0.1 Lecture 4

Thursday 19th March, 2020. Compiled: Thursday 28th May, 2020. Alice.

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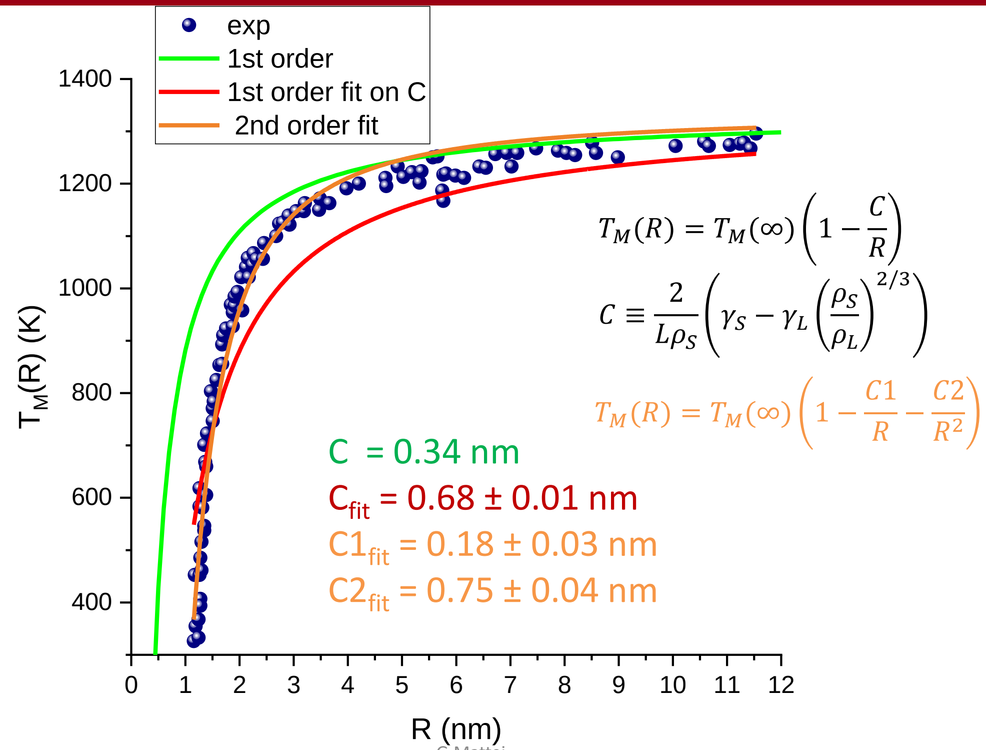
Thermodynamic Size Effect

NanoScience/ NanoPhysics



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Expanding to 1st order:

$$L(\Theta - 1) + 2\left(\frac{\gamma_S}{R_S\rho_S} - \frac{\gamma_L}{R_L\rho_L}\right) = 0$$

$$L(1-\Theta) - \frac{2}{R_S\rho_S}\Delta\gamma = 0$$

$$\begin{cases} \dfrac{T}{T_0} \equiv \Theta \\ \gamma_S - \gamma_L\left(\dfrac{\rho_S}{\rho_L}\right)^{2/3} \equiv \Delta\gamma \end{cases}$$

Espanding to 2nd order:

$$L(1-\Theta) - \frac{2}{R_S\rho_S}\left[\Delta\gamma + \Delta\gamma_2 T_0(1-\Theta)\right] + \frac{\Delta C_P}{2}T_0(1-\Theta)^2 + \frac{2}{R_S^2\rho_S}\Delta\gamma_3 = 0$$

$$(1-\Theta) - \frac{C_1}{R_S}\left[1 + C_2(1-\Theta)\right] + C_3(1-\Theta)^2 + \frac{C_4}{R_S^2} = 0$$

$$A_1(1-\Theta)^2 + \left(1 - \frac{A_2}{R_S}\right)(1-\Theta) - \frac{A_3}{R_S} + \frac{A_4}{R_S^2} = 0$$

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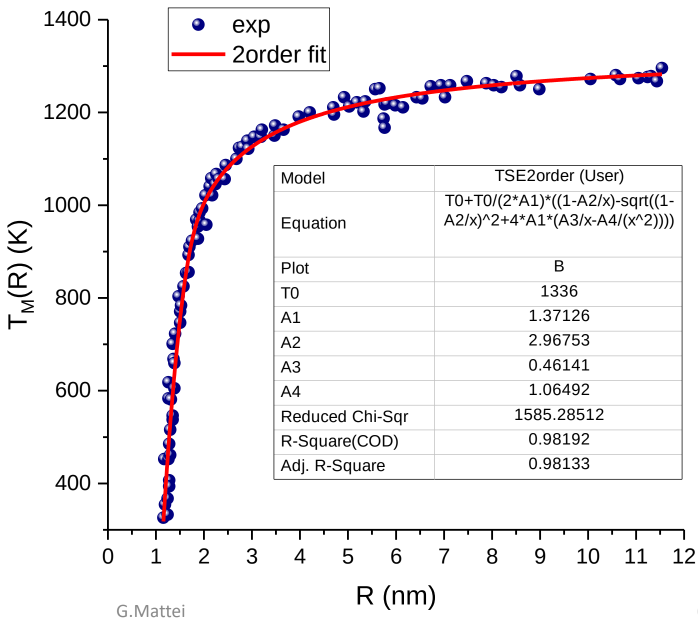
$$A_1(1-\Theta)^2 + \left(1-\frac{A_2}{R_S}\right)(1-\Theta) - \frac{A_3}{R_S} + \frac{A_4}{R_S^2} = 0$$

$$X \equiv 1-\Theta$$

$$AX^2 + BX + C = 0$$

$$T = T_0\left(1+\frac{B}{2A} - \frac{\sqrt{B^2-4AC}}{2A}\right)$$

$$\begin{cases} A = A_1 \\ B = \left(1-\dfrac{A_2}{R_S}\right) \\ C = -\dfrac{A_3}{R_S} + \dfrac{A_4}{R_S^2} \end{cases}$$



Model	TSE2order (User)
Equation	T0+T0/(2*A1)*((1-A2/x)-sqrt((1-A2/x)^2+4*A1*(A3/x-A4/(x^2))))
Plot	B
T0	1336
A1	1.37126
A2	2.96753
A3	0.46141
A4	1.06492
Reduced Chi-Sqr	1585.28512
R-Square(COD)	0.98192
Adj. R-Square	0.98133

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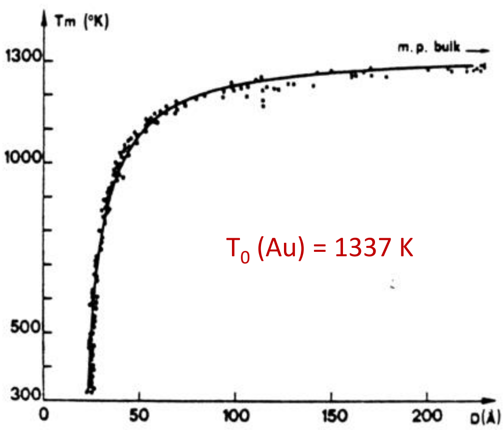
Experiment

Ph. Buffat, J-P. Borel, Phys. Rev. A 13 (1976) 2287

(electron diffraction)

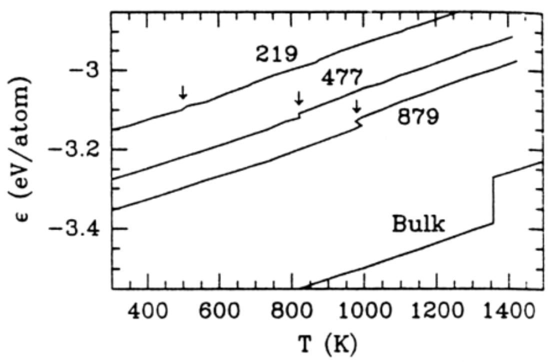


T_0 (Au) = 1337 K

Numerical simulation

F. Ercolessi *et al.*, Phys. Rev. Lett. 66 (1991) 911

(Molecular Dynamics: energy/atom)



N_{atoms}	T_M (K)
219	500
477	820
879	980
∞	1340

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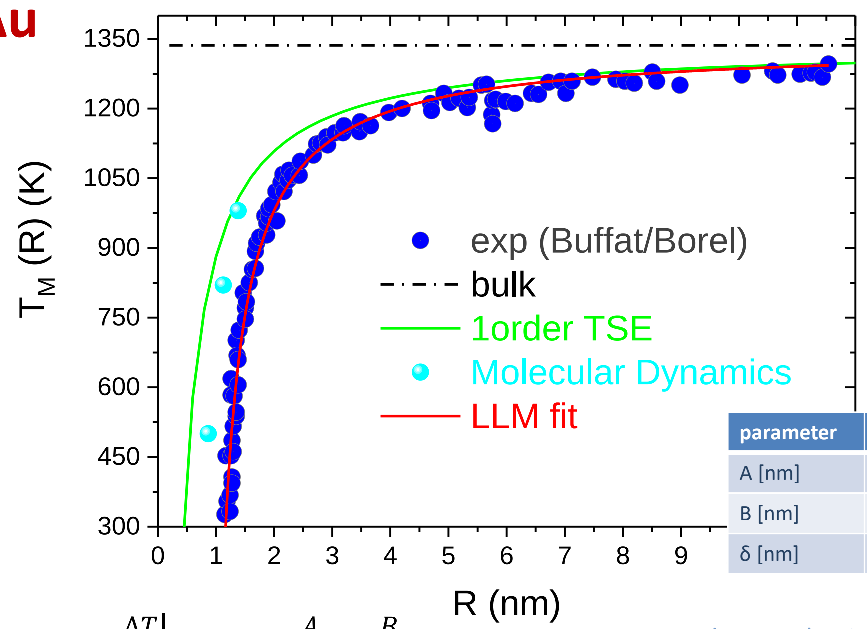
Au



parameter	value
A [nm]	0.27 ± 0.08
B [nm]	0.10 ± 0.05
δ [nm]	0.78 ± 0.08

$$\left.\frac{\Delta T}{T_0}\right|_{LLM} = -\frac{A}{R-\delta} - \frac{B}{R}$$

1. How do we obtain the liquid layer?
2. Is it experimentally observable?

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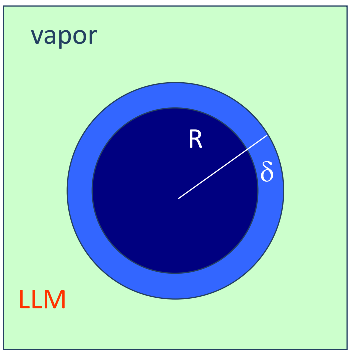
Improvements:

1. Second-order expansion for $\mu(T, P)$
2. Liquid layer model (LLM)

Liquid layer model (LLM)



$$\frac{\Delta T}{T_0} = -\frac{2}{L\rho_S}\left(\frac{\gamma_{SL}}{R-\delta} + \frac{\gamma_{LV}}{R}\left(1 - \frac{\rho_S}{\rho_L}\right)\right) < 0$$

$$\Delta T = T - T_0$$

For Au:

γ_{SL} = 1.135 J/m^2 (*solid-liquid surface tension*)

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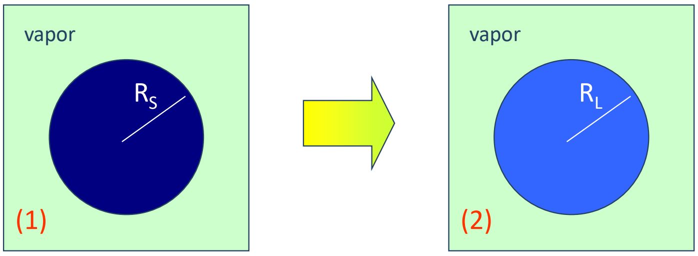
First-order transition from 1 to 2 (Pawlow fTD)

$$G_1 = N\mu_s + 4\pi R_S^2 \gamma_{SV}$$

N: atoms solid phase
γ : interfacial energy



$$G_2 = N\mu_L + 4\pi R_L^2 \gamma_{LV}$$
$$\Delta G_{2,1} \equiv G_2 - G_1$$
$$= N(\mu_L - \mu_S) + 4\pi R^2 \left[\gamma_{LV} \left(\frac{\rho_S}{\rho_L} \right)^{2/3} - \gamma_{SV} \right]$$
$$\Delta G_{2,1} = \frac{4\pi R^3}{3} \rho_S L \frac{T_0 - T}{T_0} + 4\pi R^2 \left[\gamma_{LV} \left(\frac{\rho_S}{\rho_L} \right)^{2/3} - \gamma_{SV} \right]$$

$$(\mu_L - \mu_S) = \frac{\Delta G_{vol}}{N} = \Delta g_{vol}$$
$$\Delta g_{vol} = \Delta h - T\Delta s$$
$$= L - T\frac{L}{T_0}$$

$$\frac{\partial \Delta G_{2,1}}{\partial R} = 0 \quad \Rightarrow \quad \left.\frac{\Delta T}{T_0}\right|_{fTD} = -\frac{2}{\rho_S L R} \left(\gamma_{SV} - \gamma_{LV} \left(\frac{\rho_S}{\rho_L} \right)^{2/3} \right)$$

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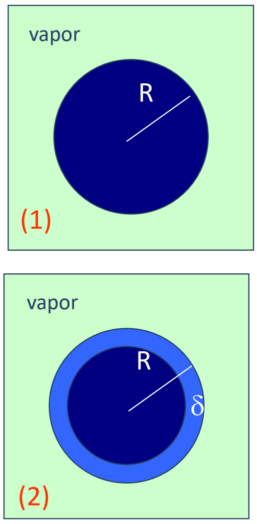
LLM

Compare the two configurations:

$$G_1 = N\mu_s + 4\pi R^2 \gamma_{SV}$$

N: atoms solid phase
N': atoms liquid phase
γ : interfacial energy



N': atoms liquid phase
L: Latent heat of fusion
V_L: Volume liquid phase
δ: liquid layer thickness

Approx: $\rho_S \cong \rho_L \cong \rho$

$$G_2 = (N - N')\mu_S + N'\mu_L + 4\pi R^2 \left[\gamma_{LV} + \gamma_{SL} \left(1 - \frac{\delta}{R} \right)^2 \right]$$

$$\Delta G_{2,1} \equiv G_2 - G_1 = N'(\mu_L - \mu_S) + 4\pi R^2 \left[\gamma_{LV} + \gamma_{SL} \left(1 - \frac{\delta}{R} \right)^2 - \gamma_{SV} \right]$$

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The volume contribution is:

$$(\mu_L - \mu_S) = \frac{\Delta G_{vol}}{N'} = \Delta g_{vol} = \Delta h - T\Delta s = L - T\frac{L}{T_0} = L\frac{T_0 - T}{T_0}$$

$$N'(\mu_L - \mu_S) = V_L \rho L \frac{T_0 - T}{T_0} = \frac{4\pi}{3}(R^3 - (R-\delta)^3)\rho L \frac{T_0 - T}{T_0}$$

$$V_L = \frac{4\pi}{3}(R^3 - (R-\delta)^3)$$

Minimize: $\frac{\partial \Delta G_{2,1}}{\partial R} = 0$ thus: $\left.\frac{\Delta T}{T_0}\right|_{LLM} = -\frac{2\gamma_{SL}}{\rho_S L(R-\delta)} = -\frac{A}{R-\delta}$

Relaxing the approx: $\rho_S \cong \rho_L \cong \rho$

$$\left.\frac{\Delta T}{T_0}\right|_{LLM} = -\frac{2\gamma_{SL}}{\rho_S L(R-\delta)} - \frac{2\gamma_{LV}}{\rho_S LR}\left(1 - \frac{\rho_S}{\rho_L}\right) = -\frac{A}{R-\delta} - \frac{B}{R}$$

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Smooth Interfaces Interaction (SII)

- More refined theory: coherence length ξ (characteristic scale of the interaction between the interfaces)
- similar results to LLM

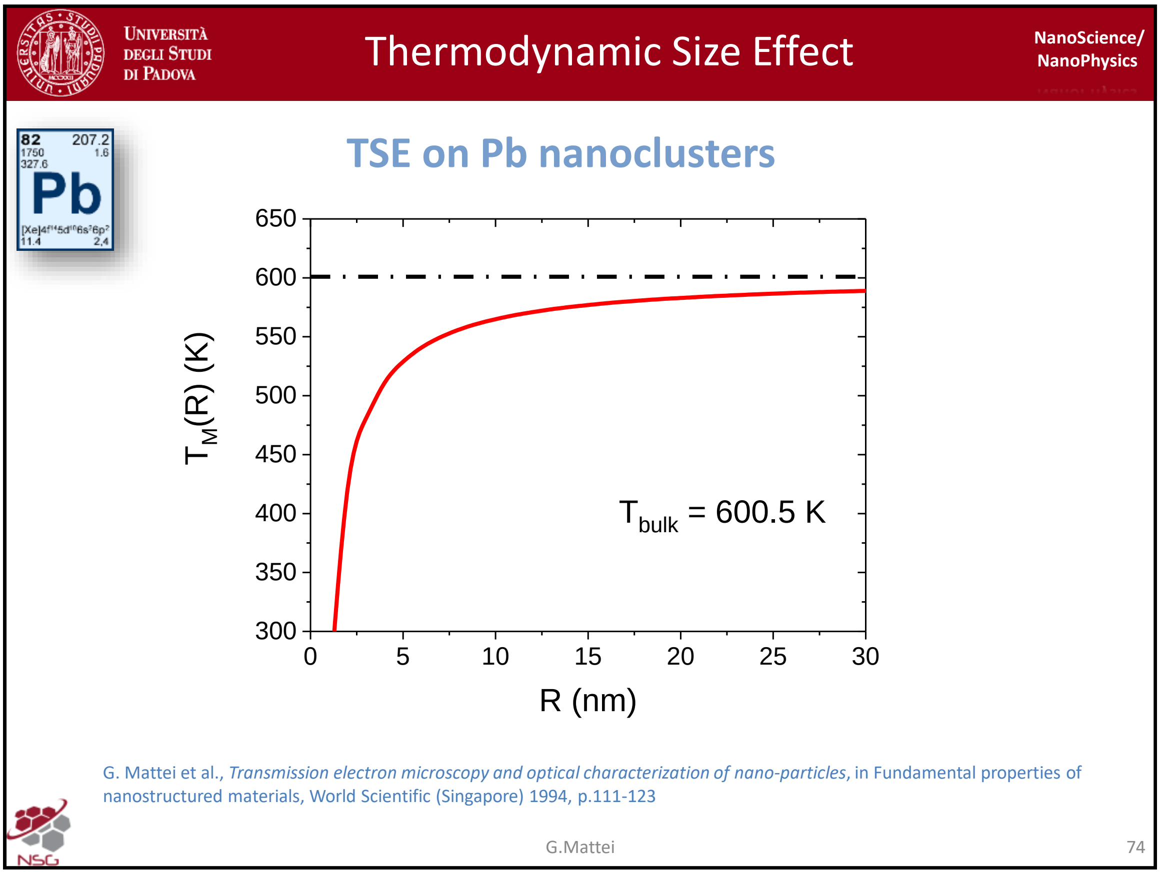
$$\Delta G = \Delta G_V + \Delta G_S$$

$$\Delta G_V = \frac{4\pi}{3}(R^3 - (R-\delta)^3)\rho L \frac{T_0 - T}{T_0}$$

$$\Delta G_S = 4\pi R^2\left[\gamma_{LV} + \gamma_{SL}\left(1 - \frac{\delta}{R}\right)^2 - \gamma_{SV}\right]\left(1 - e^{-\frac{\delta}{\xi}}\right) \qquad \Gamma \equiv \gamma_{SV} - \left[\gamma_{LV} + \gamma_{SL}\left(1 - \frac{\delta}{R}\right)^2\right]$$

$$\left.\frac{\Delta T}{T_0}\right|_{SII} = -\frac{2\gamma_{SL}}{\rho_S L(R-\delta)}\left(1 - e^{-\delta/\xi}\right) - \frac{\Gamma R^2}{\rho_S L\xi(R-\delta)^2}e^{-\delta/\xi} = -\frac{A}{R-\delta} - \frac{B\Gamma R^2}{(R-\delta)^2}$$

$$\left.\frac{\Delta T}{T_0}\right|_{SII} \xrightarrow[\xi \to 0]{} \left.\frac{\Delta T}{T_0}\right|_{LLM}$$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82 207.2
1750 1.6
327.6
Pb
TSE on Pb nanoclusters
650
600
550
500
450
400
350
300
T_M(R) (K)
T_bulk = 600.5 K
0 5 10 15 20 25 30
R (nm)
G. Mattei et al., Transmission electron microscopy and optical characterization of nano-particles, in Fundamental properties of nanostructured materials, World Scientific (Singapore) 1994, p.111-123
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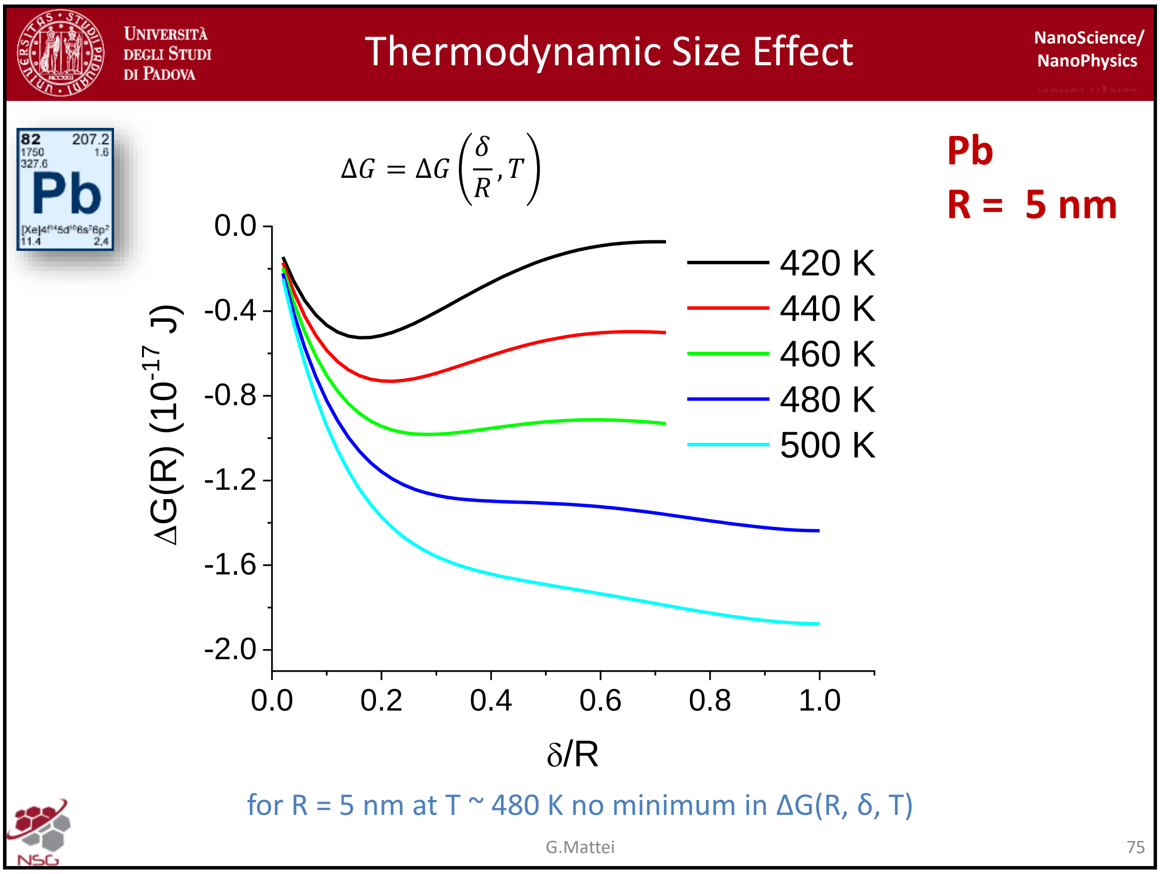
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Thermodynamic Size Effect
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82 207.2
1750 1.6
327.6
Pb
$\Delta G = \Delta G\left(\frac{\delta}{R}, T\right)$
Pb
R = 5 nm
0.0
-0.4
-0.8
-1.2
-1.6
-2.0
ΔG(R) (10^-17 J)
420 K
440 K
460 K
480 K
500 K
0.0 0.2 0.4 0.6 0.8 1.0
δ/R
for R = 5 nm at T ~ 480 K no minimum in ΔG(R, δ, T)
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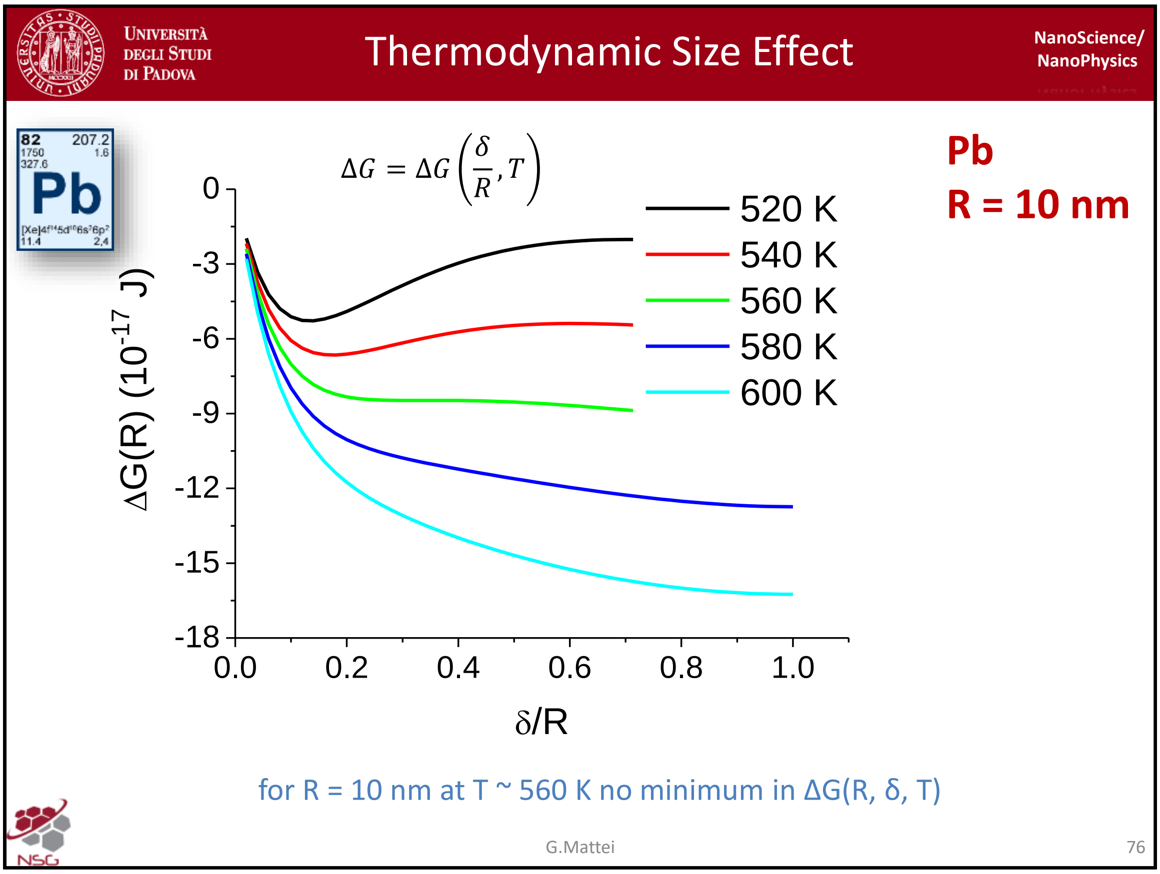

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Pb
R = 10 nm
$\Delta G = \Delta G\left(\frac{\delta}{R}, T\right)$
ΔG(R) (10^{-17} J)
δ/R
520 K
540 K
560 K
580 K
600 K
for R = 10 nm at T ~ 560 K no minimum in ΔG(R, δ, T)
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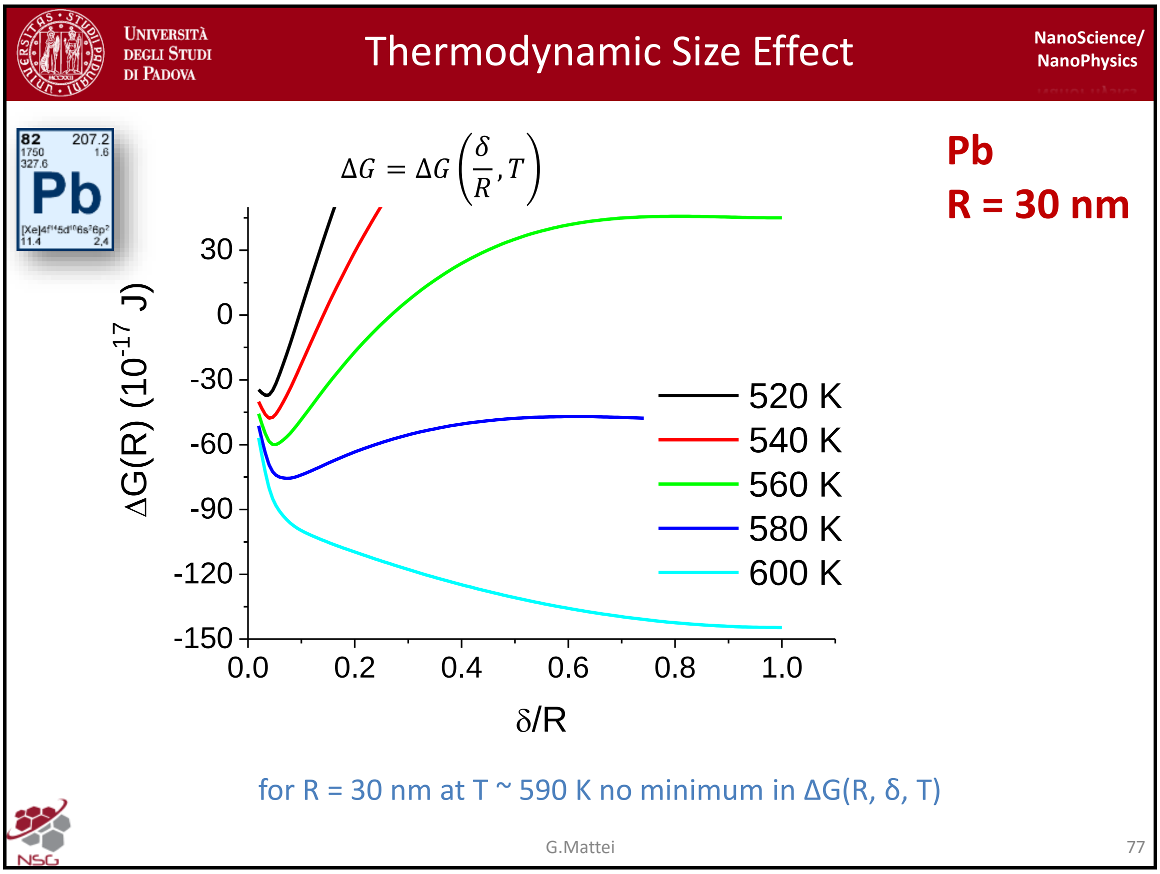

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Pb
R = 30 nm
$\Delta G = \Delta G\left(\frac{\delta}{R}, T\right)$
ΔG(R) (10^{-17} J)
δ/R
520 K
540 K
560 K
580 K
600 K
for R = 30 nm at T ~ 590 K no minimum in ΔG(R, δ, T)
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Pb 207.2 82

Pb
R = 30 nm

$$\Delta G = \Delta G\left(\frac{\delta}{R}, T\right)$$

When R = 30 nm the system is close to the bulk behaviour

$$F = \frac{n_{\text{sup}}}{n} = \frac{4}{n^{1/3}} = 4\frac{R_0}{R}$$

R_0 (Pb, fcc) = 0.175 nm

F(Pb, 30nm) = 0.023 = 2.3%

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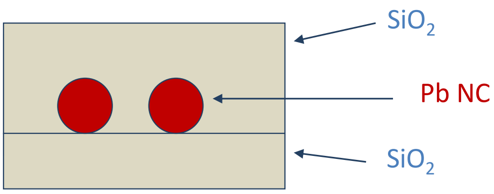
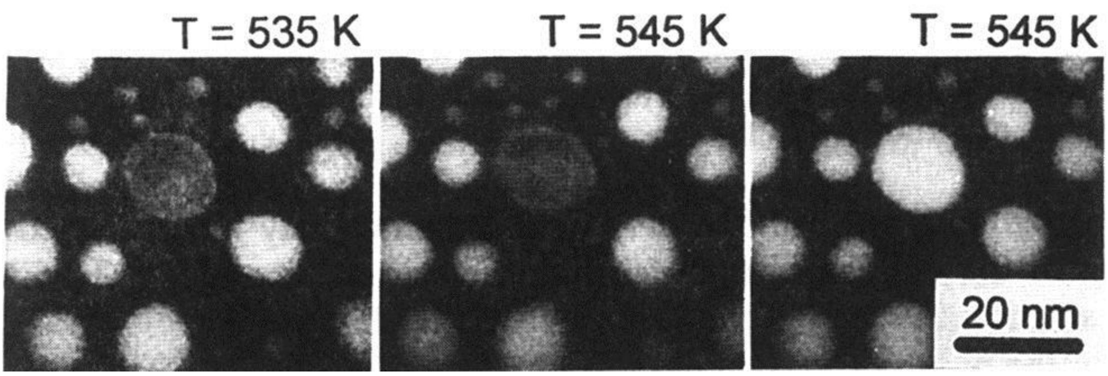


Gas Phase synthesis of Pb NCs (Pb evaporation/condensation on a SiO_2 substrate)

T_M(bulk) = 600 K

Dark-field TEM Image of Pb NCs in SiO_2



40 ms frame rate acquisition

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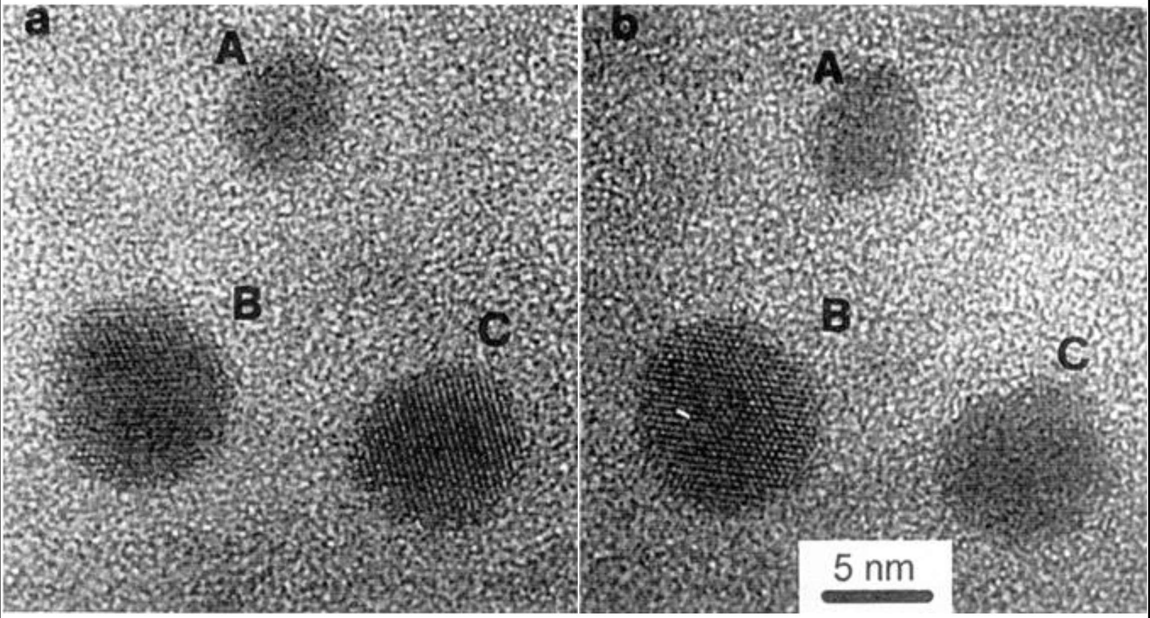
High-resolution TEM Image of Pb NCs in SiO_2



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Phase fluctuation in Pb NCs

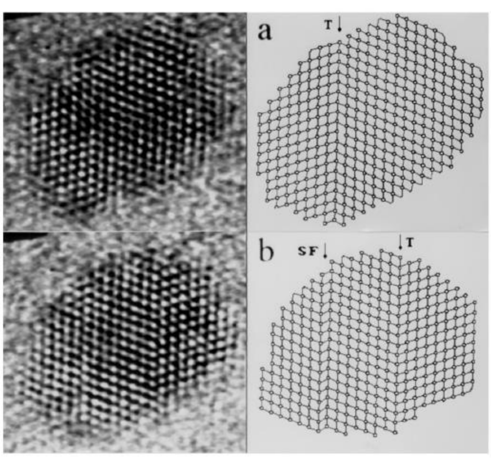

FIG. 3. Configuration transition, involving vanishing of a twin (T) on the left side, leaving a stalking fault (SF), and appearance of twin on the right side. (The first configuration was stable for 1.5 sec, the second configuration was stable for 6.5 sec, the transition time is less than 0.04 sec.)

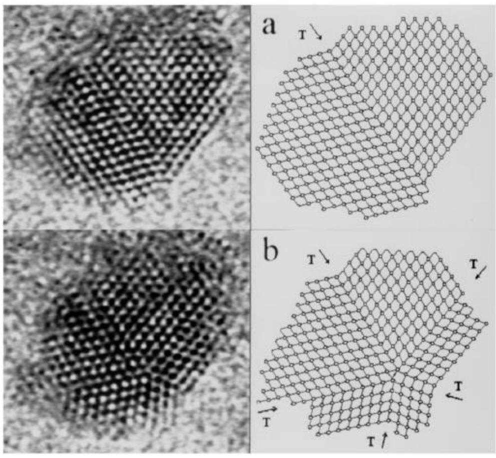

FIG. 4. Configuration transition, between single twin structure and a five-fold structure, by introducing four additional twins (marked with arrows). (The first configuration was stable for 7 sec; the second configuration was stable for 0.5 sec; the transition time is less than 0.04 sec.)