Lecture: P1_Wk2_L3

Connecting Surface Energies to Hamaker Constants

The Derjaguin Approximation

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2012

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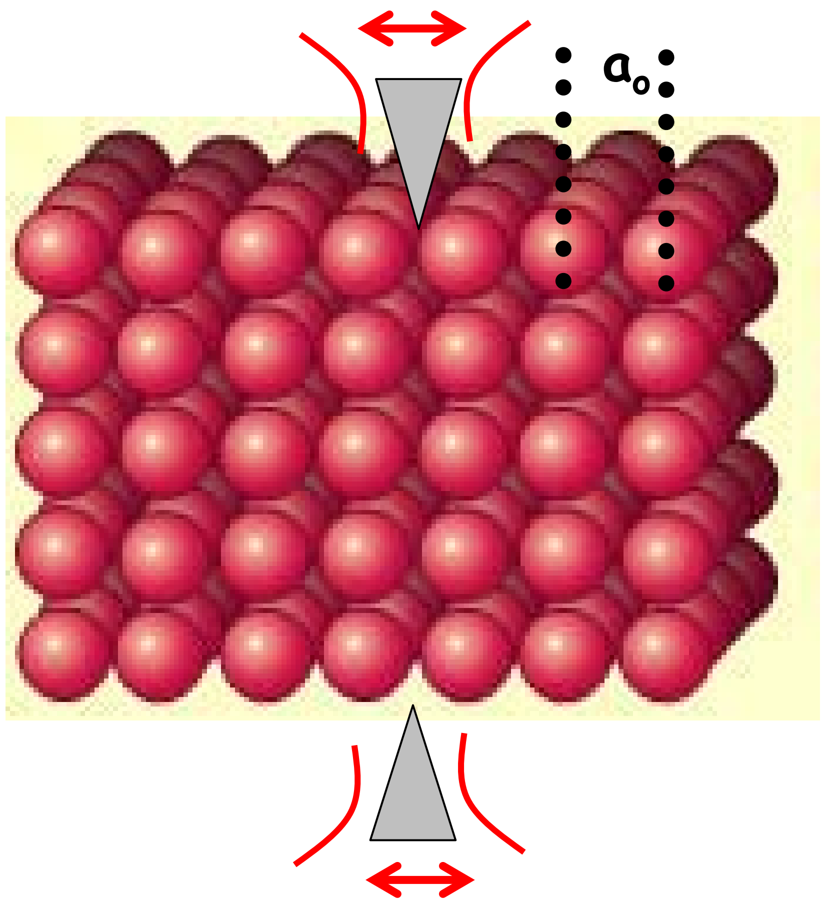
Surface Energetics

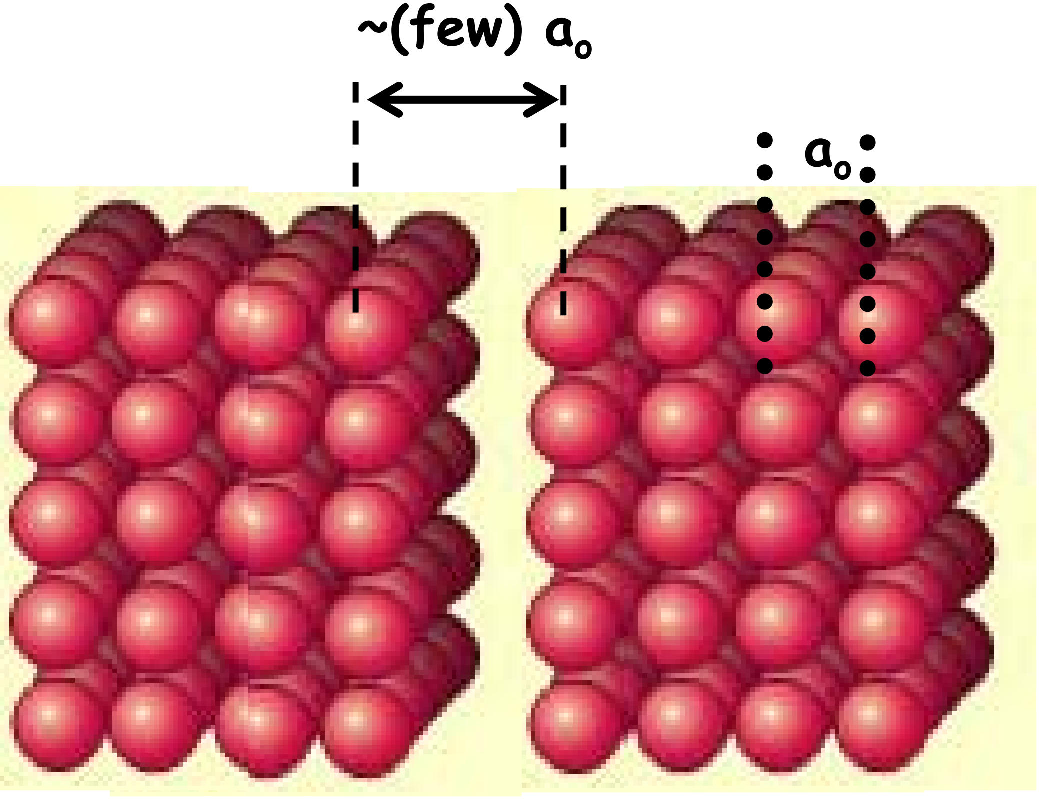
Atoms (or molecules) in the bulk of a material have a low relative energy due to nearest neighbor interactions (e.g. bonding).

Performing work on the system to create an interface can disrupt this situation...



(Excess) Surface Energy

Atoms (or *molecules*) at an interface are in a state of higher free energy than those in the bulk due to the lack of nearest neighbor interactions.



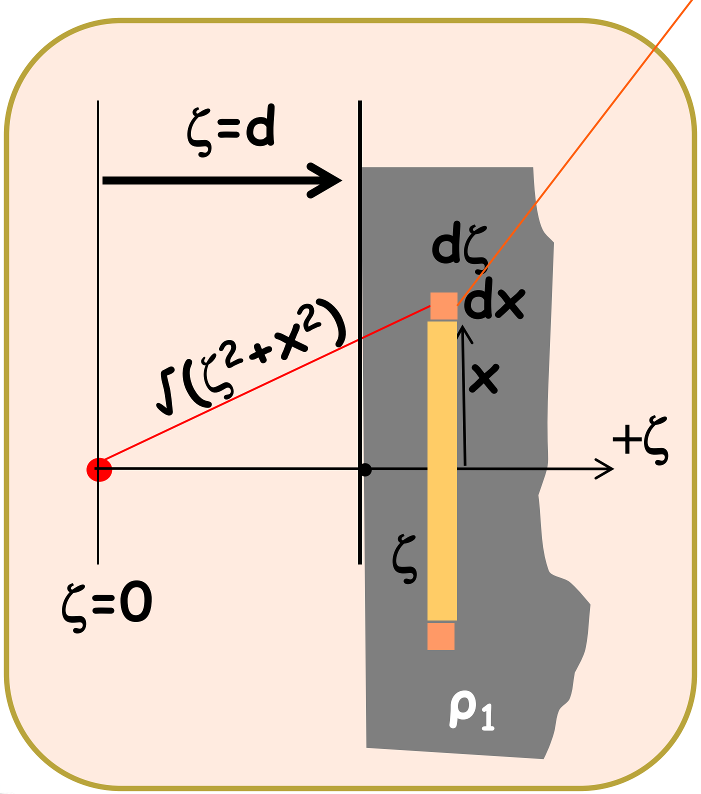
Recall the Molecule-Plane Interaction

ρ_1 = number density of atoms/molecules in an infinitesimal ring of the material

= $m_{\text{atom or molecule}} \times \rho_{\text{mass density}}$

ring volume is $dV = (2\pi x\, dx\, d\zeta)$

N= No. atoms/molecules in ring $=\rho_1 dV$



$$dU_{ring} = -N \frac{C_{vdW}}{\left(\sqrt{\zeta^2 + x^2}\right)^6} = -\frac{2\pi\rho_1 C_{vdW}\, x\, dx\, d\zeta}{\left(\zeta^2 + x^2\right)^3}$$

$$U_{vdW}(d) = -2\pi\rho_1 C_{vdW} \int_{\zeta=d}^{\zeta=\infty} d\zeta \left(\int_{x=0}^{x=\infty} \frac{x\, dx}{\left(\zeta^2 + x^2\right)^3} \right)$$

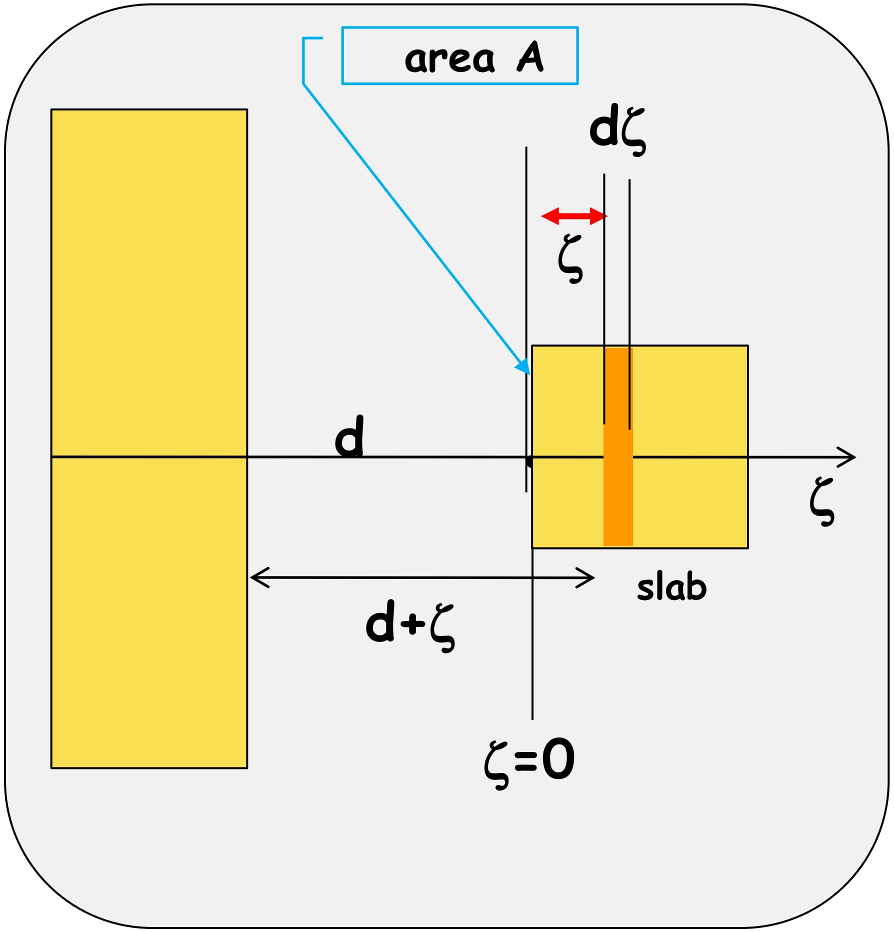
$$= -2\pi\rho_1 C_{vdW} \int_{\zeta=d}^{\zeta=\infty} \left(\frac{1}{4} \cdot \frac{1}{\zeta^4} \right) d\zeta = -\frac{2\pi\rho_1 C_{vdW}}{4} \left(-\frac{1}{3\zeta^3} \right) \Bigg|_{\zeta=d}^{\zeta=\infty}$$

$$= -\frac{2\pi\rho_1 C_{vdW}}{4} \left(\frac{1}{3} \right) \frac{1}{d^3}$$

$$U_{VdW}(d) = \frac{-\pi\rho_1 C_{vdW}}{6d^3}$$

The Plane-Plane Interaction

It is possible calculate the interaction energy **due to vdW forces** of two planar surfaces a distance 'd ' apart. Number of atoms in slab of cross-sectional area A is $\rho_2 dV = \rho_2 A\, d\zeta$. This slab interacts with an infinite flat material as shown.



$$U_{plane-plane}(d) = -\frac{\pi\rho_1 C_{vdW}}{6}\int_{\zeta=0}^{\zeta=\infty}\frac{\rho_2\, dV_{slab}}{(d+\zeta)^3}$$

$$= -\frac{\pi\rho_1\rho_2 C_{vdW}}{6}\int_{\zeta=0}^{\zeta=\infty}\frac{A d\zeta}{(d+\zeta)^3}$$

$$= -\frac{\pi\rho_1\rho_2 C_{vdW}}{6}A\left(-\frac{1}{2(d+\zeta)^2}\right)\Bigg|_{\zeta=0}^{\zeta=\infty}$$

$$= -\frac{\pi\rho_1\rho_2 C_{vdW}}{6}A\left(\frac{1}{2d^2}\right)$$

$$\therefore \quad \frac{U_{plane-plane}(d)}{A} = -\frac{H}{12\pi d^2}$$

with $H = \pi^2\rho_1\rho_2 C_{vdW}$ *as before*

H *: Hamaker's constant (also* A *or* A_H*)*

Typical Values for Hamaker Constant

Typically, for solids interacting across a vacuum,
$C_{vdW} \approx 10^{-77}$ Jm^6 and $\rho \approx 3\times10^{28}$ m^{-3}

$$H(or\ A_H) \approx \pi^2 \cdot 10^{-77}\, J\, m^6 \cdot \left(3\times10^{28} m^{-3}\right)^2$$

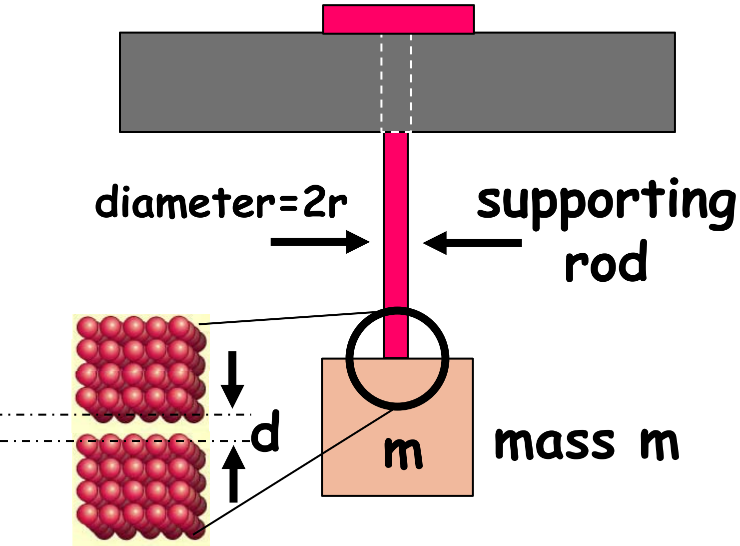
$$\simeq 10^{-19}\, J$$

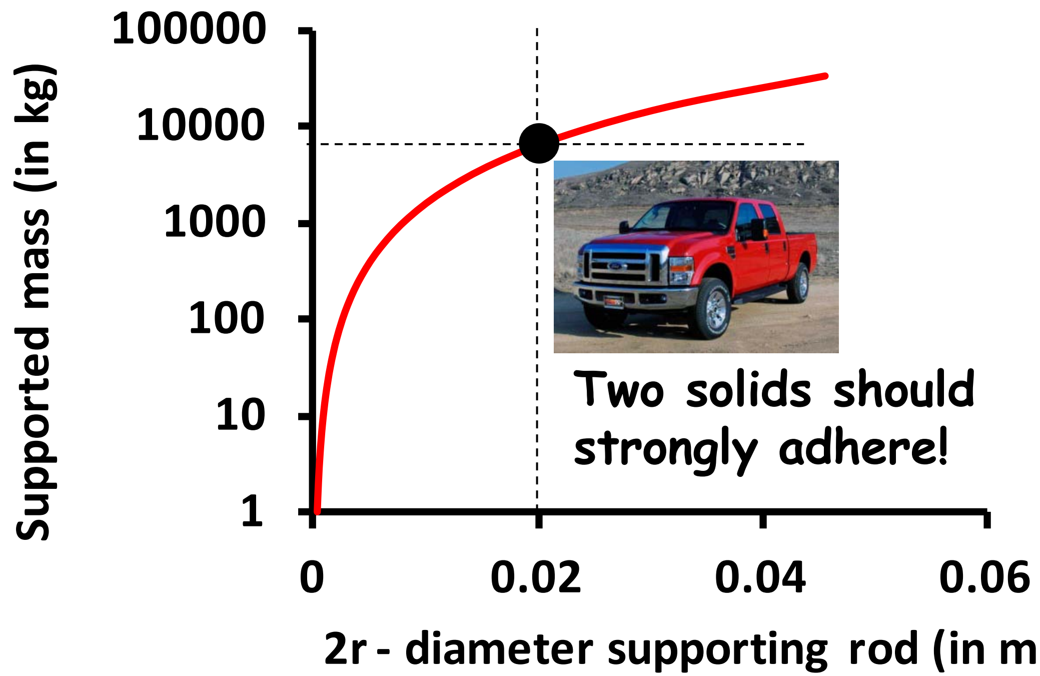
Typically, most solids have

$$H\left(or\ A_H\right) \simeq (0.4-4.0)\times10^{-19}\, J$$

see Butt, Cappella, and Kappl, Surf. Sci. Reps., **59**, 50 (2005) for more complete list

How strong is the vdW surface force?





$$\frac{U_{plane\text{-}plane}(d)}{A} = -\frac{H}{12\pi d^2}$$

$$\frac{F}{A} = -\frac{\partial}{\partial d}\left[\frac{U_{plane\text{-}plane}(d)}{A}\right] = -\frac{H}{6\pi d^3}$$

when $d \simeq a_o$,

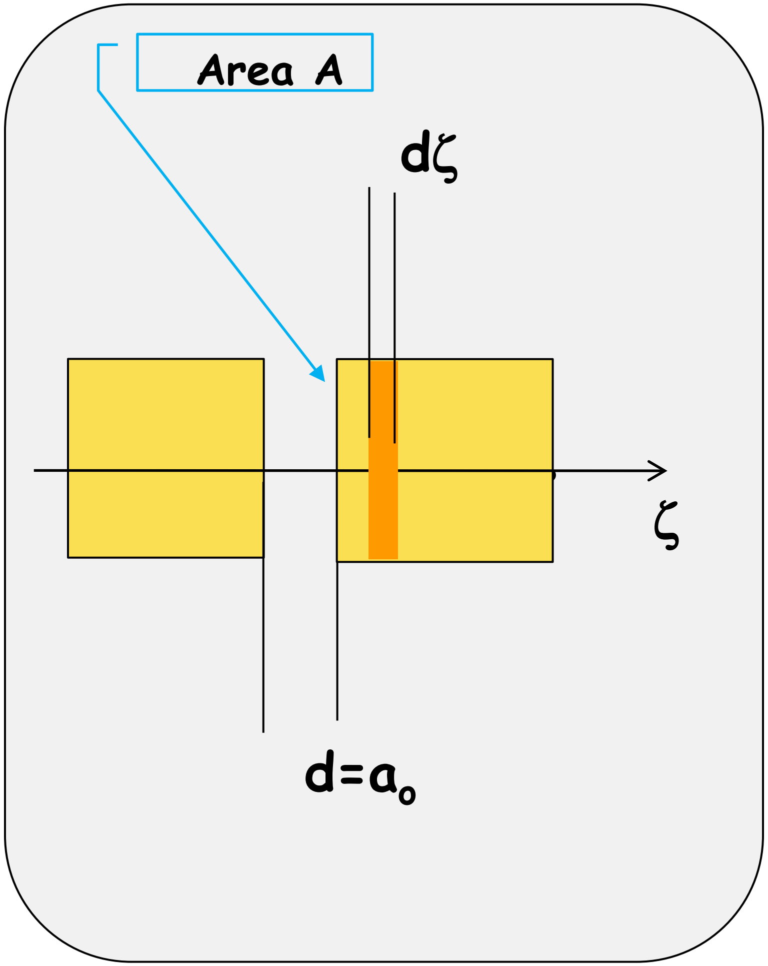
$$|F| = \frac{H}{6\pi a_o^3} A = mg = \frac{H}{6\pi a_o^3}\left(\pi r^2\right)$$

$$m = \frac{r^2 H}{6 g a_o^3} \Rightarrow r = \sqrt{\frac{6 g a_o^3}{H} m}$$

$$r \approx \left(\sqrt{\frac{6\cdot\left(9.8\,{}^{m}/_{s^2}\right)\cdot\left(\sim 0.3\times 10^{-9}\,m\right)^3}{\sim 1\times 10^{-19}\,J}}\right)\left(\sqrt{m}\right)$$

$$\text{diameter} = 2r = 2.5\times 10^{-4}\left(\sqrt{m}\right)\ \text{meters}$$

Estimating the surface energy due to vdW forces



When d≈a_o, then we should have:

$$\frac{U_{plane-plane}(d=a_o)}{A} = \frac{H}{12\pi(a_o)^2}$$

$$= \frac{dW_{11}}{dA} = 2\gamma_1$$

$$\gamma_1 = \frac{H}{24\pi(a_o)^2}$$

This approach neglects the atomicity of both surfaces. Often requires an "effective" a_o.

The Derjaguin approximation

Plane-plane interaction energies are fundamental quantities and it is useful to correlate the **tip-sample force** to known values of **plane-plane surface interaction energies**.

For a plane-sphere interaction we have:

$$U_{plane-sphere}(d) = -\frac{\pi^2 \rho_1 \rho_2 C_{vdW}}{6} R_{tip} \cdot \left(\frac{1}{d}\right)$$

$$\Rightarrow F_{plane-sphere}(d) = -\frac{\partial U_{plane-sphere}(d)}{\partial d} = -\frac{\pi^2 \rho_1 \rho_2 C_{vdW}}{6} R_{tip} \cdot \left(\frac{1}{d^2}\right)$$

attractive force

For a plane-plane interaction we already have:

$$\frac{U_{plane-plane}(d)}{A} = -\frac{\pi \rho_1 \rho_2 C_{vdW}}{6} \left(\frac{1}{2d^2}\right)$$

$$\therefore \; F_{plane-sphere}(d) = 2\pi R_{tip} \left(\frac{U_{plane-plane}(d)}{A}\right) = 2\pi R_{tip} \times \begin{Bmatrix} 2\gamma_1 \\ \gamma_1 + \gamma_2 - \gamma_{12} \end{Bmatrix}$$

geometry **material properties**

Likewise, it can be shown that for two interacting sphere of different radii

$$F_{sphere-sphere}(d) = 2\pi\left(\frac{R_1R_2}{R_1+R_2}\right)\left(\frac{U_{plane-plane}(d)}{A}\right)$$

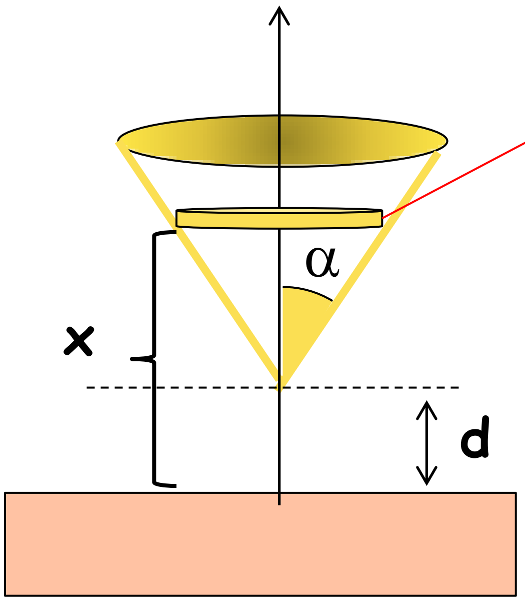
In general, Derajaguin's approximation relates the force f(x) acting between two **planes** separated by a distance x, to the force F(d) between two objects of arbitrary shape by

$$F(d) = \int_d^{\infty} f(x)\frac{dA}{dx}dx$$

where dA/dx describes how the cross-sectional area of the objects varies with separation x

Example

What's the vdW force between a cone of half-angle α an d a flat plane separated by a distance d?



$$Area \equiv A = \pi\left[(x-d)\tan\alpha\right]^2 \quad x > d$$

$$\frac{dA}{dx} = 2\pi\left[(x-d)\right]\tan^2\alpha$$

$$\frac{U_{plane-plane}(x)}{A} = -\frac{H}{12\pi x^2}$$

$$f(x) = -\frac{\partial}{\partial x}\left(-\frac{H}{12\pi x^2}\right) = -\frac{H}{6\pi x^3}$$

$$F(d) = \int_d^\infty f(x)\frac{dA}{dx}dx = -\frac{H}{6\pi}\int_d^\infty \frac{1}{x^3}2\pi\left[(x-d)\right]\tan^2\alpha\, dx$$

$$= -\frac{H}{6\pi}2\pi\tan^2\alpha\int_d^\infty\left[\frac{x-d}{x^3}\right]dx = -\frac{H}{3}\tan^2\alpha\left[-\frac{1}{x}+\frac{d}{2x^2}\right]_d^\infty$$

$$= -\frac{H}{6d}\tan^2\alpha$$

Implications of Derjaguin's approximation

- We discussed the case when $U(z)=-C/z^6$ - however the discussion is valid for any force law - attractive or repulsive or oscillatory – acting between two rigid spheres.
- As mentioned before, if two spheres are **in contact** (assuming no contamination), then $d=a_o$.
- The value of $U(d=a_o)_{plane\text{-}plane}$ is basically dW_{11} the conventional surface energy per unit area to create a solid surface. Thus:

$$F_{adhesion} \equiv F_{sphere-sphere}(d=a_o) = 2\pi \underbrace{\frac{U_{plane-plane}(d=a_o)}{A}}_{dW_{11}/dA=2\gamma_1} \cdot \left(\frac{R_1 R_2}{R_1+R_2}\right)$$

- This approximation is useful because it converts measured $F_{adhesion}$ to surface energy γ_1