

Chapter 07

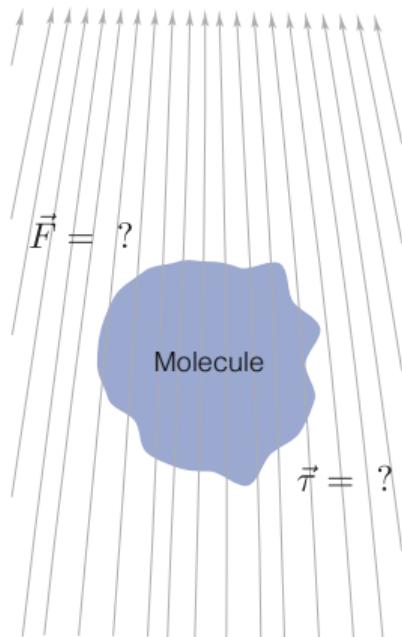
Electrostatic Interactions

Prof. Grandinetti

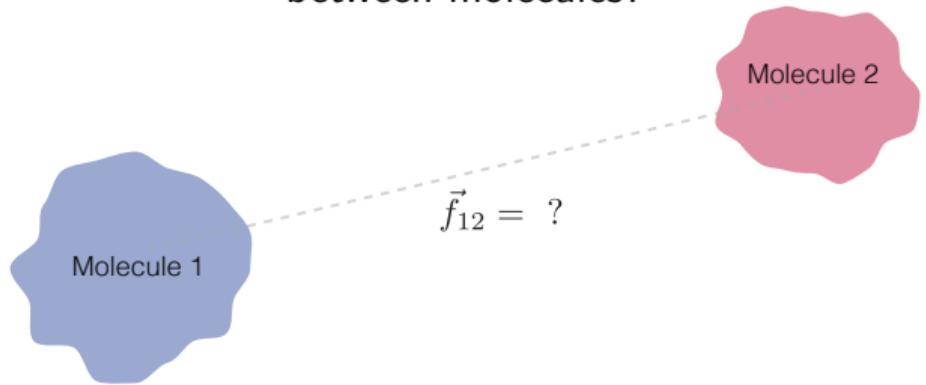
Chem. 4300

Electrostatic Interactions of Molecules

What is the force on a molecule in an electric field?



What is the origin of attractive and repulsive forces between molecules?



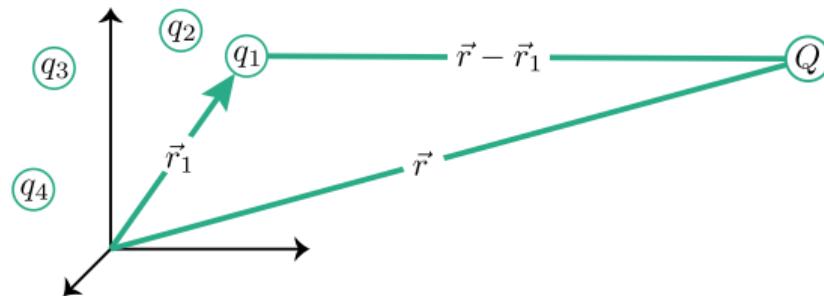
Electrostatic Interactions of Molecules

Electrostatic interactions between molecules are responsible for the formation of liquid and solid phases, friction and lubrication, adhesion and wetting phenomena, molecular self-assembly, biological membranes, protein folding, and life itself.



Electric Field and Force from a Charge Distribution

Force that discrete charges, q_i , fixed in space exert on charge Q is



$$\vec{F} = \sum_{\alpha} \vec{F}_{\alpha} = \frac{Q}{4\pi\epsilon_0} \sum_{\alpha} q_{\alpha} \frac{\vec{r} - \vec{r}_{\alpha}}{|\vec{r} - \vec{r}_{\alpha}|^3} = Q \vec{\mathcal{E}}(\vec{r}) \quad \text{Coulomb's law}$$

Electric field at \vec{r} is given by

$$\vec{\mathcal{E}}(\vec{r}) = \frac{1}{4\pi\epsilon_0} \sum_{\alpha} q_{\alpha} \frac{\vec{r} - \vec{r}_{\alpha}}{|\vec{r} - \vec{r}_{\alpha}|^3}$$

Treating atom or molecule as continuous charge distribution, where $\rho(\vec{r})$ is charge density, we have

$$\vec{\mathcal{E}}(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\vec{r} - \vec{r}'}{|\vec{r} - \vec{r}'|^3} \rho(\vec{r}') d\tau' \quad \text{where } d\tau' = dx' dy' dz'$$

Electric scalar potential, $\varphi(\vec{r})$, from a Charge Distribution

Electric field $\vec{\mathcal{E}}(\vec{r})$ is calculated from gradient of *Electrostatic Scalar Potential* $\varphi(\vec{r})$,

$$\vec{\mathcal{E}}(\vec{r}) = -\nabla \varphi(\vec{r})$$

Electric potential at distance \vec{r} from a continuous charge distribution, $\rho(\vec{r})$,

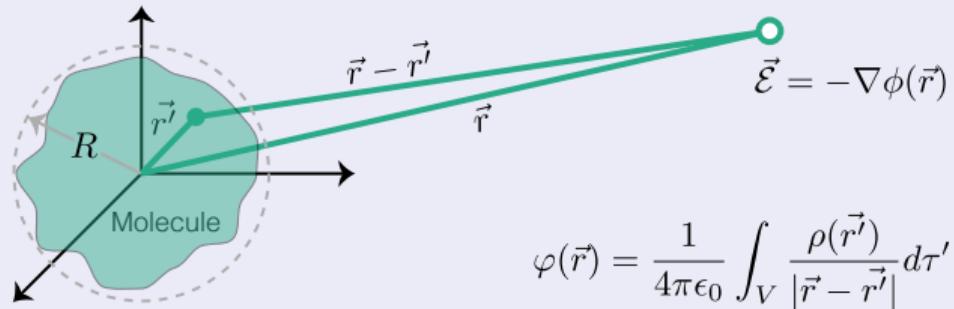
$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau'$$

Volume integral is over all charge density, $\rho(\vec{r}')$

Electric field generated by atom or molecule

Multipole Moments of a Charge Distribution

Atom or molecule consists of distribution of charges, i.e., electrons and protons. How do we calculate $\vec{\mathcal{E}}$ generated by these charges at \vec{r} ?



If $|\vec{r}| \gg R$ we can do Taylor series expansion about $\vec{r}' = 0$

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{1}{r} - (\vec{r}' \cdot \nabla) \frac{1}{r} + \frac{1}{2} (\vec{r}' \cdot \nabla)^2 \frac{1}{r} - \dots$$

Multipole Moments of a Charge Distribution

Multipole expansion of electric potential

Insert Taylor expansion of $\frac{1}{|\vec{r} - \vec{r}'|}$ and re-express $\varphi(\vec{r})$ from molecular charge distribution as

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \left[\frac{\textcolor{blue}{q}}{r} + \frac{\vec{\mu} \cdot \vec{r}}{r^3} + \frac{1}{2} \frac{\vec{r} \cdot \textcolor{violet}{Q} \cdot \vec{r}}{r^5} + \dots \right]$$

where

Electric monopole: $\textcolor{blue}{q} = \int_V \rho(\vec{r}) d\tau, \quad \text{or} \quad \textcolor{blue}{q} = \sum_{\alpha=1}^N q_\alpha$

Electric dipole: $\vec{\mu} = \int_V \vec{r} \rho(\vec{r}) d\tau, \quad \text{or} \quad \vec{\mu} = \sum_{\alpha=1}^N \vec{r}_\alpha q_\alpha$

Electric quadrupole: $\textcolor{violet}{Q}_{ij} = \int_V (3r_i r_j - r^2 \delta_{ij}) \rho(\vec{r}) d\tau, \quad \text{or} \quad \textcolor{violet}{Q}_{ij} = \sum_{\alpha=1}^N (3r_{i,\alpha} r_{j,\alpha} - r_\alpha^2 \delta_{ij}) q_\alpha.$

$\textcolor{violet}{Q}$ is a second-rank symmetric tensor quantity.

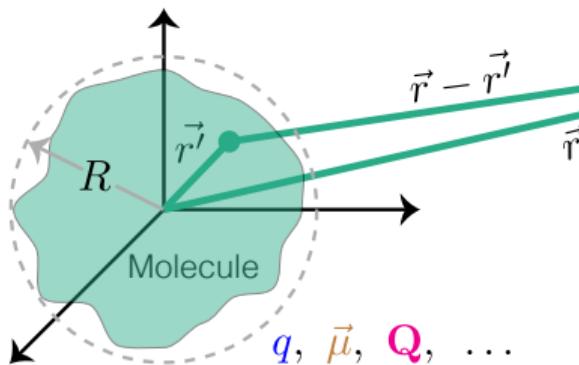
Multipole Moments of a Charge Distribution

Multipole expansion of electric potential

Instead of

$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \int_V \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau'$$

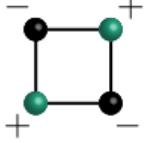
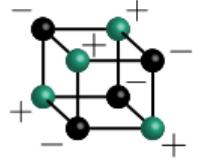
we have



$$\varphi(\vec{r}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q}{r} + \frac{\vec{\mu} \cdot \vec{r}}{r^3} + \frac{1}{2} \frac{\vec{r} \cdot \mathbf{Q} \cdot \vec{r}}{r^5} + \dots \right]$$
$$\vec{\mathcal{E}} = -\nabla \phi(\vec{r})$$

Dependence of electric field strength on multipole moment rank, ℓ .

$$\vec{\mathcal{E}}(\vec{r}) = -\nabla \varphi(\vec{r})$$

Multipole	ℓ	$1/r^{\ell+2}$	
Monopole	0	$1/r^2$	
Dipole	1	$1/r^3$	
Quadrupole	2	$1/r^4$	
Octupole	3	$1/r^5$	
Hexadecapole	4	$1/r^6$	

Molecular Dipole

If molecule has no net charge (i.e., neutral) then leading term is electric dipole term. SI unit for dipole moment is coulomb-meters ($C \cdot m$) but on atomic and molecular scale it is common to use non-SI unit debye (D):

$$1D = 3.33664 \times 10^{-30} C \cdot m$$

Definition

A *physical dipole* has two equal and opposite charges separated by finite distance, d .



$$\vec{\mu} = q\vec{r}_+ - q\vec{r}_- = q(\vec{r}_+ - \vec{r}_-) = q\vec{d}$$

vector \vec{d} is from negative to positive charge.

Molecule	μ/D
HF	1.826
HCl	1.109
CO	-0.1096
OCS	-0.7152
HCN	2.984
H_2O	1.855
H_3N	1.47
$(CH_3)_2CO$	2.88
C_5H_5N	2.19
CH_3CN	3.913

Warning!: many chemistry texts draw dipole moment vectors backwards.

Electric multipole moments depend on choice of origin

Electric multipole moments depend on origin choice but ...

*Lowest non-vanishing multipole moment is always independent of origin choice
while all higher multipole moments depend on origin choice.*

In other words...

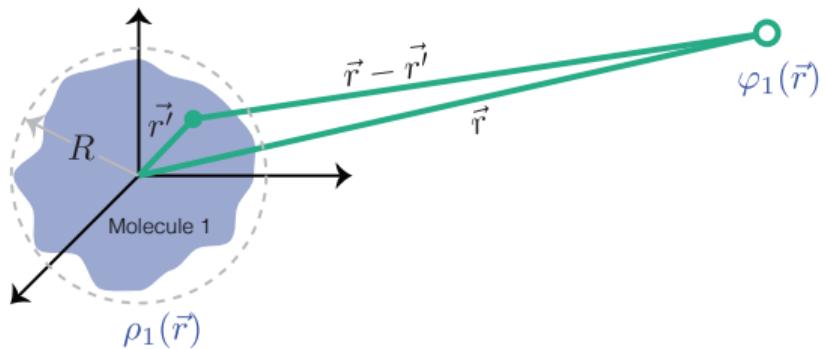
- monopole is always independent of origin.
- if lowest non-zero moment is monopole,
then dipole, quadrupole, octapole, etc, depend on origin.
- if lowest non-zero moment is dipole,
then dipole is independent of origin,
and quadrupole, octapole, hexadecapole, etc, depend on origin.
- if lowest non-zero moment is quadrupole,
then quadrupole is independent of origin,
and octapole, hexadecapole, etc, depend on origin.
- and so on...

Atom or molecule in an electric field

Atom or Molecule in an Electric Field

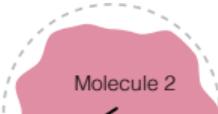
- Electric force is conservative, $\vec{F}(\vec{r}) = -\vec{\nabla}V(\vec{r})$.
- Potential energy of point charge, Q , in $\varphi(\vec{r})$ is $V(\vec{r}) = Q\varphi(\vec{r})$

Consider electrostatic scalar potential, $\varphi_1(\vec{r})$, generated by $\rho_1(\vec{r})$.



- $\rho_2(\vec{r})$ is charge distribution of molecule 2.
- From potential energy of a molecule 2, $\rho_2(\vec{r})$, in electric field of molecule 1:

$$V(\vec{r}) = \int_V \rho_2(\vec{r}) \varphi_1(\vec{r}) d\tau$$



we can calculate force (attractive or repulsive),

Atom or Molecule in an Electric Field

Use Taylor series expansion of $\varphi_1(\vec{r})$ about origin in molecule 2:

$$\varphi_1(\vec{r}) = \varphi_1(0) + \vec{r} \cdot \nabla \varphi_1(0) + \frac{1}{2} \sum_i \sum_j r_i r_j \frac{\partial^2 \varphi_1(0)}{\partial r_i \partial r_j} + \dots$$

Using $\vec{\mathcal{E}} = -\nabla \varphi(\vec{r})$ and dropping “1” subscript we obtain

$$\varphi(\vec{r}) = \varphi(0) - \vec{r} \cdot \vec{\mathcal{E}}(0) + \frac{1}{2} \sum_i \sum_j r_i r_j \frac{\partial \vec{\mathcal{E}}_j(0)}{\partial r_i} + \dots$$

Substituting back into $V(\vec{r}) = \int_V \rho_2(\vec{r}) \varphi(\vec{r}) d\tau$ gives

$$V = \textcolor{blue}{q}_2 \varphi(0) - \textcolor{brown}{\vec{\mu}}_2 \cdot \vec{\mathcal{E}}(0) - \frac{1}{6} \textcolor{pink}{\mathbf{Q}}_2 \cdot \left(\frac{\partial \vec{\mathcal{E}}(0)}{\partial \vec{r}} \right) + \dots$$

$\textcolor{blue}{q}_2$, $\textcolor{brown}{\vec{\mu}}_2$, and $\textcolor{pink}{\mathbf{Q}}_2$ are the multipole moments of $\rho_2(\vec{r})$, i.e., molecule 2.

Atom or Molecule in an Electric Field

$$V = q \varphi(0) - \vec{\mu} \cdot \vec{\mathcal{E}}(0) - \frac{1}{6} \mathbf{Q} \cdot \left(\frac{\partial \vec{\mathcal{E}}(0)}{\partial \vec{r}} \right) + \dots$$

- 1st term is molecule's monopole charge interaction with electric potential,
- 2nd term is molecule's dipole moment interaction with electric field,
- 3rd term is molecule's electric quadrupole moment interaction with electric field gradient.

Assumed atom or molecule charge distribution remains unchanged by electric field.

Polarizability of Atom or Molecule in an Electric Field

- If positions of charges in atom or molecule aren't locked then we would expect that electric field would pull electrons and nuclei in opposite directions.
- If electric field is strong enough it could even pull electrons out of their bound states of atom or molecule.
- At lower electric field strengths, forces pulling electrons and nuclei in opposite directions is balanced out by attractive force between them, but not without affecting electric multipole moments beyond monopole.

Polarizability of Atom or Molecule in External Electric Field

- Effect on electric dipole is addition of an *induced dipole*.

$$\vec{\mu} = \vec{\mu}_0 + \vec{\mu}_{\text{induced}} = \vec{\mu}_0 + \boldsymbol{\alpha} \cdot \vec{\mathcal{E}} \quad \text{where } \boldsymbol{\alpha} \text{ is 2nd rank polarizability tensor}$$

$$\boldsymbol{\alpha} = \begin{pmatrix} \frac{\partial \mu_x}{\partial \mathcal{E}_x} & \frac{\partial \mu_x}{\partial \mathcal{E}_y} & \frac{\partial \mu_x}{\partial \mathcal{E}_z} \\ \frac{\partial \mu_y}{\partial \mathcal{E}_x} & \frac{\partial \mu_y}{\partial \mathcal{E}_y} & \frac{\partial \mu_y}{\partial \mathcal{E}_z} \\ \frac{\partial \mu_z}{\partial \mathcal{E}_x} & \frac{\partial \mu_z}{\partial \mathcal{E}_y} & \frac{\partial \mu_z}{\partial \mathcal{E}_z} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{xzy} & \alpha_{zz} \end{pmatrix}, \quad \text{and has units of m}\cdot\text{C}^2/\text{N}.$$

- $\boldsymbol{\alpha}$ gives magnitude and direction of induced dipole vector from product with $\vec{\mathcal{E}}$ vector.
- Trace of $\boldsymbol{\alpha}$ (sum of diagonal components) is independent of coordinate frame orientation.
- Average or isotropic polarizability is $\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$
Observed polarizability when molecule is rotating in a fluid phase and has all orientations wrt $\vec{\mathcal{E}}$.

Polarizability of Atom or Molecule in External Electric Field

Calculate potential energy by integrating work in bringing neutral non-polar species from infinitely far away where $\vec{\mathcal{E}} = 0$ to distance r where field is $\vec{\mathcal{E}}(\vec{r})$,

$$V = - \int_0^{\vec{\mathcal{E}}} \vec{\mu} \cdot d\vec{\mathcal{E}}$$

Substitute $\vec{\mu} = \vec{\mu}_0 + \alpha \cdot \vec{\mathcal{E}}$ and integrating gives

$$V = -\vec{\mu}_0 \cdot \vec{\mathcal{E}} - \frac{1}{2} \vec{\mathcal{E}} \cdot \alpha \cdot \vec{\mathcal{E}}$$

- 1st term is potential energy of permanent dipole in $\vec{\mathcal{E}}$ field
- 2nd term is potential energy of induced dipole in $\vec{\mathcal{E}}$ field
- Alternative quantity, α_0 , often used, called *polarizability volume*, is given by

$$\alpha_0 = \frac{\alpha}{4\pi\epsilon_0}$$

- α_0 is comparable to effective volume of electronic charge cloud of atom or molecule.

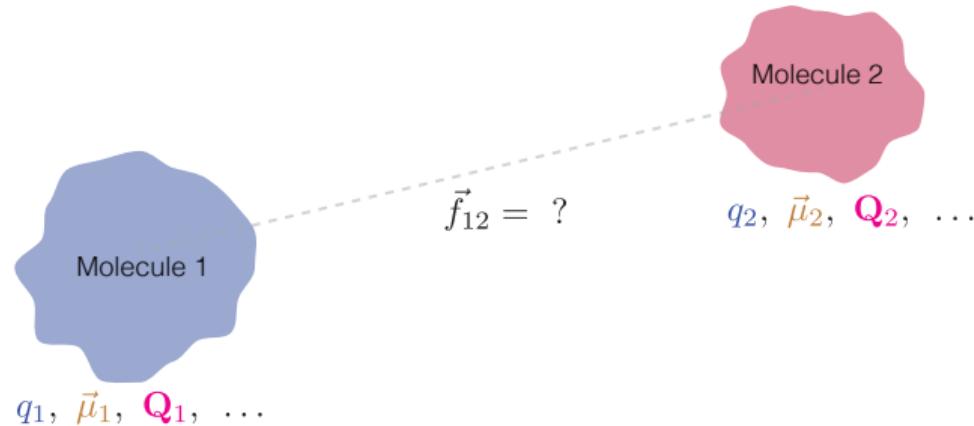
Polarizability of Atoms

Static Average Electric Dipole Polarizabilities for Ground State Atoms in units of Å³.

IA																VIIIA	
0.667 1H	5.60 3Li															0.205 2He	
24.33 3Li	5.60 4Be															3.03 5B	1.67 6C
24.11 11Na	10.6 12Mg															1.10 7N	0.802 8O
43.06 19K	22.8 20Ca	17.8 21Sc	14.6 22Ti	12.4 23V	11.6 24Cr	9.4 25Mn	8.4 26Fe	7.5 27Co	6.8 28Ni	6.2 29Cu	5.75 30Zn	8.12 31Ga	5.84 32Ge	4.31 33As	3.77 34Se	3.05 35Br	2.484 36Kr
47.24 37Rb	27.6 38Sr	22.7 39Y	17.9 40Zr	15.7 41Nb	12.8 42Mo	11.4 43Tc	9.6 44Ru	8.6 45Rh	4.8 46Pd	6.78 47Ag	7.36 48Cd	10.2 49In	6.28 50Sn	6.6 51Sb	5.5 52Te	5.35 53I	4.044 54Xe
59.42 55Cs	39.7 56Ba	31.1 57La	16.2 72Hf	13.1 73Ta	11.1 74W	9.7 75Re	8.5 76Os	7.6 77Ir	6.5 78Pt	5.8 79Au	5.02 80Hg	7.6 81Tl	6.98 82Pb	7.4 83Bi	6.8 84Po	6.0 85At	5.3 86Rn
48.60 87Fr	38.3 88Ra	32.1 89Ac															

Lanthanide Series	29.6 58Ce	28.2 59Pr	31.4 60Nd	30.1 61Pm	28.8 62Sm	27.7 63Eu	23.5 64Gd	25.5 65Tb	24.5 66Dy	23.6 67Ho	22.7 68Er	21.8 69Tm	20.9 70Yb	21.9 71Lu
Actinide Series	32.1 90Th	25.4 91Pa	24.9 92U	24.8 93Np	24.5 94Pu	23.3 95Am	23.0 96Cm	22.7 97Bk	20.5 98Cf	19.7 99Es	23.8 100Fm	18.2 101Md	16.4 102No	16.4 103Lr

Intermolecular forces



$$\boxed{\varphi_1(\vec{r}) = \frac{1}{4\pi\epsilon_0} \left[\frac{q_1}{r} + \frac{\vec{\mu}_1 \cdot \vec{r}}{r^3} + \frac{1}{2} \frac{\vec{r} \cdot \mathbf{Q}_1 \cdot \vec{r}}{r^5} + \dots \right] \quad \text{recalling } \vec{\mathcal{E}}_1(\vec{r}) = -\nabla \varphi_1(\vec{r})}$$

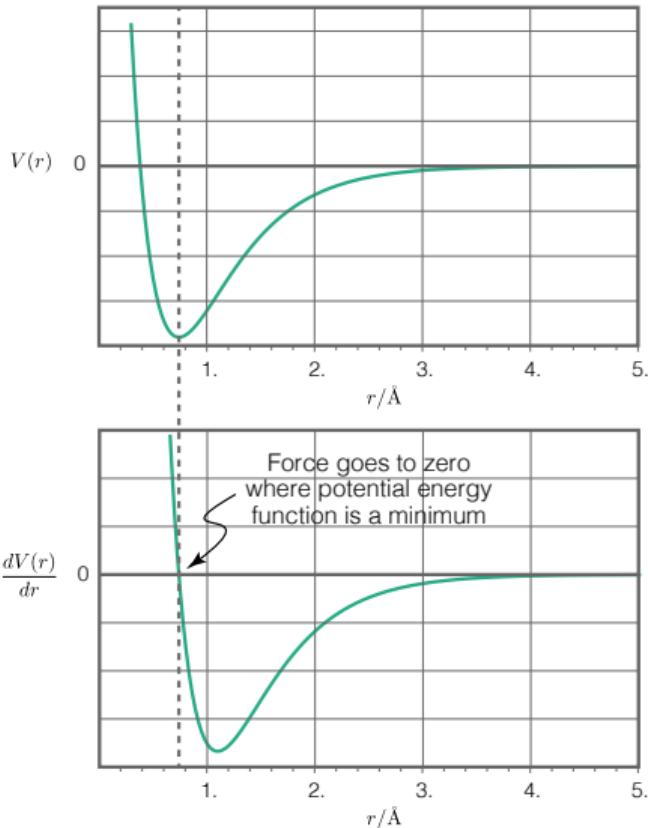
Substitute into

$$\boxed{V_2 = q_2 \varphi_1(0^*) - \vec{\mu}_2 \cdot \vec{\mathcal{E}}_1(0^*) - \frac{1}{6} \mathbf{Q}_2 \cdot \left(\frac{\partial \vec{\mathcal{E}}_1(0^*)}{\partial \vec{r}} \right) + \dots \quad \text{recalling } \vec{f}_{12} = -\vec{\nabla} V_2}$$

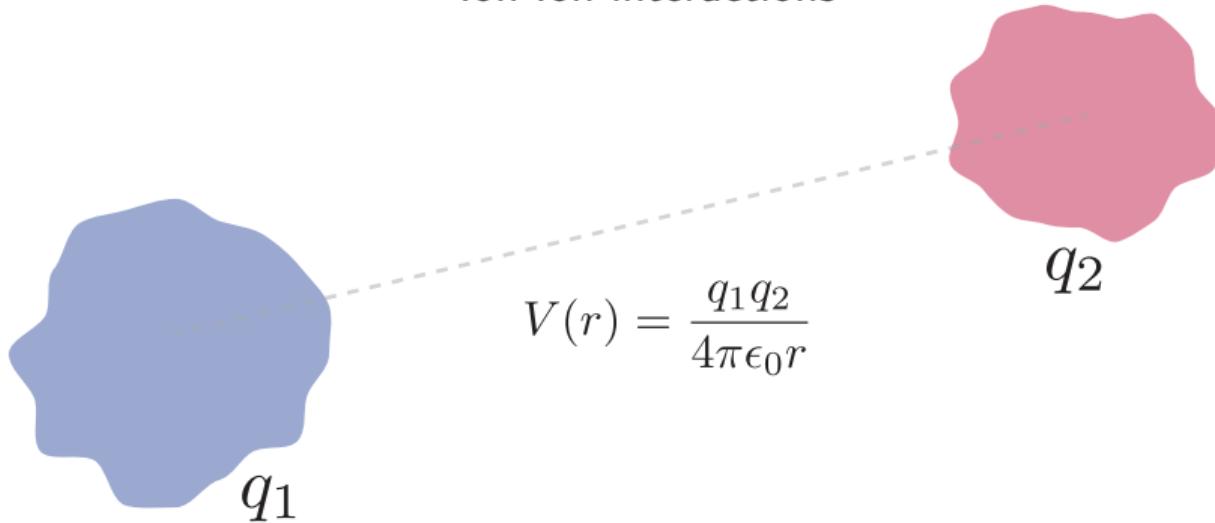
$0^* \equiv \text{origin inside molecule 2.}$

Intermolecular forces

- There will be an additional repulsive force at very short intermolecular distance molecules which arises from electron–electron interactions — not included in treatment so far, e.g, the force between cations and anions eventually becomes repulsive at short distance.
- Assume all forces acting between molecules are conservative
- Force between atoms and molecules goes to zero where the $V(r)$ is a minimum.



Ion-Ion interactions



Ion-Ion interactions

- Between cation and anion, e.g., Na^+ and Cl^- , potential energy is

$$V(r) = \frac{q_{\text{Na}}q_{\text{Cl}}}{4\pi\epsilon_0 r}$$

- Can't be whole story, since potential energy predicts Na^+ and Cl^- crash into each other at $r = 0$ and give infinitely negative potential energy.
- Need repulsive force to describe repulsions between electrons and nuclei of atoms.
- One popular choice is

$$V_{\text{repulsive}} = b/r^n \quad \text{where } n \approx 8 - 12$$

where n is called the *Born exponent*.

Ion-Ion interactions

Adding repulsion to electrostatic potential gives

$$V(r) = \frac{q_{\text{Na}}q_{\text{Cl}}}{4\pi\epsilon_0 r} + \frac{b}{r^n}$$

Calculate force and set it equal to zero

$$F = -\frac{dV}{dr} \Big|_{r=r_e} = -\frac{q_{\text{Na}}q_{\text{Cl}}}{4\pi\epsilon_0 r_e^2} - \frac{nb}{r_e^{n+1}} = 0$$

r_e is equilibrium distance where $F = 0$

Solve for b

$$b = -\frac{q_{\text{Na}}q_{\text{Cl}}}{4\pi\epsilon_0 n} r_e^{n-1}$$

Putting b back into expression for $V(r)$ gives

$$V_e = \frac{q_{\text{Na}}q_{\text{Cl}}}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

V_e is potential when $r = r_e$

Ion-Ion Repulsions - Born Exponents

Attractive/repulsive potential energy for single cation-anion pair, M^+X^-

$$V_e = \frac{q_M q_X}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

Ion type	<i>n</i>
He, Li ⁺	5
Ne, Na ⁺ , F ⁻	7
Ar, K ⁺ , Cu ⁺ , Cl ⁻	9
Kr, Rb ⁺ , Ag ⁺ , Br ⁻	10
Xe, Cs ⁺ , Au ⁺ , I ⁻	12

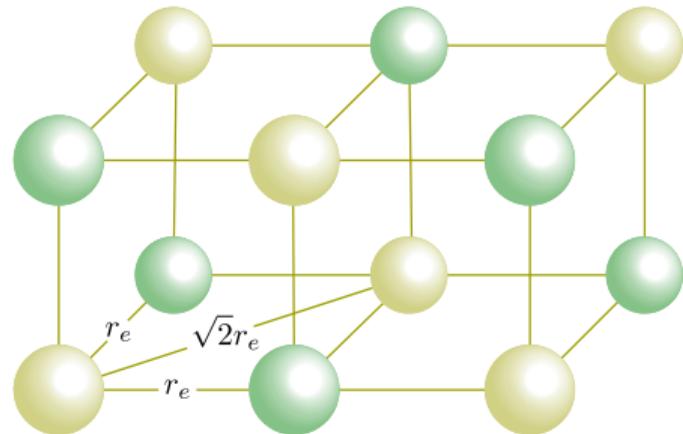
For crystal with mixed-ion type, approximate with average of *n* in right table (6 for LiF, for example).

Lattice Energy of NaCl crystal

Attractive/repulsive potential energy for single cation-anion pair, $\text{Na}^+ - \text{Cl}^-$

$$V_e = \frac{q_{\text{Na}} q_{\text{Cl}}}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

Need to consider full 3D NaCl crystal structure.

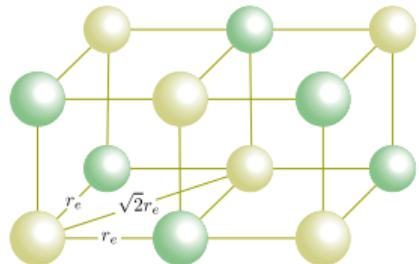


Each Na^+ surrounded by 6 Cl^- at r_e . V_e from these interactions is

$$V_e = -\frac{6q_e^2}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right) + \dots$$

q_e is fundamental charge constant.

Lattice Energy of NaCl crystal



Next nearest neighbors are 12 Na^+ ions at $\sqrt{2}r_e$, so

$$V_e = -\frac{6q_e^2}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right) + \frac{12q_e^2}{4\pi\epsilon_0 \sqrt{2}r_e} \left(1 - \frac{1}{n}\right) + \dots$$

Continuing this approach we find 8 Cl^- at $\sqrt{3}r_e$, 6 Na^+ at $\sqrt{4}r_e$, 24 Cl^- at $\sqrt{5}r_e$, 24 Na^+ at $\sqrt{6}r_e$, and so on.

$$V_e = -\frac{q_e^2}{4\pi\epsilon_0 r_e} \underbrace{\left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} + \dots\right)}_{\text{Converges to } A = 1.7476} \left(1 - \frac{1}{n}\right)$$

A is the *Madelung constant* for NaCl.

Typical Madelung constants

Structure	Crystal form	A
NaCl	FCC	1.74756
CsCl	BCC	1.76267
CaCl ₂	Cubic	2.365
CaF ₂	Cubic	2.51939
ZnS	Hexagonal	1.63805

Lattice Energy of NaCl crystal

For mole of cations experiencing this potential

$$V_e(\text{cation}) = -\frac{N_A A q_e^2}{4\pi \epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

Moving anion to center of calculation we find for mole of anions

$$V_e(\text{anion}) = -\frac{N_A A q_e^2}{4\pi \epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

Taken together total potential for 1 mole of NaCl

$$\overline{V}_e = \frac{1}{2} (V_e(\text{cation}) + V_e(\text{anion})) = -\frac{N_A A q_e^2}{4\pi \epsilon_0 r_e} \left(1 - \frac{1}{n}\right)$$

Multiply by $\frac{1}{2}$ to avoid double counting.

Lattice Energy of NaCl crystal

Example

Calculate *lattice energy* of NaCl with $n = 8.4$ using sum of Na^+ and Cl^- radii as r_e .

Radii are $r_{\text{Na}^+} = 1.02 \text{ \AA}$ and $r_{\text{Cl}^-} = 1.81 \text{ \AA}$ which has sum $r_e = 2.83 \text{ \AA}$.

$$\overline{V}_e = -\frac{N_A(1.7476)q_e^2}{4\pi\epsilon_0(2.83 \text{ \AA})} \left(1 - \frac{1}{8.4}\right) = -756 \text{ kJ/mol}$$

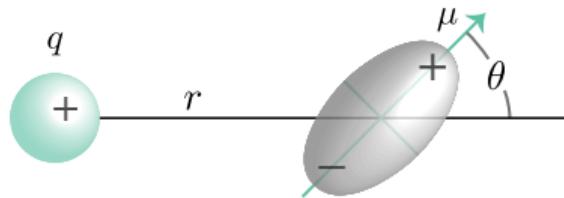
Compares well to lattice energy of -787 kJ/mol obtained with Born-Haber cycle.

Ion-Dipole interactions



Ion-Dipole interactions

Consider ion interacting with neutral molecule with permanent electric dipole moment.



Potential has form

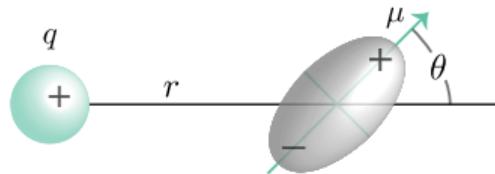
$$V(r, \theta) = -\frac{\mu q}{4\pi\kappa\epsilon_0} \frac{\cos\theta}{r^2}$$

κ is relative permittivity of the medium.

Attractive or repulsive depending on relative orientation of dipole.

Strength falls off with $1/r^2$.

Ion-Dipole interactions - Thermal Average in Fluid Phase



In fluid phase isotropic tumbling of dipole averages away interaction but doesn't average completely to zero.

Interaction energy leads to preferred orientations and temperature dependent non-zero average is

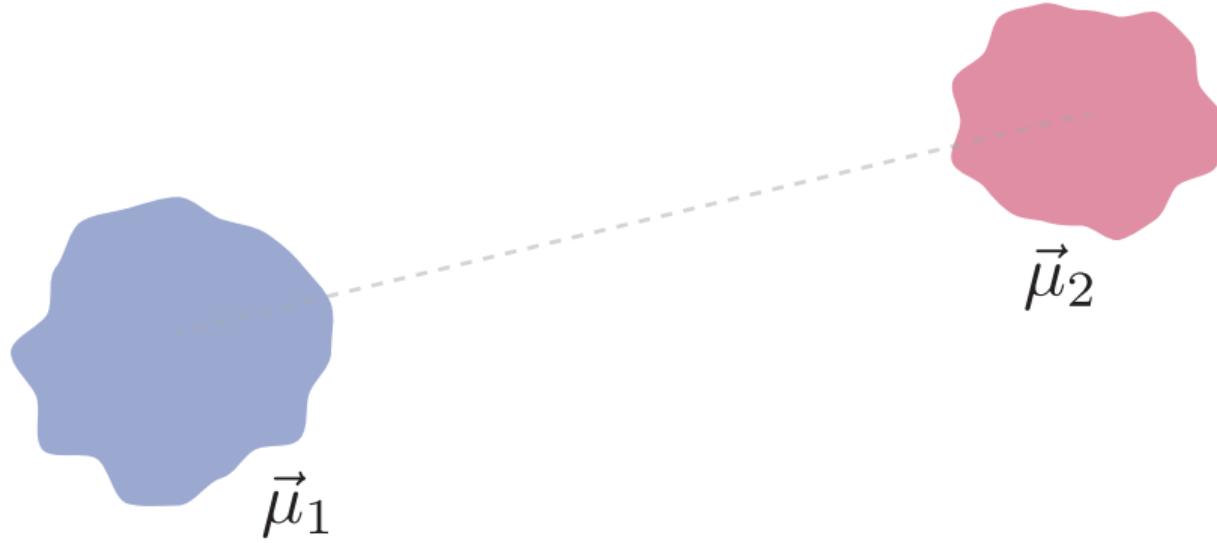
$$\langle V(r) \rangle = \frac{-q^2 \mu^2}{96\pi^2 \kappa^2 \epsilon_0^2} \frac{1}{r^4} \frac{1}{k_B T}$$

Thermal averaged interaction is always attractive.

Falls off with a $1/r^4$ dependence—short compared to $1/r^2$ of static.

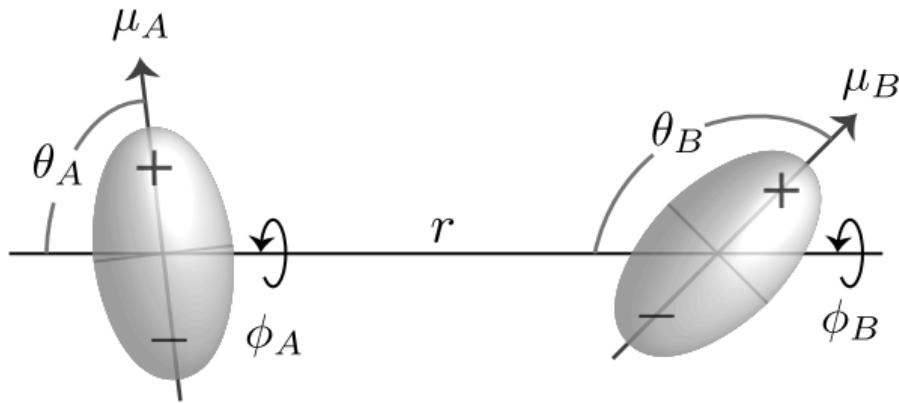
Decreases in magnitude with increasing temperature.

Dipole-Dipole interactions



Dipole-Dipole interactions

Consider interaction of 2 neutral molecules, both having permanent electric dipole moment.

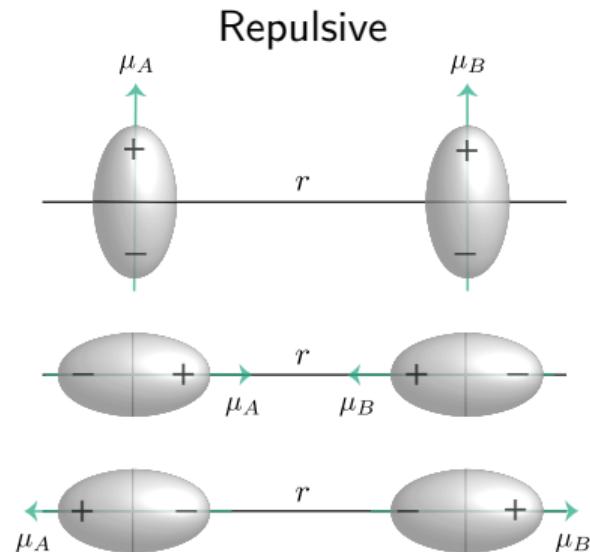
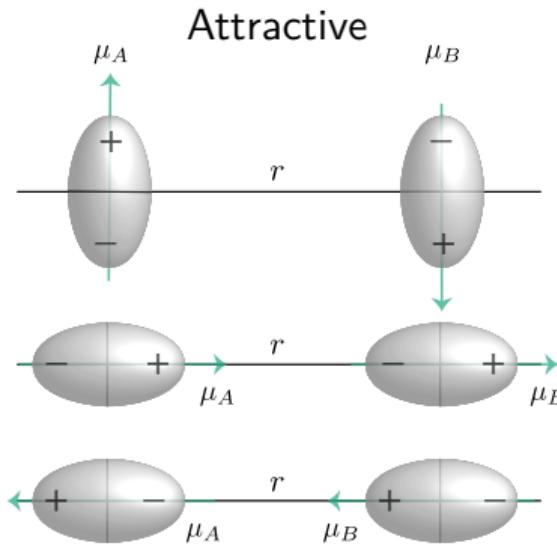


Potential energy for interaction of 2 dipoles has form

$$V(r, \theta_A, \theta_B, \phi_A, \phi_B) = -\frac{\mu_A \mu_B}{4\pi\kappa\epsilon_0} \frac{[2 \cos \theta_A \cos \theta_B - \sin \theta_A \sin \theta_B \cos(\phi_B - \phi_A)]}{r^3}$$

Dipole-Dipole interactions

Depending on their relative orientations the interaction can be



Dipole-Dipole interactions - - Thermal Average in Fluid Phase

Each dipole randomly reorients due to thermal fluctuations and average potential is

$$\langle V(r) \rangle = -\frac{1}{3} \frac{\mu_a^2 \mu_B^2}{(4\pi\kappa\epsilon_0)^2} \frac{1}{r^6} \frac{1}{k_B T}$$

- Called the *Keesom energy*.
- Falls off faster, $1/r^6$, than static interaction, $1/r^3$.
- Decreases in magnitude with increasing temperature.

Induced Dipole interactions

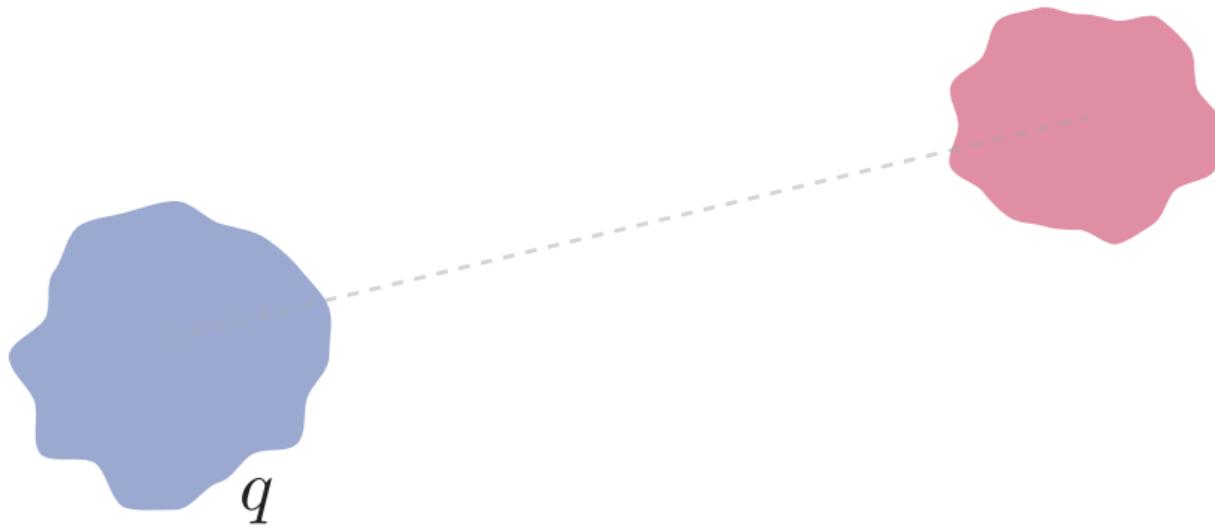


Case 1: Ion attracted to nonpolar neutral species



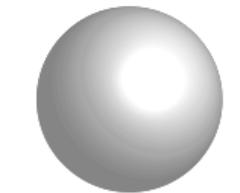
Case 2: Dipole attracted to nonpolar neutral species

Ion–induced dipole interaction

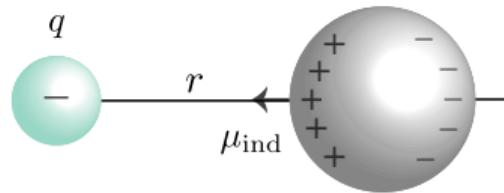


Ion-induced dipole interaction

Nearby ion can induces dipole on non-polar species.



neutral
no ions present



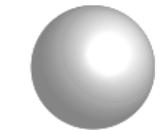
induced dipole
with ion present

Induced dipole is proportional to electric field produced at non-polar neutral species by distant ion or dipole,

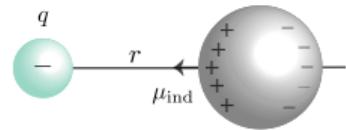
$$\vec{\mu}_{\text{ind}} = \alpha \cdot \vec{\mathcal{E}}$$

where α is polarizability tensor.

Ion-induced dipole interaction



neutral
no ions present



induced dipole
with ion present

Potential energy calculated by integrating work required to bring neutral non-polar species from ∞ where $\vec{\mathcal{E}} = 0$ to r where field is $\vec{\mathcal{E}}(\vec{r})$

$$V(r) = - \int_0^{\vec{\mathcal{E}}} \vec{\mu}_{\text{induced}} \cdot d\vec{\mathcal{E}} = - \int_0^{\vec{\mathcal{E}}} \alpha \cdot \vec{\mathcal{E}} d\vec{\mathcal{E}}$$

Taking electric field of an ion as

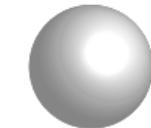
$$\vec{\mathcal{E}} = \frac{q}{4\pi\epsilon_0 r^2} \vec{e}_r$$

we find

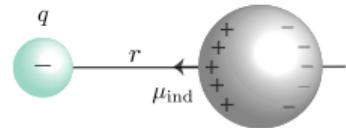
$$V(r) = -\frac{1}{2} \frac{\alpha q^2}{(4\pi\kappa\epsilon_0)^2 r^4} = -\frac{\alpha_0 q^2}{8\pi\kappa\epsilon_0} \frac{1}{r^4}$$

α is average or isotropic polarizability.

Ion-induced dipole interaction



neutral
no ions present



induced dipole
with ion present

$$V(r) = -\frac{1}{2} \frac{\alpha q^2}{(4\pi\kappa\epsilon_0)^2 r^4} = -\frac{\alpha_0 q^2}{8\pi\kappa\epsilon_0} \frac{1}{r^4}$$

No need for thermal average since dipole is always induced along \vec{r} .

The more polarizable a species is the greater the attraction.

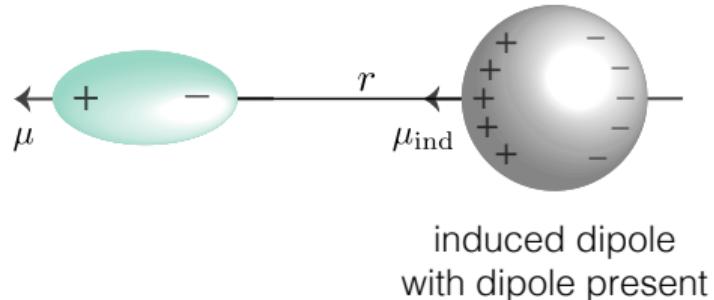
Atom	$\alpha_0/10^{-30} \text{ m}^3$	Molecule	$\alpha_0/10^{-30} \text{ m}^3$
He	0.20	H_2	0.80
Ne	0.40	N_2	1.74
Ar	1.66	CO_2	2.91
Kr	2.54	NH_3	2.26
Xe	4.15	CH_4	2.61
Cs	42.0	C_6H_6	10.4
		CCl_4	11.7

Dipole–induced dipole interaction



Dipole–induced dipole interaction

A dipole can induce a dipole in a non-polar neutral species.



For electric field of dipole we obtain interaction potential

$$V(r) = -\frac{\alpha \mu^2}{(4\pi\kappa\epsilon_0)^2} \frac{(3 \cos^2 \theta + 1)}{r^6}.$$

Called *Debye energy*

Averaging of all orientations of the dipole gives

$$\langle V(r) \rangle = -\frac{2\alpha \mu^2}{(4\pi\kappa\epsilon_0)^2} \frac{1}{r^6}.$$

Induced Dipole - Induced Dipole Interaction



Dispersion (London) forces

Dispersion (London) interactions

What about attractions between neutral, non-polar molecules or atoms?



He atoms are neutral and non-polar, yet still attract each other.
He boiling point is 4 K.

Correlated motion of electrons in atoms that leads to net attraction.



$$V(r) = -\frac{3}{2} \frac{I_A I_B}{I_A + I_B} \frac{\alpha_A \alpha_B}{r^6}$$

I_A and I_B are ionization energies and α_A and α_B are the polarizabilities.

The higher the polarizability the more easily the electrons can become correlated to motion of electrons on neighboring atoms or molecules.