Light, Liquids & Interfaces
Micro-390

Lecture 3

Sylvie Roke

EPFL

Key concepts Lecture 1 and 2

Energy and probability (P)
Boltzmann Distribution (BD)
Average Thermal Energy – importance of kT
Transformations and use of BD – predict likelihood of transformations
Thermodynamics reminder
Free energy = energy available to do work with

Material to study, Lecture 1 and 2
D. Ben-Amotz: Understanding Physical Chemistry:
Chapter 1: page 15 (start at section 1.2) – 50 (halfway section 1.5)

Lecture 3

Topic 1: Probability and thermodynamics
Topic 2: Specific Interactions in liquids

Materials to study, Lecture 3:

JN Israelachvilli: Intermolecular and surface forces:

Chapter 1: 1.6

Chapter 2: paragraphs: 2.1, 2.2, 2.3, 2.4, 2.6, 2.7.

Remainder of topic 1:
Probability and thermodynamics

Energy and probability
Boltzmann Distribution (BD)
Average Thermal Energy
Transformations and use of BD
Thermodynamics reminder
Free energy
Interaction energy & pair potential
Long & short-ranged interactions

Materials to study, Lecture 3:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 1: 1.6
Chapter 2: paragraphs: 2.1, 2.2, 2.3, 2.4, 2.6, 2.7.

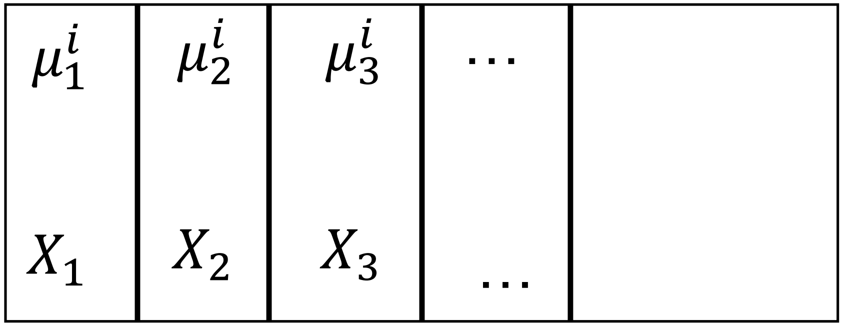
Chemical Equilibrium

The interaction energy can be coupled to the Boltzmann distribution

In a system that has many regions n with different partial concentrations X_n and interaction energies μ_n^i under chemical equilibrium and constant P, T we have:

$$\boxed{\mu_n^i + \mathrm{kT}\ln X_n = \mu}$$

Constant μ in the whole system (distribution of states / molecules such that this condition is achieved)



Chemical Equilibrium

Thermal energy (TS)
S=$k \ln X_n$

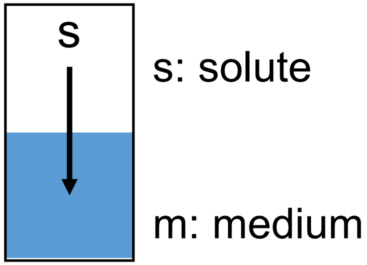
$$\boxed{\mu_n^i + kT \ln X_n = \mu}$$

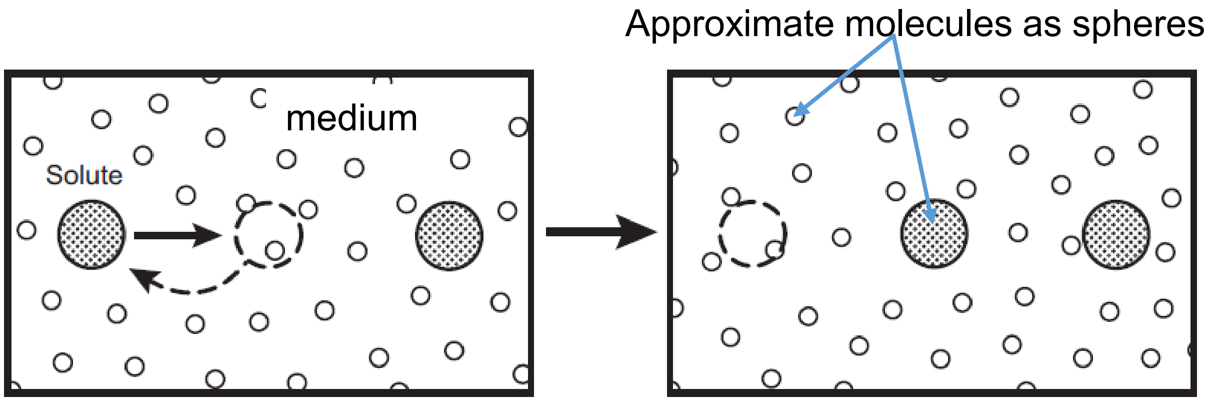
Interaction energy of species n
(determined by the specific interactions we will treat next & related to the pair interaction energy w(r))

Chemical potential
= total average free energy per molecule

Interactions in liquids

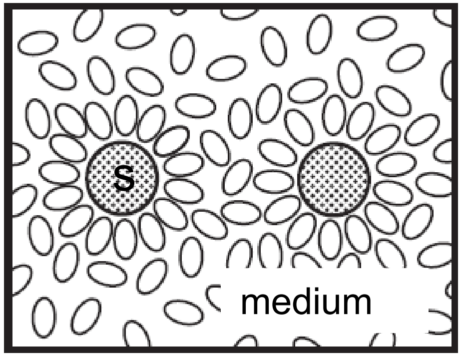
In a liquid every molecule interacts with other molecules, changing partners and having sometimes multiple types of interactions. These many-body interactions are of different nature – some general examples:



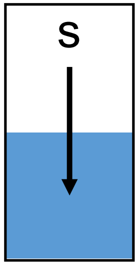


Movement of a solute s requires the displacement of medium molecule m to make place for molecule s (making and breaking interactions between s and m)

Interactions in liquids

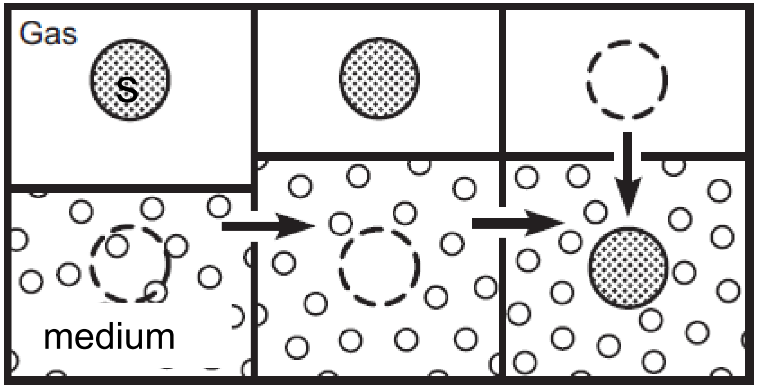


Rearrangement of m by s
But also: m changes properties of s



s: solute

m: medium



Making place for s:
Form a hole (cavity);
move m out of the way
and displace s

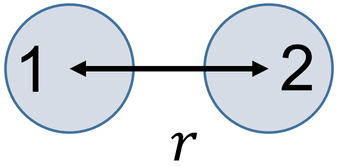
Interactions in liquids

Definitions for the interaction energy of a molecule n in a medium:

$$\mu_n^i = \sum all\ interactions$$

= Interaction energy
or Self energy
or Cohesive energy

The interaction between 2 molecules is given by the <u>pair potential</u> w(r):



$$F(r) = -\frac{dw(r)}{dr}$$

Pair potential [J]

Force of 1 on 2 (& vice versa) [N]

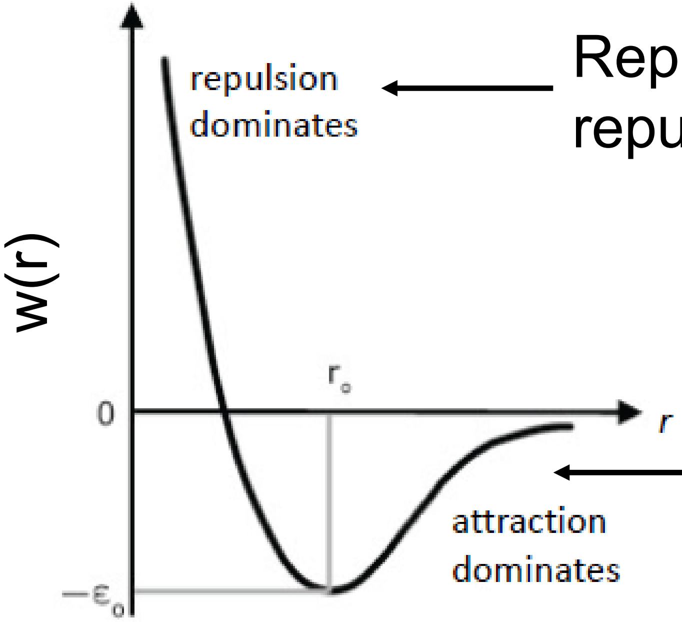
Interactions in liquids

Definitions for the interaction energy of a molecule n in a medium:

$$\mu_n^i = \sum all\ interactions$$

= Interaction energy
or Self energy
or Cohesive energy

The interaction between 2 molecules is given by the pair potential w(r):
=The average interaction of one molecule with another.



Repulsion between electron clouds (Pauli repulsion) – for all molecules

Attractive & more weakly repulsive interactions vary and depend on structure & charge distribution

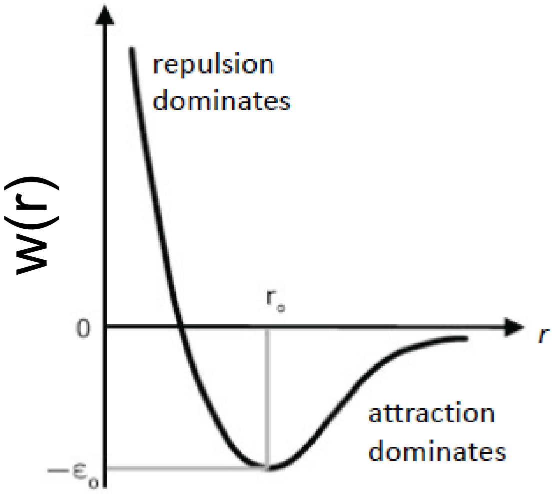
Interactions in liquids

Definitions for the interaction energy of a molecule n in a medium:

$$\mu_n^i = \sum all\ interactions$$

= Interaction energy
or Self energy
or Cohesive energy

The interaction between 2 molecules is given by the pair potential w(r):

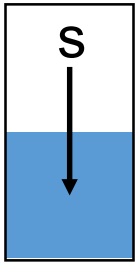


Thermal energy = kT
= ~ energy available to do work with.

If $|w(r_0)| < kT$, the thermal energy is strong enough to break the pair-wise interaction
If $|w(r_0)| > kT$, the thermal energy cannot overcome the pair-wise potential barrier

Interactions in liquids

How are the interaction energy (μ_n^i) and pair potential ($w(r)$) in a liquid related?



s: solute

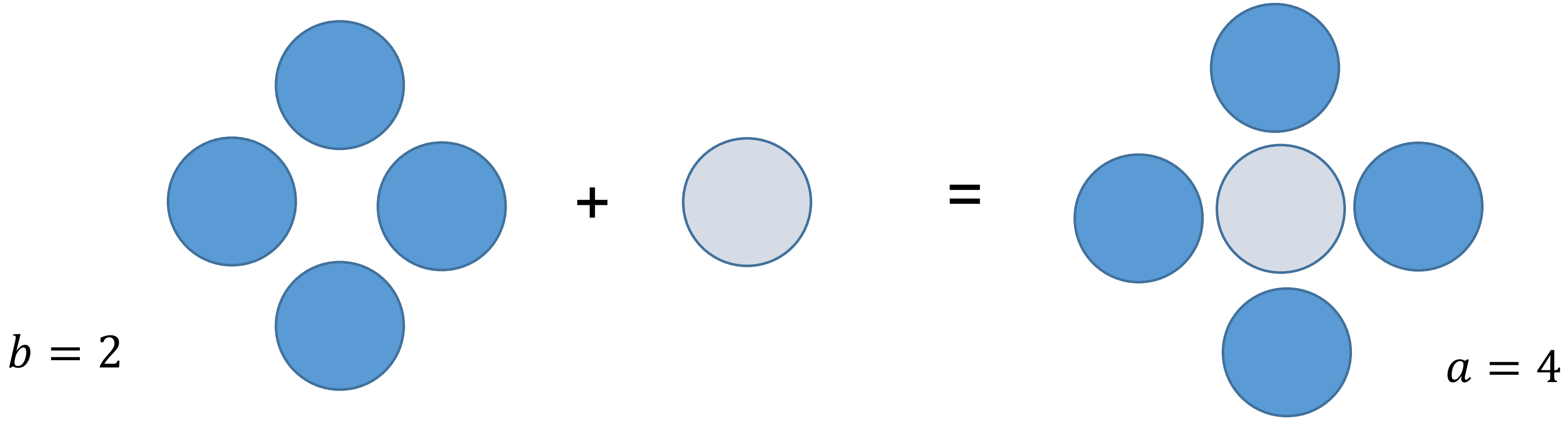
m: medium

$$\mu_n^i = a\, w_{ms} - b\, w_{mm}$$

Pair interactions that are formed between s and m

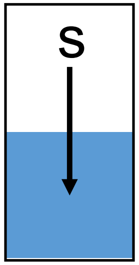
Pair interactions that are broken between m and m

Example of breaking and forming bonds:



Interactions in liquids

How are the interaction energy (μ_n^i) and pair potential (w) in a liquid related?



s: solute

m: medium

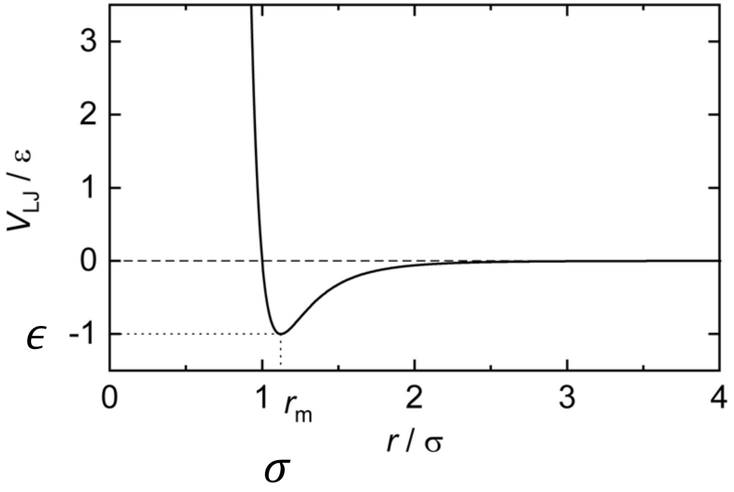
$$\mu_n^i = a\, w_{ms} - b\, w_{mm}$$

Pair interactions that are formed between s and m

Pair interactions that are broken between m and m

For a hard sphere (Lennard-Jones) liquid this is: $\mu_n^i = 12 w_{ms} - 6 w_{mm}$

$$w(r) = 4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right\}$$



One more general thing:
What is the length scale of interactions?

This depends on the functional form of the pair potential

Topic 1: Probability and thermodynamics

Energy and probability
Boltzmann Distribution (BD)
Average Thermal Energy
Transformations and use of BD
Thermodynamics reminder
Free energy
Interaction energy & pair potential
Long & short ranged interactions

Material to study for Topic 1
D. Ben-Amotz: Understanding Physical Chemistry:
Chapter 1: page 15 (start at section 1.2) – 50 (halfway section 1.5); if this is new for you
Chapter 2: paragraphs: 2.1, 2.2, 2.3, 2.4, 2.6, 2.7.

Topic 2: Driving forces and interactions in liquids

Overview
Covalent interactions
Interactions involving charges
Interactions involving polar molecules
Interactions involving non-polar groups

Material to study for Topic 2: Chapters 3-6:
JN Israelachvili: Intermolecular and surface forces:
Notes & Chapter 3: paragraphs: 3.1 – 3.8
Notes & Chapter 4: paragraphs: 4.1 – 4.7; 4.9-4.11
Notes & Chapter 5: paragraphs: 5.1 - 5.4; 5.6;
Notes & Chapter 6: paragraph: 6.1;

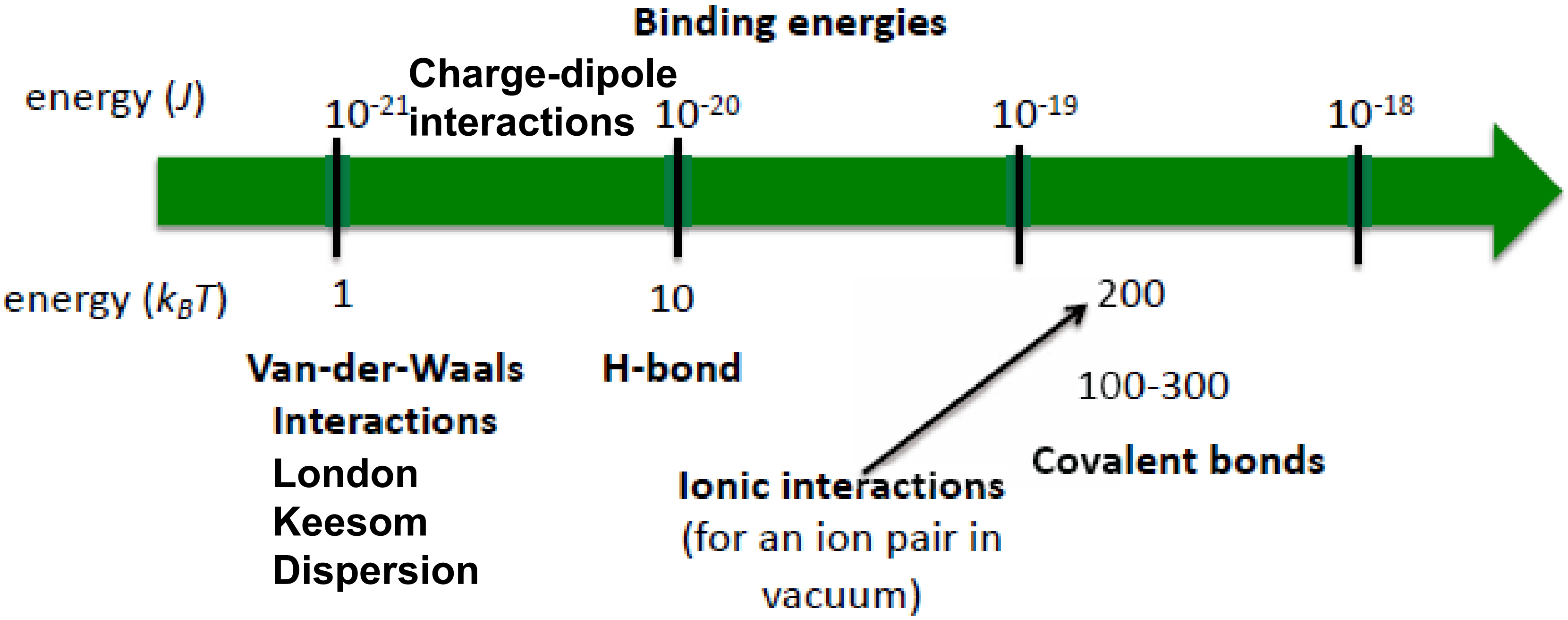
Topic 2: Driving forces and interactions in liquids

Lecture 3:

Overview
Covalent interactions
Interactions involving charges:
Ion-ion interactions in crystals
Ion-ion interactions in liquids – Debye-Hückel theory

Material to study for Lecture 3:
JN Israelachvilli: Intermolecular and surface forces:
Chapter 3.1 – 3.8

Specific interactions in liquids



These interactions are considered as pair potentials (w(r)) to understand the interplay of many body interactions – they are all of importance for understanding liquids

Slide: E. Amstad; Soft Matter

L 3

L 4

L 5

L 6

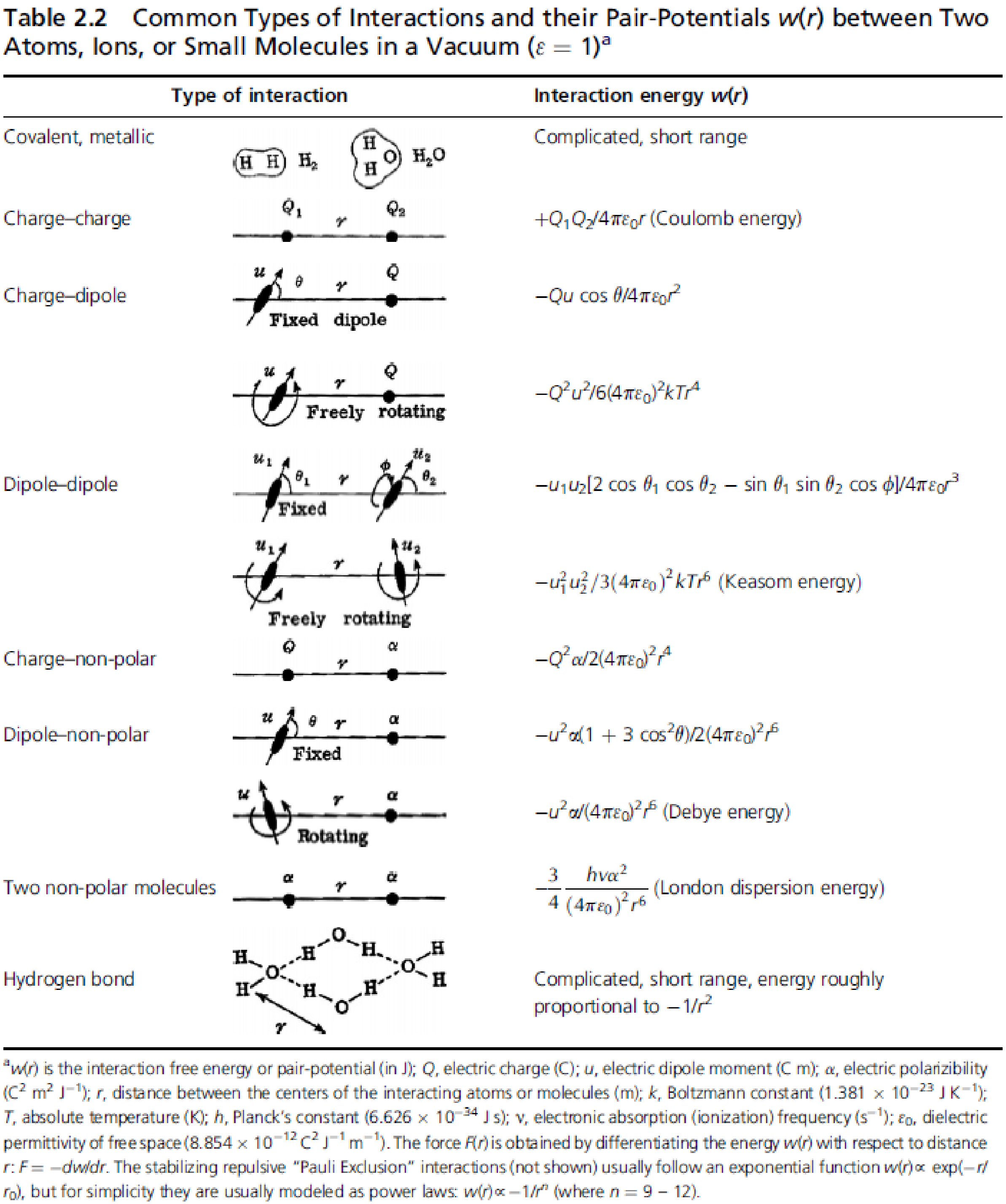


Table 2.2 Common Types of Interactions and their Pair-Potentials $w(r)$ between Two Atoms, Ions, or Small Molecules in a Vacuum ($\varepsilon = 1$)[a]

Type of interaction	Interaction energy $w(r)$
Covalent, metallic	Complicated, short range
Charge–charge	$+Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2kTr^4$
Dipole–dipole Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
Freely rotating	$-u_1^2u_2^2/3(4\pi\varepsilon_0)^2kTr^6$ (Keasom energy)
Charge–non-polar	$-Q^2\alpha/2(4\pi\varepsilon_0)^2r^4$
Dipole–non-polar Fixed	$-u^2\alpha(1+3\cos^2\theta)/2(4\pi\varepsilon_0)^2r^6$
Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules	$-\frac{3}{4}\frac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond	Complicated, short range, energy roughly proportional to $-1/r^2$

[a] $w(r)$ is the interaction free energy or pair-potential (in J); Q, electric charge (C); u, electric dipole moment (C m); α, electric polarizibility ($C^2\ m^2\ J^{-1}$); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space ($8.854 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$). The force $F(r)$ is obtained by differentiating the energy $w(r)$ with respect to distance r: $F = -dw/dr$. The stabilizing repulsive "Pauli Exclusion" interactions (not shown) usually follow an exponential function $w(r) \propto \exp(-r/r_0)$, but for simplicity they are usually modeled as power laws: $w(r) \propto -1/r^n$ (where $n = 9 - 12$).

Useful table

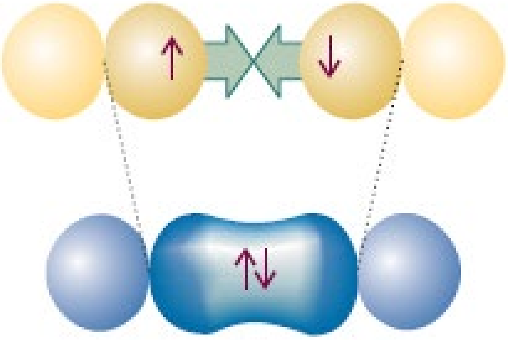
Expressions will always be provided during the exam

Knowing the general form (e.g. $1/r^6$, $1/r^2$, T dep. etc. is useful)

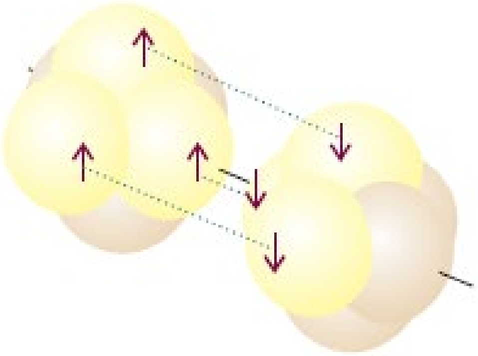
Covalent Interactions

Covalent bonds arise from mixing of quantum mechanical states determined by symmetry considerations.

- Constructive interference of electronic wave functions: bonding orbitals
- Destructive interference of electronic wave functions: antibonding orbitals

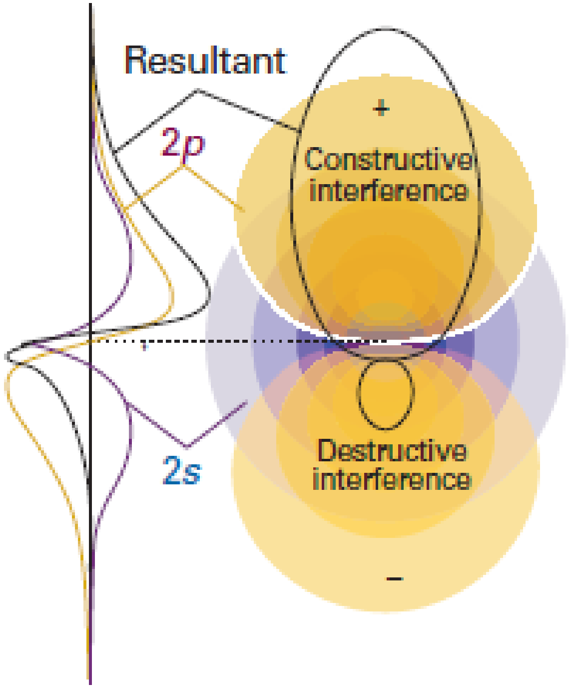


Aligned p_z orbitals mixing to form a σ bond



Aligned p_x, p_y orbitals mixing to form a π bond

N_2

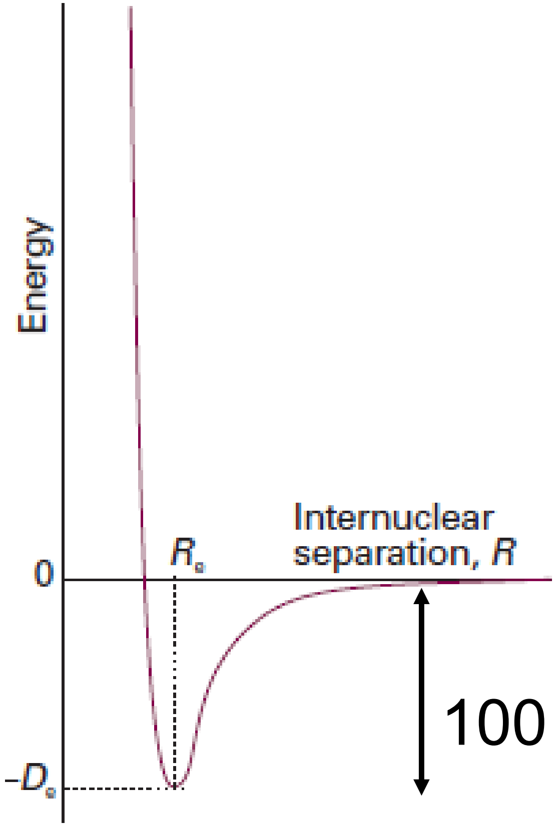


sp^3 hybridization (e.g. CH_4)

Covalent Interactions

Covalent bonds arise from mixing of quantum mechanical states determined by symmetry considerations.

- Constructive interference of electronic wave functions: bonding orbitals
- Destructive interference of electronic wave functions: antibonding orbitals



100 – 300 kT

Properties:

- Directional
- Geometry dependent
- Stoichiometric
- Short-ranged (steep well)
- Do not generally participate in phase transitions, rather in chemical reactions

Topic 2: Driving forces and interactions in liquids

- Overview
- Covalent interactions
- Interactions involving charges
- Ion-ion interactions in crystals
- Ion-ion interactions in liquids – Debye-Hückel theory

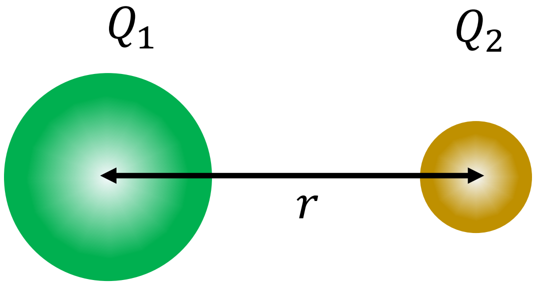
Material to study, lecture 3:
JN Israelachvili: Intermolecular and surface forces:
Chapter 3.1 – 3.8

Interactions in liquids

Liquids have statistical positioning of molecules with medium ranged interactions: interactions are generally not strongly directional, specific or stoichiometric.

Interactions between charges and dipoles, induced dipoles and non-polar groups & H-bonds (semi-directional) are all important

Charge-charge interaction: Coulombic force

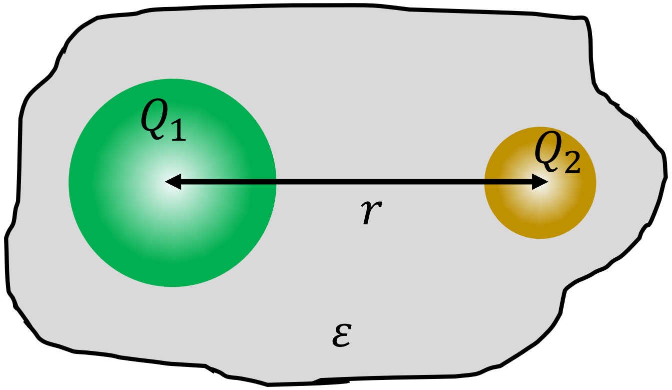


$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 \varepsilon r^2}$$

- Solubility of ions
- Ion-ion interactions in crystals or in a liquid
- Born energy

Coulombic interactions

Charge-charge interaction:



$$F = \frac{Q_1 Q_2}{4\pi\varepsilon_0\varepsilon r^2}$$

Coulombic force

$$\mathrm{w}(r) = -\frac{Q_1 Q_2}{4\pi\varepsilon_0\varepsilon r}$$

Pair-potential

Properties:

- Isotropic
- Not geometry dependent
- Long ranged, w~ 1/r (but damped by counter ions / high dielectric constant)
- 200 kT or less; depends on medium

Electrostatics Reminder

Force [N]

$$F(r) = \frac{Q_1 q}{4\pi\varepsilon_0\varepsilon r^2}$$

$$E = \frac{F}{q}$$

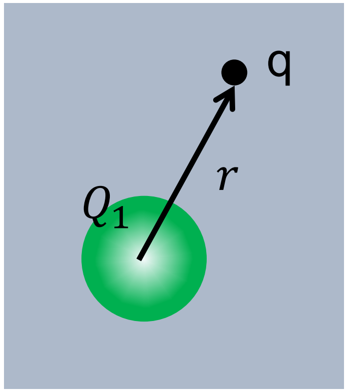
$$F = Eq$$

Field [N/C]=[V/m]

$$E(r) = \frac{Q_1}{4\pi\varepsilon_0\varepsilon r^2}$$

$$\mathrm{w}(r) = -\int F(r)dr$$

$$F(r) = -\frac{dw(r)}{dr}$$



$$\psi(r) = -\int E(r)dr$$

$$\mathrm{E}(r) = -\frac{d\psi(r)}{dr}$$

$$\mathrm{w}(r) = -\frac{Q_1 q}{4\pi\varepsilon_0\varepsilon r}$$

$$\psi = \frac{w}{q}$$

$$w = \psi q$$

$$\psi(r) = -\frac{Q_1}{4\pi\varepsilon_0\varepsilon r}$$

Pair potential [Nm]=[J]

Electrostatic potential [J/C]=[V]

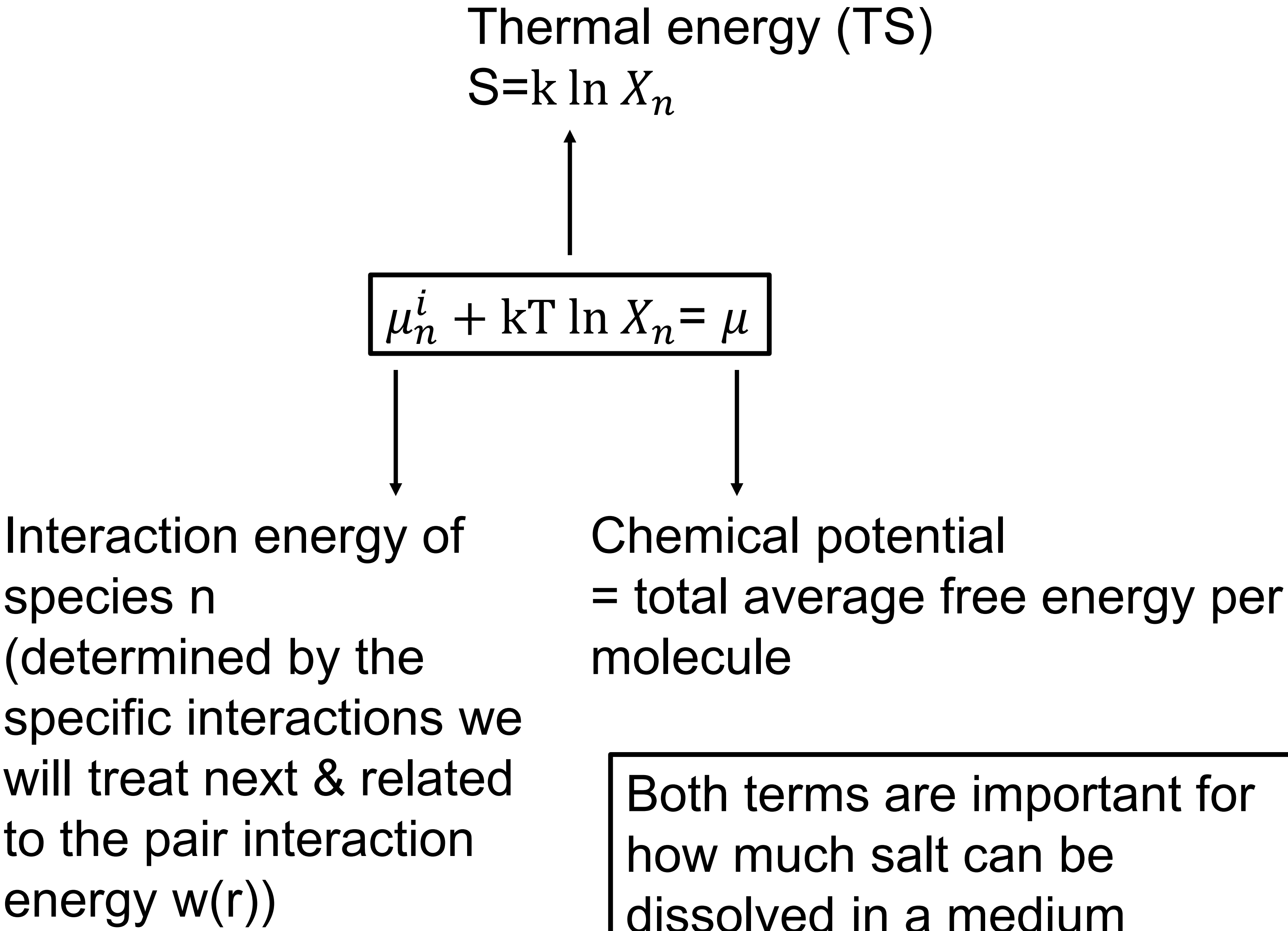
+ **Gauss law**:

E-field flux through a closed surface = enclosed charge / $\varepsilon_0\varepsilon$

Predicting ion solubility:

Combining the Boltzmann distribution and Coulombic interactions

Solubility: chemical equilibrium



Thermal energy (TS)
S=$\mathrm{k}\ln X_n$

$$\boxed{\mu_n^i + \mathrm{kT}\ln X_n = \mu}$$

Interaction energy of species n (determined by the specific interactions we will treat next & related to the pair interaction energy w(r))

Chemical potential
= total average free energy per molecule

Both terms are important for how much salt can be dissolved in a medium

The Born Energy

The Born energy is the electrostatic energy needed to keep electrostatic charge localized on an ion. This is the self-energy of a charged ion.

It can be computed in two ways:

- By charging a neutral sphere the size of an atom and computing the work done
- By computing the electrostatic field energy of an ion

The Born energy can be used to compare:
(1) how well ions dissolve
(2) How ions distribute across (partition in) different media.

The Born energy can predict ion partitioning

Key concepts Lecture 3

- The interaction energy is the average sum of all interactions for a given molecule; depends on position
- The pair potential is interaction energy between a pair
- Relationship between interaction energy and pair potential
- Importance of kT

- Properties of covalent bonds
- Force relevant for charge-charge interactions
- Properties of Coulombic interactions
- The Born energy and its use