ECE5320

Lecture #5

NANO-PARTICLE FUSION REVISITED

REMEMBER:

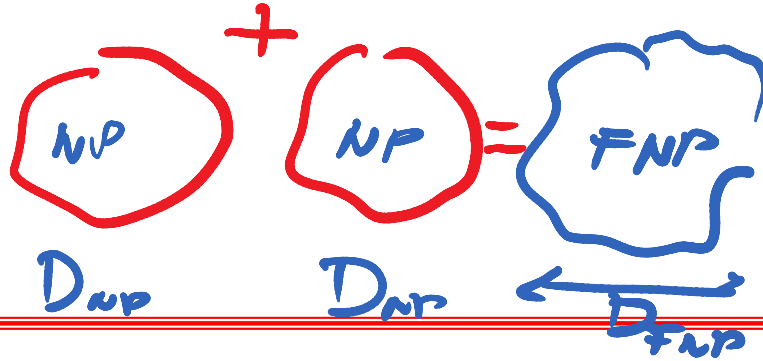
$$\Delta T_{FUS} = \frac{\Delta h_N}{\rho_{NP} \cdot c_p} \cdot \frac{6}{\pi D_{NP_F}} \quad (1)$$

↑ FUSED NP

$$\Delta h_N = \Delta U_f = \gamma \Delta a_{\uparrow} = \gamma \pi D^2 (2 - 2^{2/3})$$

AREA DECREASE

$$\Delta T_{FUS} = \frac{\gamma}{\rho c_p} \cdot \frac{0.413}{D_{FNP}} \quad (2)$$



NANO-PARTICLE FUSION – REVISITED

MELTING IS POSIBLE DURING NP FUSION

$$T_{NP} = T_{BULK} - \Delta T(D)$$

$$T_{NP} = T_{BULK} - \frac{6 M T_{BULK} \gamma_m}{D \Delta U_m \rho_m} \cdot \alpha \quad (7)$$

$$\alpha = \left[1 - \left(\frac{\gamma_s}{\sigma_a}\right) \cdot \left(\frac{\rho_l}{\rho_s}\right)^{2/3}\right]$$

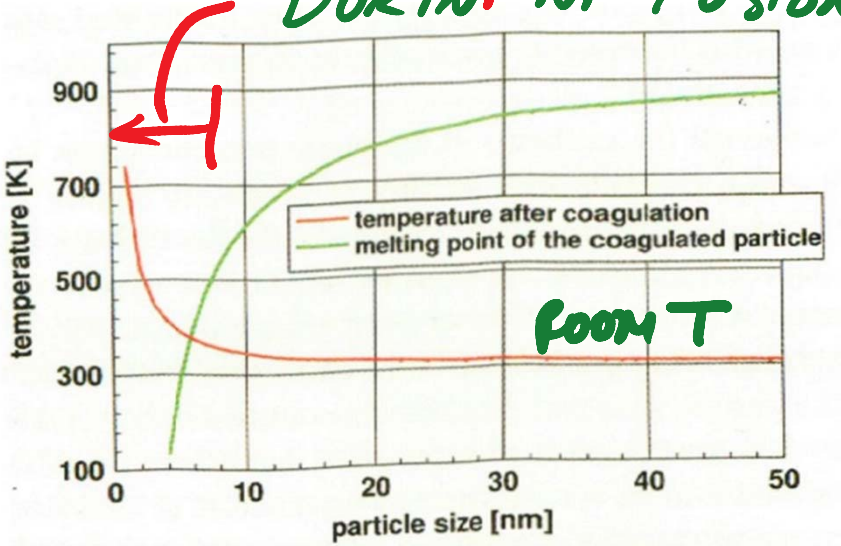


Figure 3.13 Temperature after coagulation of two aluminum particles of equal size. The melting temperature of aluminum nanoparticles is plotted as a function of particle size. Temperature flashing during coagulation may cause melting of the coagulated particle.

COMBINING (7) AND (1) WITH 2

STRUCTURES OF NP

- EXP. OBSERVATION:
NP TAKE STRUCTURE OF THE HIGH TEMP-STABLE BULK PHASE

- WHY: ?

- ONE REASON $T_{M/PT}$ ↓

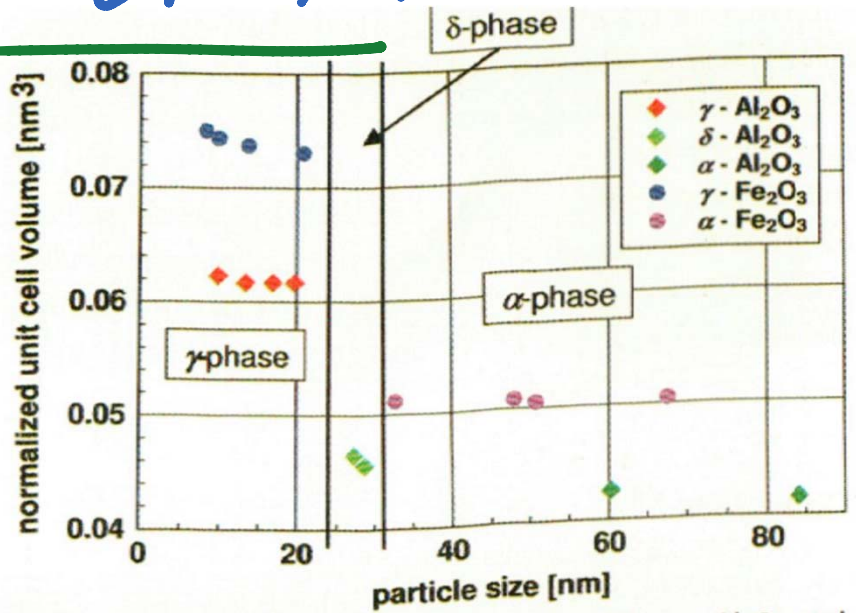
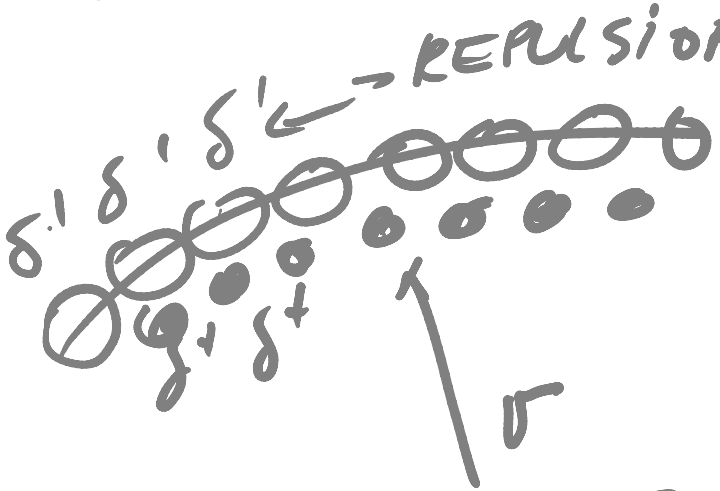


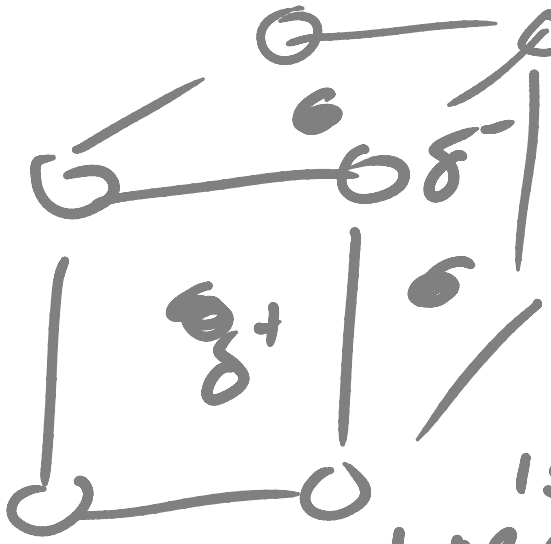
Figure 3.14 Normalized unit cell volume for different Al_2O_3 and Fe_2O_3 phases as a function of grain size [15]. Normalization provides a constant number of formula units per unit cell; otherwise, comparison is impossible. In the γ-phase, the unit cell volume is increased as the particle size decreases. A preference for high-temperature structures as the particle size decreases is clearly visible.

STRUCTURE OF NPs

- GENERAL RULE: NP TAKE THE PHASE THAT HAS MORE SYMETRIC ARRANGEMENT.

- OXIDES:



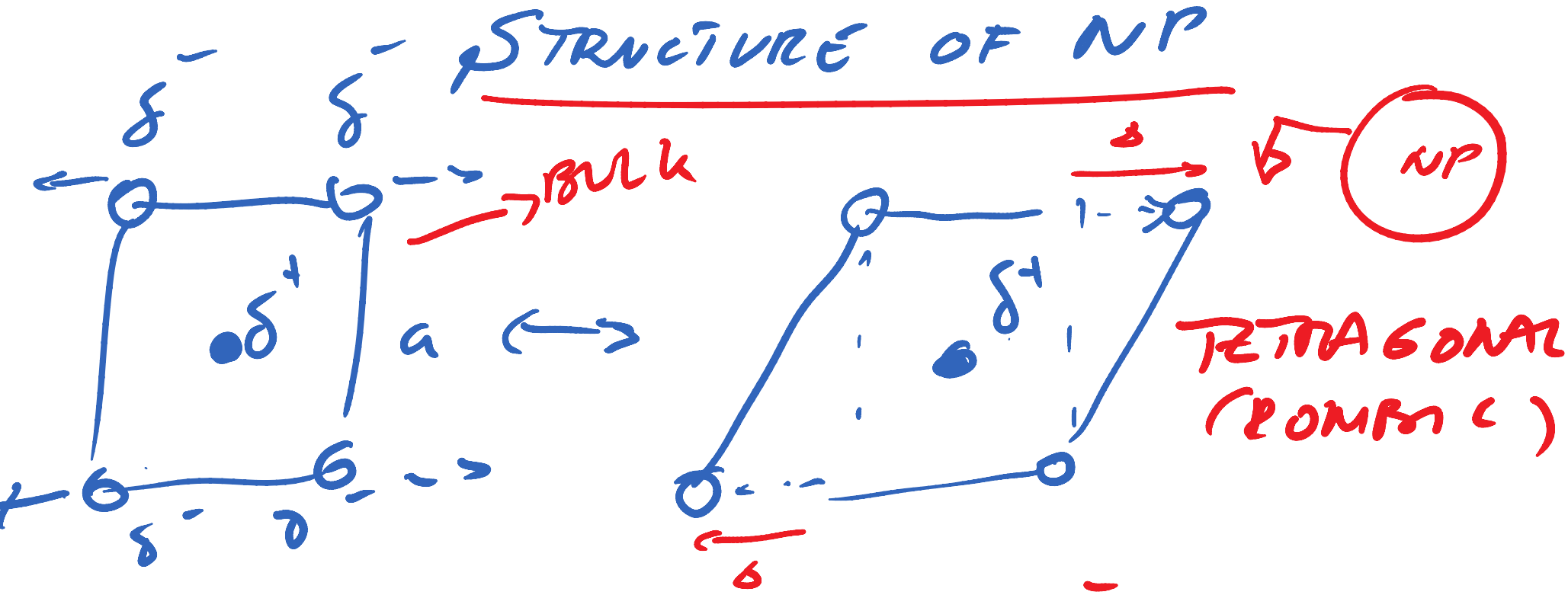


Γ ↓

$F_{\delta^-\delta^-}$ ↑

- IF THERE IS PHASE WITH LARGER SEPARAT. BETWEEN OXIGEN, THIS ONE IS TAKEN BY NP.

STRUCTURE OF NP

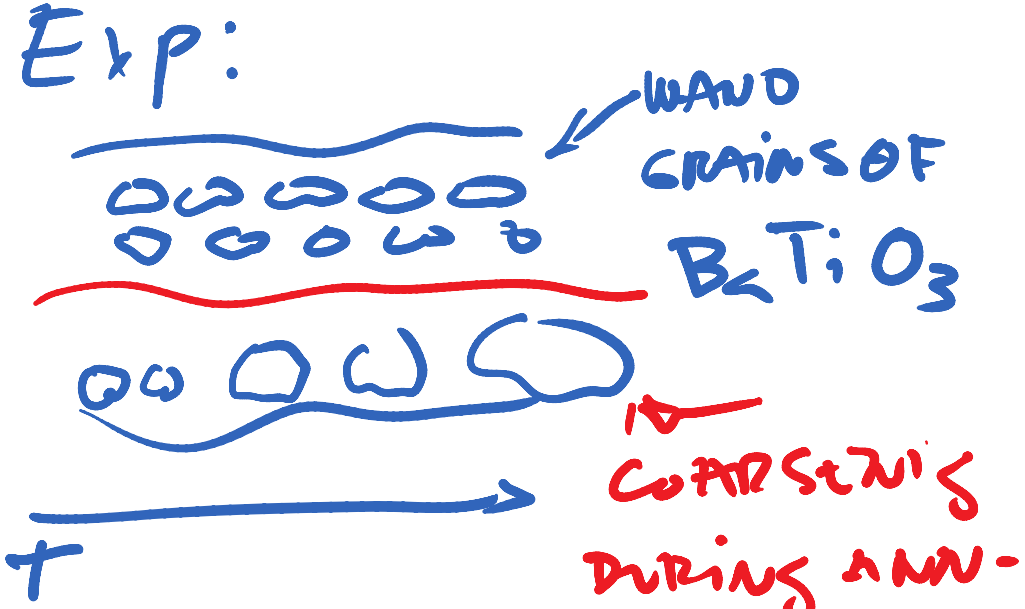


→ DUE TO OXIGEN δ^- - REPULSION

PHASE THAT IS STABLE AT ↑T, IS TAKEN!

STRUCTURE OF NP

EXP:



NP/NG → D - INCREASE

NANOGRAINS

LATTICE CONTRACTS

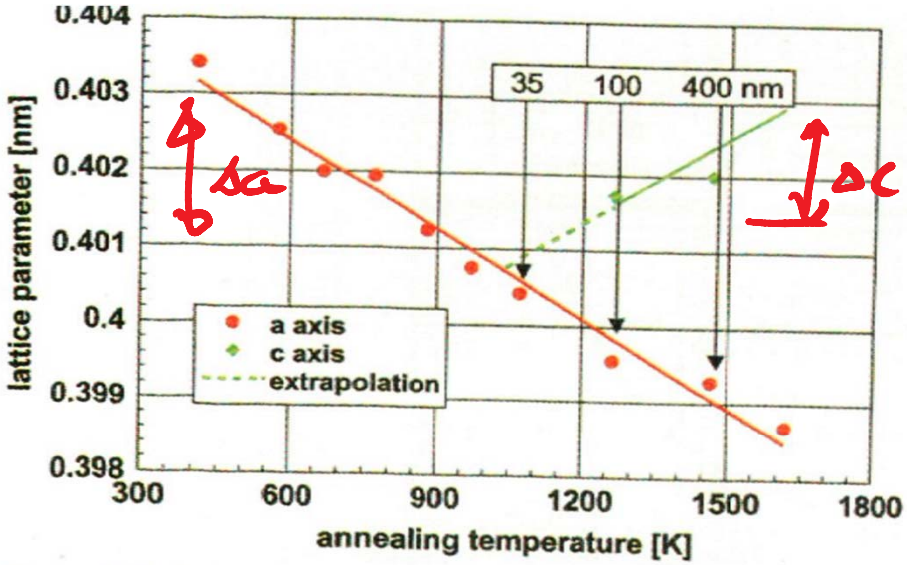
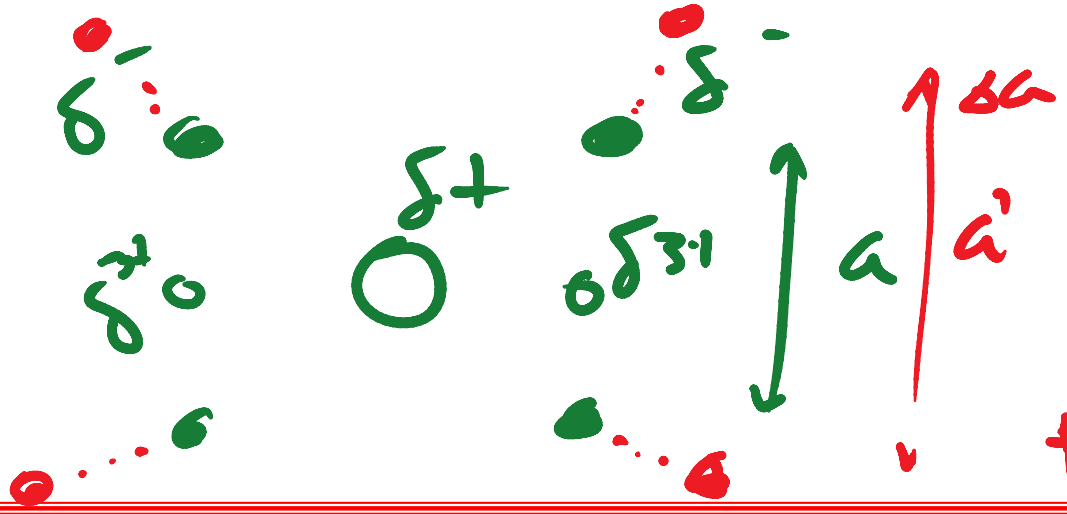


Figure 3.15 Lattice parameter of nanoparticulate $BaTiO_3$, a ferroelectric material with perovskite structure, as a function of the annealing temperature. During annealing, grain growth occurred [16]; hence, an increasing annealing temperature was equivalent to an increasing grain size. All lattice parameters were measured at room temperature, and particle sizes determined by electron microscopy. For details, see the text.

Different Exp. Same Conclus.

$BaTiO_3$ - cubic struct

- no different high T stable structure



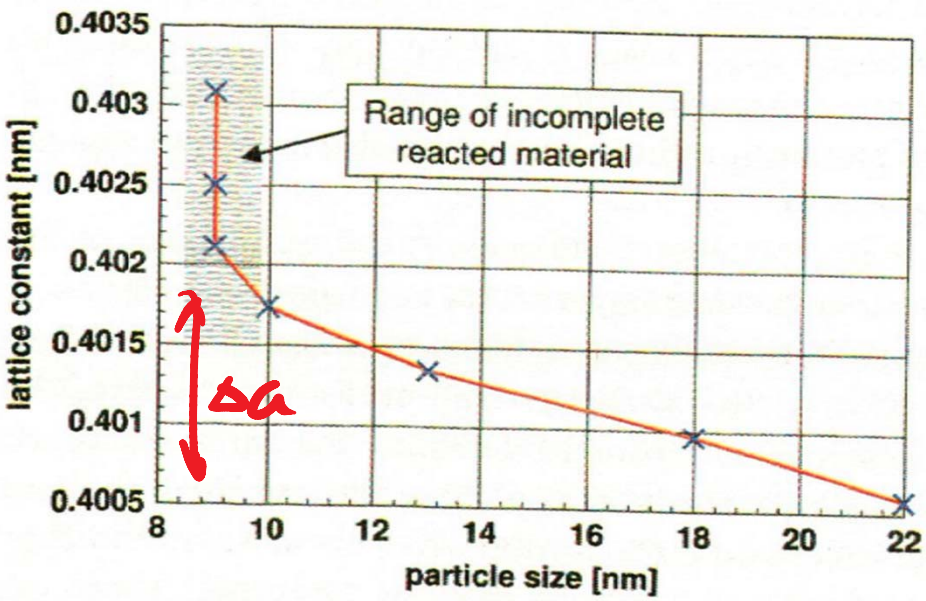


Figure 3.16 Lattice constant of $BaTiO_3$ in the cubic structure as a function of particle size [16]. The lattice constant decreases with increasing particle size. Values in the shaded area were deemed unreliable as the material was not completely reacted.

For D↓ a↑

STRUCTURE OF NPs

- FERROELECTRIC MATERIALS
- HIGH T PHASE IS DISORDERED
- LOW T PHASE IS ORDERED

NP - DISORDERED PHASE

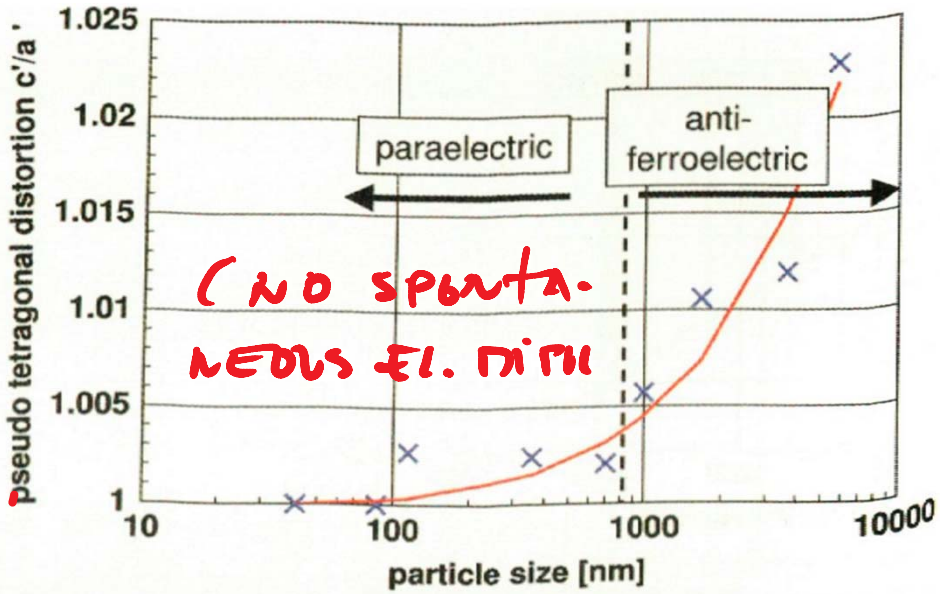


Figure 3.17 Pseudotetragonal distortion and the transition paraelectric–antiferroelectric of $PbZrO_4$ as a function of grain size [15]. A reduction in grain size had a similar effect as an increase in temperature. The paraelectric, cubic phase was the high-temperature phase; the antiferroelectric, tetragonal distorted phase was the low-temperature phase.

STRUCTURE OF NPs

- CURIE TEMP, T_c:
ORDER DISORDER
PHASE TRANSITION T
- V ↓, ΔT ↑, T_c ↓
- EFECT IS THE SAME
AS INCRESING T

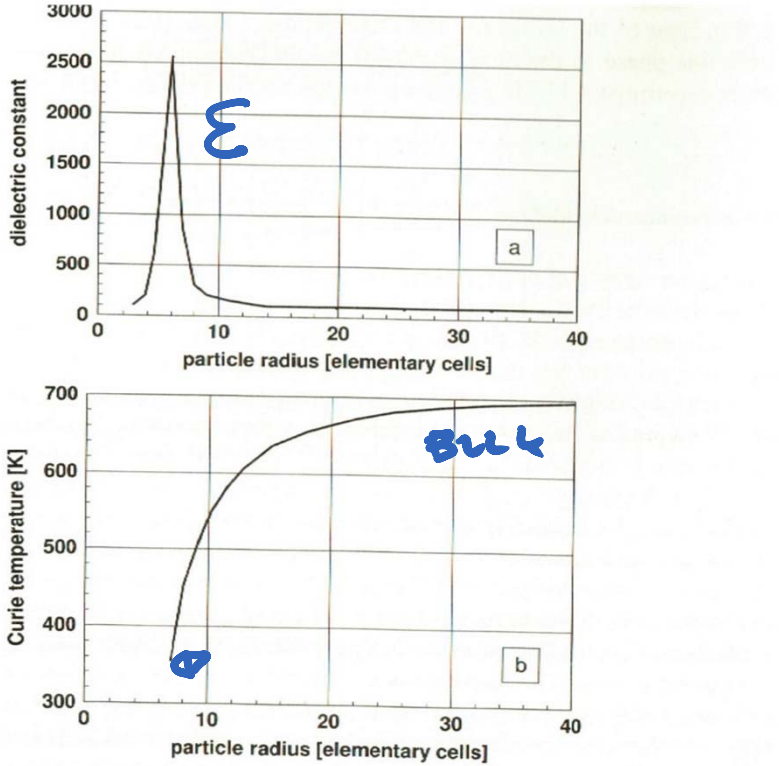


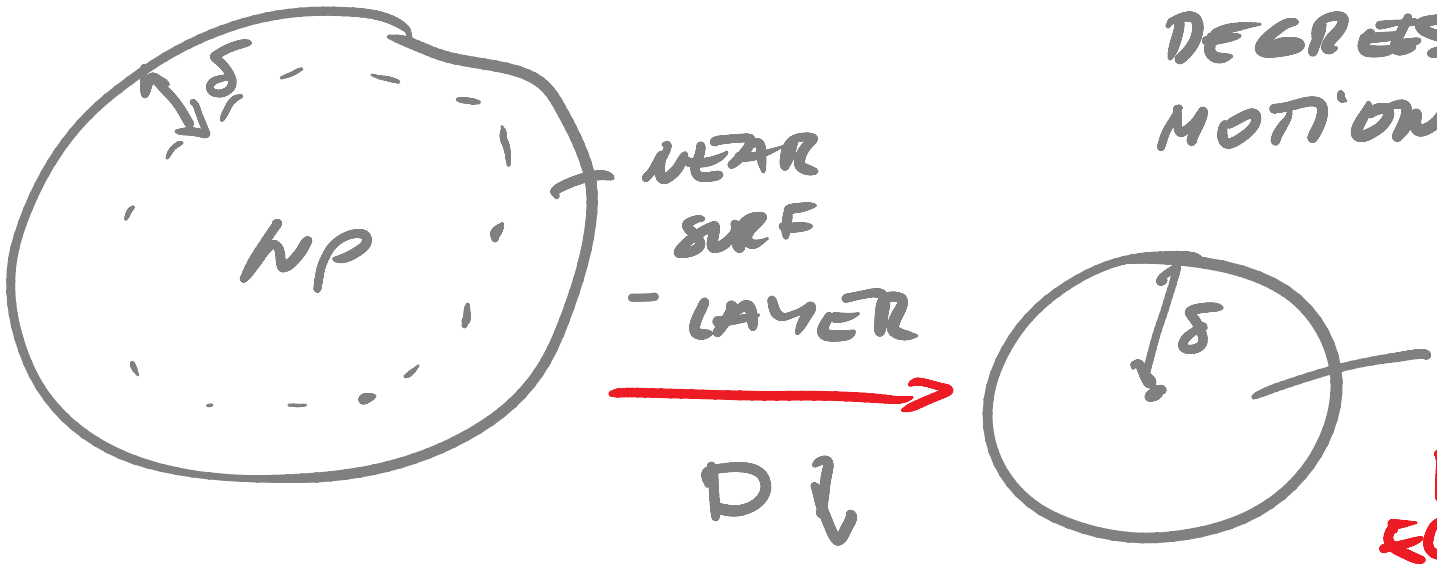
Figure 3.18 Dielectric constant and *Curie* temperature of $PbZr_{0.3}Ti_{0.7}O$ [17]. For small particle sizes transition occurs to the paraelectric, high-temperature phase. A reduction in particle size and high temperature has similar effects on particle structure and properties. The lattice constant ($a = 0.8$ nm) was selected as the dimension for the ordinate. (a) Dielectric constant of $PbZr_{0.3}Ti_{0.7}O_3$. At small particle sizes (< 5.6 lattice constants; the material was in the paraelectric, temperature phase, whereas at large sizes the material was ferroelectric. (temperature of $PbZr_{0.3}Ti_{0.7}O_3$. Belov size of eight lattice constants, the *Cu* temperature was no longer defined. Tl was paraelectric, independent of the temperature.

LANDAU'S ORDER PARAM. M

$M = 1$ - IDEAL CRYSTAL

$M = 0$ - MELT (LIQUID)

} M IS ENTROPICAL DESCRIPTION OF CRYSTAL ORDER AND DEGREES OF ATOM MOTION/FREEDOM.



VOLUME FRACTION OF THE WHOLE NP IS 1 AFFECTED BY SURF.

M FOR NP

M → 0 AS

D → 0

DISORDER IN NP INCREASES AS NP DIAMETER DECREASE (METAL NP!)

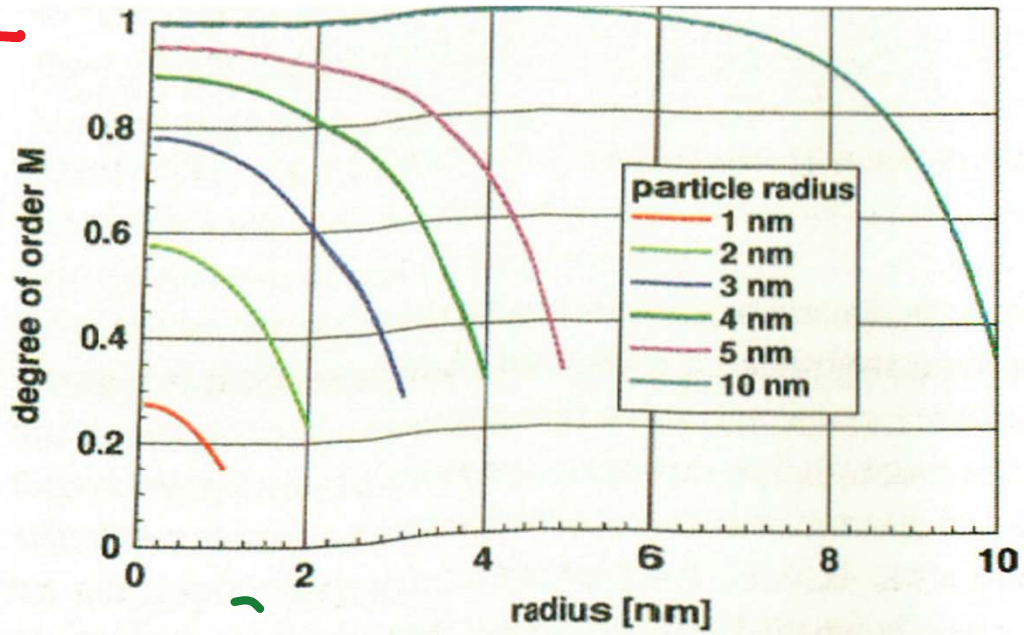
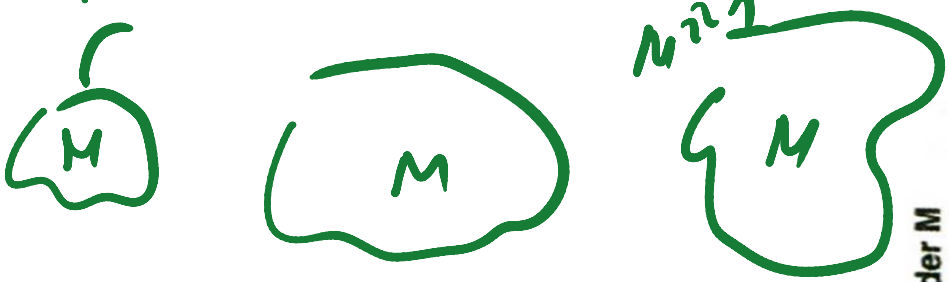


Figure 3.19 *Landau's* order parameter M for nanoparticles of tin as a function of radius and particle size [18]. The degree of order decreased with decreasing particle radius, and also from the interior to the surface. For perfectly crystallized particles $M = 1$; for melted particles, $M = 0$.

M FOR NP



T ↑ COUL. V ↑

M → 1

M - IS AN AVERAGE OF ATOMS ORDERING IN NP.

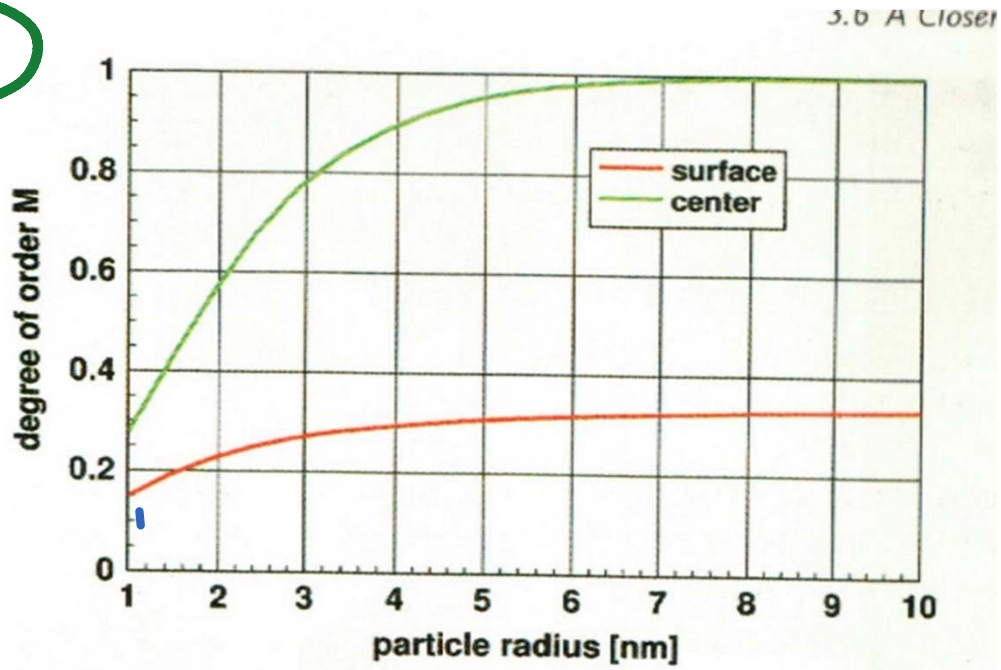


Figure 3.20 *Landau*'s order parameter *M* in the center and at the surface of nanoparticles [18]. Small nanoparticles with radii <5 nm never show perfect crystallization.

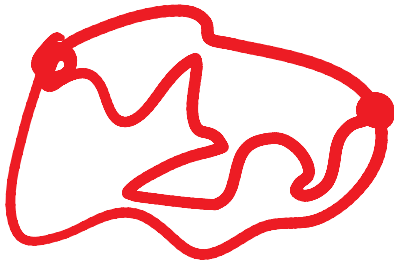
SURF. SUBCORD. EFECT. AND T_m

Shape Fluctuation of NP

$x^2 = Dt$

$10^{-16}\ m^2 \quad 10^{-12}\ \frac{m^2}{s}$

$t = 10^{-4}\ s$; 100 μs



SURFACE IS VERY DYNAMIC

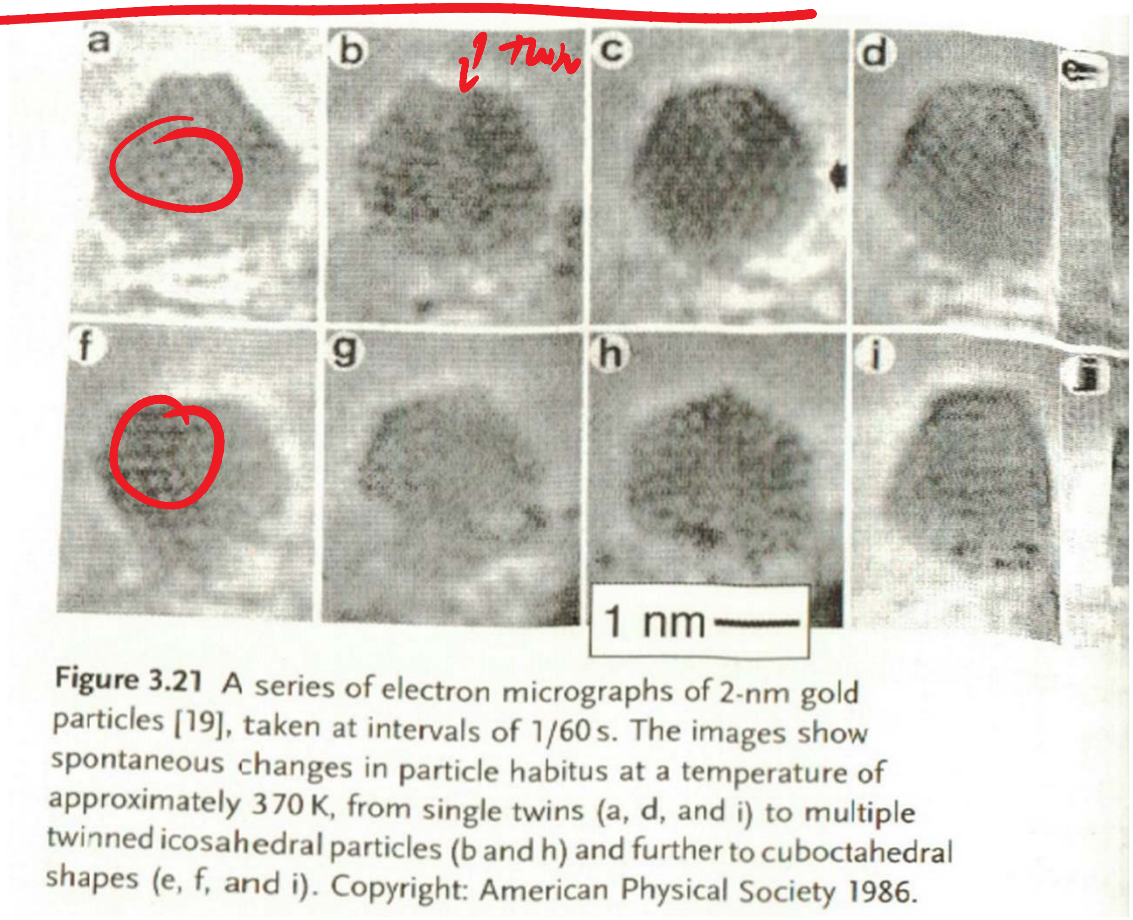


Figure 3.21 A series of electron micrographs of 2-nm gold particles [19], taken at intervals of 1/60 s. The images show spontaneous changes in particle habitus at a temperature of approximately 370 K, from single twins (a, d, and i) to multiple twinned icosahedral particles (b and h) and further to cuboctahedral shapes (e, f, and i). Copyright: American Physical Society 1986.

NP – Phase Diagram

- Combination of $T_m(V)$ and surf subordination.. results in stabili ty regimes which are $f(V)$ for NP meth!

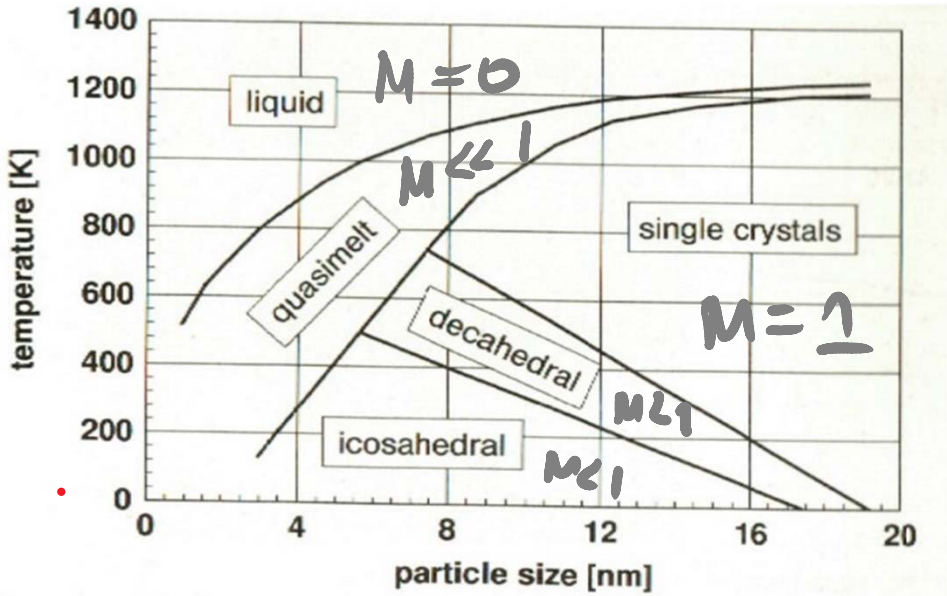


Figure 3.22 Phase diagram of gold nanoparticles, showing regions of different well-defined habitus. A region termed quasimelt is also indicated where the particles change their habitus spontaneously [20].

Au NP

TEM EVIDENCE

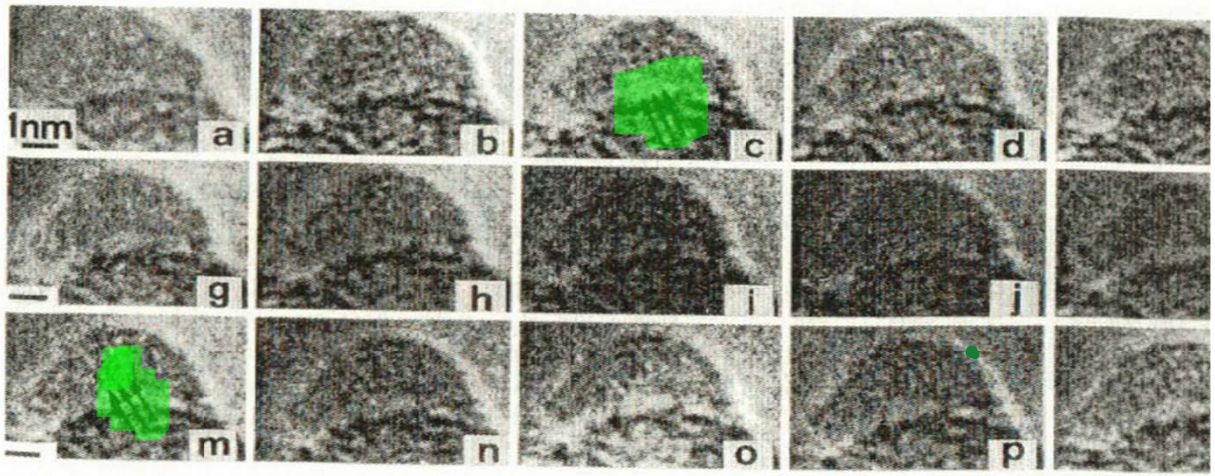


Figure 3.23 A series of electron micrographs of tin particles, taken at intervals of 1/60 s [21]. In these images the appearance and disappearance of small crystallized regions, called embryos, can be seen within the particles (frames c and m). The phenomenon of "pseudocrystallin particles" can be attributed to a well-d particle size–temperature range in a pl diagram (Reprinted with permission fr Copyright: Springer 1993.)

DIFFICULT TO OBSERVE TRA. NSITIONS 1/60s PER IMAGE:

MD SIMULATION

MD Simulations of NP dynamics

STRUCTURE OF NP

ROOM T :

- VERY FAST DYNAMIC,
- RESURFACING OF NP IS DONE WITHIN $\sim 10^{-3}$ s.

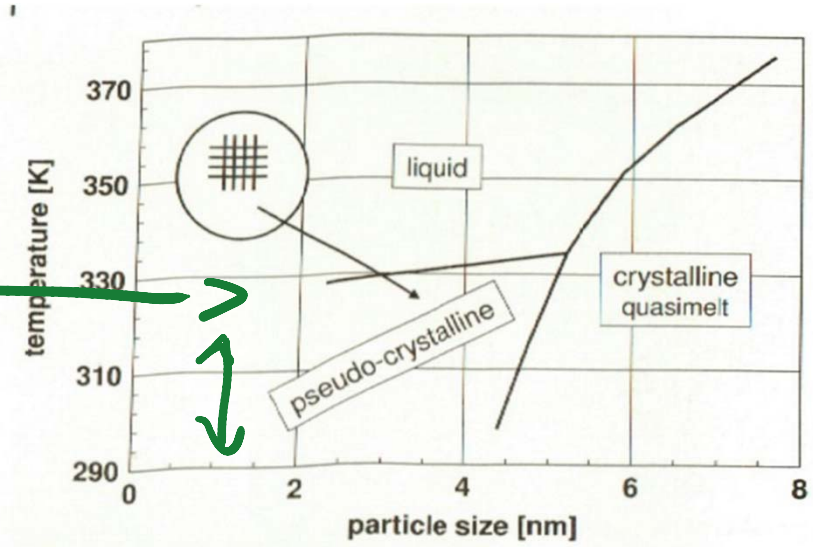


Figure 3.24 Temperature–particle size phase diagram for tin nanoparticles according to Oshima and Takayanagi [21]; conditions as noted for pseudocrystalline particle formation in Figure 3.23 were observed. A schematic drawing of the pseudocrystalline particles is also shown. In the region denominated as crystalline quasimelt, the particles fluctuate between the different possibilities of their habitus.

STRUCTURAL FLUCTUATIONS

kT – MEASURE OF THERMAL FLUCTUATIONS.

– SUPERPARAMAGNETISM.

$K_u \cdot \sigma_{ND} \approx kT$

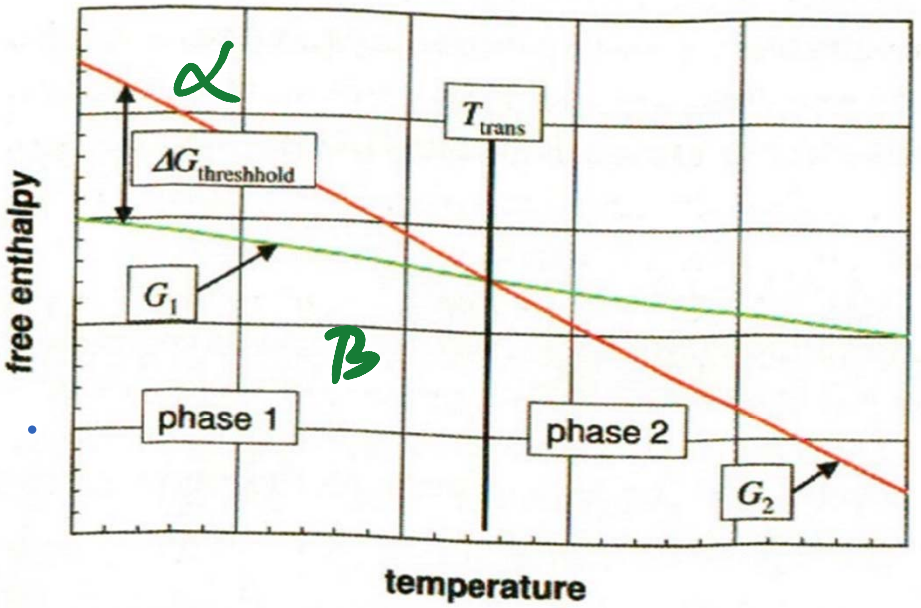


Figure 3.26 Free enthalpy as a function of temperature in the vicinity of a phase transformation. Two areas occur where phases 1 and 2 are stable. However, when $\Delta g_{threshhold} < kT$ is fulfilled, spontaneous fluctuations of the individual particles are possible.

STRUCTURAL FLUCTUATIONS

$$\Delta g_m = \Delta G_m \frac{w}{M}$$

$$\Delta g_m \leq kT$$

$$\Delta g_m \sim |T - T_{trans}|$$

$$\Delta g_m = \frac{\delta V_{rms} \pi D_\alpha^3 g_\alpha}{6M} - T\Delta S_m \cdot \frac{\pi D_\alpha g_\alpha}{6M} +$$

$$+ \gamma_\alpha^{\sim} \pi D_\alpha^2 - \gamma_\beta \pi D_\beta^2 = kT$$

STRUCTURE FL.

– AFTER RE-ARRANGEMENT.

$$T_{FL} = \frac{\Delta U_{TMS} + \gamma_\alpha \frac{GM}{D_\alpha \rho_\alpha} - \gamma_\beta \cdot \frac{GM}{\rho_\alpha D_\alpha} \left(\frac{\rho_\alpha}{\rho_{MS}}\right)^{2/3}}{\Delta S_{TMS} + k \cdot \frac{GM}{\pi D_\alpha^3 \rho_\alpha}}$$

$T_{FL} \neq T_M$

D - SMALL

$T_{FL} \approx T_M$

D -> LARGE

DL TERM DOMINATES

STRUCTURE FL.

- TEMPERATURE T_{FL}
- IS VERY IMPORTANT THAN T_m FOR NP.

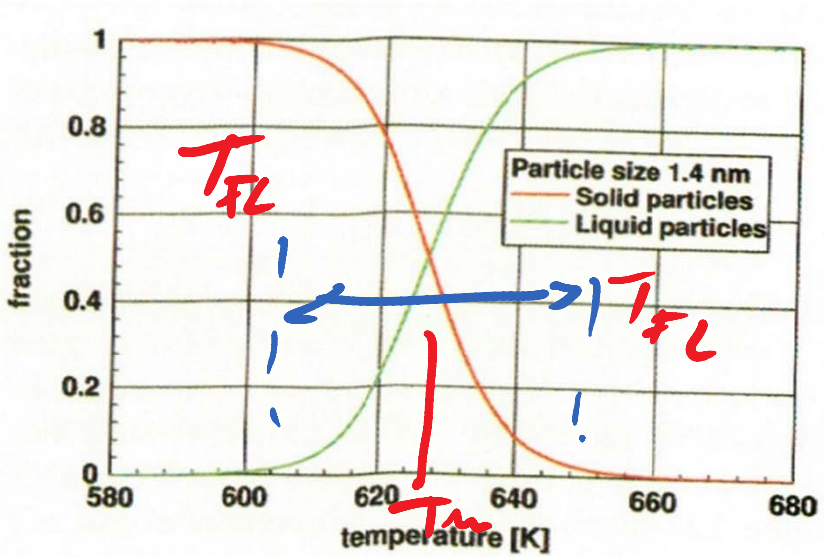


Figure 3.28 Number fractions of gold particles with a diameter of 1.4 nm. Both phases are stable over a broad temperature range [22].

SEE THE MD MOVIES AGAIN!

https://www.youtube.com/watch?v=MJj5XWQHUFE

https://www.youtube.com/watch?v=NWGoE9hwuoo

https://www.youtube.com/watch?v=AQc_mGjjErAl