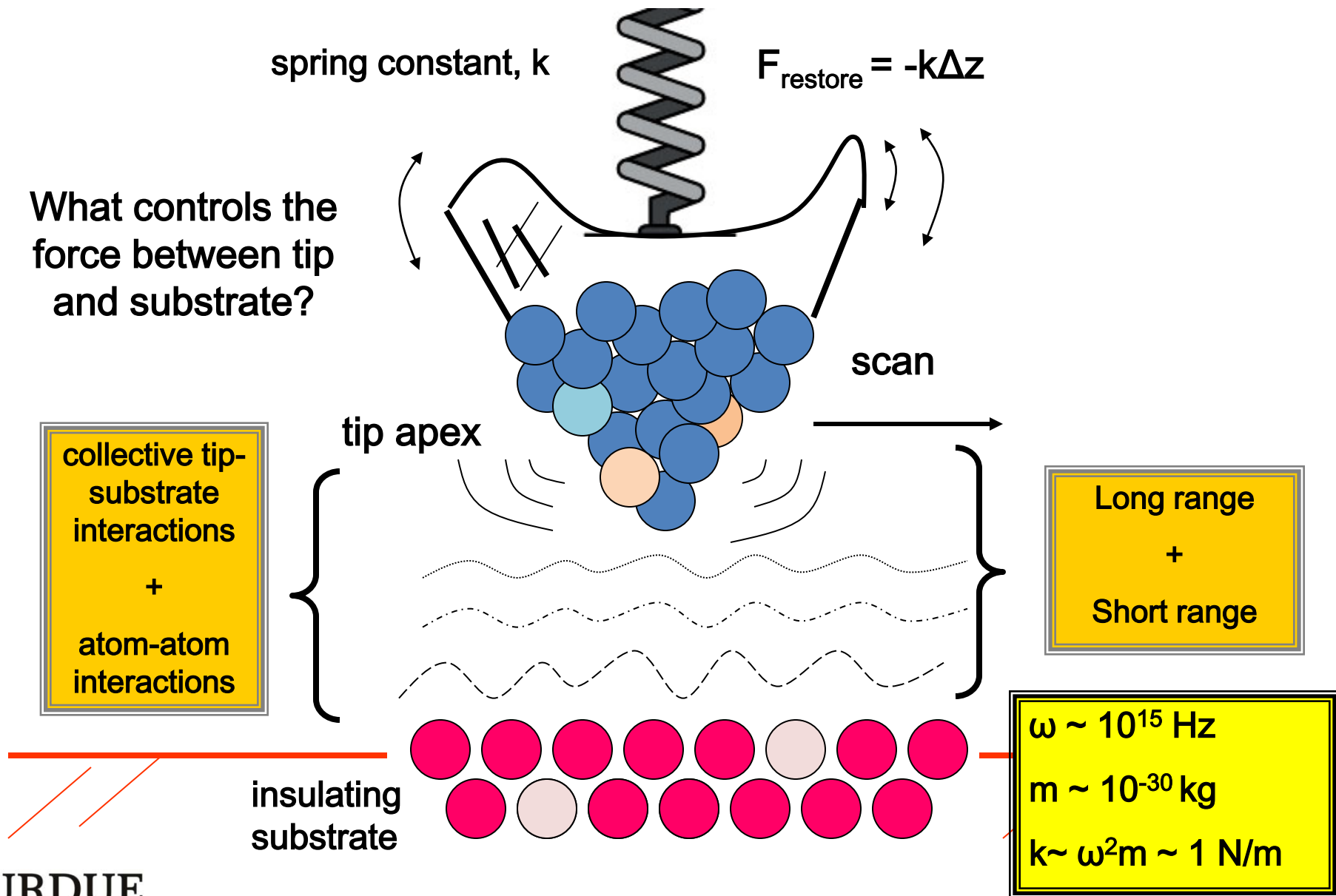# Lecture 5
Interaction forces I –

From interatomic and intermolecular forces to tip-sample interaction forces

Ron Reifenberger
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Further reading

- J. Israelachvilli, "Intermolecular and surface forces".
- H. J.Butt,B. Cappella, M. Kappl, "Force measurements with the atomic force microscope: technique, interpretation and applications" *Surface Science Reports*, Vol. 59 (1-6), 1-152, 2005.
- K. L. Johnson "Contact Mechanics".
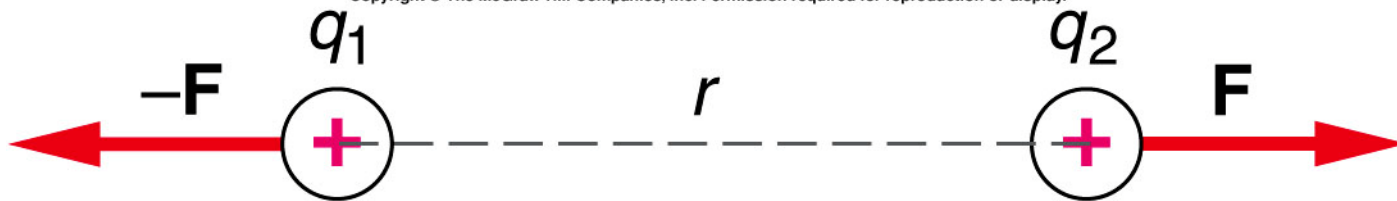
Probing the Interaction Potential

spring constant, k

$F_{restore} = -k\Delta z$

What controls the force between tip and substrate?

scan

tip apex

collective tip-substrate interactions

+

atom-atom interactions

Long range

+

Short range

insulating substrate

$\omega \sim 10^{15}$ Hz

$m \sim 10^{-30}$ kg

$k \sim \omega^2 m \sim 1$ N/m

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The Electrostatic Force: Quick review

Coulomb's Law

$$|\vec{F}| = \frac{1}{4\pi\varepsilon_o}\frac{q_1 q_2}{r^2} = k\frac{q_1 q_2}{r^2}$$
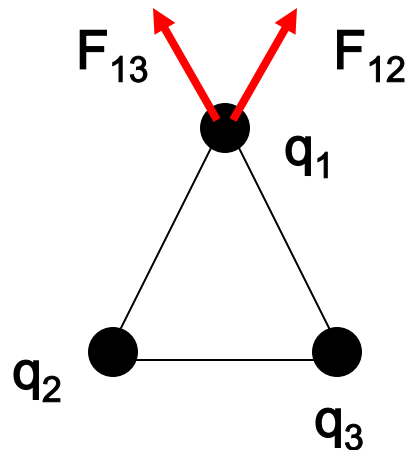
$$\varepsilon_o = 8.85\times10^{-12}\ C^2/Nm^2$$

$$k = 9\times10^9\ Nm^2/C^2$$

In vacuum

Force is a vector!

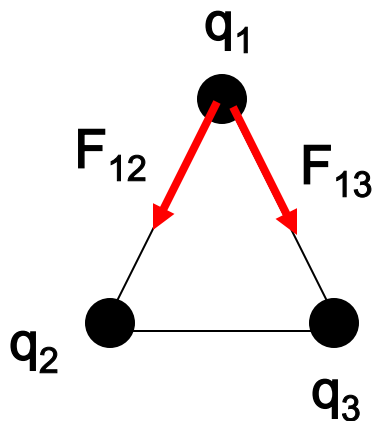### (same problem with four different choices for charge polarity)
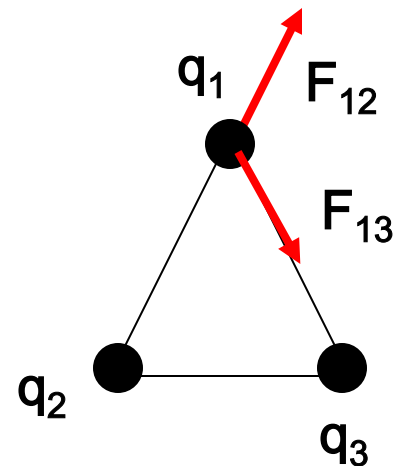
q_1	q_2	q_3
+	+	+
-	-	-

F_{13} F_{12}

q_1

q_2 q_3

q_1	q_2	q_3
-	+	-

F_{13} q_1

F_{12}

q_2 q_3

q_1	q_2	q_3
-	+	+

q_1

F_{12} F_{13}

q_2 q_3

q_1	q_2	q_3
+	+	-

q_1 F_{12}

F_{13}

q_2 q_3

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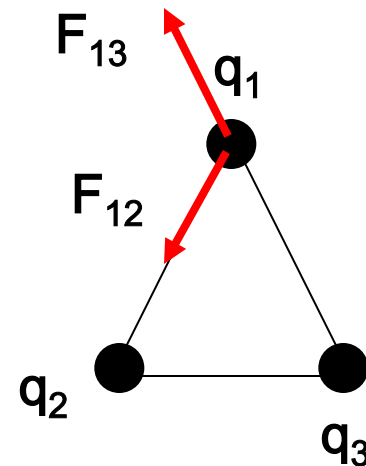
The Electric Field produced by a Positive Point Charge
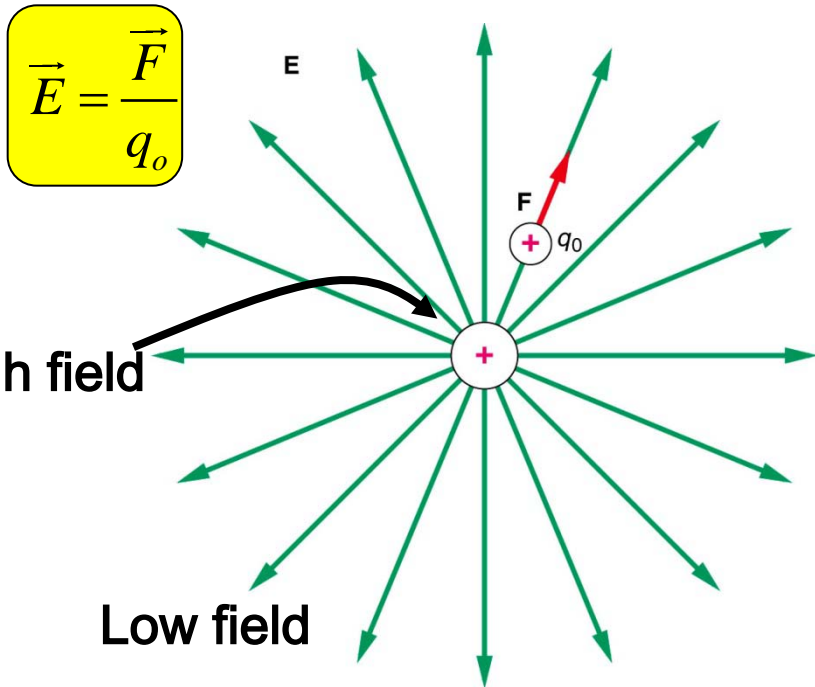
The Electric Field produced by a Negative Point Charge

$$\vec{E} = \frac{\vec{F}}{q_o}$$

E

F

q_0

High field

Low field

$$\vec{E} = \frac{\vec{F}}{q_o}$$

E

$+$ q_0

F
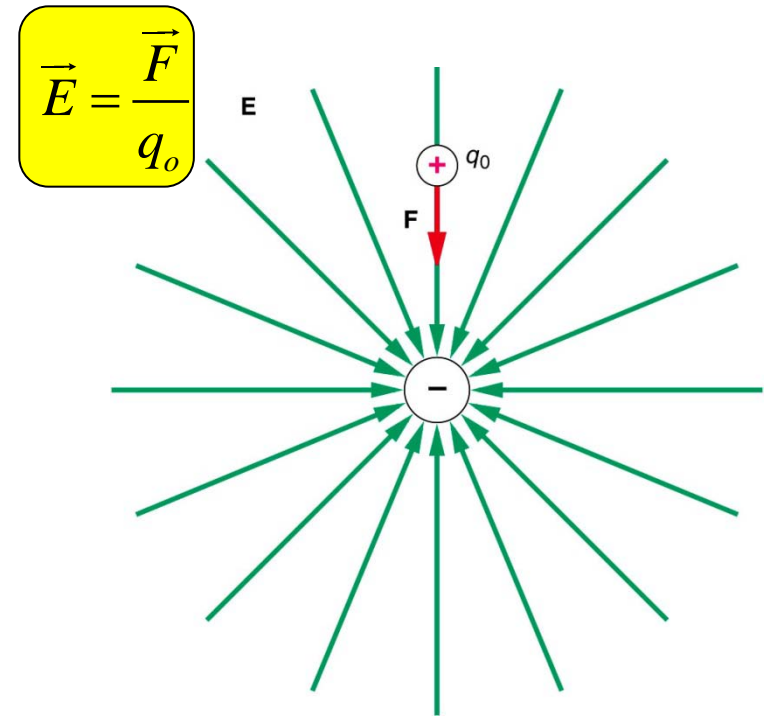
Bottom line: If there is an electric field at some point in space and you place a charge q_o at that point, the charge q_o will feel an electrostatic force.

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Electric Fields Produced by Two Point Charges of Equal Magnitude but Opposite Polarity: the Electric Dipole

physical dipole

$$\vec{p} = q\vec{d}$$

$$\left|\vec{p}\right| = qd$$
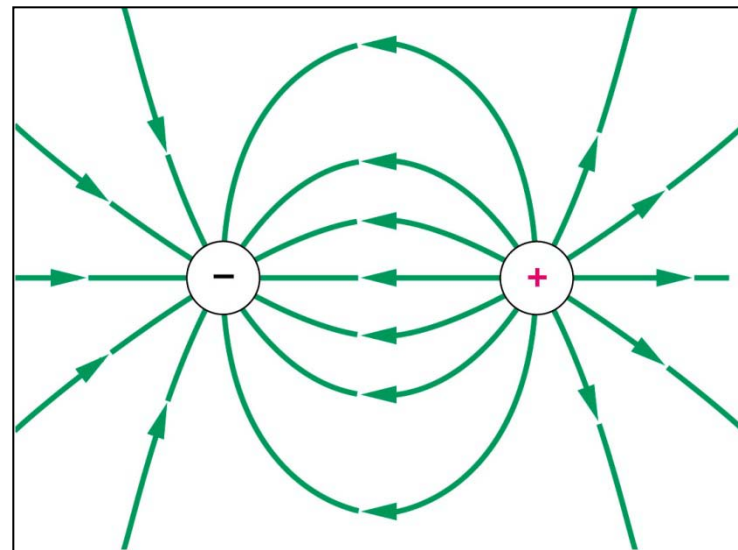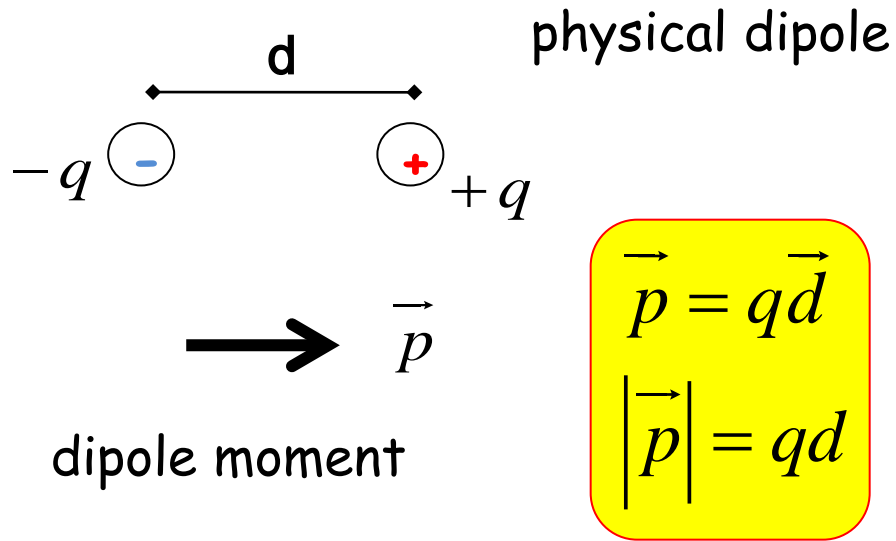
dipole moment

Historically the standard unit size of a dipole moment was defined by considering two charges of opposite sign but with equal magnitude of 10^{-10} statcoulomb (also called e.s.u. - the electrostatic unit in older literature), which were separated by 1 Angstrom = 1.0×10^{-8} cm.

This gives the following unit for molecular dipole moments:

$$1 \text{ Debye} = (1 \times 10^{-10} \text{ statC})(1 \times 10^{-8} \text{ cm}) = 1 \times 10^{-18} \text{ statC·cm}$$

$$= 10^{-10} \text{ esu·Å}$$

$$= 1/299{,}792{,}458 \times 10^{-21} \text{ C·mm}$$

$$\approx 3.33564 \times 10^{-30} \text{ C·m}$$

A few common solvent molecules

Material	ε, dielectric constant	Dipole Moment (in Debye)
Acetone	21	2.9
Isopropanol	18.3	1.7
Ethanol	24	1.7
Methanol	33	1.7
Toluene	2.4	0.4
Freon-11 (CCL_3F)	2.0	0.45
Water	80	1.8

Potential Energy

	Mechanics	Electrostatics
Work	$W = \int \vec{F} \cdot \vec{dr}$	$W = \int \vec{E} \cdot \vec{dl}$
Potential Energy, V	$V(r) = -W$	$U(r) = -W$

If Force is conservative (not a function of time), then Potential Energy at point P (for linear motion) can be defined as:
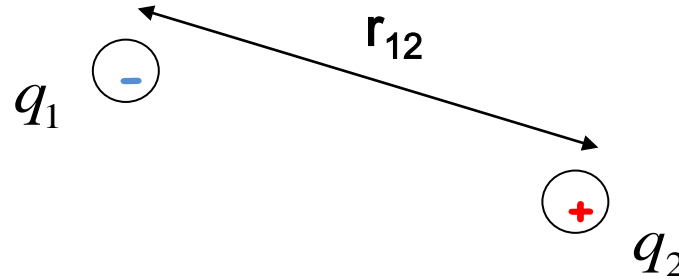
$$V_P(x) \equiv -\int_{ref}^{P} F(x)d\,x \Rightarrow F(x) = -\frac{\partial V_P(x)}{\partial x}$$

If Electric field is conservative (not a function of time), then Potential Energy at point P for electrostatic motion can be defined as:

$$U_P(\vec{r}) \equiv -\int_{\infty}^{P} \vec{E} \cdot d\vec{\ell} \Rightarrow \vec{F} = -\vec{\nabla} U_P(\vec{r})$$
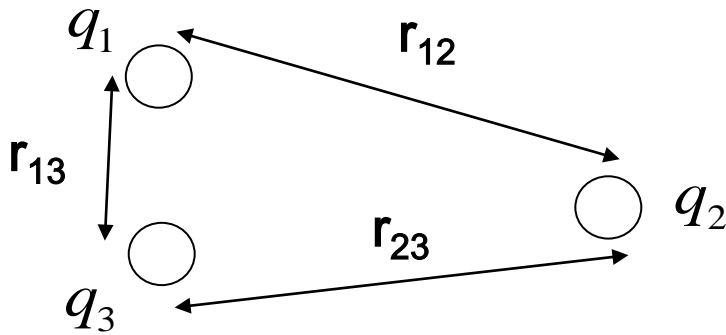
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Electrostatic Potential Energy

Two charges:

q_1 $-$ **r$_{12}$** $+$ q_2

$$U = \frac{1}{4\pi\varepsilon_o}\left[\frac{(q_1)(q_2)}{r_{12}}\right] = \frac{1}{4\pi\varepsilon_o}\left[\frac{(-q_1)q_2}{r_{12}}\right] = -\frac{1}{4\pi\varepsilon_o}\left[\frac{q_1 q_2}{r_{12}}\right]$$

Three charges:

q_1 **r$_{12}$**

r$_{13}$ q_2

r$_{23}$

q_3

$$U = \frac{1}{4\pi\varepsilon_o}\left[\frac{(q_1)(q_2)}{r_{12}} + \frac{(q_2)(q_3)}{r_{23}} + \frac{(q_1)(q_3)}{r_{13}}\right]$$

Connecting charges and electric fields to the microscopic world

Charge Distribution	Classical E&M	Real World	Examples	Chemical Formula
point charges	$+Q$ or $-Q$	ions	Li^+, Mg^{++}, Cl^-	
permanent dipoles	$p = Q\,d$	polar molecules	acetone, acetonitrile, ethanol, methanol, Freon-41, water	$(CH_3)_2CO$ CH_3CN C_2H_5OH CH_3OH CH_3F H_2O
fluctuating dipoles	$p(t) = Q\,d$	non-polar molecules, neutral atoms	hexane, benzene, toluene	C_6H_{14} C_6H_6 C_7H_8 (or $C_6H_5CH_3$)
surface charge distribution	σ	charged objects	metal plate with voltage	
volume charge distribution	ρ	charged objects	charged non-conductors	

Interatomic and intermolecular forces

$\updownarrow$ picometers   up to few nanometers $\updownarrow$
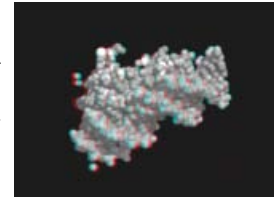
A wide variety of forces act between atoms and molecules can be loosely classified as follows (Israelachvilli):

Coulombic in origin

- **Electrostatic forces**: interactions between charged ions, permanent dipoles etc. fall into this category

- **Polarization forces**: these forces occur due to dipoles induced in some molecules in response to electric fields from nearby charges or permanent dipoles

- **Dispersion forces**: these are fundamentally electrodynamic in nature and   occur between atoms and molecules even if they are charge neutral and without permanent dipoles

Quantum in origin

- **Covalent bond forces**: when two or more atoms come together to form a molecule and share electrons, the forces that tightly bind the atoms together are called covalent forces.

- **Pauli repulsion forces**: At very small interatomic distances the electron clouds of atoms overlap and a strong repulsive force determines how close two atoms or molecules can ultimately approach each other.
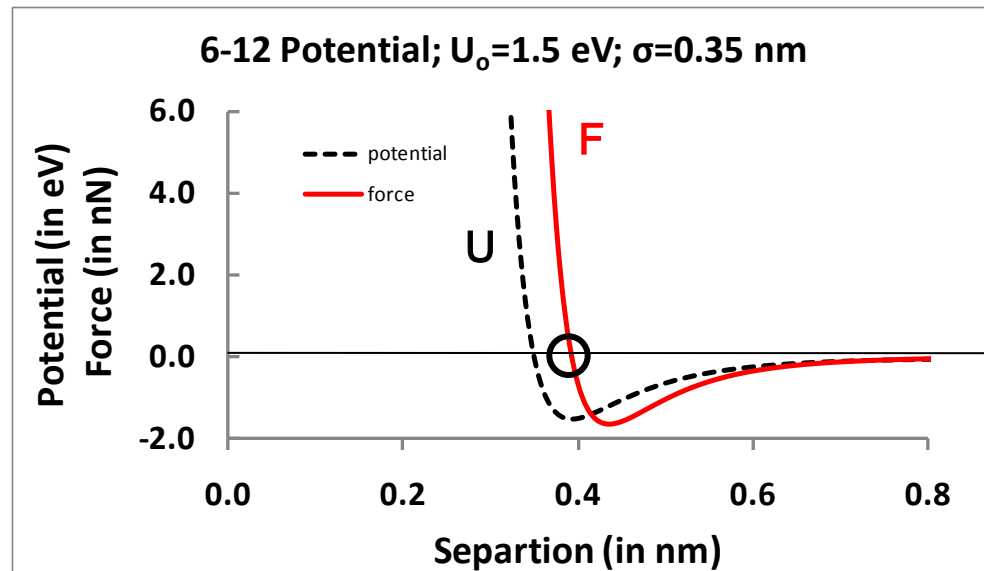
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The Lennard-Jones interatomic potential

Let's start with atom-atom interactions:

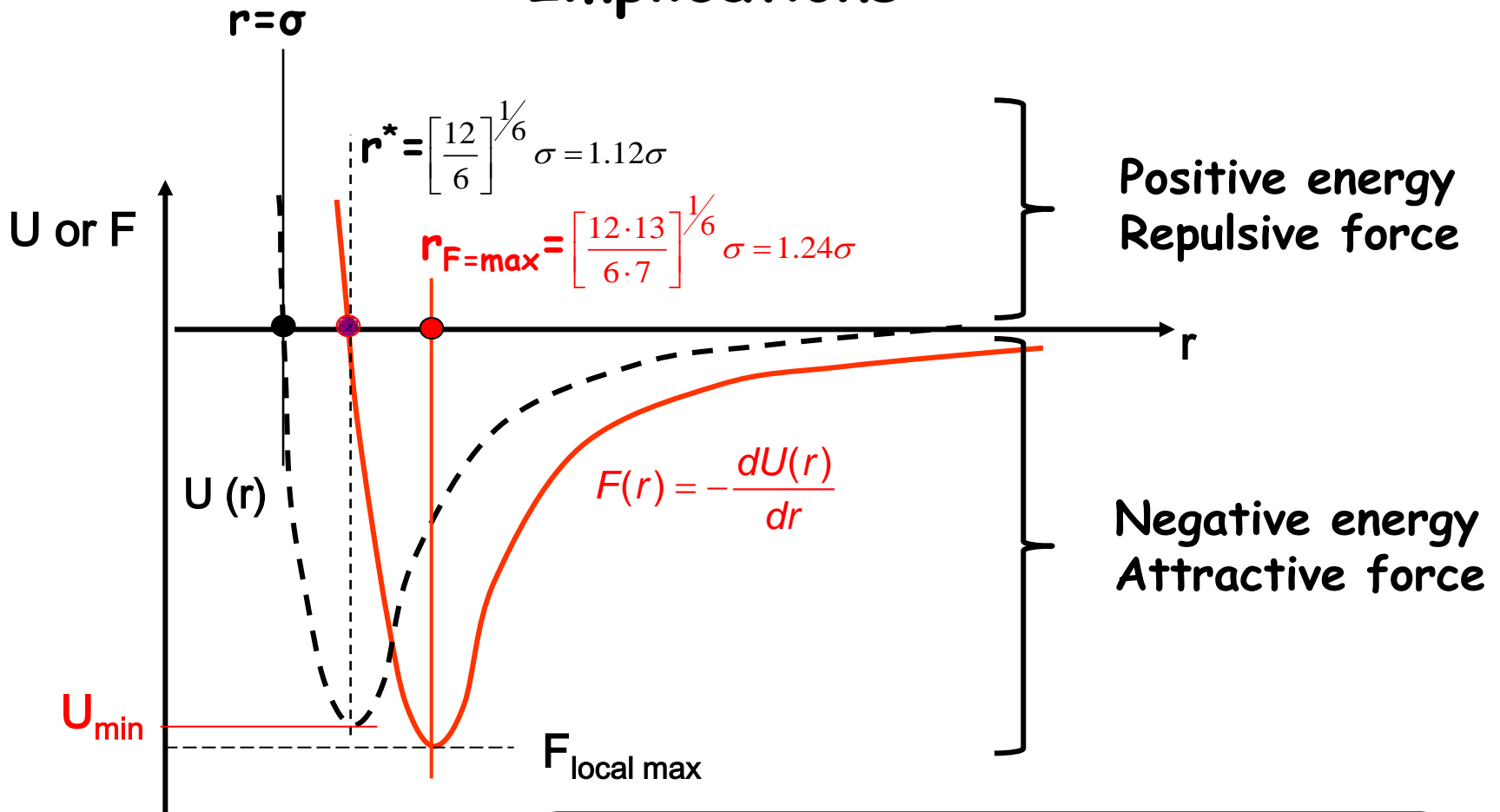- Simple *ad hoc* model that tries to couple dispersion forces and Pauli repulsion.

$$U(r) = 4U_o * \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

- U_o is depth of potential, σ is value at which $U_o(r=\sigma)=0$
- **F** = -dU(r)/dr
- While attractive part follows that from the general dispersion relation, the repulsive part is *adhoc*.

6-12 Potential; U_o=1.5 eV; σ=0.35 nm

Implications

$r=\sigma$

$r^{*}=\left[\dfrac{12}{6}\right]^{\frac{1}{6}}\sigma=1.12\sigma$

$r_{F=max}=\left[\dfrac{12\cdot 13}{6\cdot 7}\right]^{\frac{1}{6}}\sigma=1.24\sigma$

Positive energy Repulsive force

U or F

U (r)

$F(r)=-\dfrac{dU(r)}{dr}$

Negative energy Attractive force

U_{min}

$F_{local\ max}$

often define $4U_{o}\,\sigma^{6}=C$ *so that*

$$U(r)=-\dfrac{C}{r^{6}}$$

typically, $C=4\cdot(0.5\,eV)\cdot(0.25\,nm)^{6}\simeq 8\times10^{-77}\,Jm^{6}$

Electrostatic interatomic and intermolecular energies

1. ion-ion interactions
2. ion-dipole interactions
3. dipole-dipole interactions
4. angle-averaged dipole-dipole interactions
5. polarization forces (Keesom)
6. dipole-induced dipole interactions (Debye)
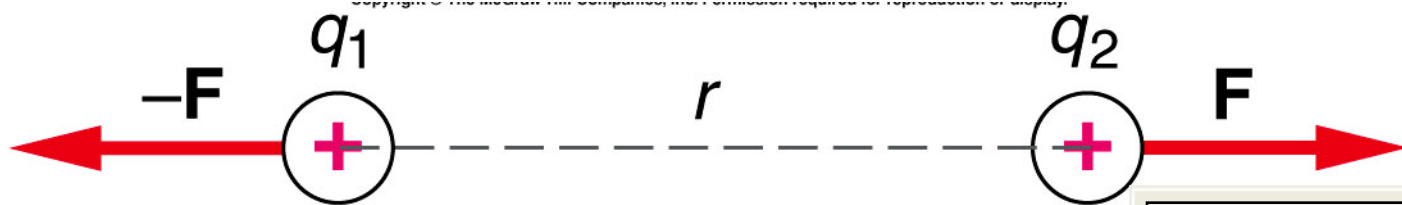7. dispersion interactions (London)

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

Electrostatic interatomic and intermolecular forces
The Electrostatic Force: Coulomb's Law

1. Charge-charge (ion-ion) interactions:

The Electrostatic Force: Coulomb's Law

$$|\vec{F}| = \frac{1}{4\pi\varepsilon_o} \frac{q_1 q_2}{r^2} = k \frac{q_1 q_2}{r^2}$$

$$U(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r}$$

$$\varepsilon_o = 8.85 \times 10^{-12} \ C^2 / Nm^2$$

$$k = 9 \times 10^9 \ Nm^2 / C^2$$

$$|F(r)| = -\frac{dU(r)}{dr} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r^2}$$

In vacuum
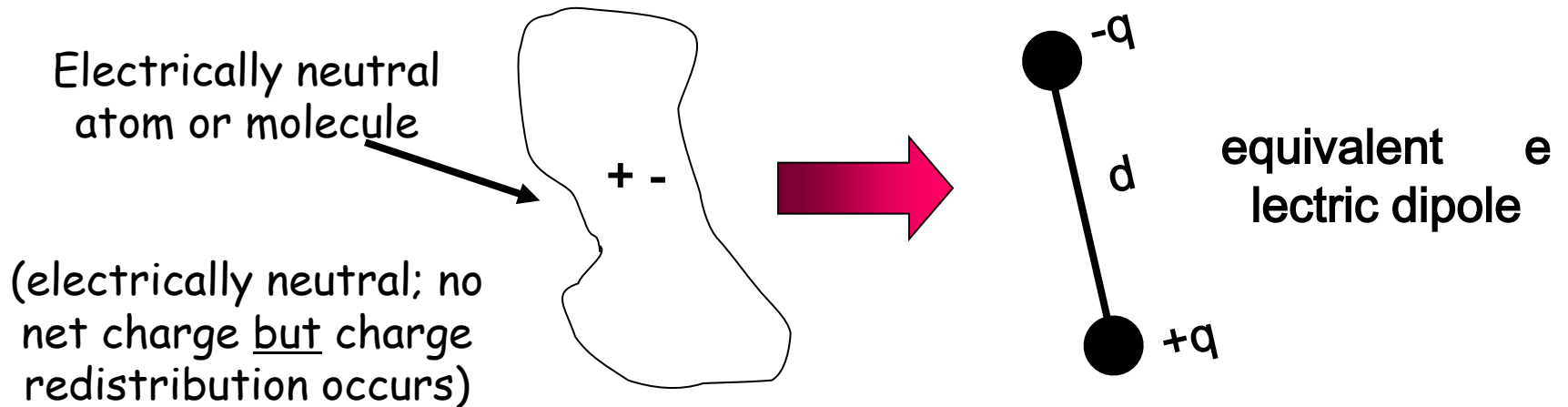
In dielectric

$$\varepsilon_o \rightarrow \varepsilon\varepsilon_o; \quad \varepsilon > 1$$

16

Electrostatic interatomic and intermolecular forces

2. Permanent dipole-charge interactions:

The permanent dipole of a molecule is the separation of charges by d in the molecule times the magnitude of the charge separated
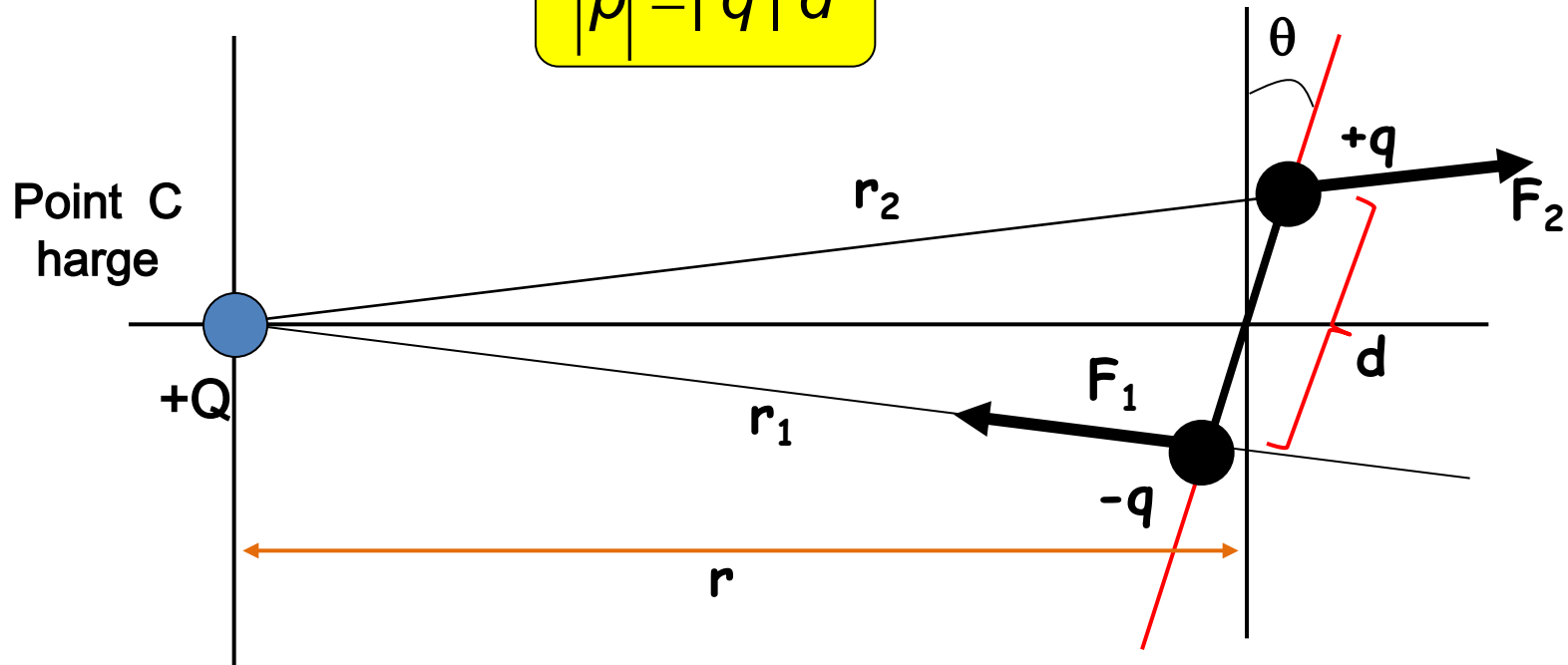
$$|p| = qd$$

Electrically neutral atom or molecule

+ -

(electrically neutral; no net charge but charge redistribution occurs)

-q

d

+q

equivalent electric dipole

1 click

17

Electrostatic interatomic and intermolecular forces

The interaction energy of a point charge Q with a dipole having a dipole moment **p**
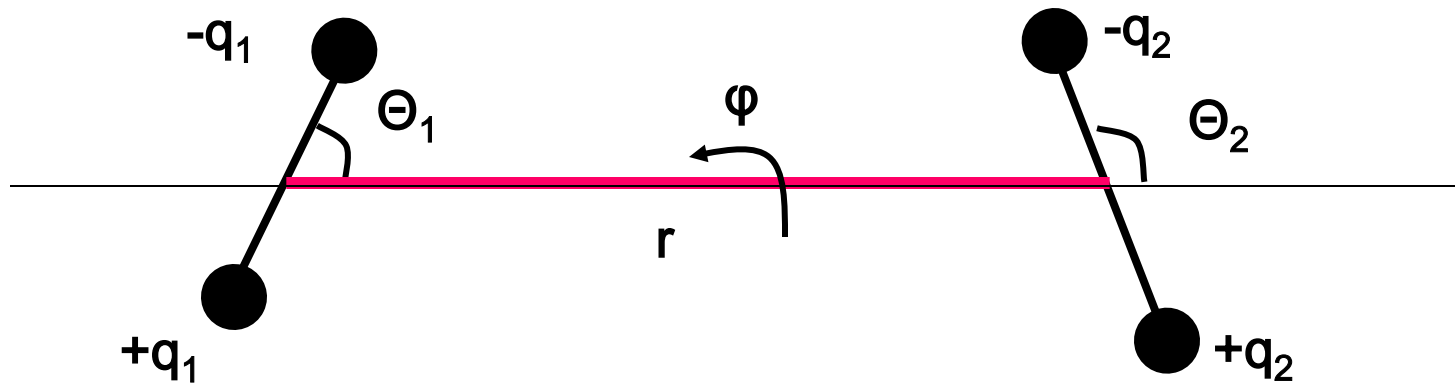
$$\left|\vec{p}\right| = |q|\,d$$

θ

+q

r_2

Point Charge

+Q

r_1

F_2

F_1

d

-q

r

1 click

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

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Electrostatic interatomic and intermolecular forces

3. Permanent dipole-permanent dipole interactions
    - fixed orientation:

already four parameters: separation distance (r) + 3 angles ($\Theta_1, \Theta_2, \varphi$)

-q₁ **-q₂**

Θ_1 φ Θ_2

r

+q₁ **+q₂**

$$U(r) = -\frac{p_1 p_2 \left[2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi) \right]}{4\pi\varepsilon\varepsilon_0} \frac{1}{r^3}$$

Electrostatic interaction between in-plane permanent dipoles

diagram for s/d ≈ 1
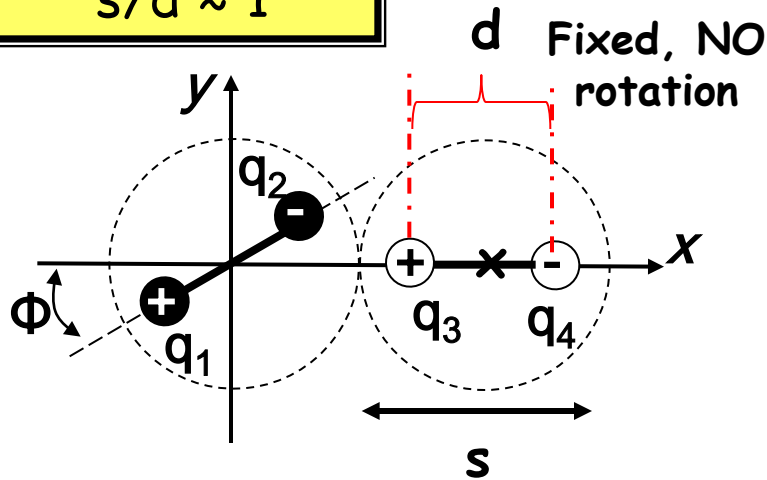
Symbol	Actual Charge
q_1	+ q
q_2	- q
q_3	+ q
q_4	- q

Note: $|p_1|=|p_2|$

$|q|=1\times10^{-18}$ C;   s=10 nm

d/s=0.75
d/s=0.50
d/s=0.30

U_{total} (in 10^{-18} J)

Φ (degrees)
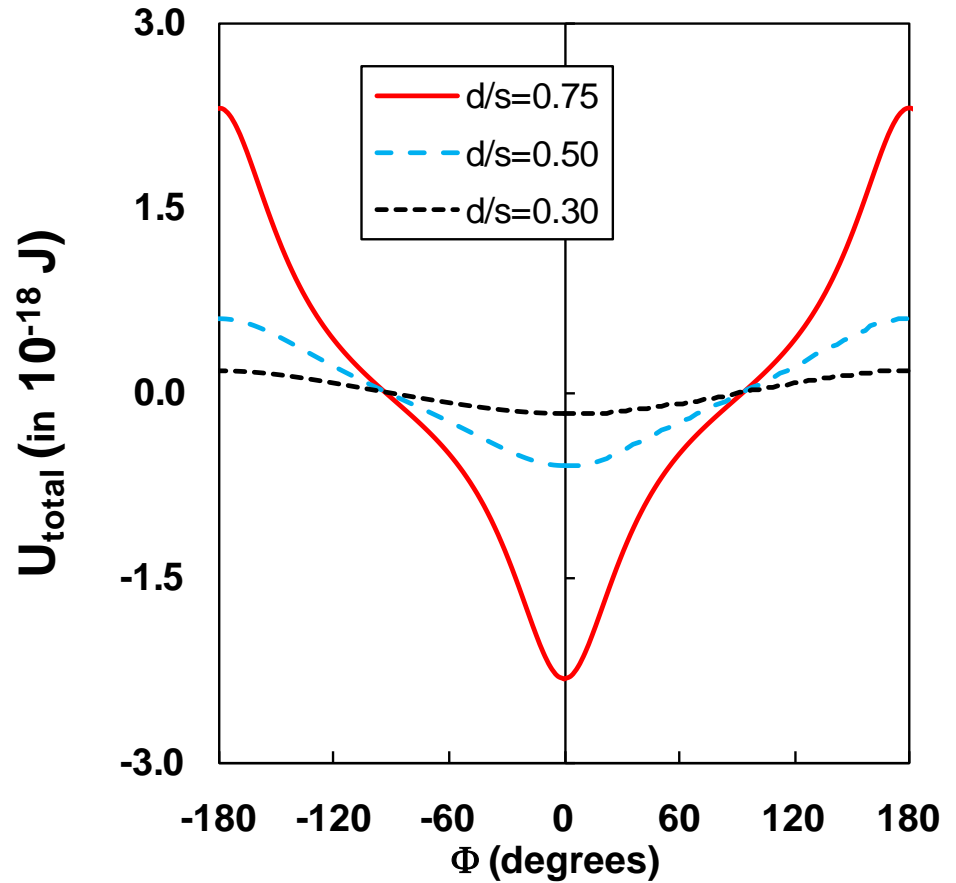
Strength of interactions

The strength of an interaction is measured by comparing the value of the potential energy at equilibrium with the typical thermal energy $k_B T$ ($k_B = 1.38 \times 10^{-23}$ J K^{-1}).

$$k_B T = 4.1 \times 10^{-21} J \ (at \ 300K) = 4.1 \ pN \bullet nm$$

For strong interactions, U ~ 100's $k_B T$

- Example 1 (2 electron charges Q=1.602×10^{-19} C at a distance of 0.276 nm (equilibrium separation of Na^+ and Cl^-) in vacuum

$$U = \frac{1}{4 \pi \varepsilon_o} \frac{q_1 q_2}{r} = -\frac{9 \times 10^9 \ Nm^2 \big/ C^2 \cdot \left(1.6 \times 10^{-19} C\right)^2}{0.276 \times 10^{-9} m}$$

$$= -8.34 \times 10^{-19} J \approx 203 \, k_B T \ at \ room \ temperature$$

- Example 2: What is the energy of interaction of two dipoles (p=1D) lined up and separated by 0.5 nm?

p_1 p_2

r
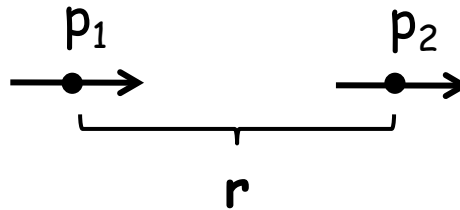
$$U(r) = -\frac{p_1 p_2 \left[2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi) \right]}{4\pi\varepsilon\varepsilon_0 r^3}$$

$$\theta_1 = 0; \quad \theta_2 = 0; \quad \phi = 0; \quad p_1 = p_2 = 1D = 3.33\times10^{-30}\,Cm; \quad \varepsilon = 1$$

$$\left| U(r) \right| = \frac{p_1 p_2 [2]}{4\pi\varepsilon_0} \frac{1}{r^3} = 9\times10^9\,Nm^2\!\!\Big/C^2 \cdot \frac{2\left(3.33\times10^{-30}\,Cm\right)^2}{(0.5\times10^{-9})^3} = 1.6\times10^{-21}\,J$$

$$\left| U(r) \right| \simeq 0.4\,k_B T$$

about 100 times weaker
than typical ion-ion interaction

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Electrostatic interatomic and intermolecular forces

4. Angle averaged dipole-dipole interactions:

At large distances, $k_B T$ makes molecules fluctuate so that a **weighted average** using classical Boltzmann statistics is required.

Partition function

Let P_r = *probability of finding a state with energy* ε_r

$$P_r = \frac{e^{-\varepsilon_r/k_B T}}{\sum_r e^{-\varepsilon_r/k_B T}} \; when \; in \; thermal \; equilibrium$$

Probability of finding any quantity y *with values* y_r :

$$\langle y \rangle = \overline{y} = \sum_r y_r P_r = \frac{\sum_r y_r e^{-\varepsilon_r/k_B T}}{\sum_r e^{-\varepsilon_r/k_B T}}$$

………when applied to dipole-dipole interactions

$$U(r) = -\frac{p_1 p_2 \left[2\langle \cos\theta_1 \rangle \langle \cos\theta_2 \rangle - \langle \sin\theta_1 \rangle \langle \sin\theta_2 \rangle \langle \cos\phi \rangle \right]}{4\pi\varepsilon\varepsilon_0} \frac{1}{r^3}$$

$where \quad \langle .... \rangle = thermal\ average\ over\ d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$

$$for\ example,\ \langle \cos\vartheta \rangle \equiv \frac{\displaystyle\int_\Omega \cos\vartheta\, e^{-U/k_B T}\, d\Omega}{\displaystyle\int_\Omega e^{-U/k_B T}\, d\Omega}$$
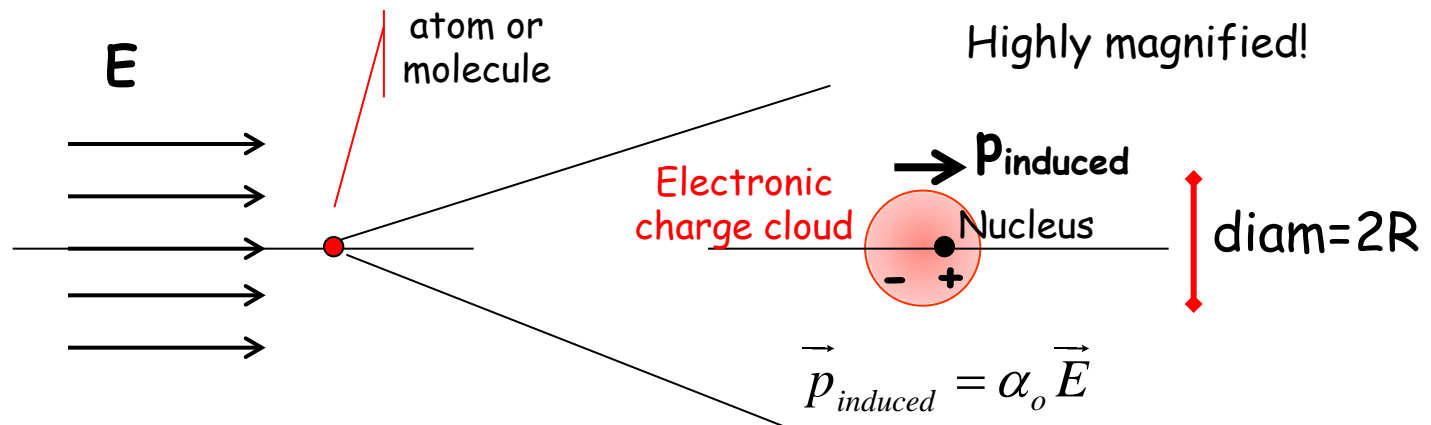
This gives (also known as the Keesom interaction):

$$U_{Keesom}(r) = -\frac{p_1^2 p_2^2}{3(4\pi\varepsilon\varepsilon_0)^2} \frac{1}{k_B T} \frac{1}{r^6}$$

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Electrostatic interatomic and intermolecular forces

5. Polarization forces

All atoms and molecules not having an intrinsic dipole moment can be polarized by an external electric field.

E

atom or molecule

Highly magnified!

$p_{induced}$

Electronic charge cloud

Nucleus

diam=2R

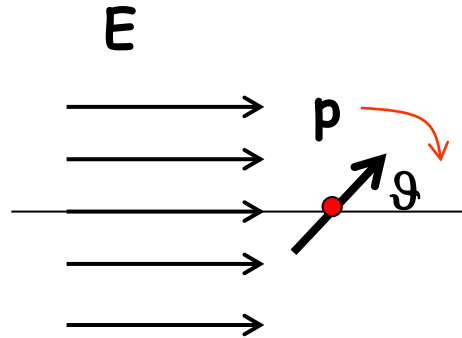$$\vec{p}_{induced} = \alpha_o \vec{E}$$

α_0 is called the **electronic polarizability** and has units of m^3, it is proportional to molecule size

$$\alpha_o = 4\pi\varepsilon_0 \times R^3$$

For water, $\alpha_0 / 4\pi\varepsilon_o = 1.48 \times 10^{-30}$ m^3
$\rightarrow$ R=0.114 nm – compare to $R_{H2O} \approx 0.135$ nm
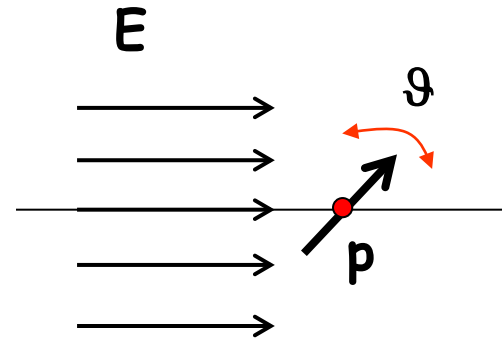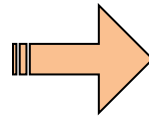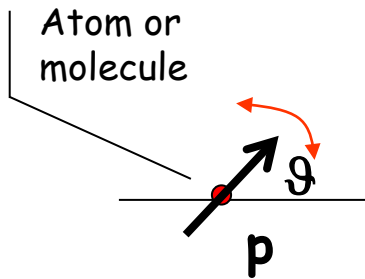
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Energetics of a static dipole in a uniform applied electric field

The interaction energy is:

$$U = -\vec{p} \cdot \vec{E} = -pE \cos \vartheta$$

If dipole fluctuates with thermal energy kT

Atom or molecule

E

$$\langle \vec{p} \rangle = \vec{p} \langle \cos \vartheta \rangle$$

where $\langle \ \rangle = thermal\ average$

$$U = -\langle \vec{p} \rangle \cdot \vec{E} = -pE \langle \cos \vartheta \rangle$$

Langevin function (1905)

$$\langle \cos \vartheta \rangle = \frac{\int\limits_{\Omega} e^{-U/k_B T} \cos \vartheta \, d\Omega}{\int\limits_{\Omega} e^{-U/k_B T} \, d\Omega} = cotanh\left[\frac{pE}{k_B T}\right] - \frac{k_B T}{pE}$$

temperature dependent contribution to the **polarizability**

$$when \ \frac{pE}{k_B T} \ll 1 \quad \langle \cos \vartheta \rangle \approx \frac{1}{3} \frac{pE}{k_B T}$$

$$\langle p \rangle = p \langle \cos \vartheta \rangle = \frac{1}{3} \frac{p^2 E}{k_B T} = \alpha_1 E \qquad \alpha_1 \equiv \frac{1}{3} \frac{p^2}{k_B T}$$

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Polarization forces

$$p_{total} = p_{induced} + \langle p \rangle$$

$$= (\alpha_o + \alpha_1) E$$

$$= \left(\alpha_o + \frac{1}{3} \frac{p^2}{k_B T} \right) E$$

$$\alpha = \alpha_0 + \frac{p^2}{3k_B T} \ (Debye - Langevin \ equation)$$

Usually, α depends on the frequency of the electric field.

Electrostatic interatomic and intermolecular forces

6. Dipole-induced dipole interaction:

By taking the electric field generated by a fixed dipole and using the above equation and thermal angle averaging according to Boltzmann statistics, one finds the Debye interaction energy

$$U_{Debye}(r) = -\frac{p_1^2\alpha_{02} + p_2^2\alpha_{01}}{(4\pi\varepsilon_0\varepsilon)^2 r^6} = -\frac{C_D}{r^6}$$

where α_{01} and α_{02} are the electronic polarizabilities of the two molecules.

If one replaces α_0 with the orientation polarizability $\alpha = p^2/3k_B T$, we recover the Keesom force.

Electrostatic interatomic and intermolecular forces

7. Dispersion Forces

• The London or Dispersion Force is the most important contributor to van der Waals forces and acts between all molecules irrespective of their polarization

• relevant distances range from 0.2 nm to 10 nm.

• fundamentally quantum mechanical in nature and arises from induced dipole-induced dipole interactions.

• quantum mechanical calculation

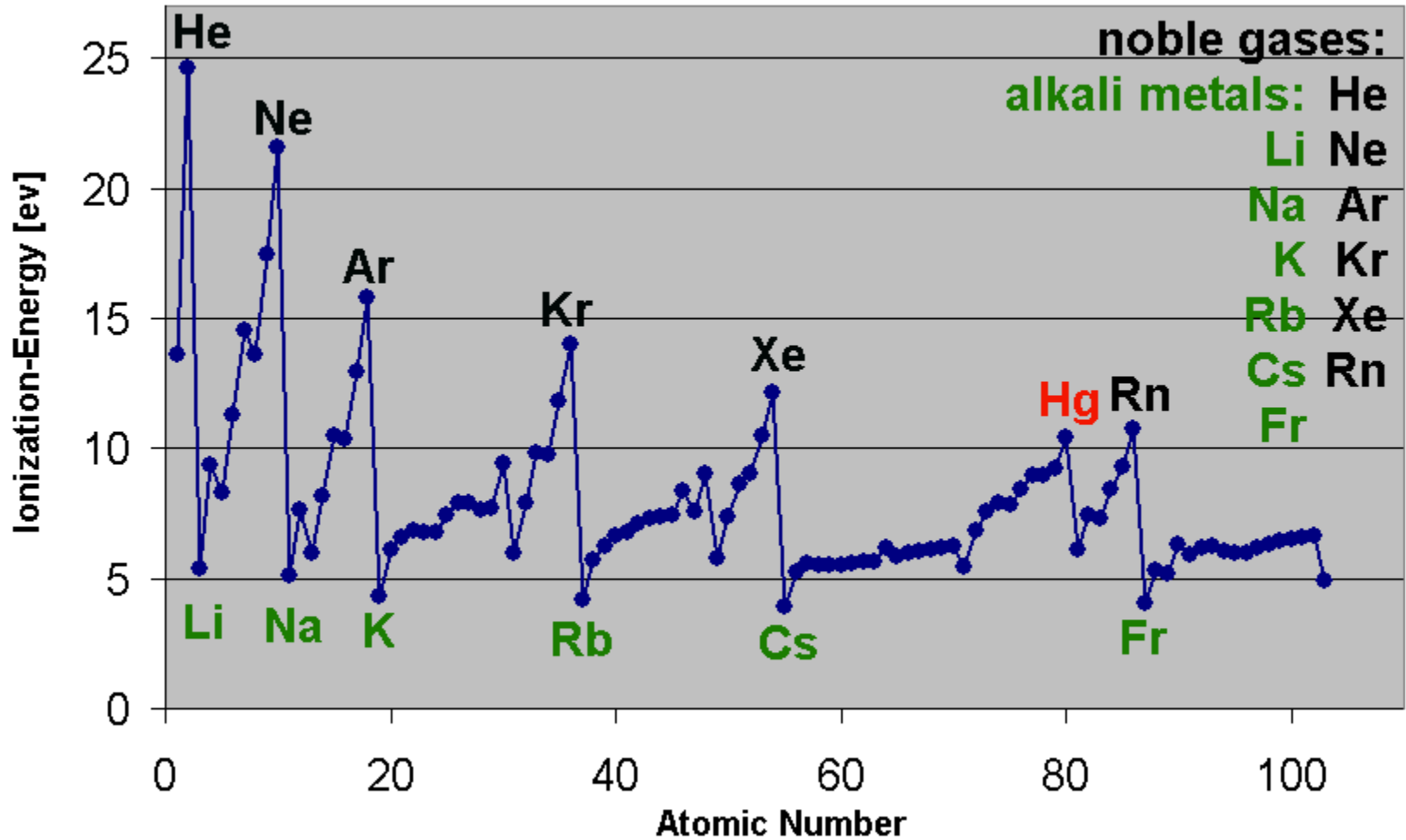It can be shown that for two similar atoms/molecules with an ionization energy I

$$U_{London}(r) = -\frac{4}{2}\frac{\alpha_0^2 I}{(4\pi\varepsilon_0\varepsilon)^2 r^6} = -\frac{C_L}{r^6}$$

For dissimilar atoms/molecules with ionization energies I_1 and I_2

$$U_{London}(r) = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0\varepsilon)^2 r^6}\frac{I_1 I_2}{I_1 + I_2} = -\frac{C_L}{r^6}$$

Ionization-Energy

Electrostatic interatomic and intermolecular forces

7. Dispersion Forces (cont.)

- Extensions to frequency dependent polarizations by McLachlan (1963)

- As distances increase (>100nm), the time taken for fluctuating dipoles to reach other atom/molecule needs to be taken into account-retardation effects (power law dependence becomes $1/r^7$)

- Casimir-Polder force is generalization to include finite conductivity

van der Waals Forces

The van der Waals forces is the sum of three different forces each of whose potential varies as $1/r^6$, where r is the separation

- **Orientation or Keesom Force**. The Keesom force is the averaged dipole-dipole interaction between two atoms or molecules.
- **Debye Force** is the angle averaged dipole-induced dipole interaction between two atoms or molecules
- **The London or Dispersion force** is the most important contributor to van der Waals forces and acts between all molecules.

$$U_{VdW}(r) = U_{Keesom}(r) + U_{Debye}(r) + U_{London}(r)$$

$$= -\frac{p_1^2 p_2^2}{3(4\pi\varepsilon\varepsilon_0)^2 k_B T}\frac{1}{r^6} - \frac{p_1^2 \alpha_{02} + p_2^2 \alpha_{01}}{(4\pi\varepsilon_0\varepsilon)^2}\frac{1}{r^6} - \frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0\varepsilon)^2}\frac{(I_1)(I_2)}{I_1 + I_2}\frac{1}{r^6} = -\frac{C}{r^6}$$
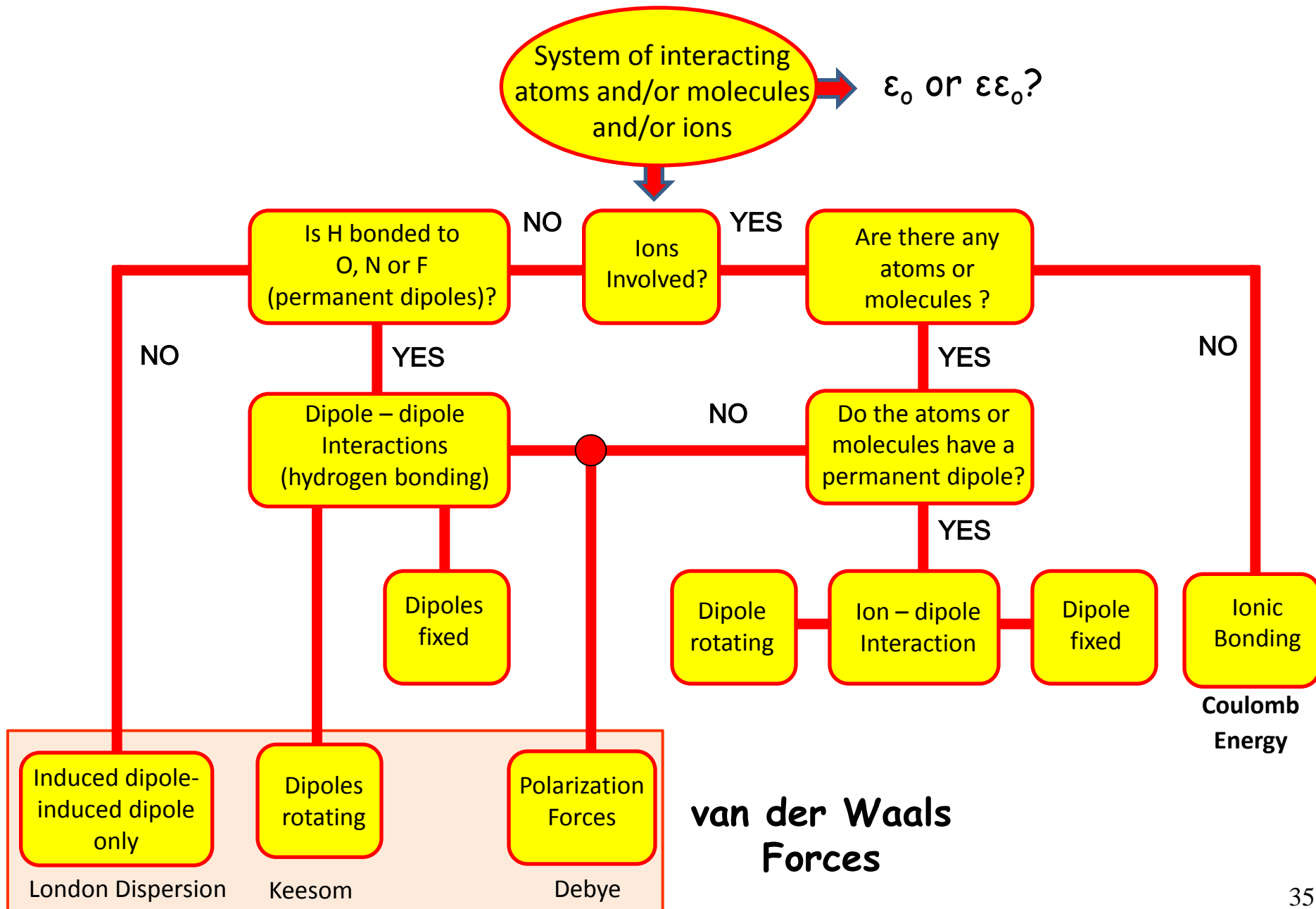
Relative values of Van der Waals force components are presented in **Table 1** [3].

Substance	$\chi, \mathrm{m}^3 \times 10^{18}$	d, D	I, eV	C_{Keesom} $\times 10^{79}\,\mathrm{J\cdot m^6}$	C_{Debye} $\times 10^{79}\,\mathrm{J\cdot m^6}$	C_{London} $\times 10^{79}\,\mathrm{J\cdot m^6}$
H	0.667	0	13.6	0	0	6.3
O_2	1.57	0	13.6	0	0	41.3
N_2	1.74	0	15.8	0	0	59.3
Ar	1.6	0	15.8	0	0	48
He	0.2	0	24.7	0	0	1.2
CO	1.99	0.12	14.3	0.0034	0.057	67.5
HCl	2.63	1.03	13.7	18.6	5.4	105
H_2O	1.48	1.84	18.0	197	10	48.8
NH_3	2.24	1.5	11.7	87	10	72.6

Table 1. Magnitudes of polarizability, dipole moment, ionization potential and energies of different weak interactions between various atoms and molecules.
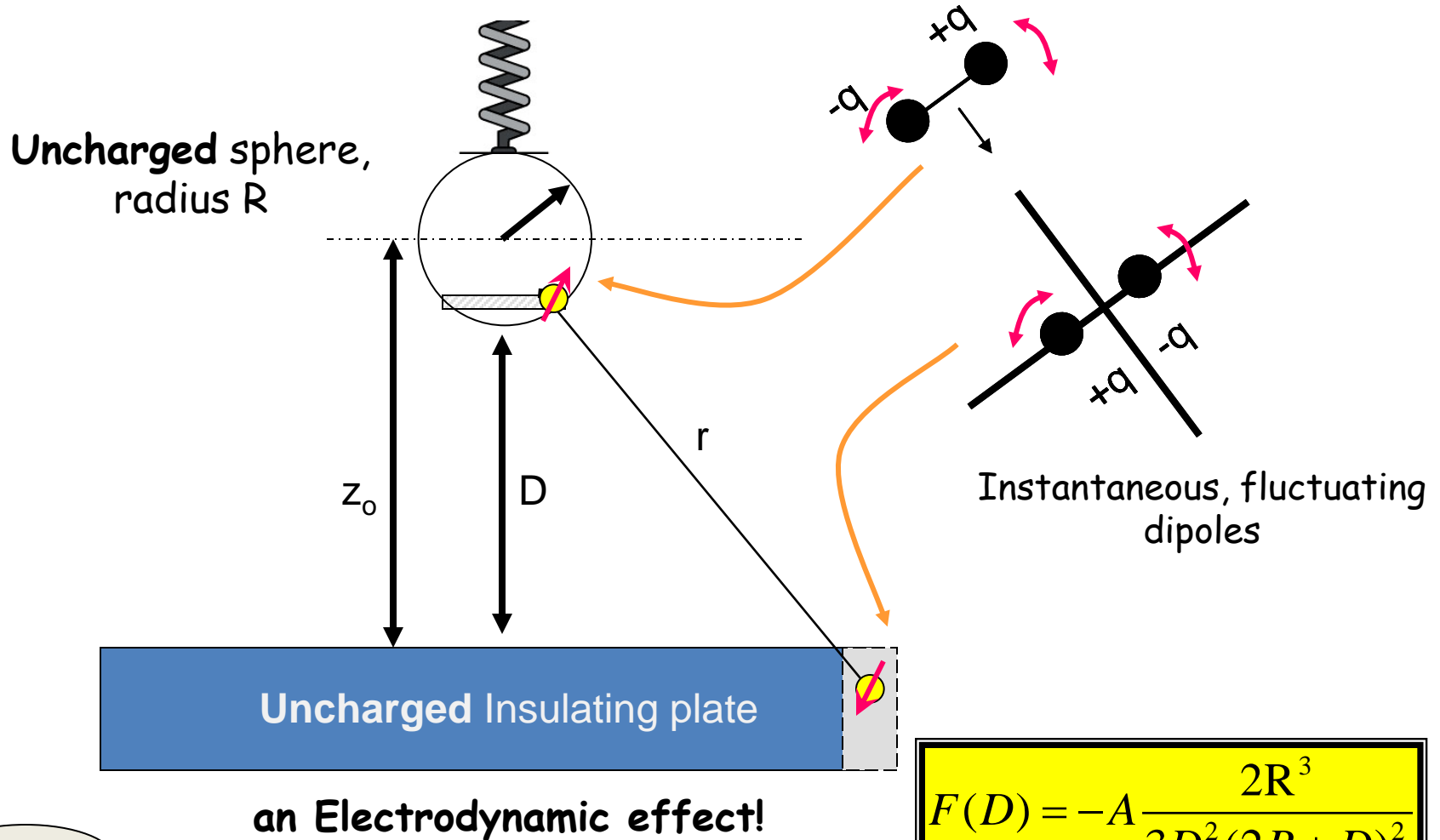
Source: http://www.ntmdt.com/spm-basics/view/intermolecular-vdv-force

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Summary of Coulombic Intermolecular Forces

System of interacting atoms and/or molecules and/or ions

ε_o or $\varepsilon\varepsilon_o$?

Is H bonded to O, N or F (permanent dipoles)?

NO

Ions Involved?

YES

Are there any atoms or molecules ?

NO

YES

Dipole – dipole Interactions (hydrogen bonding)

NO

Do the atoms or molecules have a permanent dipole?

YES

Dipoles fixed

Dipole rotating

Ion – dipole Interaction

Dipole fixed

Ionic Bonding

Coulomb Energy

Induced dipole-induced dipole only

Dipoles rotating

Polarization Forces

van der Waals Forces

London Dispersion

Keesom

Debye

35

Interaction between electrically NEUTRAL objects!

Dispersive or van der Waals Force

Uncharged sphere, radius R

z_0

D

r

Uncharged Insulating plate

an Electrodynamic effect!

1 click

+q

-q

-q

+q

Instantaneous, fluctuating dipoles

$$F(D) = -A\frac{2R^3}{3D^2(2R+D)^2}$$

A=Hamaker's constant

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Putting in some numbers

R=10 nm; Q= 8 electrons

Attractive Force (nN)

Charged sphere

sphere, radius R

D

Uncharged plate

Neutral sphere

Dielectric plate

Metal plate

a_o

I

0.020

0.010

0.000

0.0   10.0   20.0   30.0   40.0

D Surface-to-Surface Separation (nm)
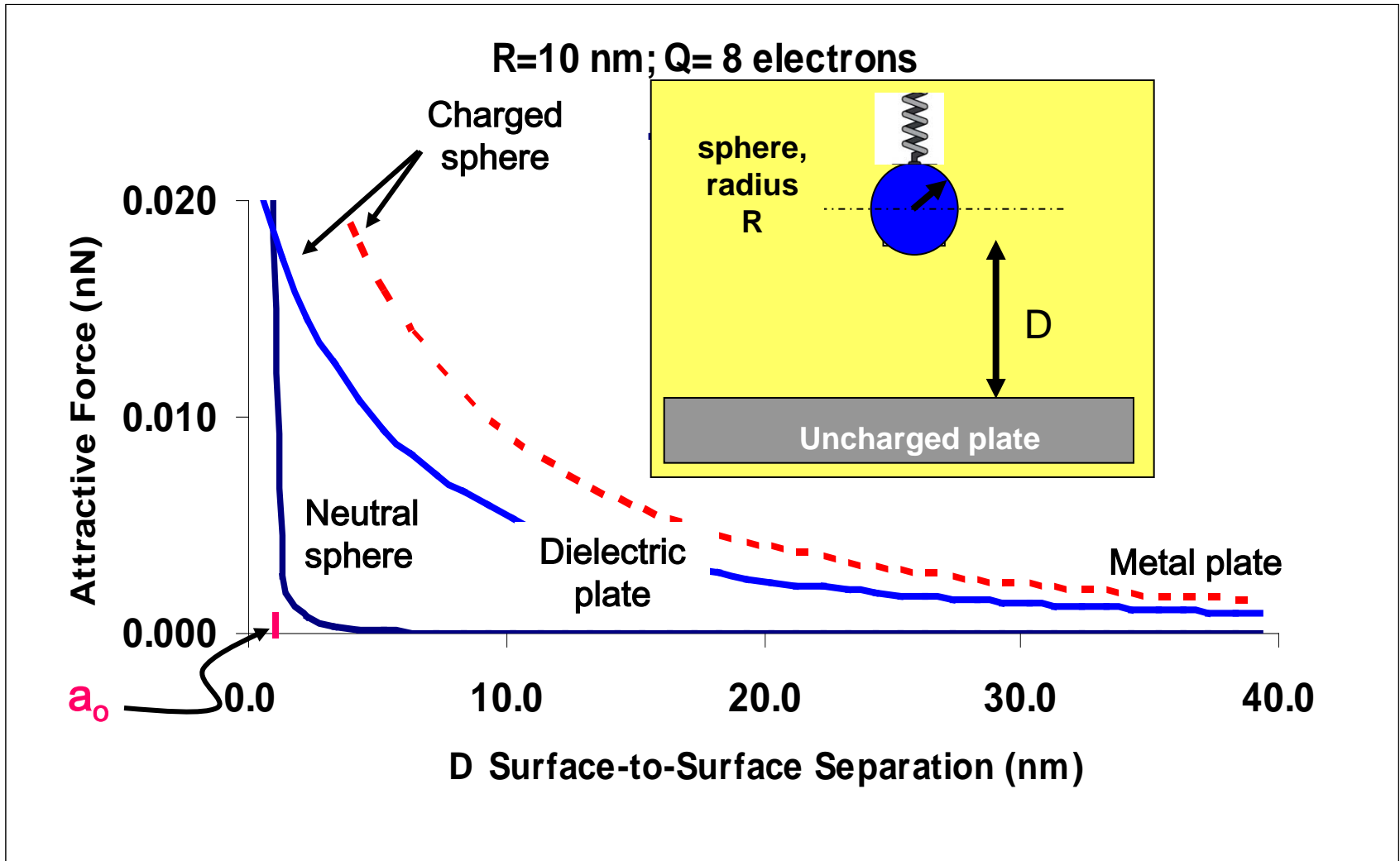
Implications for AFM

- In AFM the tip usually has native oxide on the tip within which small trapped charges or permanent dipoles can exist. As debris accumulates more permanent dipoles and charges accumulate on tip

- Dispersion potential U(r) scales as r^{-6} while electrostatics scales as

  r^{-1} (ion-ion), or

  r^{-2} (ion-dipole), or

  r^{-3} (dipole-dipole)

- In reality attractive forces are due to combination of vdW and short range electrostatics (i.e. covalent forces)

Summary: Tip-sample interaction forces in AFM

Nanosensors Gmbh
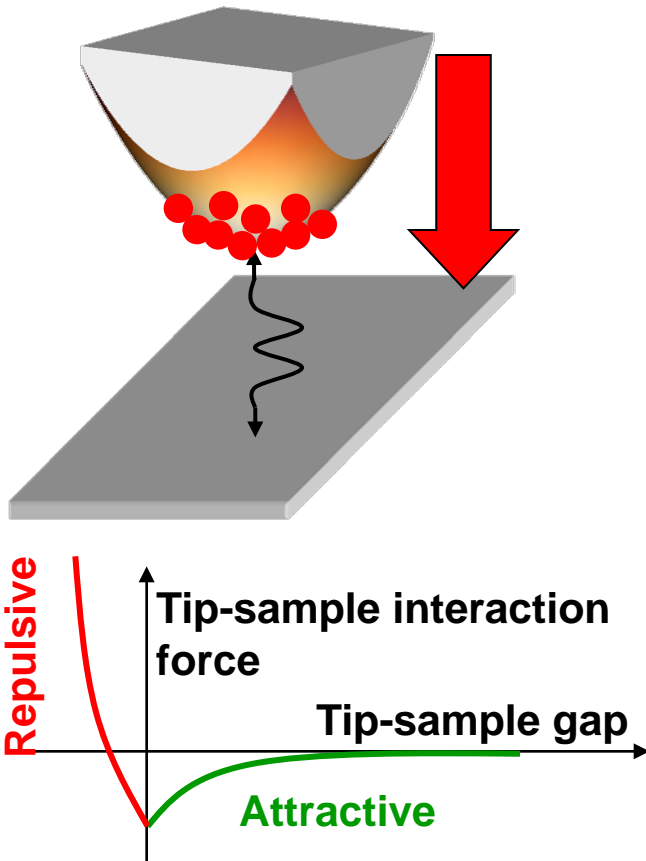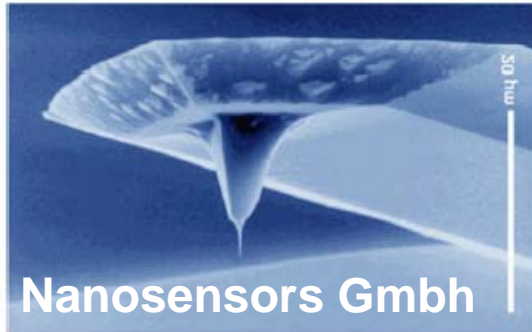
- Long-range electrostatic and magnetic forces (up to 100 nm)
- Short-range electrostatic forces
- Short-range polarization forces
- Dispersion forces (few nm) that are fundamentally quantum mechanical in nature
- van der Waals and Casimir forces
- Capillary forces (few nm)
- Short-range chemical forces (fraction of nm)
- Pauli repulsion
- Contact forces
- Electrostastic double-layer forces
- Solvation forces
- Hydrophobic and hydrophillic forces
- Nonconservative forces (Dürig (2003))

Repulsive

Tip-sample interaction force

Tip-sample gap

Attractive

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