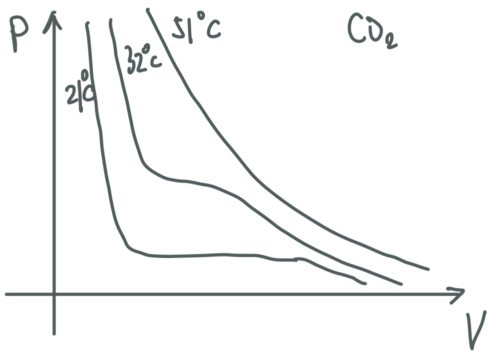
# Van der Waals interactions between molecules

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)

$PV = nRT$ (ideal gas law)

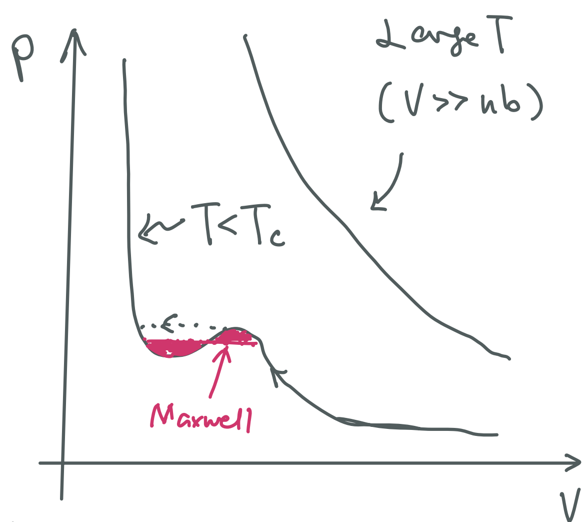
$\downarrow$

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

$n = N/N_A$ number of moles

b - volume of a mole of particles

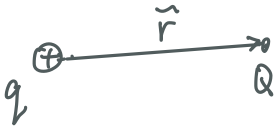
a - a measure of average attraction between particles



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

H – Cl          Na – Cl
+     −              +      −

### • Potential of a charge



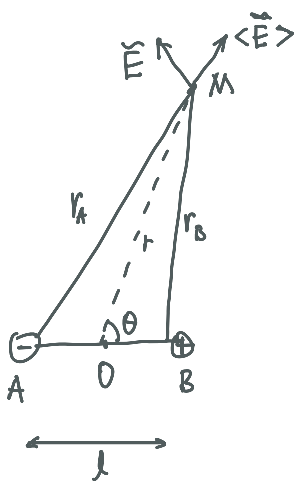

$$V(\tilde{r}) = \frac{q}{4\pi\varepsilon r}\,. \qquad r = |\tilde{r}|.$$

↑ Permittivity 介电常数.

→ Electrical field $\tilde{E} = \tilde{\nabla} V$

### • Potential of a dipole

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




$$V = \frac{q}{4\pi\varepsilon_0}\left(-\frac{1}{r_A} + \frac{1}{r_B}\right)$$

$$r_{A,B} = \left(\frac{l^2}{4} + r^2 \pm l \times r\cos\theta\right)^{1/2}$$

$$= r\left(1 \pm \frac{l}{r}\cos\theta + \frac{l^2}{4r^2}\right)^{1/2}$$

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

$$\rightarrow V \simeq \frac{q}{4\pi\varepsilon_0 r}\left(\frac{1}{1-\frac{l}{2r}\cos\theta} - \frac{1}{1+\frac{l}{2r}\cos\theta}\right) = \frac{\overbrace{ql}^{\mu}}{4\pi\varepsilon_0 r^2}\cos\theta \qquad \text{when } l \gg r$$

The field $\tilde{E}$ at point M caused by dipole AB of $\mu$ is given by $\tilde{\nabla} V$

$$\rightarrow E_r = -\frac{\partial V}{\partial r} = \frac{\mu}{2\pi\varepsilon_0 r^3}\cos\theta\,, \qquad E_\theta = -\frac{1}{r}\frac{\partial V}{\partial\theta} = \frac{\mu}{4\pi\varepsilon_0 r^3}\sin\theta$$

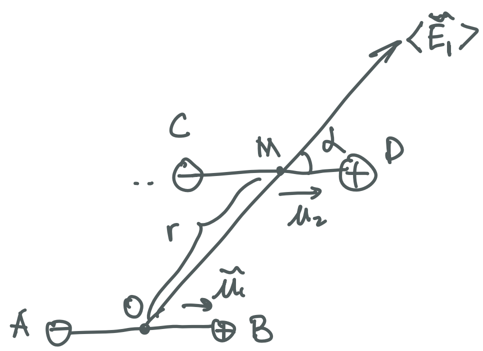
$$E = |\tilde{E}| = \sqrt{E_r^2 + E_\theta^2} = \frac{\mu}{4\pi\varepsilon_0 r^3}\sqrt{1+3\cos^2\theta}$$

If the dipole is free to rotate, with equal probability, there is a mean field

ALONG $\overrightarrow{OM}$:

$$\langle f \rangle = \frac{\int_0^{2\pi} d\phi \int_0^{\pi} f(\theta) \sin\theta \, d\theta}{\underbrace{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta}_{=4\pi}} \Rightarrow \langle E \rangle = \frac{\sqrt{2}\mu}{4\pi\varepsilon_0 r^3}$$

- Dipole in an electric field.




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

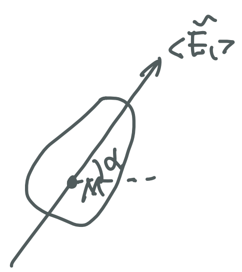
Therefore, Dipole-Dipole interaction $U \sim \frac{\mu_1 \mu_2}{\varepsilon_0 r^3}$

$\mu \sim 1.6 \times 10^{-19} C \times 0.1 \text{ nm}$, $\varepsilon_0 \sim 8.854 \times 10^{-12} C^2/(Jm)$, $k \sim 1.38 \times 10^{-23} J/K$, $T \sim 300K$

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

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.




$$P(\alpha) \propto \exp\left[-U(\alpha)/kT\right] = Ae^{z\cos\alpha}, \quad z = \frac{\mu_2 \langle E_1 \rangle}{kT} \ll 1$$

The prefactor A is so that:

$$\int Ae^{z\cos\alpha} d\Omega = 1, \text{ where } d\Omega = d\theta \sin\alpha \, d\alpha = 2\pi \int_{\pi}^{0} d(\cos\alpha)$$

$$\langle U\rangle = -\int d\Omega \, p(\alpha)\, \mu_2 \langle E_1\rangle \cos\alpha$$

$$= -\mu_2\langle E_1\rangle \frac{\cancel{2\pi}\int_0^{\pi} e^{z\cos\alpha}\cos\alpha \, d(\cos\alpha)}{\underbrace{\cancel{2\pi}\int_0^{\pi} e^{z\cos\alpha}\, d(\cos\alpha)}_{=1/A}}$$

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

$$= -\mu_2\langle E_1\rangle \frac{\int_{-1}^{1} x e^{zx} dx}{\int_{-1}^{1} e^{zx} dx} = -\mu_2\langle E_1\rangle \frac{1}{I}\frac{dI}{dz}$$

Hyperbolic cotangent 双曲余切

$$= -\mu_2\langle E_1\rangle \underbrace{\left(\coth z - \frac{1}{z}\right)}$$

← Langevin's function

Note that $\coth = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2z^5}{945} + O(z^7)$ when $|z| \ll 1$, we then have

$$\Rightarrow \boxed{\langle U\rangle = -\frac{1}{3}\mu_2\langle E_1\rangle z = -\frac{1}{3}\frac{\mu_2^2\langle E_1\rangle^2}{kT} = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{2\mu_1^2\mu_2^2}{3kT}\frac{1}{r^6}}$$

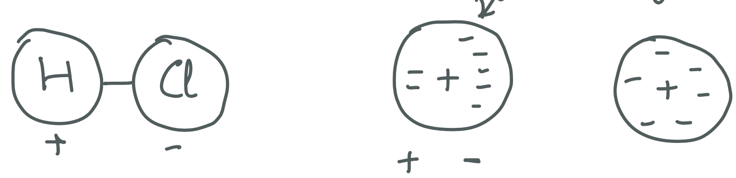
Correction is needed to describe the influence of $\vec{\mu}_2$ on the orientation probability of dipole 1 ("sligtly" longer)

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 <u>NOT</u> agree with experiments!?

(vdW is almost $T$-independent)

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

more negative (induced dipole)



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

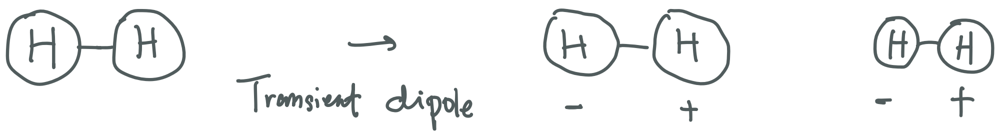
$$\mu_{in} = \alpha_0 E$$

by deformation of electronic cloud, where $\alpha_0 \propto V \times 4\pi\varepsilon_0$

$$U \propto -\alpha_{02}\langle E_1\rangle \times \langle E_1\rangle - \alpha_{01}\langle E_2\rangle \times \langle E_2\rangle = -\frac{1}{(4\pi\varepsilon_0)^2}\frac{\alpha_{02}\mu_1^2 + \alpha_{01}\mu_2^2}{r^6}$$

However, such induced forces are too weak!

• The London Theory (1930): dispersion force. Instanteous dipole – induced dipole interation.




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

Polarizability

Planck constant $\nu_0$ – electronic absorption frequency

• $U = \frac{-1}{(4\pi\varepsilon_0)^2}\frac{3\alpha^2 \hbar \nu_0}{4}\frac{1}{r^6}$ for two molecules

| 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. $CH_4$ (16) vs. $CH_3CH_2CH_2CH_3$ ($C_3H_{10}$, 58)?

- $$U = -\underbrace{\frac{1}{(4\pi\varepsilon_0)^2}\frac{3\alpha_A\alpha_B h\nu_A\nu_B}{2(\nu_A+\nu_B)}}_{\text{London constant. } \sim 10^{-79}\ \mathrm{J\,m^6}}\frac{1}{r^6}$$ for two dissimilar molecules

A A B B → A–A + B–B   $U_1 \propto \frac{3}{4}\alpha_A^2\nu_A + \frac{3}{4}\alpha_B^2\nu_A$

→ A–B + A–B   $U_2 \propto 3\alpha_A\alpha_B\nu_A\nu_B/(\nu_A+\nu_B)$

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

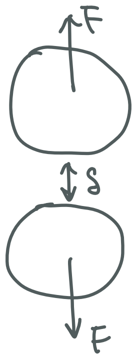
In a mixture, attraction between similar molecules is energetically more favourable than between dissimilar molecules.

- Non-retarted vdW forces : $U(r) = -\frac{C}{r^6}$

| | 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% |
| $H_2O$ – $H_2O$ | 10 | 96 | 33 | 24% |

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

• Retarded vdW forces (Macroscopic theory, Dzyaloshinskii, Lifshitz & Pitaevskii 1961)




A correction of $1/r$ to account for the time effect on the interaction over long distances

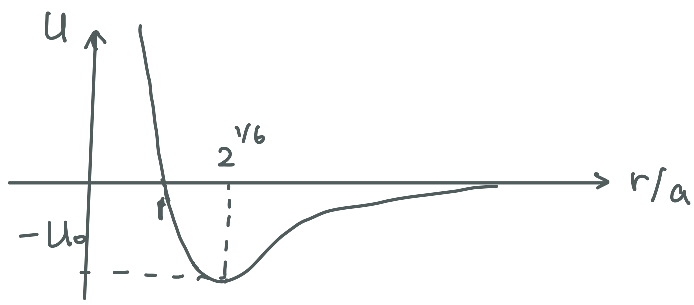
$$U = \begin{cases} -\dfrac{C}{r^6} & r < 50\ \text{nm} \\ -\dfrac{C_{12}}{r^7} & r > 500\ \text{nm} \end{cases}$$

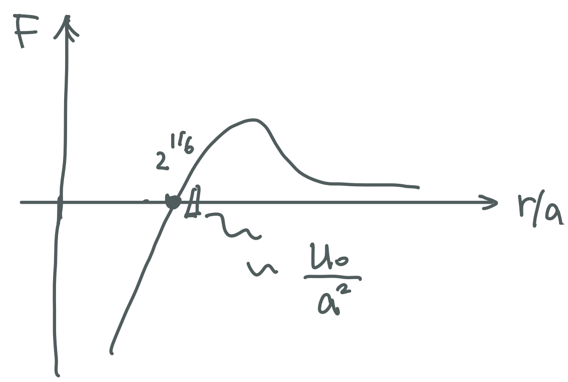
## • Lennard - Jones Potential

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 $n \geq 10$.

Born repulsion (empirical)

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

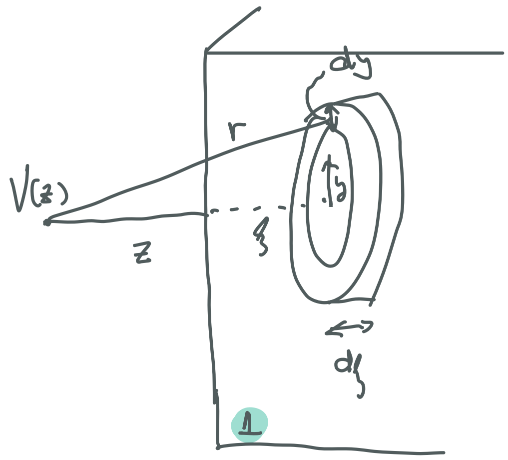


# Van der Waals Interaction Between Solids

- VdW attraction between two surfaces

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




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

Interaction between a molecule and solid 1

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

$$= \int_{\xi=0}^{\infty}\int_{y=0}^{\infty} \frac{-2\pi n_1 C_{12}\, y\, dy\, d\xi}{[(z+\xi)^2+y^2]^3}$$

$$\left(\frac{\text{Atoms}}{\text{Vol}}\right) = n_1 = \frac{\rho_1 N_A}{M_{w1}}$$

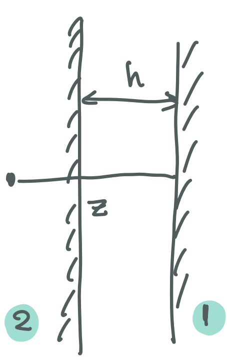
mass density; $N_A$ ~ Avogadro const.; $M_{w1}$ ~ Molar mass

$$dV = 2\pi y\, dy\, d\xi$$

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

$$= \int_{\xi=0}^{\infty} \frac{1}{2}\pi n_1 C_{12} \frac{1}{[(z+\xi)^2+y^2]^{\cancel{3}2}}\Bigg|_0^{\infty} d\xi = -\frac{1}{6}\pi n_1 C_{12} \frac{1}{(z+\xi)^3}\Bigg|_0^{\infty} = -\frac{\pi n_1 C_{12}}{6z^3}$$

Interaction between solid 2 and solid 1 (per unit area)




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

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

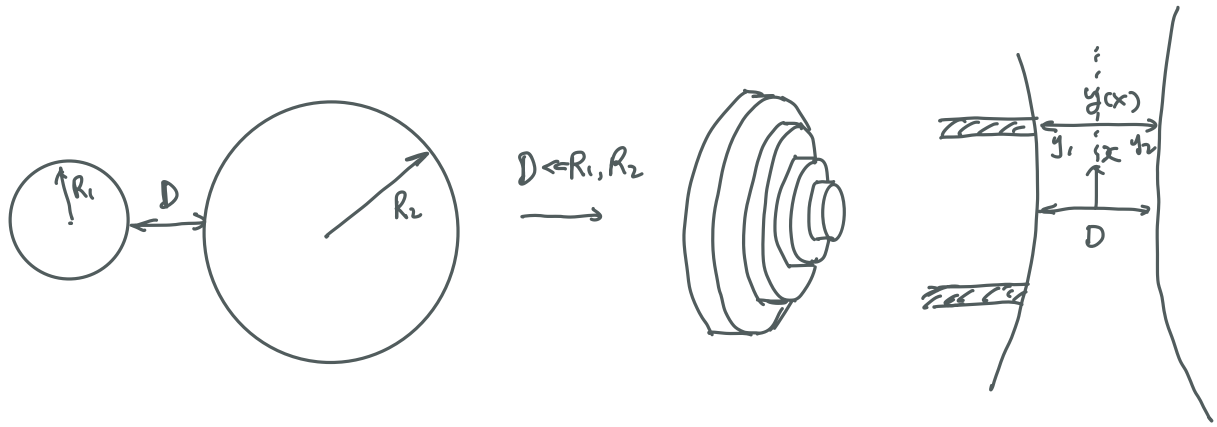
Interaction force per unit area: $\boxed{F = -\frac{dV}{dh} = -\frac{A_{12}}{6\pi h^3}}$ (Repulsive)

$$A_{12} = \pi^2 n_1 n_2 C_{12} = \frac{\pi^2 N_0^2 \rho_1 \rho_2 C_{12}}{M_{w1} \cdot M_{w2}} \sim O\left(10^{-21} - 10^{-19}\ J\right).$$

This is a large value

$$h \sim 0.1\ nm \rightarrow V \sim \frac{10^{-20}\ J}{6\pi\ (0.1\ nm)^2} \sim 10^{-1}\ J/m^2,\quad F \sim \frac{10^{-1}\ J/m^2}{0.1\ nm} \sim 1\ GPa$$

- VdW attraction between two spheres (Derjaguin approximation).




Force/area between two surfaces

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

How to approximate $y(x)$?

$\simeq \left(R_1 - \frac{x^2}{2R_1}\right)$ when $x \ll R_1$

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

or $\nabla^2 y = \kappa = \frac{1}{R} \Rightarrow y_1 = \frac{D}{2} + \frac{1}{2R_1}x^2$ & $y_2 = \frac{D}{2} + \frac{1}{2R_2}x^2$

curvature

$$\Rightarrow y(x) = D + \frac{1}{2}\underbrace{\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}_{=\frac{1}{R_{eff}}}x^2 \quad \& \quad dy = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) x\, dx$$

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

$$W(D) = -\underbrace{\frac{R_1R_2}{R_1+R_2}}_{R_{eff}}\frac{A_{12}}{6D} \qquad \left(F_{Attractive} = +\frac{dW}{dD}\right)$$

When one of the spheres becomes a half-space, say $R_1 \to \infty$, $R_2 = R$, $R_{eff} \to R$

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

- Retarded interaction between two surfaces

$$W_{m-m}(r) = \begin{cases} \dfrac{-C}{r^6}, & \text{Small } r \\ -\dfrac{C'}{r^7}, & \text{Large } r \end{cases} \Rightarrow \underset{Attractive}{F(h)} = \begin{cases} \dfrac{\overset{\text{1 and 2 cross 3}}{A_{132}}}{6\pi h^3}, & \text{Small } h \\ \dfrac{B_{132}}{h^4}, & \text{Large } h \end{cases}$$

Lifshitz (1956) (3 = Vacuum), Dzyaloshinski, Lifshitz, Pitaevski (1961) (3 Any medium)

$$A_{132} = \frac{3\hbar\overline{\omega}}{4\pi}, \quad \overline{\omega} = \int_0^\infty \left[\frac{\varepsilon_1(i\xi)-\varepsilon_3(i\xi)}{\varepsilon_1(i\xi)+\varepsilon_3(i\xi)}\right]\left[\frac{\varepsilon_2(i\xi)-\varepsilon_3(i\xi)}{\underset{\uparrow \text{Dielectric permittivity}}{\varepsilon_2(i\xi)}+\varepsilon_3(i\xi)}\right]d\xi$$

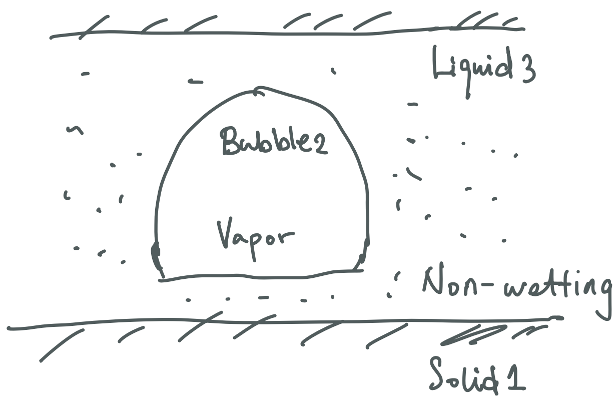
$$B_{132} = \frac{\pi^2\hbar c}{240}\frac{1}{\sqrt{\varepsilon_{30}}}\left(\frac{\varepsilon_{10}-\varepsilon_{30}}{\varepsilon_{10}-\varepsilon_{30}}\right)\left(\frac{\varepsilon_{20}-\varepsilon_{30}}{\varepsilon_{20}+\varepsilon_{30}}\right)\varphi(\varepsilon_{10}, \varepsilon_{20}, \varepsilon_{30})$$

Similarly, the interaction between a sphere and a wall becomes:

$$F(D) \propto \begin{cases} \dfrac{R}{D^2} & (\text{Non-retarded, } D \lesssim 10 \text{ nm}) \\ \dfrac{R}{D^3} & (\text{Retarded, } D \gtrsim 100 \text{ nm}) \end{cases}$$

## • Examples

### Example 1 : Stick or slip?

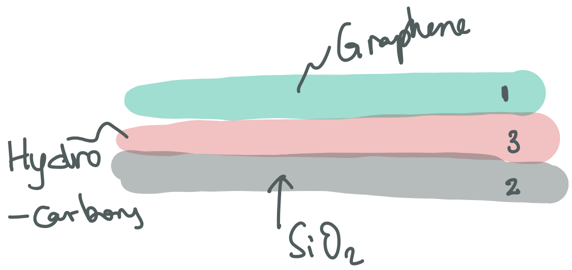




$A_{132} > 0$ , Liquid does not wet .

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

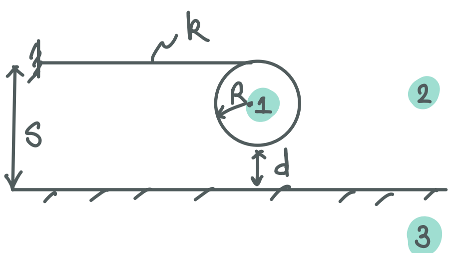
### Example 2 : Atomic cleaning ?

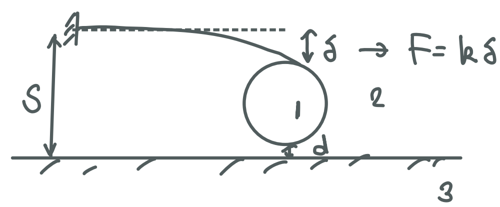



$A_{132} > 0$ Attractive force between 1 & 2 (Fluid 3 squeezed out)

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

### Example 3 : Pull-in instability



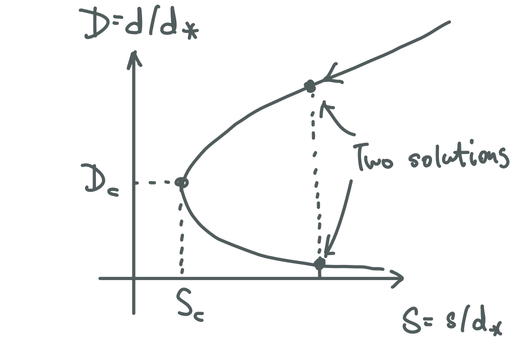




At which S, d, or F, the sphere jumps to the surface ?

$$\begin{cases} S = d + \delta + S_0 \;\leftarrow \text{Ref.} \\ \delta = F/k \\ F = \dfrac{A_{123} R}{6 d^2} \end{cases} \longrightarrow \quad S = d + \frac{A_{123} R}{6 k d^2} + S_0$$

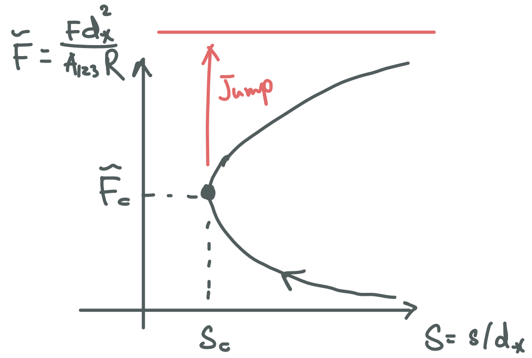
$$d_x = \left(\frac{A_{123} R}{k}\right)^{1/3}, \quad S = \frac{s}{d_x}, \quad D = \frac{d}{d_x}, \quad \tilde{F} = \frac{F d_x^2}{A_{123} R} = F\left(\frac{1}{A_{123} R k^2}\right)^{1/3}$$

$$\begin{cases} S = D + \dfrac{1}{6D^2} + \cancel{S_0} \;\leftarrow \text{Neglect} \\ \tilde{F} = \dfrac{1}{6D^2} \end{cases}$$




$$\left.\frac{dS}{dD}\right|_{D_c} = 1 - \frac{1}{3D_c^3} = 0 \rightarrow D_c = 3^{-1/3} \quad \text{or} \quad d_c = \left(\frac{A_{123}R}{3k}\right)^{1/3}$$

$$S_c = \frac{3^{1/3}}{2} \quad \text{or} \quad s_c = \left(\frac{3A_{123}R}{8}\right)^{1/3}$$




$$\tilde{F}_c = \frac{1}{6D_c^2}, \quad F_c = \left(\frac{A_{123}k^2R_s}{24}\right)^{1/3}$$