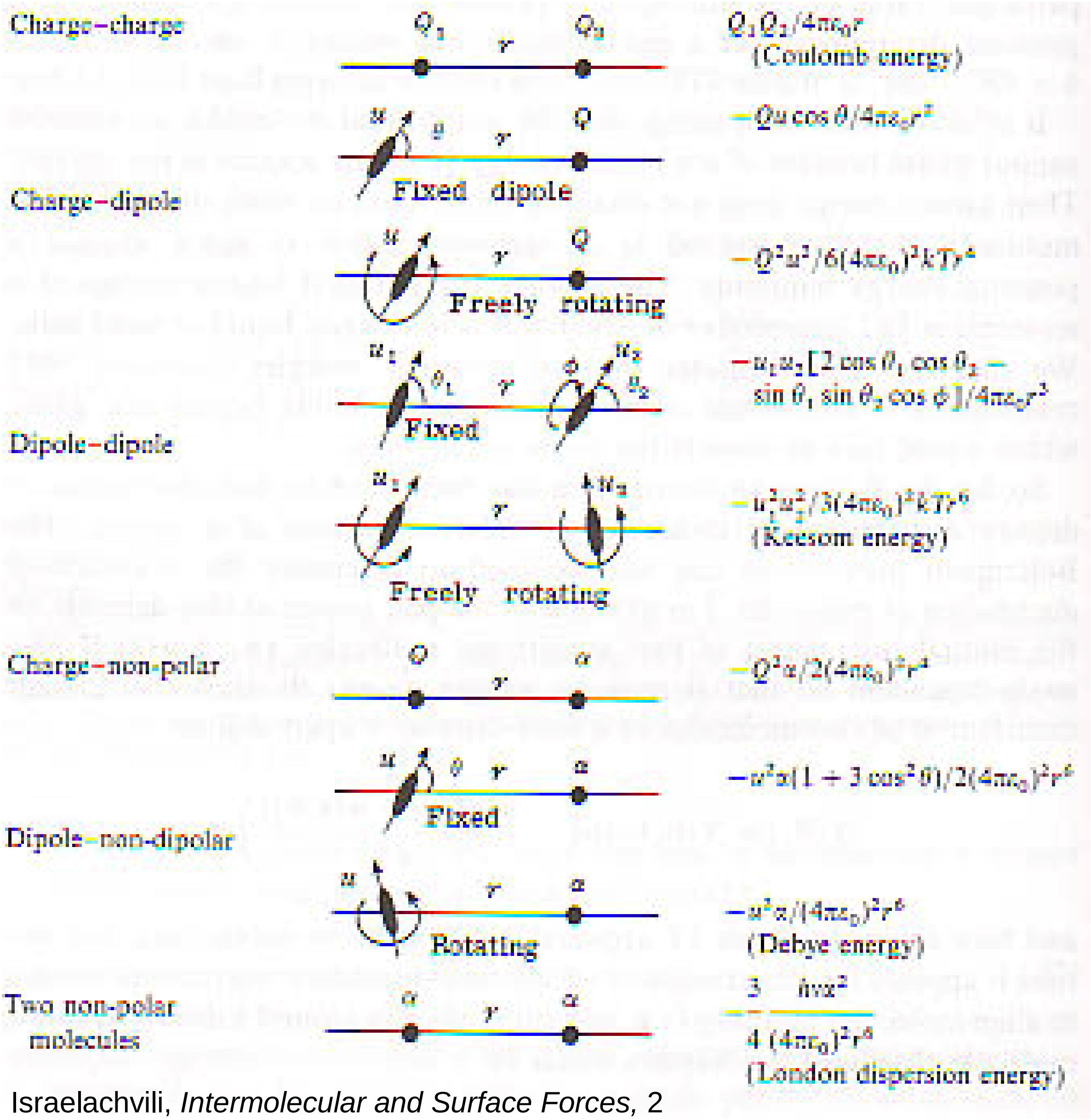
Overview of Intermolecular Forces

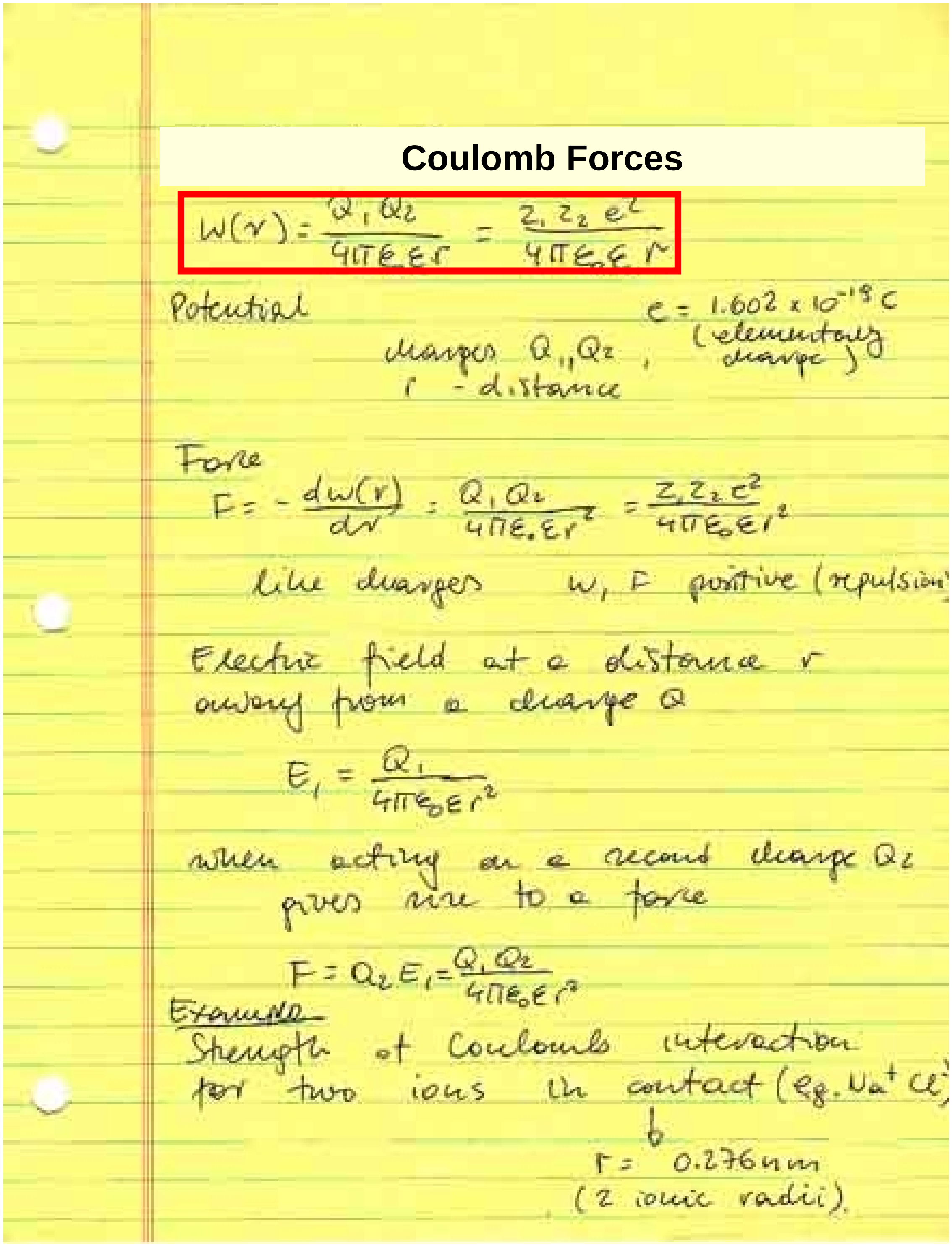
(Based on the textbook *Intermolecular and Surface Forces* by Jacob Israelachvili)

This lecture reviews major intermolecular forces, emphasizing their electrostatic background.



J. Israelachvili, *Intermolecular and Surface Forces,* 2 edition, p.28, Academic Press (1992).

Coulomb Forces



$$\boxed{w(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 \varepsilon r} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 \varepsilon r}}$$

Potential

charges Q_1, Q_2, $e = 1.602 \times 10^{-19}$ C (elementary charge)

r - distance

Force

$$F = -\frac{dw(r)}{dr} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 \varepsilon r^2} = \frac{z_1 z_2 e^2}{4\pi\varepsilon_0 \varepsilon r^2}$$

like charges w, F positive (repulsion)

Electric field at a distance r away from a charge Q

$$E_1 = \frac{Q_1}{4\pi\varepsilon_0 \varepsilon r^2}$$

when acting on a second charge Q_2 gives rise to a force

$$F = Q_2 E_1 = \frac{Q_1 Q_2}{4\pi\varepsilon_0 \varepsilon r^2}$$

Example

Strength of Coulomb interaction for two ions in contact (e.g. $Na^+ Cl^-$)

$r = 0.276$ nm

(2 ionic radii)

$$w(r) = \frac{-(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12})(0.276 \times 10^{-9})} =$$

$$= -8.4 \times 10^{-19}\ J$$

compare with kT at R.T

$kT = 1.38 \times 10^{-23}\ J/K \cdot 300K = 4.1 \times 10^{-21}\ J$.

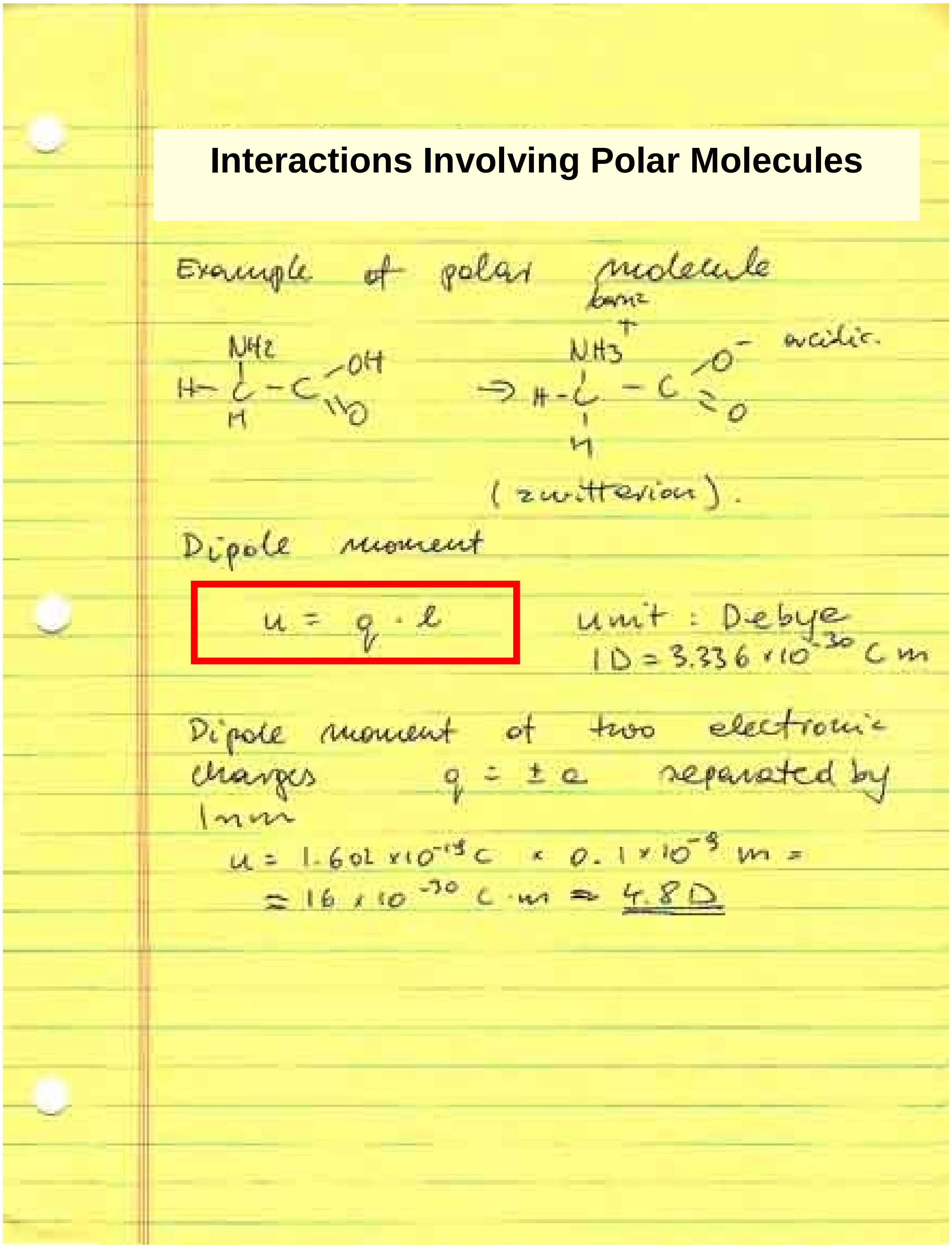
coulomb interaction ~ 200kT per ion pair in vacuum.

At what distance will it fall below kT?

$$\frac{1}{r_x} = \frac{1}{200} \cdot \frac{1}{r_0} \qquad r_x = 200 \cdot 0.28\ nm =$$

$$= 56\ nm$$

Interactions Involving Polar Molecules



Example of polar molecule

(zwitterion).

Dipole moment

$$\boxed{u = q \cdot l}$$

unit : Debye

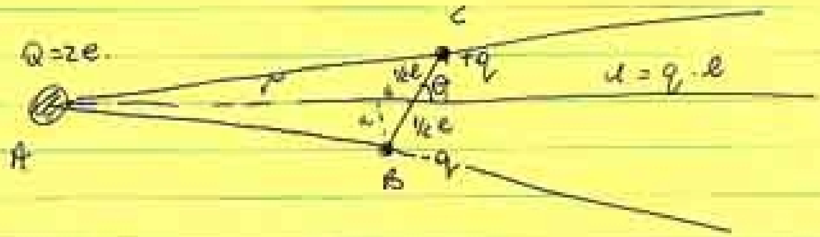
$1 D = 3.336 \times 10^{-30}$ C m

Dipole moment of two electronic charges $q = \pm e$ separated by 1nm

$$u = 1.602 \times 10^{-19} C \times 0.1 \times 10^{-9} m =$$

$$\simeq 16 \times 10^{-30} C \cdot m \simeq \underline{4.8 D}$$

Ion-Dipole Interactions



$$w(r) = \frac{Qq}{4\pi\varepsilon\varepsilon_0}\left(-\frac{1}{AB} + \frac{1}{AC}\right)$$

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

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

if $r \gg l$.

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

$$= \frac{Qq}{4\pi\varepsilon\varepsilon_0}\;\frac{-l\cos\theta}{r^2+\frac{l^2}{4}\cos^2\theta} \approx$$

$$\approx \frac{-Qql\cos\theta}{4\pi\varepsilon\varepsilon_0 r^2} = \boxed{\frac{-Q\mu\cos\theta}{4\pi\varepsilon\varepsilon_0 r^2}}$$

Dipole-Dipole Interactions

$$\boxed{\begin{aligned} &w(r, \theta_1, \theta_2, \phi) = \\ &= \frac{-u_1 u_2}{4\pi\varepsilon_0 \varepsilon r^3}\left[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi\right] \end{aligned}}$$

maximum for $\theta_1 = \theta_2 = 0$

$$w(r, 0, 0, \phi) = -\frac{2u_1 u_2}{4\pi\varepsilon_0 \varepsilon r^3}$$

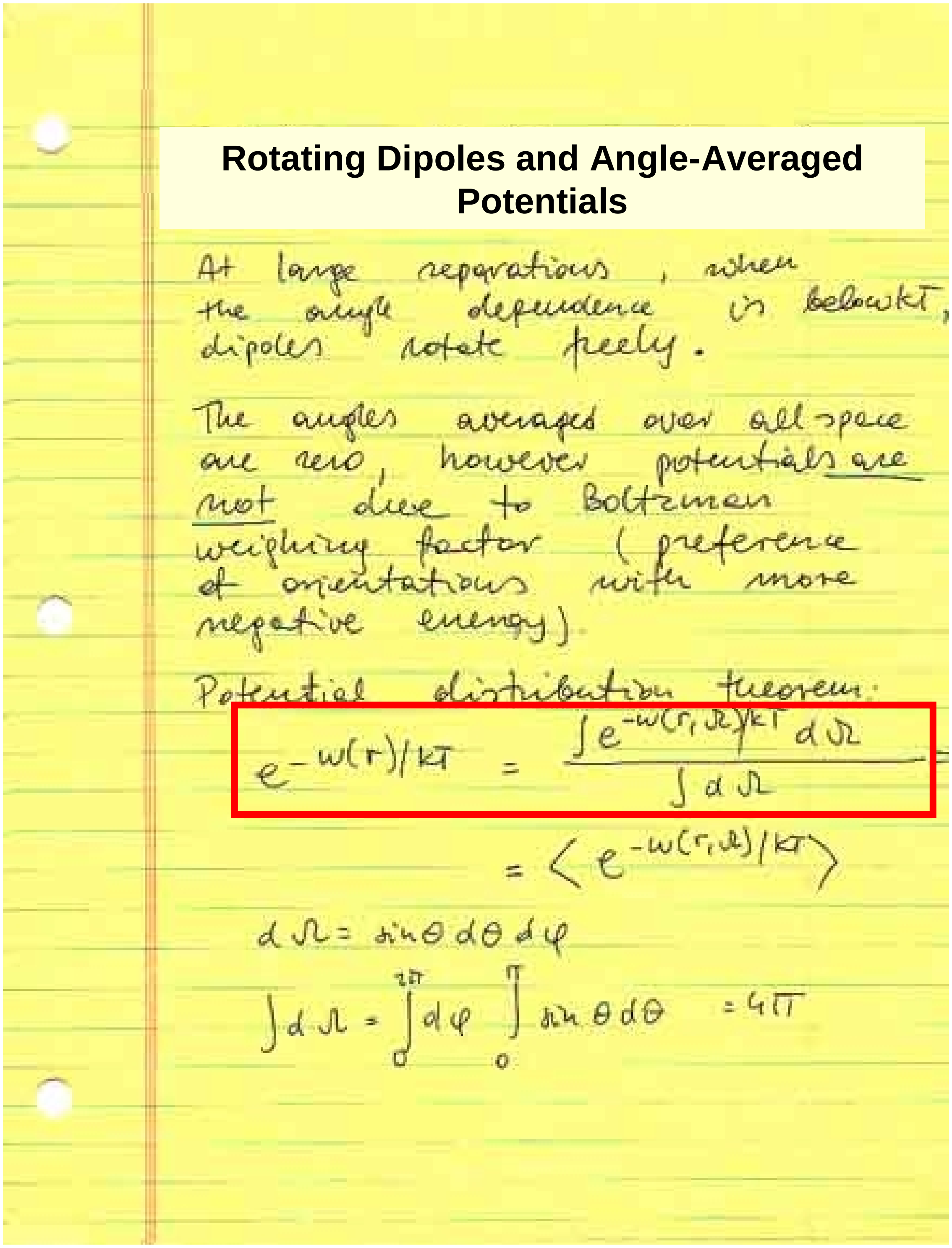
Two equal dipoles of moment 1D

interaction is of the order of kT

at r = 0.36nm when in line

and at r = 0.29 nm when ||

Rotating Dipoles and Angle-Averaged Potentials



At large separations, when the angle dependence is below kT, dipoles rotate freely.

The angles averaged over all space are zero, however potentials are not due to Boltzmann weighting factor (preference of orientations with more negative energy).

Potential distribution theorem:

$$\boxed{e^{-w(r)/kT} = \frac{\int e^{-w(r,\Omega)/kT}\, d\Omega}{\int d\Omega}}$$

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

$$d\Omega = \sin\theta\, d\theta\, d\varphi$$

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

$$e^{-w(r)/kT} = \frac{1}{4\pi}\int_0^{4\pi} d\varphi \int_0^{\pi} e^{-w(r,\theta,\varphi)} \sin\theta \, d\theta$$

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

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

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

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

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

when $w(r,\Omega) < kT$

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

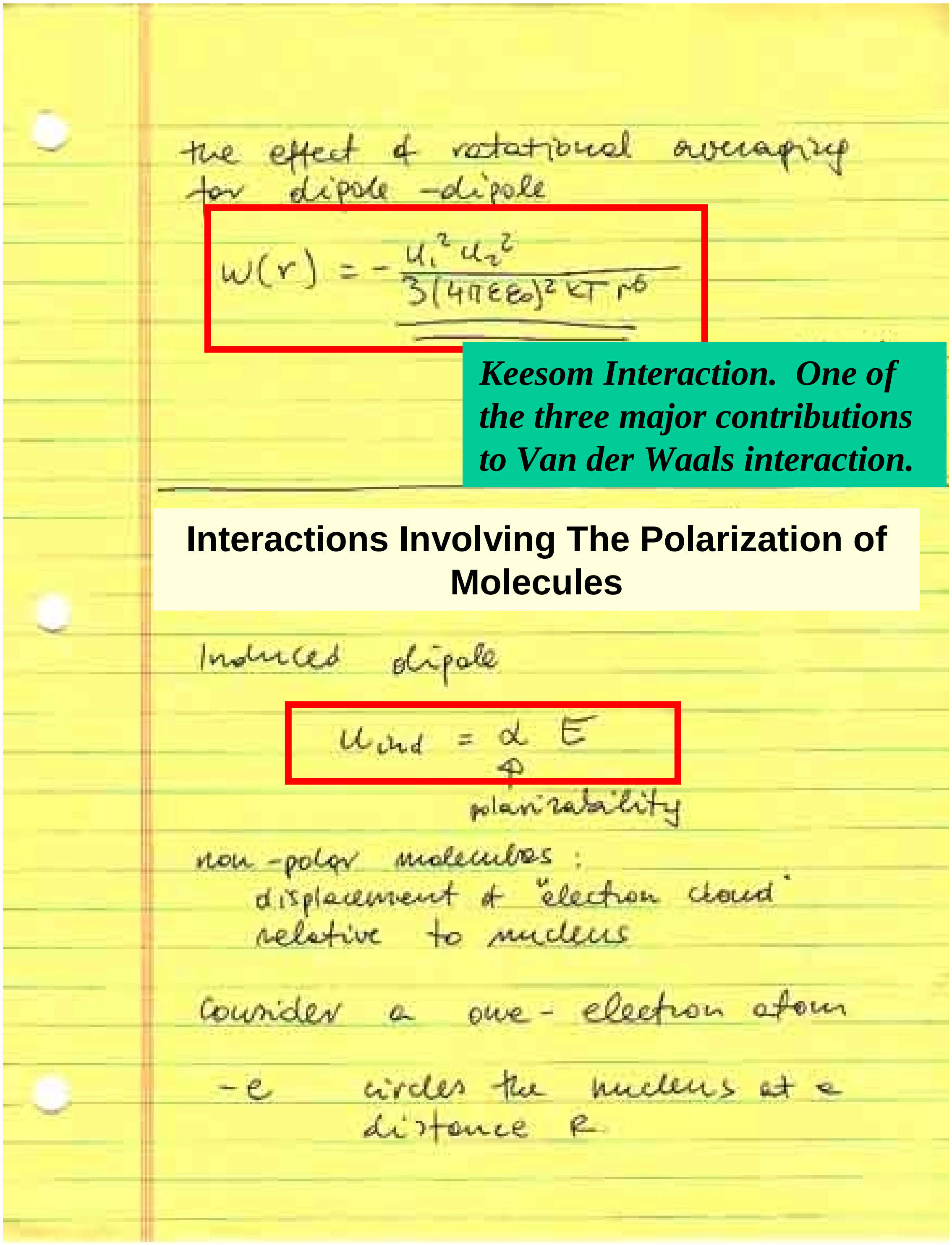
thus

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

for <u>charge -dipole</u>

$$w(r) = \left\langle -\frac{Qu\cos\theta}{4\pi\varepsilon_0\varepsilon r^2} - \left(\frac{Qu}{4\pi\varepsilon_0\varepsilon r^2}\right)^2 \frac{\cos^2\theta}{2kT} + \dots \right\rangle$$

$$\approx \boxed{-\frac{Q^2u^2}{6(4\pi\varepsilon\varepsilon_0)^2 kTr^4}} \quad \text{for } kT > \frac{Qu}{4\pi\varepsilon\varepsilon_0 r^2}$$



the effect of rotational averaging for dipole-dipole

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

Keesom Interaction. One of the three major contributions to Van der Waals interaction.

Interactions Involving The Polarization of Molecules

Induced dipole

$$\boxed{u_{ind} = \underset{\uparrow}{\alpha} \; E}$$

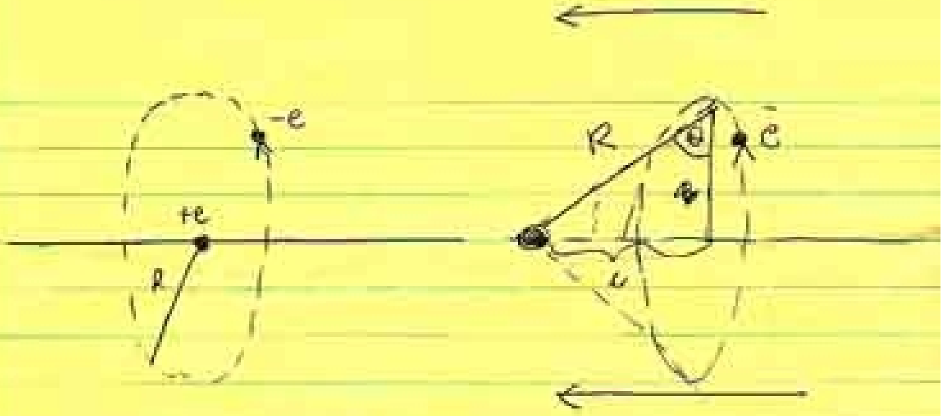
polarizability

non-polar molecules:

displacement of "electron cloud" relative to nucleus

consider a one-electron atom

$-e$ circles the nucleus at a distance R



$$\mu_{ind} = \alpha_0 E = l e$$

$$F_{ext} = E e \qquad \underline{\sin\theta = \frac{l}{R}}$$

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

$$= \frac{e}{4\pi\varepsilon\varepsilon_0 R^3}\,\mu_{ind}.$$

At equilibrium

$$F_{ext} = F_{int}$$

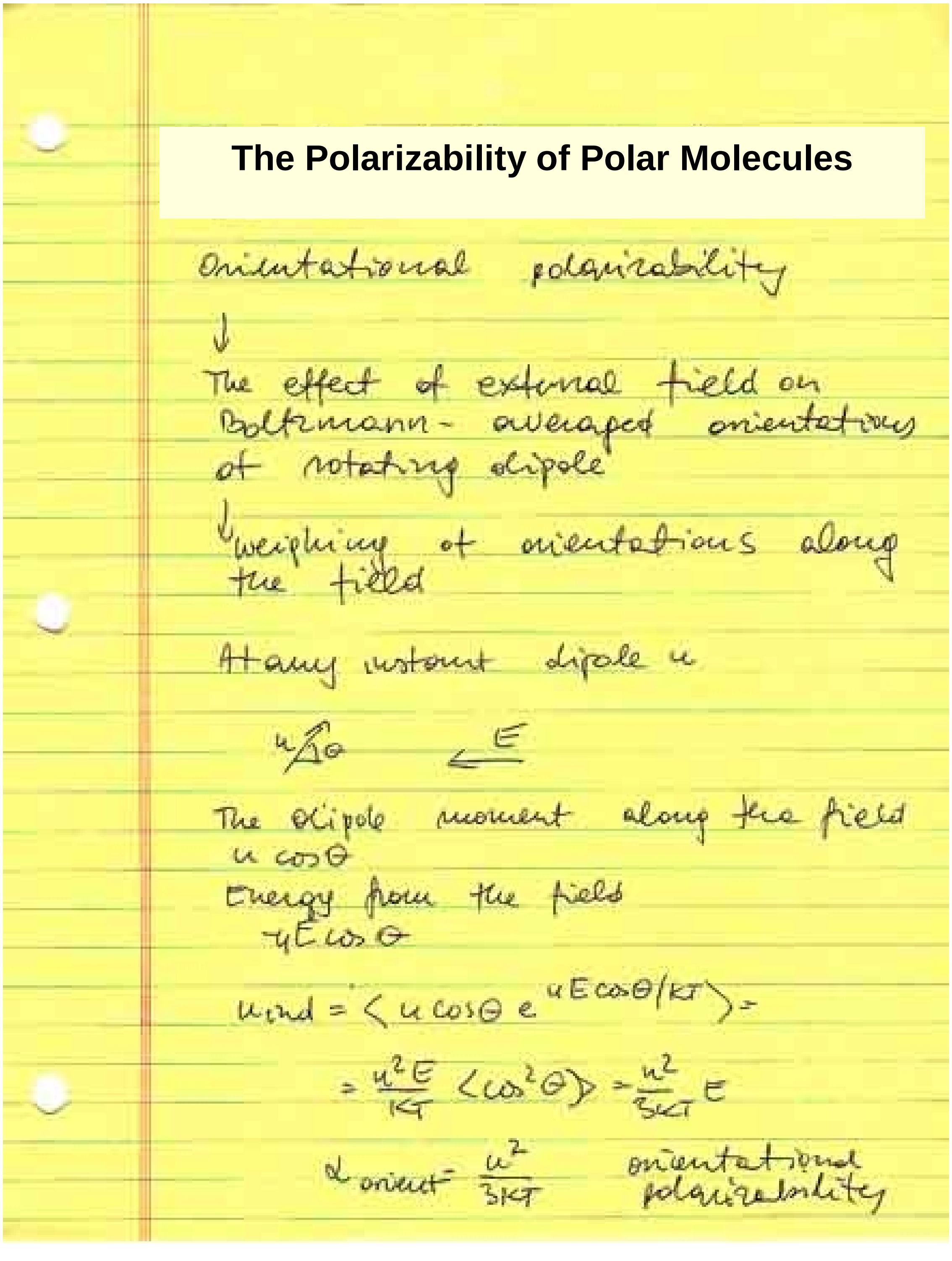
$$E e = \frac{e}{4\pi\varepsilon\varepsilon_0 R^3}\,\mu_{ind}$$

$$\mu_{ind} = \underline{4\pi\varepsilon\varepsilon_0 R^3}\,E = \alpha_0 E$$

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

Polarizability is expressed in terms of $4\Pi\varepsilon_0$

The Polarizability of Polar Molecules



Orientational polarizability

↓

The effect of external field on Boltzmann-averaged orientations of rotating dipole

↓ weighing of orientations along the field

At any instant dipole μ

The dipole moment along the field

$\mu \cos\theta$

Energy from the field

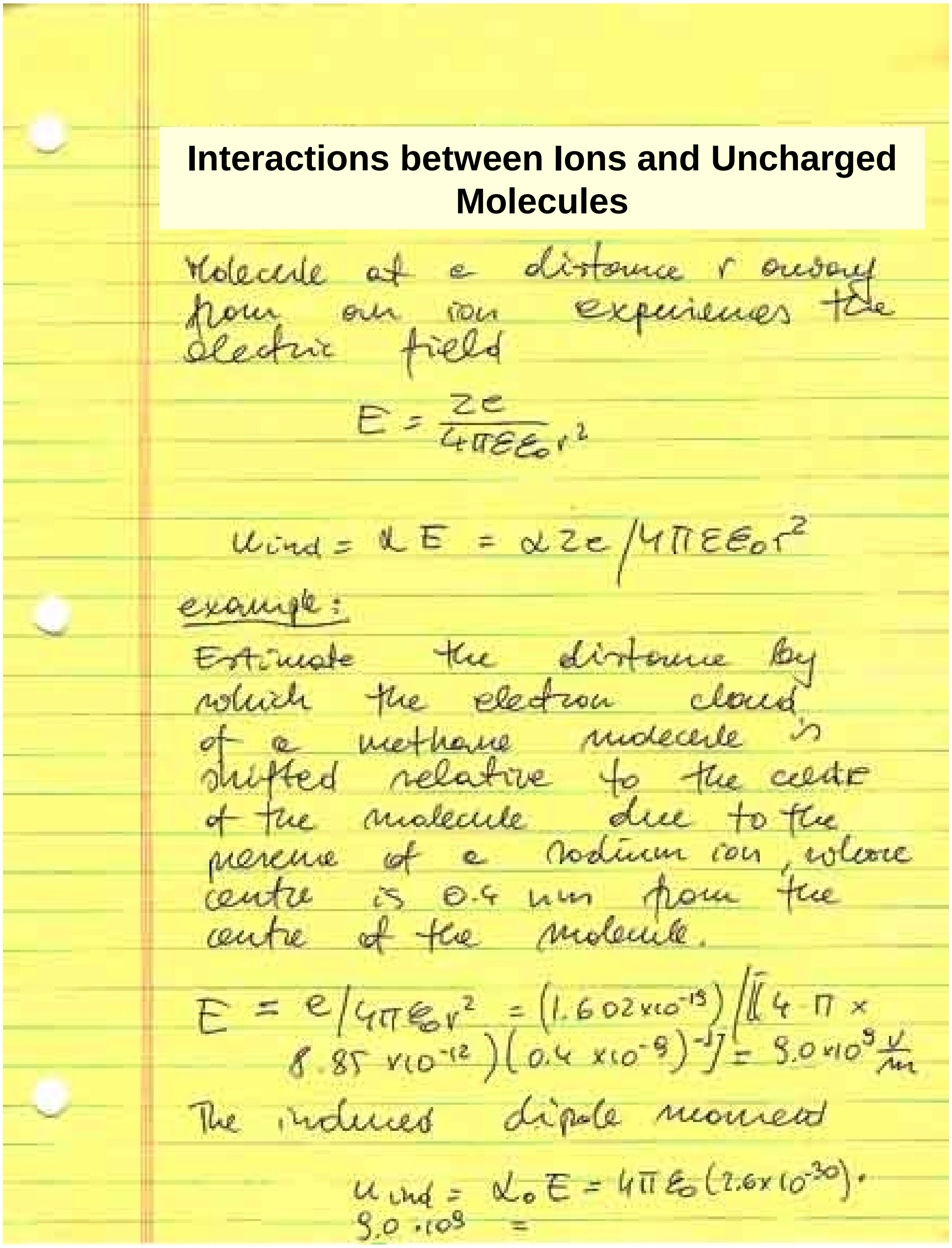
$-\mu E \cos\theta$

$$\mu_{ind} = \langle \mu \cos\theta \, e^{\mu E \cos\theta / kT} \rangle =$$

$$= \frac{\mu^2 E}{kT} \langle \cos^2\theta \rangle = \frac{\mu^2}{3kT} E$$

$$\alpha_{orient} = \frac{\mu^2}{3kT}$$ orientational polarizability

Interactions between Ions and Uncharged Molecules



Molecule at a distance r away from an ion experiences the electric field

$$E = \frac{ze}{4\pi\varepsilon\varepsilon_0 r^2}$$

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

example:

Estimate the distance by which the electron cloud of a methane molecule is shifted relative to the centre of the molecule due to the presence of a sodium ion, whose centre is 0.4 nm from the centre of the molecule.

$$E = e/4\pi\varepsilon_0 r^2 = (1.602\times10^{-19})/[(4\pi\times 8.85\times10^{-12})(0.4\times10^{-9})^{2}] = 9.0\times10^{9}\,\frac{V}{m}$$

The induced dipole moment

$$\mu_{ind} = \alpha_0 E = 4\pi\varepsilon_0(2.6\times10^{-30})\cdot 9.0\times10^{9} =$$

$$E = {}^{ze}\!/_{4\pi\varepsilon\varepsilon_0 r^2}$$

$\mu_{ind} = q \cdot l = \alpha E$

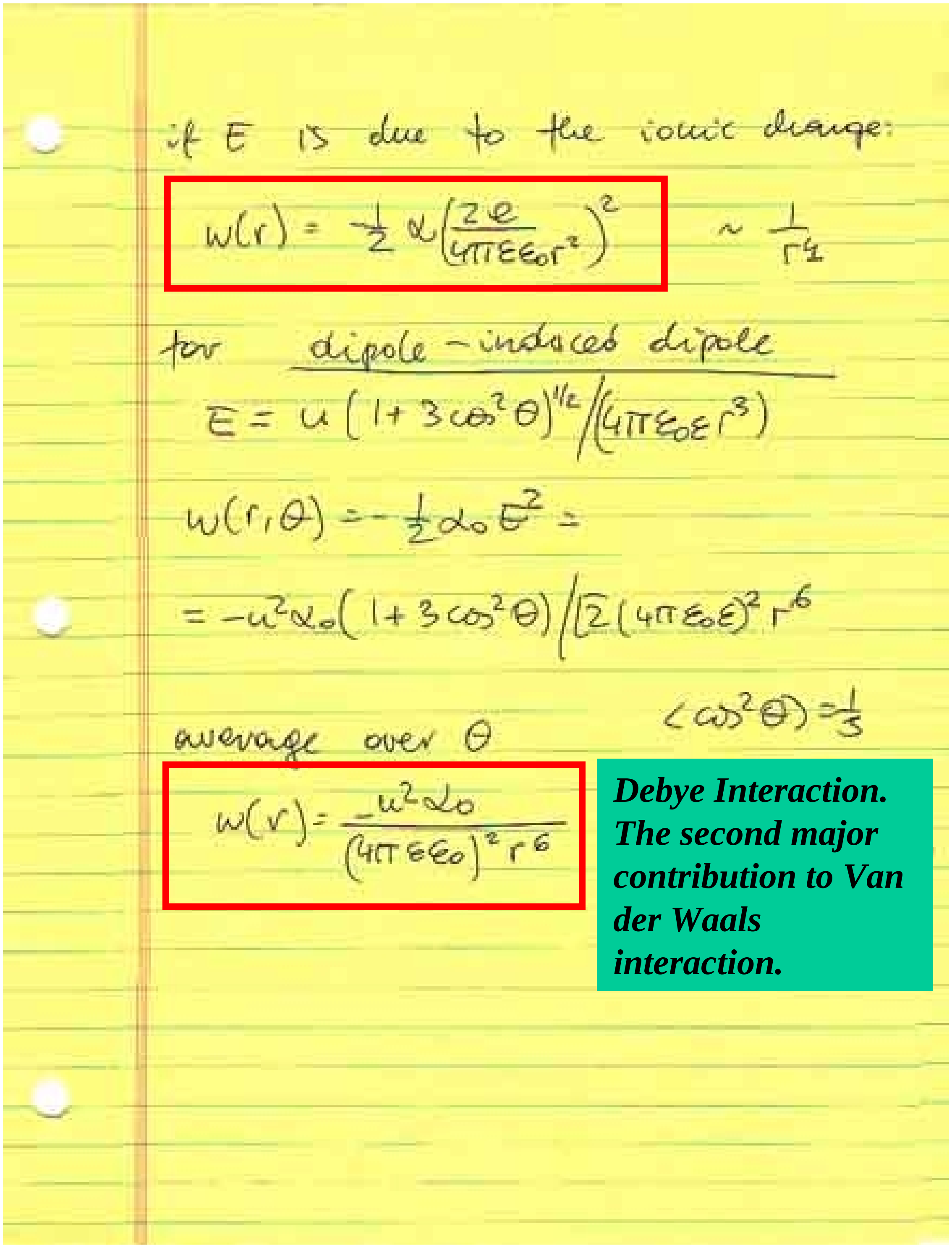
the resulting force on the neutral molec.

$F = q\,\Delta E$ ← difference in E at each end.

$$F = q\,\underbrace{\frac{dE}{dr}\cdot l} = \alpha E\,\frac{dE}{dr}$$

interaction energy

$$w(r) = -\int F\,dr = -\int \alpha E\,dE = \underline{-\frac{1}{2}\alpha E^2}$$



if E is due to the ionic charge:

$$\boxed{w(r) = -\frac{1}{2}\alpha\left(\frac{ze}{4\pi\varepsilon\varepsilon_0 r^2}\right)^2} \sim \frac{1}{r^4}$$

for <u>dipole – induced dipole</u>

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

$$w(r,\theta) = -\frac{1}{2}\alpha_0 E^2 =$$

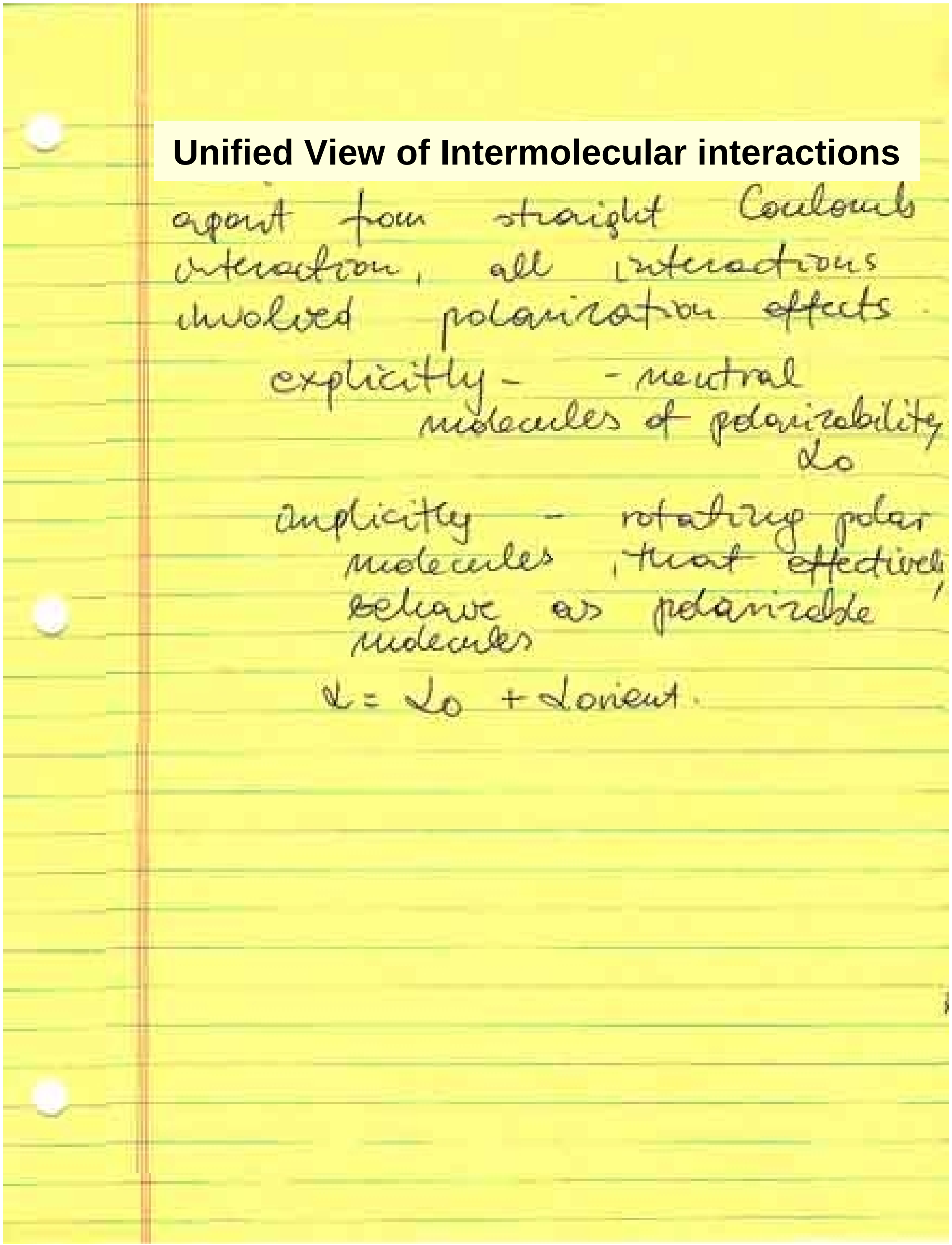
$$= -u^2\alpha_0\left(1+3\cos^2\theta\right)/\left[2\left(4\pi\varepsilon_0\varepsilon\right)^2 r^6\right]$$

average over θ $\quad \langle\cos^2\theta\rangle = \frac{1}{3}$

$$\boxed{w(r) = \frac{-u^2\alpha_0}{\left(4\pi\varepsilon\varepsilon_0\right)^2 r^6}}$$

Debye Interaction. The second major contribution to Van der Waals interaction.

Unified View of Intermolecular interactions



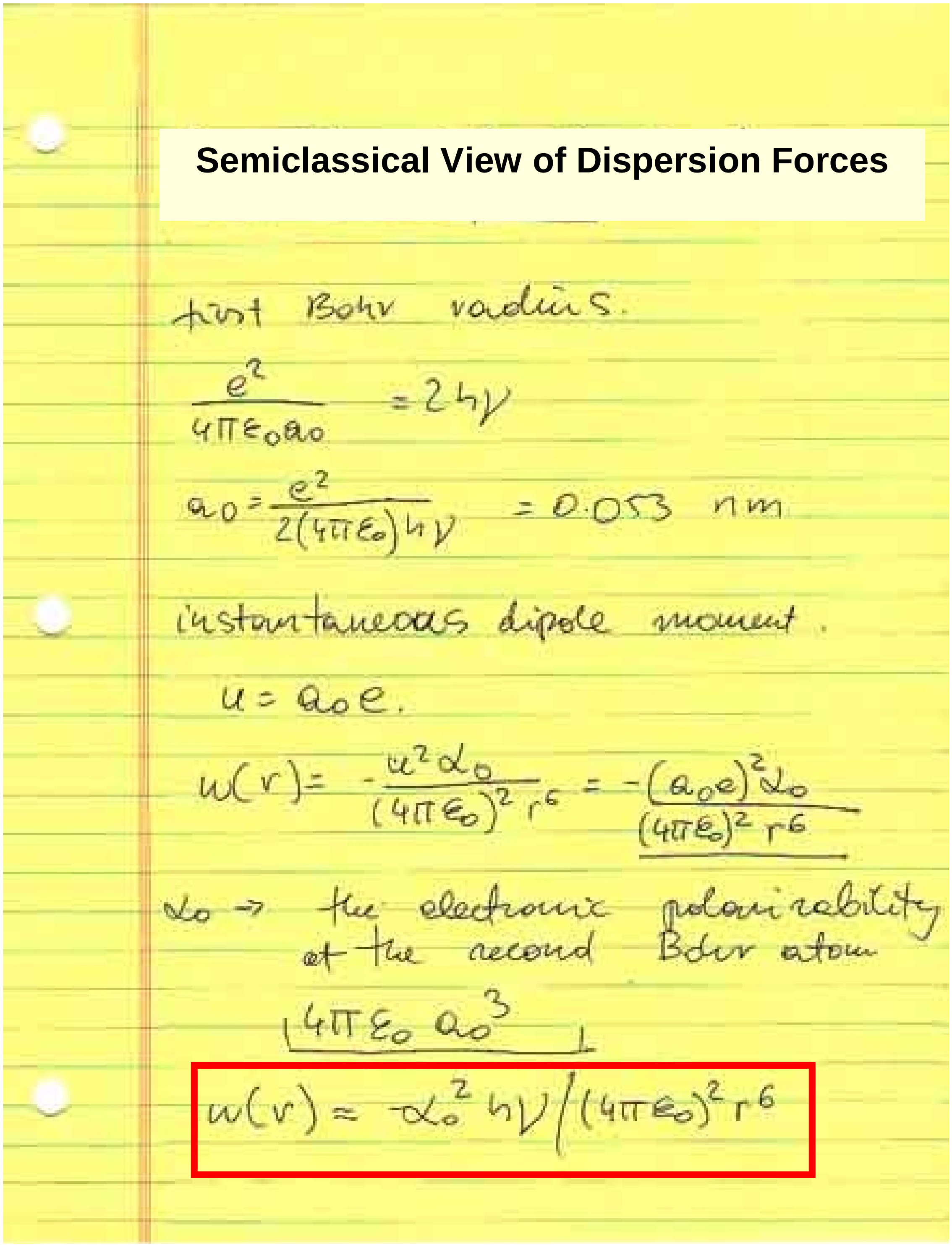
apart from straight Coulomb interaction, all interactions involved polarization effects.

explicitly – – neutral molecules of polarizability α_0

implicitly – rotating polar molecules, that effectively behave as polarizable molecules

$\alpha = \alpha_0 + \alpha_{orient}$.

Semiclassical View of Dispersion Forces



first Bohr radius.

$$\frac{e^2}{4\pi\varepsilon_0 a_0} = 2h\nu$$

$$a_0 = \frac{e^2}{2(4\pi\varepsilon_0)h\nu} = 0.053\ \text{nm}$$

instantaneous dipole moment.

$u = a_0 e.$

$$w(r) = -\frac{u^2\alpha_0}{(4\pi\varepsilon_0)^2 r^6} = \underline{-\frac{(a_0 e)^2\alpha_0}{(4\pi\varepsilon_0)^2 r^6}}$$

α_0 → the electronic polarizability of the second Bohr atom

$$\underline{4\pi\varepsilon_0 a_0^3}$$

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

very good agreement with London's expression for the dispersion interaction energy: just this factor.

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

Strength of the interaction:

two small molecules with

$\alpha_0 / 4\pi\varepsilon_0 \approx 1.5 \times 10^{-30}\ m^3$

$I = h\nu = 2\times 10^{-18}\ J$

if $r = \sigma \approx 0.3\ nm$

$w(\sigma) = -4.6 \times 10^{-21}\ J$

of the order of kT