Van der Waals Forces (2)
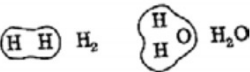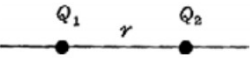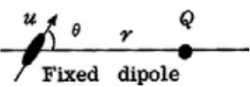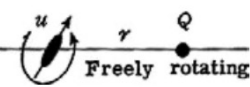
Reference text:

Intermolecular and Surface Forces, Jacob N. Israelachvili

Colloidal Science and Nanoscale Engineering, Orlin Velev
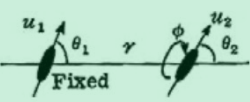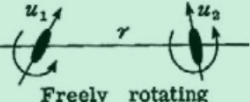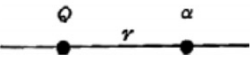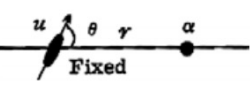
Colloidal Systems, Darrell Velegol

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

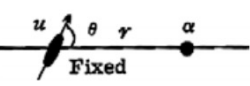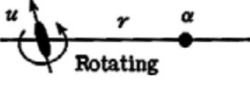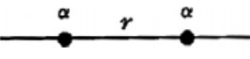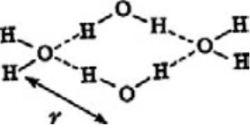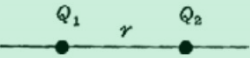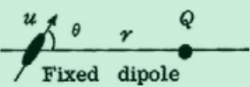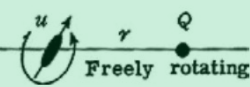| Type of interaction		Interaction energy $w(r)$
Covalent, metallic	$\text{(H H)} \ H_2$ $\quad H_2O$	Complicated, short range
Charge–charge	$Q_1 \quad r \quad Q_2$	$+Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	$Q \quad \alpha$	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	$\alpha \quad r \quad \alpha$	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (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 polarizibility (C^2 m^2 J^{-1}); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-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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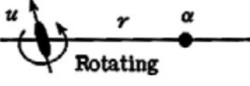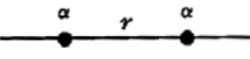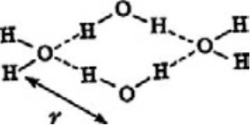
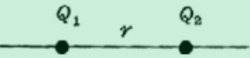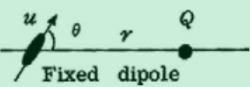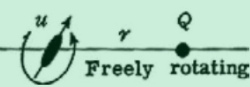| Type of interaction		Interaction energy $w(r)$
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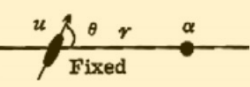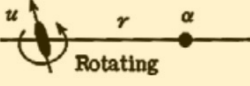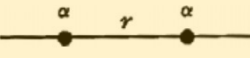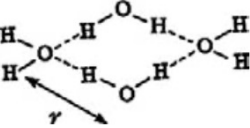| Type of interaction		Interaction energy $w(r)$
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Charge–non-polar	$Q \quad r \quad \alpha$	$-Q^2 \alpha / 2(4\pi\varepsilon_0)^2 r^4$
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Basic types of long-range molecular interactions
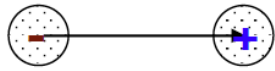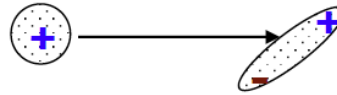
Charge - Charge   Charge - Dipole   Dipole - Dipole
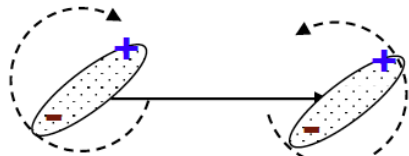
Two Rotating Dipoles   Charge – Rotating Dipole
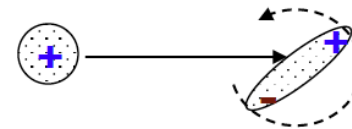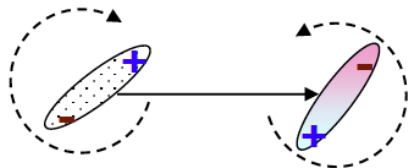
Dipole - Polarizable   Charge - Polarizable
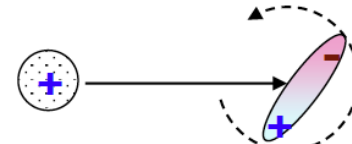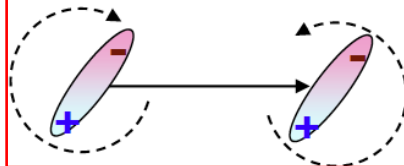
Polarizable – Polarizable
Dispersion forces

All of these are attractive (Why?)

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)

(b)

a one-electron "Bohr" atom

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

The internal (restoring) force is

$$F_{int} = \frac{-e^2}{4\pi\varepsilon_0 R^2}\sin\theta \approx \frac{-e^2 l}{4\pi\varepsilon_0 R^3} \approx \frac{-eu_{ind}}{4\pi\varepsilon_0 R^3}$$

• Polarizing an atom in the electric field

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

$$u_{ind} = 4\pi\varepsilon_0 R^3 E = \alpha_0 E$$

$$\alpha_0 = 4\pi\varepsilon_0 R^3$$

Electronic polarizability
[C² m² J⁻¹]

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

• Polarizing a molecule in the field of an ion

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 θ, and its energy in the field is uE cos θ: $\quad w(r, \theta) = -uE(r)\cos\theta$

- so the angle-averaged induced dipole moment is given by

$$u_{\text{ind}} = \left\langle u\cos\theta e^{uE\cos\theta/kT} \right\rangle$$

$$= \frac{u^2 E}{kT}\left\langle \cos^2\theta \right\rangle = \frac{u^2}{3kT}\, E, \qquad uE \ll kT$$

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

$$w(r) = w(r,\theta) = -\frac{Qq}{4\pi\varepsilon_0\varepsilon}\left[\frac{1}{r - \frac{1}{2}l\cos\theta} - \frac{1}{r + \frac{1}{2}l\cos\theta}\right]$$

$$= -\frac{Qq}{4\pi\varepsilon_0\varepsilon}\left[\frac{l\cos\theta}{r^2 - \frac{1}{4}l^2\cos^2\theta}\right]$$

$$= -\frac{Qu\cos\theta}{4\pi\varepsilon_0\varepsilon r^2} = -\frac{(ze)u\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}.$$

- Note that since the electric field of the charge acting on the dipole is $E(r) = Q/4\pi\varepsilon_0\varepsilon r^2$

in general the energy of a permanent dipole u in a field E may be written as

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

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

Total polarizability = molecular + orientational

Debye-Langevin equation

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

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

Charge – Rotating Dipole

Dipole - Polarizable

Charge - Polarizable

Polarizable – Polarizable
Dispersion forces

All of these are attractive (Why?)

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 $E = ze/4\pi\varepsilon_0\varepsilon r^2$ will induce in the molecule a dipole moment of

$$u_{\text{ind}} = \alpha E = \alpha ze/4\pi\varepsilon_0\varepsilon r^2$$

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 ($\varepsilon = 1$)

$$u_{\text{ind}} = \alpha E = \alpha z e / 4\pi\varepsilon_0\varepsilon r^2$$

- A: 0.016 nm

- B: 0.16 nm

- C: 1.6 nm

- D: 16 nm

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_2H_6	4.5
H_2O	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_3OH	3.2	C_6H_6	10.3
CO	1.95	Xe	4.0	CCl_4	10.5

[a]Polarizabilities α_0 are given in volume units of $(4\pi\varepsilon_0)\text{Å}^3 = (4\pi\varepsilon_0)10^{-30}$ m^3 $= 1.11 \times 10^{-40}$ C^2 m^2 J^{-1}.

$$u_{ind} = ql = \alpha_o E$$

the molecular radius of methane (of 0.2 nm)

Long URL   https://forms.gle/QZAScSrbQ8Jmhzhh9

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

$$u_{ind} = \alpha E = \alpha z e / 4\pi\varepsilon_0\varepsilon r^2$$

$$E = e/4\pi\varepsilon_0 r^2 = (1.602 \times 10^{-19})$$
$$/(4 \times 3.142 \times 8.854 \times 10^{-12})(0.4 \times 10^{-9})^2$$
$$= 9.0 \times 10^9 \text{ V m}^{-1}$$

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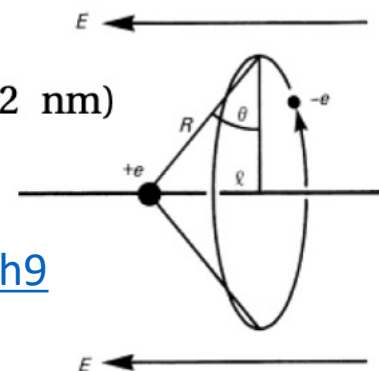
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The induced dipole moment on a methane molecule is

$$u_{ind} = \alpha_0 E = 4\pi\varepsilon_0(2.6 \times 10^{-30})(9.0 \times 10^9)$$
$$= 2.60 \times 10^{-30} \text{ C m}$$
$$= 2.60 \times 10^{-30}/3.336 \times 10^{-30} = 0.78 \text{ D}$$

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

the molecular radius of methane (of 0.2 nm)

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 ($\varepsilon = 1$)

$$u_{ind} = \alpha E = \alpha z e / 4\pi\varepsilon_0\varepsilon r^2$$

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

$$E = e/4\pi\varepsilon_0 r^2 = (1.602 \times 10^{-19})$$
$$/(4 \times 3.142 \times 8.854 \times 10^{-12})(0.4 \times 10^{-9})^2$$
$$= 9.0 \times 10^9 \text{ V m}^{-1}$$

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_2H_6	4.5
H_2O	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_3OH	3.2	C_6H_6	10.3
CO	1.95	Xe	4.0	CCl_4	10.5

The induced dipole moment on a methane molecule is

[a]Polarizabilities α_0 are given in volume units of $(4\pi\varepsilon_0)\text{Å}^3 = (4\pi\varepsilon_0)10^{-30}$ m³ $= 1.11 \times 10^{-40}$ C² m² J⁻¹.

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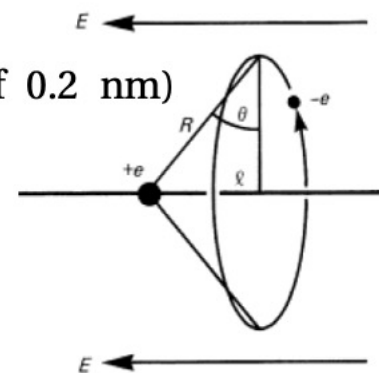
$$u_{ind} = ql = \alpha_0 E$$

the molecular radius of methane (of 0.2 nm)

this corresponds to a unit charge separation in the molecule of

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

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 $E = ze/4\pi\varepsilon_0\varepsilon r^2$ will induce in the molecule a dipole moment of

$$u_{\text{ind}} = \alpha E = \alpha ze/4\pi\varepsilon_0\varepsilon r^2$$

- From this example we see that the induced dipole moments can be of order 1 Debye, which is quite large. We may therefore anticipate that the forces associated with induced dipole moments may likewise be quite large.

Interactions between Ions and Uncharged Molecules

- Consider the interaction between an ion and an uncharged molecule. The induced dipole will point away from the ion if it is a cation and toward the ion if it is an anion. In either case this will lead to an attractive force between the ion and the polarized molecule.

Ion

Nonpolar molecule

l

ze

r

$-q$ $+q$

E

Polarizing field

u_{ind}

E

E_r "Reaction field" from induced dipole
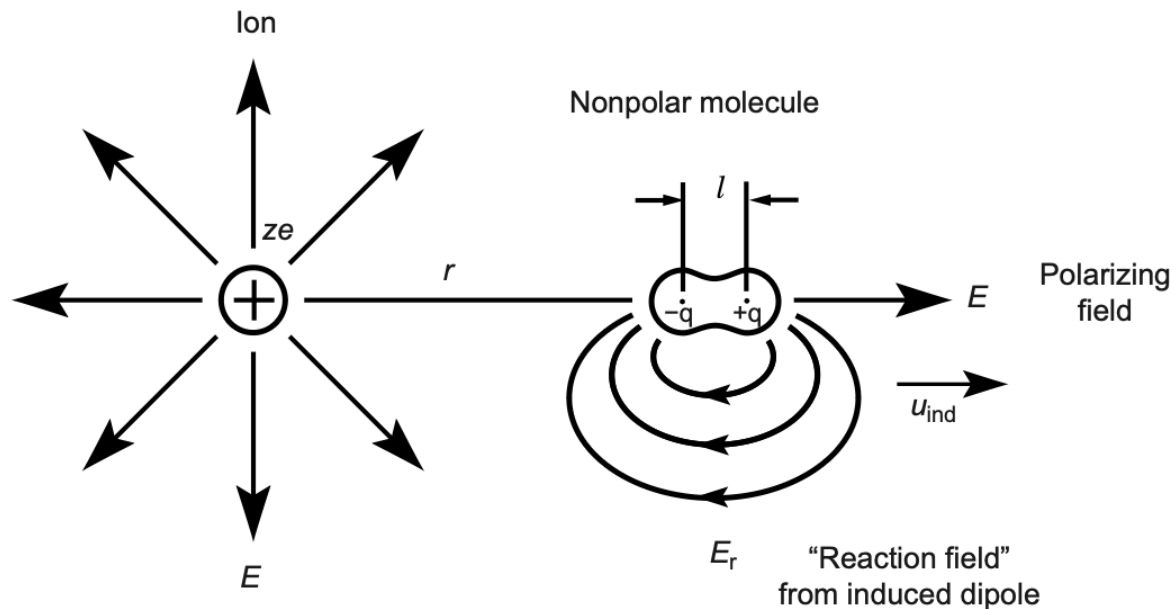
- The "reflected" or "reaction" field of the induced dipole E_r acting back on the ion is

$$E_r = -2u_{ind}/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha E/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha(ze)/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

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

$$E_\parallel = (E_- - E_+)\cos(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{2l}{r}\cos\theta$$

$$E_\perp = (E_- + E_+)\sin(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{l}{r}\sin\theta$$

- The magnitude and direction ψ of the resulting dipolar field at A is therefore given by

$$E_u = \sqrt{E_\parallel^2 + E_\perp^2} = (ql/4\pi\varepsilon_0 r^3)\sqrt{4\cos^2\theta + \sin^2\theta}$$

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

- therefore, $F = QE_u = \dfrac{Qu\,(1+3\cos^2\theta)^{1/2}}{4\pi\varepsilon_0 r^3}$

- with $\tan\psi = \dfrac{\tan\theta}{2}$

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

$$\boxed{w(r) = -\int_\infty^r F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2}$$

$$E_r = -2u_{\mathrm{ind}}/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha E/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha(ze)/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

Interactions between Ions and Uncharged Molecules

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- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

$$E_r = -2u_{\mathrm{ind}}/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha E/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha(ze)/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

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- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

- Note that this energy is half that expected for the interaction of an ion with a similarly aligned **permanent** dipole, which we derived before as: (θ = 0°)

$$w(r) = -uE = -\alpha E^2$$

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

$$w(r) = w(r,\theta) = -\frac{Qq}{4\pi\varepsilon_0\varepsilon}\left[\frac{1}{r - \frac{1}{2}l\cos\theta} - \frac{1}{r + \frac{1}{2}l\cos\theta}\right]$$

$$= -\frac{Qq}{4\pi\varepsilon_0\varepsilon}\left[\frac{l\cos\theta}{r^2 - \frac{1}{4}l^2\cos^2\theta}\right]$$

$$= -\frac{Qu\cos\theta}{4\pi\varepsilon_0\varepsilon r^2} = -\frac{(ze)u\cos\theta}{4\pi\varepsilon_0\varepsilon r^2}.$$

- Note that since the electric field of the charge acting on the dipole is $E(r) = Q/4\pi\varepsilon_0\varepsilon r^2$

in general the energy of a permanent dipole u in a field E may be written as

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

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

$$w(r) = -\int_{\infty}^{r} F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2$$

- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

- Note that this energy is half that expected for the interaction of an ion with a similarly aligned **permanent** dipole, which we derived before as: ($\theta = 0°$)

$$w(r) = -uE = -\alpha E^2$$

- This happens because when a dipole moment is induced (rather than being permanent or fixed), some energy is taken up in polarizing the molecule.

- From the Poll question, we see that this is the energy absorbed internally in displacing the positive and negative charges in the molecule.

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 ($\varepsilon = 1$)

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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Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

$$w(r) = -\int_\infty^r F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2$$

- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

- Note that this energy is half that expected for the interaction of an ion with a similarly aligned **permanent** dipole, which we derived before as: ($\theta = 0°$)

$$w(r) = -uE = -\alpha E^2$$

- We can calculate this energy by integrating the internal force $\mathbf{F_{int}}$ with respect to the charge separation from 0 to l:

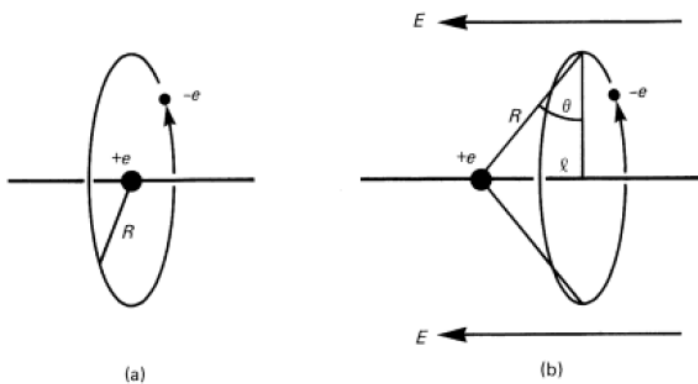$$w_{int}(r) = \int_0^l F_{int}\,dl = \int_0^l \frac{e^2 l\,dl}{4\pi\varepsilon_0 R^3} = \frac{(el)^2}{8\pi\varepsilon_0 R^3} = \frac{(\alpha E)^2}{2\alpha} = \frac{1}{2}\alpha E^2$$

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

The internal (restoring) force is

$$F_{\text{int}} = \frac{-e^2}{4\pi\varepsilon_0 R^2}\sin\theta \approx \frac{-e^2 l}{4\pi\varepsilon_0 R^3} \approx \frac{-eu_{\text{ind}}}{4\pi\varepsilon_0 R^3}$$

• Polarizing an atom in the electric field

a one- electron "Bohr" atom

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

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

$$u_{\text{ind}} = 4\pi\varepsilon_0 R^3 E = \alpha_0 E$$

$$\alpha_0 = 4\pi\varepsilon_0 R^3$$

Electronic polarizability
[C² m² J⁻¹]

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

• Polarizing a molecule in the field of an ion

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

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- We can calculate this energy by integrating the internal force **F$_{int}$** with respect to the charge separation from 0 to l:

$$w_{\text{int}}(r) = \int_0^l F_{\text{int}}\mathrm{d}l = \int_0^l \frac{e^2 l\,\mathrm{d}l}{4\pi\varepsilon_0 R^3} = \frac{(el)^2}{8\pi\varepsilon_0 R^3} = \frac{(\alpha E)^2}{2\alpha} = \frac{1}{2}\alpha E^2$$

- Thus, a factor $+\frac{1}{2}\alpha E^2$ must be added to $-\alpha E^2$ to obtain the **free energy** for the **ion-induced dipole interaction** as derived above: $w(r) = -\frac{1}{2}\alpha E^2$

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

$$w(r) = -\int_{\infty}^{r} F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2$$

- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

- We may now insert the value for the **total polarizability** of polar molecules

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

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

Total polarizability = molecular + orientational

Debye-Langevin equation

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

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}.

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

$$w(r) = -\int_\infty^r F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2$$

- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.

- We may now insert the value for the **total polarizability** of polar molecules

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

- And obtain the **net ion-induced dipole interaction** **free energy** as

$$w(r) = -\frac{(ze)^2\alpha}{2(4\pi\varepsilon_0\varepsilon)^2 r^4} = -\frac{(ze)^2}{2(4\pi\varepsilon_0\varepsilon)^2 r^4}\left(\alpha_0 + \frac{u^2}{3kT}\right)$$

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

| Type of interaction		Interaction energy $w(r)$
Covalent, metallic	$\boxed{H\ H}$ H_2 $\overset{H}{\underset{H}{O}}$ H_2O	Complicated, short range
Charge–charge	$\underset{Q_1 \quad r \quad Q_2}{\bullet \quad\quad \bullet}$	$+Q_1 Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	Freely rotating	$-Q^2 u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	Fixed	$-u_1 u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	$\underset{Q \quad\quad r \quad\quad \alpha}{\bullet \quad\quad \bullet}$	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	$\underset{\alpha \quad\quad r \quad\quad \alpha}{\bullet \quad\quad \bullet}$	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (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 polarizibility (C^2 m^2 J^{-1}); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-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).

Having considered **charge**-**induced dipole** **interactions**, we are ready to move on to the **dipole**-**induced dipole** **interactions**

Basic types of long-range molecular interactions
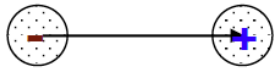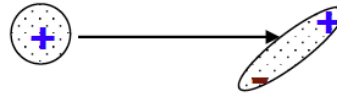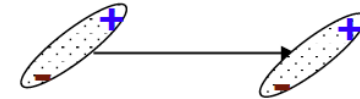
Charge - Charge

Charge - Dipole
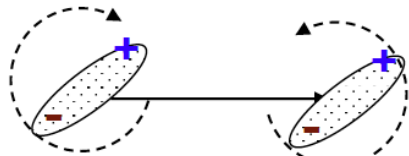
Dipole - Dipole

Two Rotating Dipoles
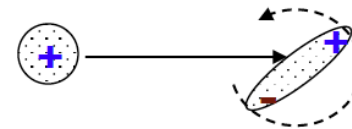
Charge – Rotating Dipole
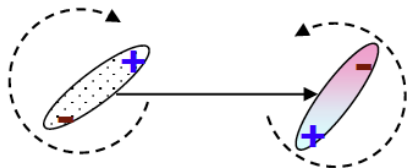
Dipole - Polarizable
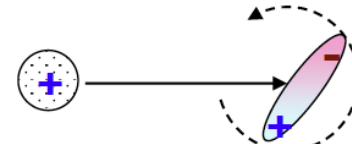
Charge - Polarizable
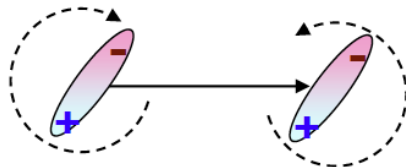
Polarizable – Polarizable
Dispersion forces

All of these are attractive (Why?)

Dipole-Induced Dipole Interactions

- The interaction between a **polar molecule** and a **nonpolar molecule** is analogous to the **ion-induced dipole interaction** just discussed except that the **polarizing field** comes from a permanent **dipole** rather than a **charge**.

- For a fixed **dipole u** oriented at an angle θ to the line joining it to a **polarizable molecule**, we derived the **electric field** of the **dipole** acting on the surrounding as

$$E = u(1 + 3\cos^2\theta)^{1/2}/4\pi\varepsilon_0\varepsilon r^3$$

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

$$E_\parallel = (E_- - E_+)\cos(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{2l}{r}\cos\theta$$

$$E_\perp = (E_- + E_+)\sin(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{l}{r}\sin\theta$$

- The magnitude and direction ψ of the resulting dipolar field at A is therefore given by

$$E_u = \sqrt{E_\parallel^2 + E_\perp^2} = (ql/4\pi\varepsilon_0 r^3)\sqrt{4\cos^2\theta + \sin^2\theta}$$

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

- therefore, $F = QE_u = \dfrac{Qu\,(1 + 3\cos^2\theta)^{1/2}}{4\pi\varepsilon_0 r^3}$

- with $\tan\psi = \dfrac{\tan\theta}{2}$

Dipole-Induced Dipole Interactions

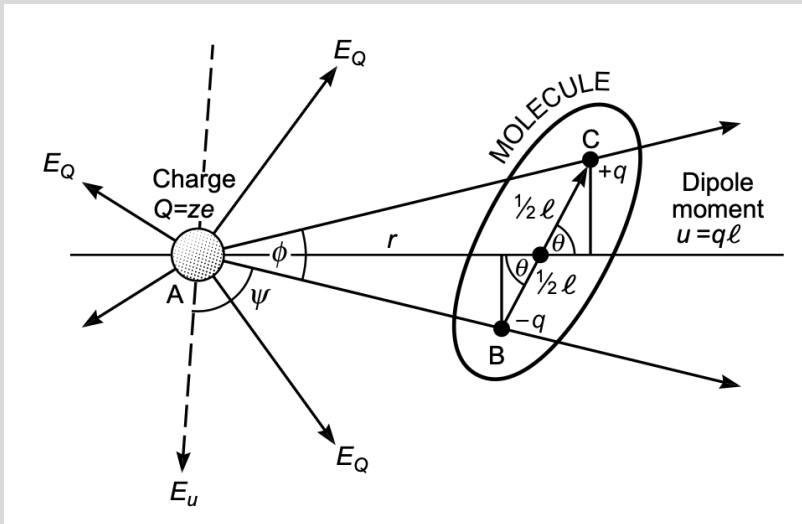- The interaction between a **polar molecule** and a **nonpolar molecule** is analogous to the **ion**-**induced dipole interaction** just discussed except that the **polarizing field** comes from a permanent **dipole** rather than a **charge**.

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$$E = u(1 + 3\cos^2\theta)^{1/2}/4\pi\varepsilon_0\varepsilon r^3$$

- In this case, this **electric field** acts on a **polarizable molecule**, the **interaction energy** therefore will be

$$\boxed{w(r,\theta) = -\frac{1}{2}\alpha_0 E^2} = -u^2\alpha_0(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0\varepsilon)^2 r^6$$

Interactions between Ions and Uncharged Molecules

- The attractive **force** and **energy** are

$$F(r) = (ze)E_r = -2\alpha(ze)^2/(4\pi\varepsilon_0\varepsilon)^2 r^5$$
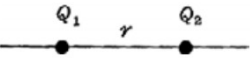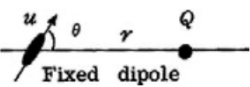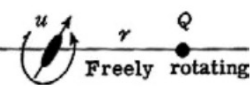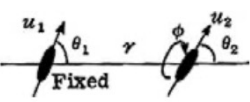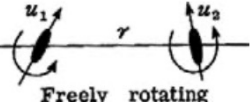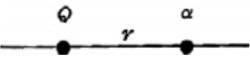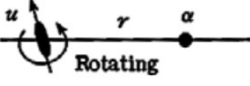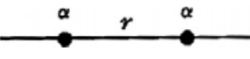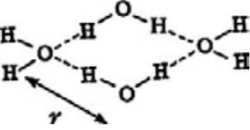
$$w(r) = -\int_\infty^r F\,dr = -\alpha(ze)^2/2(4\pi\varepsilon_0\varepsilon)^2 r^4 = -\frac{1}{2}\alpha E^2$$

- Recall $E = ze/4\pi\varepsilon_0\varepsilon r^2$ is the field acting on the molecule.
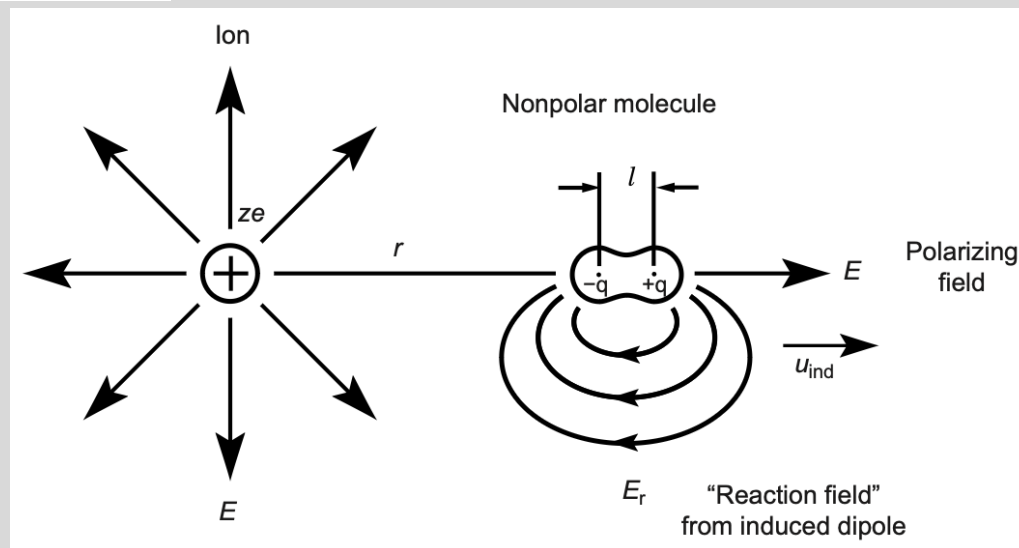
$$E_r = -2u_{\text{ind}}/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha E/4\pi\varepsilon_0\varepsilon r^3 = -2\alpha(ze)/(4\pi\varepsilon_0\varepsilon)^2 r^5$$

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

Type of interaction		Interaction energy $w(r)$
Covalent, metallic	(H H) H_2 (H O H) H_2O	Complicated, short range
Charge–charge	Q_1 —— r —— Q_2	$+Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	u, θ, r, Q Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	u, r, Q Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	u_1, θ_1, r, ϕ, u_2, θ_2 Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	u_1, r, u_2 Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	Q, α, r	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	u, θ, r, α Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	u, r, α Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	α, r, α	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond	H, O, H, O, H (hydrogen-bonded cluster) r	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 polarizibility (C^2 m^2 J^{-1}); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-12} C^2 J^{-1} m^{-1}). The force $F(r)$ is obtained by differentiating the energy $w(r)$ with respect to distan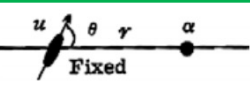ce r: $F = -dw/dr$. The stabilizing repulsive "Pauli Exclusion" interactions (not shown) usually follow an exponential function $w(r) \propto \exp(-r/r_0)$, but for simplicity they are usually modeled as power laws: $w(r) \propto +1/r^n$ (where $n = 9$–12).

Dipole-Induced Dipole Interactions

- The interaction between a **polar molecule** and a **nonpolar molecule** is analogous to the **ion**-**induced dipole interaction** just discussed except that the **polarizing field** comes from a permanent **dipole** rather than a **charge**.

- For a fixed **dipole u** oriented at an angle θ to the line joining it to a **polarizable molecule**, we derived the **electric field** of the **dipole** acting on the surrounding as

$$E = u(1 + 3\cos^2 \theta)^{1/2}/4\pi\varepsilon_0\varepsilon r^3$$

- In this case, this **electric field** acts on a **polarizable molecule**, the **interaction energy** therefore will be

$$w(r, \theta) = -\frac{1}{2}\alpha_0 E^2 = -u^2\alpha_0(1 + 3\cos^2 \theta)/2(4\pi\varepsilon_0\varepsilon)^2 r^6$$

- For typical values of **u** and α_0, the strength of this interaction is not sufficient to mutually orient the molecules, as occurs in **ion**-**dipole** or strong **dipole**-**dipole** interactions.

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- For typical values of **u** and α_0, the strength of this interaction is not sufficient to mutually orient the molecules, as occurs in **ion-dipole** or strong **dipole-dipole** interactions. The **effective interaction** is therefore the angle-averaged energy.

- Since the angle average of $\cos^2\theta$ is 1/3, this interaction energy becomes

$$w(r) = -u^2\alpha_0/(4\pi\varepsilon_0\varepsilon)^2 r^6$$

Recall for spherical coordinates

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

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

$$\langle \sin^2 \phi \rangle = \langle \cos^2 \phi \rangle = \frac{1}{2},$$
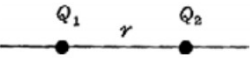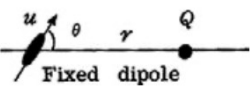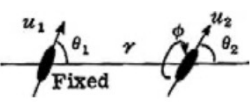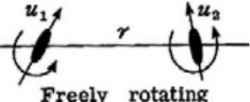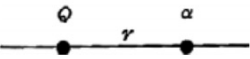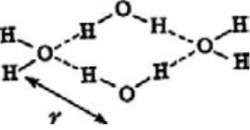
$$\langle \sin \theta \rangle = \langle \cos \theta \rangle = \langle \sin \theta \cos \theta \rangle = 0,$$

$$\langle \sin \phi \rangle = \langle \cos \phi \rangle = \langle \sin \phi \cos \phi \rangle = 0.$$
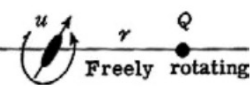
This is in three dimensions. In two dimensions—for example, on a surface—the only difference is that $\langle \cos^2 \theta \rangle = \langle \sin^2 \theta \rangle = \frac{1}{2}$.

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	u_1 r u_2 Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	Q α r	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	u θ r α Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	u r α Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	α r α	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond	H–O···H–O–H···O–H (with r)	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 polarizibility ($C^2\ m^2\ J^{-1}$); 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 ($s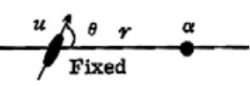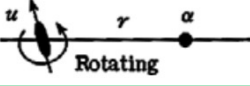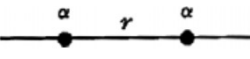^{-1}$); ε_0, dielectric permittivity of free space ($8.854 \times 10^{-12}\ C^2\ J^{-1}\ m^{-1}$). The force $F(r)$ is obtained by differentiating the energy $w(r)$ with respect to distance r: $F = -dw/dr$. The stabilizing repulsive "Pauli Exclusion" interactions (not shown) usually follow an exponential 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 $n = 9\text{–}12$).

Dipole-Induced Dipole Interactions

- more <u>generally</u>, for **two molecules** possessing permanent dipole moments $\mathbf{u_1}$ and $\mathbf{u_2}$ and polarizabilities α_{01} and α_{02}, their net **dipole-induced dipole energy** is

$$w(r) = -\frac{[u_1^2 \alpha_{02} + u_2^2 \alpha_{01}]}{(4\pi\varepsilon_0\varepsilon)^2 r^6}$$

$$w(r) = -u^2 \alpha_0 / (4\pi\varepsilon_0\varepsilon)^2 r^6$$

Interaction between rotating dipolar and polarizable molecules

Debye or induction interaction – second major component of vdW forces

• Full dipole-polarizable dipole

$$w(r) = -\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{\left(4\pi\varepsilon\varepsilon_0\right)^2 r^6}$$

Total polarizability = molecular + orientational

Debye-Langevin equation

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

Dipole-Induced Dipole Interactions

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$$w(r) = -\frac{[u_1^2 \alpha_{02} + u_2^2 \alpha_{01}]}{(4\pi\varepsilon_0\varepsilon)^2 r^6}$$

- This is often referred to as the **Debye interaction** or the **induction interaction**. It constitutes the **second** of **three** <u>inverse sixth power </u>contributions to the total **van der Waals** interaction energy between molecules.
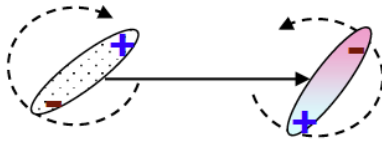
Dipole-Induced Dipole Interactions

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- The **first** we have already encountered in the <u>angle-averaged **dipole-dipole**</u> or **Keesom interaction**, which incidentally may also be obtained from the above expression by replacing α_{01} and α_{02} by $\boxed{\alpha_{\text{dip}} = u^2/3kT}$ so that for **two dipoles** $\mathbf{u_1}$ and $\mathbf{u_2}$, we recover the **Keesom free energy**:

$$w(r) = -\frac{u_1^2 u_2^2}{3(4\pi\varepsilon_0\varepsilon)^2 kT r^6}$$

Basic types of long-range molecular interactions
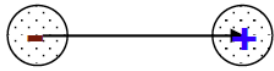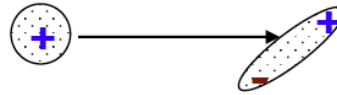
Charge - Charge

Charge - Dipole
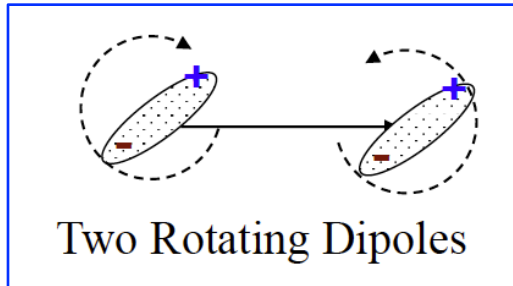
Dipole - Dipole

Two Rotating Dipoles
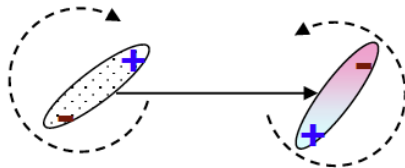
Charge – Rotating Dipole
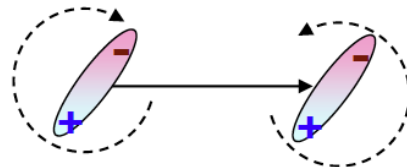
Dipole - Polarizable

Charge - Polarizable

Polarizable – Polarizable
Dispersion forces

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

Angle-Averaged Rotating Dipole - Dipole Interaction

- Angle-averaging vs. the thermal energy for $kT > w(r, \Omega)$
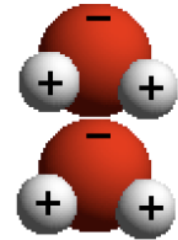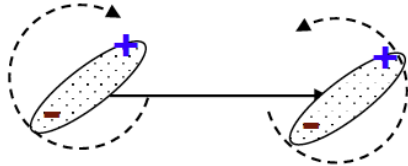
Polar attraction between water molecules

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

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

What happens to the averaged 1st term?

$$w(r) \approx -\frac{u_1^2 \, u_2^2}{3\left(4\pi\varepsilon\varepsilon_0\right)^2 kT \, r^6}$$
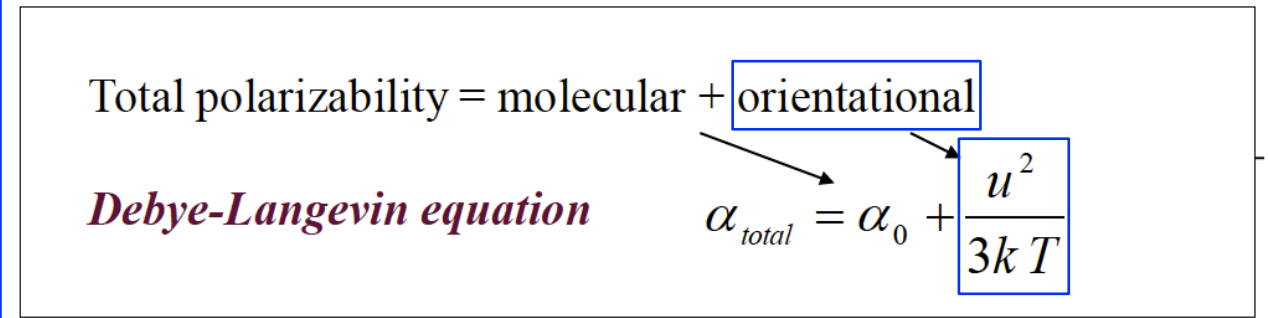
Orientation or Keesom molecular dipole interaction

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.

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

Total polarizability = molecular + orientational

Debye-Langevin equation $\qquad \alpha_{total} = \alpha_0 + \dfrac{u^2}{3kT}$

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}**.
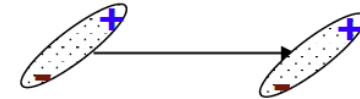
Basic types of long-range molecular interactions

Charge - Charge

Charge - Dipole

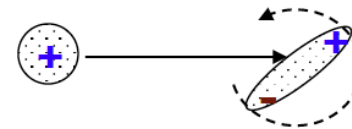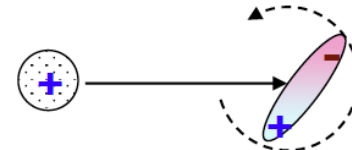Dipole - Dipole

Two Rotating Dipoles

Charge – Rotating Dipole

Dipole - Polarizable

Charge - Polarizable

Polarizable – Polarizable
Dispersion forces

All of these
are attractive
(Why?)

London Dispersion Force between Nonpolar Molecules

- The various types of physical forces described so far are fairly easy to understand, since they arise from straightforward **electrostatic interactions** involving **charged** or **dipolar molecules**.

- But there is **another type of force** that—like the gravitational force—acts between **all** atoms and molecules, even totally **nonpolar ones** such as helium, carbon dioxide, and hydrocarbons.

- These forces have been variously known as **dispersion forces**, **London forces**, **charge-fluctuation** forces, **electrodynamic** forces, and **induced-dipole-induced-dipole** forces.

- The origin of this name has to do with their relation to the dispersion of light in the visible and UV regions of the spectrum, as we shall see.

- **Dispersion forces** make up the **third** and perhaps **most important** contribution to the total **van der Waals** force between atoms and molecules, and they are **always** present (in contrast to the other types of forces that may or may not be present, depending on the properties of the molecules).

London Dispersion Force between Nonpolar Molecules

- Dispersion forces are **quantum mechanical in origin** and amenable to a host of theoretical treatments of varying complexity.

- For a simple semiquantitative understanding of how these forces arise, we may consider the following model based on the interaction between **two Bohr atoms**.

- In the **Bohr atom** an **electron** is pictured as **orbiting** around a **proton**. The **smallest distance** between the **electron** and **proton** is known as the **first Bohr radius a_0** and is the **radius** at which the **Coulomb energy** $e^2/4\pi\varepsilon_0 a_0$ is equal to **$h\nu$**, that is:

$$a_0 = e^2/8\pi\varepsilon_0 h\nu = 0.053 \text{ nm}$$

- where **h** is the **Planck constant** and ν the orbiting frequency of the electron.

- For a **Bohr atom**, $\nu = 3.3 \times 10^{15} \text{ s}^{-1}$, so that $h\nu = 2.2 \times 10^{-18} \text{ J}$. This is the **energy of an electron** in the **first Bohr radius** and is equal to the energy needed to ionize the atom—the **first ionization potential**, **I**.

London Dispersion Force between Nonpolar Molecules

- The **Bohr atom** has **no permanent dipole moment**. However, at any instant there exists an instantaneous dipole of moment, **u** = ql = a_0e, whose field will **polarize** a nearby **neutral atom**, giving rise to an **attractive interaction** that is entirely analogous to the **dipole**-**induced dipole** (Debye) interaction discussed previously

- The **energy** of this interaction in a vacuum is given by

$$w(r) = -u^2\alpha_0/(4\pi\varepsilon_0\varepsilon)^2 r^6 = -(a_0 e)^2\alpha_0/(4\pi\varepsilon_0)^2 r^6$$

Dipole-Induced Dipole Interactions
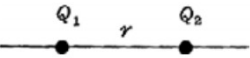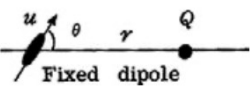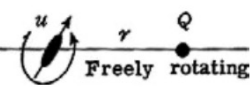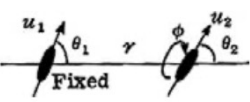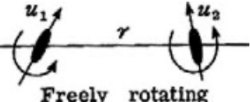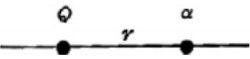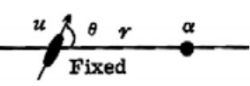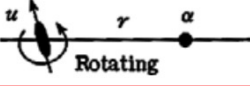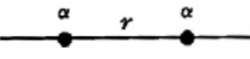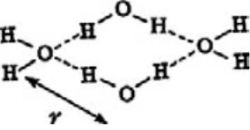
- more <u>generally</u>, for **two molecules** possessing permanent dipole moments $\mathbf{u_1}$ and $\mathbf{u_2}$ and polarizabilities α_{01} and α_{02}, their net **dipole-induced dipole energy** is

$$w(r) = -\frac{[u_1^2 \alpha_{02} + u_2^2 \alpha_{01}]}{(4\pi\varepsilon_0\varepsilon)^2 r^6}$$

- This is often referred to as the **Debye interaction** or the **induction interaction**. It constitutes the **second** of **three** <u>inverse sixth power</u> contributions to the total **van der Waals** interaction energy between molecules.

$$w(r) = -u^2 \alpha_0 / (4\pi\varepsilon_0\varepsilon)^2 r^6$$

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

Type of interaction		Interaction energy $w(r)$
Covalent, metallic	(H H) H_2, H_2O	Complicated, short range
Charge–charge	Q_1 — r — Q_2	$+Q_1 Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	Freely rotating	$-Q^2 u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	Fixed	$-u_1 u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	Q — r — α	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	α — r — α	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (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 polarizibility (C^2 m^2 J^{-1}); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-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).

London Dispersion Force between Nonpolar Molecules

- The **Bohr atom** has **no permanent dipole moment**. However, at any instant there exists an instantaneous dipole of moment, **u** = ql = a_0e, whose field will **polarize** a nearby **neutral atom**, giving rise to an **attractive interaction** that is entirely analogous to the **dipole**-**induced dipole** (Debye) interaction discussed previously

- The **energy** of this interaction in a vacuum is given by

$$w(r) = -u^2\alpha_0/(4\pi\varepsilon_0\varepsilon)^2 r^6 = -(a_0 e)^2\alpha_0/(4\pi\varepsilon_0)^2 r^6$$

- where α_0 is the **electronic polarizability** of the second **Bohr atom**, which from our previous results $\alpha_0 \approx 4\pi\varepsilon_0 a_0^3$

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)

a one-electron "Bohr" atom

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

The internal (restoring) force is

$$F_{int} = \frac{-e^2}{4\pi\varepsilon_0 R^2}\sin\theta \approx \frac{-e^2 l}{4\pi\varepsilon_0 R^3} \approx \frac{-eu_{ind}}{4\pi\varepsilon_0 R^3}$$

• Polarizing an atom in the electric field

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

$$u_{ind} = 4\pi\varepsilon_0 R^3 E = \alpha_0 E$$

$$\boxed{\alpha_0 = 4\pi\varepsilon_0 R^3}$$

Electronic polarizability
$[\text{C}^2 \text{ m}^2 \text{ J}^{-1}]$

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

• Polarizing a molecule in the field of an ion

London Dispersion Force between Nonpolar Molecules

- The **Bohr atom** has **no permanent dipole moment**. However, at any instant there exists an instantaneous dipole of moment, **u** = ql = a_0e, whose field will **polarize** a nearby **neutral atom**, giving rise to an **attractive interaction** that is entirely analogous to the **dipole**-**induced dipole** (Debye) interaction discussed previously

- The **energy** of this interaction in a vacuum is given by

$$w(r) = -u^2 \alpha_0 / (4\pi\varepsilon_0\varepsilon)^2 r^6 = -(a_0 e)^2 \alpha_0 / (4\pi\varepsilon_0)^2 r^6$$

- where α_0 is the **electronic polarizability** of the second **Bohr atom**, which from our previous results $\alpha_0 \approx 4\pi\varepsilon_0 a_0^3$

- Combined with the definition of the **Bohr radius** $a_0 = e^2 / 8\pi\varepsilon_0 h\nu$, we find that the above **interaction energy** can be written approximately as

$$w(r) \approx -\alpha_0^2 h\nu / (4\pi\varepsilon_0)^2 r^6$$

London Dispersion Force between Nonpolar Molecules

- Except for a numerical factor, this is the same as that derived by London in 1930 using quantum mechanical perturbation theory. **London's expression** for the **dispersion interaction energy** between two **identical** atoms or molecules is

$$w(r) = \frac{-C_{\text{disp}}}{r^6} = -\frac{3}{4}\alpha_0^2 h\nu/(4\pi\varepsilon_0)^2 r^6 = -\frac{3}{4}\alpha_0^2 I/(4\pi\varepsilon_0)^2 r^6$$

$$w(r) \approx -\alpha_0^2 h\nu/(4\pi\varepsilon_0)^2 r^6$$

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- and for two **dissimilar** atoms

$$w(r) = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1 + \nu_2)} = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{I_1 I_2}{(I_1 + I_2)}$$

Interactions between Neutral Polarizable Molecules: van der Waals Forces

How do these neutral molecules polarize each other?

• **Instantaneous** dipole moment due to electron-proton displacement

$$w(r) = -\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{2(4\pi\varepsilon\varepsilon_0)^2 r^6}$$

$$w(r) = -\frac{3\alpha_0^2 h\nu}{4(4\pi\varepsilon_0)^2 r^6}$$

Between similar atoms

London 's equations

$$w(r) = -\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1+\nu_2)}$$

Between dissimilar atoms

ν = ionization frequency

$h\nu$ = first ionization potential

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Type of interaction		Interaction energy $w(r)$
Covalent, metallic	$(H\ H)$ H_2 H_2O	Complicated, short range
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Charge–dipole	u θ r Q Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	u r Q Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	u_1 θ_1 r ϕ u_2 θ_2 Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	u_1 r u_2 Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	Q α r	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	u θ r α Fixed	$-u^2\alpha(1 + 3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	u r α Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	α r α	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond	H–O–$H \cdots O$–H ... r	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 polarizibility ($C^2\ m^2\ J^{-1}$); 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).

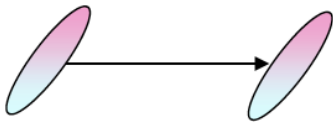# London Dispersion Force between Nonpolar Molecules

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$$w(r) = \frac{-C_{\text{disp}}}{r^6} = -\frac{3}{4}\alpha_0^2 h\nu/(4\pi\varepsilon_0)^2 r^6 = -\frac{3}{4}\alpha_0^2 I/(4\pi\varepsilon_0)^2 r^6$$
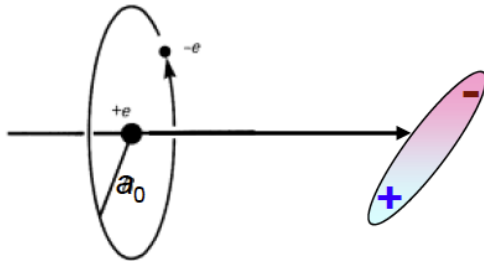
- and for <u>two **dissimilar**</u> atoms

$$w(r) = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1 + \nu_2)} = -\frac{3}{2}\frac{\alpha_{01}\alpha_{02}}{(4\pi\varepsilon_0)^2 r^6}\frac{I_1 I_2}{(I_1 + I_2)}$$

- From the above simple model we see that while **dispersion forces** are quantum mechanical (in determining the instantaneous, but fluctuating, dipole moments of neutral atoms), the **ensuing interaction is still essentially electrostatic**—a sort of **quantum mechanical polarization force**.

- And we may further note that the **$1/r^6$ distance dependence** is the same as that of the two other polarization interactions, the **Keesom** and **Debye** forces discussed before, that together contribute to the net van der Waals force.

General expression for the van der Waals force

$$w_{VDW}(r) = -\left[\frac{u_1^2 u_2^2}{3kT} + \left(u_1^2 \alpha_{02} + u_2^2 \alpha_{01}\right) + \frac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(\nu_1+\nu_2)}\right] \frac{1}{(4\pi\varepsilon_0)^2 r^6}$$
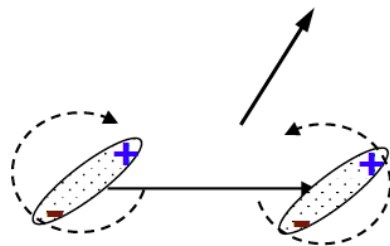
Dipole - Dipole
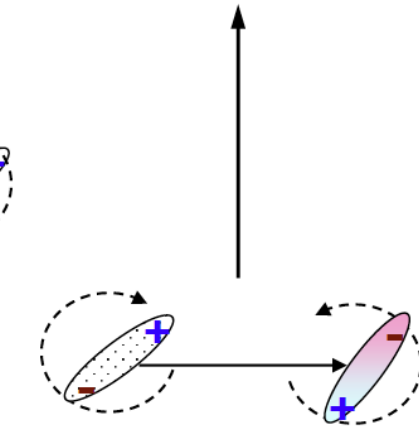
Dipole - Polarizable
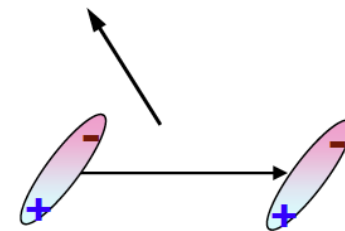
Polarizable – Polarizable

- *Lumping together all molecular and physical constants*

$$w_{VDW}(r) = -\left[C_{orient} + C_{ind} + C_{disp}\right]\frac{1}{r^6} = -\frac{C_{VDW}}{r^6}$$

Table 6.3 Induction, Orientation, and Dispersion Free Energy Contributions to the Total Van der Waals Energy in a Vacuum for Various Pairs of Molecules at 293 K

				Van der Waals Energy Coefficients C (10^{-79} J m^6)					
Similar Molecules							*Total VDW Energy* C_{VDW}		
Interacting Molecules	**Electronic Polarizability** $\dfrac{\alpha_0}{4\pi\varepsilon_0}$ (10^{-30}m^3)	**Permanent Dipole Moment** u (D) [a]	**Ionization Potential** $I = h\nu_I$ (eV) [b]	C_{ind} $\dfrac{2u^2\alpha_0}{(4\pi\varepsilon_0)^2}$	C_{orient} $\dfrac{u^4}{3kT(4\pi\varepsilon_0)^2}$	C_{disp} $\dfrac{3\alpha_0^2 h\nu_I}{4(4\pi\varepsilon_0)^2}$	**Theoretical Eq. (6.17)**	**From Gas Law Eq. (6.14)**	**Dispersion Energy Contribution to Total (Theoretical) (%)**
Ne−Ne	0.39	0	21.6	0	0	4	4	4	100
CH$_4$−CH$_4$	2.60	0	12.6	0	0	102	102	101	100
HCl−HCl	2.63	1.08	12.7	6	11	106	123	157	86
HBr−HBr	3.61	0.78	11.6	4	3	182	189	207	96
HI−HI	5.44	0.38	10.4	2	0.2	370	372	350	99
CH$_3$Cl−CH$_3$Cl	4.56	1.87	11.3	32	101	282	415	509	68
NH$_3$−NH$_3$	2.26	1.47	10.2	10	38	63	111	162	57
H$_2$O−H$_2$O	1.48	1.85	12.6	10	96	33	139	175	24

Dissimilar Molecules				$\dfrac{u_1^2\alpha_{02} + u_2^2\alpha_{01}}{(4\pi\varepsilon_0)^2}$	$\dfrac{u_1^2 u_2^2}{3kT(4\pi\varepsilon_0)^2}$	$\dfrac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(4\pi\varepsilon_0)^2(\nu_1+\nu_2)}$			
Ne−CH$_4$				0	0	19	19[c]	—	100
HCl−HI				7	1	197	205	—	96
H$_2$O−Ne				1	0	11	12	—	92
H$_2$O−CH$_4$				9	0	58	67	—	87

[a] 1 D = 3.336×10^{-30} Cm.
[b] 1 eV = 1.602×10^{-19} J.
[c] This approximate value may be compared with the ab initio calculation by Fowler et al., (1989) that gives 23×10^{-79} J m^6.

Lecture 12 Poll: the three components of VdW interactions

In general, which of these interactions has the largest contribution to the VdW energy?

- A: Keesom-orientation
- B: Debye-induction
- C: London-dispersion

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Similar Molecules				Van der Waals Energy Coefficients C $(10^{-79}$ J m$^6)$				Total VDW Energy C_{VDW}		
Interacting Molecules	Electronic Polarizability $\frac{\alpha_0}{4\pi\varepsilon_0}$ $(10^{-30}$m$^3)$	Permanent Dipole Moment u (D) ^{a}	Ionization Potential $I = h\nu_I$ (eV) ^{b}	C_{ind} $\frac{2u^2\alpha_0}{(4\pi\varepsilon_0)^2}$	C_{orient} $\frac{u^4}{3kT(4\pi\varepsilon_0)^2}$	C_{disp} $\frac{3\alpha_0^2 h\nu_I}{4(4\pi\varepsilon_0)^2}$	Theoretical Eq. (6.17)	From Gas Law Eq. (6.14)	Dispersion Energy Contribution to Total (Theoretical) (%)
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H$_2$O–H$_2$O	1.48	1.85	12.6	10	96	33	139	175	24

Dissimilar Molecules	$\frac{u_1^2\alpha_{02}+u_2^2\alpha_{01}}{(4\pi\varepsilon_0)^2}$	$\frac{u_1^2 u_2^2}{3kT(4\pi\varepsilon_0)^2}$	$\frac{3\alpha_{01}\alpha_{02}h\nu_1\nu_2}{2(4\pi\varepsilon_0)^2(\nu_1+\nu_2)}$			
Ne–CH$_4$	0	0	19	19^c	—	100
HCl–HI	7	1	197	205	—	96
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Short URL   https://shorturl.at/cmAL4

Contributions of the various interactions to the total van der Waals force

Interacting Molecules	$\gamma_{dipole-dipole}$ (Keesom)	$\gamma_{dipole-ind. dipole}$ (Debye)	$\gamma_{ind. dipole-ind. dipole}$ (London)	Total vdW Energy	$\gamma_{ind-ind}$ (% theoretical)
Ne–Ne	0	0	4	4	100
CH_4–CH_4	0	0	102	102	100
CH_3Cl–CH_3Cl	101	32	282	415	68
H_2O–H_2O	96	10	33	139	24

Dissimilar Molecules

Ne–CH_4	0	0	19	19	100
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H_2O–CH_4	0	9	58	67	87

In units of 10^{-79} J m^{-6}

Induced attraction is the largest energy component

Dominance of dispersion forces. Dispersion forces generally exceed the dipole-dependent induction and orientation forces except for small highly polar molecules, such as water.

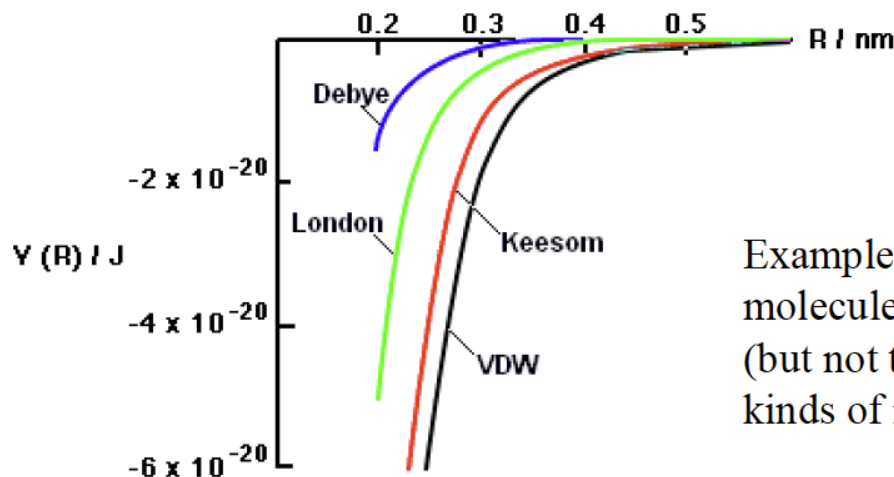Example – two water molecules at 293 K (but not typical for all kinds of molecules)

Contributions of the various interactions to the total van der Waals force

Interacting Molecules	$V_{dipole-dipole}$ (Keesom)	$V_{dipole-ind.\,dipole}$ (Debye)	$V_{ind.\,dipole-ind.\,dipole}$ (London)	Total vdW Energy	$V_{ind-ind}$ (% theoretical)
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In units of 10^{-79} J m^{-6}

> *Induced attraction is the largest energy component*

- London dispersion forces are present in all molecules, and the strength is directly proportional to the polarizability of the molecule.

- Molecules are more polarizable with increasing numbers of electrons and with increasing surface area.

- Keesom and Debye forces are present only in molecules with permanent dipole moments. If the molecules are highly polarizable, and are not very polar, then the Keesom and Debye forces are weaker than the London dispersion forces.

Unification of Polarization Interactions

- Apart from the straight Coulomb interaction between two charges, all the other interactions we have considered have involved **polarization effects**, either explicitly for nonpolar molecules of polarizability α_0 or **implicitly** for rotating polar molecules that effectively behave as polarizable molecules of polarizability

$$\alpha = \alpha_0 + \alpha_{\text{dip}}$$

- For completeness, we may note that all these **angle-averaged interactions** may be expressed in one general equation; thus, for a **charged polar molecule 1** interacting with a second **polar molecule 2**, we may write

$$w(r) = -\left(\frac{Q_1^2}{2r^4} + \frac{3kT\alpha_1}{r^6}\right)\frac{\alpha_2}{(4\pi\varepsilon_0\varepsilon)^2} = -\left[\frac{Q_1^2}{2r^4} + \frac{3kT}{r^6}\left(\frac{u_1^2}{3kT} + \alpha_{01}\right)\right]\left(\frac{u_2^2}{3kT} + \alpha_{02}\right)\Bigg/\left(4\pi\varepsilon_0\varepsilon\right)^2$$

- Here Q_1 is the charge of the **first molecule** and u_1, u_2, α_{01}, α_{02} are the dipole moments and electronic polarizabilities of the two molecules.

Unification of Polarization Interactions
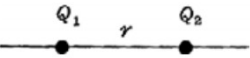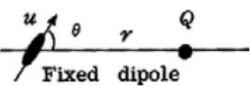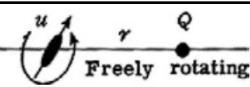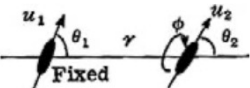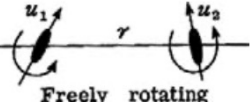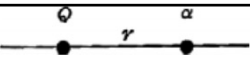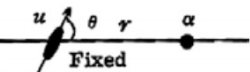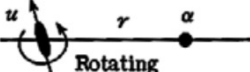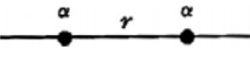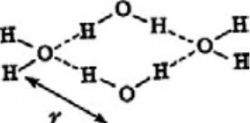
$$W(r) = -\frac{1}{(4\pi\epsilon\epsilon_0)^2}\cdot\left\{\frac{Q_1^2}{2r^4}+\frac{3kT}{r^6}\left(\frac{u_1^2}{3kT}+\alpha_{01}\right)\right\}\left(\frac{u_2^2}{3kT}+\alpha_{02}\right)$$

$$=-\frac{1}{(4\pi\epsilon\epsilon_0)^2}\left\{\frac{Q_1^2 u_2^2}{2r^4\,3kT}+\frac{Q_1^2\alpha_{02}}{2r^4}+\frac{u_1^2 u_2^2}{3kT\,r^6}+\frac{u_1^2\alpha_{02}}{r^6}+\frac{u_2^2\alpha_{01}}{r^6}\right.$$

$$\left.+\frac{3kT\,\alpha_{01}\alpha_{02}}{r^6}\right\}$$

dipole – dipole (Keesom energy)

non polar – non polar
(London dispersion energy)

Charge non-polar

charge dipole (freely rotating)

dipole – non-polar
(Debye energy)

- The **unification** of these various interactions is conceptually important, for it shows them all to be essentially **polarization-type forces**.

- If none of the molecules carries a net charge ($Q_1 = 0$), this gives the (1) Keesom-orientation, the (2) Debye-induction, and the (3) London-dispersion contributions to the total van der Waals force between two molecules.

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

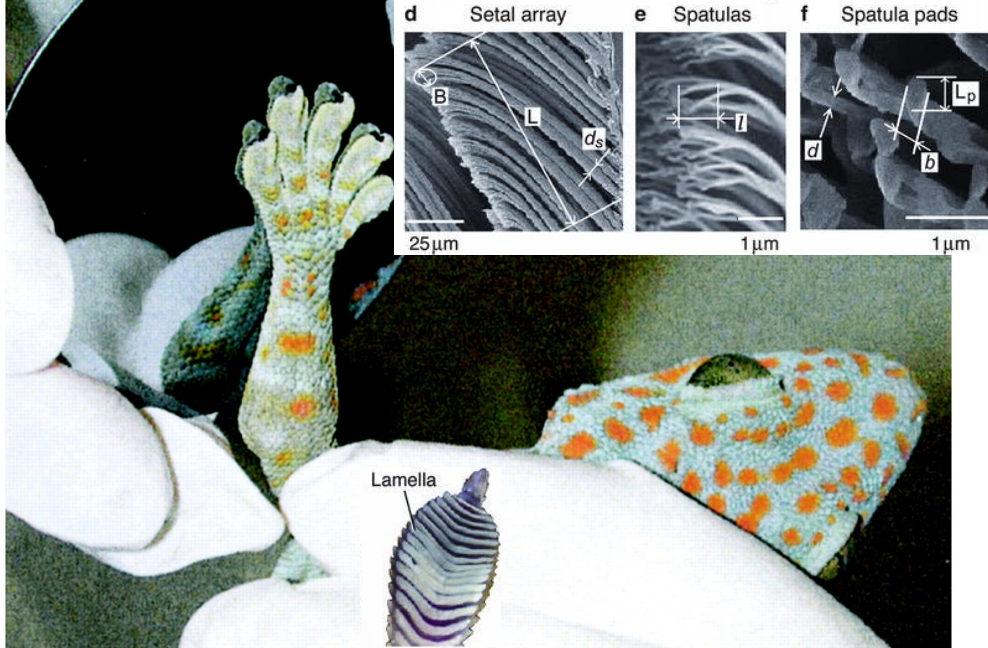| Type of interaction		Interaction energy $w(r)$
Covalent, metallic	(H H) H_2 H O H H_2O	Complicated, short range
Charge–charge	Q_1 r Q_2	$+Q_1Q_2/4\pi\varepsilon_0 r$ (Coulomb energy)
Charge–dipole	u θ r Q Fixed dipole	$-Qu\cos\theta/4\pi\varepsilon_0 r^2$
	u r Q Freely rotating	$-Q^2u^2/6(4\pi\varepsilon_0)^2 kTr^4$
Dipole–dipole	u_1 θ_1 r ϕ u_2 θ_2 Fixed	$-u_1u_2[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi]/4\pi\varepsilon_0 r^3$
	u_1 r u_2 Freely rotating	$-u_1^2 u_2^2/3(4\pi\varepsilon_0)^2 kTr^6$ (Keesom energy)
Charge–non-polar	Q r α	$-Q^2\alpha/2(4\pi\varepsilon_0)^2 r^4$
Dipole–non-polar	u θ r α Fixed	$-u^2\alpha(1+3\cos^2\theta)/2(4\pi\varepsilon_0)^2 r^6$
	u r α Rotating	$-u^2\alpha/(4\pi\varepsilon_0)^2 r^6$ (Debye energy)
Two non-polar molecules	α r α	$-\dfrac{3}{4}\dfrac{h\nu\alpha^2}{(4\pi\varepsilon_0)^2 r^6}$ (London dispersion energy)
Hydrogen bond	H O H · · · H O H H O · · · H O H r	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 polarizibility (C^2 m^2 J^{-1}); r, distance between the centers of the interacting atoms or molecules (m); k, Boltzmann constant (1.381×10^{-23} J K^{-1}); T, absolute temperature (K); h, Planck's constant (6.626×10^{-34} J s); ν, electronic absorption (ionization) frequency (s^{-1}); ε_0, dielectric permittivity of free space (8.854×10^{-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 $n = 9–12$).

d Setal array   e Spatulas   f Spatula pads

25 μm   1 μm   1 μm

Lamella

Tokay gecko (Gekko gecko) adhering to molecularly smooth hydrophobic GaAs semiconductor. The strong adhesion between the hydrophobic surface of the gecko's toes and the hydrophobic GaAs surfaces demonstrates that the mechanism of adhesion in geckos is van der Waals force.

The ability of geckos – which can hang on a glass surface using only one toe – to climb on sheer surfaces has been for many years mainly attributed to the van der Waals forces between these surfaces and the spatulae, or microscopic projections, which cover the hair-like setae found on their footpads.

https://royalsocietypublishing.org/doi/10.1098/rspb.2009.0946
https://www.pnas.org/doi/full/10.1073/pnas.192252799
https://link.springer.com/referenceworkentry/10.1007/978-0-387-92897-5_470

Microfiber cloth makes use of van der Waals force to remove dirt without scratches.

https://www.explainthatstuff.com/microfibercloths.html

www.explainthatstuff.com

www.explainthatstuff.com
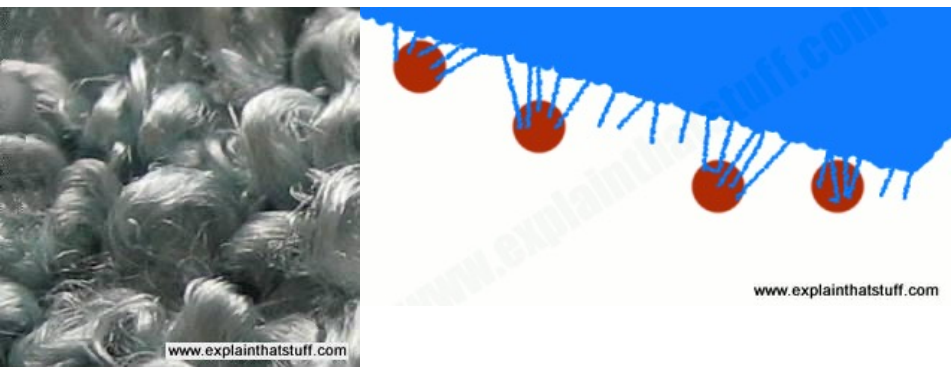
2D Materials – Flexible Electronic Circuit Elements

Graphene — Conductor

MoS₂ — **Semi**-conductor

hBN — Insulator

Electronically — **Tunable**

Mechanically — **Flexible**

Nature Mat. (**2015**)

Gr/MoS₂/hBN Transistor
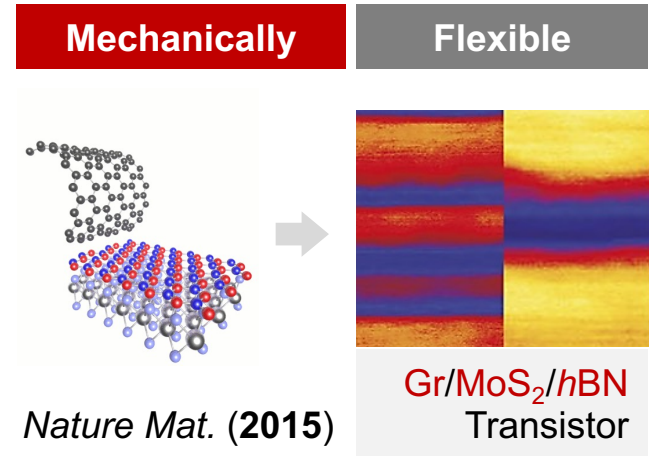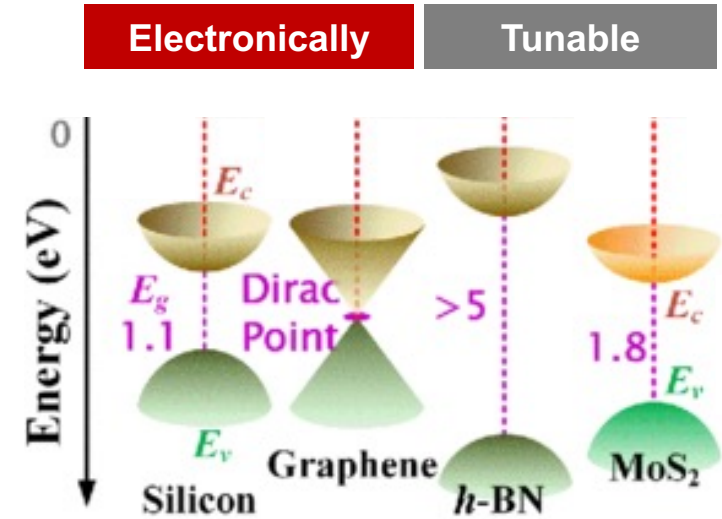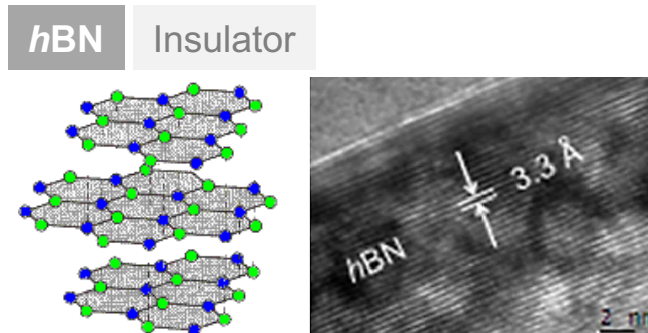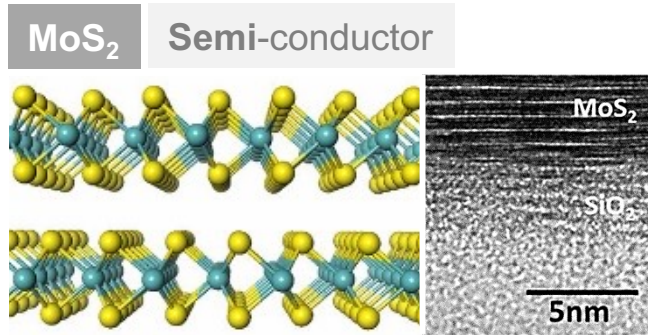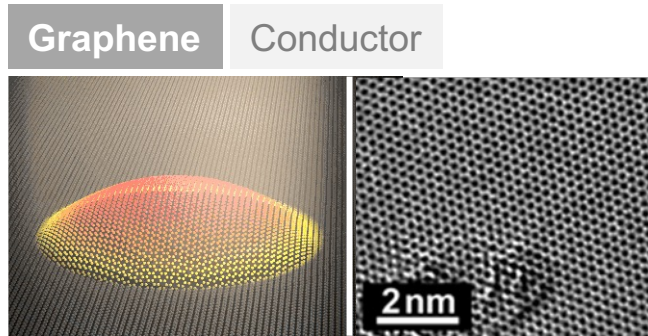
Van der Waals interactions are what holds 2D materials together

- Because van der Waals forces are relatively weak, mechanical motion can break the intermolecular attraction. The best-known example is graphite pencils, where the mechanical motion of the pencil going across the paper cleaves off graphite layers onto the paper.

- The carbon atoms in graphene are sp^2 hybridized, so there is one free π-electron per carbon atom in a graphene particle. This means that the graphene particle can attract other graphene particles, and other materials, toward it.

- When two or more graphene-like materials are stacked, their properties change, opening the possibility of designing novel nano-devices. The properties of these hybrid materials can be controlled by twisting the two stacked layers, providing a unique degree of freedom for the nanoscale control of next generation composite materials and nano-devices without any chemical bonds as they are bound together only by van der Waals forces.
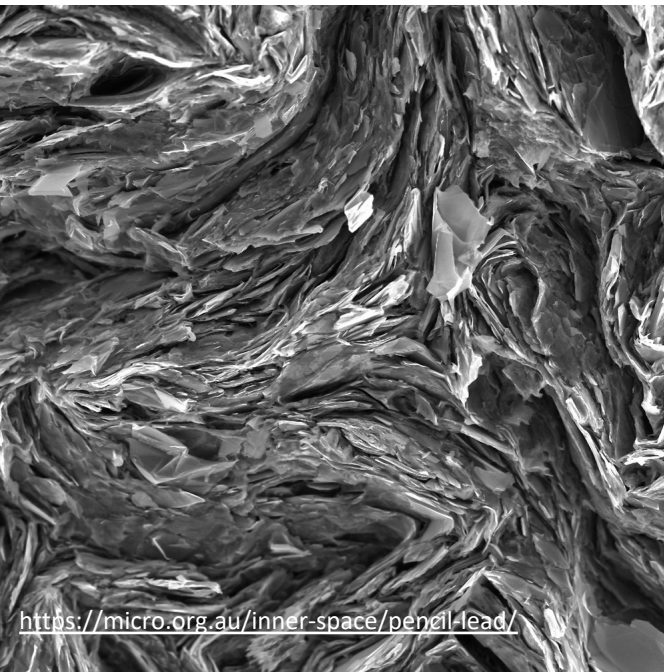
- The van der Waals interactions hold the different 2D material layers in place and the properties of these heterostructures can be vastly different than the sum of its parts. Without van der Waals forces, it wouldn't be possible to stack graphene and other 2D materials.

- The versatility of van der Waals heterostructures is vast—as is the material properties that you can generate. This is due to the sheer number of 2D materials out there that can be stacked on top of one another in different configurations, with each layer laid on top of each other directly, or in some cases, twisted slightly to change the electronic properties of the heterostructure.

moiré patterns are large-scale **interference patterns** that can be produced when a partially opaque ruled pattern with transparent gaps is overlaid on another similar pattern. For the moiré interference pattern to appear, the two patterns must not be completely identical, but rather **displaced**, **rotated**, or have **slightly different pitch**. https://en.wikipedia.org/wiki/Moir%C3%A9_pattern
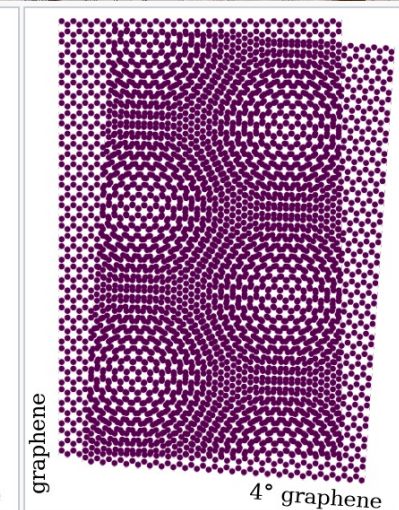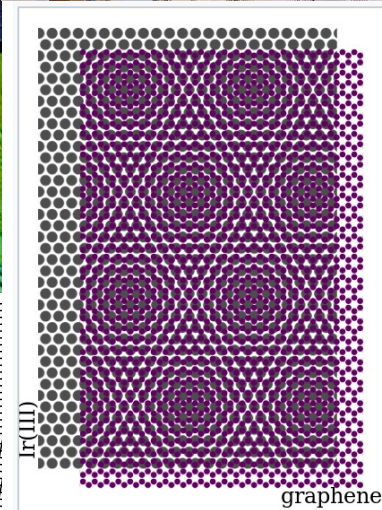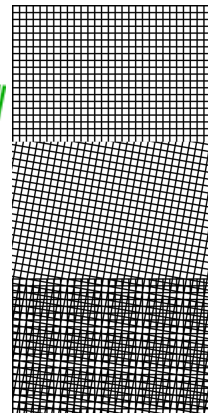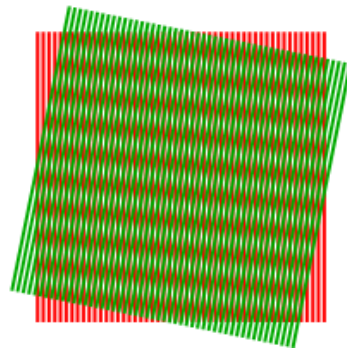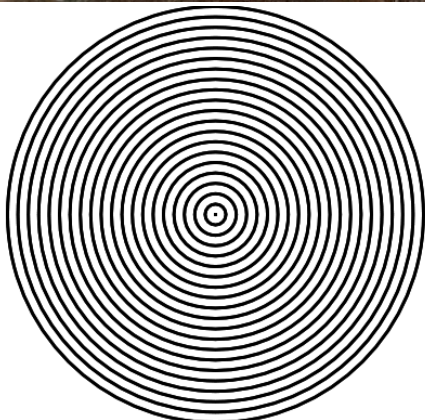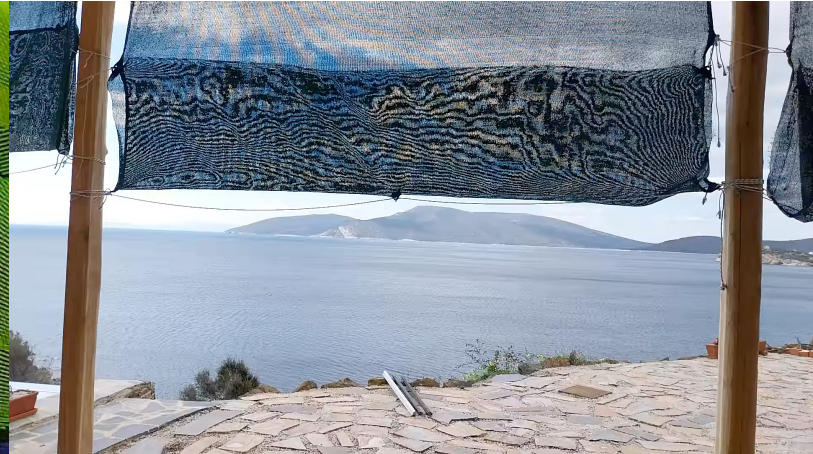
When graphene is grown on the (111) surface of iridium, its long-wavelength height modulation can be thought of as a moiré pattern arising from the superposition of the two mismatched hexagonal lattices.

Moiré pattern arising from the superposition of two graphene lattices twisted by 4°

Van der Waals interactions – a generalized perspective

- Of all the forces that must be examined for colloidal particles – depletion forces, solvation forces, solvophobic forces, hydrogen bonding – the most ubiquitous is the VDW force.
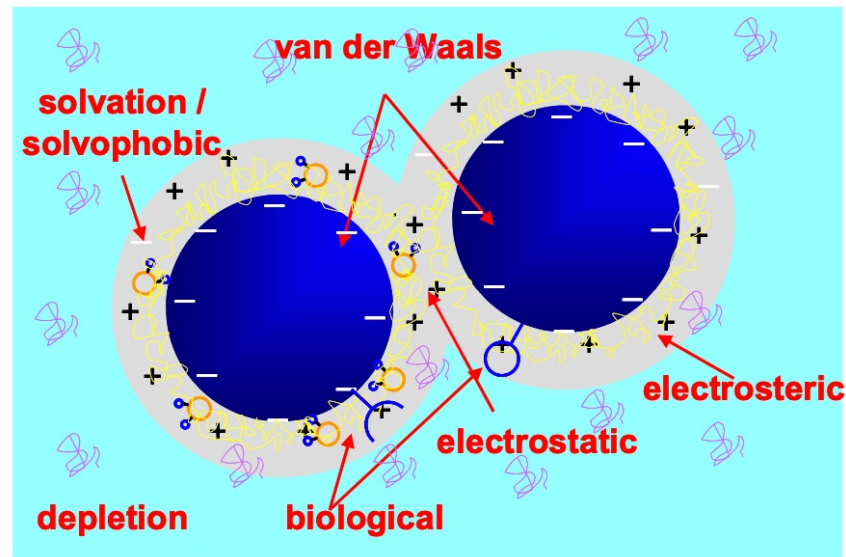
Nature Materials, 8, 543-557 123 (2009)

- VDW interactions are weak for atomic or molecular systems – often giving energies less than 0.1 kT. On the other hand, for colloidal system, where the particles typically contain 10^3 to 10^{12} atoms, VDW interactions can readily amount to several 100 kT of attraction, due to the larger size of the particles.

Van der Waals interactions – a generalized perspective

- The physics of the VDW interaction is quantum mechanical. Within the atoms of an electron, the electrons are continually performing their quantum mechanical dance.

- As a result of the electron movement, small and instantaneous dipoles form within the atoms.
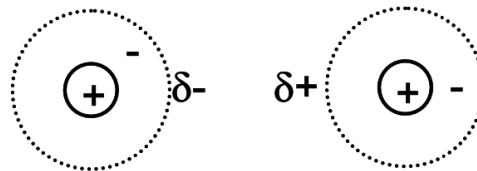
Figure 3-2. Instantaneous temporary dipole and induced dipole on two hydrogen atoms. The electron in the atom on the left has spontaneously moved to one side of the atom, and this in turn causes the electron in the atom on the right to move to the far right side, since like charges repel. The resulting dipoles are arranged with the negative tail of one dipole near to the positive end of the other. Attraction results.

- The detailed physics for VDW attraction between two hydrogen atoms, starting with second order perturbations to the orbital solutions of quantum mechanics for the hydrogen atom, have been known for three-fourths of a century.

Pauling, Linus; Wilson, E. Bright. Introduction to Quantum Mechanics, McGraw- Hill (New York) 1935.
This wonderful book lays out the solution clearly.

Van der Waals interactions – a generalized perspective

- London found that the change in energy ($\Delta V_{VDW,2}$) of two atoms when they are brought from infinite separation to a finite center-to-center separation (r) is

$$\Delta V_{VDW,2} = -\frac{3\hbar\omega_0\alpha_0^2}{4(4\pi\varepsilon_0)^2 r^6}$$

- $\hbar = h / 2\pi$, where $h = 6.626 \times 10^{-34}$ J-s is Planck's constant.

- The atom is characterized by a static (zero frequency) polarizability (α_0) and a characteristic angular frequency (ω_0).

- The polarizability provides a measure of how easily the electrons are moved to one side of the atom in the presence of an electric field, whereas the characteristic angular frequency indicates how quickly the electrons change polarization within the atom.

$$\omega_0 = \frac{2\pi}{\tau}, where\ \tau \equiv period, and\ \nu = \frac{1}{\tau}, therefore\ \omega_0 = 2\pi \cdot \nu$$

Interactions between Neutral Polarizable Molecules: van der Waals Forces

How do these neutral molecules polarize each other?

• *Instantaneous* dipole moment due to electron-proton displacement

(a)

$$w(r) = -\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{2(4\pi\varepsilon\varepsilon_0)^2 r^6}$$

$$w(r) = -\frac{3\alpha_0^2 h\nu}{4(4\pi\varepsilon_0)^2 r^6}$$

Between similar atoms

London 's equations

$$w(r) = -\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1+\nu_2)}$$

Between dissimilar atoms

ν = ionization frequency
$h\nu$ = first ionization potential

London Dispersion Force between Nonpolar Molecules

- Except for a numerical factor, this is the same as that derived by London in 1930 using quantum mechanical perturbation theory. **London's expression** for the **dispersion interaction energy** between two **identical** atoms or molecules is

$$w(r) = \frac{-C_{\text{disp}}}{r^6} = -\frac{3}{4}\alpha_0^2 h\nu/(4\pi\varepsilon_0)^2 r^6 = -\frac{3}{4}\alpha_0^2 I/(4\pi\varepsilon_0)^2 r^6$$

$$w(r) \approx -\alpha_0^2 h\nu/(4\pi\varepsilon_0)^2 r^6$$

The coupled dipole method (CDM)

- In order to derive that numerical factor, we have to use insights from quantum mechanics.

- I will present the "coupled dipole method" (CDM), which is a simplified approach that captures the essential parts of the quantum mechanics.

- The CDM treats all atoms or groups of atoms as being polarizable when an electric field (**E**) is applied. That is, the electrons respond to **E** to give a net dipole. The applied **E** field can in fact change in time with some frequency (ω). At zero or low frequency, the electrons within a given atom have plenty of time to respond to the electric field, and so they polarize to the maximum extent.

- As a result, the atom takes on a dipole (**p**), with units of C-m, which is charge times distance, according to **p** = α**E**.

- In essence, we have stuffed the complex quantum mechanics of the electrons' motion into the single polarizability (α).

Langmuir, 23, 1735-1740 (2007). Seeds of the coupled dipole method date back to London.

The coupled dipole method (CDM)

- As the frequency of **E** increases, the electrons have to move back and forth within the atom.

- At a frequency of say 1000 s^{-1}, the electrons are easily able to keep up. It is almost as if a static **E** field were being applied.

- As the frequency gets higher, perhaps 10^{14} s^{-1}, the electrons no longer have time to accelerate completely, so they are not able to polarize the atom to the maximum extent.

- At very high frequencies, say 10^{18} s^{-1}, the E field is reversing so quickly that before an electron can move in one direction, due to mass inertia, the **E** field has already changed direction. In this case, on average, the electrons do not polarize at all.

- As we see, the polarization depends on the frequency of how fast **E** is being reversed. Thus, the polarizability (α) is not a single number, but a function that depends on frequency.

Langmuir, 23, 1735-1740 (2007). Seeds of the coupled dipole method date back to London.

The coupled dipole method (CDM)

- One common equation for expressing the frequency-dependent polarizability $\alpha(\omega)$ is the Drude model:

$$\alpha(\omega) = \frac{\alpha_0}{1 - (\omega/\omega_0)^2}$$

- as before, α_0 is the static (zero frequency) polarizability and ω_0 is the characteristic frequency, or resonant frequency. When the E field is applied at a frequency $\omega = \omega_0$, it is like pushing a child on a swing at the resonant frequency of the pendulum: A little push causes the child to swinger ever higher. Mathematically, α becomes infinite when $\omega = \omega_0$.
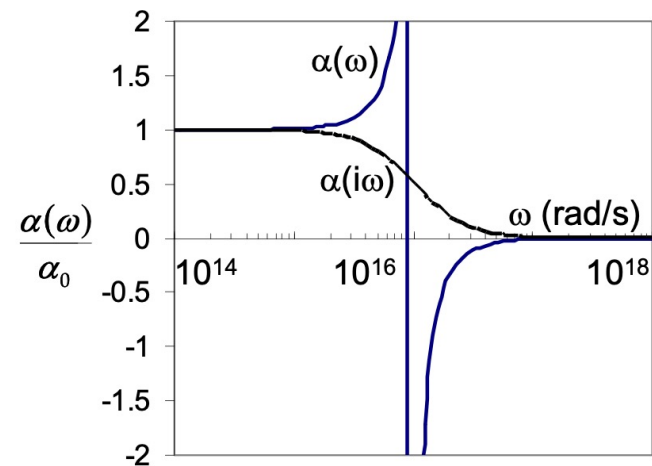
Figure 3-3. Polarizability function. This atom has $\omega_0 = 10^{16}$ rad/s. When expressing α as a function of frequency ω (rad/s = Hz), the function diverges at ω_0. Sometimes the polarizability is expressed as a function of "complex frequency" ($i\omega$), which has no physical meaning but is useful mathematically, since this function does not diverge and is monotonic.

The coupled dipole method (CDM)
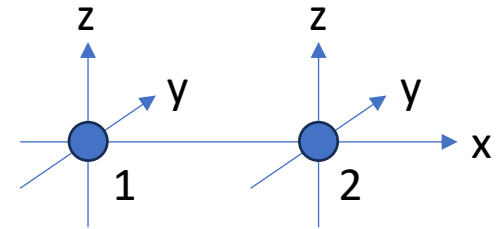
- Now imagine that we have two identical atoms in the universe. Every energy must have a reference point, so that I can define where "zero energy" exists. For the VDW energy, the reference state is set where the atoms are separated by an infinite distance.

$$\Delta V_{VDW}(r) = V(r) - V(r \to \infty)$$

- where V is the work required to position the atoms in given locations. By subtracting the work required to assemble the system at infinite separation, we remove energies such as assembling the nucleus and similar physics, enabling us to focus on the VDW interaction alone.

- Let's define the position of one atom as being at the origin ($x_1 = 0$), and the other atom we will place along the x-axis at $x_2 = r$. For these atoms the polarizations are:

$$\mathbf{p}_1 = \alpha \mathbf{E}(\mathbf{x}_1), \ \mathbf{p}_2 = \alpha \mathbf{E}(\mathbf{x}_2)$$

- where α_0 is the polarizability of each atom, which is the first place where quantum mechanics enters this problem. The electric field at x_1 and x_2 could be due to an applied field (E_0), but it could also be due to a dipole field resulting from the other atom.

The coupled dipole method (CDM)
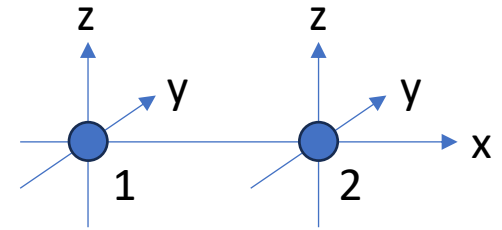
- We may write the dipole electric field at x_1 resulting from a dipole (p_2) at x_2 as

$$\mathbf{E}(\mathbf{x}_1) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_2}{4\pi\varepsilon_0 r^3}$$

$$\mathbf{E}(\mathbf{x}_2) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_1}{4\pi\varepsilon_0 r^3}$$

- In this case the normal vector (**n**) from dipole 1 to 2 is simply **n** = **i$_x$**, the unit vector along the x-axis, since the atoms are along the x-axis. ($n_x = 1$, $n_y = 0$, $n_z = 0$)

- A dyad like **nn** is a "tensor" quantity. The normal vector can be written as **n** = n_x**i$_x$** + n_y**i$_y$** + n_z**i$_z$**, and then the expression 3**nn** − **I** could be written as

$$3\begin{pmatrix} n_x n_x & n_x n_y & n_x n_z \\ n_y n_x & n_y n_y & n_y n_z \\ n_z n_x & n_z n_y & n_z n_z \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 3\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

The coupled dipole method (CDM)

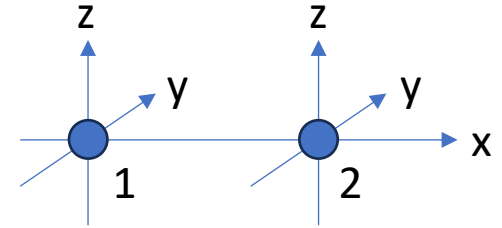- We may write the dipole electric field at x_1 resulting from a dipole (p_2) at x_2 as

$$\mathbf{E}(\mathbf{x}_1) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_2}{4\pi\varepsilon_0 r^3}$$

$$\mathbf{E}(\mathbf{x}_2) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_1}{4\pi\varepsilon_0 r^3}$$

- In this case the normal vector (**n**) from dipole 1 to 2 is simply **n** = $\mathbf{i_x}$, the unit vector along the x-axis, since the atoms are along the x-axis. ($n_x = 1$, $n_y = 0$, $n_z = 0$)

- Therefore, the top equation becomes (assuming no external field or $\mathbf{E_0 = 0}$):

$$\begin{pmatrix} E_{1x} \\ E_{1y} \\ E_{1z} \end{pmatrix} = \frac{1}{4\pi\varepsilon_0 r^3} \begin{pmatrix} 2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} P_{2x} \\ P_{2y} \\ P_{2z} \end{pmatrix}$$

$$E_{1x} = \frac{2}{4\pi\varepsilon_0 r^3} P_{2x} \qquad E_{1y} = -\frac{1}{4\pi\varepsilon_0 r^3} P_{2y} \qquad E_{1z} = -\frac{1}{4\pi\varepsilon_0 r^3} P_{2z}$$

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

$$E_{\parallel} = (E_- - E_+)\cos(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{2l}{r}\cos\theta$$

$$E_{\perp} = (E_- + E_+)\sin(\phi/2) \approx (q/4\pi\varepsilon_0 r^2)\frac{l}{r}\sin\theta$$

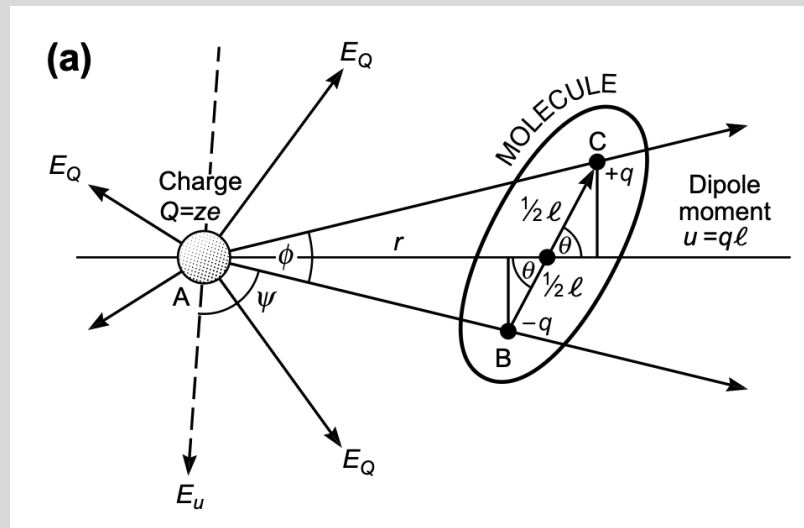- The magnitude and direction ψ of the resulting dipolar field at A is therefore given by

$$E_u = \sqrt{E_{\parallel}^2 + E_{\perp}^2} = (ql/4\pi\varepsilon_0 r^3)\sqrt{4\cos^2\theta + \sin^2\theta}$$

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

- therefore, $F = QE_u = \dfrac{Qu\,(1+3\cos^2\theta)^{1/2}}{4\pi\varepsilon_0 r^3}$

- with $\tan\psi = \dfrac{\tan\theta}{2}$

(a)

- For a fixed **dipole u** oriented at an angle θ to the line joining it to a **polarizable molecule**, we derived the **electric field** of the **dipole** acting on the surrounding as

$$E = u(1 + 3\cos^2\theta)^{1/2}/4\pi\varepsilon_0\varepsilon r^3$$

$$\tan\psi = \frac{\tan\theta}{2}$$

Input interpretation

plot | tan(x)

Plots

Input interpretation

plot | cos(x)

Plots

Input interpretation

solve | $\tan(x) = \frac{1}{2}\tan\left(\frac{\pi}{2} + 0.001\right)$

Result

$x = 3.14159\,n - 1.5688$ and $n \in \mathbb{Z}$

The coupled dipole method (CDM)

- We may write the dipole electric field at x_1 resulting from a dipole (p_2) at x_2 as

$$\mathbf{E}(\mathbf{x}_1) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_2}{4\pi\varepsilon_0 r^3}$$

$$\mathbf{E}(\mathbf{x}_2) = \mathbf{E}_0 + \frac{(3\mathbf{nn} - \mathbf{I}) \cdot \mathbf{p}_1}{4\pi\varepsilon_0 r^3}$$

- Recall $\quad \mathbf{p}_1 = \alpha\mathbf{E}(\mathbf{x}_1), \ \mathbf{p}_2 = \alpha\mathbf{E}(\mathbf{x}_2) \quad$ and $\quad \alpha(\omega) = \dfrac{\alpha_0}{1 - (\omega/\omega_0)^2}$

- We obtain two vector equations for two vector quantities ($\mathbf{p}_1$ and $\mathbf{p}_2$).

$$\omega_0^2 \mathbf{p}_1 - \alpha_0 \omega_0^2 \left(\frac{3\mathbf{nn} - \mathbf{I}}{4\pi\varepsilon_0 r^3} \right) \cdot \mathbf{p}_2 = \omega^2 \mathbf{p}_1$$

$$-\alpha_0 \omega_0^2 \left(\frac{3\mathbf{nn} - \mathbf{I}}{4\pi\varepsilon_0 r^3} \right) \cdot \mathbf{p}_1 + \omega_0^2 \mathbf{p}_2 = \omega^2 \mathbf{p}_2$$

The coupled dipole method (CDM)

- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$

$$\begin{pmatrix} P_{1x} \\ P_{1y} \\ P_{1z} \end{pmatrix} - \begin{pmatrix} 2\gamma & 0 & 0 \\ 0 & -1\gamma & 0 \\ 0 & 0 & -1\gamma \end{pmatrix} \begin{pmatrix} P_{2x} \\ P_{2y} \\ P_{2z} \end{pmatrix} = \left(\frac{\omega}{\omega_0}\right)^2 \begin{pmatrix} P_{1x} \\ P_{1y} \\ P_{1z} \end{pmatrix}$$

$$- \begin{pmatrix} 2\gamma & 0 & 0 \\ 0 & -1\gamma & 0 \\ 0 & 0 & -1\gamma \end{pmatrix} \begin{pmatrix} P_{1x} \\ P_{1y} \\ P_{1z} \end{pmatrix} + \begin{pmatrix} P_{2x} \\ P_{2y} \\ P_{2z} \end{pmatrix} = \left(\frac{\omega}{\omega_0}\right)^2 \begin{pmatrix} P_{1x} \\ P_{1y} \\ P_{1z} \end{pmatrix}$$

$$\omega_0^2 \mathbf{p}_1 - \alpha_0 \omega_0^2 \left(\frac{3\mathbf{nn} - \mathbf{I}}{4\pi\varepsilon_0 r^3}\right) \cdot \mathbf{p}_2 = \omega^2 \mathbf{p}_1$$

$$- \alpha_0 \omega_0^2 \left(\frac{3\mathbf{nn} - \mathbf{I}}{4\pi\varepsilon_0 r^3}\right) \cdot \mathbf{p}_1 + \omega_0^2 \mathbf{p}_2 = \omega^2 \mathbf{p}_2$$

The coupled dipole method (CDM)

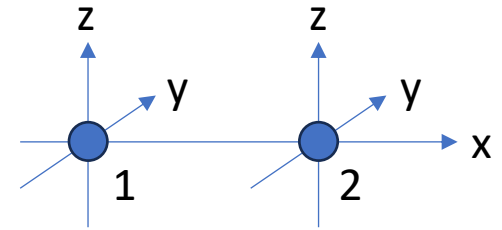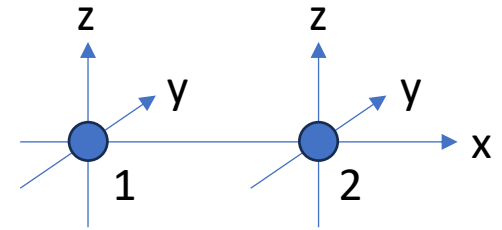- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$
- This can be further consolidated into 6 scalar equations:

$$
\begin{pmatrix}
1 & 0 & 0 & -2\gamma & 0 & 0 \\
0 & 1 & 0 & 0 & \gamma & 0 \\
0 & 0 & 1 & 0 & 0 & \gamma \\
-2\gamma & 0 & 0 & 1 & 0 & 0 \\
0 & \gamma & 0 & 0 & 1 & 0 \\
0 & 0 & \gamma & 0 & 0 & 1
\end{pmatrix}
\cdot
\begin{pmatrix}
p_1^x \\
p_1^y \\
p_1^z \\
p_2^x \\
p_2^y \\
p_x^z
\end{pmatrix}
= \left(\frac{\omega}{\omega_0} \right)^2
\begin{pmatrix}
p_1^x \\
p_1^y \\
p_1^z \\
p_2^x \\
p_2^y \\
p_x^z
\end{pmatrix}
$$

- This is an **eigenvalue** problem. Solving it will give 6 **eigenvalues** for $(\omega/\omega_0)^2$.
- Physically, this linear set of equations describes the coupling between the two atoms – it describes their "dipole conversation". The **eigenvalues** gives the **frequencies** "at which the dipoles talk".

The coupled dipole method (CDM)

- Dividing both sides by $\omega_0{}^2$ and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$

- The eigenvalues can be solved as:

$$\left(\frac{\omega}{\omega_0}\right)^2 = \{1-2\gamma, 1-\gamma, 1-\gamma, 1+2\gamma, 1+\gamma, 1+\gamma\}$$

- The frequencies (ω/ω$_0$) are always positive, and so taking the square root of each of these 6 values gives the characteristic frequencies of the system:

$$\frac{\omega}{\omega_0} = \left\{\sqrt{1-2\gamma}, \sqrt{1-\gamma}, \sqrt{1-\gamma}, \sqrt{1+2\gamma}, \sqrt{1+\gamma}, \sqrt{1+\gamma}\right\}$$

- Now we approximate each atom as a **quantum harmonic oscillator**. Quantum mechanics tells us the energy of a **harmonic oscillator**. Each of the two atoms can have oscillations in each of 3 directions – 6 modes of oscillation.

The coupled dipole method (CDM)

- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$
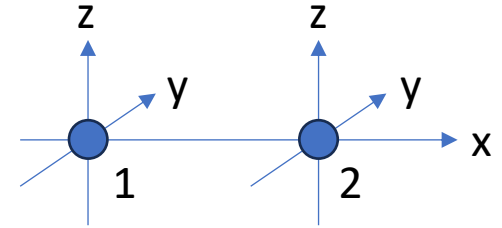
- The eigenvalues can be solved as:

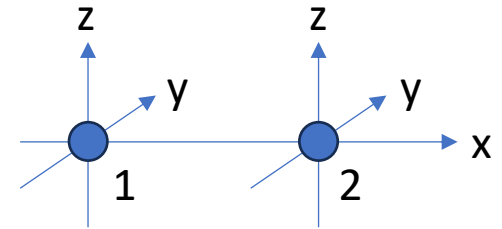$$\left(\frac{\omega}{\omega_0}\right)^2 = \{1-2\gamma, 1-\gamma, 1-\gamma, 1+2\gamma, 1+\gamma, 1+\gamma\}$$

- The frequencies (ω/ω_0) are always positive, and so taking the square root of each of these 6 values gives the characteristic frequencies of the system:

$$\frac{\omega}{\omega_0} = \left\{\sqrt{1-2\gamma}, \sqrt{1-\gamma}, \sqrt{1-\gamma}, \sqrt{1+2\gamma}, \sqrt{1+\gamma}, \sqrt{1+\gamma}\right\}$$

- When the atoms have an infinite separation they behave independently, and since the energy of each mode of oscillation is $\hbar\omega_0/2$ from quantum mechanics, this results in $6\hbar\omega_0/2$. The overall energy changes when two atoms are brought from an infinite separation to a finite separation (r): (where the ω_i are from the eigenvalues listed above)

$$\Delta V_{VDW} = \sum_{i=1}^{6} \frac{\hbar\omega_i}{2} - 6\frac{\hbar\omega_0}{2}$$

The coupled dipole method (CDM)

- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$

- For small values of γ, perform Taylor expansion for the frequencies (ω/ω_0)

$$\frac{\omega}{\omega_0} \approx \{1-\gamma-\gamma^2/2,\ 1-\gamma/2-\gamma^2/8,\ 1-\gamma/2-\gamma^2/8,$$

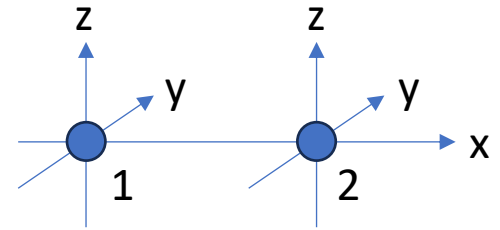$$1+\gamma/2-\gamma^2/8,\ 1+\gamma/2-\gamma^2/8,\ 1+\gamma-\gamma^2/2\}$$

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$$\frac{\omega}{\omega_0} = \left\{\sqrt{1-2\gamma},\sqrt{1-\gamma},\sqrt{1-\gamma},\sqrt{1+2\gamma},\sqrt{1+\gamma},\sqrt{1+\gamma}\right\}$$

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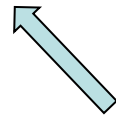
The coupled dipole method (CDM)

- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$

- For small values of γ, perform Taylor expansion for the frequencies (ω/ω_0)

$$\frac{\omega}{\omega_0} \approx \{1-\gamma-\gamma^2/2,\ 1-\gamma/2-\gamma^2/8,\ 1-\gamma/2-\gamma^2/8,$$

$$1+\gamma/2-\gamma^2/8,\ 1+\gamma/2-\gamma^2/8,\ 1+\gamma-\gamma^2/2\}$$

- Insert these approximated frequencies into the ΔV_{VDW} expression:

$$\Delta V_{VDW} = \frac{\hbar}{2}\omega_0\left(6-\frac{3\gamma^2}{2}\right) - 6\frac{\hbar\omega_0}{2} = -\frac{\hbar}{2}\omega_0\left(\frac{3\gamma^2}{2}\right) \implies \boxed{\Delta V_{VDW} = -\frac{3\hbar\omega_0}{4}\left(\frac{\alpha_0}{4\pi\varepsilon_0 r^3}\right)^2}$$

which is identical with London's result

$$\Delta V_{VDW} = \sum_{i=1}^{6} \frac{\hbar\omega_i}{2} - 6\frac{\hbar\omega_0}{2}$$
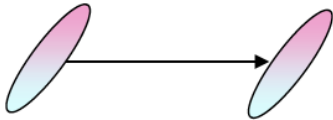
Van der Waals interactions – a generalized perspective

- London found that the change in energy ($\Delta V_{VDW,2}$) of two atoms when they are brought from infinite separation to a finite center-to-center separation (r) is

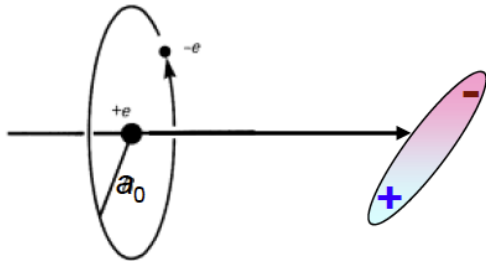$$\Delta V_{VDW,2} = -\frac{3\hbar\omega_0\alpha_0^2}{4(4\pi\varepsilon_0)^2 r^6}$$

- $\hbar = h / 2\pi$, where $h = 6.626 \times 10^{-34}$ J-s is Planck's constant.

- The atom is characterized by a static (zero frequency) polarizability (α_0) and a characteristic angular frequency (ω_0).

- The polarizability provides a measure of how easily the electrons are moved to one side of the atom in the presence of an electric field, whereas the characteristic angular frequency indicates how quickly the electrons change polarization within the atom.

$$\omega_0 = \frac{2\pi}{\tau}, where\ \tau \equiv period, and\ \nu = \frac{1}{\tau}, therefore\ \omega_0 = 2\pi \cdot \nu$$

Interactions between Neutral Polarizable Molecules: van der Waals Forces

How do these neutral molecules polarize each other?

(a)

- **Instantaneous** dipole moment due to electron-proton displacement

$$w(r) = -\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{2(4\pi\varepsilon\varepsilon_0)^2 r^6}$$

$\rightarrow$

$$w(r) = -\frac{3\alpha_0^2 h\nu}{4(4\pi\varepsilon_0)^2 r^6}$$
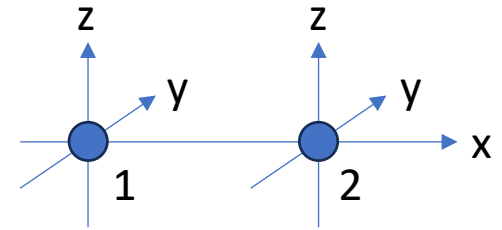
Between similar atoms

London 's equations

$$w(r) = -\frac{3\alpha_{01}\alpha_{02}}{2(4\pi\varepsilon_0)^2 r^6}\frac{h\nu_1\nu_2}{(\nu_1+\nu_2)}$$

Between dissimilar atoms

ν = ionization frequency
$h\nu$ = first ionization potential

The coupled dipole method (CDM)

- Dividing both sides by ω_0^2 and defining $\gamma = \alpha_0 / 4\pi\varepsilon_0 r^3$

- For small values of γ, perform Taylor expansion for the frequencies (ω/ω_0)

$$\frac{\omega}{\omega_0} \approx \{1 - \gamma - \gamma^2/2,\; 1 - \gamma/2 - \gamma^2/8,\; 1 - \gamma/2 - \gamma^2/8,$$

$$1 + \gamma/2 - \gamma^2/8,\; 1 + \gamma/2 - \gamma^2/8,\; 1 + \gamma - \gamma^2/2\}$$

- Insert these approximated frequencies into the ΔV_{VDW} expression:

$$\Delta V_{VDW} = \frac{\hbar}{2}\omega_0\left(6 - \frac{3\gamma^2}{2}\right) - 6\frac{\hbar\omega_0}{2} = -\frac{\hbar}{2}\omega_0\left(\frac{3\gamma^2}{2}\right) \implies \Delta V_{VDW} = -\frac{3\hbar\omega_0}{4}\left(\frac{\alpha_0}{4\pi\varepsilon_0 r^3}\right)^2$$

- In the end, with only two pieces of quantum information – 1) the expression for the energy of a harmonic oscillator and 2) the polarizability of each atom – the dipole conversation has been re-framed as an eigenvalue problem that gives the van der Waals attractive energy between two atoms.

- The VDW energy results from the slight change in frequency of the modes of the system, when the atoms are brought to a finite separation (r).
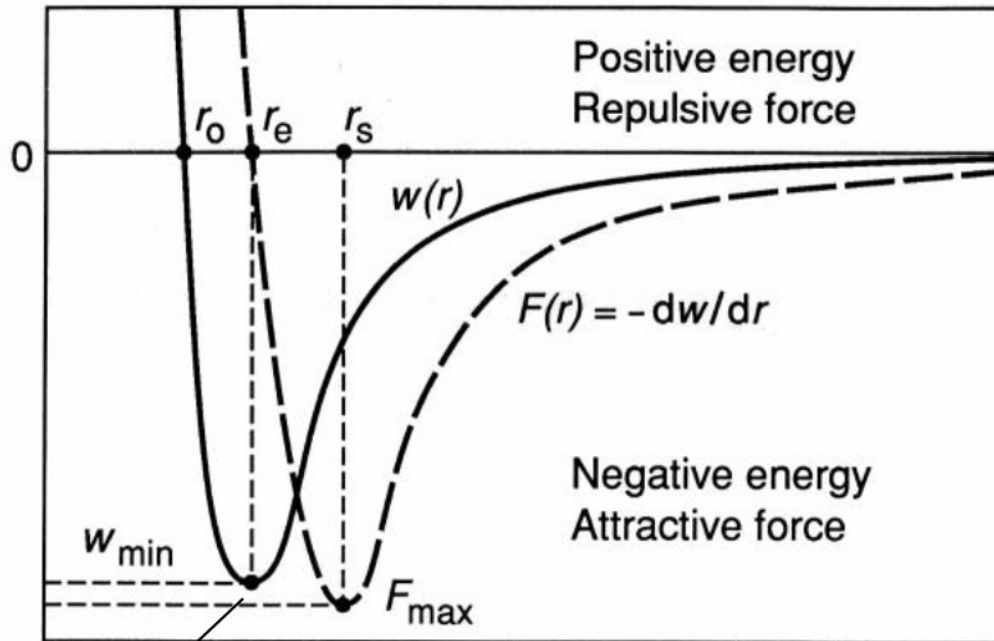
Van der Waals interactions – a generalized perspective

- We see that the VDW energy vary as $1/r^6$. This same dependence on r is the origin of the second term in the Lennard- Jones parameterization of the interaction energy between atoms, which is given by

$$\Delta V_{L-J}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

- where ω gives the depth of the potential well, and r = σ gives the distance where ΔV_{L-J} = 0.

- The twelfth power on the first term simply provides a simple way to express the hard-sphere repulsion between the atoms.

$$\Delta V_{VDW} = -\frac{3\hbar\omega_0}{4} \left(\frac{\alpha_0}{4\pi\varepsilon_0 r^3} \right)^2$$

Basics of Molecular Interactions: Force and Energy

Positive energy
Repulsive force

$w(r)$

$F(r) = -dw/dr$

Negative energy
Attractive force

w_{min}

F_{max}

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