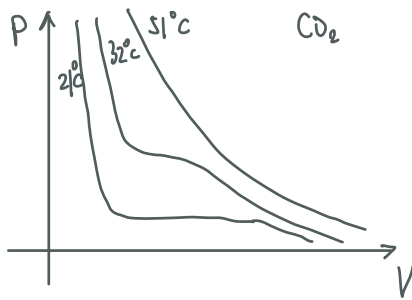


Van der Waals interactions between molecules

Strong bonds: ionic bond, covalent bond, metallic bond, hydrogen bond. & vdW forces

VdW: Distance-dependent interactions between molecules or atoms.

- Liquefaction of gas (Andrew 1869)



The existence of critical temperature and critical pressure for the phase change

- VDW equation of state (1873, Nobel prize 1910)

$$pV = nRT \quad (\text{ideal gas law})$$

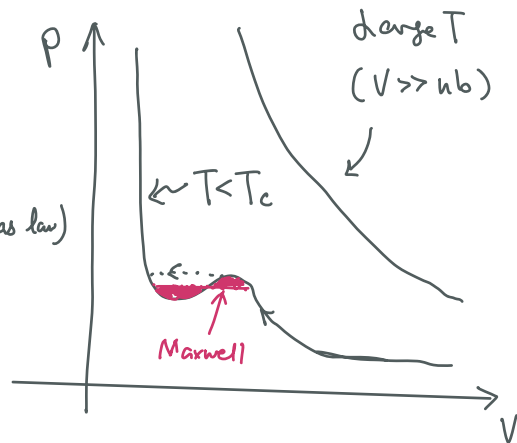
↓

$$\left(p + \frac{n^2 a}{V}\right) (V - nb) = nRT \quad (\text{Real gas law})$$

$$n = N/n_A \quad \text{number of moles}$$

b - volume of a mole of particles

a - a measure of average attraction between particles

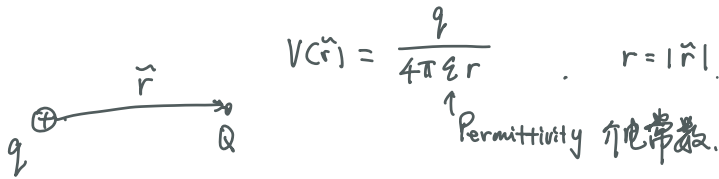


Keesom Theory (1921): Forces between permanent dipoles 永久偶极子.

(2)

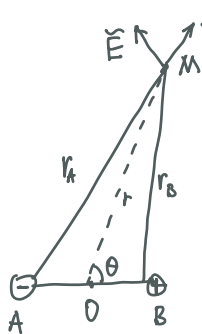


• Potential of a charge



• Potential of a dipole

Dipole: A combination of two opposite electric charges $+q$ & $-q$ set apart by a small l . $\vec{\mu} = ql$ is dipolar moment. ($l \sim 0.1 \text{ nm}$)



$$V = \frac{q}{4\pi\epsilon_0} \left(\frac{1}{r_A} + \frac{1}{r_B} \right)$$

$$r_{A,B} = \left(\frac{l^2}{2} + r^2 \pm l r \cos\theta \right)^{1/2}$$

$$= r \left(1 \pm \frac{l}{r} \cos\theta + \frac{l^2}{2r^2} \right)^{1/2}$$

$$\approx r \left[1 \pm \frac{l}{2r} \cos\theta + O\left(\frac{l}{r}\right)^2 \right]$$

$$V \approx \frac{q}{4\pi\epsilon_0 r} \left(\frac{1}{1 - \frac{l}{2r} \cos\theta} - \frac{1}{1 + \frac{l}{2r} \cos\theta} \right) = \frac{q l}{4\pi\epsilon_0 r^2} \cos\theta$$

The field \vec{E} at point M caused by dipole AB of μ :

③

$$E_r = -\frac{\partial V}{\partial r} = \frac{\mu}{2\pi\epsilon_0 r^3} \cos\theta$$

$$E_\theta = -\frac{1}{r} \frac{\partial V}{\partial \theta} = \frac{\mu}{4\pi\epsilon_0 r^3} \sin\theta$$

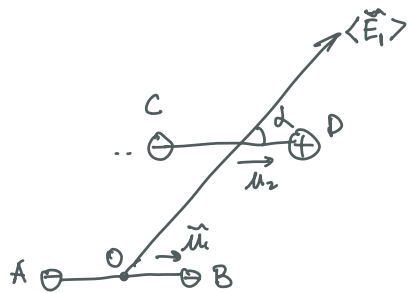
$$E = |\vec{E}| = \sqrt{E_r^2 + E_\theta^2} = \frac{\mu}{4\pi\epsilon_0 r^3} \sqrt{1 + 3\cos^2\theta}$$

If the dipole is free to rotate, with equal probability, there is a mean field **ALONG \vec{OM}** :

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

$$\Rightarrow \langle E \rangle = \frac{\sqrt{3}\mu}{4\pi\epsilon_0 r^3} \quad \star^0$$

• Dipole in an electric field.



Potential energy $U = -\vec{\mu}_2 \cdot \langle \vec{E}_1 \rangle = -\mu_2 \langle E_1 \rangle \cos\alpha$

Dipole-Dipole interaction $U \sim \frac{\mu_1 \mu_2}{\epsilon_0 r^3}$

$\mu \sim 1.6 \times 10^{-19} \text{ C} \times 0.1 \text{ nm}$, $\epsilon_0 \sim 8.854 \times 10^{-12} \text{ C}^2/(\text{Vm})$, $k \sim 1.38 \times 10^{-23} \text{ J/K}$, $T \sim 300 \text{ K}$

$$\frac{U}{kT} \sim \left(\frac{0.36 \text{ nm}}{r} \right)^3 \ll 1 \quad \text{as } r \gtrsim 1 \text{ nm}$$

With thermal energy, both dipoles can rotate "freely" $\rightarrow \langle \cos\alpha \rangle = 0$?

Angle-averaged potential is not ZERO cause there is always Boltzmann Weighting factor that gives weight to orientations that have a lower energy.



$$P(\alpha) \propto \exp[-U(\alpha)/kT] = Ae^{z \cos \alpha}, \quad z = \frac{\mu_0 \langle E_1 \rangle}{kT} \ll 1$$

$$\text{so that } \int Ae^{z \cos \alpha} d\Omega = 1, \quad d\Omega = d\theta \sin \theta d\alpha = 2\pi \int_{-1}^1 d(\cos \alpha)$$

$$\langle U \rangle = - \int d\Omega P(\alpha) \mu_0 \langle E_1 \rangle \cos \alpha$$

$$= -\mu_0 \langle E_1 \rangle \frac{2\pi \int_0^\pi e^{z \cos \alpha} \cos \alpha d(\cos \alpha)}{2\pi \int_0^\pi e^{z \cos \alpha} d(\cos \alpha)} \quad \leftarrow \text{K 1/A}$$

$$\text{Let } x = \cos \alpha, \text{ Let } I = \int_{-1}^1 e^{zx} dx = \frac{2 \sinh z}{z}$$

$$= -\mu_0 \langle E_1 \rangle \frac{\int_{-1}^1 x e^{zx} dx}{\int_{-1}^1 e^{zx} dx} = \mu_0 \langle E_1 \rangle \frac{1}{I} \frac{dI}{dz}$$

Mathematics.

$$= -\mu_0 \langle E_1 \rangle \left(\text{coth } z - \frac{1}{z} \right) \quad \leftarrow \text{Langevin's function}$$

↙ Hyperbolic cotangent 双曲余切

$$\text{coth } z = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2z^5}{945} + O(z^7) \quad (\text{Note } z \ll 1)$$

$$\Rightarrow \langle U \rangle = -\frac{1}{3} \mu_0 \langle E_1 \rangle z = -\frac{1}{3} \frac{\mu_0^2 \langle E_1 \rangle^2}{kT} = -\frac{1}{(4\pi \epsilon_0)^2} \frac{2\mu_0^2 \mu_p^2}{3kT} \frac{1}{r^6}$$

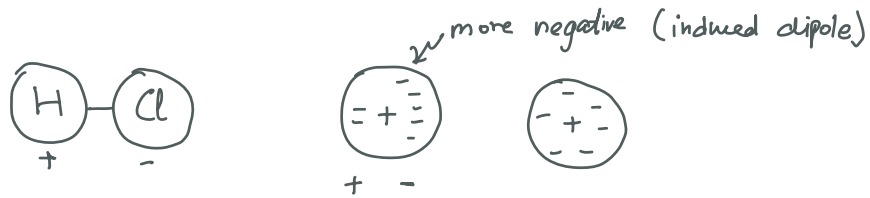
Correction is needed to describe the influence of $\vec{\mu}_2$ on the orientation probability of dipole 1 ("slightly" longer)

(5)

Keesom's theory gives a force law r^{-7} , of the proper order of magnitude.

However, numerical values from $\mu_1\mu_2$ and variation with T do NOT agree with experiments (vdW is almost T -independent).

The Debye Theory (1920): Dipole-induced dipole interaction



In an electric field E , a molecule takes an induced dipolar moment

$$\mu_{in} = \alpha_0 E$$

by deformation of electronic cloud, $\alpha_0 \propto V \times 4\pi \epsilon_0$

$$U \approx -\alpha_{02} \langle E_1 \rangle \times \langle E_1 \rangle - \alpha_{01} \langle E_2 \rangle \times \langle E_2 \rangle$$

$$= -\frac{1}{(4\pi\epsilon_0)^2} \frac{\alpha_{02}\mu_1^2 + \alpha_{01}\mu_2^2}{r^6}$$

However, such induced forces are too weak!

The London Theory (1930): dispersion force. Instantaneous dipole

- induced dipole interaction.

⑥



Attraction forces come from the coupling of oscillations of two neighbouring molecules vibrating in resonance, explaining the cohesion of liquid or solid rare gases whose atoms are spherical with no permanent dipolar moment.

$$U = -\frac{1}{(4\pi\epsilon_0)^2} \frac{3\alpha^2 h\nu_0}{4} \frac{1}{r^6} \quad \text{for two molecules}$$

Labels: α - Polarizability, $h\nu_0$ - Planck constant ν_0 - electronic absorption frequency

Molar weight	Molecules	Boiling point	Electrons.
38	F ₂ (g)	-188°C	9e ⁻
70.9	Cl ₂ (g)	-34°C	17e ⁻
159.8	Br ₂ (l)	59°C	35e ⁻
253.8	I ₂ (s)	114°C	53e ⁻

Eg. CH₄ (16) vs. CH₃CH₂CH₂CH₃ (C₄H₁₀, 58) ?

$$U = -\frac{1}{(4\pi\epsilon_0)^2} \frac{3\alpha_A\alpha_B h\nu_A\nu_B}{2(\nu_A+\nu_B)} \frac{1}{r^6} \quad \text{for two dissimilar molecules}$$

London constant. $\sim 10^{-79} \text{ Jm}^6$



$$\Delta U = U_1 - U_2 \propto \frac{\alpha_B^2 U_B^2}{V_A + V_B} \left[\left(\frac{\alpha_A V_A}{\alpha_B V_B} - 1 \right)^2 + \frac{V_A}{V_B} \left(\frac{\alpha_A}{\alpha_B} - 1 \right)^2 \right] > 0$$

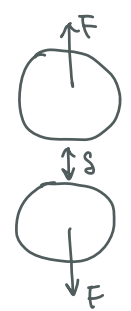
In a mixture, attraction between similar molecules is energetically more favourable than between dissimilar molecules.

Non-retarded, additive: $U(r) = -\frac{C}{r^6}$

	Debye	Keesom	Dispersion/London	Disp. Contribution
Ne-He	0	0	4	100%
HCL-HCL	6	11	106	86%
HI-HI	2	0.2	370	99%
{ NH ₃ -NH ₃	10	38	63	56%
	H ₂ O-H ₂ O	10	96	33

Dispersion forces prevail over orientation/induction forces, except for VERY polarized molecules.

- Retarded vdW forces (macroscopic theory by Dzyaloshinski, Lifshitz & Pitaevskii 1961)



A correction of $\frac{1}{r^6}$ to account for the time effect on the interaction over long distances

$$U = \begin{cases} -\frac{C}{r^6} & r < 50 \text{ nm} \\ -\frac{C_{12}}{r^7} & r > 500 \text{ nm} \end{cases}$$

Lennard - Jones Potential.

Quantum mechanics leads to an energy of repulsion related to $\exp(r_0/r)$

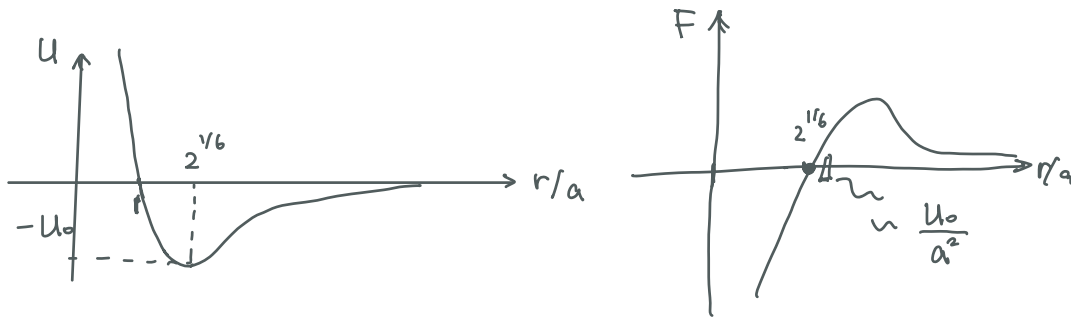
as r goes to 0. For mathematical convenience, it is written as $1/r^n$

with $n > 10$.

$$U = \frac{D}{r^{12}} - \frac{C}{r^6}$$

Born repulsion (empirical)

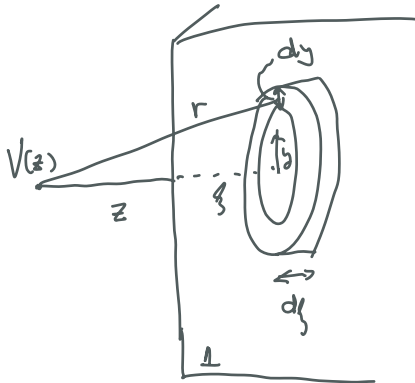
$$= 4U_0 \left[\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r}\right)^6 \right]$$



Van der Waals Interaction Between Solids

VdW attraction between two surfaces

Assuming that vdw forces are additive (non-retarded). de Boer (1936) Hamaker (1937)



$$w(r) = -\frac{C_{12}}{r^6} \text{ for m-m interaction}$$

Interaction between a molecule and solid 1

$$V_1(z) = \int_V w(r) \left(\frac{\text{Atoms}}{\text{Volume}} \right) dV$$

$$r^2 = (z+y)^2 + y^2$$

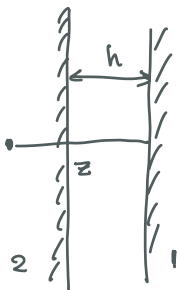
$$\left(\frac{\text{Atoms}}{\text{Vol}} \right) = n_1 = \frac{\rho_1 N_A}{M W_1}$$

$$= \int_0^\infty \int_0^\infty -\frac{2\pi n_1 C_{12} y dy dz}{[(z+y)^2 + y^2]^3}$$

$$dV = 2\pi y dy dz$$

$$= \int_0^\infty \frac{1}{2} \pi n_1 C_{12} \frac{1}{[(z+y)^2 + y^2]^2} \Big|_0^\infty dz$$

$$= -\frac{1}{6} \pi n_1 C_{12} \frac{1}{(z+y)^3} \Big|_0^\infty = -\frac{\pi n_1 C_{12}}{6z^3}$$



$$V_{12} = \int_h^\infty -\frac{\pi n_1 C_{12}}{6z^3} n_2 dz = +\frac{\pi n_1 n_2 C_{12}}{12z^2} \Big|_0^\infty = -\frac{\pi n_1 n_2 C_{12}}{12h^2}$$

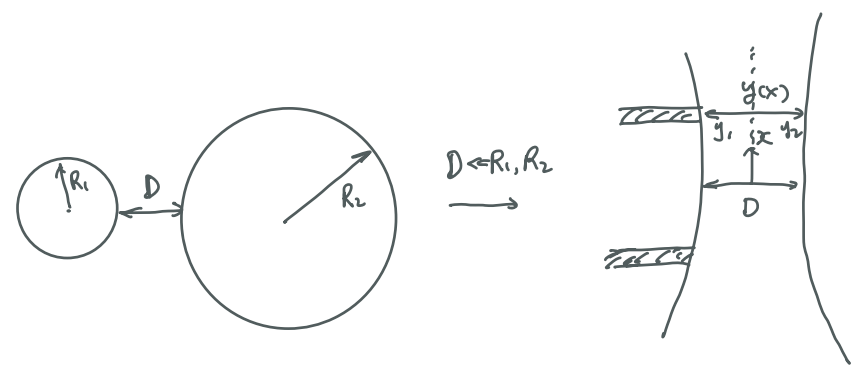
Interaction energy / unit area $V = -\frac{A_{12}}{12\pi h^2}$ Hamaker constant

Interaction force / unit area: $F = - \frac{dV}{dh} = - \frac{A_{12}}{6\pi h^3}$

$A_{12} = \pi^2 n_1 n_2 C_{12} = \frac{\pi^2 N_0^2 \rho_1 \rho_2 C_{12}}{(Mw_1)(Mw_2)} \sim O(10^{-19} - 10^{-20} J)$

$h \sim 0.3 \text{ nm} \rightarrow V \sim -30 \text{ mJ/m}^2, F \sim 100 \text{ MPa}$

VdW attraction between two spheres (Derjaguin approximation)



$F(D) = \int_D^\infty f(y) 2\pi x dx = \int_0^\infty \frac{A_{12}}{6\pi y^3} 2\pi x dx$ (Attractive force)

Force/area between two surfaces

$\star \begin{cases} y_1 = \frac{D}{2} + \frac{1}{2R_1} x^2 \\ y_2 = \frac{D}{2} + \frac{1}{2R_2} x^2 \end{cases} \leftarrow \nabla^2 y = k = \frac{1}{R}$

Or $\left[y_1 - \left(\frac{D}{2} + R_1 \right) \right]^2 + x^2 = R_1^2 \Rightarrow y_1 = -\sqrt{R_1^2 - x^2} + \frac{D}{2} + R_1$

$R_1 \sqrt{1 - \frac{x^2}{R_1^2}} = R_1 \left(1 - \frac{1}{2} \frac{x^2}{R_1^2} \right)$

$= \frac{D}{2} + \frac{1}{2} \frac{x^2}{R_1}$

- Accurate for $x \ll R_1, R_2$
- Breakdown when $x \sim R_1, R_2$. An correction expected scaling as $F_c \sim \frac{A}{R^3} x R^2 = \frac{A}{R}$

(11)

$$\Rightarrow y(x) = D + \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) x^2 \rightarrow dy = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) x dx$$

$$\text{Therefore, } F(D) = \int_0^\infty \frac{A_{12}}{6\pi y^3} 2\pi \frac{R_1 R_2}{R_1 + R_2} dy = \left(\frac{R_1 R_2}{R_1 + R_2} \right) \frac{A_{12}}{6D^2}$$

$$\rightarrow W(D) = - \left(\frac{R_1 R_2}{R_1 + R_2} \right) \frac{A_{12}}{6D}$$

$$\text{Note that } \Delta F_{\text{Total}} = F(D) + F_c = \bar{R} \frac{A_{12}}{6D^2} + \frac{A_{12}}{\bar{R}} = \bar{R} \frac{A_{12}}{6D^2} \left[1 + O\left(\frac{D^2}{\bar{R}^2}\right) \right]$$

↑
Far from D

$$\textcircled{2} F_{\text{sphere-wall}} = \frac{R A_{12}}{6D^2}, \quad W_{\text{sphere-wall}} = - \frac{A_{12} R}{6D}$$

Retarded interaction between two surfaces

$$W_{\text{min}}(r) = \begin{cases} -\frac{c}{r^6} & \text{small } r \\ -\frac{c'}{r^7} & \text{large } r \end{cases}$$

$$F(h) = \begin{cases} \frac{A_{132}}{6\pi d^3} & \text{small } r \\ \frac{B_{132}}{d^4} & \text{large } r \end{cases} \quad \text{1 and 2 cross 3}$$

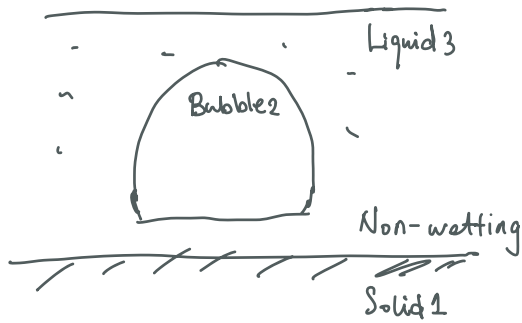
Lifshitz (1956) ($\beta = \text{Vacuum}$), Dzyaloshinski, Lifshitz, Pitaevski (1961) ($\beta \text{ Any medium}$)

$$A_{132} = \frac{3\hbar \bar{\omega}}{4\pi}, \quad \bar{\omega} = \int_0^\infty \left[\frac{\epsilon_1(i\xi) - \epsilon_3(i\xi)}{\epsilon_1(i\xi) + \epsilon_3(i\xi)} \right] \left[\frac{\epsilon_2(i\xi) - \epsilon_3(i\xi)}{\epsilon_2(i\xi) + \epsilon_3(i\xi)} \right] d\xi$$

↑
Dielectric permittivity

$$B_{132} = \frac{\pi^2 \hbar c}{240} \frac{1}{\sqrt{\epsilon_{30}}} \left(\frac{\epsilon_{10} - \epsilon_{20}}{\epsilon_{10} - \epsilon_{30}} \right) \left(\frac{\epsilon_{20} - \epsilon_{30}}{\epsilon_{20} + \epsilon_{30}} \right) \varphi(\epsilon_{10}, \epsilon_{20}, \epsilon_{30})$$

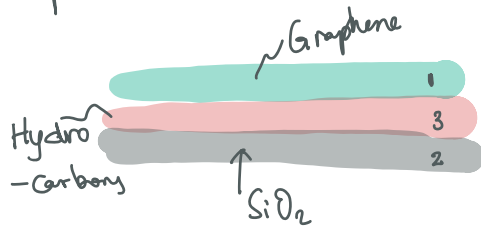
Example 1:



$A_{132} > 0$. Liquid does not wet .

$A_{132} < 0$, Liquid completely wets .

Example 2:



$A_{132} > 0$ Attractive force between 1 & 2
(Fluid 3 squeezed out)

$A_{132} < 0$ Repulsive force between 1 & 2
(Fluid 3 wets) .

Retarded interaction between a sphere and a wall

$$F(D) \propto \begin{cases} \frac{R}{D^2} & \text{(Non-retarded, small } D \text{)} \\ \frac{R}{D^3} & \text{(Retarded, large } D \text{)} . \end{cases}$$