

The Born Energy of an Ion

The free energy density of an electric field E arising from a charge is $\frac{1}{2}(\epsilon_0 \epsilon E^2)$ per unit volume

Integrating the energy density of an ion over all of space = Born energy:

$$\mu^i = \frac{1}{2}\epsilon_0\epsilon \int E^2 dV = \frac{1}{2}\epsilon_0\epsilon \int_a^\infty \frac{Q^2}{(4\pi\epsilon_0\epsilon r^2)^2} 4\pi r^2 dr = + \frac{Q^2}{8\pi\epsilon_0\epsilon a} \quad (5)$$

The change in free energy on transferring an ion from a medium of low dielectric constant ϵ_1 to one of high dielectric constant ϵ_2 :

$$\Delta\mu^i = - \frac{z^2 e^2}{8\pi\epsilon_0 a} \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right] \quad (6)$$

one mole of ions:

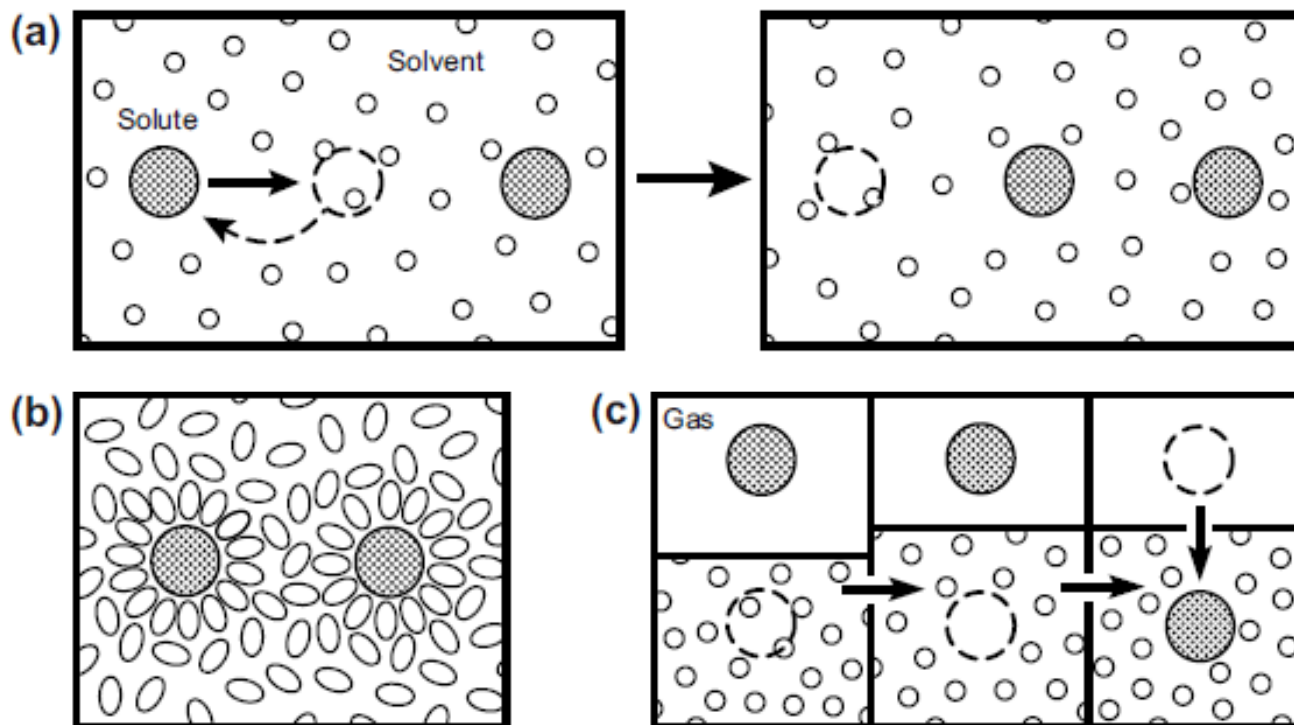
$$\Delta G = N_o \Delta\mu^i = - \frac{69z^2}{a} \left[\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right] \text{ kJ mol}^{-1} \quad (7)$$

One mole of monovalent cations and anions are transferred from the gas phase ($\epsilon = 1$) into water ($\epsilon = 78$), $a = 0.14$ nm : maintaining a NaCl ionic crystal

$$\Delta G = - \frac{2 \times 69}{0.14} \left[1 - \frac{1}{78} \right] \approx - 1000 \text{ kJ mol}^{-1}$$

The Interaction of Molecules in a Medium

Medium (solvent) effects:



Solute-solvent interactions can change the properties of dissolved molecules, such as their dipole moment and el. charge. The properties of dissolved molecules may be different in different media.

Solubility of Ions in Different Solvents

The free energy change on separating two monovalent ions(Na^+ , Cl^-):

$$\Delta\mu^i \approx \frac{+e^2}{4\pi\epsilon_0\epsilon(a_+ + a_-)} \quad (8)$$

The concentration X_s of ions forming a saturated solution in equilibrium with the solid

$$X_s = e^{-\Delta\mu^i/kT} = \exp\left[-\frac{e^2}{4\pi\epsilon_0\epsilon(a_+ + a_-)kT}\right] \quad (9)$$

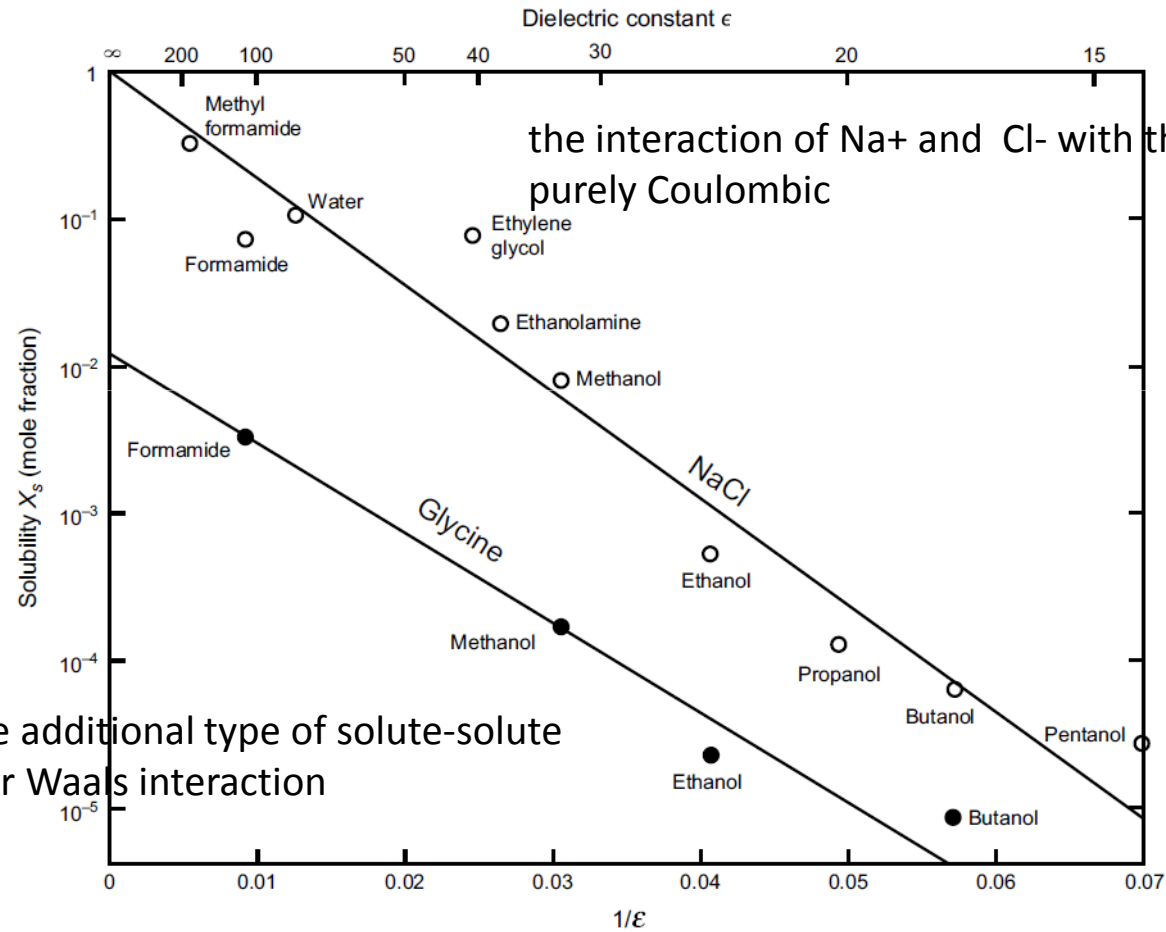
For NaCl in water, where $(a_+ + a_-) = 0.276 \text{ nm}$, $\epsilon = 78$ at $T = 298 \text{ K}$

$X_s = e^{-26} = 0.075$ in mole fraction unit
experimental value $X_s = 0.11$

Solubility of Ions in Different Solvents

$$X_S = e^{-\Delta\mu^i/kT} = \exp\left[-\frac{e^2}{4\pi\epsilon_0\epsilon(a_+ + a_-)kT}\right]$$

→ larger ions are more soluble than smaller ions

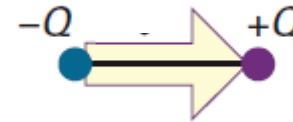


Alkali halides in water:

CsBr and KI, are generally much **more soluble** in various solvents than NaF and LiF

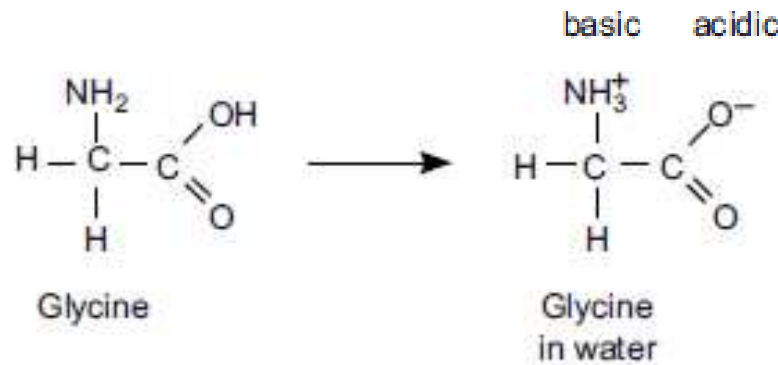
Interactions Involving Polar Molecules

All heteronuclear diatomic molecules are polar.



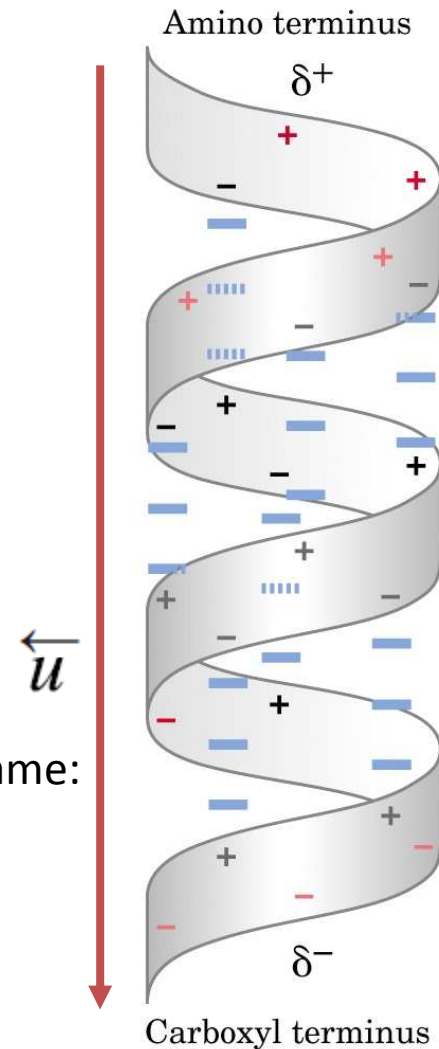
The dipoles of some molecules depend on their environment:

zwitterionic molecule



The magnitude of the positive and negative charges are not the same:
dipolar ions

Proteins have a net dipole moment.



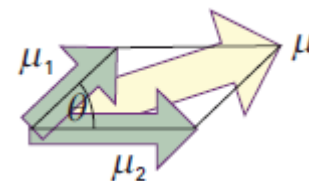
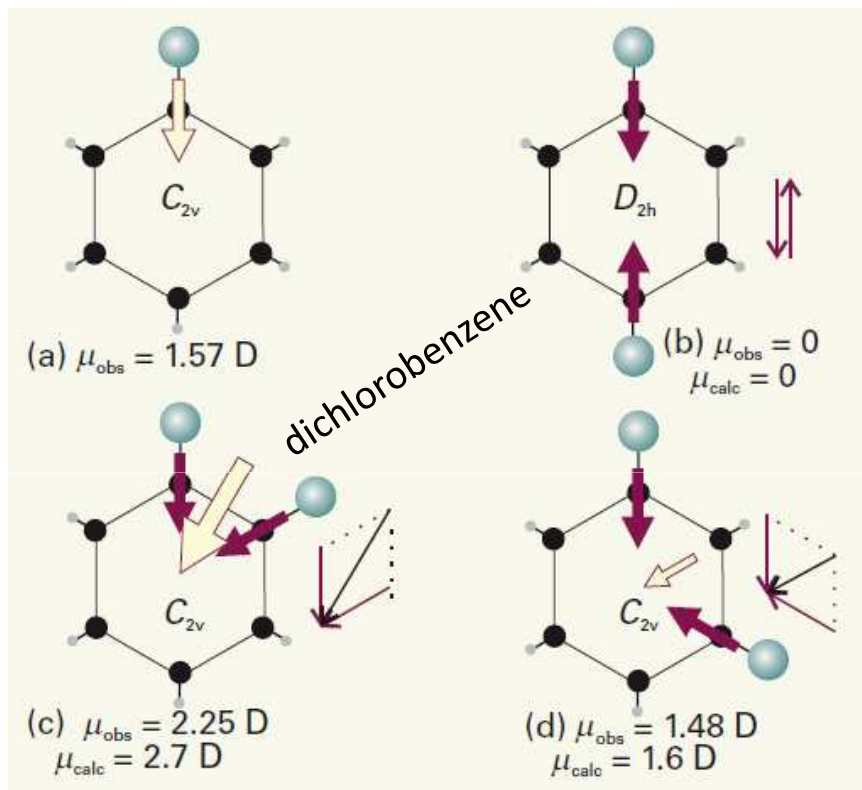
Dipole Moments of Molecules, Bonds, and Molecular Groups (in Debye Units)

$$1 \text{ Debye} = 1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

| Molecules | | | | | |
|---|---------|----------------------------------|---------|--|-------------------|
| Alkanes | | 0^b | | H ₂ O | 1.85 ^c |
| C ₆ H ₆ (benzene) | | 0^d | | C _n H _{2n+1} OH (alcohols) | 1.7 |
| CCl ₄ | | 0 | | C ₆ H ₁₁ OH (cyclohexanol) | 1.7 |
| CO ₂ | | 0^e | | OMCTS ^f | 0.42 |
| CO | | 0.11 | | CH ₃ COOH (acetic acid) | 1.7 |
| CHCl ₃ (chloroform) | | 1.06 | | C ₂ H ₄ O (ethylene oxide) | 1.9 |
| HCl | | 1.08 | | CH ₃ COCH ₃ (acetone) | 2.9 |
| HF | | 1.91 ^c | | HCONH ₂ (formamide) | 3.7 ^c |
| NH ₃ | | 1.47 | | C ₆ H ₅ OH (phenol) | 1.5 |
| CH ₃ Cl | | 1.87 | | C ₆ H ₅ NH ₂ (aniline) | 1.5 |
| NaCl | | 8.5 | | C ₆ H ₅ Cl (chlorobenzene) | 1.8 |
| CsCl | | 10.4 | | C ₆ H ₅ NO ₂ (nitrobenzene) | 4.2 |
| Bond Moments | | | | | |
| C-H ⁺ | 0.4 | C-C | 0 | C ⁺ -Cl | 1.5-1.7 |
| N-H ⁺ | 1.31 | C=C | 0 | N ⁺ -O | 0.3 |
| O-H ⁺ | 1.51 | C ⁺ -N | 0.22 | C ⁺ =O | 2.3-2.7 |
| F-H ⁺ | 1.94 | C ⁺ -O | 0.74 | N ⁺ =O | 2.0 |
| Group Moments | | | | | |
| C ⁻ +CH ₃ | 0.4 | C ⁻ +COOH | 1.7 | Adenine | ~3 |
| C ⁻ +OH | 1.65 | C ⁻ +OCH ₃ | 1.3 | Thymine | ~4 |
| C ⁻ +NH ₂ | 1.2-1.5 | C ⁺ -NO ₂ | 3.1-3.8 | Guanine | ~7 |
| | | | | Cytosine | ~8 |

Dipole Moments of Molecules

chlorobenzene



$$\mu_{\text{res}} = (\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos \theta)^{1/2}$$

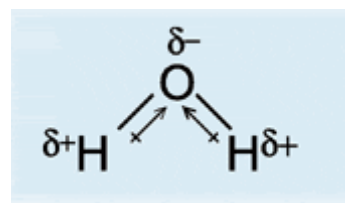
$$\mu_{\text{res}} = 2\mu_1 \cos \frac{1}{2}\theta$$

Ex: Gaseous water

$$\theta = 104.5^\circ$$

$$\mu_{\text{H}_2\text{O}} = 2 \times 1.51 \cos(52.25^\circ) = 1.85 \text{ D}$$

With partial charges



$$\mu_x = \sum_j \delta_j x_j$$

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

Dipole Self-Energy

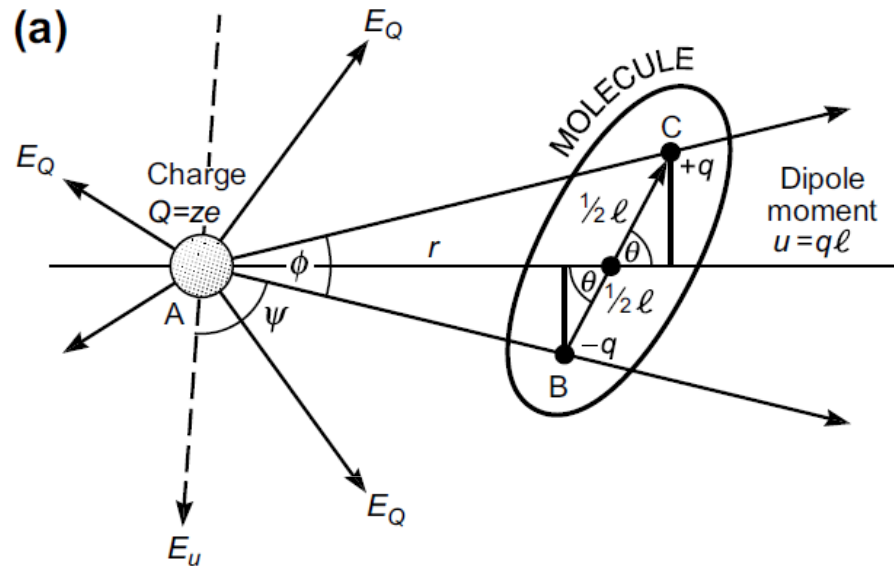
$$\mu^i = \frac{1}{4\pi\epsilon_0\epsilon} \left[\frac{q^2}{2a} + \frac{q^2}{2a} - \frac{q^2}{r} \right] = + \frac{q^2}{8\pi\epsilon_0\epsilon a}$$

→ Born energy of an individual ion

This equation is not as useful as the Born equation for ions.

- a moment of $u = 1\text{D}$
 - $\pm e$ separated by $l = 0.02\text{ nm}$
 - $\pm \frac{1}{2}e$ separated by $l = 0.04\text{ nm}$.
- the dipole moment u can vary from solvent to solvent
- there are additional large energy terms arising from non-electrostatic solute-solvent interactions

Ion-Dipole Interactions



$$AB = \left[\left(r - \frac{1}{2}l \cos \theta \right)^2 + \left(\frac{1}{2}l \sin \theta \right)^2 \right]^{1/2} \approx r - \frac{1}{2}l \cos \theta,$$

$$AC = \left[\left(r + \frac{1}{2}l \cos \theta \right)^2 + \left(\frac{1}{2}l \sin \theta \right)^2 \right]^{1/2} \approx r + \frac{1}{2}l \cos \theta,$$

$r \gg l$

$$w(r) = -\frac{Qq}{4\pi\epsilon_0\epsilon} \left[\frac{1}{AB} - \frac{1}{AC} \right] \quad (10)$$

Point dipole approximation limit:

$$w(r) = w(r, \theta) = -\frac{Qq}{4\pi\epsilon_0\epsilon} \left[\frac{1}{r - \frac{1}{2}l \cos \theta} - \frac{1}{r + \frac{1}{2}l \cos \theta} \right]$$

$$= -\frac{Qq}{4\pi\epsilon_0\epsilon} \left[\frac{l \cos \theta}{r^2 - \frac{1}{4}l^2 \cos^2 \theta} \right]$$

$$= -\frac{Qu \cos \theta}{4\pi\epsilon_0\epsilon r^2} = -\frac{(ze)u \cos \theta}{4\pi\epsilon_0\epsilon r^2} \leftarrow$$

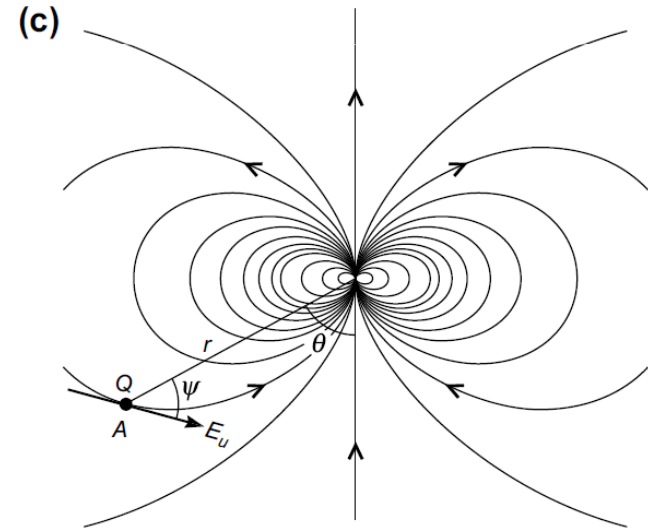
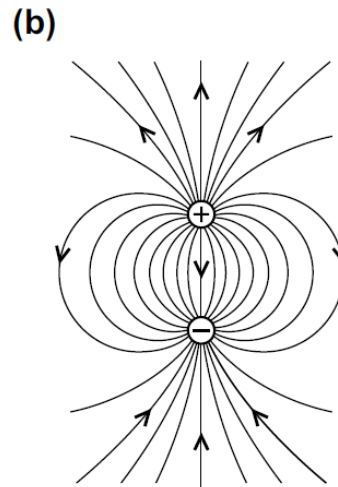
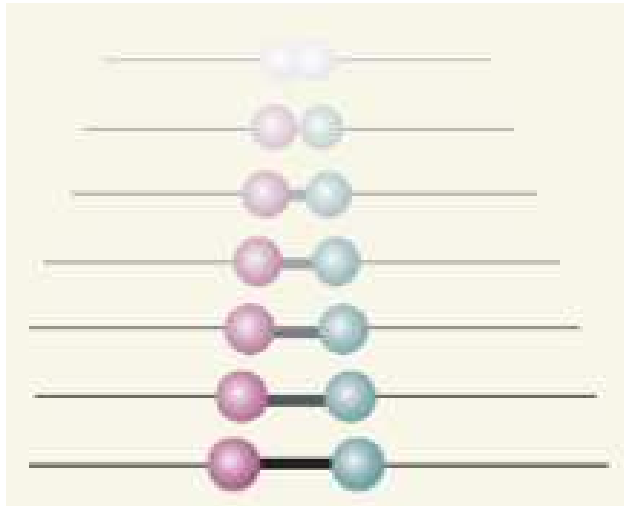
(11)

Ion-Dipole Interactions

$$E(r) = Q/4\pi\epsilon_0\epsilon r^2 \longrightarrow w(r, \theta) = -uE(r)\cos \theta \quad (12)$$

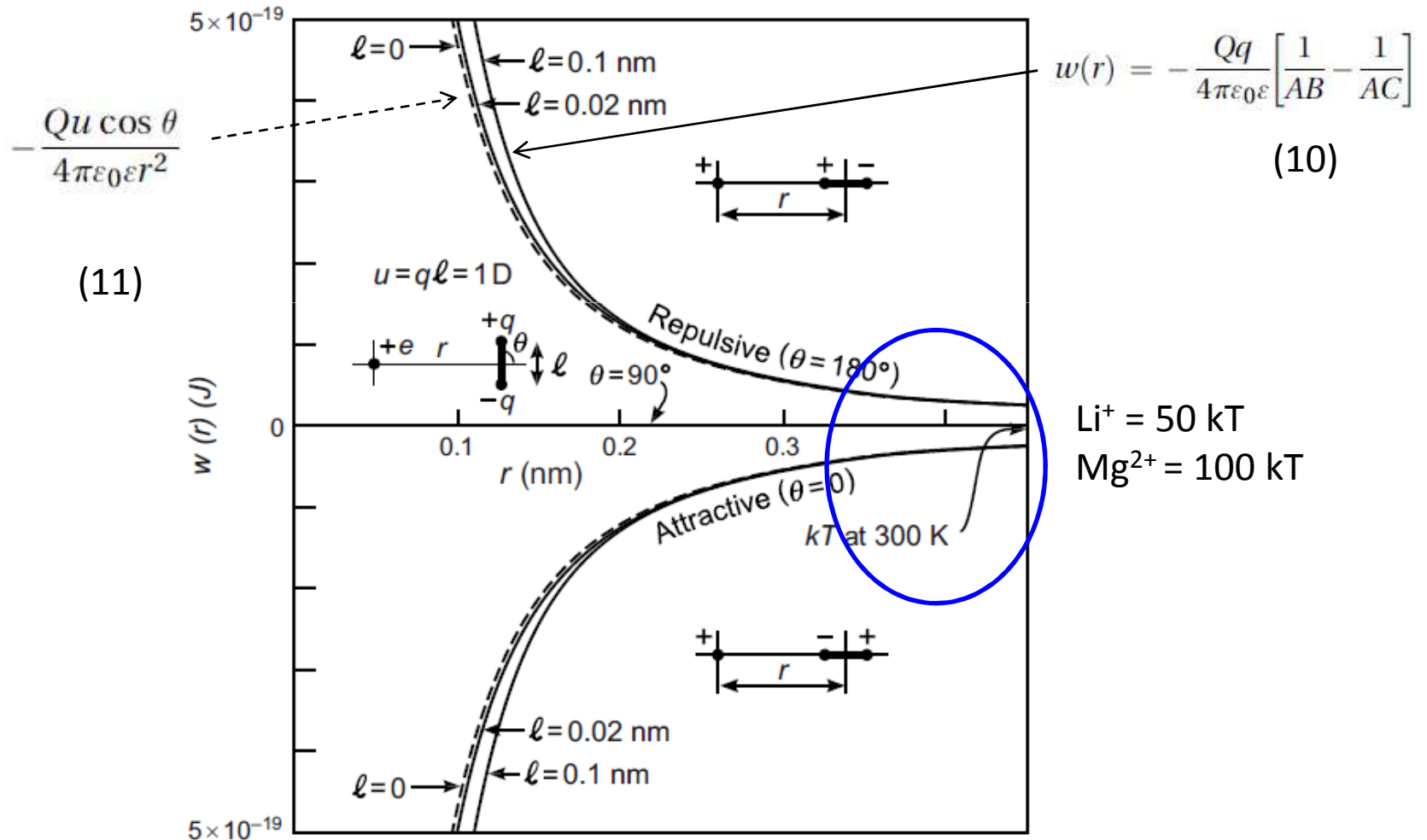
$\theta = 0$, attractive force

$\theta = \pi$, repulsive force



Ion-Dipole Interactions

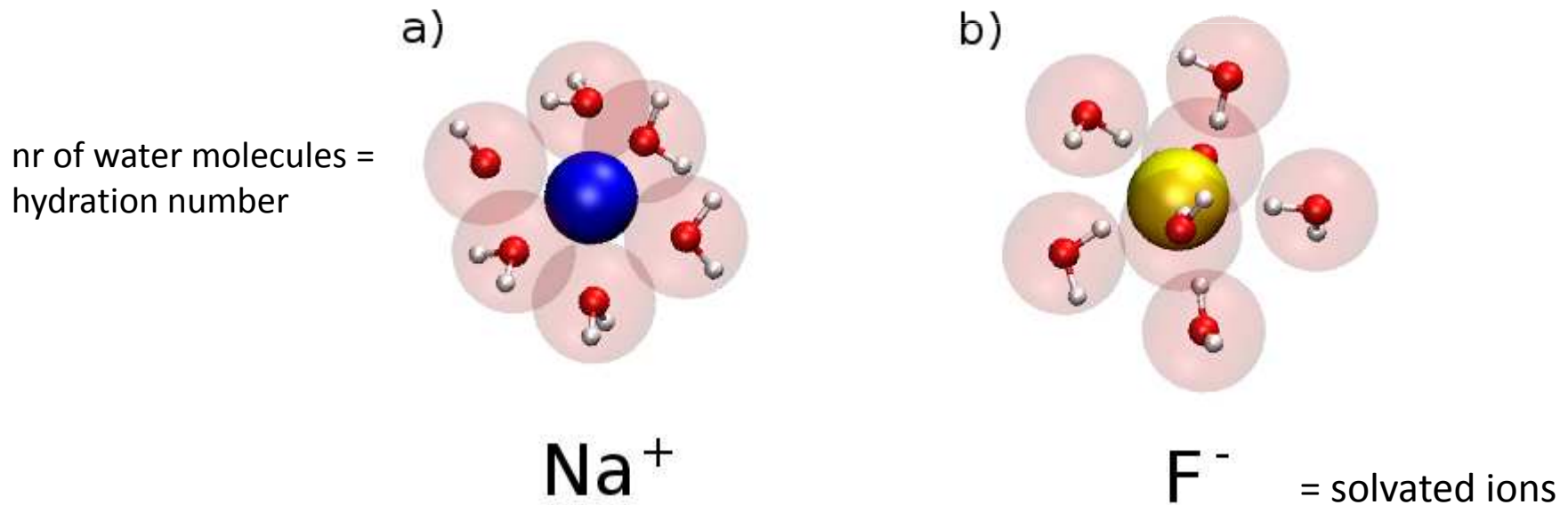
Charge-dipole interaction energy in vacuum ($\epsilon = 1$) between a unit charge e and a dipole of moment $u = q \ell = 1 \text{ D}$ oriented at different angles θ to the charge.



Ion-Dipole Interactions in Water: Hydrated Ions

$$w(r) = w(r, \theta) = -\frac{Qu \cos \theta}{4\pi\epsilon_0\epsilon r^2} = -\frac{(ze)u \cos \theta}{4\pi\epsilon_0\epsilon r^2}$$

A water molecule in bulk water is in a different state from a water molecule near an ion.



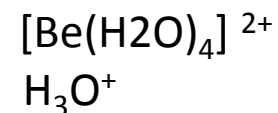
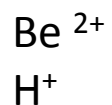
The first shell of water molecules around a strongly solvated ion = **first or primary hydration shell.**

Hydrated radii and Hydration Numbers of Ions in Water

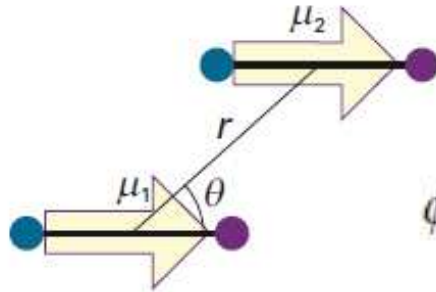
| Ion | Bare ion radius (nm) | Hydrated radius (nm) | Hydration number (± 1) | Lifetime/exchange rate (s) |
|---|----------------------|----------------------|------------------------------|----------------------------|
| H ₃ O ⁺ | — | 0.28 | 3 | — |
| Li ⁺ | 0.068 | 0.38 | 5 | 5×10^{-9} |
| Na ⁺ | 0.095 | 0.36 | 4 | 10^{-9} |
| K ⁺ | 0.133 | 0.33 | 3 | 10^{-9} |
| Cs ⁺ | 0.169 | 0.33 | 1 | 5×10^{-10} |
| Be ²⁺ | 0.031 | 0.46 | 4 ^a | 10^{-3} |
| Mg ²⁺ | 0.065 | 0.43 | 6 ^a | 10^{-6} |
| Ca ²⁺ | 0.099 | 0.41 | 6 | 10^{-8} |
| Al ³⁺ | 0.050 | 0.48 | 6 ^a | 0.1–1 |
| Cr ³⁺ | 0.052 | — | 6 ^a | >3 hrs |
| OH ⁻ | 0.176 | 0.30 | 3 | |
| F ⁻ | 0.136 | 0.35 | 2 | |
| Cl ⁻ | 0.181 | 0.33 | 1 | $\sim 10^{-11}$ |
| Br ⁻ | 0.195 | 0.33 | 1 | $\sim 10^{-11}$ |
| I ⁻ | 0.216 | 0.33 | 0 | $\sim 10^{-11}$ |
| NO ₃ ⁻ | 0.264 | 0.34 | 0 | |
| N(CH ₃) ₄ ⁺ | 0.347 | 0.37 | 0 | |

The average time that water molecules remain bound to ions:

- pure liquid at room temperature the water molecules tumble about with a mean reorientation time of about 10^{-11} s
- the water molecules are near ion: 10^{-11} s to many hours



Dipole-Dipole Interactions



The potential energy $V = -\mathcal{E}_1 \cdot \boldsymbol{\mu}_2$ (13)

Distribution of charges Q_i at r_i (x_i, y_i, z_i)

The Coulomb potential at R (x, y, z):

$$\phi = \sum_i \frac{Q_i}{4\pi\epsilon_0} \frac{1}{\{(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2\}^{1/2}} \quad (14)$$

$$r_i \ll r$$

$$\begin{aligned} \phi(\mathbf{r}) &= \sum_i \frac{Q_i}{4\pi\epsilon_0} \times \left\{ \frac{1}{r} + \left(\frac{\{(x - x_i)^2 + (y - y_i)^2 + (z - z_i)^2\}^{1/2}}{x_i} \right)_{x_i=0} x_i + \dots \right\} \\ &= \sum_i \frac{Q_i}{4\pi\epsilon_0} \left\{ \frac{1}{r} + \frac{xx_i}{r^3} + \dots \right\} \end{aligned}$$

$$\sum_i Q_i x_i = \mu_x$$

$$\phi = \frac{1}{4\pi\epsilon_0 r^3} (\mu_x x + \mu_y y + \mu_z z) = \frac{1}{4\pi\epsilon_0 r^3} \boldsymbol{\mu}_1 \cdot \mathbf{r} \quad (15)$$

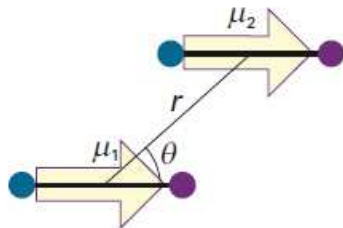
Dipole-Dipole Interactions

The electric field strength $\mathcal{E} = \nabla\phi$

$$\mathcal{E}_1 = \frac{1}{4\pi\epsilon_0} \nabla \frac{\boldsymbol{\mu}_1 \cdot \mathbf{r}}{r^3} = -\frac{\boldsymbol{\mu}_1}{4\pi\epsilon_0 r^3} - \frac{\boldsymbol{\mu}_1 \cdot \mathbf{r}}{4\pi\epsilon_0} \nabla \frac{1}{r^3} \quad (16)$$

The potential energy:

$$V = \frac{\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2}{4\pi\epsilon_0 r^3} - 3 \frac{(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})}{4\pi\epsilon_0 r^5} \quad (17)$$

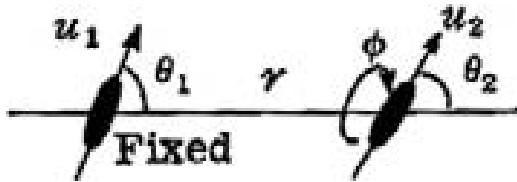


$$\boldsymbol{\mu}_1 \cdot \mathbf{r} = \mu_1 r \cos \theta$$

$$\boldsymbol{\mu}_2 \cdot \mathbf{r} = \mu_2 r \cos \theta$$

$$V = \frac{\mu_1 \mu_2 f(\theta)}{4\pi\epsilon_0 r^3} \quad f(\theta) = 1 - 3 \cos^2 \theta \quad (18)$$

Dipole-Dipole Interactions



$$w(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi] \quad (19)$$

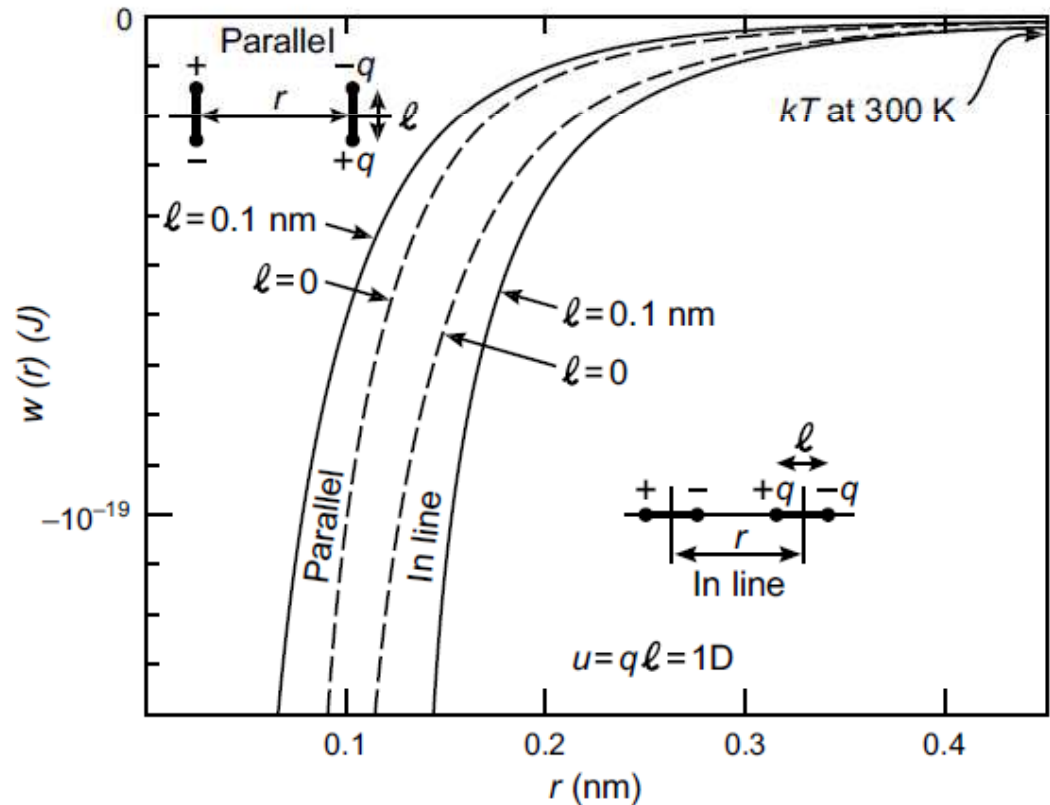
$$\text{Maximum: } w(r, 0, 0, \phi) = -2u_1 u_2 / 4\pi\epsilon_0\epsilon r^3 \quad (20)$$

For two equal dipoles of moments 1D, the interaction energy in a vacuum = kT at $r = 0.36$ nm when the dipoles are in line.

Dipolar interactions are strong enough to bind only very polar molecules.



cigar-shaped molecules



Rotating Dipoles: Keesom interaction

Potential distribution theorem

$$e^{-w(r)/kT} = \int e^{-w(r,\Omega)/kT} d\Omega / \int d\Omega \quad d\Omega = \sin \theta d\theta d\phi \quad (21)$$

Denominator: $\int d\Omega = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta = 4\pi$

$$e^{-w(r)/kT} = \langle e^{-w(r,\theta,\phi)/kT} \rangle = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi e^{-w(r,\theta,\phi)/kT} \sin \theta d\theta \quad (22)$$

$w(r, \Omega) \ll kT, e^x = 1+x :$

$$e^{-w(r)/kT} = 1 - \frac{w(r)}{kT} + \dots = \left\langle 1 - \frac{w(r, \Omega)}{kT} + \frac{1}{2} \left(\frac{w(r, \Omega)}{kT} \right)^2 - \dots \right\rangle$$

$$w(r) = \left\langle w(r, \Omega) - \frac{w(r, \Omega)^2}{2kT} + \dots \right\rangle \quad (23)$$

Rotating Dipoles: Keesom interaction

The angle-averaged free energy for the **charge-point dipole** interaction

$$w(r) = \left\langle -\frac{Qu \cos \theta}{4\pi\epsilon_0\epsilon r^2} - \left(\frac{Qu}{4\pi\epsilon_0\epsilon r^2}\right)^2 \frac{\cos^2 \theta}{2kT} + \dots \right\rangle \approx -\frac{Q^2 u^2}{6(4\pi\epsilon_0\epsilon)^2 kT r^4} \quad (24)$$

$$kT > \frac{Qu}{4\pi\epsilon_0\epsilon r^2}$$

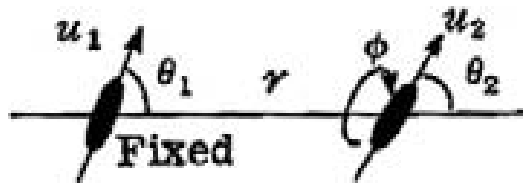
$$\langle \cos^2 \theta \rangle = \frac{1}{4\pi} \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = \frac{1}{3}$$

A monovalent ion interacting with the polar solvent molecules of a medium ϵ :

$$Q = e, u = 1.85 \text{ D}, \epsilon = 80 \quad r = \sqrt{Qu/4\pi\epsilon_0\epsilon kT} = 0.2 \text{ nm}$$

Rotating Dipoles: Keesom interaction

Dipole-dipole interaction, angle averaged interaction free energy:



$$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\epsilon_0\epsilon)^2 kTr^6} \quad \text{for} \quad kT > \frac{u_1 u_2}{4\pi\epsilon_0\epsilon r^3} \quad (25)$$

Keesom interaction

Neither ion-dipole nor dipole-dipole forces can produce long-range alignment effects in liquids.

Pair of molecule with $\mu = 1\text{D}$ at $t = 25^\circ\text{C}$, $r = 0.5\text{ nm}$ $w(r) = -0.06\text{ kJ mol}^{-1}$

average molar kinetic energy $\frac{3}{2}RT = 3.7\text{ kJ mol}^{-1}$

Strengths of Covalent Bonds

| Bond Type | Strength (kJ mol^{-1}) | Bond Type | Strength (kJ mol^{-1}) |
|--|-----------------------------------|--------------------------------|-----------------------------------|
| $\text{C}\equiv\text{N}$ (HCN) | 870 | Si-O | 370 |
| $\text{C}=\text{O}$ (HCHO) | 690 | C-C (C_2H_6) | 360 |
| $\text{C}=\text{C}$ (C_2H_4) | 600 | C-O (CH_3OH) | 340 |
| O-H (H_2O) | 460 | N-O (NH_2OH) | 200 |
| C-H (CH_4) | 430 | F-F (F_2) | 150 |

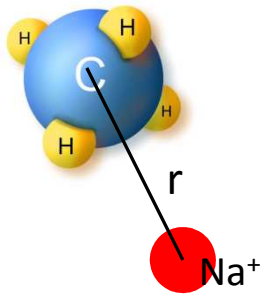
Ion-induced Dipole Interaction

A molecule of polarizability α at a distance r from an ion of charge ze .
Induced electric dipole:

$$u_{\text{ind}} = \alpha E = \alpha ze / 4\pi\epsilon_0\epsilon r^2 \quad (26)$$

Ex:

Estimate the distance by which the electron cloud of a CH_4 molecule ($\alpha = 2.6 \times 10^{-40} \text{C}^2 \text{m}^2 \text{J}^{-1}$) is shifted relative to the center of the molecule due to the presence of a bare sodium ion whose center is 0.4 nm from the center of the molecule. Assume that the interaction occurs in air ($\epsilon = 1$) and the molecular radius of methane is 0.2 nm.



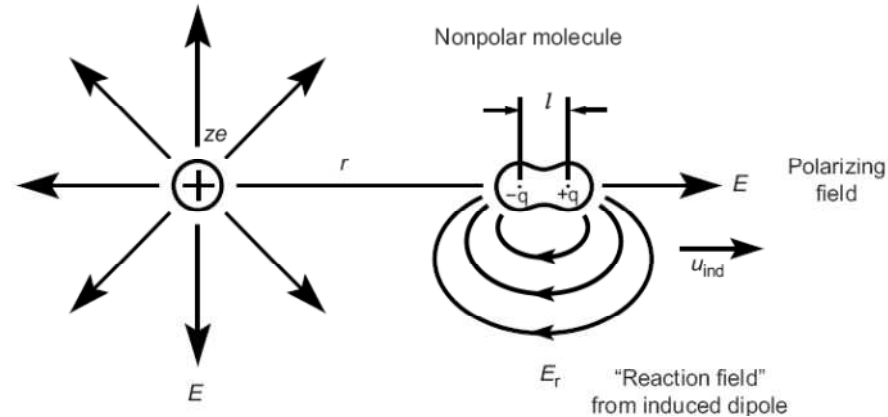
$$E = e / 4\pi\epsilon_0 r^2 = 9.0 \times 10^9 \text{ V m}^{-1}$$

$$u_{\text{ind}} = \alpha E = 0.78 \text{ D}$$

$$l = u_{\text{ind}} / e = 0.016 \text{ nm} \quad \text{8\% of the molecular radius of methane}$$

4 hydrogen electrons in CH_4 may be displaced simultaneously: $l = 0.004 \text{ nm}$
2 % of the molecular radius of methane

Ion-induced Dipole Interaction



The “reaction” field:

$$E_r = -2u_{\text{ind}}/4\pi\epsilon_0\epsilon r^3 = -2\alpha E/4\pi\epsilon_0\epsilon r^3 = -2\alpha(ze)/(4\pi\epsilon_0\epsilon)^2 r^5 \quad (27)$$

Force: $F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\epsilon_0\epsilon)^2 r^5 \quad (28)$

Energy: $w(r) = -\int_{\infty}^r Fdr = -\alpha(ze)^2/2(4\pi\epsilon_0\epsilon)^2 r^4 = -\frac{1}{2}\alpha E^2 \quad (29)$

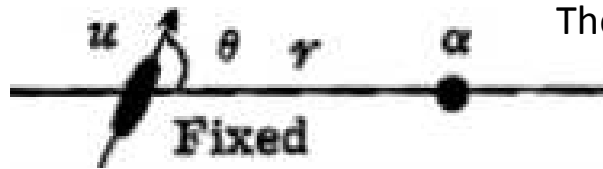
Ion-permanent dipole interaction: $w(r) = -uE = -\alpha E^2$

$E = ze/4\pi\epsilon_0\epsilon r^2$

Net ion-induced dipole interaction free energy $\alpha = \alpha_0 + u^2/3kT$

$$w(r) = -\frac{(ze)^2\alpha}{2(4\pi\epsilon_0\epsilon)^2 r^4} = -\frac{(ze)^2}{2(4\pi\epsilon_0\epsilon)^2 r^4} \left(\alpha_0 + \frac{u^2}{3kT} \right)$$

Dipole-Induced Dipole Interactions



The electric field of the dipole acting on the polarizable molecule:

$$E = u (1 + 3 \cos^2 \theta)^{1/2} / 4\pi\epsilon_0\epsilon r^3$$

Interaction energy:

$$w(r, \theta) = -\frac{1}{2}\alpha E^2 = -u^2\alpha_0(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0\epsilon)^2 r^6 \quad (30)$$

The angle-averaged energy:

$$w(r) = -u^2\alpha / (4\pi\epsilon_0\epsilon)^2 r^6 \quad (31)$$

2 molecules with permanent dipole moments u_1 and u_2 and polarizabilities α_{01} and α_{02}

$$w(r) = -\frac{[u_1^2\alpha_{02} + u_2^2\alpha_{01}]}{(4\pi\epsilon_0\epsilon)^2 r^6} \quad \text{Debye interaction} \quad (32)$$

Dipole-induced dipole Keesom interaction

$$\alpha_{or} = u^2/3kT$$

$$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\epsilon_0\epsilon)^2 kT r^6} \quad (33)$$

Unification of Polarization Interactions

α_0 polarizability of neutral molecules

rotating polar molecules $\alpha = \alpha_0 + u^2/3kT$

The total attractive interaction energy between rotating molecules:
sum of the ion-induced dipole and dipole-induced dipole interaction discussed above

$$w(r) = -\left(\frac{Q_1^2}{2r^4} + \frac{3kT\alpha_1}{r^6}\right) \frac{\alpha_2}{(4\pi\epsilon_0\epsilon)^2} \quad (34)$$

$$= -\left[\frac{Q_1^2}{2r^4} + \frac{3kT}{r^6}\left(\frac{u_1^2}{3kT} + \alpha_{01}\right)\right] \left(\frac{u_2^2}{3kT} + \alpha_{02}\right) / (4\pi\epsilon_0\epsilon)^2 \quad (35)$$

polarization-type forces

The relative strengths of charge, dipole, and electronic polarizability contributions in an interaction:

$$Q_1 = e = 1.6 \times 10^{-19} \text{ C}, u_1 = 1 \text{ D} = 3.3 \times 10^{-30} \text{ C m}, \alpha_{01} = (4\pi\epsilon_0)3 \times 10^{-30} \text{ m}^3$$

$r = 0.5 \text{ nm}$, at $T = 300 \text{ K}$

| | | | | | |
|----------------------|---|---------------------|---|------------------------------|---------|
| $\frac{Q_1^2}{2r^4}$ | : | $\frac{u_1^2}{r^6}$ | : | $\frac{3kT\alpha_{01}}{r^6}$ | 800:3:1 |
|----------------------|---|---------------------|---|------------------------------|---------|

| | | |
|--------|---------------------|------|
| Water: | $u^2 : 3kT\alpha_0$ | 20:1 |
|--------|---------------------|------|