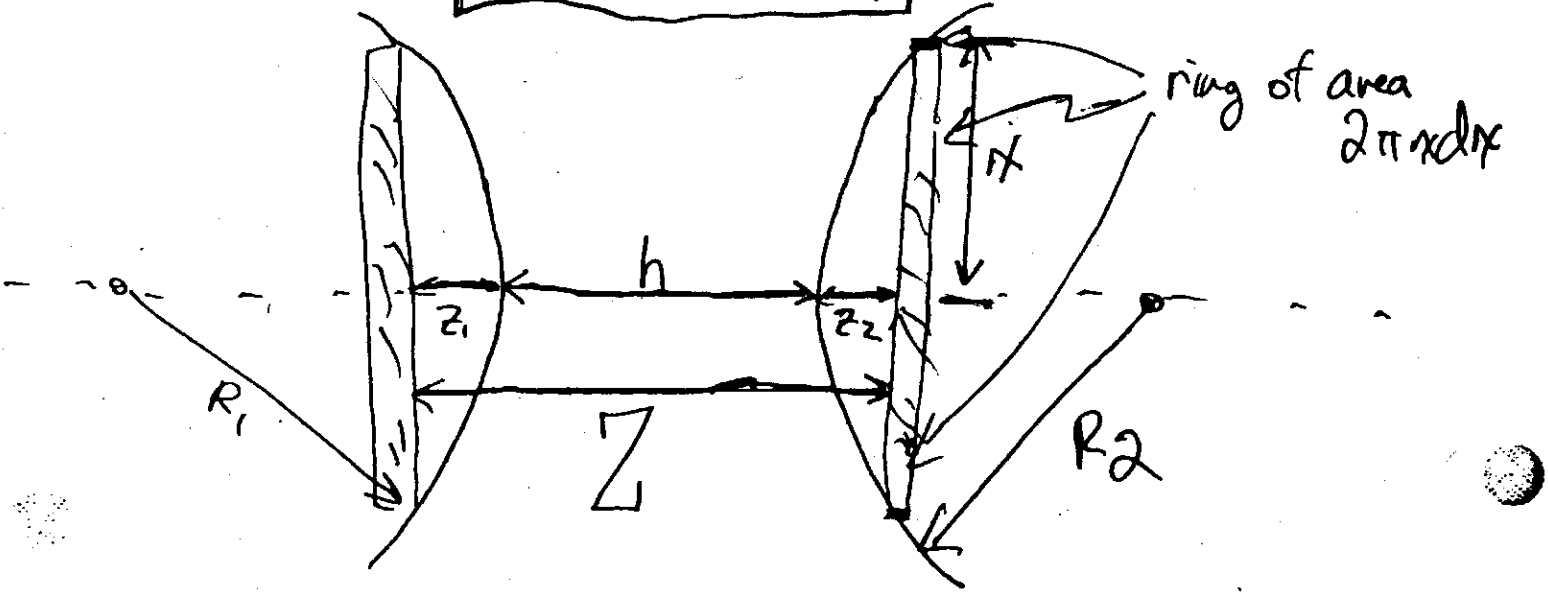
The Derjaquin Approximation.

(How to account for curvature)

– Consider 2 spheres of radii R_1 & R_2 separated by h. $\boxed{(h \ll R_1, R_2)}$



Distance between rings $(Z) = z_1 + h + z_2$

Now: $F(h) = \int_{Z=h}^{Z=\infty} 2\pi x \, (F/A) \, dx$

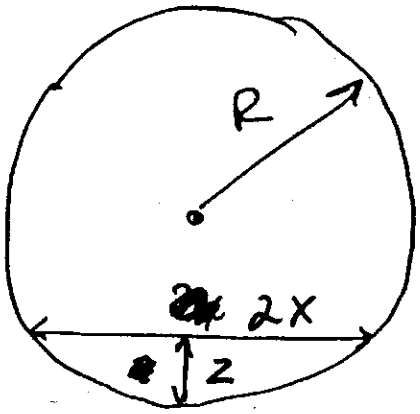
integral in x

Limits in Z

(Recall F/A is a function of sep'n distance (h))

How to get from X to Z ②

- Chord theorem:



$$x^2 = (2R - z)z \cong 2Rz \qquad (z \ll R)$$

$$x^2 \cong 2R_1 z_1 = 2R_2 z_2 \qquad \left(\text{constant } x \text{ for integration}\right)$$

Now, $z_1 = \frac{x^2}{2R_1}$ & $z_2 = \frac{x^2}{2R_2}$

$$Z = z_1 + h + z_2 = \frac{x^2}{2R_1} + h + \frac{x^2}{2R_2}$$

$$Z = h + \frac{x^2}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

$$dZ = \left(\frac{1}{R_1} + \frac{1}{R_2}\right) x\, dx$$

$$x\, dx = \frac{dZ}{\left(\frac{1}{R_1} + \frac{1}{R_2}\right)} = \left(\frac{R_1 R_2}{R_1 + R_2}\right) dZ$$

Back to integral:

$$F(h) = \int_{Z=h}^{Z=\infty} 2\pi x \left(\frac{E}{A}\right) dx = \int_{h}^{\infty} 2\pi \left(\frac{E}{A}\right)\left(\frac{R_1 R_2}{R_1+R_2}\right) dZ$$

$$F(h) = 2\pi\left(\frac{R_1 R_2}{R_1+R_2}\right)\int_{h}^{\infty} \left(\frac{E}{A}\right) dZ$$

- ok, now define the energy of interaction:

$$U(h) = -\int_{\infty}^{h} F(x)\,dx$$

$$F = -\frac{dU}{dx}$$

x = sep'n distance.

$$F(h) = 2\pi\left(\frac{R_1 R_2}{R_1+R_2}\right)\frac{U(h)}{A}$$

$F(h)$ ↑ 2 spheres.

$\frac{U(h)}{A}$ ↑ flat plates

$$F_{<<(h)} = 2\pi\left(\frac{R_1 R_2}{\quad}\right) U_{\ldots\ldots(h)}$$

result of "Derjaguin approx."

- Very important relationship... handles changes in geometry.
- Valid for any type of force profile, as long as $h \ll R$. (where would it not work?)
- Often, easiest to derive energy of int. for flat plates
  ↳ force between spheres more practical.

ex) - From last time:

$$\frac{F}{A}(h) = \underbrace{64\,kT\,c_\infty^*\tanh^2\left(\frac{ze\phi_0}{4kT}\right)}_{\equiv "B"} \exp(-\kappa h)$$

$$\frac{F}{A}(h) = B\exp(-\kappa h)$$

$$\frac{U_{ww}}{A}(h) = \int_h^\infty \frac{F}{A}(h')\,dh' = \int_h^\infty B\exp(-\kappa h')\,dh'$$

$$\frac{U_{ww}}{A}(h) = -\frac{B}{\kappa}\left[\frac{1}{\exp(\kappa h')}\right]_h^\infty = \frac{B}{\kappa}\left[\frac{1}{\exp(\kappa h')}\right]_\infty^h$$

$$\boxed{\frac{U_{ww}(h)}{A} = \frac{B}{\kappa}\exp(-\kappa h)}$$

- Now, Derjaquin:

$$F_{ss}(h) = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) \frac{U_{ww}(h)}{\text{area}}$$

$$\boxed{F_{ss}(h) = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) \left(\frac{B}{\kappa} \right) \exp(-\kappa h)}$$

EDL ~~energy~~ force between spheres, weak overlap limit.

- Energy between spheres? $\boxed{F = -\frac{dU}{dh}}$

$$U_{ss}(h) = \int_h^\infty F_{ss}(h')\, dh'$$

$$= \int_h^\infty 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) \left(\frac{B}{\kappa} \right) \exp(-\kappa h')\, dh'$$

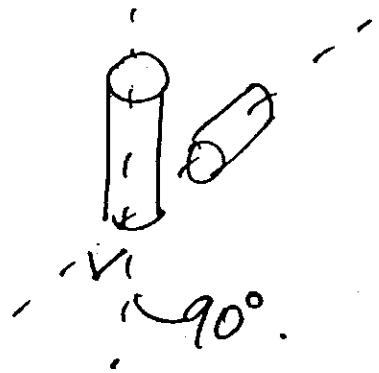
$$\boxed{U_{ss}(h) = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) \left(\frac{B}{\kappa^2} \right) \exp(-\kappa h)}$$

EDL energy between spheres, weak overlap limit.

- other forms of Derjaguin:

sphere / wall. $\boxed{F_{sw}(h) = 2\pi R \frac{U_{ww}(h)}{A}}$ $(R_2 \to \infty)$.

crossed cylinders. $\boxed{F_{xc}(h) = 2\pi\sqrt{R_1 R_2}\frac{U_{ww}(h)}{A}}$



(others exist).

+ ~~van der Waals interactions between macroscopic~~

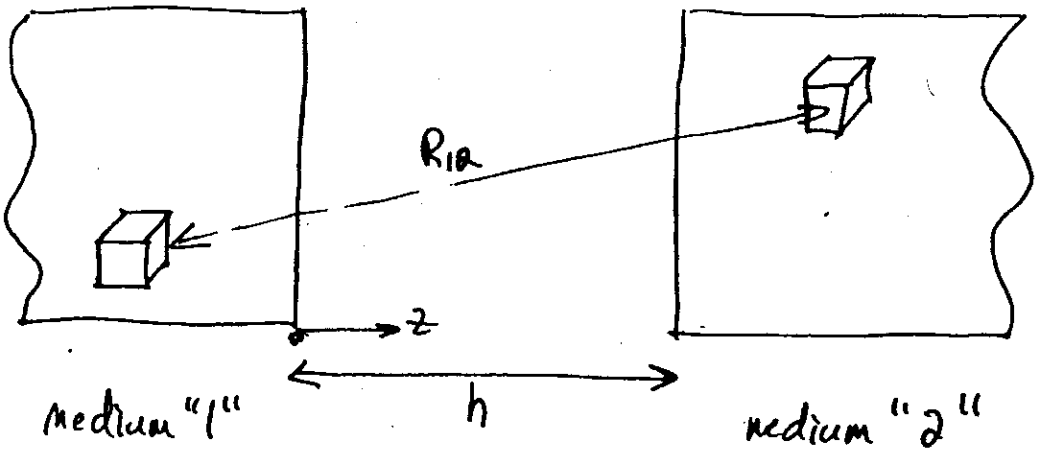
- interparticle van der Waals interactions.

Recall that: $\boxed{V_{ij}(r) = \frac{-C_1}{r^6}}$ (VDW int.).

$C \propto \alpha_1 \alpha_2$ [redacted]

- To calculate the interaction between two particles, we'll first assume we can just add all contributions from VDW. (pairwise-additivity, only really valid for London kinds)

- Now, for two semi-∞ slabs ...



$$dU_{12} = \frac{-C_{12}\rho_1\rho_2\, dV_1\, dV_2}{\left\{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right\}^3}$$

R "pyth. thrm"

$$U_{12} = C_{12}\rho_1\rho_2 \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{h}\int_{0}^{\infty} \frac{dx_1\,dx_2\,dy_1\,dy_2\,dz_1\,dz_2}{\left\{(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right\}^3}$$

(z's.)

solve by subst.

$$x = (x_2 - x_1)$$

$$x' = (x_2 + x_1)$$

$$y = (y_2 - y_1)$$

$$y' = (y_2 + y_1)$$

$$\frac{U_{ww}(h)}{\text{area}} = \frac{U_{12}}{dx\,dy} = C_{12}\rho_1\rho_2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{h}^{\infty} \frac{dx\,dy\,dz_1\,dz_2}{\left\{x^2+y^2+(z_2-z_1)^2\right\}^3}$$

$$\frac{U_{ww}(h)}{\text{area}} = -\frac{C_{12}\rho_1\rho_2\pi}{12}\left(\frac{1}{h^2}\right)$$

Define a material-dependent "Hamaker constant" . . .

$$H_{12} \equiv \pi^2 C_{12}\rho_1\rho_2$$

← C_{12} is a func. of polarizability, α

$$\boxed{\frac{U_{ww}(h)}{\text{area}} = -\frac{H_{12}}{12\pi}\left(\frac{1}{h^2}\right)}$$ (VDW energy of int. between flat plates).

$$\boxed{U_{sw}(h) = -\frac{H_{12}R}{6}\left(\frac{1}{h}\right)}$$ (sphere-wall VDW energy)

$$\boxed{U_{ss}(h) = -\frac{H_{12}}{6}\left(\frac{R_1R_2}{R_1+R_2}\right)\left(\frac{1}{h}\right)}$$ (sphere-sphere VDW energy).

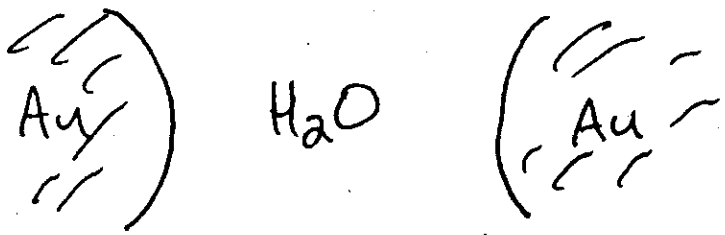
$$\boxed{U_{xc}(h) = -H_{12}\sqrt{R_1R_2}\left(\frac{1}{h}\right)}$$ / crossed-cylinders.)

- So what is this Hamaker constant?
  - Units of energy. H_{12}: $\boxed{10^{-19} \sim 10^{-20}\ J}$

↑ for almost all materials in vacuum!

Material	$H_{12} \times 10^{20}$ J	
Water	4.35	
Polystyrene	7.8 ~ 9.8	
Silver	39.8	} Why higher? (larger atoms, more e⁻)
Gold	45.3	}
n-octane	4.5	
liquid He	0.057	(very low ∴ nonpolar).

- What about interactions across a medium?



"1" "3" "1".

What is the Hamaker Constant Related to?

London Forces

$$V_{ij,\,London}(R) = -\frac{3}{2}\left(\frac{I_1 I_2}{I_1 + I_2}\right)\left(\frac{\alpha_1 \alpha_2}{(4\pi\varepsilon_0)^2}\right)\frac{1}{r^6}$$

$\Downarrow$ Pairwise Summation (of Hiesom + Debye forces to)

Hamaker constant

Polarizability

Both London Forces $\Rightarrow$ Hamaker Constant

function of material Polarizability

α $\Longleftrightarrow$ Macroscopic

microscopic $\Downarrow$ use Lorenz-Lorentz Eqn.

$$\frac{\alpha}{(4\pi\varepsilon_0)} = \left(\frac{n^2-1}{n^2+2}\right)\frac{3v}{4\pi}$$

n is index of refraction

The Hamaker constant is related to the index of refraction!!

The magnitude of H_{12} between materials is proportional to the difference in n_1 & n_2

$$|H_{12}| \propto |n_1 - n_2|$$

In a practical sense →

Hamaker constant between

(PS) water (PS)

(Au) water (Au)

(oil) water (oil)

	n_D
PS	1.515
water	1.33
oil	~ 1.4
Au	>> 1

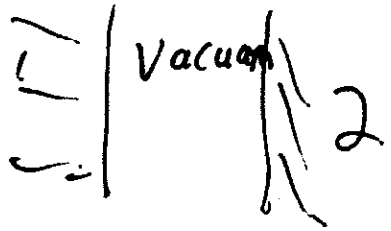
⇒ Hamaker const.

$H_{gold} > H_{PS} > H_{oil}$

- "Combining relations" (Based on Lifschitz theory of London int.)

$$\boxed{A_{12} \cong \sqrt{H_{11} \cdot H_{22}}}$$

1↦2 in vacuum.



$$\boxed{H_{131} \cong H_{313} \cong H_{11} + H_{33} - 2H_{13}}$$

For like materials always attractive (always attractive).

$$\boxed{H_{132} \cong \left[\sqrt{H_{11}} - \sqrt{H_{33}}\right]\left[\sqrt{H_{22}} - \sqrt{H_{33}}\right]}$$

(can be positive or negative!)

ex) Quartz / octane / quartz
1 3 1

$H_{octane} = 4.5 \times 10^{-20}$ J
$H_{quartz} = 6.3 \times 10^{-20}$ J

$$H_{131} = H_{11} + H_{33} - 2H_{13} = H_{11} + H_{33} - 2\sqrt{H_{11} \cdot H_{33}}$$

$$= 6.3 + 4.5 - 2\sqrt{(6.3)(4.5)} = \boxed{0.15 \times 10^{-20}\ \text{J}}$$

c) Quartz / octane / air. $H_{air} = 0$ (Ideal gas law).

$$H_{132} = \left(\sqrt{H_{11}} - \sqrt{H_{33}}\right)\left(\sqrt{H_{22}} - \sqrt{H_{33}}\right)$$

$$= \left(\sqrt{6.3} - \sqrt{4.5}\right)\left(0 - \sqrt{4.5}\right)$$

$$= \boxed{-0.82 \times 10^{-20}\ \text{J}}$$ ← int. between quartz & octane are stronger!

- other issues.

- Retardation: at distances > 5 nm, $\frac{1}{r}$ deviation.

$\sim \frac{1}{r^7}$ or greater

(due to the ~~distance~~ time to travel from "1" to "2" = time for fluctuations).

- Pairwise additivity only good for London, but error is lumped in H_{12}.

- Difficult to measure experimentally, but not impossible

- may be hard to measure, but vital to dispersion stability