ECE5320

Lecture #4

CURVATURE EFECTS

RECALL:

$$|\Delta\mu_1| > |\Delta\mu_2|$$

$$\boxed{\Delta\mu = \frac{4\gamma V_m}{D}} \Leftarrow \left\{ \begin{array}{l} P(r) = P_\infty \exp\left(\dfrac{4\gamma V_m}{RT\cdot D}\right) \\ \Delta\mu = RT\ln\dfrac{P(r)}{P_\infty} \end{array} \right.$$

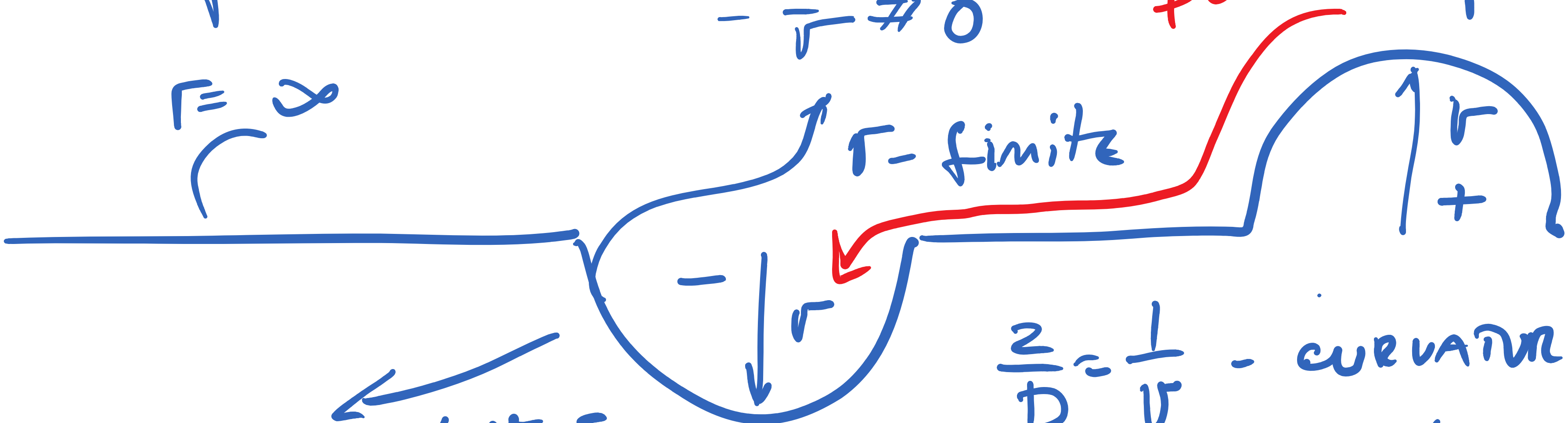
CURVATURE EFECT

$\frac{1}{r}=0$

$r=\infty$

$-\frac{1}{r}\neq 0$

$+\frac{1}{r}\neq 0$



$\frac{2}{D}=\frac{1}{r}$ - CURVATURE

$$\Delta\mu = -\frac{4\gamma V_m}{D}$$

$$\Delta\mu < 0$$

CURVATURE DRIVEN SURF. RELAXATION

$$\Delta\mu = +\frac{4\gamma V_m}{D}$$

$$\Delta\mu > 0$$

CURVATURE EFECT

- TRANSPORT FROM $+\frac{1}{r}$ TO $-\frac{1}{r}$ VIA DIFFUSION

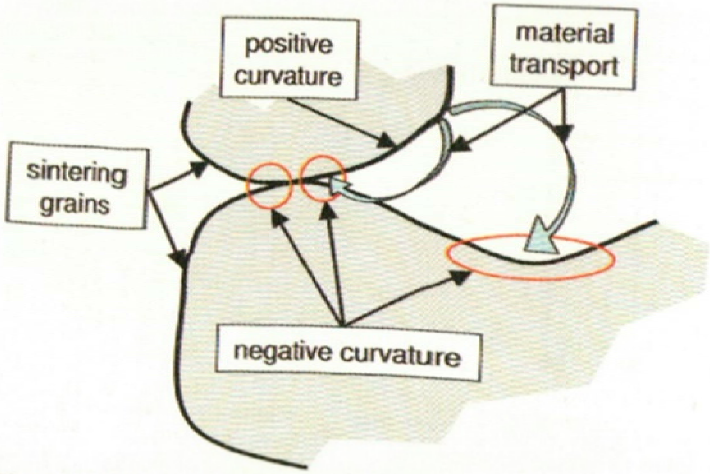


Figure 2.19 Two sintering grains. The diagram indicates ranges with positive and negative curvature, and material transport associated with the curvature-dependent vapor pressure.

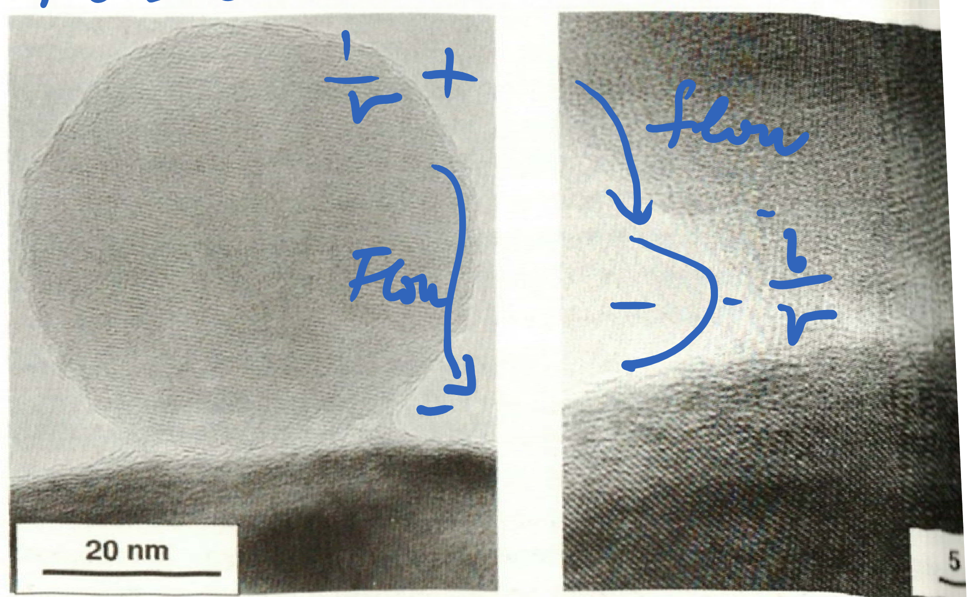
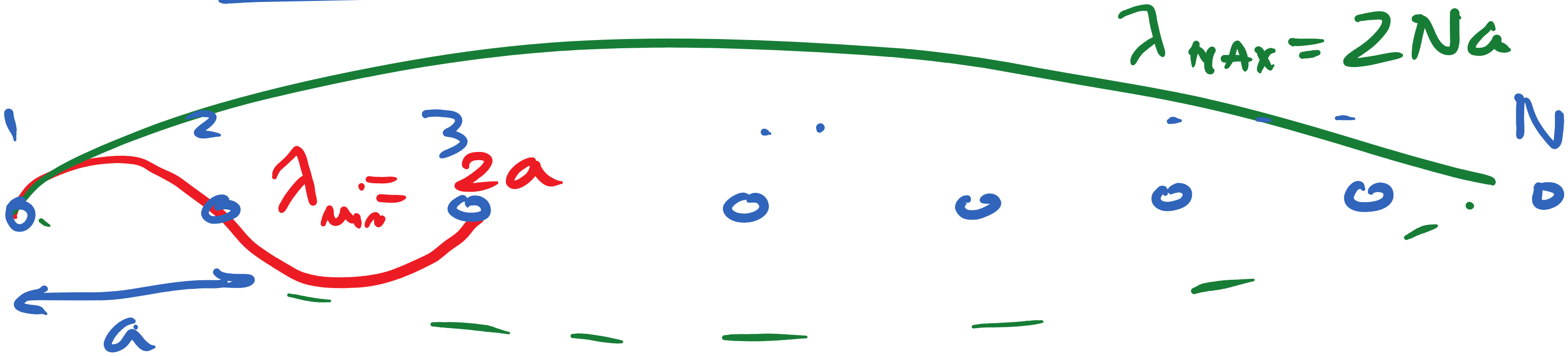


Figure 2.20 Two sintering alumina particles. The curvature-dependent vapor pressure causes material to evaporate at the positively curved surfaces of the particles, and to condense in the wedge (or neck) between the two particles, where the curvature is negative.

- SINTERING

Heat Capacity of NP



CRYSTAL LATTICE

$\nu_{max} = \frac{c}{2a}$ C – SPEED OF SOUND

$\nu_m = \frac{c}{2Na}$

HEAT CAPACITY OF NP

- INTERNAL ENERGY U

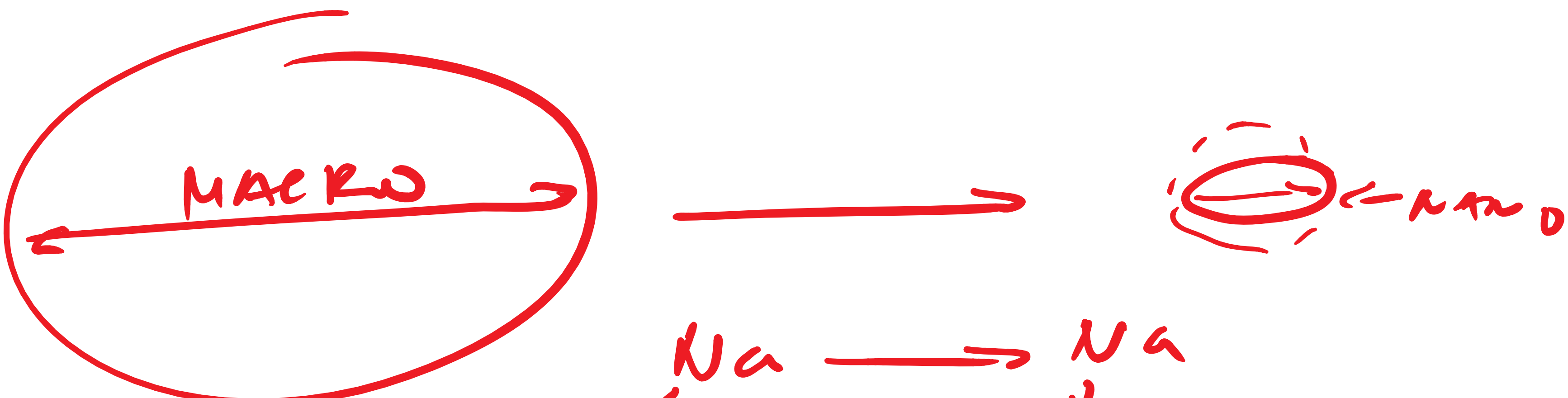
$$U = \sum_{1}^{n} n_i \nu_i h \qquad n_i - \text{MODE OF VIBRATIONS}$$

$$\lambda = \frac{2Na}{1};\ \frac{2Na}{2} \ldots \frac{2Na}{n}$$

$$\nu_i = \frac{c}{2Na},\ \frac{2c}{2Na},\ \ldots \frac{nc}{2Na}$$

Heat Capacity of NPs

$$C_V = -\frac{\partial U}{\partial T}\Big|_{V=const} = T\frac{\partial S}{\partial T}\Big|_{V=const}.$$



$Na \longrightarrow Na$

$10^9 - 10^{20}$ $\sim 10 - 1000$

Heat Capacity of NP

$U = \sum_{1}^{n} n_i \cdot \nu_i h$

- ν_i, n_i — size dependent.
- sum is size dependent

$n_i \rightarrow$ DECRESES

ν_i TAKES HIGHER TERMS

$u \ [\frac{J}{mol}]$

$N \downarrow \ L \downarrow \ n_i \downarrow$

$U = \sum_{1}^{n} n_i \cdot \nu_i h$

FOR THE SAME NUMBER OF ATOMS, $U_{NP} < U_B$

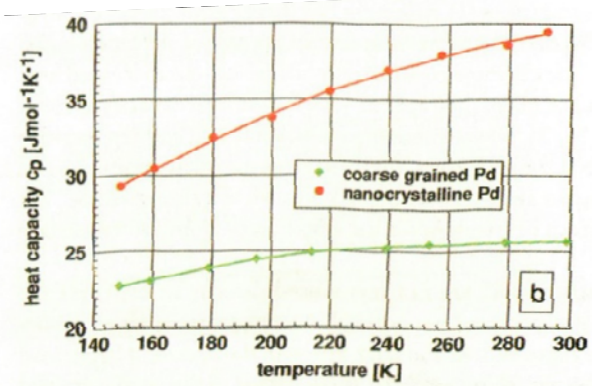
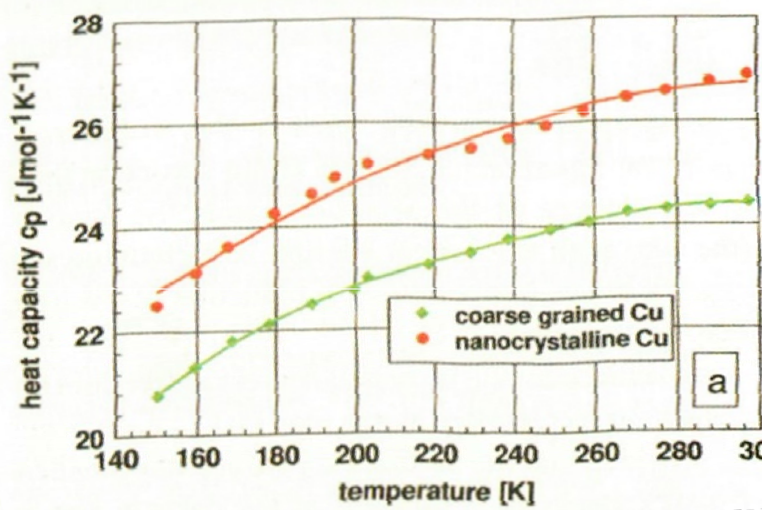


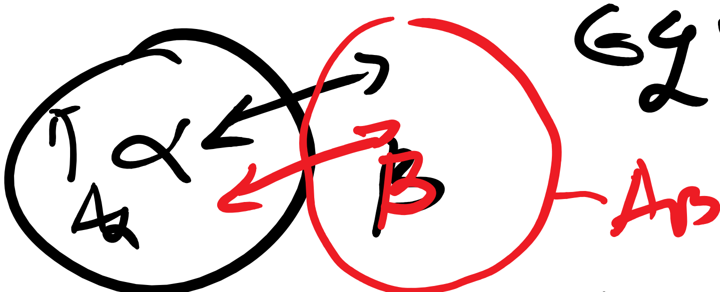
Figure 3.4 Comparative heat capacity for sintered metallic nanocrystalline materials and coarse-grained material [2]. (a) Copper materials; (b) palladium materials. In both cases, the heat capacity for nanocrystalline is greater than for coarse-grained material.



Phase Transformation in NP

$$U_\alpha - TS_\alpha + \gamma_\alpha A_\alpha = U_\beta - TS_\beta + \gamma_\beta A_\beta$$

equilibrium



$$S_\alpha - S_\beta = \Delta S \qquad U_\alpha - U_\beta = \Delta U = \Delta H$$

$$\Delta G = 0; \quad \Delta G = \Delta U - T\Delta S + \gamma_\alpha A_\alpha + \gamma_\beta A_\beta$$

PHASE TRAST. IN NP

$$A_{NP,1}\left[\frac{m^2}{mol}\right] = \frac{6M}{\rho D}$$

ρ – DENSITY $\left[\frac{kg}{m^3}\right]$

D – DIAMET. NP

M – MOLAR WEIGHT $\left[\frac{kg}{mol}\right]$

AS THE ONE PHASE GROW

D_α CHANGES AS WEL AS D_B !

$$\frac{D_B}{D_\alpha} = \left(\frac{V_{m,B}}{V_{m,\alpha}}\right)^{1/3} = \left(\frac{\rho_{m,\alpha}}{\rho_{m,B}}\right)^{1/3} = \left(\frac{\rho_\alpha}{\rho_B}\right)^{1/3}$$

Phase Transf. in NP

$$\Delta G = \Delta U - T\Delta S + \gamma_B \cdot \frac{6M}{\rho_B D_B} - \gamma_\alpha \frac{6M}{\rho_\alpha D_\alpha}$$

$$\Delta G = \Delta U - T\Delta S + \gamma_B \frac{6M}{\rho_B D_B} - \gamma_\alpha \cdot \frac{6M}{\rho_\alpha D_B} \left(\frac{\rho_\alpha}{\rho_B}\right)^{2/3}$$

$$\boxed{D_\alpha = \left(\frac{\rho_B}{\rho_\alpha}\right)^{1/3} D_B}$$

$$\frac{\Delta U}{\Delta S} = T_{Bulk}$$

$$\Delta G = 0 \Rightarrow$$

PHASE TRANSF. IN NP

$$\underbrace{\frac{\Delta U}{\Delta S}}_{\substack{\downarrow \\ T_{\text{TRANSF. FOR BULK}}}} - \underbrace{\frac{6M\gamma_B}{\rho_B D_B \Delta S}\left[1-\left(\frac{\gamma_B}{\gamma_\alpha}\right)\left(\frac{\rho_B}{\rho_\alpha}\right)^{2/3}\right]}_{\substack{\Delta T \\ \text{(FINITE SIZE)}}} = T_{NP}$$

$$\Delta T = T_{\text{BULK}} - T_{NP} = \frac{6M\gamma_B}{\rho_B D_B \Delta S}\left[1-\left(\frac{\gamma_B}{\gamma_\alpha}\right)\left(\frac{\rho_B}{\rho_\alpha}\right)^{2/3}\right]$$

Phase Transf. in NP

$$T_{bulk} = \frac{\Delta U}{\Delta S} \Rightarrow \Delta S = \frac{\Delta U}{T_{bulk}} = \frac{\Delta U}{T}$$

$$\boxed{\Delta T = \frac{6 M T_{bulk} \gamma_B}{D_B \, \Delta U \, \rho_B} \left[1 - \left(\frac{\gamma_\alpha}{\gamma_B} \right) \left(\frac{\rho_B}{\rho_\alpha} \right) \right]}$$

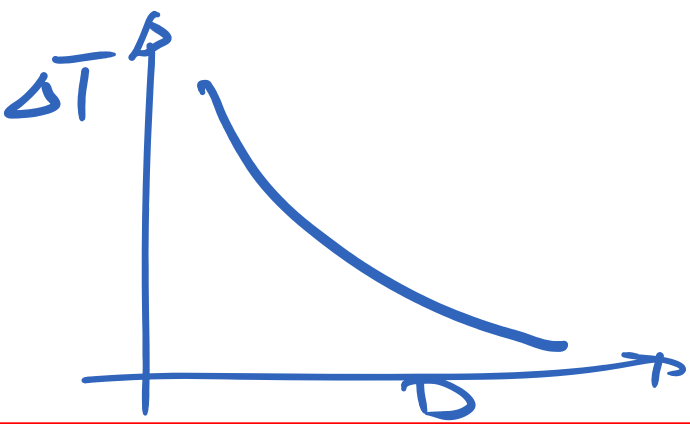
Gibbs-Thomson eq. restated.

G-T Eq.

$$\alpha = \left[1 - \frac{\gamma_\alpha}{\gamma_B} \cdot \left(\frac{\rho_B}{\rho_\alpha}\right)^{2/3}\right]$$

$$\Delta T = \alpha \cdot \frac{\gamma T_{Bulk}}{\Delta U D} \cdot \frac{6M}{\rho}$$ in many situations

$$\Delta T \approx \frac{\gamma T_{Bulk}}{\Delta U D} \cdot \frac{6M}{\rho}$$



$$\alpha \approx 1$$

G-T EXAMPLE

RELEVANT PARAMETERS OF G-T EQ.

Table 3.1 Characteristic constants (β) [according to Equation (3.8)] responsible for changes in the liquid–solid transition temperature for metals, as derived from their materials data.

Metal	$\frac{\gamma_{liquid}}{\gamma_{solid}}$	$\left(\frac{\rho_{solid}}{\rho_{liquid}}\right)$	$\left(\frac{\rho_{solid}}{\rho_{liquid}}\right)^{2/3}$	$\frac{\gamma_{liquid}}{\gamma_{solid}}\left(\frac{\rho_{solid}}{\rho_{liquid}}\right)^{2/3}$
Copper	0.90	1.11	1.07	0.97
Gold	0.87	1.11	1.07	0.93
Silver	0.82	1.12	1.08	0.89

$\rho_{solid}/\rho_{liquid} < 1$ OR > 1 $\qquad 0 < \Delta T < 0$!

G-T. e.g. EXAMPLES vs. EXPERIMENT.

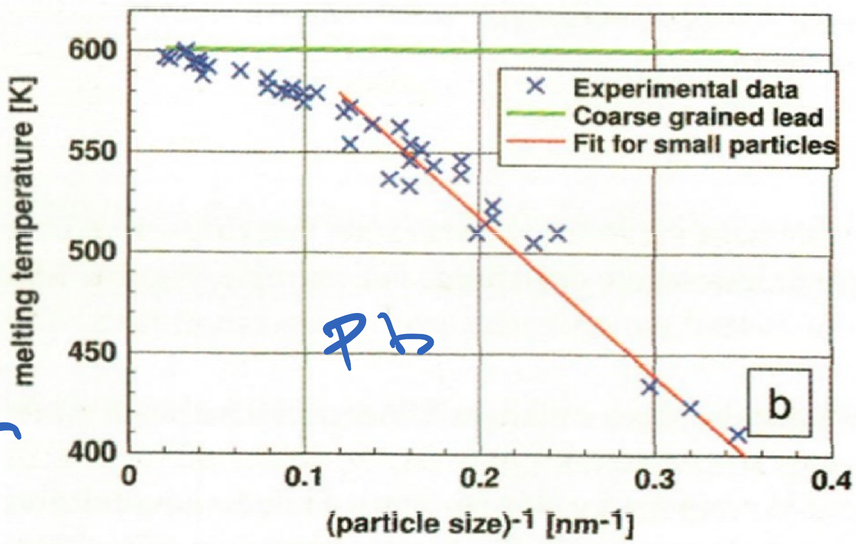
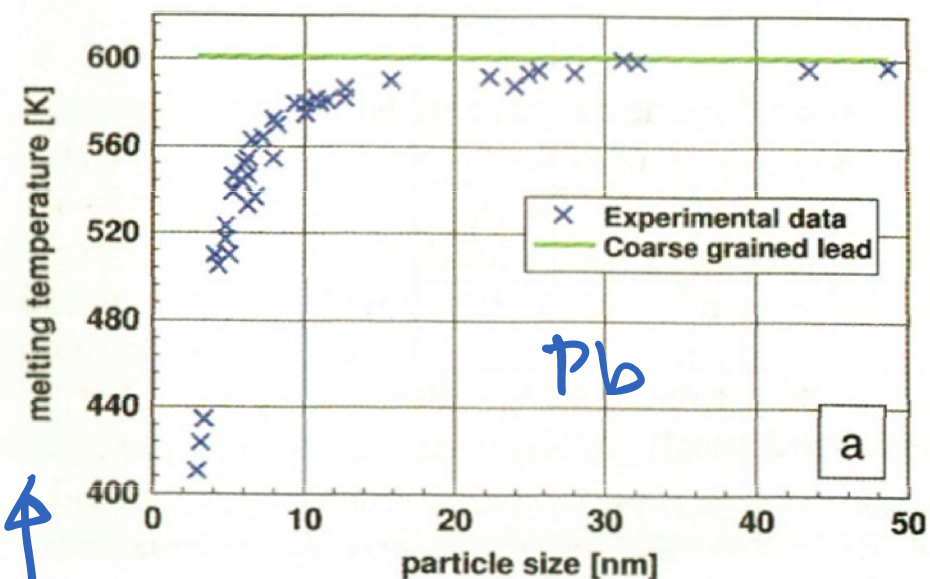


Figure 3.9 The melting point of lead as a function of particle size,

T-ΔT



T-ΔT

Eq vs. EXPERIMENTS

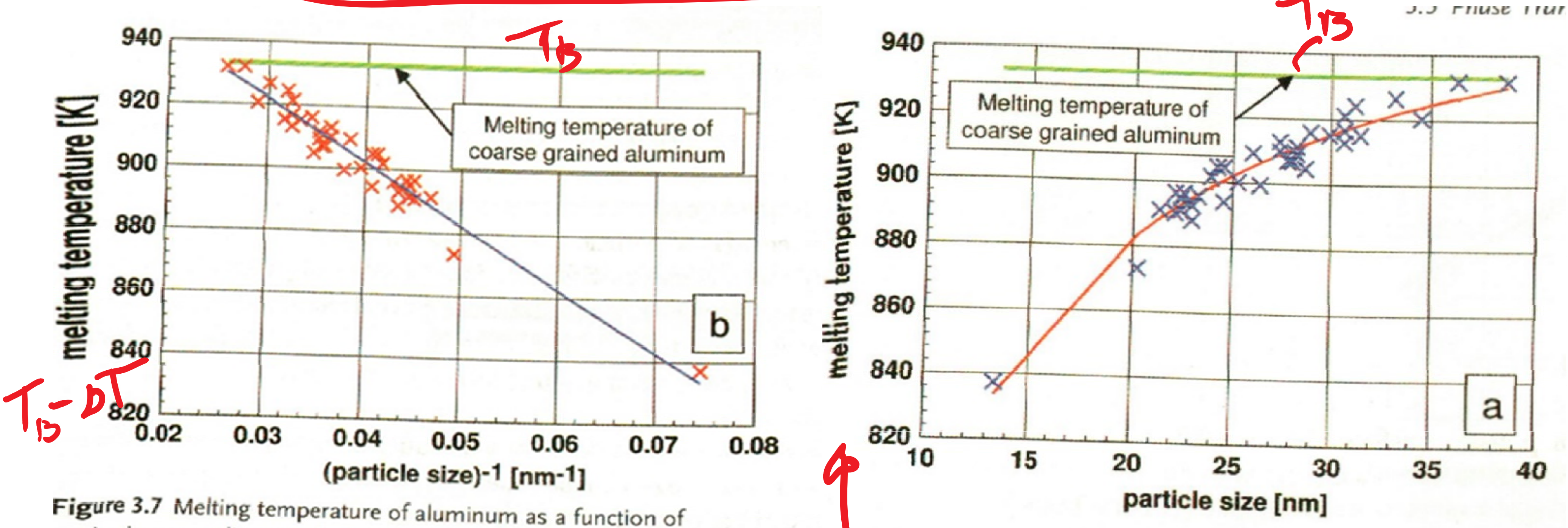


Figure 3.7 Melting temperature of aluminum as a function of grain size, according to Eckert *et al.* [11]. The melting temperature of the bulk material is indicated by the bold line. (a) Aluminum melting points plotted versus particle size; (b) aluminum melting points plotted versus inverse particle size. Note the inverse proportionality as described in Equation (3.7).