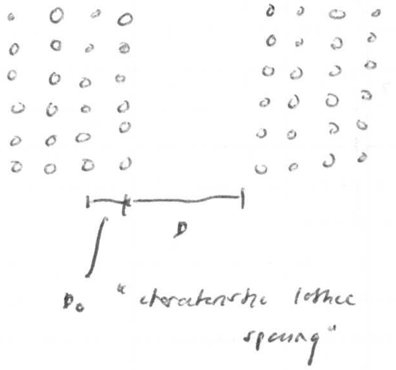
surface and adhesion energy

let's return to the plane-plane case and calculate the total energy

$$W = \underbrace{-(\text{constant})}_{\substack{\text{bulk cohesive energy} \\ E_{1_b}}} + \underbrace{\text{energy of unsatisfied bonds @ surface}}_{\substack{\frac{A}{12\pi D_0^2} \\ E_{1_s}}}$$

+ VDW energy ("from body 1 to body 2")



if we neglect the bulk energy, then

$$W = \frac{A}{12\pi}\left(\frac{1}{D_0^2}\right) - \frac{A}{12\pi}\left(\frac{1}{D^2}\right) = \frac{A}{12\pi D_0^2}\left(1 - \frac{D_0^2}{D^2}\right) \quad \text{per unit area}$$

if $D >> D_0$, then

$$W = \frac{A}{12\pi D_0^2} = 2\gamma, \quad \gamma = \text{"surface energy"}$$

so, γ = half energy needed to separate the material from solid to ∞.

if we consider the arrangement of atoms in the lattice, then

$$\gamma = \frac{A}{24\pi\left(\sigma/2.5\right)^2}, \quad \sigma = \text{lattice spacing (lattice parameter)}$$

this gives very good agreement for all but highly polar liquids.

surface energies of metals are typically higher because of close electron exchange interactions ⇒ metallic bonding

e.g., for 2 metal surfaces,

$$w(D) = -2\gamma \left[1 - \frac{(D-D_0)}{\lambda_m} \right] \exp\left({}^{-(D-D_0)/\lambda_m} \right) \quad \text{per unit area}$$

λ_m = characteristic decay length

we define the work of adhesion as the free energy change required to separate 2 surfaces from contact to ∞ (in vacuum)

$W_{11} = 2\gamma_{11}$:

when we have 2 different materials in contact, e.g. 2 liquids, we define interfacial tension γ_{12}

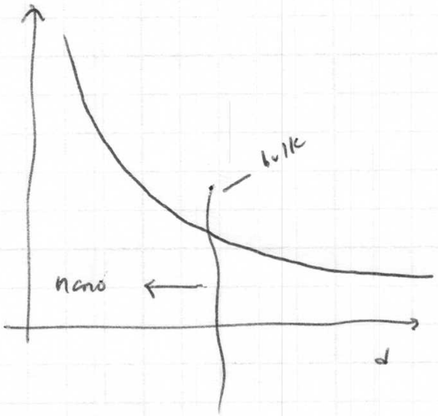
$$\gamma_{12} = \underbrace{\frac{1}{2} W_{11}}_{\substack{\text{create} \\ \text{(open)}}} + \underbrace{\frac{1}{2} W_{22}}_{\substack{\text{create} \\ \text{(open)}}} - \underbrace{W_{12}}_{\substack{\text{connect} \\ \text{(close)}}} = \frac{1}{2} W_{121} = \frac{1}{2} W_{212}$$

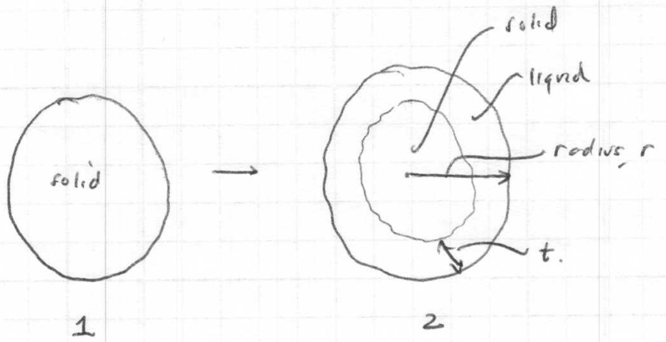
therefore, for 2 spheres in contact,

$$F = 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) W_{132}$$ work of adhesion

NM - nanoscale melting behavior

pawlow's model (1909)





define gibbs' free energy: maximum mechanical work that can be extracted w/o volume expansion or heat transfer

$$dG = \underbrace{\cancel{V\,dP}}_{\text{constant } P} - S\,dT + \underbrace{\cancel{\Sigma \mu_i\,dn_i}}_{\text{no volume change}}$$

$$\Delta G_{\text{melting}} = \underbrace{\Delta G^b}_{\text{bulk}} + \underbrace{\Delta G^s}_{\text{surface}}$$

1/ find ΔG^b

$$\Delta G^b = G_2 - G_1$$

$$= V_\ell \underbrace{g_\ell}_{\text{per unit volume}} + V_s g_s - \underbrace{V_t}_{V \text{ total}} g_s$$

$$= V_\ell g_\ell + V_s g_s - (V_\ell + V_s)\, g_s$$

$$\Delta G^b = V_\ell (g_\ell - g_s)$$

$$= V_\ell \Delta g$$ ← what is Δg?

definition: $\frac{dg}{dT}\Big|_p = -s$ — entropy / volume

so $\Delta g = \int_{T_{m,b}}^{T} -s\,dT$, assume $s(T)$ = constant for each phase

$$\Rightarrow \Delta g^l = (-s^l)(T - T_{mb})$$

$$\Delta g^s = (-s^s)(T - T_{mb})$$

$$\Delta g = \Delta g^l - \Delta g^s = \underbrace{(s^l - s^s)}_{\text{heat of melting } = \frac{h_o}{T_{mb}}}(T_{mb} - T)$$

latent heat of melting (phase change)

$$\Rightarrow \Delta G^b = v_l \frac{h_o}{T_{mb}}(T_{mb} - T)$$

$$= \frac{4}{3}\pi\left(r^3 - (r-t)^3\right)(T_{mb} - T)\left(\frac{h_o}{T_{mb}}\right)$$

2/ find ΔG^s

destroy γ_s
create γ_l
create γ_{sl}

} surface energies, σ equivalent symbol

$$\Delta G^s = 4\pi r^2 \gamma_l + 4\pi (r-t)^2 \gamma_{sl} - 4\pi r^2 \gamma_s$$

$$= 4\pi r^2 (\gamma_l - \gamma_s) + 4\pi (r-t)^2 \gamma_{sl}$$

so $\Delta G^M = \Delta G^s + \Delta G^B$

$$= \frac{4\pi}{3} \frac{h_0}{T_{Mb}} (T_{Mb} - T)\left(r^3 - (r-t)^3\right)$$

$$+ 4\pi r^2 (\gamma_l - \gamma_s) + 4\pi (r-t)^2 \gamma_{sl}$$

imagine we've melted a thickness t, → would it be favorable to melt the rest?

$\Rightarrow$ yes, if $\frac{d\Delta G}{dt} < 0$ (ΔG is maximum)

so let's find where $\frac{d\Delta G}{dt} = 0$

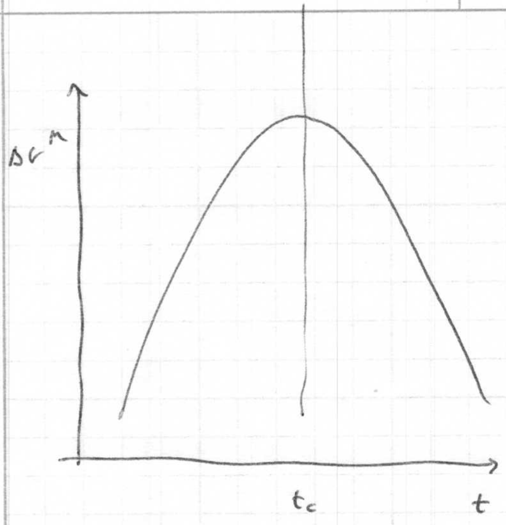
$$\frac{d\Delta G}{dt} = -\cancel{3}\left(\frac{\cancel{4\pi}}{\cancel{3}}\right)\left(\frac{h_0}{T_{Mb}}\right)(r-t)^{\cancel{2}}\,(T_{Mb}-T) - 2\cancel{(4\pi)}\cancel{(r-t)}\gamma_{sl}$$

$$= \frac{-h_0}{T_{Mb}} (r-t)(T_{Mb} - T) - 2\gamma_{sl}$$

$$\Rightarrow \quad t = r - \frac{2 T_{Mb} \gamma_{sl}}{h_0 (T_{Mb} - T)}$$

→ $= t_c$ "critical thickness"

gives t_c as $f(T)$



can show $\frac{d^2 \Delta G}{dt^2} < 0$

$\Rightarrow \frac{d\Delta G}{dt} = 0$ is a maximum

melting happens spontaneously if $t_c \to 0$

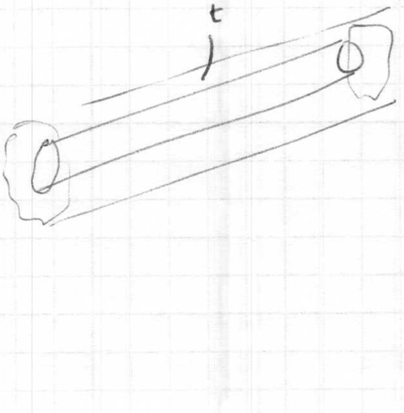
$$: \quad r = \frac{2 T_{mb} \gamma_{sl}}{h_0 (T_{mb} - T)}$$

$$\Rightarrow \quad T_{mb} - T = \frac{2 T_{mb} \gamma_{sl}}{h_0 r}$$

$$★ \quad \Rightarrow \quad \underline{T_M = T_{mb}\left(1 - \frac{2\gamma_{sl}}{h_0 r}\right)}$$

suppressed melting point of a small particle

could do the same for a wire, like



neglecting shell at ends.

in general, we have 3 models of NP melting suppression

$$\frac{T}{T_{mb}} = 1 - \frac{2 l_{in}}{R}\left(\frac{1}{\rho_s h}\right)$$

homogeneous melting : $l_{in} = \sigma_s - \sigma_l \left(\rho_s/\rho_l\right)^{2/3}$

liquid - shell : $l_{in} = \frac{\sigma_{sl}}{1-\delta} + \sigma_l\left(1 - \rho_s/\rho_l\right)$, δ = liquid layer thickness $\delta << 1$

liquid nucleation : $l_{in} = \left[\sigma_{sl},\ 1.5\left(\sigma_s - \sigma_l\left(\rho_s/\rho_l\right)\right)\right]$

if $\rho_s = \rho_l \Rightarrow$ all go to our simple

density - independent model,

↑ here we assume density does not change on melting.

alternative approach : average cohesive energy per atom (Nanda) 2002

total cohesive energy of a NP is $\overbrace{\quad\quad\quad\quad}$ binding energy, energy for moving atoms from lattice positions to infinite separation

$$E_b = \underset{\substack{\uparrow \\ \text{energy/atom} \\ \text{(bulk value)}}}{a_v} \overset{\text{\# atoms}}{N} - (\text{surface area})(\overset{\text{surface energy}}{\gamma})$$

$$\frac{E_b}{N} = a_{v,\,np} = \underline{a_v - \frac{(SA)(\gamma)}{N}}$$

for a sphere, $\dfrac{SA(\gamma)}{N} = \dfrac{4\pi r^2 \gamma}{\frac{4}{3}\pi r^3 \big/ \left(\frac{4}{3}\pi r_a^3\right)}$ — v_a = volume of atom

$$\Rightarrow a_{v,np} = a_v - \frac{3\gamma v_a}{r} = \underline{a_v - \frac{6\gamma v_a}{d}}$$

it has been shown that bulk melting point, T_m

$$T_m = n a_v f^2 / 3k_B z$$

n = exponent of repulsive interatomic potential

f = (atomic displacement at T_m) / lattice constant

z = valency of atoms $\approx$ # of bonds formed by each atom empirically, $a_v = c_1 T_{Mb} + c_2$

$\to c_1 = 5.74\text{e}{-4}$ } → straight lines for (a_s, a_v) versus T_{Mb}.

$a_s = 0.82\, a_v$

so, let's estimate $T_{M,np}$ using the principle of cohesive energy

$$a_{v,np} = c_1 T_{M,np} + c_2$$

universal relationship between cohesive and surface energy

$$c_1 T_{M,np} + c_2 = c_1 T_{Mb} + c_2 - \frac{6\gamma v_a}{d}$$

$$T_{M,np} = T_{Mb} - \frac{6\gamma v_a}{d}\left(\frac{1}{c_1}\right)$$

$$\frac{T_{Mnp}}{T_{Mb}} = 1 - \frac{6}{d}\left(\frac{\gamma v_a}{T_{Mb}\, c_1}\right)$$

$$= 1 - 6\beta/d$$ ← for a sphere.

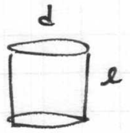
should be dimensionless vs β/d.

generally then

$$\frac{T_{Mnp}}{T_{Mb}} = 1 - \beta\left(SA/vol\right)$$

↑ material properties

cylinders : $\frac{SA}{V} = \frac{2\pi d^2/4 + \pi d l}{\pi d^2/4 \cdot l}$



$$= \frac{4}{d} + \frac{2}{l}$$

$$\Rightarrow \frac{T_{mn}}{T_{mb}} = 1 - \beta\left(\frac{4}{d} + \frac{2}{l}\right)$$

nanowires : $l >> d$

$$\Rightarrow \left(\frac{4}{d}\right)$$

thin films : $l << d$

$$\Rightarrow \left(\frac{2}{l}\right), \quad l = t \Rightarrow \left(\frac{2}{t}\right)$$

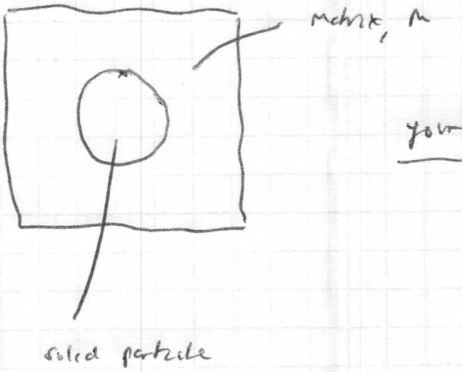
so $\frac{T_{mb} - T_{mn}}{T_{mb}} = \Delta \bar{T}$

sphere, d; wire, d; film, t

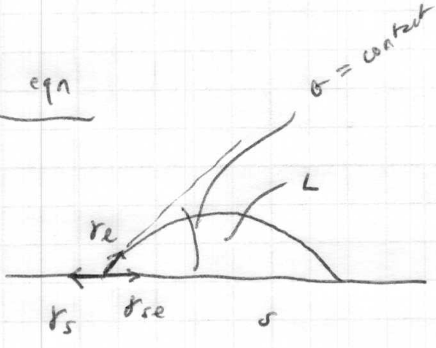
$$= 3 : 2 : 1$$

$$\frac{6}{d} : \frac{4}{d} : \frac{2}{t}$$

finally let's consider the effect of a matrix on melting



young's eqn



if we sum forces, $\gamma_\ell \cos\theta = \gamma_s - \gamma_{s\ell}$

if liquid wets fully, $\gamma_\ell = \gamma_s - \gamma_{s\ell} \Rightarrow \underline{\gamma_{s\ell} = \gamma_s - \gamma_\ell}$

if in a matrix, $\gamma_{s\ell} = \gamma_{sm} - \gamma_{\ell m}$

then, $T_M = T_{Mb}\left(1 - \dfrac{2(\gamma_{sm} - \gamma_{\ell m})}{L_0 r}\right)$

if $\gamma_{\ell m} > \gamma_{sm} \Rightarrow$ superheating!

matrix prevents melting because it "grabs" the outer atoms.

e.g., in some ceramic composites