

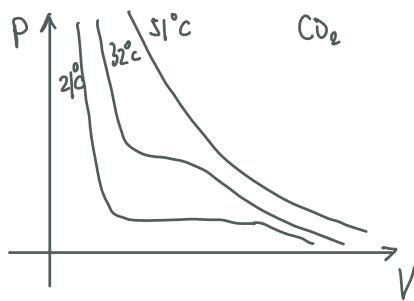
①

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.

- Liquidation of gas (Andrew 1869)



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

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

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

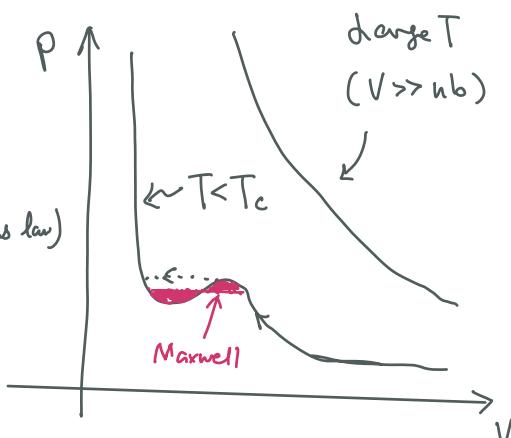


$$\left(P + \frac{n^2 a}{V}\right) (V - nb) = nRT \quad (\text{Real gas law})$$

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

b - volume of a mole of particles

a - a measure of average attraction between particles



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



• Potential of a charge

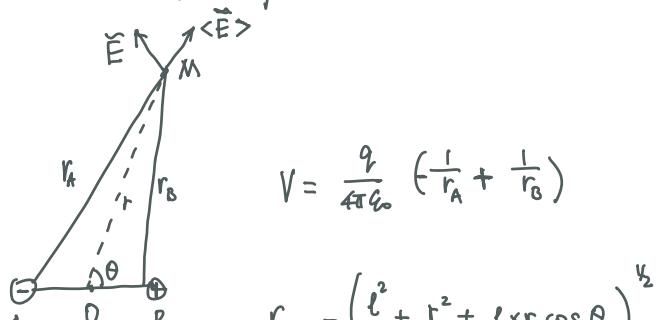
$$V(\vec{r}) = \frac{q}{4\pi\epsilon_0 r} \quad . \quad r = |\vec{r}|$$

↑ Permittivity 介电常数.

• Potential of a dipole

Dipole: A combination of two opposite electric charges $+q$ & $-q$

Set apart by a small ℓ . $\vec{\mu} = q\vec{\ell}$ is dipolar moment. ($1 \times 10^{-30} \text{ Cm}$)



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

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

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

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

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

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

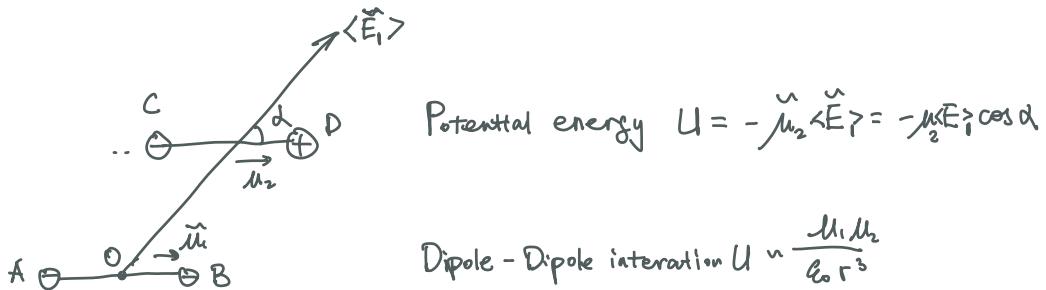
$$E = |\vec{E}| = \sqrt{E_r^2 + E_\theta^2} = \frac{\mu}{4\pi\epsilon_0 r^3} \sqrt{1 + 3 \cos^2\theta}$$

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

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

$$\Rightarrow \boxed{\langle E \rangle = \frac{\sqrt{2}\mu}{4\pi\epsilon_0 r^3}} \quad \text{?}$$

- Dipole in an electric field.



$$\mu \approx 1.6 \times 10^{-19} \text{ C} \times 0.1 \text{ nm}, \epsilon_0 \approx 8.854 \times 10^{-12} \text{ C}^2/\text{Nm}, k \approx 1.38 \times 10^{-25} \text{ J/K}, T \approx 300 \text{ K}$$

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

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

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

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

so that $\int A e^{z \cos \alpha} dS = 1, \quad dS = d\theta \sin \alpha d\alpha = 2\pi \int_0^\pi d(\cos \alpha)$

$$\langle U \rangle = - \int dS \rho d\alpha \mu_s \langle E_i \rangle \cos \alpha$$

$$= -\mu_s \langle E_i \rangle \frac{2\pi \int_0^\pi e^{z \cos \alpha} \cos \alpha d(\cos \alpha)}{2\pi \int_0^\pi e^{z \cos \alpha} d(\cos \alpha)} \quad R \rightarrow 1/A$$

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

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

Mathematica.

$$= -\mu_s \langle E_i \rangle \left(\underbrace{\coth z - \frac{1}{z}}_{\text{Langevin's function}} \right) \quad \begin{matrix} \text{Hyperbolic cotangent } \coth z \approx \frac{1}{z} \\ \text{for } z \ll 1 \end{matrix}$$

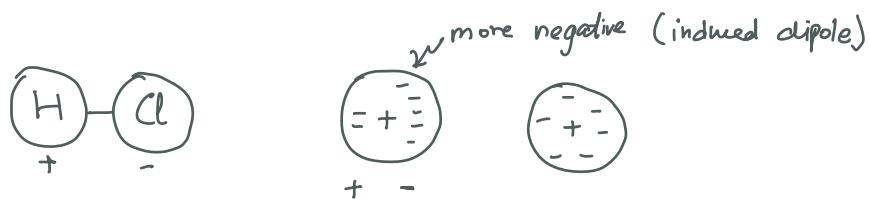
$$\coth z = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{z^5}{945} + O(z^7) \quad (\text{Note } z \ll 1)$$

$$\Rightarrow \boxed{\langle U \rangle = -\frac{1}{3} \mu_s \langle E_i \rangle z = -\frac{1}{3} \frac{\mu_s^2 \langle E_i \rangle^2}{kT} = -\frac{1}{(4\pi \epsilon_0)^2} \frac{2\mu_1^2 \mu_2^2}{3kT} \frac{1}{r^6}}$$

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

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

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

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

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

However, such induced forces are too weak!

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

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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.

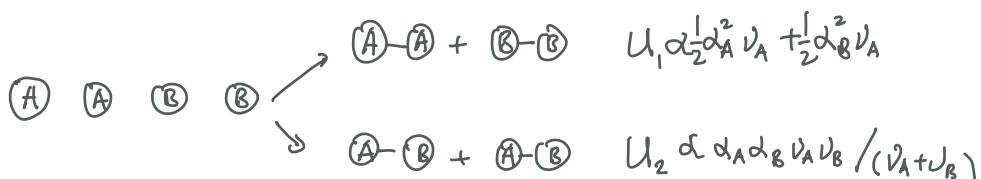
$\bullet U = \frac{-1}{(4\pi\epsilon_0)^2} \frac{3\alpha^2 h\nu_0}{4} \frac{1}{r^6}$ for two molecules

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

$\bullet U = -\frac{1}{(4\pi\epsilon_0)^2} \underbrace{\frac{3\alpha_A\alpha_B h\nu_A\nu_B}{2(\nu_A + \nu_B)}}_{\text{London constant. } \sim 10^{-79} \text{ J m}^6} \frac{1}{r^6}$ for two dissimilar molecules



$$\Delta U = U_1 - U_2 \propto \frac{d_B^2 v_B^2}{v_A + v_B} \left[\left(\frac{d_A v_A}{d_B v_B} - 1 \right)^2 + \frac{v_A}{v_B} \left(\frac{d_A}{d_B} - 1 \right)^2 \right] > 0 \quad (7)$$

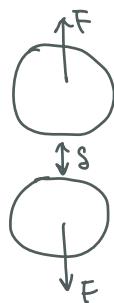
In a mixture, attraction between similar molecules is energetically more favourable than between dissimilar molecules.

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 | 24% |

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

- Retarded rdW forces (Macroscopic theory by Dzyaloshinski, Lifshitz, Pitaevskii 1961)



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

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

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Lennard - Jones Potential.

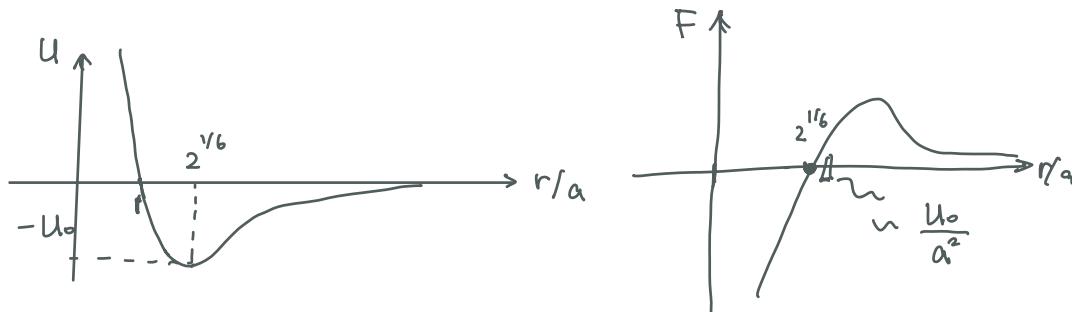
Quantum mechanics leads to an energy of repulsion related to $\exp(r_0/r)$

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

with $n > 10$.

$$U = \frac{D}{r^{12}} - \frac{C}{r^6} \quad \text{Born repulsion (empirical)}$$

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

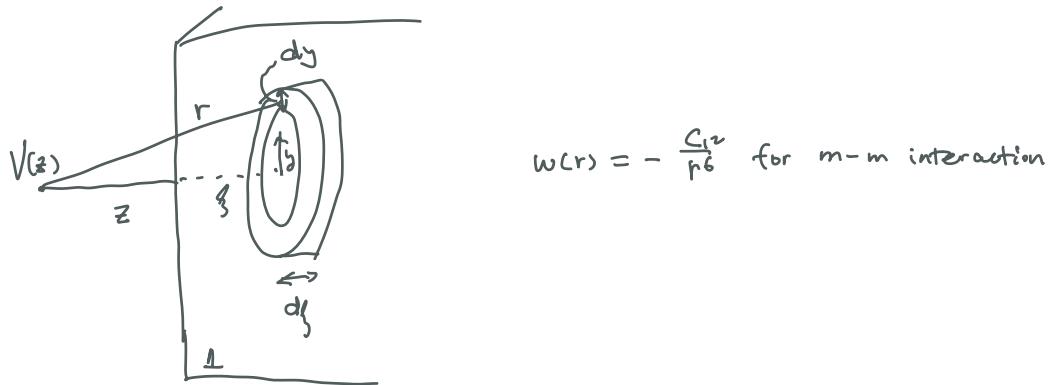


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Van der Waals Interaction Between Solids

VdW attraction between two surfaces

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



Interaction between a molecule and solid 1

$$\begin{aligned}
 V_1(z) &= \int_V W(r) \left(\frac{\text{Atoms}}{\text{Volume}} \right) dV \\
 &= \int_0^\infty \int_0^\infty -\frac{2\pi n_1 C_{12} y dy dz}{[(z+y)^2 + y^2]^2} \\
 &= \int_0^\infty \frac{1}{2} \pi n_1 C_{12} \frac{1}{[(z+y)^2 + y^2]^2} \Big|_0^\infty dz \\
 &= -\frac{1}{6} \pi n_1 C_{12} \frac{1}{(z+y)^3} \Big|_0^\infty = -\frac{\pi n_1 C_{12}}{6z^3}
 \end{aligned}$$

The diagram shows two parallel vertical plates labeled 1 and 2, separated by distance h . A small area element dz is shown at distance z from plate 1.

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

Interaction energy / unit area

$$V = -\frac{A_{12} k_B T}{12\pi h^2}$$

Hamaker constant

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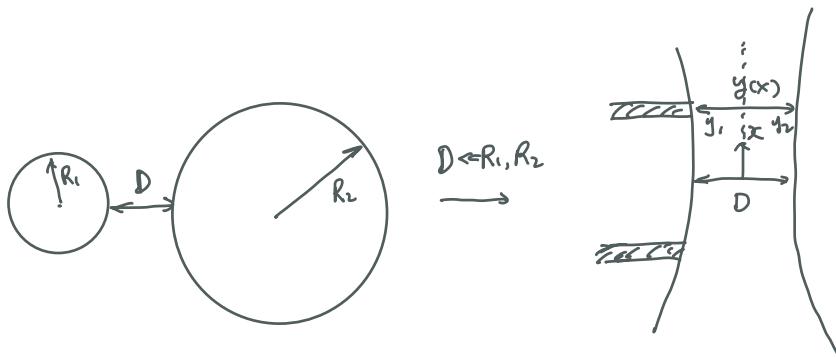
Interaction force / unit area:

$$F = -\frac{dV}{dh} = -\frac{A_{12}}{6\pi h^3}$$

$$A_{12} = \pi^2 n_1 n_2 C_{12} = \frac{\pi^2 N_0^2 \rho_1 \rho_2 C_{12}}{(Mw_1)(Mw_2)} \sim 0(10^{-19} - 10^{-20} J).$$

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

Vdw attraction between two spheres (Derjaguin approximation)



Force/area between two surfaces

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

★ $\begin{cases} y_1 = \frac{D}{2} + \frac{1}{2R_1} x^2 \\ y_2 = \frac{D}{2} + \frac{1}{2R_2} x^2 \end{cases} \Leftrightarrow \nabla^2 y = K = \frac{1}{R}$

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

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

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

- Accurate for $x \ll R_1, R_2$

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

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

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

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

$$\text{Note that } \oint F_{\text{true}} = F(D) + F_c = \bar{R} \frac{A_n}{6D^2} + \underbrace{\frac{A_n}{R}}_{\text{far from } D} = \bar{R} \frac{A_{12}}{6D^2} \left[1 + O\left(\frac{D^2}{R^2}\right) \right]$$

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

Retarded interaction between two surfaces

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

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

Lifshitz (1956) ($3 = \text{vacuum}$) , Dzyaloshinsky, Lifshitz, Pitaevski (1961) ($3 = \text{Any medium}$)

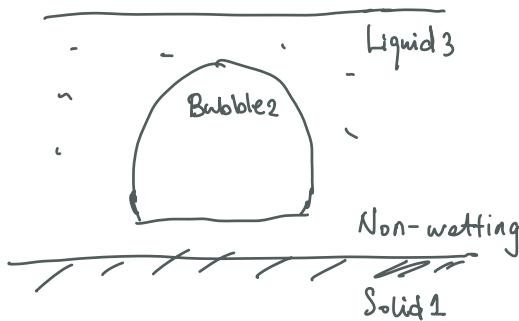
$$A_{132} = \frac{3\hbar\bar{\omega}}{4\pi}, \quad \bar{\omega} = \int_0^\infty \left[\frac{\epsilon_1(iq) - \epsilon_3(iq)}{\epsilon_1(iq) + \epsilon_3(iq)} \right] \left[\frac{\epsilon_2(iq) - \epsilon_3(iq)}{\epsilon_2(iq) + \epsilon_3(iq)} \right] dq$$

\uparrow Dielectric permittivity

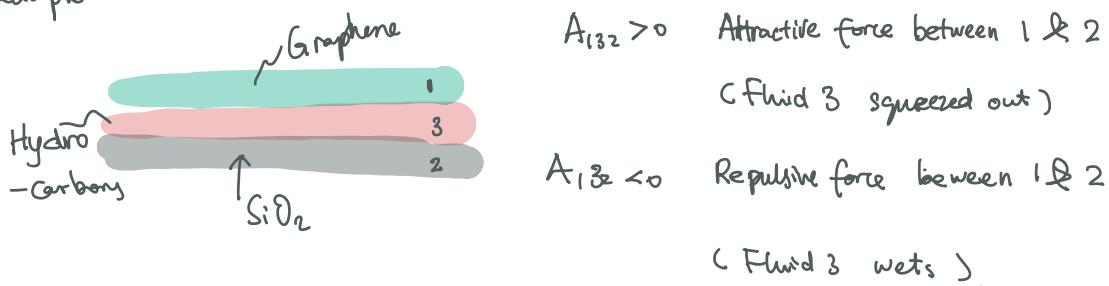
$$B_{132} = \frac{\pi^2 \hbar c}{240} \frac{1}{\sqrt{\epsilon_{30}}} \left(\frac{\epsilon_{10} - \epsilon_{20}}{\epsilon_{10} + \epsilon_{20}} \right) \left(\frac{\epsilon_{20} - \epsilon_{30}}{\epsilon_{20} + \epsilon_{30}} \right) \varphi(\epsilon_{10}, \epsilon_{20}, \epsilon_{30})$$

(12)

Example 1:

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

Example 2:



- Retarded interaction between a sphere and a wall

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