(1a)

$$\frac{T_m - T_m^b}{T_m^b} = \frac{2(\gamma_{LW} - \gamma_{SW})}{H \rho \Delta_m h} \quad \text{——①}$$

where T_m^b = bulk melting temp.

γ_{LW} & γ_{SW} = liquid-wall & solid-wall surface tension

$\rho = \frac{N}{V}$ = density

$\Delta_m h = h_L - h_S$ ⇒ latent heat of melting

Gibbs-Thomson eqn

$$T_m(H) = T_T^b + \frac{2(\gamma_{LW} - \gamma_{SW})}{\rho_S \Delta_m s H} \quad \text{——②}$$

In the $\mu A_w HT$ ensemble, the thermodynamic potential is the grand potential

$$\Omega = U - TS - \mu N = -PA_w H + 2\gamma A_w \quad \text{——③}$$

with internal energy

$$U = TS - PA_w H + 2\gamma A_w + \mu N$$

where S = entropy

P = pressure

γ = surface tension

@ coexistence between the liquid & solid phases;

$$\Omega_L = \Omega_S$$

but $$P_L - P_S = \frac{2(\gamma_{LW} - \gamma_{SW})}{H} \quad \text{——④}$$

this depends on the difference in surface tension between the liquid & the walls between the solid & walls, respectively as well as on the pore size (H)

$$d\Omega = -S_L dT - P A_w dH + (2\gamma - PH) dA_w - N d\mu \quad \text{——— (5)}$$

$$(S_L - S_s) dT + \frac{2A_w(\gamma_{LW} - \gamma_{SW})}{H} dH + (N_L - N_s) d\mu = 0 \quad \text{— (6)}$$

Integrating eqn (6) ultimately $[H \to \infty]$

$$\frac{dH}{H^2} = -\frac{dT}{2(\gamma_{LW} - \gamma_{SW})} \left[(\rho_L S_L - \rho_s S_s) + (\rho_L - \rho_s) \frac{d\mu}{dT} \right] \quad \text{— (7)}$$

where $\rho = \frac{N}{V}$ = density

entropy / particle, $s = \frac{S}{N}$

Also; $$\frac{d\mu}{dT} = \frac{\rho_L^b s_L^b - \rho_G^b s_G^b}{\rho_L^b - \rho_G^b} = -s_L^b \quad \text{——— (8)}$$

where b (superscript) = bulk (unconfined) liquid & gas phases.

In the case of isobaric - isothermic liquid phase, the result would be exactly $-s_L^b$

$$\therefore \frac{dH}{H^2} = -\frac{(\rho_L - \rho_s)(s_L - s_L^b) + \rho_s (s_L - s_s)}{2(\gamma_{LW} - \gamma_{SW})} dT \quad \text{— (9)}$$

For sufficiently large confining distances (correspondingly small shift in the melting temp, $T_m - T_m^b$)

Assumption: $|\rho_L - \rho_s| \ll \rho_s$

$$\frac{dH}{H^2} = -\frac{\rho_s^b \Delta_m s^b}{2(\gamma_{LW} - \gamma_{SW})} dT \qquad (10)$$

with $\Delta_m s^b = s_L^b - s_s^b$ being the bulk entropy of melting

temp.

Integrating eqn (10) along a thermodynamic path connecting the confined system for finite H & corresponding T_m and an ~~unconfined~~ unconfined one [$H \to \infty$ and bulk melting temp T_m^b)

Assumption: ratio on RHS is independent of temp. & confining distance over the considered range.

Under these condition;

$$\int_H^{+\infty} \frac{dH}{H^2} = -\frac{\rho_s^b \Delta_m s^b}{2(\gamma_{LW} - \gamma_{SW})} \int_{T_m}^{T_m^b} dT$$

$$\therefore \quad T_m(H) = T_T^b + \frac{2(\gamma_{LW} - \gamma_{SW})}{H \rho_s^b \Delta_m s^b}$$

(16) Using a "confined Clapeyron" approach in the $\mu A_w HT$ ensemble:

The slit pore has a surface area A_w, a width H & a pore volume $V = A_w H$ [from the fig in the paper]

Assumption: both confining walls are make of the same material so that their interaction with the confined fluid or solid are identical

$$\Omega = U - TS - \mu N = -PA_w H + 2\gamma A_w$$

with internal energy

$$U = TS - PA_w H + 2\gamma A_w + \mu N$$

where S = entropy

P = pressure

γ = surface tension

@ coexistence between the liquid & solid phases, thermodynamic potentials of the 2 phases are equal $\Omega_l = \Omega_s$

(c) Ostwald – Freundlich Eqn

$$\Rightarrow x_a = x_a^{\infty} \exp\left[\frac{2V_a\gamma}{R_a T R_{seq}}\right]$$

where X_a = mole fraction

V = molar volume

R_{seq} = radius

γ = interfacial tension

R_a = gas constant

T = temp

Kelvin eqn $\Rightarrow$ $\ln\left(\frac{p(r)}{p}\right) = \frac{2\gamma V_{molecule}}{k_B T_r}$ OTE

$$\frac{dP}{dT} = \frac{PL}{T^2 R}$$

$$p(r_1, r_2) = P - \frac{\gamma \rho_{vapor}}{(\rho_{liquid} - \rho_{vapor})}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

If particles is assumed to be spherical, then $r = r_1 = r_2$

$$\therefore p(r) = P - \frac{2\gamma \rho_{vapor}}{(\rho_{liquid} - \rho_{vapor})r}$$

Since $\rho_{liquid} >> \rho_{vapor}$, then $\rho_{liquid} - \rho_{vapor} \approx \rho_{liquid}$

$$\therefore p(r) \approx P + \frac{2\gamma \rho_{vapor}}{\rho_{liquid} \cdot r}$$

Assuming vapor obeys the ideal gas law;

$$\rho_{vapor} = \frac{M_{vapor}}{V} = \frac{MW \cdot n}{V} = \frac{MW \cdot P}{RT} = \frac{MW \cdot P}{N_A k_B T}$$

Since $\frac{MW}{N_A}$ = mass of one molecule of vapor/liquid

$$\therefore \frac{\frac{MW}{N_A}}{\rho_{liquid}} = \text{volume of one molecule} = V_{molecule}$$

$$\therefore p(r) \approx P + \frac{2\gamma V_{molecule} P}{k_B T r} = P + \frac{R_{critical} P}{r} \quad \text{where } R_{critical} = \frac{2\gamma V_{mol}}{k_B T}$$

Thus; $\frac{p(r) - P}{P} \approx \frac{R_{critical}}{r}$

Since; $\frac{p(r)}{P} = 1 - \frac{P - p(r)}{P}$

then, $\log\left(\frac{p(r)}{P}\right) = \log\left(1 - \frac{P - p(r)}{P}\right)$

since $p(r) \approx P$, then $\frac{P - p(r)}{P} << 1$

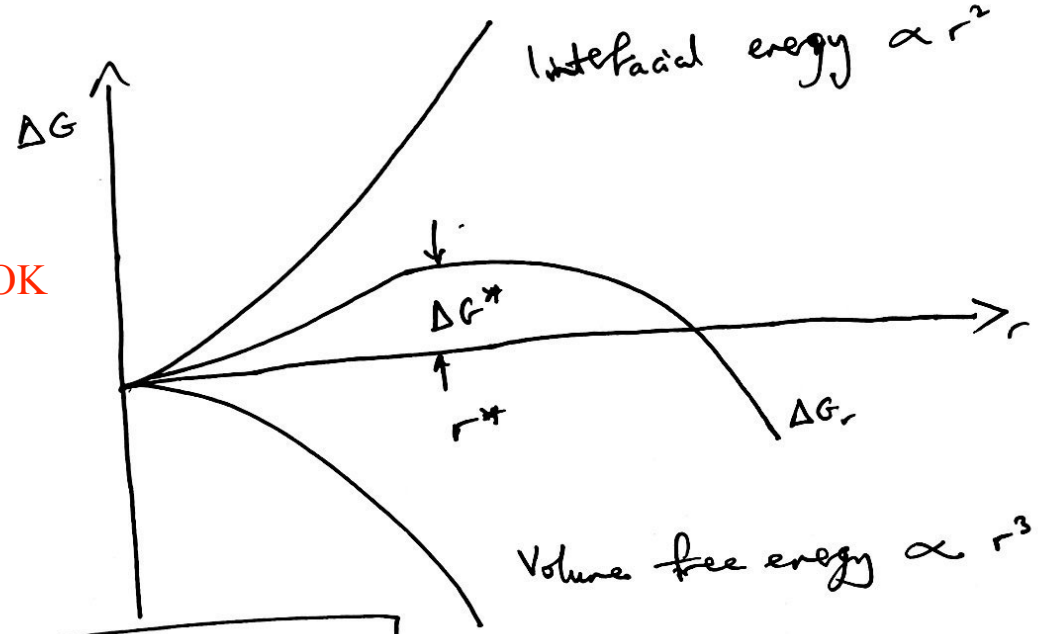
If $x << 1$, then $\log(1-x) \approx -x$

Hence; $\log\left(\frac{\rho(r)}{\rho}\right) \approx \frac{\rho(r) - \rho}{\rho}$

$\therefore \log\left(\frac{\rho(r)}{\rho}\right) \approx \frac{R_{critical}}{r}$

d) -20

(1e)



OK

Homogeneous nucleation

Below T_m, ΔG_v is positive, so formation of small volume of solid has negative contribution

If γ_{SL} is isotropic, the shape should be sphere with radius r

$$\Rightarrow \Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

$$r^* = \frac{2\gamma_{SL}}{\Delta G_v} = \left(\frac{2\gamma_{SL} T_m}{L_v}\right)\frac{1}{\Delta T}$$

Heterogeneous nucleation

$$\Delta G_{heterogeneous} = \Delta G_{homogeneous} \times f(\theta)$$

where $$f(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

$$r^* = -\frac{2\gamma_{\alpha\beta}}{\Delta G_v}$$

(2a) Type of system: fully isomorphous OK

Determination of composition & amounts of phases

⇒ Lever rule [Using a tie-line]

One would expect that as temperature is reduced and the spherical domains start to form.

α ⇒ 85 at% Ni

L ⇒ 75 at% Ni

(2b) Phase region : Eutectic

OK Triple point : Eutectic

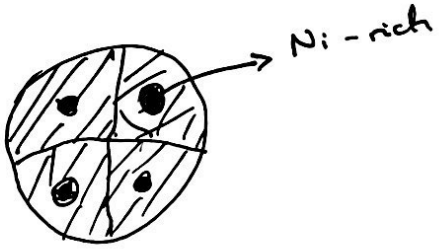
Reaction : $L \rightarrow Ni + Zr_2Ni_3$

Gibb's Phase Rule:

$F = C - P + 1$ [at constant pressure]

$F = 2 - 3 + 1$

$F = 0$



(2d) An intermetallic phase is a chemical compound consisting of 2 or more metals

-15

@ Room temp (R.T) → [1170°C] ; Zr_5Ni_3 = 15 at% Zr

@ = = = → [1438°C] ; Zr_7Ni_3 = 22 at% Zr

@ = = = → [920°C] ; Zr_5Ni_3 = 25 at% Zr

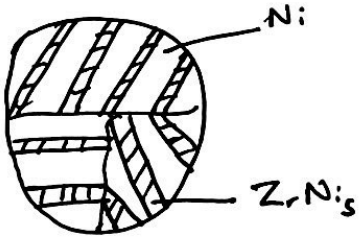
@ = = = → [1163°C] ; $Zr_{7}Ni_{10}$ = 41 at% Zr

@ = = = → [1180°C] ; Zr_9Ni_{11} = 28 at% Zr

@ 975°C → [1157°C] ; Zr_9Ni_{11} = 45 at% Zr

(2c)

-5



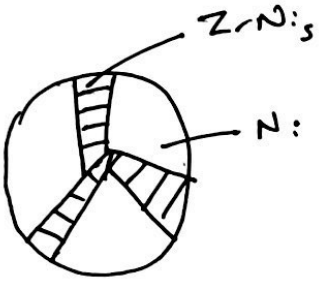
Quench to the bottom

Phase Fraction of Ni = 0.67

Zr = 0.33

Composition of Ni = 100% Ni

= = Zr_5Ni_3 = 85% Ni



Slow cool

Phase fraction of Ni = $\frac{15-5}{15-0}$ = 0.67

= = = Zr_2 = 1 − 0.67 = 0.33

Composition of Ni = 100% Ni

Composition of Zr_2Ni_5 = 85% Ni

(2e)