Van der Waals Forces between Nanoscale Objects.

Lennard-Jones Potential

repulsive forces

exchange repulsion

hard core repulsion

steric repulsion

$$w(r) = \frac{A}{r^{12}} - \frac{B}{r^{6}} = \boxed{4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]}$$

$w(r) = 0$ at $r = \sigma$ ← minimum force $F = -\frac{dw}{dr}$

minimum energy:

$r = 2^{1/6}\sigma \approx 1.12\sigma$

minimum energy =

$w(r) = -\epsilon$

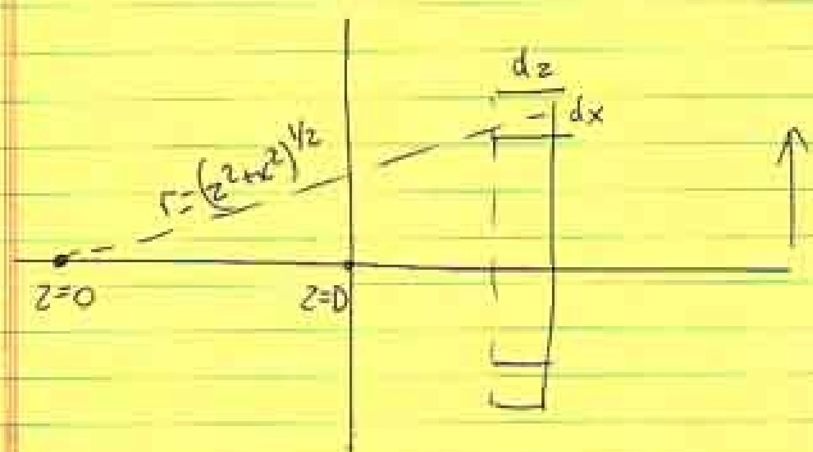
with the attractive contribution

$A = 10^{-77}$ J m^{6} $B = 10^{-134}$ J m^{12}

Molecule-Surface Interactions

Assumption: pair-wise additivity of interaction potential

$w(r) = -C/r^n$



The number of molecules in the ring

$$2\pi \rho x \, dx \, dz$$

ρ - number density of molecules in the solid

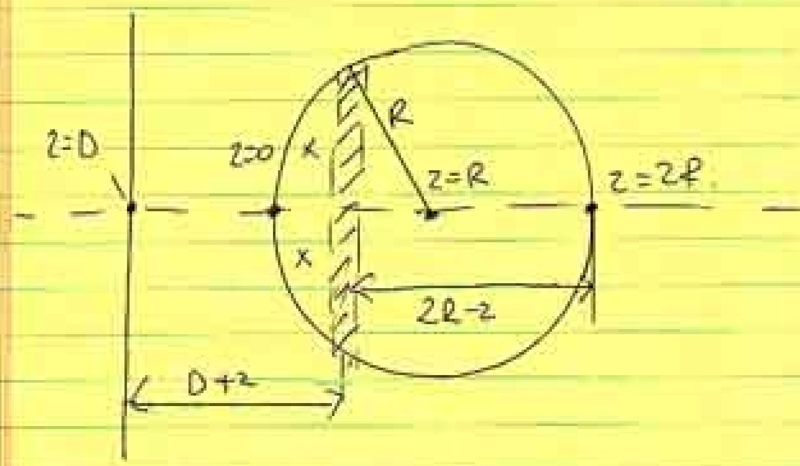
The net interaction

$$w(D) = -2\pi\rho C \int_{z=D}^{z=\infty} dz \int_{x=0}^{\infty} \frac{x\,dx}{(z^2+x^2)^{n/2}} =$$

$$\boxed{n=6 \quad w(D) = \frac{-\pi C\rho}{6D^3}} \qquad = \frac{2\pi C\rho}{(n-2)} \int_D^{\infty} \frac{dz}{z^{n-2}} = \frac{-2\pi C\rho}{(n-2)(n-3)D^{n-3}}$$

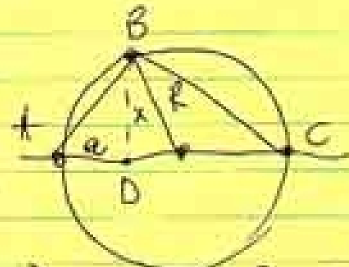
Sphere-Surface Interaction

(Integration of the molecule-surface potential)



chord theorem:

$$x^2 = (2R - z)z$$



$$AC^2 = AB^2 + BC^2 = AD^2 + BD^2 + BD^2 + DC^2$$

$$4R^2 = a^2 + 2x^2 + (2R - a)^2$$

$$x^2 = (2R - a)a.$$

Consider a thin circular section

$\pi x^2 dz = \pi (2R - z) z\, dz$

number of molecules in this section

$\pi \rho (2R - z) z\, dz$

all these molecules are at the distance $D+z$ from the planar surface

$w(D) =$

$$= -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{z=0}^{z=2R} \frac{(2R-z)z}{(D+z)^{n-3}}\, dz$$

for $D \ll R$

$$w(D) = -\frac{2\pi^2 C \rho^2}{(n-2)(n-3)} \int_0^\infty \frac{2Rz\, dz}{(D+z)^{n-3}} =$$

$$\boxed{= -\frac{4\pi^2 C \rho^2 R}{(n-2)(n-3)(n-4)(n-5)\, D^{n-5}}}$$

$$\boxed{\text{for } n=6 \quad w(D) = -\pi^2 C \rho^2 R / 6D}$$

$$\boxed{A = \pi^2 C \rho^2 \quad \text{— Hamaker constant}}$$

(typically of the order of 10^{-19} J)

For two dissimilar materials

$$\boxed{A = \pi^2 C \rho_1 \rho_2}$$

Hamaker constant for two phases 1 and 2 interacting through medium 3, calculated from Lifshitz theory:

$$A = \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right)\left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right)$$

$$+ \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}\left\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\right\}}$$

where ε_i, n_i are dielectric permittivities and coefficients of refraction

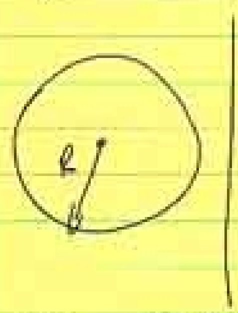
Summary of Interaction Potentials for Model Objects Obtained by Integration of $w(r) = -C/r^6$

$w = -C/r^6$

atom - surface

$w = -\pi C \rho / 6D^3$

sphere surface

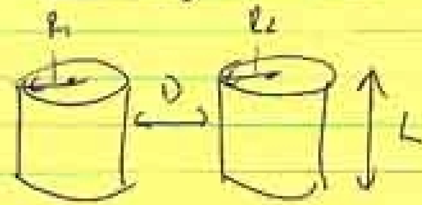


$W = -AR/6D$

Two spheres

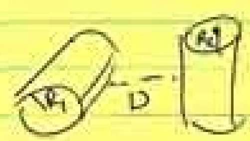
$W = -\frac{A}{6D} \frac{R_1 R_2}{R_1 + R_2}$

Two cylinders



$W = \frac{AL}{12\sqrt{2}\, D^{3/2}} \left(\frac{R_1 R_2}{R_1 + R_2} \right)^{1/2}$

Two crossed cylinders

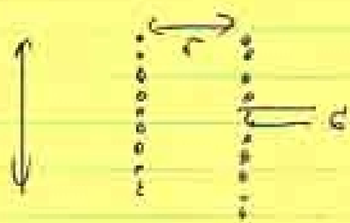


$W = -A\sqrt{R_1 R_2}/6D$

Two surfaces

$$W = -\frac{A}{2\pi D^2}$$ per unit area.

Two parallel chain molecules



$$W = \frac{-3\pi C L}{8\sigma^2 r^5}$$