Light, Liquids & Interfaces
Micro-390

Lecture 5

Sylvie Roke

Organizational comments

Upcoming:

Nov. 7 - Week 8: Intermediate Test (ELG 116)
Material: Lecture 1 - 5

Key concepts Lecture 4

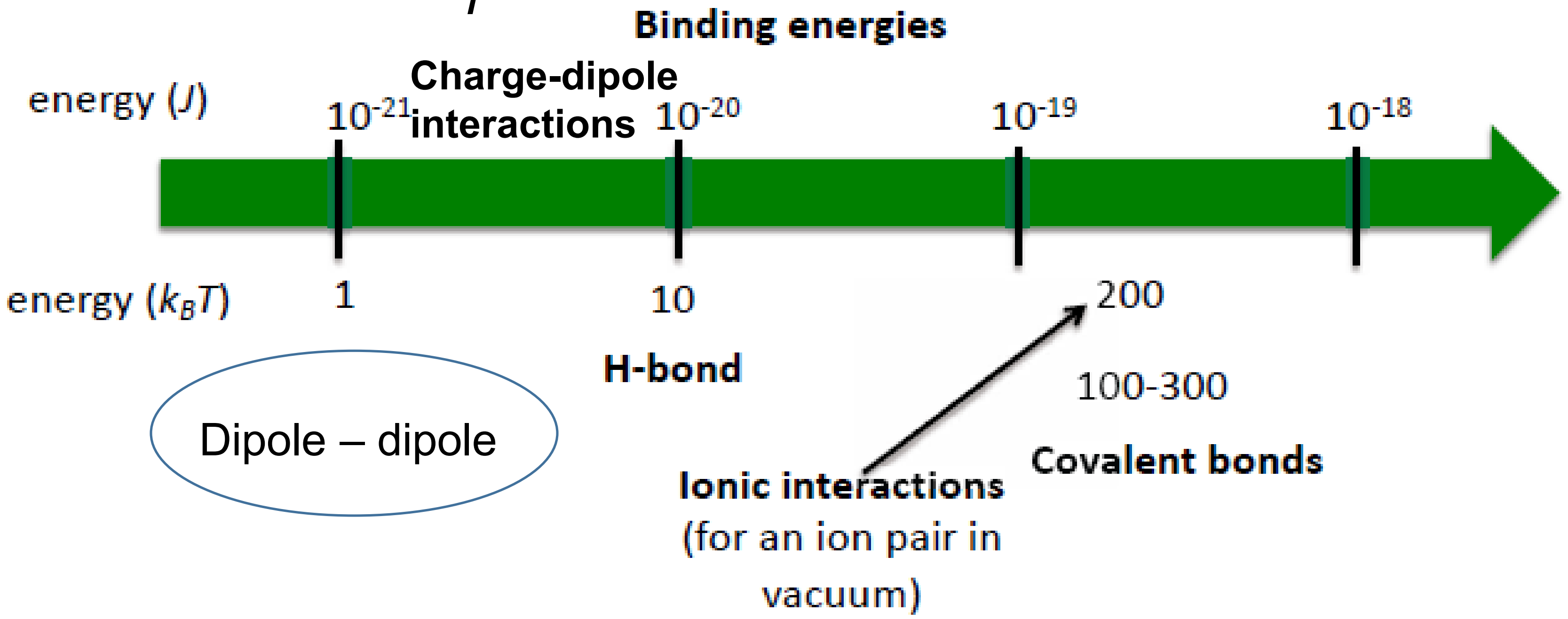
- Ions interact in liquids through screened potentials that arise from + and – charges interacting via Boltzmann weighted interactions
- Debye-Hueckel theory describes this interaction in the limit of a weak potential compared to thermal energy
- Impacts surface structure, protein folding, self-assembly

Dipole-charge interactions

- Dipolar self-energy
- Force relevant for charge-dipole interactions
- Properties of charge-dipole interactions
- Hydration shell definition

Interactions in liquids

$$\frac{1}{r^2}$$



Binding energies

Charge-dipole interactions

energy (J)

10^{-21}

10^{-20}

10^{-19}

10^{-18}

energy (k_BT)

1

10

200

Dipole – dipole

H-bond

100-300

Covalent bonds

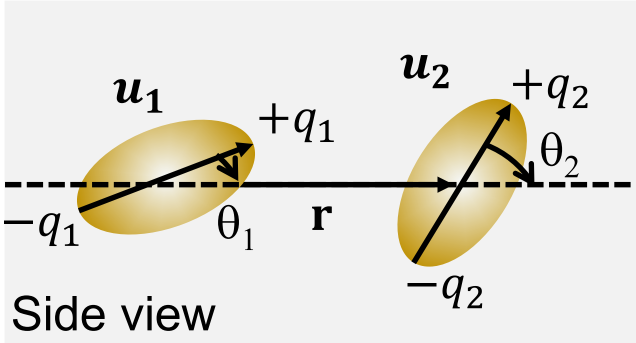
Ionic interactions (for an ion pair in vacuum)

$$\frac{1}{r}$$

Slide: E. Amstad; Soft Matter

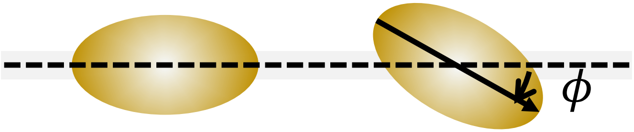
Dipole-Dipole interactions

Are important to understand liquid-liquid and dipolar solute-solvent interactions



ϕ: out of plane tilt

Top view



Properties:

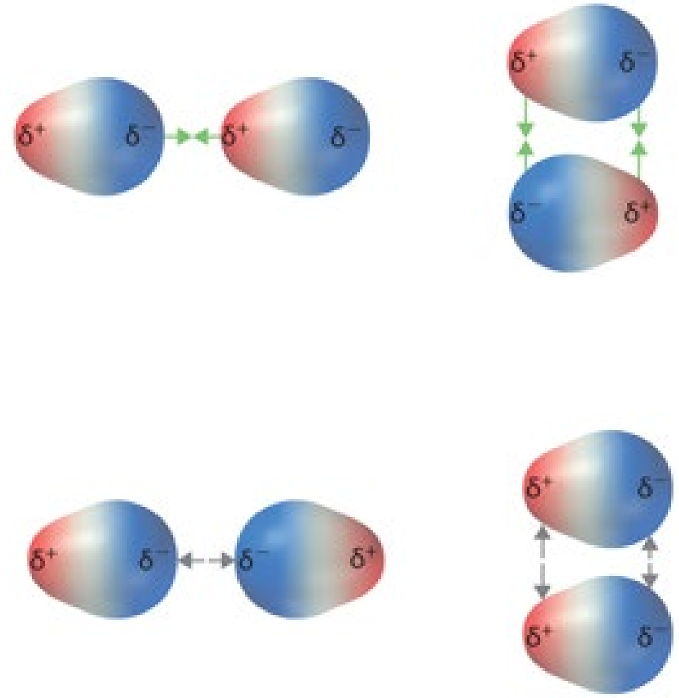
- Depend on orientation of dipoles
- Intermediate range ($w \sim 1/r^3$)
- Strength: ~ kT

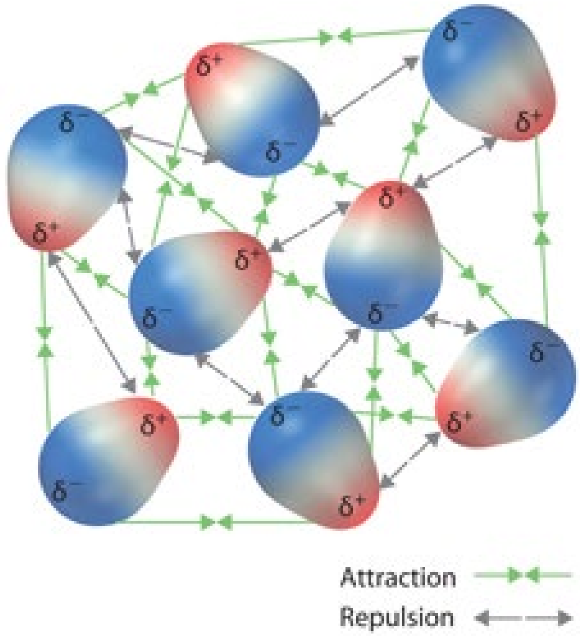
$$w(r,\theta_1,\theta_2,\phi) = -\frac{u_1 u_2}{4\pi\varepsilon_0\varepsilon r^3}[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]$$

Dipole-Dipole interactions

$$w(r,\theta_1,\theta_2,\phi) = -\frac{u_1 u_2}{4\pi\varepsilon_0\varepsilon r^3}[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]$$

This can be attractive or repulsive depending on the orientation



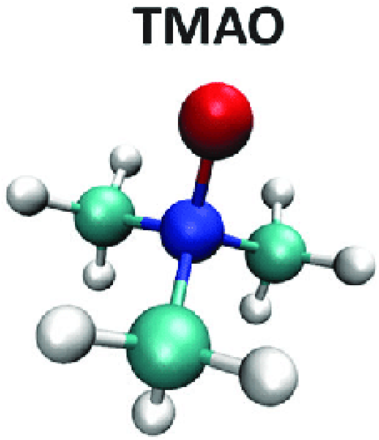


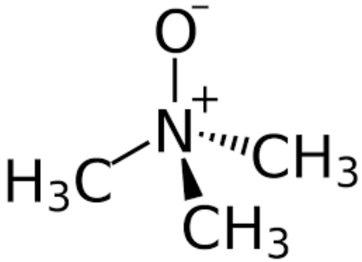
Dipole-Dipole interactions

Some examples of small dipolar molecules with a biological function:

TMAO – 5.4 D (9.3 D in water)

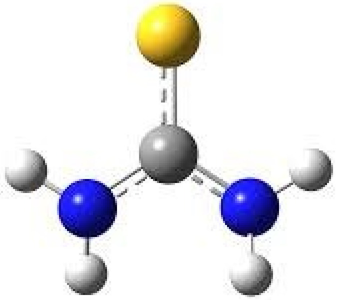
- Osmolyte – preserves osmotic pressure in marine animals
- Stabilizes proteins
- Humans: associated with cardiovascular disease an kidney malfunction

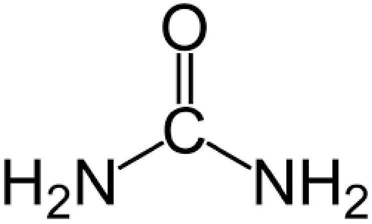




Urea – 4.6 D

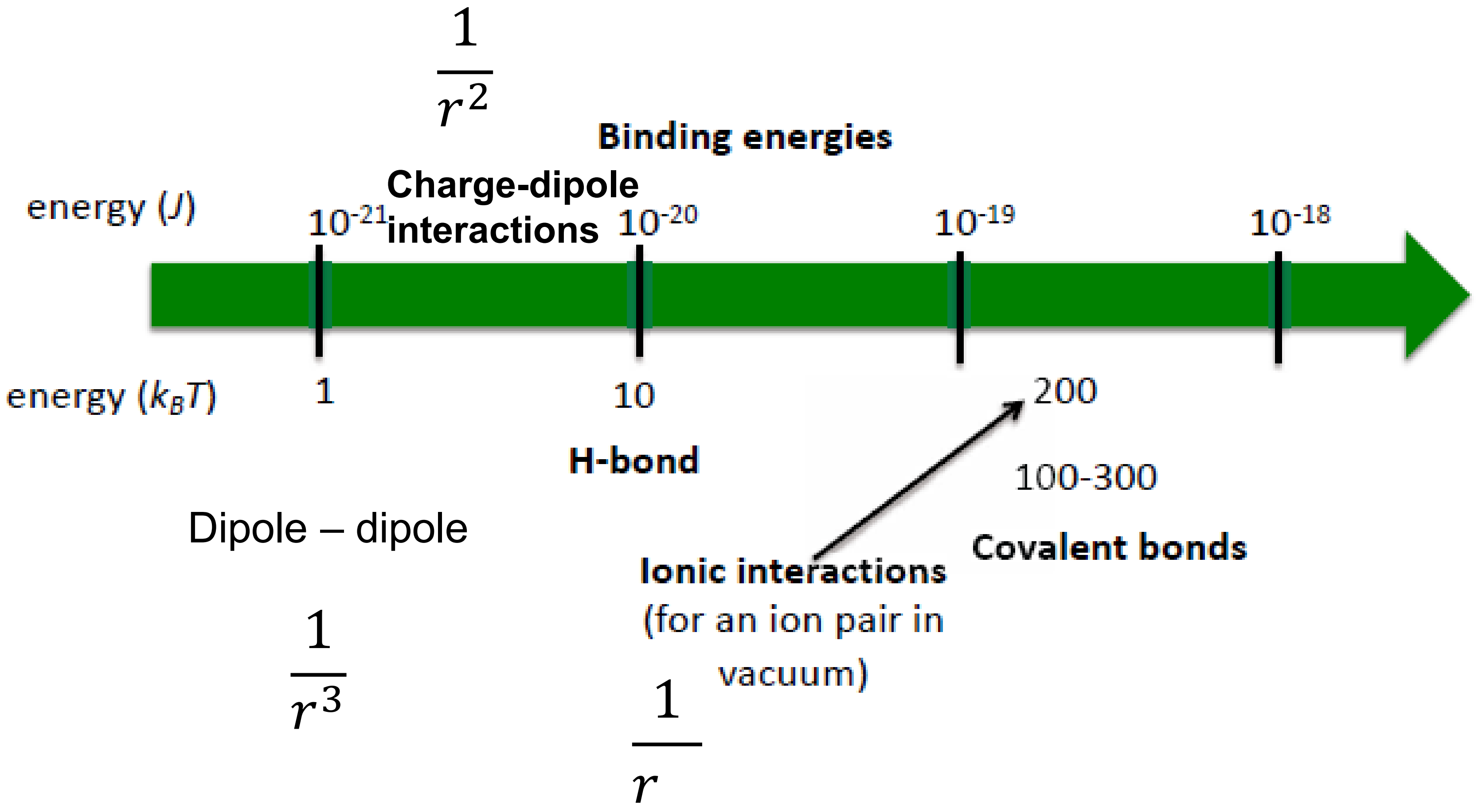
- Fertilizer
- Nitrogen metabolism
- Destabilizes proteins





Examine the orientation dependence of the pair potential of 2 dipoles

Specific interactions in liquids



$$\frac{1}{r^2}$$

Binding energies

Charge-dipole interactions

energy (J)

10^{-21} 10^{-20} 10^{-19} 10^{-18}

energy (k_BT)

1 10 200

H-bond

100-300

Dipole – dipole

Covalent bonds

Ionic interactions (for an ion pair in vacuum)

$$\frac{1}{r^3}$$

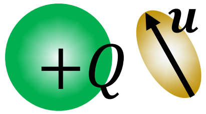
$$\frac{1}{r}$$

But the interactions depend on orientation – this means we will have to consider how rotation changes the pair potential and what it will be on average.

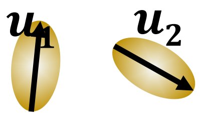
Slide: E. Amstad; Soft Matter

Angle Averaged Potentials

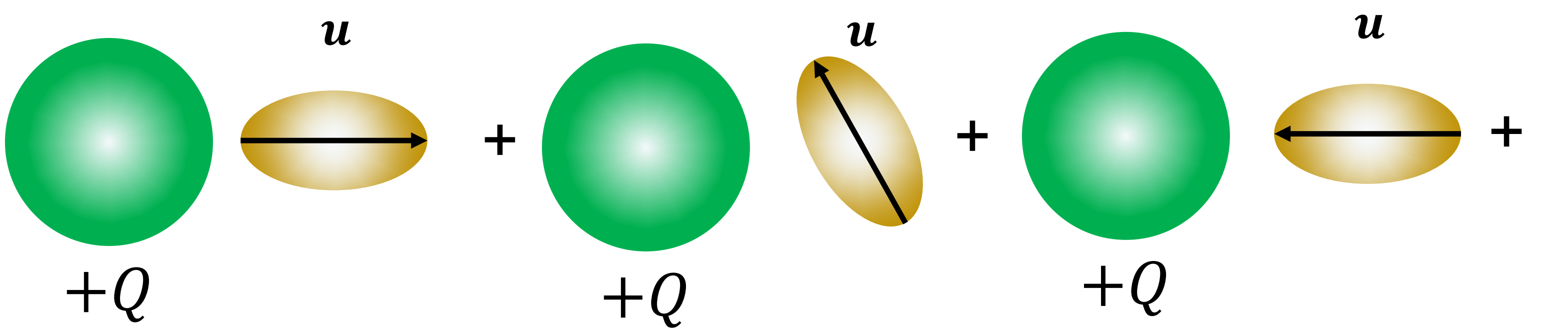
$$w(r) = -\frac{Qu\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}$$



$$w(r,\theta_1,\theta_2,\phi) = -\frac{u_1u_2}{4\pi\varepsilon_0\varepsilon r^3}[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]$$



When the dipoles are free to move in solution they will experience different orientations and thus different interaction potentials. Although cos and sin θ are 0 when averaged over all angles, w(r) is not because the Boltzmann distribution determines how often a certain orientation occurs:



All possible orientations

More favorable: larger weighing factor

Less favorable: smaller weighing factor

Angle-Averaged Potentials

To describe the angle averaged pair potential we need to use the potential distribution theorem that connects the angle averaged potential energy $w(r)$ to the potential at an instantaneous orientation dependent position $w(r, \Omega)$

$$e^{-w(r)/kT} = \int e^{-w(r,\Omega)/kT} d\Omega \Big/ \int d\Omega = \left\langle e^{-w(r,\Omega)/kT} \right\rangle_{\Omega}$$

$\Omega = [\theta, \phi]$

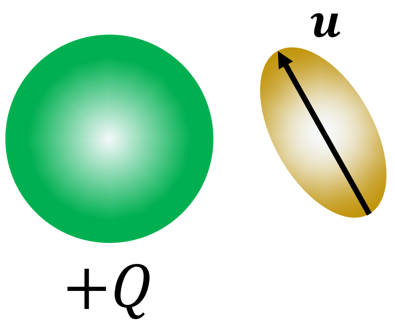
$d\Omega = \sin\theta \, d\theta d\phi$

Limit $w(r) < kT$ i.e. outside hydration shell

Apply this expression – how does it modify the interaction?

Angle-Averaged Potentials

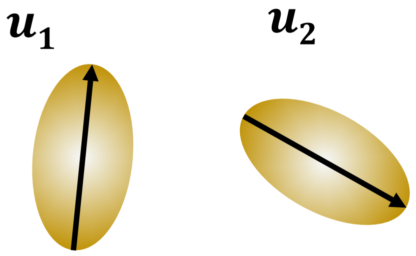
$$w(r) \approx -\frac{Q^2 u^2}{6(4\pi\varepsilon_0\varepsilon)^2 kTr^4} \quad \text{for} \quad kT > \frac{Qu}{4\pi\varepsilon_0\varepsilon r^2}$$



Properties:

- Temperature dependent
- Short range ($w \sim 1/r^4$)
- Strength w < kT;

$$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_0\varepsilon)^2 kTr^6} \quad \text{for} \quad kT > \frac{u_1 u_2}{4\pi\varepsilon_0\varepsilon r^3}$$



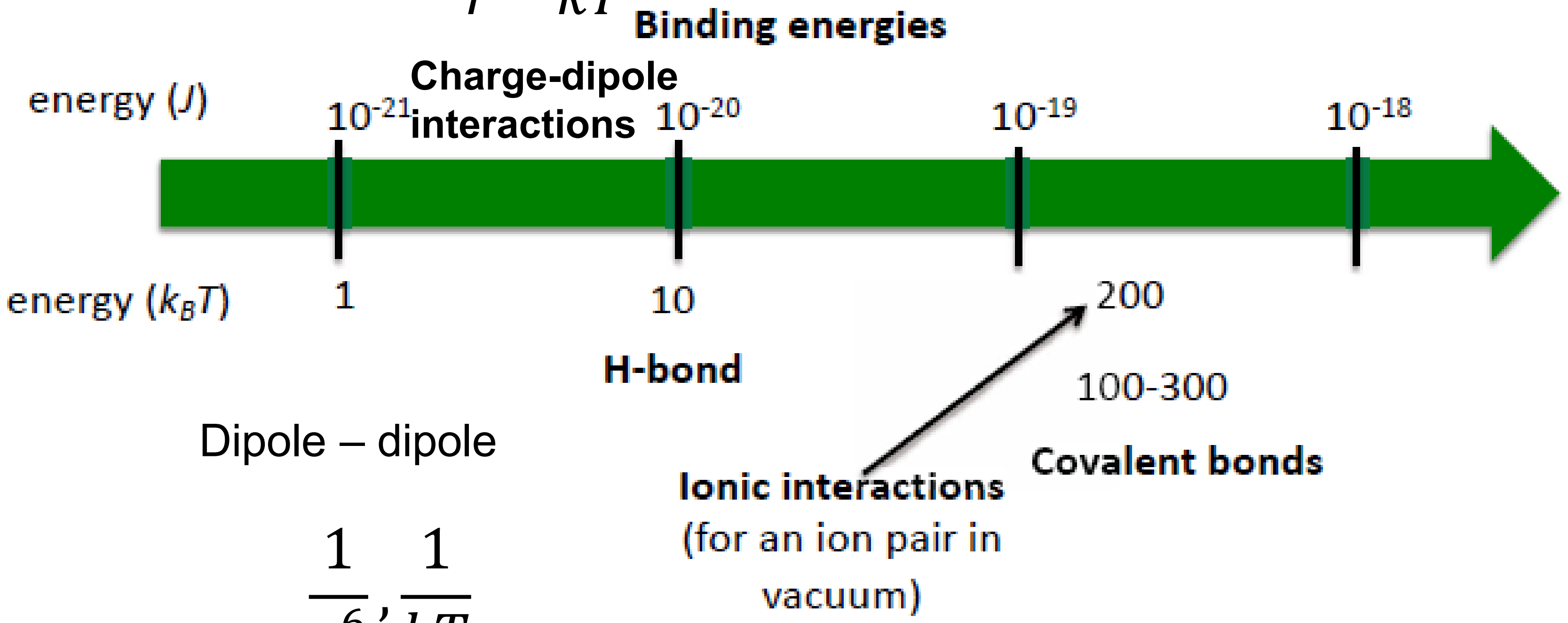
Properties:

- Temperature dependent
- Short range ($w \sim 1/r^6$)
- Strength w < kT;
- =Keesom interaction (1 of 3 VDW interactions)

Interactions in liquids – effect of averaging

$$\frac{1}{r^4}, \frac{1}{kT}$$

Charge-dipole interactions



Binding energies

energy (*J*) 10^{-21} 10^{-20} 10^{-19} 10^{-18}

energy (k_BT) 1 10 200

H-bond

100-300

Covalent bonds

Ionic interactions
(for an ion pair in vacuum)

Dipole – dipole

$$\frac{1}{r^6}, \frac{1}{kT}$$

$$\frac{1}{r}$$

Slide: E. Amstad; Soft Matter

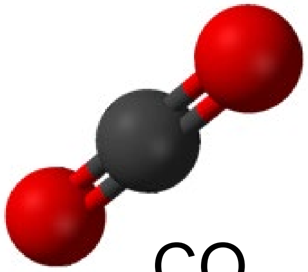
Topic 2: Interactions in liquids

Non-polar molecules
Interactions involving non-polar molecules
Polarizability (molecular & macroscopic)
Van der Waals interactions

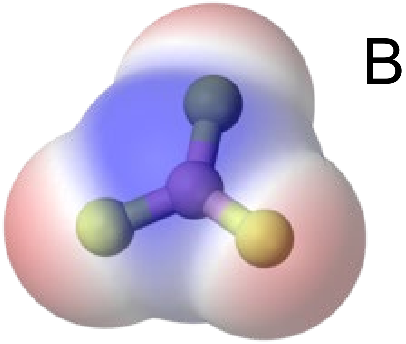
Material to study:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 5: paragraph: 5.1,5.2, 5.3-5.4, 5.6
Chapter 6: paragraph: 6.1
Chapter 7: paragraph: 7.1-7.3

Non-polar molecules

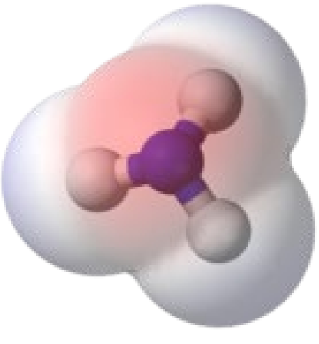
Non-polar molecules are single atom substances (He, Ne , Ar,…), or have bonds with equal charge distributions (O_2,N_2) or there is a symmetric arrangement of polar bonds.



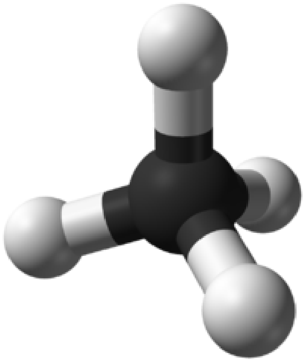
CO_2



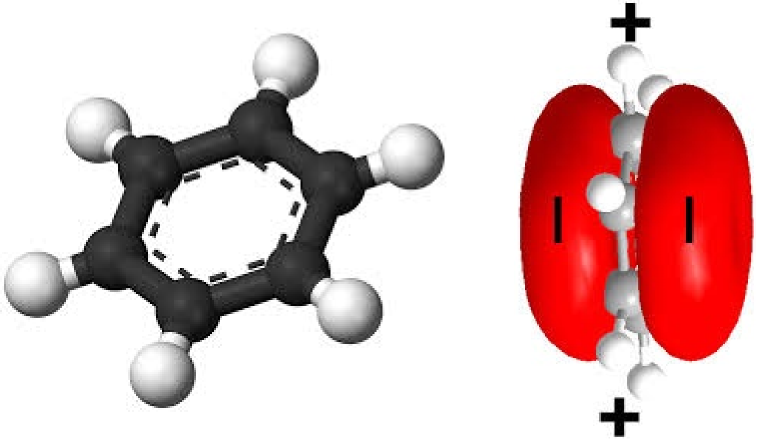
BF_3



NH_3



CH_4



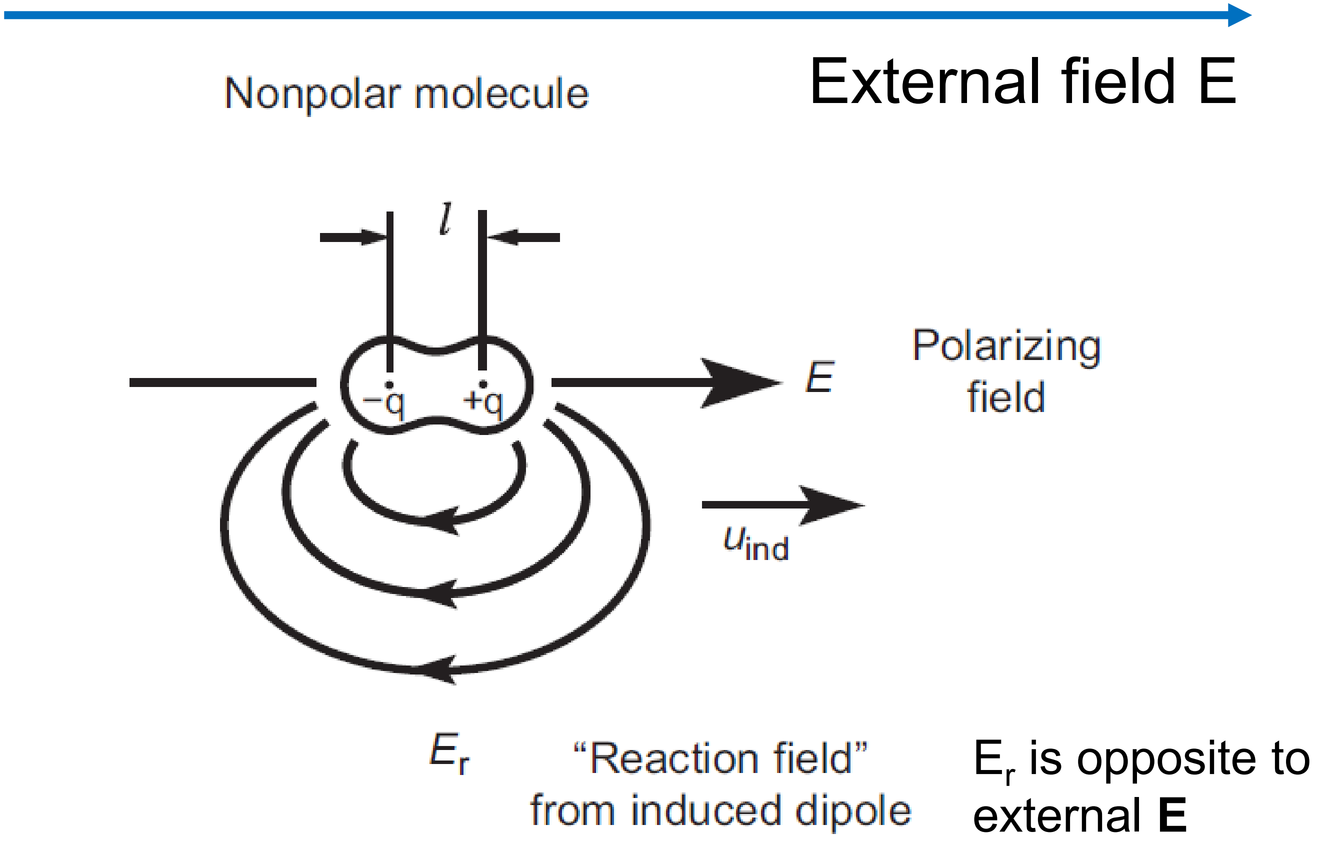
C_6H_6

(which one is not non-polar?)

What is the effect of an electrostatic field (external, or e.g. from an ion or a dipole) on a non-polar molecule?

E-field can induce a dipole

An electrostatic field can interact with the charge distribution in a non-polar molecule and create charge separation



External field E

E_r is opposite to external **E**

This is a source of **polarization**: The ability of a molecule or material to counteract the effect of an external electrostatic field

Molecular electronic polarizability

Molecular polarizability is the quantity that connects the external field and the induced dipole:

$$u_{ind,i} = \underset{\substack{\downarrow \\ \text{molecular polarizability}}}{\alpha_{ij}} E_j$$

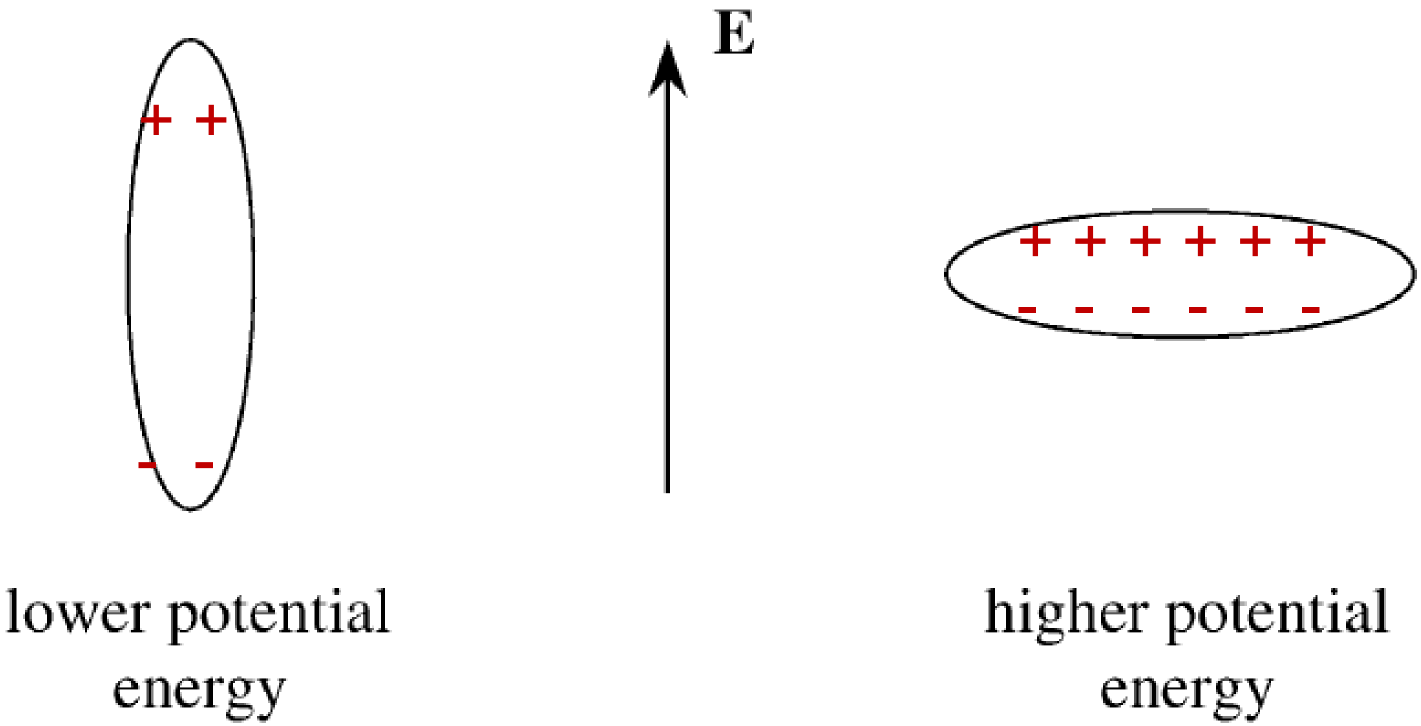
Electronic polarizability: redistribution of charge within a molecule (determined by symmetry of orbitals)

Bond polarizabilities within a molecule are additive

Are there other contributions to the polarizability of a molecule that arise from an electrostatic field interacting with dipolar or non-polar non-spherical molecules?

Non spherical non-polar molecules

The potential energy of a non spherical non-polar molecule depends on its orientation:

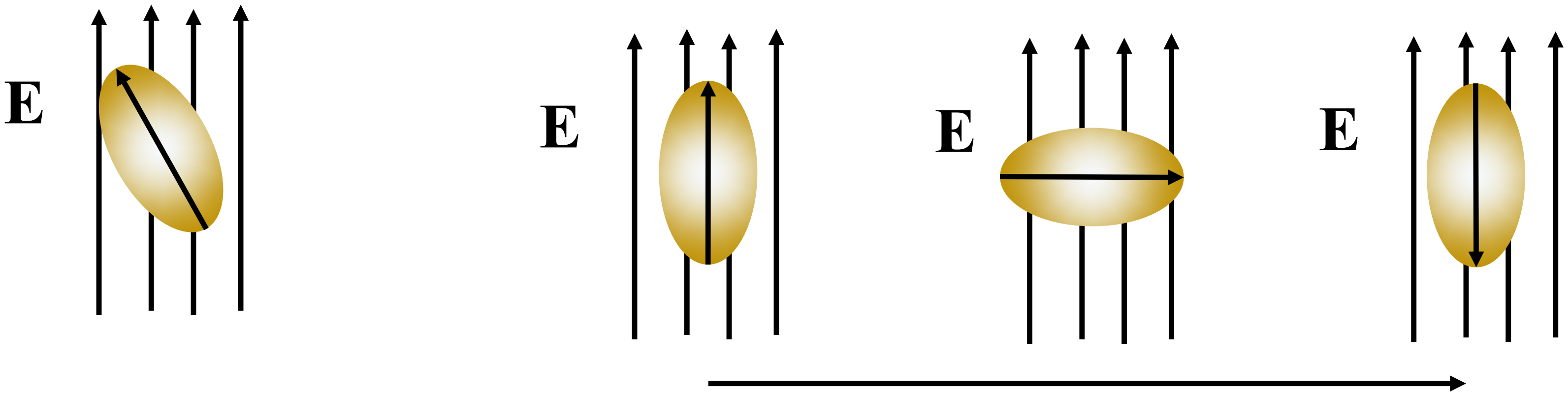


For these molecules α has multiple values determined by the polarizability tensor α_{ij}

E-field can orient permanent dipoles

The field on the outer radius of a Na$^+$ is: 1.4×10^{11} V/m

E field orients dipoles:



Higher potential energy

This type of polarization occurs in molecules that have a permanent internal charge separation

Molecular polarizability

Molecular polarizability is the quantity that connects the external field and the (induced) dipole:

$$u_{ind,i} = \alpha_{ij}E_j$$

molecular polarizability

$$\alpha_{ij}=\alpha_{0,ij} + \frac{u_{ij}^2}{3kT}$$

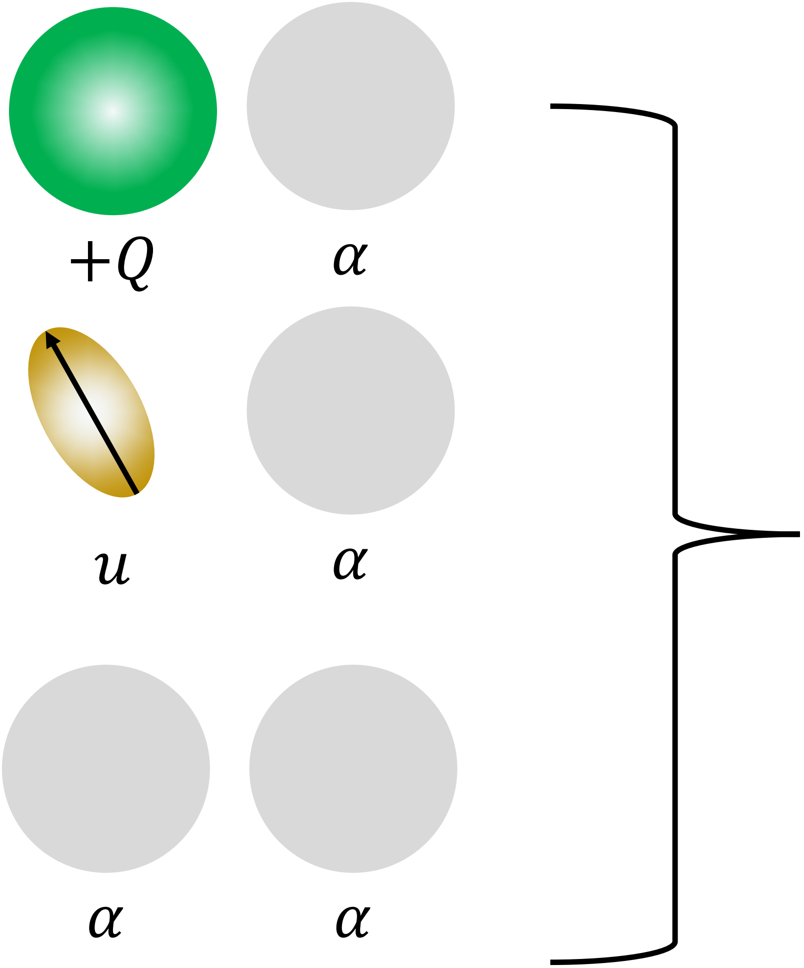
Electronic polarizability: redistribution of charge within a molecule (determined by symmetry of orbitals – all molecules)

Orientational polarizability:
Ability to orient along direction of external field (for dipolar molecules)

Bond polarizabilities are additive

Interactions of non-polar molecules

Each moiety that emits an electrostatic field can induce a polarization.

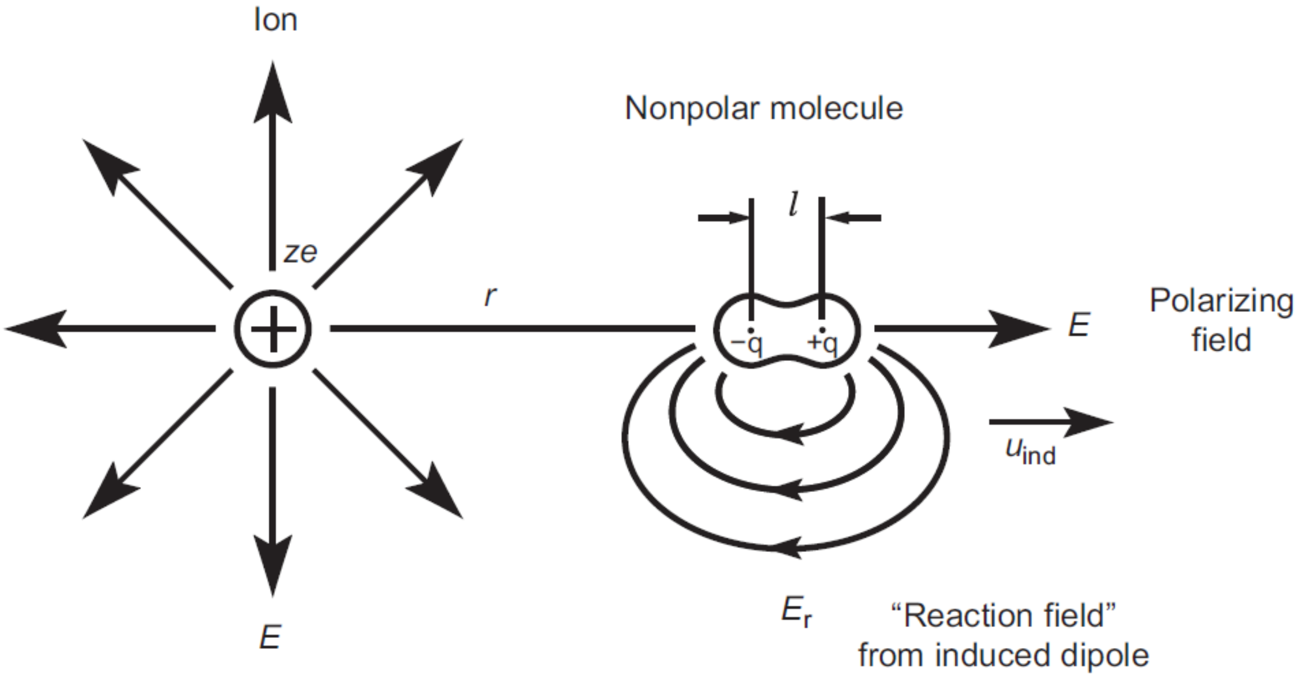


All determined by induction of charge separation in the non-polar molecule by the (temporary) E field of the charge distribution

Let’s consider them in detail…

Charge – non-polar interactions

An electrostatic field from **a charge** can interact with the charges in a non-polar molecule and create charge separation



For induced dipole moment:

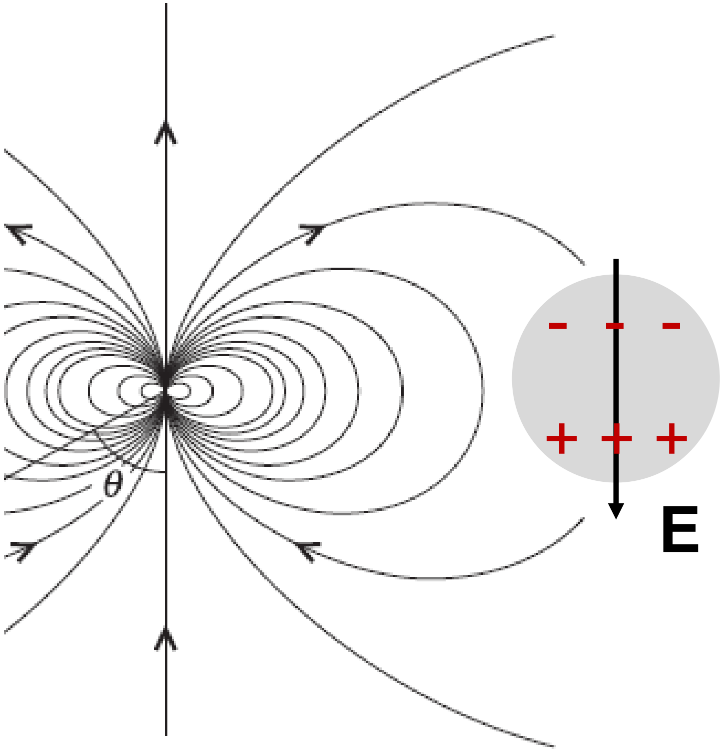
$$w(r) = -\frac{1}{2}\alpha E(r)_Q^2$$

Reminder for permanent dipole moment:

$$w(r) = -uE(r)_Q = \alpha E(r)_Q^2$$

Dipole – non-polar interactions

An electrostatic field from **a dipole** can interact with the charges in a non-polar molecule and create charge separation



$$w(r) = -\frac{1}{2}\alpha E(r)_D^2$$

$$w(r) = -\frac{u^2\alpha_0}{(4\pi\varepsilon_0\varepsilon)^2 r^6}$$

This interaction has 2 different names:
Induction interaction
Debye interaction

Non-polar – Non-polar interactions

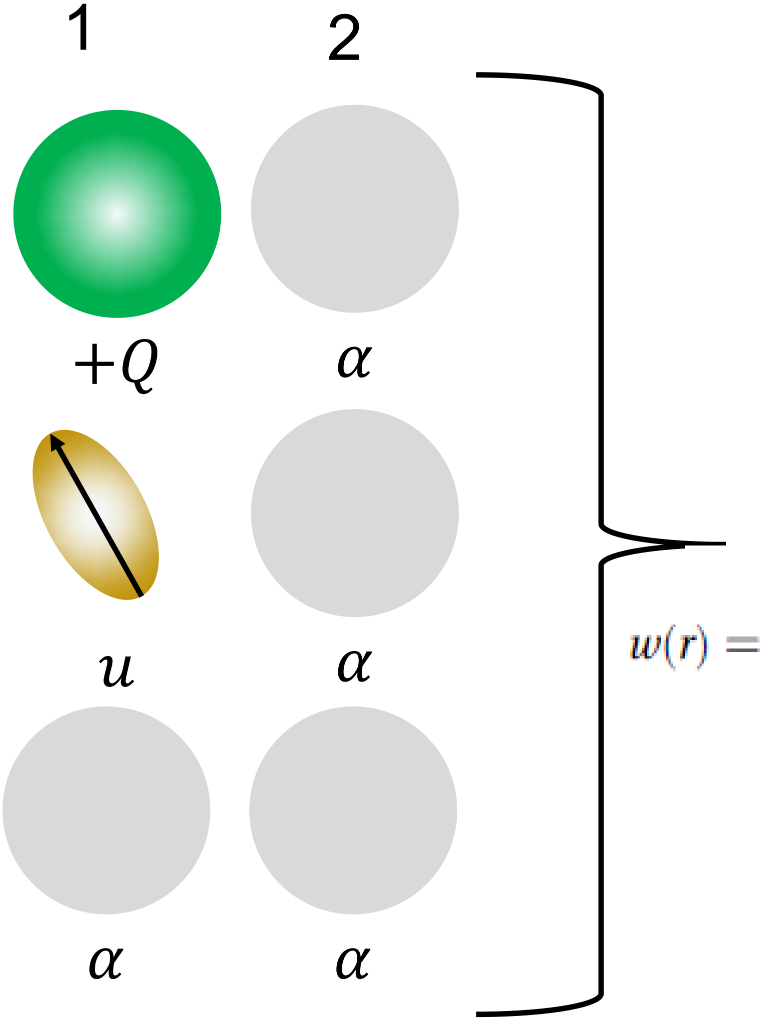
Non-polar molecules have **fluctuating charge distributions**, due to the probabilistic nature of the wave functions. These fluctuating charge distributions induce fluctuating charge distributions in other non-polar molecules. These are dispersive (frequency dependent) interactions

$$w(r) \sim -\frac{\alpha_0 \nu}{r^6}$$

Properties:
Quantum mechanical in nature
Not additive
Every molecule contributes
Size & structure determines the strength of the interaction
Magnitude: < kT

Name of interaction:
Dispersive interactions

Interactions of non-polar molecules



Combined expression that takes into account all interactions:

$$w(r) = -\left[\frac{Q_1^2}{2r^4} + \frac{3kT}{r^6}\left(\frac{u_1^2}{3kT} + \alpha_{01}\right)\right]\left(\frac{u_2^2}{3kT} + \alpha_{02}\right)\Big/(4\pi\varepsilon_0\varepsilon)^2,$$

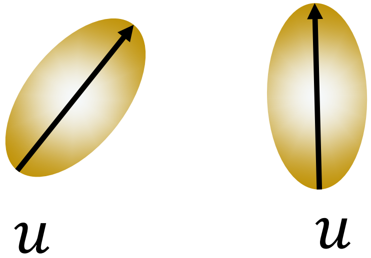
Note that 1 and 2 each refer to a single molecule or group within a molecule

We often encounter the term
‘van der Waals interactions’

What is this ?

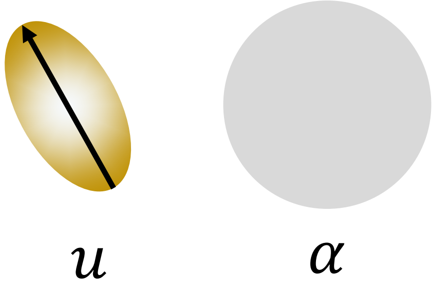
Combining term: Van der Waals interactions

Van der Waals interactions = a grouping of 3 types of attractive interactions that have a **$1/r^6$ dependence**



$$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_0\varepsilon)^2 kTr^6}$$

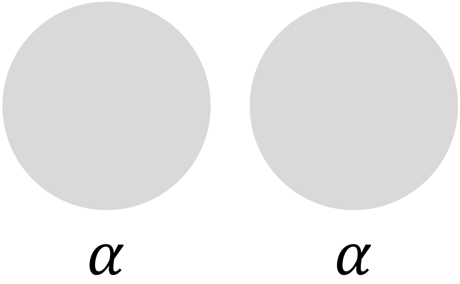
Keesom interaction



$$w(r) = -\frac{u^2\alpha_0}{(4\pi\varepsilon_0\varepsilon)^2 r^6}$$

Induction interaction

Debye interaction



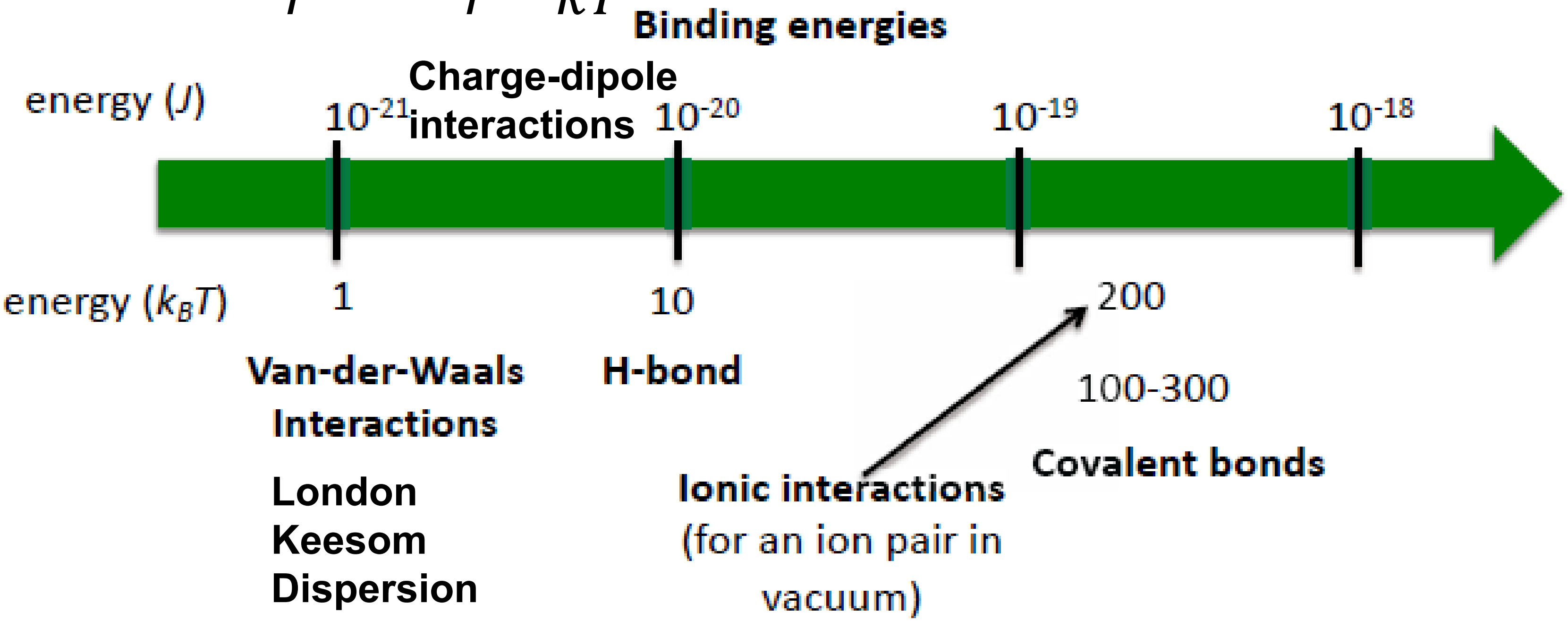
$$w(r) \sim -\frac{\alpha_0 \nu}{r^6}$$

Dispersive interaction

London interaction

Interactions in liquids

$\frac{1}{r^2}$ or $\frac{1}{r^4}, \frac{1}{kT}$



Binding energies

Charge-dipole interactions

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energy (k_BT) 1 10 200

Van-der-Waals Interactions

London
Keesom
Dispersion

H-bond

Ionic interactions
(for an ion pair in vacuum)

100-300

Covalent bonds

$\frac{1}{r^3}$ or $\frac{1}{r^6}, \frac{1}{kT}$

$\frac{1}{r}$

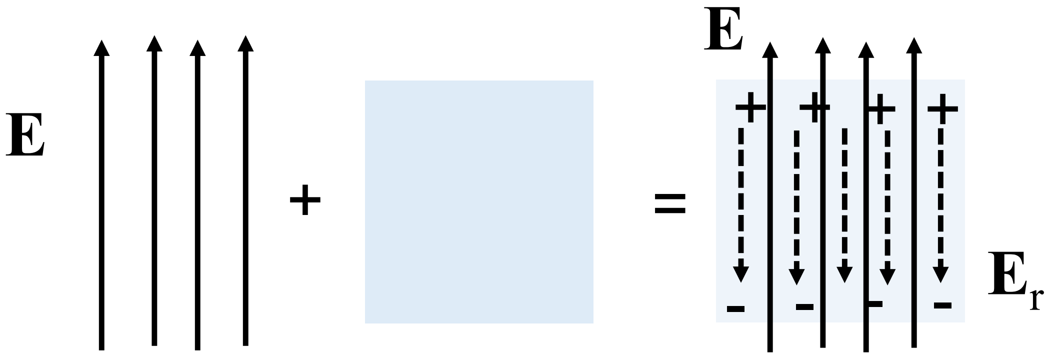
Slide: E. Amstad; Soft Matter

Lets now examine again the effects of fields in a macroscopic medium: this is the combined effect of all interactions

Fields in a medium

Macroscopic polarizability is the ability of a medium to respond to and reduce the magnitude of an external electromagnetic field (**E**).

Interaction of electric field (**E**) with medium:



Medium consist of charged electrons and nuclei which will be displaced by external **E** field

E field distorts atoms & molecules: separates / <u>displace</u>s charges & induce dipoles & orients them; it also changes the free charge distribution (if present)

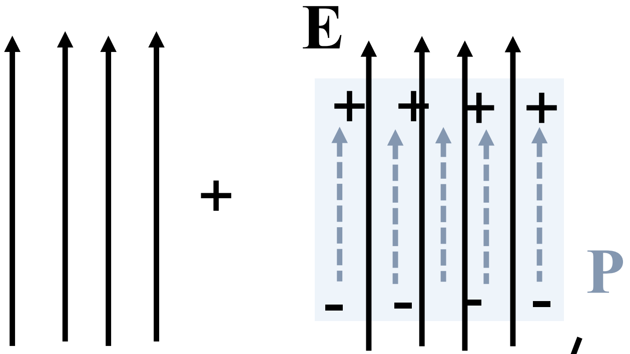
These charge displacements create a response field ($\mathbf{E}_r$)

These two field <u>interfere & reduce:</u> $\mathbf{E}_{\mathrm{eff}}=\mathbf{E}+\mathbf{E}_r$

Macroscopic Polarizability (**P**)

Polarizability (**P**) is the field that is present in the medium

Displacement field (**D**) in a medium =



D= ε_0**E** + **P**

Displacement field in vacuum

Polarization

D is a field, but it is *not* an electric field. Unit: [C/m^2]. It is a ‘density of dipoles’ [(Cm)/m^3] created by the action of the external field

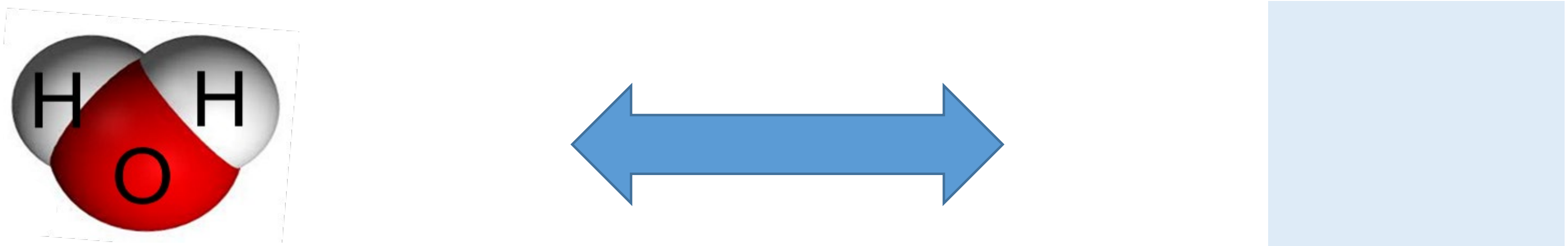
P = $\varepsilon_0\ \chi^{(1)}$**E** is macroscopic material contribution to **D** in medium:

$\varepsilon = 1 + \chi^{(1)}$, ε is the dielectric permittivity, frequency dependent

$n^2 = 1 + \chi^{(1)}$, n is the refractive index

Linear susceptibility

Molecular vs Macroscopic polarization



Molecular polarization:
u or **p*** [Cm] (permanent dipole)

Molecular induced dipole:
$\mathbf{u}_{\mathrm{ind}}$ or $\mathbf{p}_{\mathrm{ind}}$

*u: used by Israelachvilli;
p: used for optics/spectroscopy

Macroscopic polarization **P**

$$\boldsymbol{P} = \sum_{all\ molecules} \boldsymbol{p}_i = N\langle \boldsymbol{p} \rangle$$

Number of molecules per unit volume contributing to the polarization

Material response:

$$\chi^{(1)} = \frac{N}{\varepsilon_0}\langle \alpha \rangle_{orientations}$$

Molecular polarization can be induced by:
1 - Separating charge within (or outside) a molecule (with or without a charge or dipole). This is electronically induced polarization.
2 – Rotating dipoles. This is dipolar induced polarization.

Key concepts Lecture 5

- Dipole-dipole interaction and its properties
- Angle-averaged potentials:

  When dipoles are free to move in solution, they will experience different orientations and thus different interaction potentials.

  Boltzmann weighting factor can give more weight to a specific orientation.

  Angle-average pair potentials are T-dependent

- Interactions of non-polar molecules
- Dipole moments can be induced in non-polar molecules
- Van der Waals forces group 3 forces with $1/r^6$ dependence
- Molecular polarizability vs. macroscopic polarizability