

Van der Waals Forces (1)

Reference text:

Intermolecular and Surface Forces, Jacob N. Israelachvili

Colloidal Science and Nanoscale Engineering, Orlin Velev

Colloidal Systems, Darrell Velegol

Journal club assignments for L10

Lecture 10 (3/26)	
Group	Paper Title
A	P2_park-doyle-2018-multifunctional-hierarchically-assembled-hydrogel-particles-with-pollen-grains-via-pickering-suspension
B	P4_shah-et-al-2024-a-universal-approximation-for-conductance-blockade-in-thin-nanopore-membranes (3)
C	P1_s41586-023-05733-1
D	P3_Angew Chem Int Ed - 2017 - Zheng - Shape-Shifting Patchy Particles

Before we dive into today's lecture...

- Why do I talk about electrostatics before Van der Waals? Because it is the basic interactions that underline VdW forces (as you will see).
- Why do I go through the derivation in (sometimes painstaking) detail rather than feeding you the results (like I did in Lecture 4)? Because this is not a higher level elective: rather than teaching you the results, I'd much rather teach you how to think, or rather, how our scientific forebearers thought about this stuff so that one day you will be able to do one better.
- Trust me that all of you already know the math. Calculus, linear algebra and differential equations are more than enough for what is needed to understand what I told and am about to tell you. The details I provide in this class, however, do not assume you still remember the details from these math classes. As long as you have taken these classes, **the math that I provide is entirely self-enclosed** and are designed to be able to draw those memories out.
- So, what I aim to teach you is already in your head, all I am trying to do is just to connect the right dots and show you the train of thought.

"Microwire" grown by electric field nanoparticle assembly

<https://www.science.org/doi/10.1126/science.1063821>



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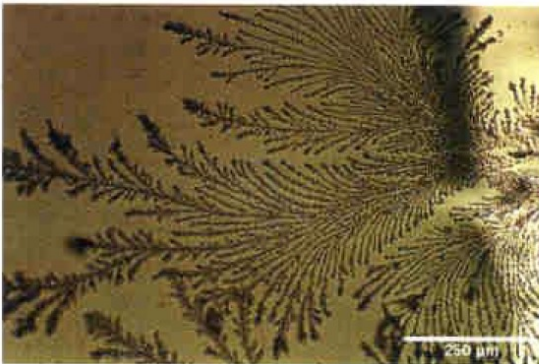
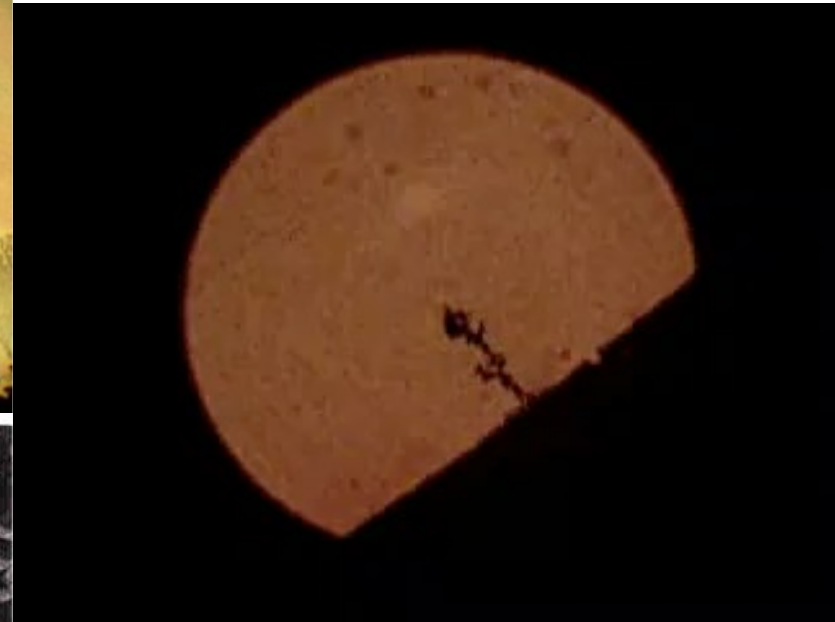
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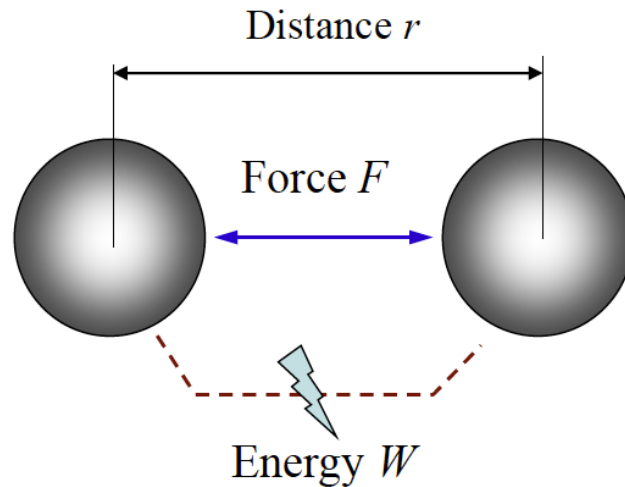
Dielectrophoretic Assembly of Electrically Functional Microwires from Nanoparticle Suspensions

KEVIN D. HERMANSON, SIMON O. LUMSDON, JACOB P. WILLIAMS, ERIC W. KALER, AND ORLIN D. VELEV [Authors Info & Affiliations](#)

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Basics of Molecular Interactions: Force and Energy



$$F(r) = -\frac{W(r)}{d r}$$



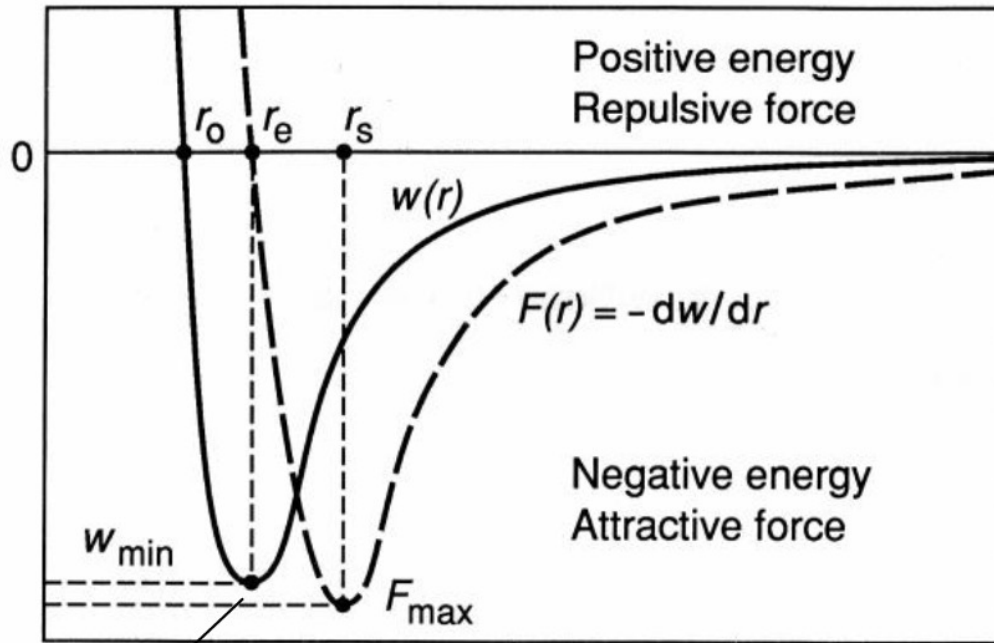
Force – measured directly,
defined for a certain separation
distance

$$W(r) = -\int F(r) d r$$



Energy: most useful in
understanding the system,
defined for a process

Basics of Molecular Interactions: Force and Energy



Energy: most common approximation:
Lennard-Jones potential

$$w(r) = + \frac{A}{r^{12}} - \frac{B}{r^6}$$

Strong short-range repulsion

Long-range attraction corresponding to the dispersion forces

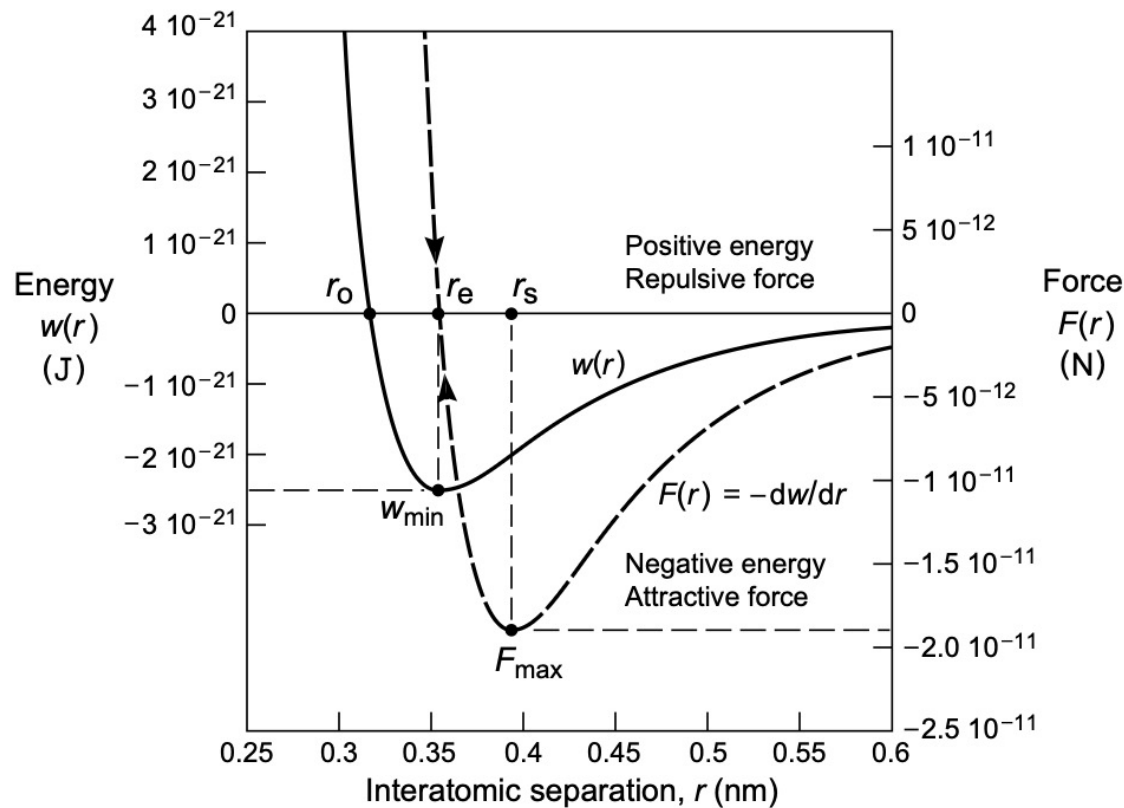
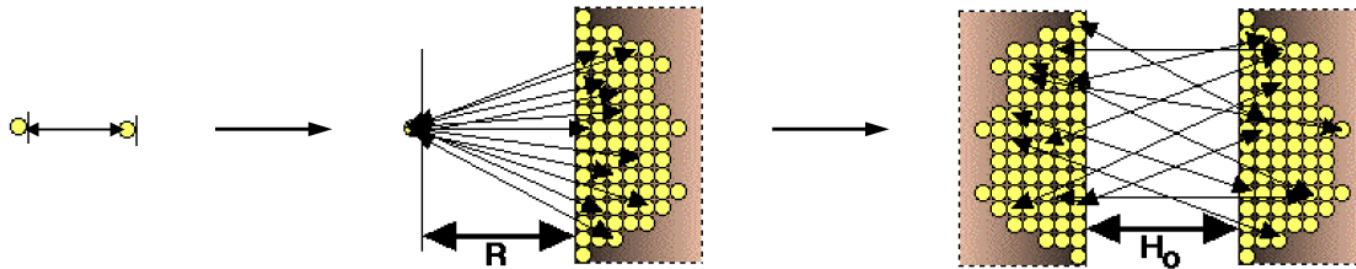


FIGURE 1.4 Typical van der Waals interaction energy (or potential) function $w(r)$ and force function $F(r) = -dw/dr$ between two atoms, which are related by $F(r) = -dw/dr$. The separation r_e is the equilibrium separation, where the force is zero and the energy is a minimum, and r_s is the point at which the two atoms or particles separate spontaneously from r_s when pulled apart by a force F_{\max} (the “adhesion” or “pull-off” force). The plotted curves are for a Lennard-Jones potential, Eq. (1.7), with parameters $A = 10^{-77} \text{ J m}^6$ and $B = 10^{-134} \text{ J m}^{12}$ (see Worked Example 1.2).

Why we need to know molecular interactions & how they operate in vacuum?

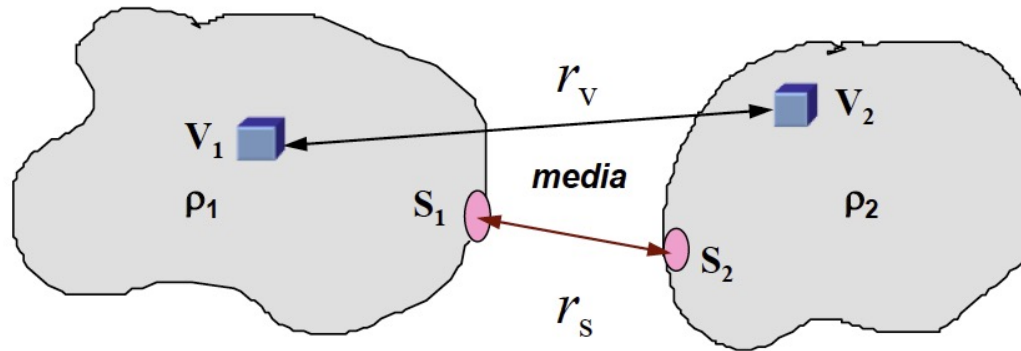
*If we sum up the interactions between **all** molecules we obtain interactions between bodies*



These forces are important in the nano-world, because the particles are not much larger and further apart than molecules

Molecular interactions in colloidal systems

Sum up all bulk and surface interactions



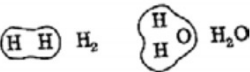
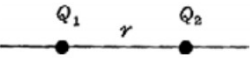
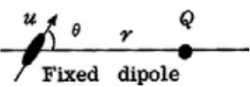
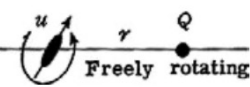
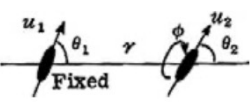
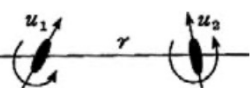
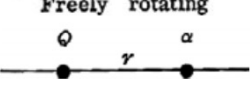
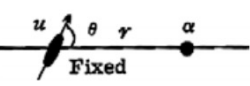
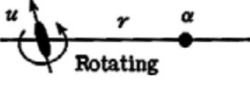
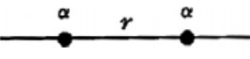
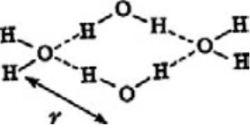
$$W(r) = \underbrace{\iint_{V_1 V_2} w_v(r_v) \rho_v d\mathbf{r}_v}_{\text{Interactions between the molecules in the bulk of the particles:}} + \underbrace{\iint_{S_1 S_2} w_s(r_s) s_s d\mathbf{r}_s}_{\text{Interactions between the surfaces of the particles:}}$$

Interaction energy between the particles

Interactions between the molecules in the bulk of the particles:
van der Waals

Interactions between the surfaces of the particles:
Electrostatic,
hydrophobic, etc

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

Type of interaction	Interaction energy $w(r)$
Covalent, metallic 	Complicated, short range
Charge-charge 	$+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy)
Charge-dipole 	$-Qu \cos \theta/4\pi\epsilon_0r^2$
	$-Q^2u^2/6(4\pi\epsilon_0)^2kTr^4$
Dipole-dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge-non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole-non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$\frac{3}{4} \frac{hv\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

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

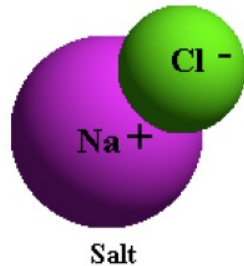
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Dipole–dipole	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
Dipole–dipole	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge–non-polar	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole–non-polar	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
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Electrical characteristics of molecules: Charge and Dipole Moment

- **Charge** $Q = z e$ [C]



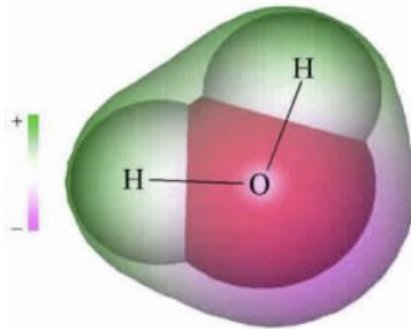
Q – total charge

z – number of electronic charges

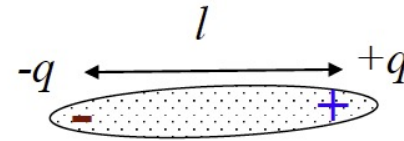
e – charge of one electron

Note that Q and z can be positive or negative

- **Dipole moment** u [C m] or [D] (1 D = 1 Debye = 3.336×10^{-30} C m)



$$u = ql$$

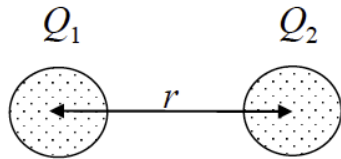


q = sub-charge on each end of molecule

l – length of molecule

Electrostatic characteristics of molecules

- **Charge Q [C]**



Two charged atoms/molecules
in media of dielectric constant ϵ

- Coulomb's law for energy
of charge-charge interaction

$$w(r) = \frac{Q_1 Q_2}{4\pi \epsilon_0 \epsilon r} = \frac{z_1 z_2 e^2}{4\pi \epsilon_0 \epsilon r}$$

Q_1, Q_2 – total charges

z_1, z_2 – number of electronic charges


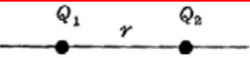
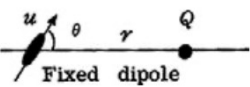
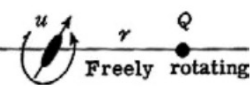
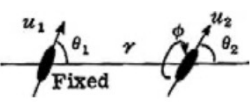
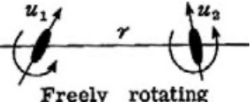
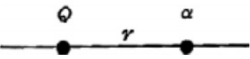
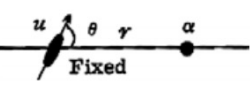
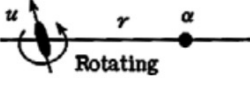
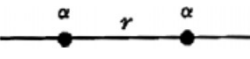
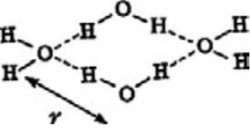
e – charge of one electron

Note that Q and z can be positive or negative

- **Long-ranged, simple force but not present often in colloidal systems**

– *Why – because the above forces are in vacuum*

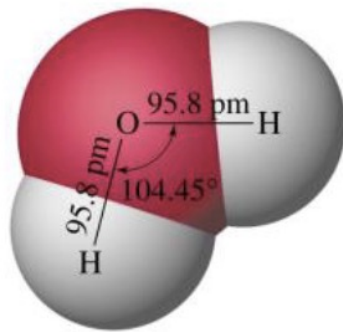
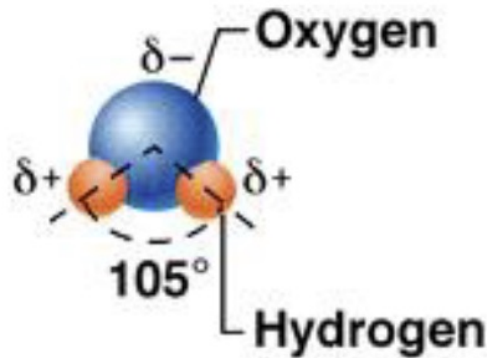
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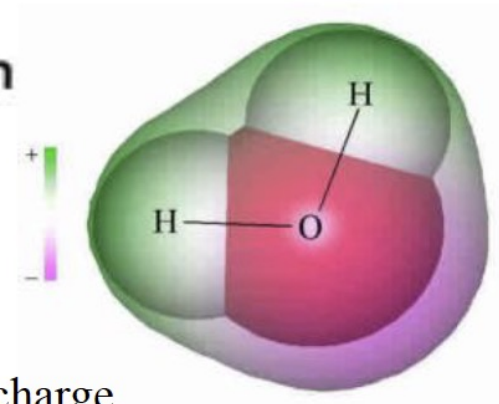
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Example of molecular electrostatics: Water

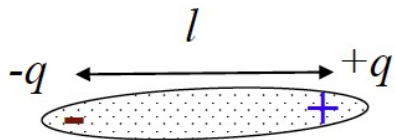
Schematic



Real size



Electronic charge

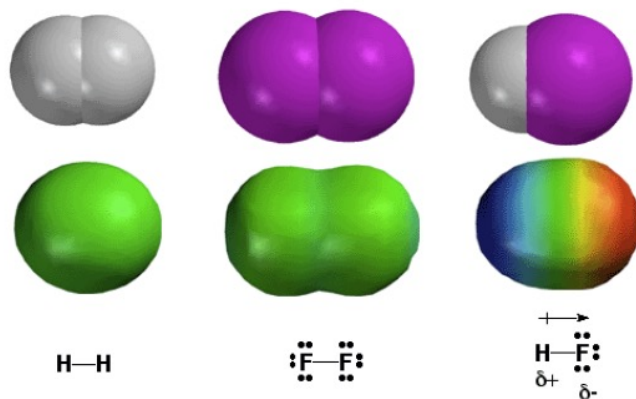


$$u = ql$$

*How is the dipole moment
superimposed on the water molecule?*

Dipole moment in molecules: Examples

Alkanes	0	NH ₃	1.47
CCl ₄	0	CH ₃ OH, C ₂ H ₅ OH	1.69
CO ₂	0	CH ₃ COOH	1.70
CHCl ₃	1.06	H ₂ O	1.85
HCl	1.08	CH ₃ COCH ₃	1.85

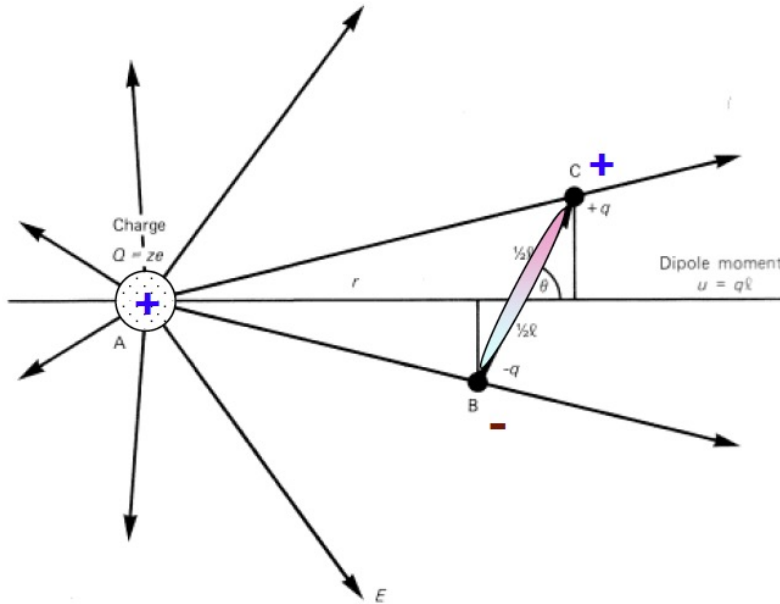


What is the major difference between molecules with large and small dipole moments?

Ion-Dipole Interactions

- One the first types of electrostatic pair interaction we shall consider is that between **a charged atom and a polar molecule**—for example, between **Na⁺ and H₂O**. As an illustrative example, we shall derive the interaction potential for this case from basic principles.

Energy of Ion-Dipole Interaction



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


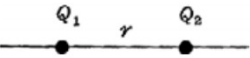
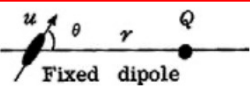
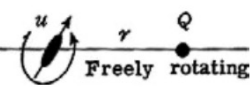
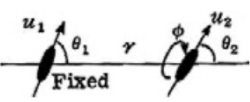
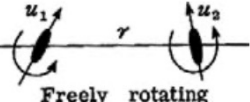
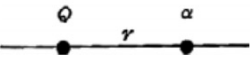
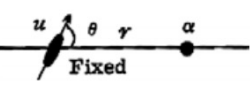
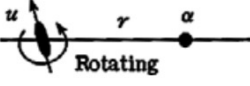
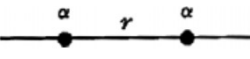
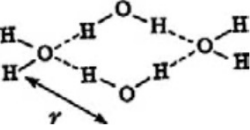
(from Coulomb law)

if $r \gg l$ then

$$AB \approx r - \frac{1}{2}l \cos\theta \quad AC \approx r + \frac{1}{2}l \cos\theta$$

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

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

Type of interaction	Interaction energy $w(r)$
Covalent, metallic 	Complicated, short range
Charge-charge 	$+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy)
Charge-dipole 	$-Qu \cos \theta/4\pi\epsilon_0r^2$
	$-Q^2u^2/6(4\pi\epsilon_0)^2kTr^4$
Dipole-dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge-non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole-non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$\frac{3}{4} \frac{hv\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

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

Some more details...

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

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

- the free energy for the interaction of a charge Q and a “point dipole” u (for which $l = 0$) in a medium is

$$\begin{aligned} w(r) = w(r, \theta) &= -\frac{Qq}{4\pi\epsilon_0\epsilon} \left[\frac{1}{r - \frac{1}{2}l \cos \theta} - \frac{1}{r + \frac{1}{2}l \cos \theta} \right] \\ &= -\frac{Qq}{4\pi\epsilon_0\epsilon} \left[\frac{l \cos \theta}{r^2 - \frac{1}{4}l^2 \cos^2 \theta} \right] \\ &= -\frac{Qu \cos \theta}{4\pi\epsilon_0\epsilon r^2} = -\frac{(ze)u \cos \theta}{4\pi\epsilon_0\epsilon r^2}. \end{aligned}$$

- Note that since the electric field of the charge acting on the dipole is $E(r) = Q/4\pi\epsilon_0\epsilon r^2$ in general the energy of a permanent dipole u in a field E may be written as

$$w(r, \theta) = -uE(r)\cos \theta$$

Ion-Dipole Interactions

- Thus, when a cation is near a dipolar molecule, maximum attraction (i.e., maximum negative energy) will occur when the dipole points away from the ion ($\theta = 0^\circ$), while if the dipole points toward the ion ($\theta = 180^\circ$) the interaction energy is positive and the force is repulsive.
- Figure shows how the pair-potential $w(r)$ varies with distance for a monovalent cation ($z = +1$) interacting with a dipolar molecule of moment 1 D in a vacuum.

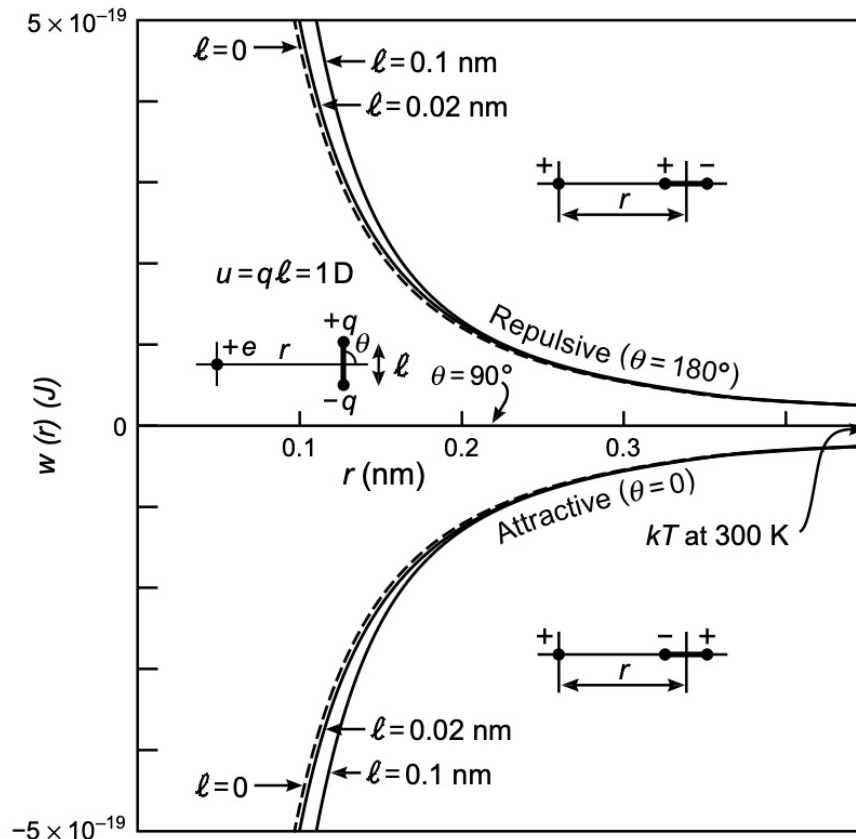
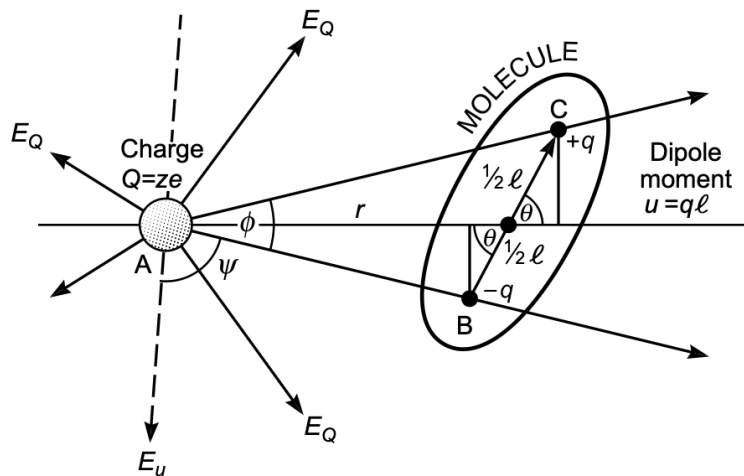


FIGURE 4.2 Charge-dipole interaction energy in vacuum ($\epsilon = 1$) between a unit charge e and a dipole of moment $u = ql = 1 \text{ D}$ (1 Debye) oriented at different angles θ to the charge. Solid lines are exact solutions, Eqs. (4.3) and (4.4), for finite sized dipoles with $l = 0.02 \text{ nm}$ and $l = 0.10 \text{ nm}$; dashed lines are exact solutions for $l = 0$, which correspond to the approximate point-dipole formula, Eq. (4.5). Note that for typical interatomic spacings ($r \approx 0.3\text{--}0.4 \text{ nm}$) the strength of the pair interaction greatly exceeds the thermal energy kT at 300 K.

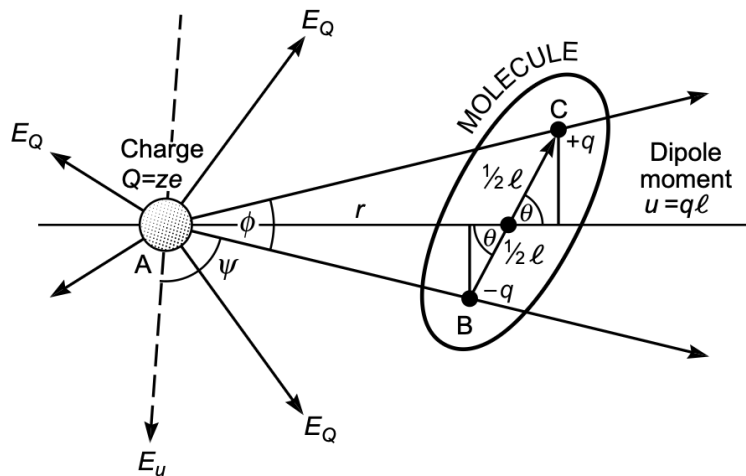
Ion-Dipole Interactions

Question: what is the net electrostatic force experienced by the ion, and in which direction does it act? What implications does your result have for (1) how a free ion moves when it is in the force field of a fixed dipolar molecule, and (2) how a free dipolar molecule moves when it is close to a fixed charge?



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- the field at A due to the charge $-q$ at B is of magnitude

$$E_- = q/4\pi\epsilon_0 \cdot AB^2 \approx (q/4\pi\epsilon_0 r^2)(1 + \frac{l}{r} \cos \theta)$$

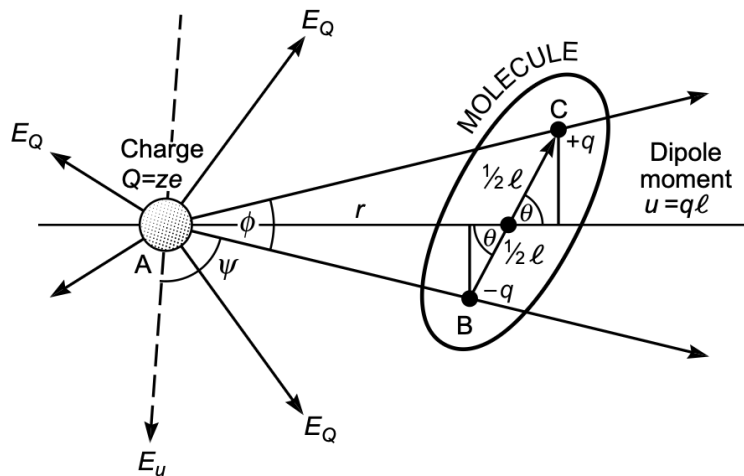
- It acts along the AB direction—that is, at an angle $-\phi/2$ to r

- Similarly, the field at A due to the charge $+q$ at C is of magnitude

$$E_+ = q/4\pi\epsilon_0 \cdot AC^2 \approx (q/4\pi\epsilon_0 r^2)(1 - \frac{l}{r} \cos \theta)$$

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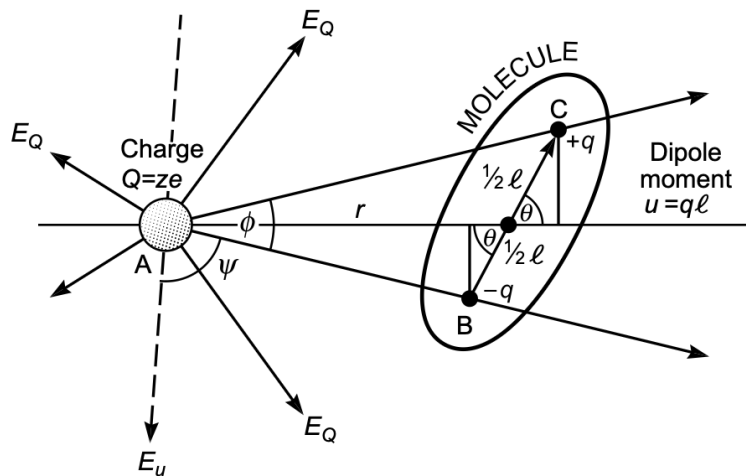
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$$E_+ = q/4\pi\epsilon_0 \cdot AC^2 \approx (q/4\pi\epsilon_0 r^2)(1 - \frac{l}{r} \cos \theta)$$
- For $r \gg l$, the angle ϕ is small and may be approximated by

$$\sin(\phi/2) \approx l \sin \theta / 2r \text{ and } \cos(\phi/2) \approx 1$$

Ion-Dipole Interactions

Question: what is the net electrostatic force experienced by the ion, and in which direction does it act? What implications does your result have for (1) how a free ion moves when it is in the force field of a fixed dipolar molecule, and (2) how a free dipolar molecule moves when it is close to a fixed charge?



- Resolving the total field at A into its components E_{\parallel} and E_{\perp} parallel and perpendicular to r , we obtain

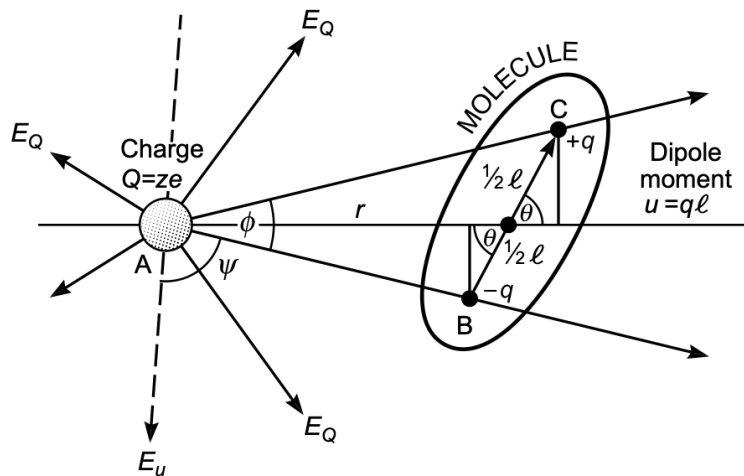
$$E_{\parallel} = (E_{-} - E_{+}) \cos(\phi/2) \approx (q/4\pi\epsilon_0 r^2) \frac{2l}{r} \cos \theta$$

$$E_{\perp} = (E_{-} + E_{+}) \sin(\phi/2) \approx (q/4\pi\epsilon_0 r^2) \frac{l}{r} \sin \theta$$

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Ion-Dipole Interactions

Question: what is the net electrostatic force experienced by the ion, and in which direction does it act? What implications does your result have for (1) how a free ion moves when it is in the force field of a fixed dipolar molecule, and (2) how a free dipolar molecule moves when it is close to a fixed charge?



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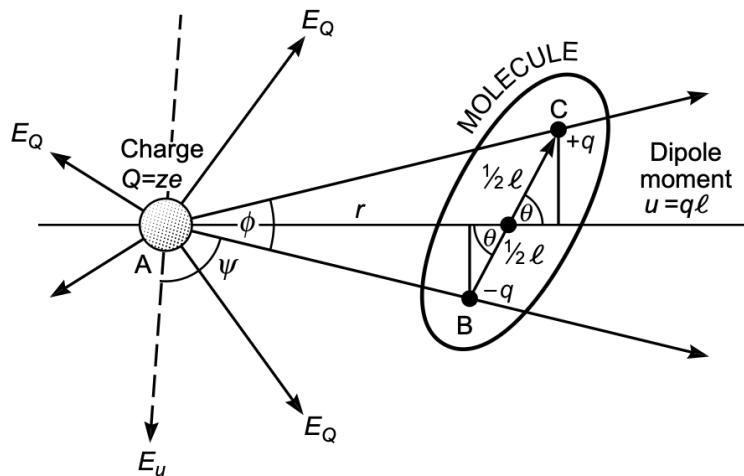
$$E_{\perp} = (E_{-} + E_{+})\sin(\phi/2) \approx (q/4\pi\epsilon_0 r^2)\frac{l}{r} \sin \theta$$
- The magnitude and direction ψ of the resulting dipolar field at A is therefore given by

$$E_u = \sqrt{E_{\parallel}^2 + E_{\perp}^2} = (ql/4\pi\epsilon_0 r^3)\sqrt{4 \cos^2 \theta + \sin^2 \theta}$$

- with $\tan \psi = E_{\perp}/E_{\parallel} = \sin \theta / 2 \cos \theta$

Ion-Dipole Interactions

Question: what is the net electrostatic force experienced by the ion, and in which direction does it act? What implications does your result have for (1) how a free ion moves when it is in the force field of a fixed dipolar molecule, and (2) how a free dipolar molecule moves when it is close to a fixed charge?



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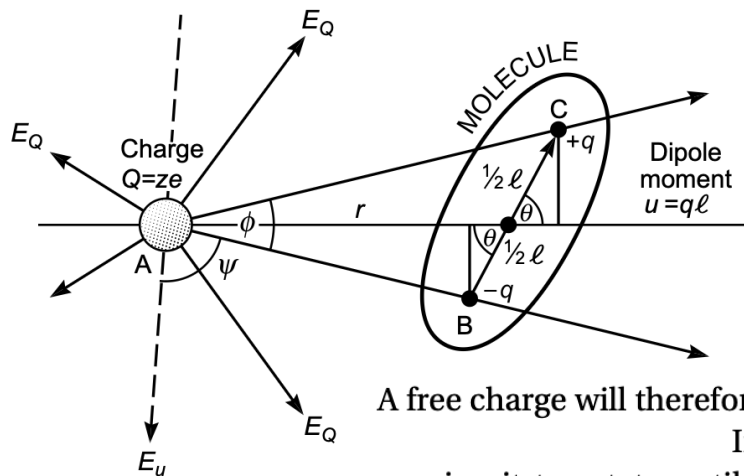
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- with $\tan \psi = E_{\perp}/E_{\parallel} = \sin \theta / 2 \cos \theta$
- therefore, $F = QE_u = \frac{Qu (1 + 3 \cos^2 \theta)^{1/2}}{4\pi\epsilon_0 r^3}$
- with $\tan \psi = \frac{\tan \theta}{2}$.

Ion-Dipole Interactions

Question: what is the net electrostatic force experienced by the ion, and in which direction does it act? What implications does your result have for (1) how a free ion moves when it is in the force field of a fixed dipolar molecule, and (2) how a free dipolar molecule moves when it is close to a fixed charge?



A free charge will therefore move along the field lines E_u or lines of force QE_u of a fixed dipole, In contrast, a free dipole near a fixed charge will experience a torque, causing it to rotate until its negative charge $-q$ points toward the positive charge $+Q$, after which it will move in a straight line (along r) toward the charge. In both cases, however, the actual trajectories will be much more complex due to inertial and viscous effects, since the full equations of motion must include both inertial terms of the type $m\ddot{x}$ and viscous terms of the type $\eta\dot{x}$. Then, on coming into contact, additional steric effects—determined by the specific sizes and shapes of the ion and dipolar molecules—ultimately determine their lowest energy configuration.

Ions in Polar Solvents

- When ion-water interactions take place in bulk water, the above energies are reduced by a factor of about 80, the dielectric constant of water. Even then, however, the strength of the interaction will exceed kT for small divalent and multivalent ions, and it is by no means negligible for small monovalent ions.

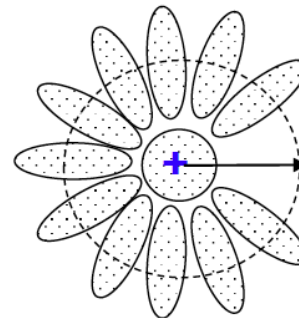
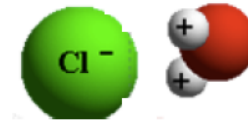
Ion - Dipole Interaction: What happens when $w(r) > kT$?

For a monovalent ion in water, single ionic charge $Q = e^-$, $u = 1.85 D$, $\epsilon = 80$

$$w_{\max} = \frac{Qu}{4\pi\epsilon\epsilon_0 r^2} > kT \quad \text{at}$$

$$r = \left(\frac{Qu}{4\pi\epsilon\epsilon_0 kT} \right)^{1/2} = 0.2 \text{ nm}$$

- *The consequences are:*



0.2 nm \approx a shell of one layer of water molecules are frozen oriented around the ion

Ions in Polar Solvents

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- For small or multivalent ions in highly polar solvents such as water, the strong orientation dependence of their ion-dipole interaction will tend to orient the solvent molecules around them, favoring ($\theta = 0^\circ$) near cations and ($\theta = 180^\circ$) near anions.

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- For small or multivalent ions in highly polar solvents such as water, the strong orientation dependence of their ion-dipole interaction will tend to orient the solvent molecules around them, favoring ($\theta = 0^\circ$) near cations and ($\theta = 180^\circ$) near anions.
- Thus, in water Li^+ , Be^{2+} (Beryllium), Mg^{2+} , and Al^{3+} ions have a number of water molecules orientationally bound to them. Such ions are called solvated ions or hydrated ions, and the number of water molecules they bind—usually between 4 and 6 is known as their hydration number.

Table 4.2 Hydrated radii and Hydration Numbers of Ions in Water (Approximate)

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 hydration number gives the number of water molecules in the primary hydration shell (Fig. 3.4), though the total number of water molecules affected can be much larger and depends on the method of measurement. Similarly, the hydrated radius depends on how it is measured. Different methods can yield radii that can be as much as 0.1 nm smaller or larger than those shown. Table compiled from data given by Nightingale (1959), Amis (1975), Saluja (1976), Bockris and Reddy (1970), and Cotton and Wilkinson (1980).

^aNumber of water molecules forming a stoichiometric complex with the ion—for example, [Be(H₂O)₄]²⁺.

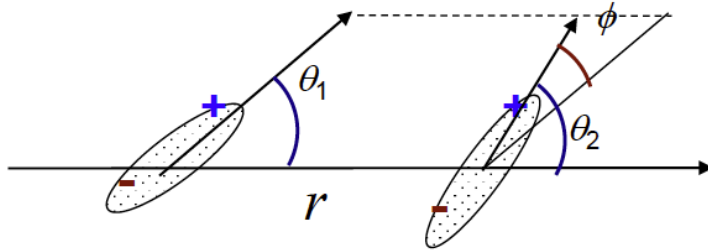
Ions in Polar Solvents

- Closely related to the hydration number is the effective radius or hydrated radius of an ion in water, which is larger than its real radius (i.e., its crystal lattice radius), as shown in Table on the previous slide.
- Because smaller ions are more hydrated due to their more intense electric field they tend to have larger hydrated radii than larger ions. However, very small ions such as Be^{2+} have lower hydration numbers because they are too small for more than 4 water molecules to pack around them.
- Hydration numbers and radii can be deduced from measurements of the viscosity, diffusion, compressibility, conductivity, solubility, and various thermodynamic and spectroscopic properties of electrolyte solutions, and the results rarely agree with one another.

Dipole-Dipole Interactions

- When two polar molecules are near each other, there is a dipole-dipole interaction between them that is analogous to that between two magnets.

Energy of Dipole-Dipole Interaction

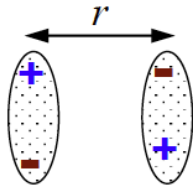


- Characterized by the distance r and three rotation angles, θ_1, θ_2 and ϕ

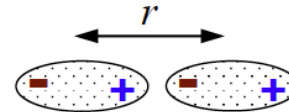
$$w(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi \epsilon_0 \epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

Workout – which attraction is stronger?

“Parallel”



← or →


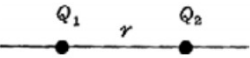
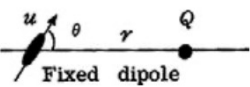
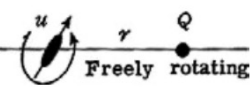
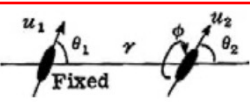
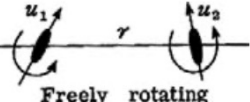
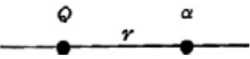
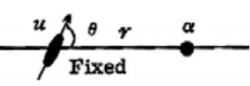
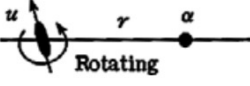
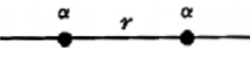
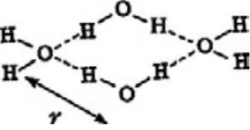


“In line”

$$w\left(r, \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) = -\frac{u_1 u_2}{4\pi \epsilon_0 \epsilon r^3}$$

$$w_{\max} = w(r, 0, 0, \phi) = -\frac{2u_1 u_2}{4\pi \epsilon_0 \epsilon r^3} \quad \checkmark$$

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Dipole–dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge–non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole–non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$\frac{3}{4} \frac{hv\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

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Dipole-Dipole Interactions

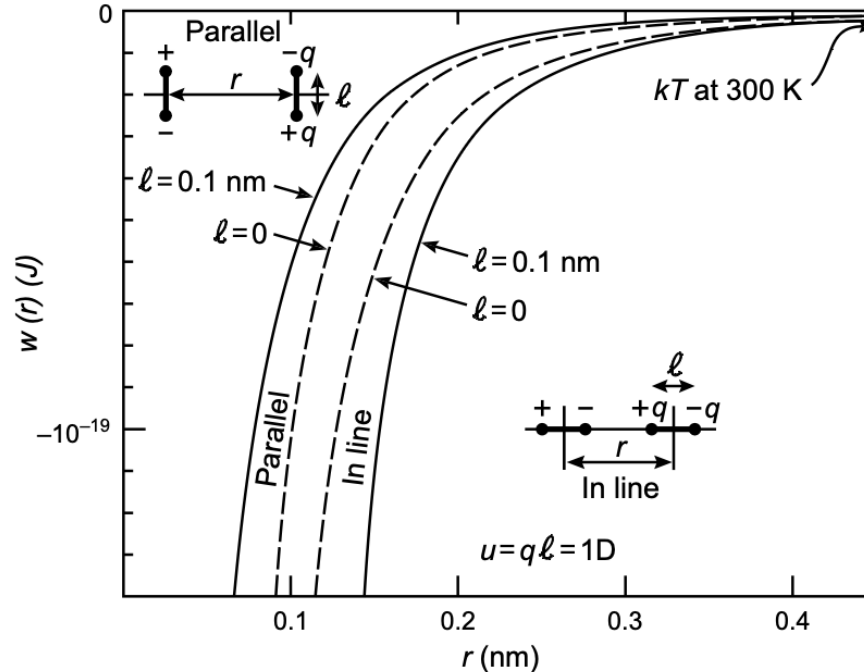
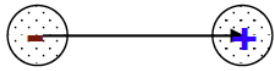


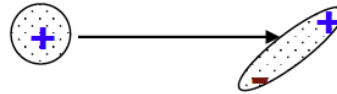
FIGURE. 4.3 Dipole-dipole interaction energy in a vacuum between two dipoles each of moment 1 D. Note how much weaker this interaction is compared to the charge-dipole interaction (Figure. 4.2) and the large effect of finite dipole size.

Caveat: This is true only for the same value of r . Most dipolar molecules are also anisotropic in shape being longer along the direction of the dipole, so in practice the centers of two such cigar-shaped molecules can come significantly closer together when they align in parallel, thereby making this interaction the more favorable one.

Basic types of long-range molecular interactions



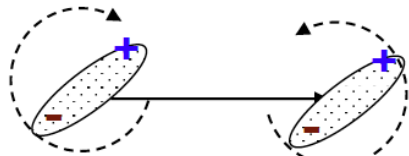
Charge - Charge



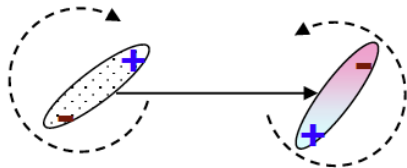
Charge - Dipole



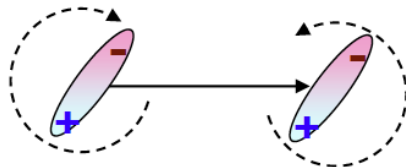
Dipole - Dipole



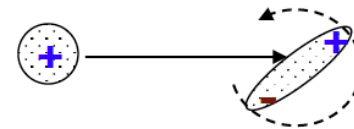
Two Rotating Dipoles



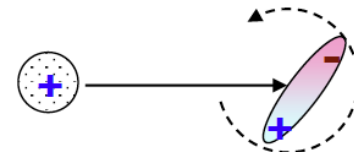
Dipole - Polarizable



Polarizable - Polarizable
Dispersion forces



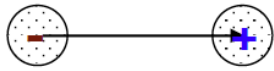
Charge - Rotating Dipole



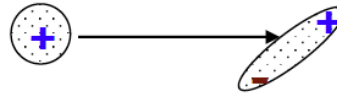
Charge - Polarizable

**All of these
are attractive
(Why?)**

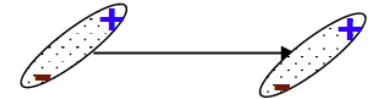
Basic types of long-range molecular interactions



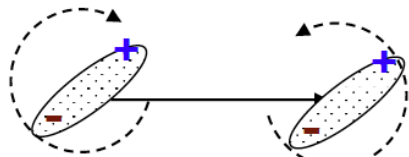
Charge - Charge



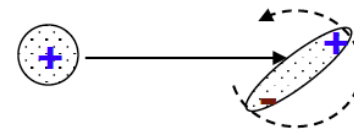
Charge - Dipole



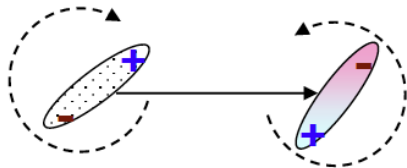
Dipole - Dipole



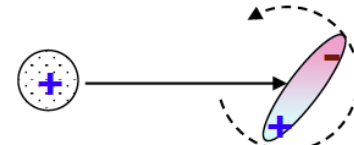
Two Rotating Dipoles



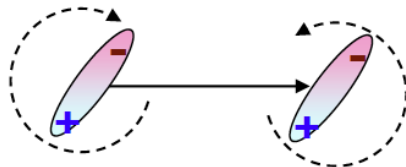
Charge - Rotating Dipole



Dipole - Polarizable



Charge - Polarizable



Polarizable - Polarizable
Dispersion forces

**All of these
are attractive
(Why?)**

Rotating Dipoles and Angle-Averaged Potentials

- At large separations or in a medium of high ϵ , when the angle dependence of the interaction energy falls below the thermal energy kT , dipoles can now rotate more or less freely.
- the values of $\cos \theta$, $\sin \theta$, and so on, when averaged over all of space are zero, the angle-averaged potentials are not zero, since there is always a Boltzmann weighting factor that gives more weight to those orientations that have a lower (more negative) energy.
- In general, the angle-averaged free energy $w(r)$ of an instantaneous orientation-dependent free energy $w(r, \Omega)$ is given by

$$e^{-w(r)/kT} = \int e^{-w(r,\Omega)/kT} d\Omega / \int d\Omega = \left\langle e^{-w(r,\Omega)/kT} \right\rangle$$

- where $d\Omega = \sin\theta d\theta d\phi$ corresponds to the polar and azimuthal angles θ and ϕ and the integration is over all of angular space. The denominator in the above equation is:

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

Recall for spherical coordinates

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

$$\langle \sin^2 \theta \rangle = \frac{2}{3},$$

$$\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = \frac{1}{2},$$

$$\langle \sin \theta \rangle = \langle \cos \theta \rangle = \langle \sin \theta \cos \theta \rangle = 0,$$

$$\langle \sin \phi \rangle = \langle \cos \phi \rangle = \langle \sin \phi \cos \phi \rangle = 0.$$

This is in three dimensions. In two dimensions—for example, on a surface—the only difference is that $\langle \cos^2 \theta \rangle = \langle \sin^2 \theta \rangle = \frac{1}{2}$.

Rotating Dipoles and Angle-Averaged Potentials

- Since the angle-averaged free energy $w(r)$ of an instantaneous orientation-dependent free energy $w(r, \Omega)$ is given by

$$e^{-w(r)/kT} = \int e^{-w(r,\Omega)/kT} d\Omega / \int d\Omega = \left\langle e^{-w(r,\Omega)/kT} \right\rangle$$

- Taylor expand:

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

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


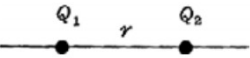
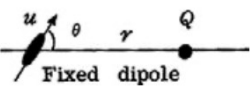
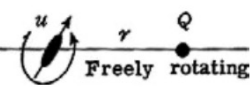
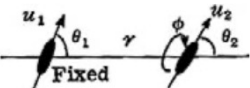
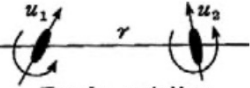
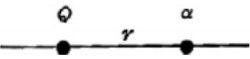
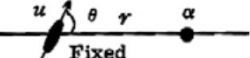
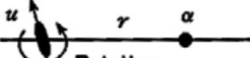
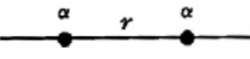
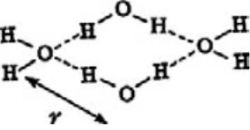
- Recall the free energy for the [charge-dipole interaction](#) is

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

- the angle-averaged free energy for the [charge-dipole interaction](#) is therefore

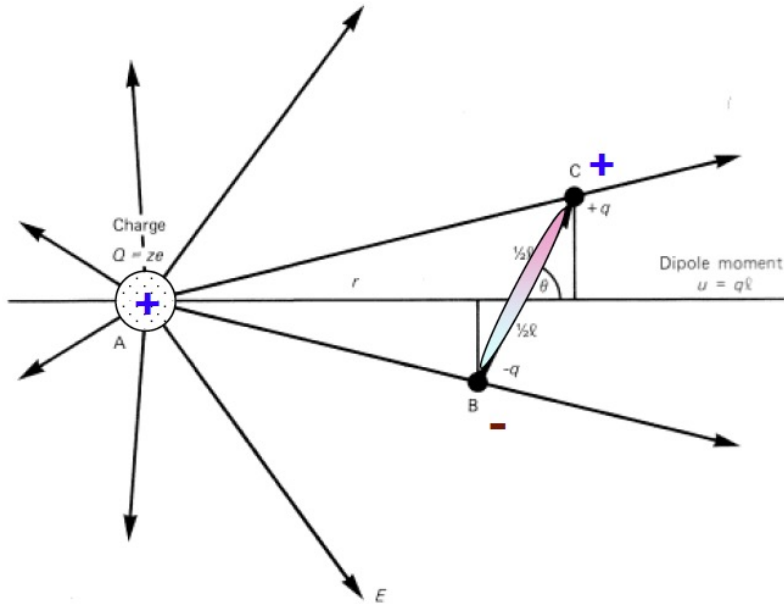
$$\implies w(r) = \left\langle -\frac{Qu \cos \theta}{4\pi\epsilon_0\epsilon r^2} - \left(\frac{Qu}{4\pi\epsilon_0\epsilon r^2} \right)^2 \frac{\cos^2 \theta}{2kT} + \dots \right\rangle \approx -\frac{Q^2 u^2}{6(4\pi\epsilon_0\epsilon)^2 kT r^4}$$

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

Type of interaction	Interaction energy $w(r)$
Covalent, metallic 	Complicated, short range
Charge-charge 	$+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy)
Charge-dipole 	$-Qu \cos \theta/4\pi\epsilon_0r^2$
	$-Q^2u^2/6(4\pi\epsilon_0)^2kTr^4$
Dipole-dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge-non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole-non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$\frac{3}{4} \frac{hv\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

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

Energy of Ion-Dipole Interaction



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

(from Coulomb law)

if $r \gg l$ then

$$AB \approx r - \frac{1}{2}l \cos\theta \quad AC \approx r + \frac{1}{2}l \cos\theta$$

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

Rotating Dipoles and Angle-Averaged Potentials

- Since the angle-averaged free energy $w(r)$ of an instantaneous orientation-dependent free energy $w(r, \Omega)$ is given by

$$e^{-w(r)/kT} = \int e^{-w(r,\Omega)/kT} d\Omega / \int d\Omega = \left\langle e^{-w(r,\Omega)/kT} \right\rangle$$

- Taylor expand:

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

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

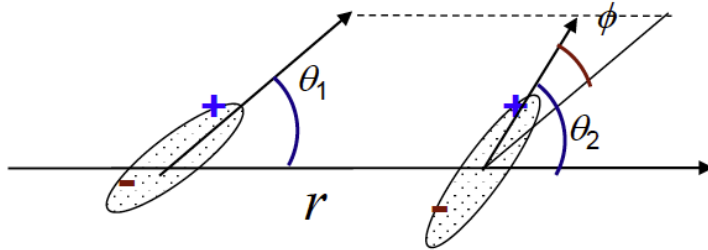
- Recall the free energy for the **dipole-dipole interaction** is

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

- the angle-averaged free energy for the **dipole-dipole interaction** is therefore

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

Energy of Dipole-Dipole Interaction

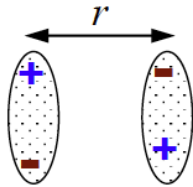


- Characterized by the distance r and three rotation angles, θ_1, θ_2 and ϕ

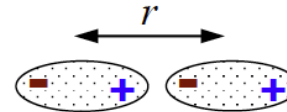
$$w(r, \theta_1, \theta_2, \phi) = -\frac{u_1 u_2}{4\pi \epsilon_0 \epsilon r^3} [2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]$$

Workout – which attraction is stronger?

“Parallel”



← or →



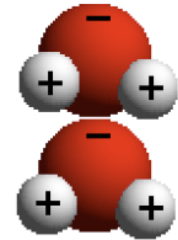
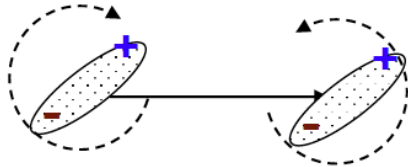
“In line”

$$w\left(r, \frac{\pi}{2}, -\frac{\pi}{2}, 0\right) = -\frac{u_1 u_2}{4\pi \epsilon_0 \epsilon r^3}$$

$$w_{\max} = w(r, 0, 0, \phi) = -\frac{2u_1 u_2}{4\pi \epsilon_0 \epsilon r^3} \quad \checkmark$$

Angle-Averaged Rotating Dipole - Dipole Interaction

- Angle-averaging vs. the thermal energy for $kT > w(r, \Omega)$



Polar attraction between water molecules

$$\exp[-w(r)/kT] = \langle \exp[-w(r, \Omega)/kT] \rangle$$

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


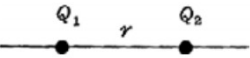
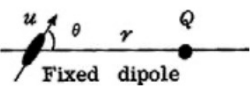
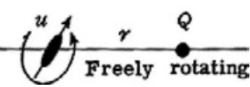
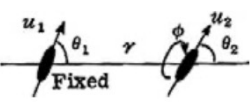
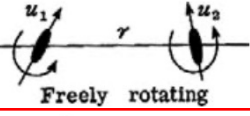
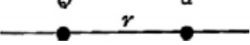
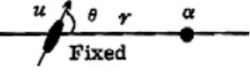
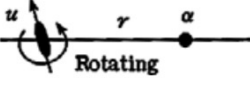
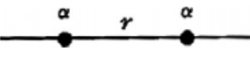
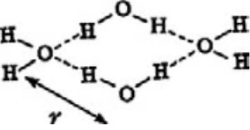
What happens to the averaged 1st term?

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

Orientation or Keesom molecular dipole interaction

The Boltzmann-averaged interaction between two permanent dipoles is usually referred to as the orientation or Keesom interaction. It is one of three important interactions, each varying with the inverse sixth power of the distance, that together contribute to the total van der Waals interaction between atoms and molecules.

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

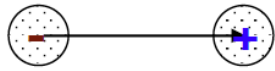
Type of interaction	Interaction energy $w(r)$
Covalent, metallic 	Complicated, short range
Charge–charge 	$+Q_1Q_2/4\pi\epsilon_0r$ (Coulomb energy)
Charge–dipole 	$-Qu \cos \theta/4\pi\epsilon_0r^2$
	$-Q^2u^2/6(4\pi\epsilon_0)^2kTr^4$
Dipole–dipole 	$-u_1u_2[2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi]/4\pi\epsilon_0r^3$
	$-u_1^2u_2^2/3(4\pi\epsilon_0)^2kTr^6$ (Keesom energy)
Charge–non-polar 	$-Q^2\alpha/2(4\pi\epsilon_0)^2r^4$
Dipole–non-polar 	$-u^2\alpha(1 + 3 \cos^2 \theta)/2(4\pi\epsilon_0)^2r^6$
	$-u^2\alpha/(4\pi\epsilon_0)^2r^6$ (Debye energy)
Two non-polar molecules 	$\frac{3}{4} \frac{hv\alpha^2}{(4\pi\epsilon_0)^2r^6}$ (London dispersion energy)
Hydrogen bond 	Complicated, short range, energy roughly proportional to $-1/r^2$

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

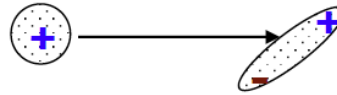
Interactions Involving the Polarization of Molecules

- We now enter the last large category of electrostatic interactions that we shall be considering: those that involve molecular polarization. This involves the dipole moments induced in molecules by the electric fields emanating from nearby molecules.

Basic types of long-range molecular interactions



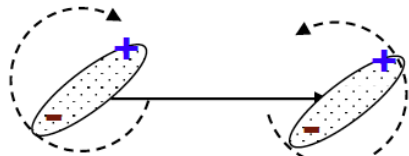
Charge - Charge



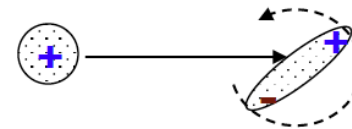
Charge - Dipole



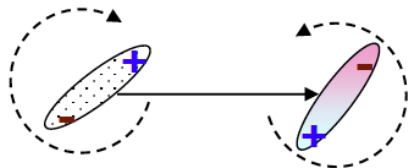
Dipole - Dipole



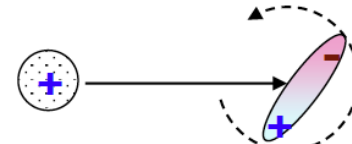
Two Rotating Dipoles



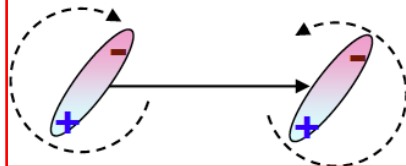
Charge - Rotating Dipole



Dipole - Polarizable



Charge - Polarizable



Polarizable - Polarizable
Dispersion forces

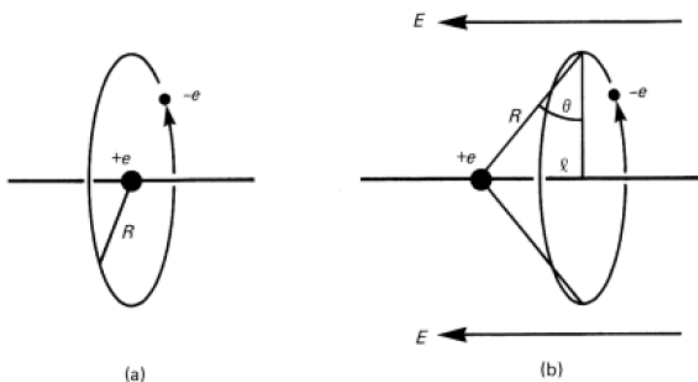
**All of these
are attractive
(Why?)**

Interactions Involving the Polarization of Molecules

- We now enter the last large category of electrostatic interactions that we shall be considering: those that involve molecular polarization. This involves the dipole moments induced in molecules by the electric fields emanating from nearby molecules.
- 3 sub-categories: (1) charge-polarizable dipole, (2) dipole-polarizable dipole, and (3) polarizable dipole – polarizable dipole interactions.
- Actually, we have already been much involved with polarization effects: whenever the macroscopic dielectric constant of a medium entered into our consideration, this was no more than a reflection of the way the molecules of the medium are polarized by the local electric field. Here we shall look at these effects in more detail, starting at the molecular level.
- All atoms and molecules are polarizable. Their (dipole) polarizability α is defined according to the strength of the induced dipole moment \mathbf{u}_{ind} they acquire in a field \mathbf{E}

For a nonpolar molecule, the polarizability arises from the displacement of its negatively charged electron cloud relative to the positively charged nucleus under the influence of an external electric field. For polar molecules, there are other contributions to the polarizability, discussed later. For the moment, we shall concentrate on the polarizabilities of nonpolar molecules, which we shall denote by α_0 .

Basics of molecular polarization



a one-electron "Bohr" atom

the external force F_{ext} on the electron due to the field E is $F_{\text{ext}} = -eE$

The internal (restoring) force is

$$F_{\text{int}} = \frac{-e^2}{4\pi\epsilon_0 R^2} \sin \theta \approx \frac{-e^2 l}{4\pi\epsilon_0 R^3} \approx \frac{-e u_{\text{ind}}}{4\pi\epsilon_0 R^3}$$

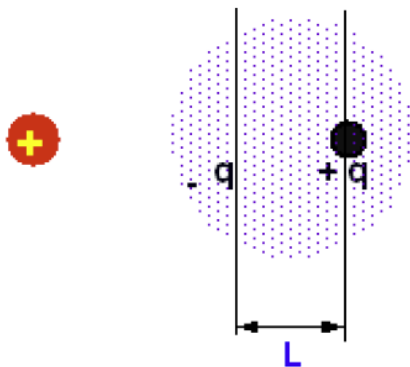
- Polarizing an atom in the electric field

$$u_{\text{ind}} = ql = \alpha_0 E$$

$$u_{\text{ind}} = 4\pi\epsilon_0 R^3 E = \alpha_0 E$$

$$\alpha_0 = 4\pi\epsilon_0 R^3$$

Electronic polarizability
[C² m² J⁻¹]



$F_{\text{ext}} = F_{\text{int}}$ at equilibrium

- Polarizing a molecule in the field of an ion

Table 5.1 Electronic Polarizabilities α_0 of Atoms, Molecules, Bonds, and Molecular Groups^a

Atoms and Molecules					
He	0.20	NH ₃	2.3	CH ₂ =CH ₂	4.3
H ₂	0.81	CH ₄	2.6	C ₂ H ₆	4.5
H ₂ O	1.45–1.48	HCl	2.6	Cl ₂	4.6
O ₂	1.60	CO ₂	2.9	CHCl ₃	8.2
Ar	1.63	CH ₃ OH	3.2	C ₆ H ₆	10.3
CO	1.95	Xe	4.0	CCl ₄	10.5
Bond Polarizabilities					
C–C aliphatic	0.48	C–H	0.65	C–Cl	2.60
C \equiv C aromatic	1.07	O–H	0.73	C–F	0.73
C=C	1.65	C–O	0.60	Si–Si	2.24
C \equiv C	2.39	C=O	1.36	Si–H	1.27
Molecular Groups					
C–O–H	1.3	–CH ₂ –	1.84	CF ₃	2.4
C–O–C	1.1	CH ₃	2.0	Si–O–Si	1.4
C–NH ₂	2.0	–CF ₂ –	2.0	Si–OH	1.6

^aPolarizabilities α_0 are given in volume units of $(4\pi\epsilon_0)\text{\AA}^3 = (4\pi\epsilon_0)10^{-30} \text{ m}^3 = 1.11 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$. Note that when molecules are dissolved in a solvent medium, their polarizability can change by up to 10%. Data compiled from *CRC Handbook of Chemistry and Physics*, 87th Edition (2006–2007), Denbigh (1940), Hirschfelder et al., (1954), and Smyth (1955).

Since the electronic polarizability is associated with displacements of electron clouds, it has long been recognized that the polarizability of a molecule can be obtained by simply summing the characteristic polarizabilities of its covalent bonds, since these are where the polarizable electrons are mostly localized. (i.e., $\alpha_{\text{CH}_4} = 4\alpha_{\text{C-H}}$)

The Polarizability of Polar Molecules

- Up till now we considered the polarizability arising solely from the electronic displacements in atoms and molecules.
- A freely rotating dipolar molecule (whose time-averaged dipole moment is zero) also has an orientational or a dipolar polarizability, arising from the effect of an external field on the Boltzmann-averaged orientations of the rotating dipole.
- Thus, in the presence of an electric field E , these orientations will no longer time-average to zero but will be weighted along the field.
- If at any instant the permanent dipole u is at an angle θ to the field E ,
- its resolved dipole moment along the field is $u \cos \theta$, and its energy in the field is $uE \cos \theta$: $w(r, \theta) = -uE(r) \cos \theta$
- so the angle-averaged induced dipole moment is given by

$$\begin{aligned} u_{\text{ind}} &= \left\langle u \cos \theta e^{uE \cos \theta / kT} \right\rangle \\ &= \frac{u^2 E}{kT} \left\langle \cos^2 \theta \right\rangle = \frac{u^2}{3kT} E, \quad uE \ll kT \end{aligned}$$

Since u_{ind} is proportional to the field E , we see that the factor $u^2/3kT$ provides an additional contribution to the molecular polarizability. This is the dipolar or orientational polarizability, defined by $\alpha_{\text{dip}} = u^2/3kT$.

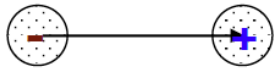
Total polarizability = molecular + orientational

Debye-Langevin equation

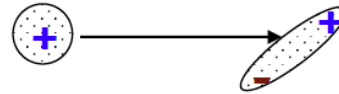
$$\alpha_{\text{total}} = \alpha_0 + \frac{u^2}{3kT}$$

For **non-polar** molecules, its polarizability is just α_0 . If it is a **dipolar molecule**, then its total polarizability will have a **molecular component** α_0 as well as an angle averaged **orientational component** α_{dip} .

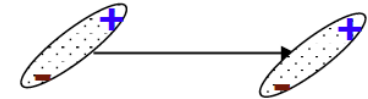
Basic types of long-range molecular interactions



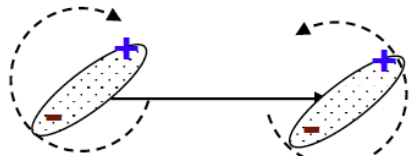
Charge - Charge



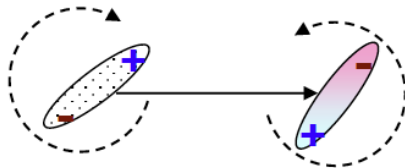
Charge - Dipole



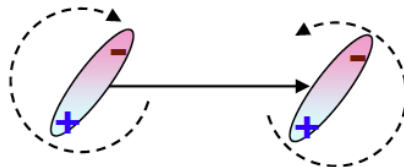
Dipole - Dipole



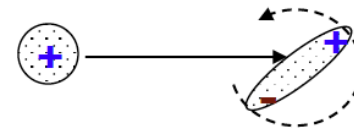
Two Rotating Dipoles



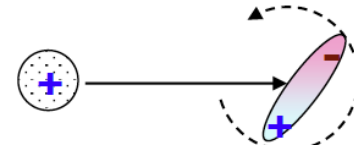
Dipole - Polarizable



Polarizable - Polarizable
Dispersion forces



Charge - Rotating Dipole



Charge - Polarizable

**All of these
are attractive
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Interactions between Ions and Uncharged Molecules

- When a molecule of polarizability α is at a distance r from an ion of charge ze , the electric field of the ion $E = ze/4\pi\epsilon_0\epsilon r^2$ will induce in the molecule a dipole moment of

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

You need to log in using your umich.edu account in order to access this poll

Lecture 10 Poll: interactions between ions and uncharged molecules

Question: Estimate the distance by which the electron cloud of a methane (CH_4) molecule 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 ($\epsilon = 1$)

- A: 0.016 nm
- B: 0.16 nm
- C: 1.6 nm
- D: 16 nm

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

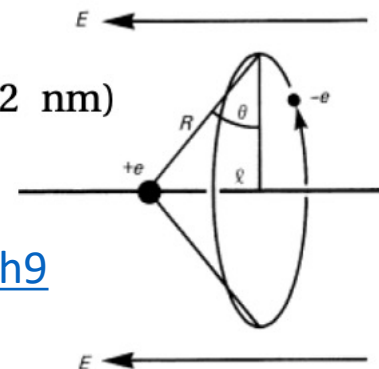
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$$u_{\text{ind}} = ql = \alpha_0 E$$

the molecular radius of methane (of 0.2 nm)



Long URL <https://forms.gle/QZAScSrbQ8Jmhzh9>

Short URL <https://shorturl.at/ahyHS>



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For a monovalent ion such as Na^+ , the electric field at a distance of 0.4 nm from its center is

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

$$E = e / 4\pi\epsilon_0 r^2 = (1.602 \times 10^{-19})$$

$$/ (4 \times 3.142 \times 8.854 \times 10^{-12}) (0.4 \times 10^{-9})^2$$

$$= 9.0 \times 10^9 \text{ V m}^{-1}$$

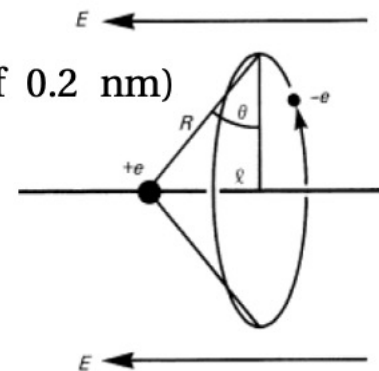
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$$u_{\text{ind}} = ql = \alpha_0 E$$

the molecular radius of methane (of 0.2 nm)



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Lecture 10 Poll: interactions between ions and uncharged molecules

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For a monovalent ion such as Na⁺, the electric field at a distance of 0.4 nm from its center is

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$$E = e / 4\pi\epsilon_0 r^2 = (1.602 \times 10^{-19}) / (4 \times 3.142 \times 8.854 \times 10^{-12})(0.4 \times 10^{-9})^2 = 9.0 \times 10^9 \text{ V m}^{-1}$$

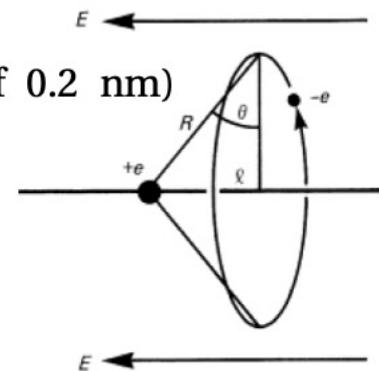
The induced dipole moment on a methane molecule is

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$$u_{\text{ind}} = \alpha_0 E = 4\pi\epsilon_0 (2.6 \times 10^{-30})(9.0 \times 10^9) = 2.60 \times 10^{-30} \text{ C m} = 2.60 \times 10^{-30} / 3.336 \times 10^{-30} = 0.78 \text{ D}$$

$$u_{\text{ind}} = ql = \alpha_0 E$$

the molecular radius of methane (of 0.2 nm)



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Lecture 10 Poll: interactions between ions and uncharged molecules

Question: Estimate the distance by which the electron cloud of a methane (CH_4) molecule 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 ($\epsilon = 1$)

For a monovalent ion such as Na^+ , the electric field at a distance of 0.4 nm from its center is

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$$E = e / 4\pi\epsilon_0 r^2 = (1.602 \times 10^{-19}) / (4 \times 3.142 \times 8.854 \times 10^{-12}) (0.4 \times 10^{-9})^2 = 9.0 \times 10^9 \text{ V m}^{-1}$$

The induced dipole moment on a methane molecule is

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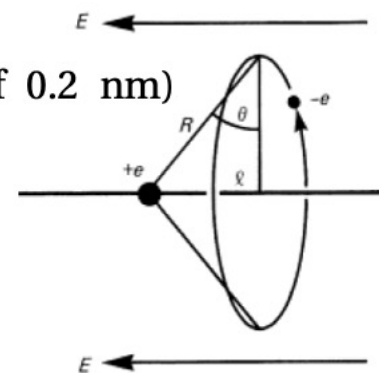
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$$u_{\text{ind}} = ql = \alpha_0 E$$

the molecular radius of methane (of 0.2 nm)

this corresponds to a unit charge separation in the molecule of

$$l = u_{\text{ind}} / e = 0.016 \text{ nm} \text{ which is about 8\% of the molecular radius of methane (of 0.2 nm).}$$



Journal club assignments for L11

Lecture 11 (4/2)	
Group	Paper Title
A	P2_doshi-et-al-2009-red-blood-cell-mimicking-synthetic-biomaterial-particles
B	P1_nmat1486
C	P3_Advanced Materials - 2012 - Maeda - Controlled Synthesis of 3D Multi-Compartmental Particles with Centrifuge-Based
D	P4_s41598-019-49244-4