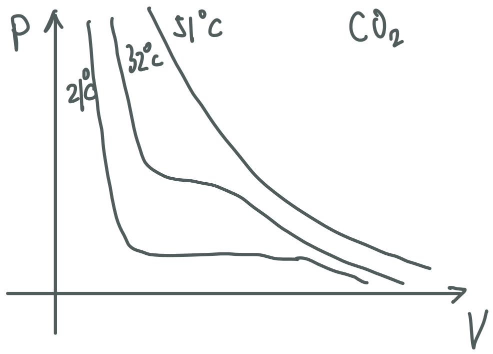
Van der Waals interactions

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)



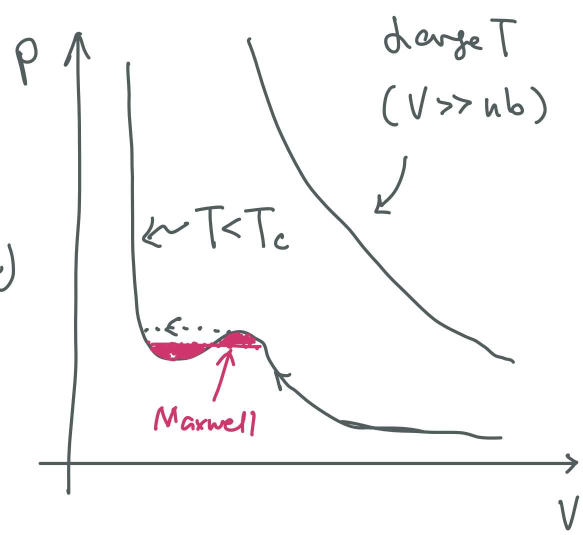
The existence of critical temperature and critical pressure for the phase change

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

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

$$\downarrow$$

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



n - number of moles

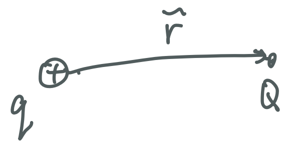
b - volume of a mole of particles

a - measure of average attraction between particles

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

H – Cl   Na – Cl
\+   −   +   −

- Potential of a charge

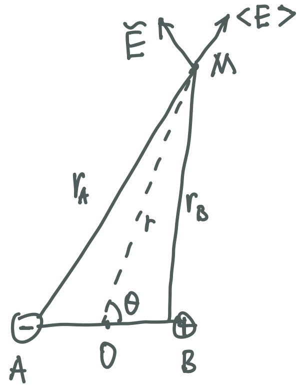


$$V(\tilde{r}) = \frac{q}{4\pi\varepsilon r} \quad . \quad r = |\tilde{r}|.$$

↑ 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. $\tilde{\mu} = q\tilde{l}$ is dipolar moment. ($l \sim 0.1$ nm)



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

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

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

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

$$V \simeq \frac{q}{4\pi\varepsilon_0 r}\left(\frac{1}{1-\frac{l}{2r}\cos\theta} - \frac{1}{1+\frac{l}{2r}\cos\theta}\right) = \frac{ql}{4\pi\varepsilon_0 r^2}\cos\theta$$

The field $\tilde{E}$ at point M caused by dipole AB of μ is $-\nabla\mu$:

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

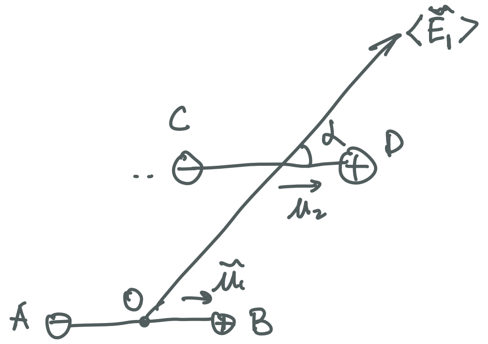
$$\rightarrow E = |\hat{E}| = \sqrt{E_r^2 + E_\theta^2} = \frac{\mu}{4\pi\varepsilon_0 r^3}\sqrt{1+3\cos^2\theta}$$

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

ALONG $\overrightarrow{OM}$:

$$\langle \cos^2\theta \rangle = \frac{\int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta}{\underbrace{\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta}_{=4\pi}} = \frac{1}{3} \rightarrow \boxed{\langle E \rangle = \frac{\sqrt{2}\,\mu}{4\pi\varepsilon_0 r^3}}$$

- Dipole in an electric field.



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

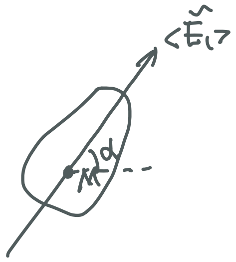
Dipole - Dipole interation $U \sim \frac{\mu_1 \mu_2}{\varepsilon_0 r^3}$

$\mu \sim 1.6\times10^{-19}\,C \times 0.1\,nm$, $\varepsilon_0 \sim 8.854\times10^{-12}\,C^2/(Jm)$, $k \sim 1.38\times10^{-23}\,J/K$, $T \sim 300\,K$

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

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

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



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

so that $\int A e^{z\cos\alpha} d\Omega = 1$, $d\Omega = d\theta \sin\alpha \, d\alpha = 2\pi \int_{\pi}^{0} d(\cos\alpha)$

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

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

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

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

Hyperbolic cotangent 双曲余切

$$= -\mu_2 \langle E_1 \rangle \underbrace{\left(\coth z - \frac{1}{z} \right)}_{\text{Langevin's function}}$$

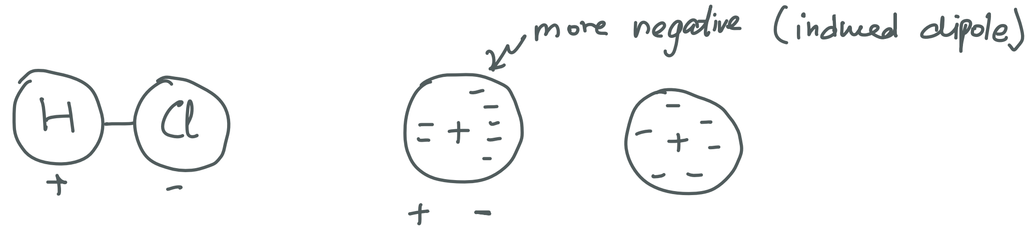
$$\coth = \frac{1}{z} + \frac{z}{3} - \frac{z^3}{45} + \frac{2z^5}{945} + O(z^7) \quad (\text{Note } z \ll 1)$$

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

Correction is needed to describe the influence of $\vec{\mu_2}$ on the orientation probability of dipole 1 ("slightly" longer)

Keesom's theory gives a force law r^{-7}, of the proper order of magnitude. However, numerical values from μ_1, μ_2 and variation with T do NOT agree with experiments, showing that 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, $\alpha_0 \propto V \times 4\pi\varepsilon_0$

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

$$= -\frac{1}{(4\pi\varepsilon_0)^2}\,\frac{\alpha_{02}\mu_1^2 + \alpha_{01}\mu_2^2}{r^6}$$

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 liquid, solid or rare gases whose atoms are spherical with no permanent dipolar moment.

Polarizability

Planck constant

ν_0 – electronic absorption frequency

- $U = \dfrac{-1}{(4\pi\varepsilon_0)^2}\,\dfrac{3\alpha^2 h\nu_0}{4}\,\dfrac{1}{r^6}$ for two molecules

Molar weight	Molecules	Boiling point	Electrons.
38	F_2 (g)	$-188^\circ C$	$9e^-$
70.9	Cl_2 (g)	$-34^\circ C$	$17e^-$
159.8	Br_2 (l)	$59^\circ C$	$35e^-$
253.8	I_2 (s)	$114^\circ C$	$53e^-$

Eg. CH_4 (16) vs. $CH_3CH_2CH_2CH_3$ (C_4H_{10}, 58) ?

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

$$Ⓐ\ Ⓐ\ Ⓑ\ Ⓑ \nearrow Ⓐ\!-\!Ⓐ + Ⓑ\!-\!Ⓑ \quad -U_1 \propto \frac{1}{4}\alpha_A^2\nu_A + \frac{1}{4}\alpha_B^2\nu_A$$

$$\searrow Ⓐ\!-\!Ⓑ + Ⓐ\!-\!Ⓑ \quad -U_2 \propto \alpha_A\alpha_B\nu_A\nu_B/(\nu_A+\nu_B)$$

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

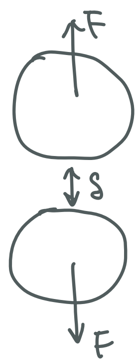
In a mixture, attraction between similar molecules is energetically more favourable than between dissimilar molecules. - The reason why the separation of two liquids by an interface into two phases can often be observed!

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

Non-retarted, additive : $U(r) = -\frac{C}{r^6}$ unit: $10^{-76}\ \mathrm{J m^6}$

	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%

- Retarded vdW forces (Macroscopic theroy by Dzyaloshinski, Lifshitz & Pitaevskii 1961)

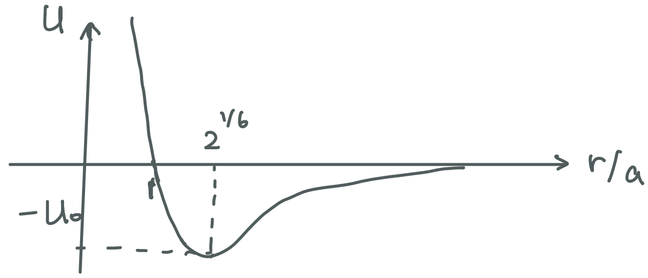


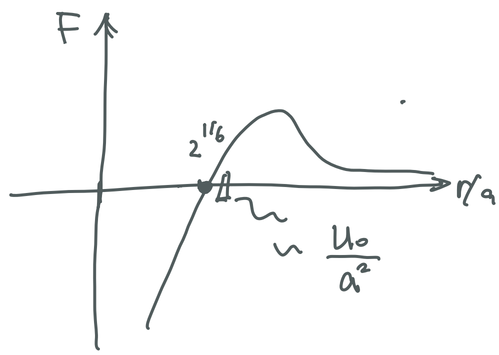
A correction of $\frac{1}{r}$ to account for the time effect on the interaction over long distances

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

- 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 $n > 10$.



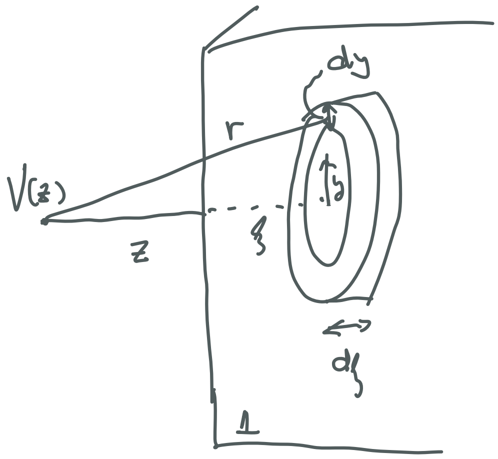


Born repulsion (empirical)

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

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

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

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

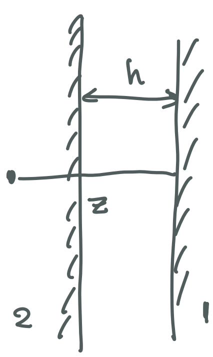
$r^2 = (z+\xi)^2 + y^2$

$\left(\frac{\text{Atoms}}{\text{Vol}}\right) = n_1 = \frac{\rho_1 N_A}{MW_1}$

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

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

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



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

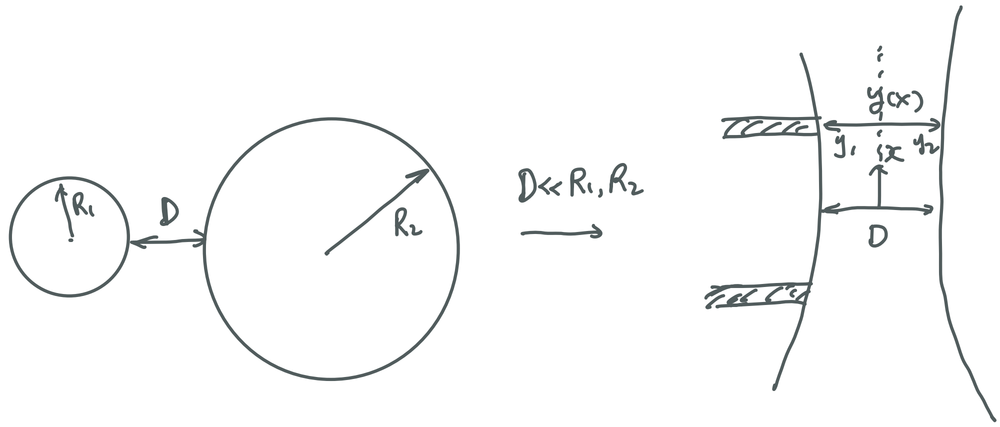
Interaction energy /unit area: $\boxed{V = -\frac{A_{12}}{12\pi h^2}}$ Hamaker constant

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

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

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

VdW attraction between two spheres (Derjaguin approximation)



Force/area between two surfaces

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

What are y_1, y_2?

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

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

$$\simeq \frac{D}{2} + \frac{1}{2}\frac{x^2}{R}$$

Or $\nabla^2 y = \kappa = \frac{1}{R}$ $\rightarrow$ $y_1 = \frac{D}{2} + \frac{1}{2R_1}x^2$

$\rightarrow$ $y_2 = \frac{D}{2} + \frac{1}{2R_2}x^2$

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

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

Therefore. $F(D)=\int_0^\infty \frac{A_{12}}{6\pi y^3} 2\pi \frac{R_1R_2}{R_1+R_2} dy = \left(\frac{R_1R_2}{R_1+R_2}\right)\frac{A_{12}}{6D^2}$

$$W(D) = -\left(\frac{R_1R_2}{R_1+R_2}\right)\frac{A_{12}}{6D}$$

Note that ① $F_{sphere-wall} = \frac{RA_{12}}{6D^2}$, $W_{sphere-wall} = -\frac{A_{12}R}{6D}$

② Retarded interaction between a sphere and a wall

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

③ 3 substances by Lifshitz (1956), Dzyaloshinski. Lifshitz. Pitaevski (1961)

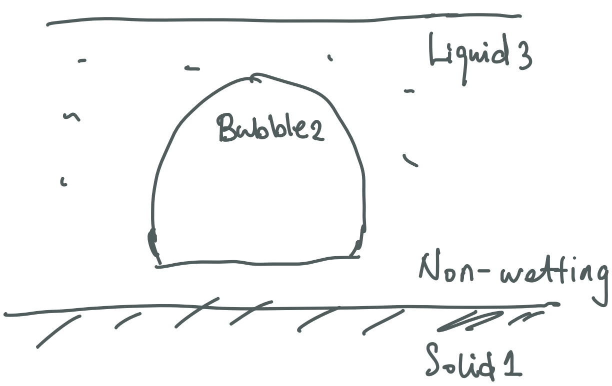
$$F(D) = \begin{cases} \frac{A_{132}}{6\pi D^3}, & \text{Small } D \\ \frac{B_{132}}{D^4}, & \text{Large } D \end{cases}$$

1 and 2 cross 3

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

Dielectric permittivity

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



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

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