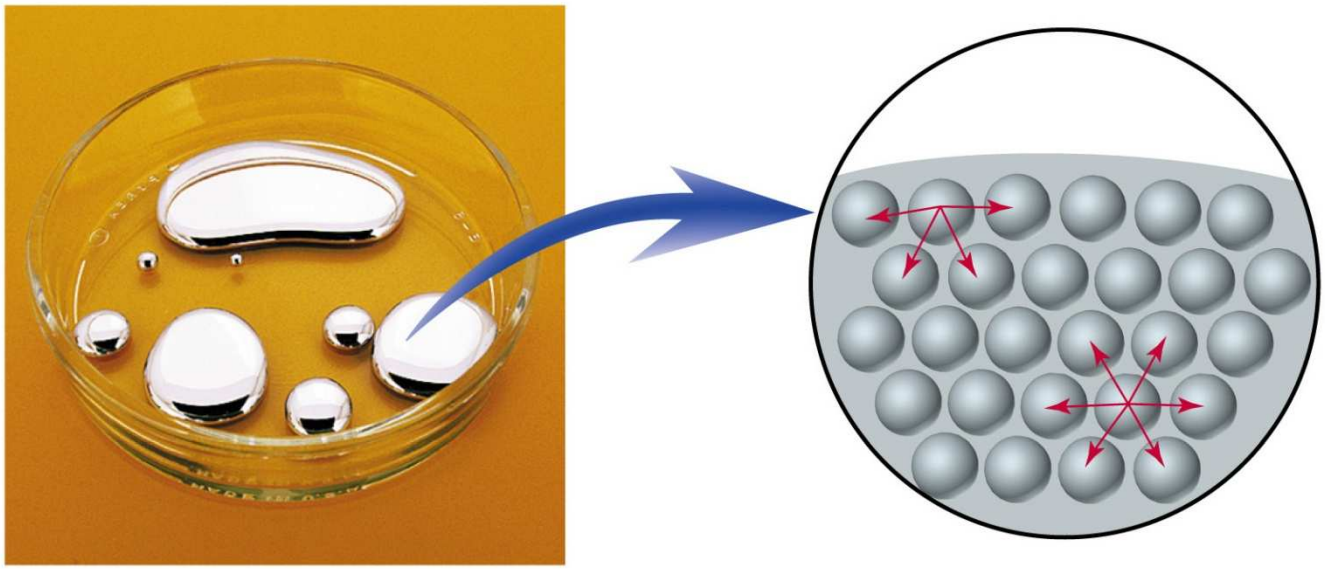


verbinding	γ [Nm^{-1}]
benzeen	29×10^{-3}
ethanol	23×10^{-3}
n-hexaan	18×10^{-3}
kwik	472×10^{-3}
water	73×10^{-3}
water (100℃)	58×10^{-3}

verbeter de waarden in Tabel 4.9

▲ FIGURE 12-10
An effect of surface tension illustrated
Despite being denser than water, the needle is supported on the surface of the water. The property of surface tension accounts for this unexpected behaviour.

Druppelvorming



interactie Hg-atomen onderling > interactie kwik-glasoppervlak

⇩ ⇩

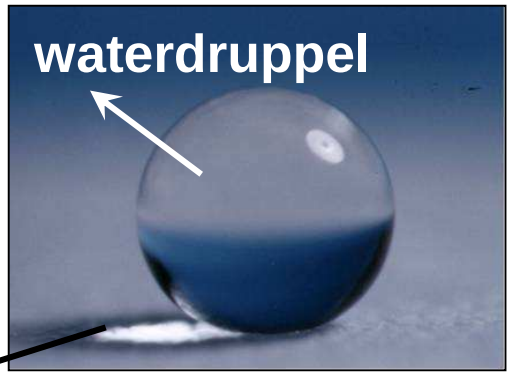
*CO*hesieve interactie *AD*hesieve interactie

Bevochtiging van oppervlakken

sterkere COadhesieve interactie water-water

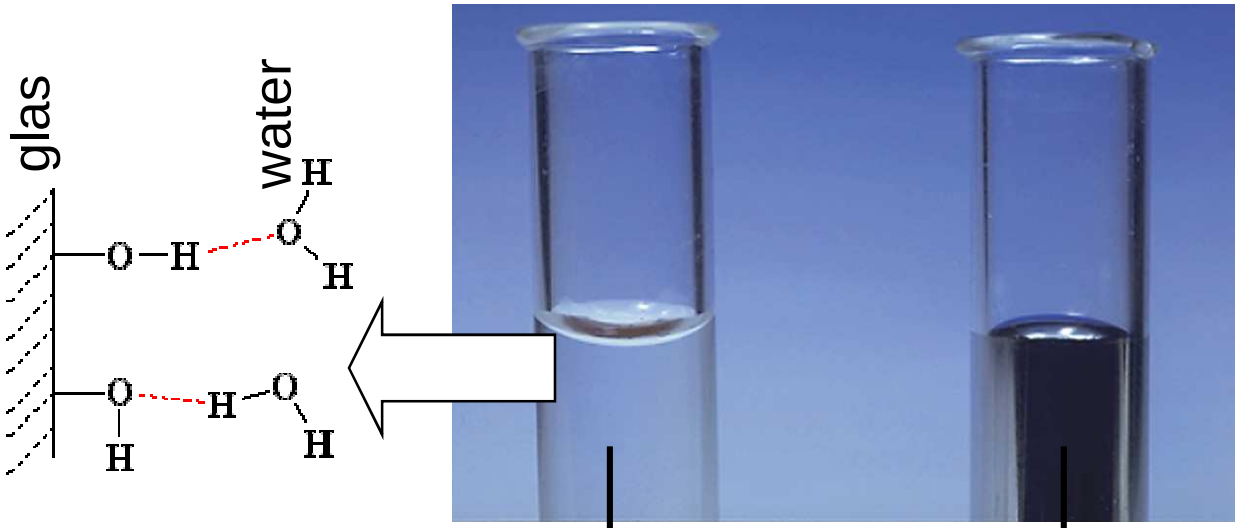
sterkere ADhesieve interactie
water-glasoppervlak

bol = kleinste oppervlak voor gegeven volume



superwaterafstotend oppervlak

Capillaire werking



cohesieve interactie water < adhesieve interactie water-glasoppervlak

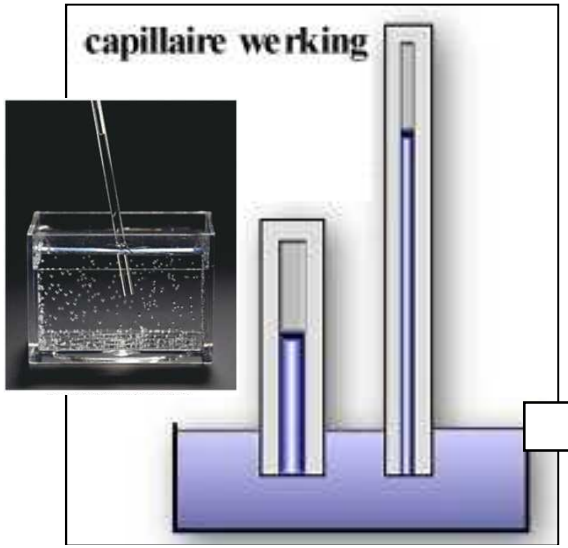
⇩

HOLLE meniscus

cohesieve interactie kwik > adhesieve interactie kwik-glasoppervlak

⇩

BOLLE meniscus

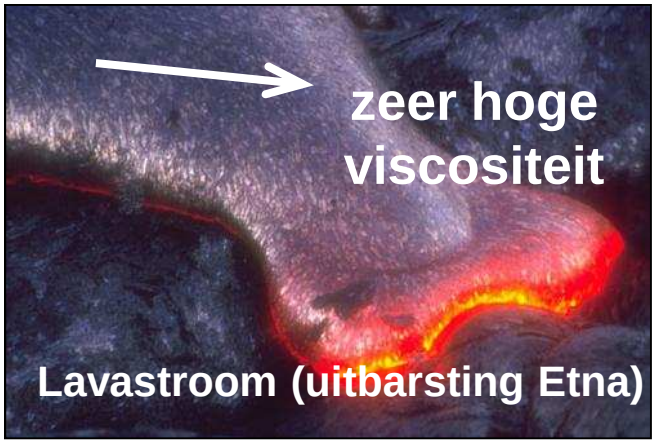


⇨ hoogte vloeistofkolom ↑ als diameter ↓

gewicht/hoogte vloeistof kolom ⇔ adhesieve interactie

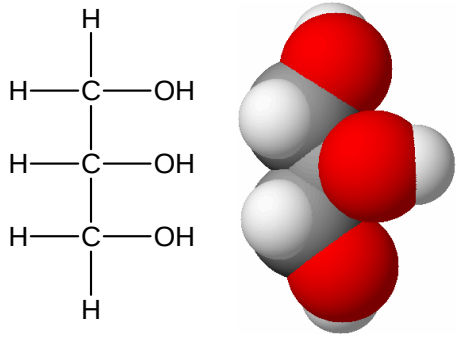
Viscositeit η

viscositeit = maat voor weerstand vloeistof tegen stroming

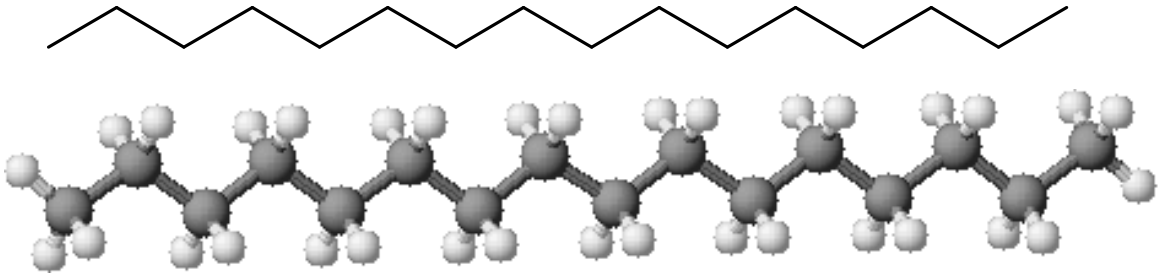


hoge viscositeit:

- verbindingen met sterke intermoleculaire interactie
- lengte/complexiteit verbindingen



glycerol



Ethyl alcohol
(ethanol)
at 20 °C: $\eta = 1.20$ cP

Ethylene glycol
(1,2-ethanediol)
at 20 °C: $\eta = 19.9$ cP

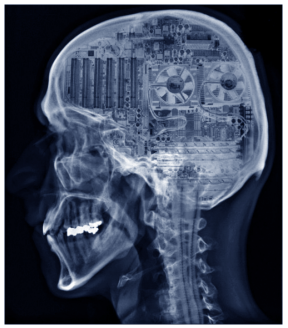
Glycerol
(1,2,3-propanetriol)
at 20 °C: $\eta = 1490$ cP

verbinding	η bij 25℃ (cP)
lucht	18.6×10^{-3}
water	0.89
ethanol	1.07
bloed	3.5
olijfolie	81
ketchup	$50\text{-}100 \times 10^{3}$

cP: centipoise

1 Pa s = 10 Poise = 1000 Centipoise

Examenstof



belangrijke vaardigheden

- bepalen polariteit van een binding/molecule
- bepalen belang van invloedsfactoren op kookpunt in een reeks van moleculen
- intermoleculaire krachten $\Leftrightarrow$ oplosbaarh/opp.spanning/viscositeit