

How Do Geckos Defy Gravity?

Lecture 9. Electrostatic Nature of Intermolecular forces

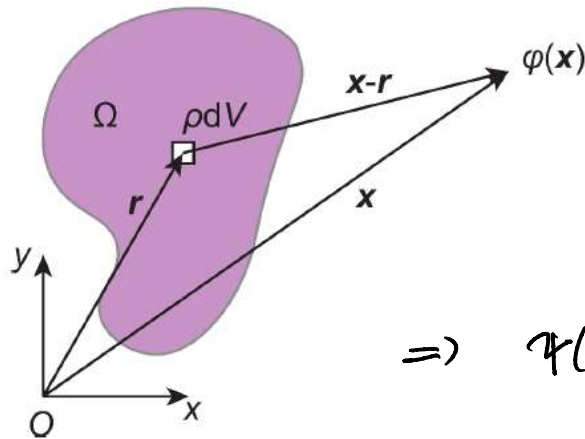
Questions to be answered

- What is the origin of intermolecular and surface forces?
- How to predict the strength?

Perspectives

- Basic derivations of intermolecular interactions
- Understanding the power laws of different interactions
- Comparison between different interactions

Extension of Coulomb's Law



$$\psi(x) = \frac{1}{4\pi\epsilon_0} \int_{\Omega} \frac{\rho(r)}{|r-x|} d^3r$$

\vec{x} very large \rightarrow Taylor expansion $\vec{r}=0, \frac{1}{|\vec{r}-\vec{x}|}$

Taylor expansion: $f(x)|_{x=0} = f(x_0) + f'(x_0)(x-x_0) + \frac{1}{2} f''(x_0)(x-x_0)^2 + \dots$

$$\Rightarrow \varphi(\vec{x}) = \frac{1}{4\pi\epsilon_0} \int \left(\frac{1}{|\vec{r}-\vec{x}|} \Big|_{r=0} + \vec{r} \cdot \vec{\nabla} \frac{1}{|\vec{r}-\vec{x}|} \Big|_{r=0} + \dots \right) \rho(r) d^3r$$

$$= \frac{1}{4\pi\epsilon_0} \left[\underbrace{\int \frac{\rho(r)}{|\vec{x}|} d^3r}_{\text{Monopole}} + \underbrace{\int \frac{\vec{r} \cdot \vec{\nabla} \rho(r)}{|\vec{x}|^3} d^3r}_{\text{Dipole}} + \dots \right]$$

\rightarrow total charge

$$q = \int_{\Omega} \rho(r) d^3r$$

\rightarrow dipole moment

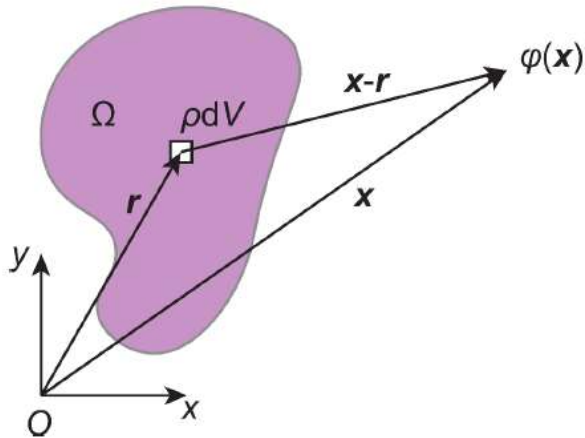
$$u = \int \vec{r} \cdot \rho(r) d^3r$$

Extension of Coulomb's Law

Example:



Dipole moment $\vec{u} = q \cdot \vec{e}$



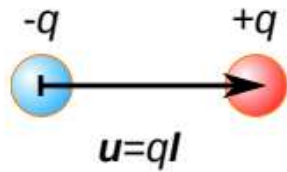
$$\varphi(\vec{x}) = \frac{1}{4\pi\epsilon_0} \frac{\vec{u} \cdot \vec{x}}{|\vec{x}|^3}$$

Dipole Moment

Dipole moment orientation: From -q to +q

$$q = \int_{\Omega} \rho(r) d^3r$$

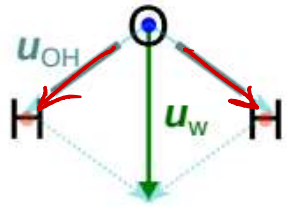
$$u = \int_{\Omega} r \rho(r) d^3r$$



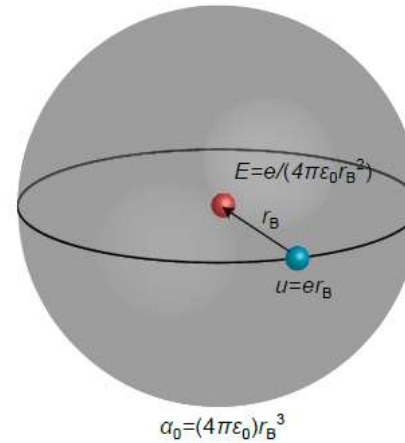
Unit: C·m (SI) or Debye $1D = 0,21e \cdot \text{\AA}$

Examples:

H₂O: $u_w = 1,85D$



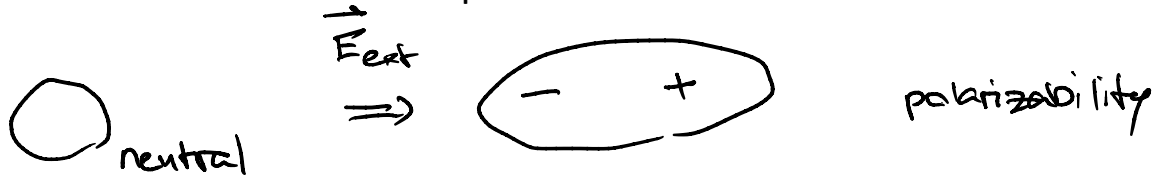
Bohr atom: transient dipole



$u_{tr} = 2,54D$

The Electric Polarizability

How much can the electron cloud be displaced under electric field? \rightarrow Polarizability $\alpha = \frac{|u|}{|E|}$



1. Electronic polarizability

Case: Bohr atom

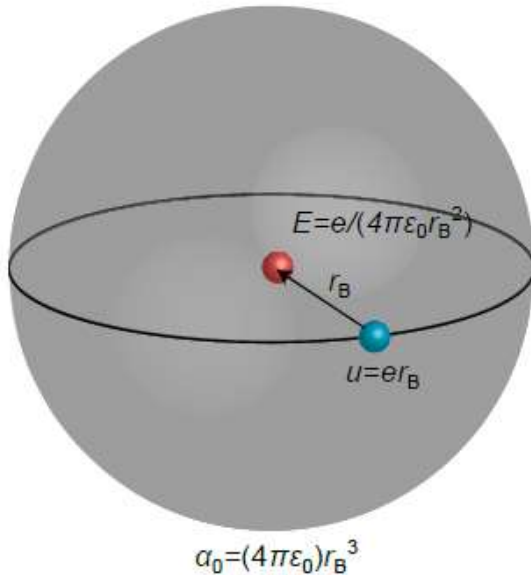
r_B : Bohr radius

$$|\vec{u}| = e \cdot r_B \quad , \quad |\vec{E}| = \frac{e}{4\pi\epsilon_0 r_B^2} \quad (\text{Coulomb's law})$$

$$\alpha_c = \frac{|\vec{u}|}{|\vec{E}|} = \underbrace{4\pi\epsilon_0}_{\text{Prefactor}} \cdot \underbrace{r_B^3}_{\text{Volume of } e^- \text{-cloud}}$$

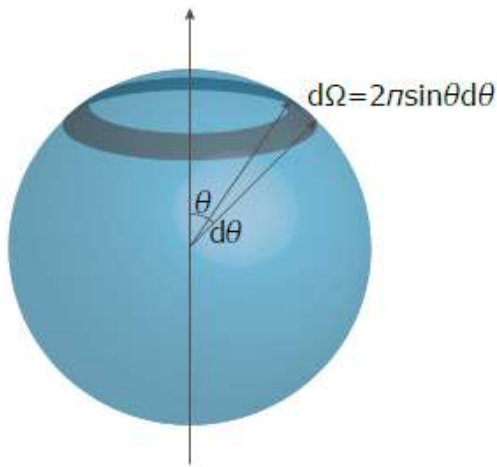
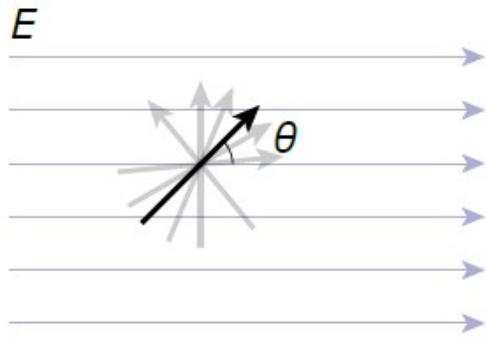
\rightarrow Larger e^- cloud, more polarizable

$$\alpha_c(\text{Ar}) \approx 4 \cdot \alpha_c(\text{Ne})$$



The Electric Polarizability

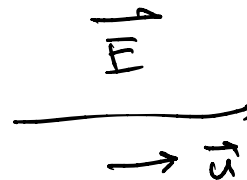
2. Dipolar polarizability (comes from orientation of permanent dipole)



Energy of \vec{u} in \vec{E} :

$$W_{uE} = -\vec{u} \cdot \vec{E} = -u \cdot E \cdot \cos \theta$$

Case:



$$W = -u \cdot E \quad (\text{low})$$



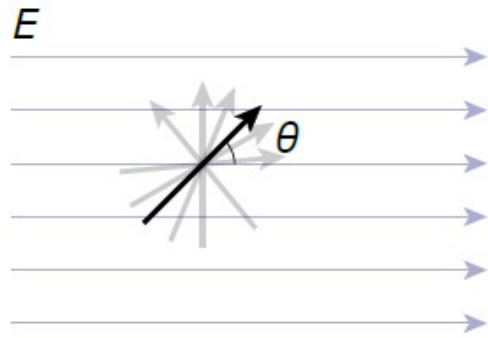
$$W = uE \quad (\text{high})$$

$$\hat{u} = \frac{\int_{\Omega} u \cdot \cos(\theta) \cdot \exp\left(\frac{-W_{uE}(\theta)}{k_B T}\right) d\Omega}{\int_{\Omega} \exp\left(\frac{-W_{uE}(\theta)}{k_B T}\right) d\Omega}$$

$$y = \cos(\theta) \quad , \quad \beta = \frac{uE}{k_B T} \quad , \quad \int_{\Omega} \dots d\Omega = \int_0^{\pi} \dots (2\pi \sin(\theta) d\theta)$$

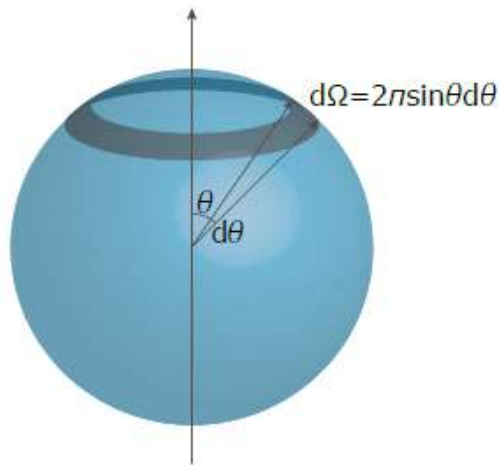
The Electric Polarizability

2. Dipolar polarizability (comes from orientation of permanent dipole)

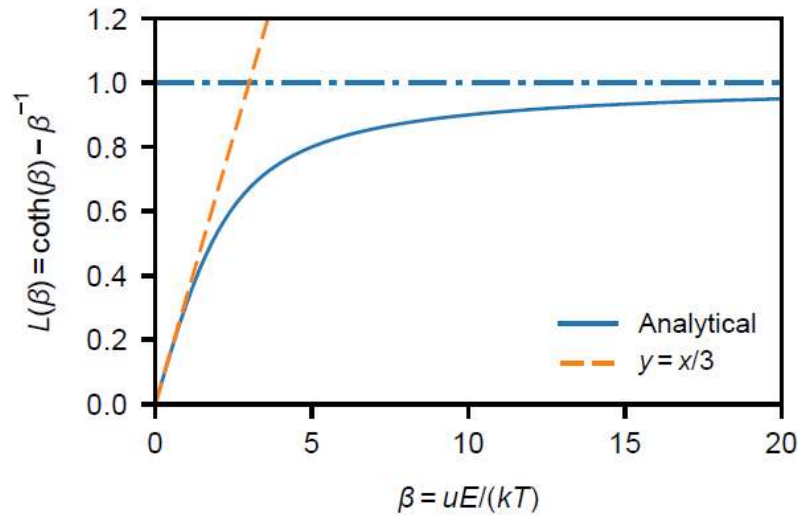


$$\hat{u} = u \left[\coth \beta - \frac{1}{\beta} \right]$$

Langevin - function



The Electric Polarizability



Case $k_B T \gg uE$ ($\beta \ll 1$)


$$\hat{u} = \frac{\beta}{3}$$

$$\Rightarrow \alpha_{\text{dip}} = \frac{\hat{u}}{E} = \frac{1}{3} \frac{u^2}{k_B T} \quad (k_B T \gg uE)$$

Total electric polarizability
($\beta \ll 1$)

$$\alpha = \alpha_0 + \alpha_{\text{dip}} = \alpha_0 + \frac{1}{3} \frac{u^2}{k_B T}$$

THERE ARE FOUR FUNDAMENTAL FORCES BETWEEN PARTICLES:
(1) **GRAVITY**, WHICH OBEYS THIS INVERSE SQUARE LAW:


$$F_{\text{gravity}} = G \frac{m_1 m_2}{d^2}$$


OK...

(2) **ELECTROMAGNETISM**, WHICH OBEYS THIS INVERSE-SQUARE LAW:

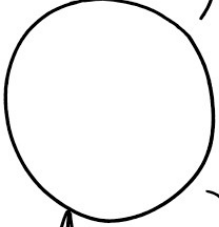
$$F_{\text{static}} = k_e \frac{q_1 q_2}{d^2}$$

AND ALSO MAXWELL'S EQUATIONS



ALSO WHAT?


(3) THE **STRONG NUCLEAR FORCE**, WHICH OBEYS, UH...
...WELL, UMM...
...IT HOLDS PROTONS AND NEUTRONS TOGETHER.



I SEE.

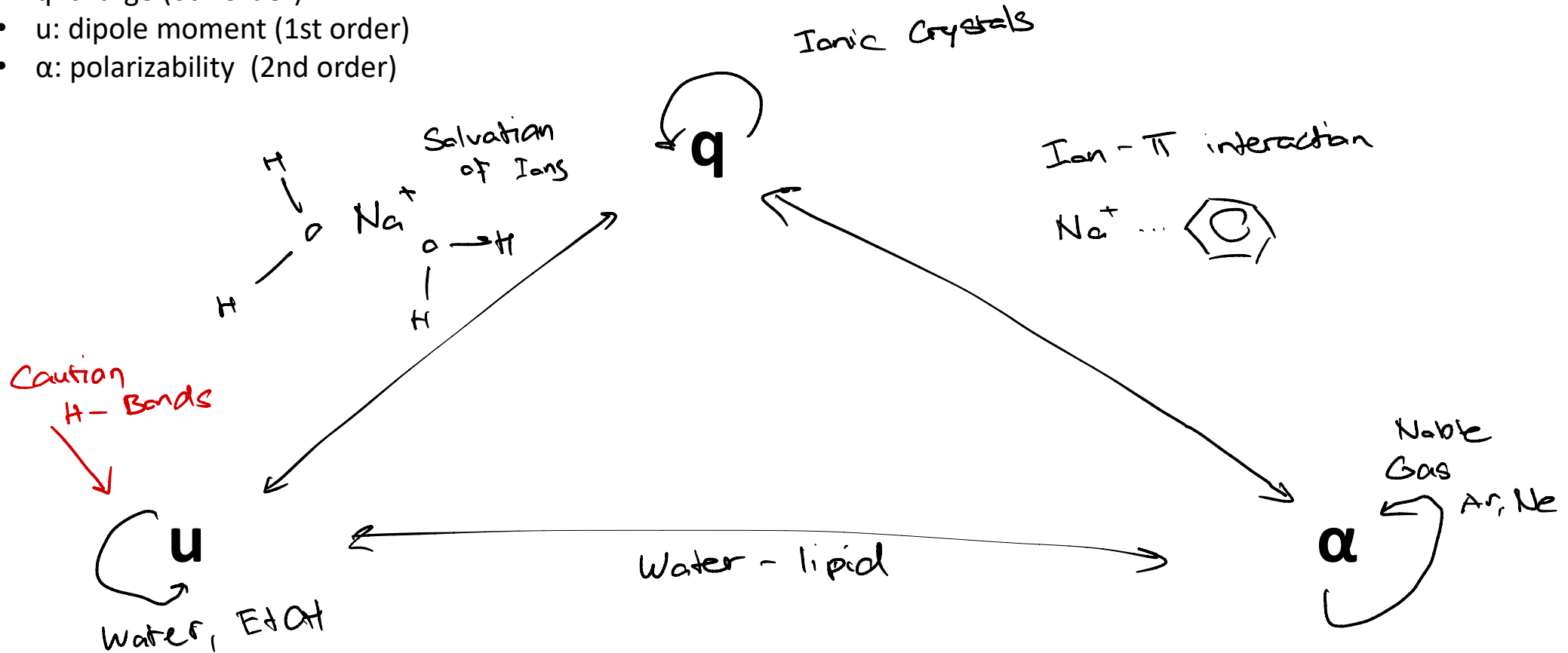
IT'S STRONG.

AND (4) THE **WEAK FORCE**. IT [MUMBLE MUMBLE] RADIOACTIVE DECAY [MUMBLE MUMBLE]
THAT'S NOT A SENTENCE. YOU JUST SAID 'RADIO-
-AND THOSE ARE THE **FOUR FUNDAMENTAL FORCES!**

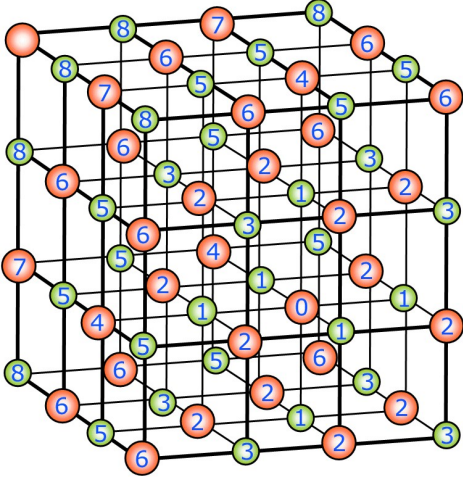


Interplay Between Charge Components

- q : charge (0th order)
- u : dipole moment (1st order)
- α : polarizability (2nd order)



Charge-Charge (Coulomb) interaction: q-q



$$w_{q_1 q_2}(r) = \frac{q_1 q_2}{4\pi \epsilon_0 \epsilon_r r} \propto r^{-1}$$

$\underbrace{\epsilon_r}_{\text{environment}}$

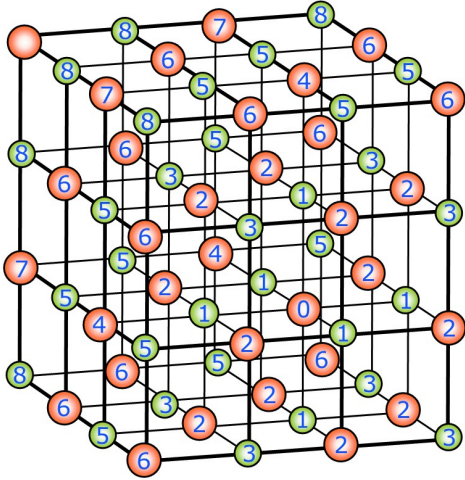
Example 1:

$$\text{Na}^+ \dots \text{Cl}^- (\text{vacuum} \Rightarrow \epsilon_r = 1) \rightarrow w_{q_1 q_2} = -200 k_B T \text{ (300K)}$$

$$\text{Na}^+ \dots \text{Cl}^- (\text{water} \Rightarrow \epsilon_r = 78) \rightarrow w_{q_1 q_2} = -2.6 k_B T$$

Caution: Not applicable for all Ionic Crystals

Charge-Charge (Coulomb) interaction: q-q



Example 2: lattice energy

$$W_{\text{FCC}} = \frac{e^2}{4\pi \epsilon_0} \cdot \sum_{i=1}^{\infty} \frac{N_i \cdot s_i}{r_i}$$

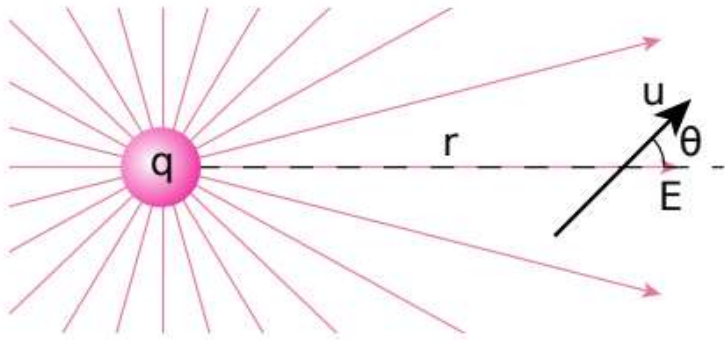
FCC
sign

↪ # Neighbors

↪ distance

$$= - \underbrace{1.748}_{\text{Madelung constant}} \cdot \frac{e^2}{4\pi \epsilon_0 \cdot r_{\text{Na-Cl}}}$$

Charge-Dipole (Coulomb) interaction: q-u



Angle-dependent energy: $E = \frac{q}{4\pi\epsilon_0\epsilon_r r^2}$

$$W_{uE} = -u \cdot E \cos\theta$$

$$= -\frac{qu \cdot \cos\theta}{4\pi\epsilon_0\epsilon_r \cdot r^2} \propto r^{-2}$$

Example

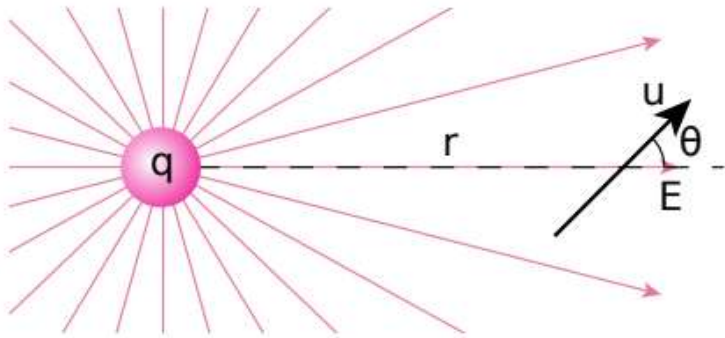
$\text{Na}^+ \dots \text{H}_2\text{O}$ (vacuum, $\epsilon_r = 1$)

$\text{Na}^+ \dots \text{H}_2\text{O}$ (water, $\epsilon_r = 78$)

$$r = 2.35 \text{ \AA}, \quad W = -40 k_B T$$

$$|W| \ll 1 k_B T$$

Charge-Dipole (Coulomb) interaction: q-u



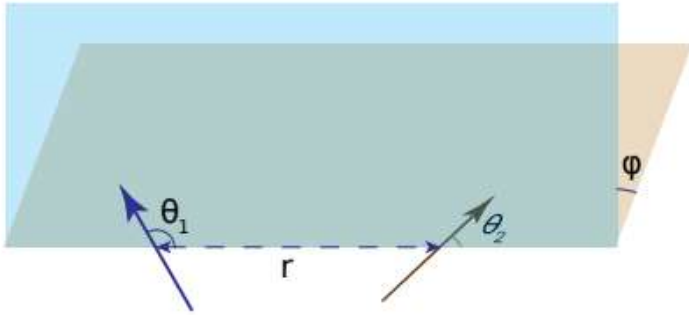
Angle-averaged energy: (Boltzmann-stat)

$$\langle \omega_{qu} \rangle = \frac{\int_{\Omega} \omega_{qu}(\theta) \cdot \exp\left(-\frac{\omega_{qu}(\theta)}{k_B T}\right) d\Omega}{\int_{\Omega} \exp\left(-\frac{\omega_{qu}(\theta)}{k_B T}\right) d\Omega}$$

$$\langle \omega_{qu} \rangle = -k_B T \beta L(\beta) \stackrel{(\beta \ll 1)}{\sim} -k_B T \cdot \frac{\beta^2}{3} = -\frac{1}{3} \frac{q^2 u^2}{(4\pi\epsilon_0 \epsilon_r)^2 r^4 k_B T} \propto r^{-4}$$

Free energy = $\frac{1}{2}$ · internal energy $\propto \epsilon_r^2$

Dipole-Dipole (Keesom) interaction: u-u



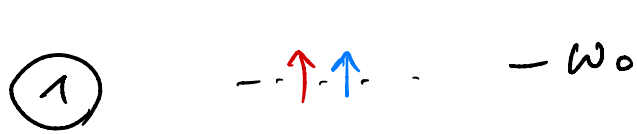
Angle-dependent energy:

4 variables: $\theta_1, \theta_2, r, \varphi$

$$W_{uu} = \frac{-u_1 u_2}{4\pi\epsilon_0 \epsilon_r r^3} [2 \cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\varphi]$$

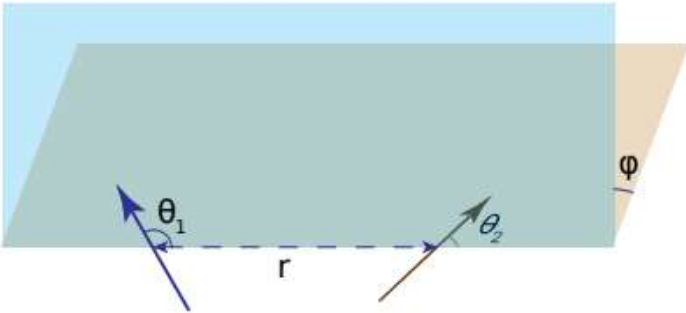
$\propto r^{-3}$ $\leftarrow := W_0 < 0$

Example: $\varphi = 0$



③ < ② < ① < ④

Dipole-Dipole (Keesom) interaction: u-u



Angle-averaged energy:

$$\hat{W}_{uu} = - \frac{2u_1^2 u_2^2}{3(4\pi \epsilon_0 \epsilon_r)^2 k_B T r^6} \propto r^{-6}$$

\downarrow
 \downarrow Langevin

\rightarrow First component of vdW interaction

Example

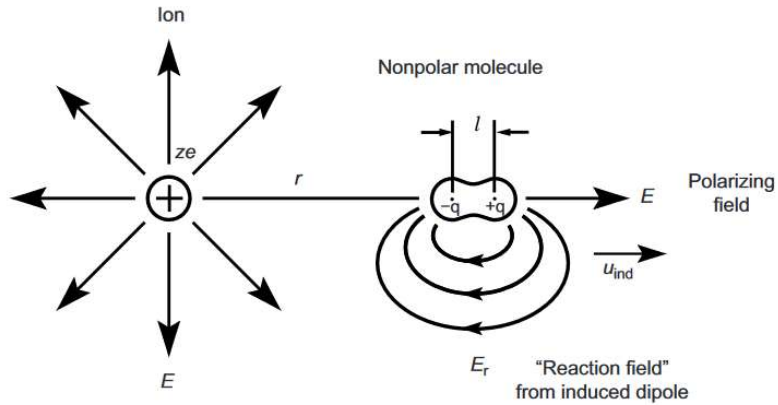
$H_2O \dots H_2O$ (Vacuum)

$H_2O \dots H_2O$ (water)

$$r = 3 \text{ \AA} \Rightarrow \hat{W}_{uu} = -6.2 k_B T$$

$$\hat{W}_{uu} = -10^{-3} k_B T$$

Charge-Induced Dipole interaction: q- α



Internal energy:

$$W_{q\alpha} = - u_{ind} \cdot E = - \alpha \cdot E^2$$

$$u_{ind} = \alpha \cdot E$$

$$\text{Free energy: } W_{free} = - \frac{1}{2} \alpha E^2$$

Similar to capacitor

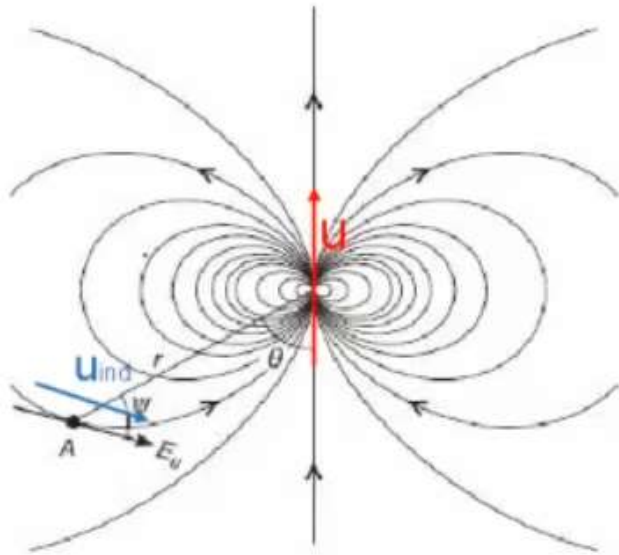
$$\alpha = \alpha_0 + \frac{1}{3} \frac{u^2}{k_B T}$$

$$W_{q\alpha} = \frac{-q^2 \left(\alpha_0 + \frac{1}{3} \frac{u^2}{k_B T} \right)}{(4\pi \epsilon_0 \epsilon_r)^2 r^4}$$

$$\propto r^{-4}$$

Example $\text{Na}^+ \dots \text{EtOH} \quad r = 3 \text{ \AA} \Rightarrow W = -0.3 k_B T$

Dipole-Induced Dipole (Debye) interaction: $u-\alpha$



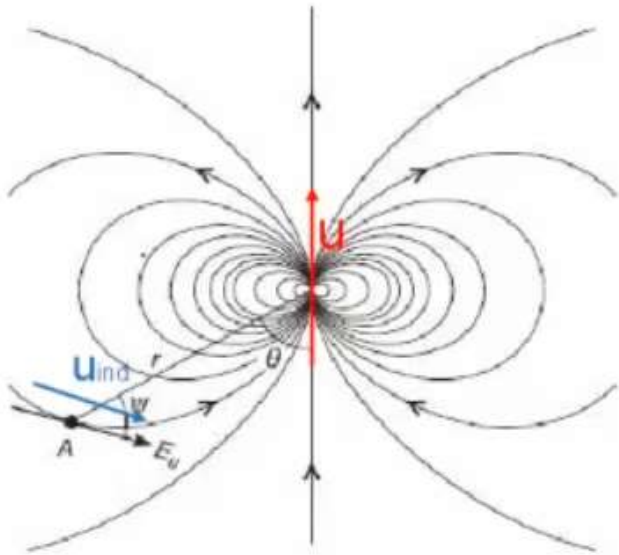
How to get angle-dependent energy:

$$u \rightarrow E(u, \theta) \rightarrow u_{ind} = \alpha E$$

$$E(u, \theta) = \frac{u \sqrt{1 + 3 \cos^2 \theta}}{4\pi \epsilon_0 \epsilon_r \cdot r^3}$$

$$W_{\alpha q} = -\alpha \cdot E^2 = \frac{-u_1 \left(\alpha_0 \epsilon_2 + \frac{1}{3} \frac{u_1^2}{k_B T} \right) \cdot (1 + 3 \cos^2 \theta)}{(4\pi \epsilon_0 \epsilon_r)^2 k_B T \cdot r^6}$$

Dipole-Induced Dipole (Debye) interaction: $u-\alpha$



Angle-averaged energy:

$$\hat{W}_{u\alpha} = \frac{-2u_1^2 \left(\alpha_{c,2} + \frac{1}{3} \frac{u_2^2}{k_B T} \right)}{(4\pi \epsilon_0 \epsilon_r)^2 k_B T \cdot r^6}$$

$\propto r^{-6}$

Debye interaction weaker than ~~keesam~~

Overview of Interaction terms

Power law comparison (excluding q-q):

$$q-u: r^{-4}$$

$$u-u: r^{-6} \text{ (Rosen)} \text{ (Rosen)}$$

$$q-\alpha: r^{-4}$$

$$u-\alpha: r^{-6} \text{ (Debye)}$$

Scaling comparison ϵ_r (excluding q-q):

$$q \sim r^{-1}, \quad u \sim r^{-3}, \quad \alpha \sim r^{-3}$$

Overview of Interaction terms

Consider 2 molecules with permanent charge q_i , dipole moment u_i and electronic polarizability $\alpha_{0,i}$ (excluding q-q):

$$w = - \prod_{i=1}^2 \frac{1}{(4\pi\epsilon_0\epsilon_r)^2} \left[\frac{q_i^2}{\sqrt{6k_B T}r} + \frac{\sqrt{2}u_i^2}{\sqrt{3k_B T}r^3} + \frac{\sqrt{6k_B T}\alpha_{0,i}}{r^3} \right]$$

- charge-dipole

$$w_{qu} = - \frac{q_1^2 u_2^2 + q_2^2 u_1^2}{3k_B T (4\pi\epsilon_0\epsilon_r)^2 r^4}$$

- charge-electronic polarizability

$$w_{q\alpha_0} = - \frac{q_1^2 \alpha_{02} + q_2^2 \alpha_{01}}{(4\pi\epsilon_0\epsilon_r)^2 r^4}$$

- dipole-dipole (Keesom energy)

$$w_{uu} = - \frac{2u_1^2 u_2^2}{3k_B T (4\pi\epsilon_0\epsilon_r)^2 r^6}$$

- dipole-electronic polarizability (Debye energy)

$$w_{q\alpha_0} = - \frac{2(u_1^2 \alpha_{02} + u_2^2 \alpha_{01})}{(4\pi\epsilon_0\epsilon_r)^2 r^6}$$

$$\alpha - \alpha \rightarrow - \frac{6k_B T \alpha_{01} \cdot \alpha_{02}}{(4\pi\epsilon_0\epsilon_r)^2 r^6} \rightarrow \text{London-Dispersion}$$

Induced Dipole-Induced Dipole (London) interaction: α - α

- Why can non-polar molecules still interact?
- How to explain the coefficient?
- What components are involved in vdW interactions?

Keesom + Debye + London
vdW

We will answer these questions in the next lecture!