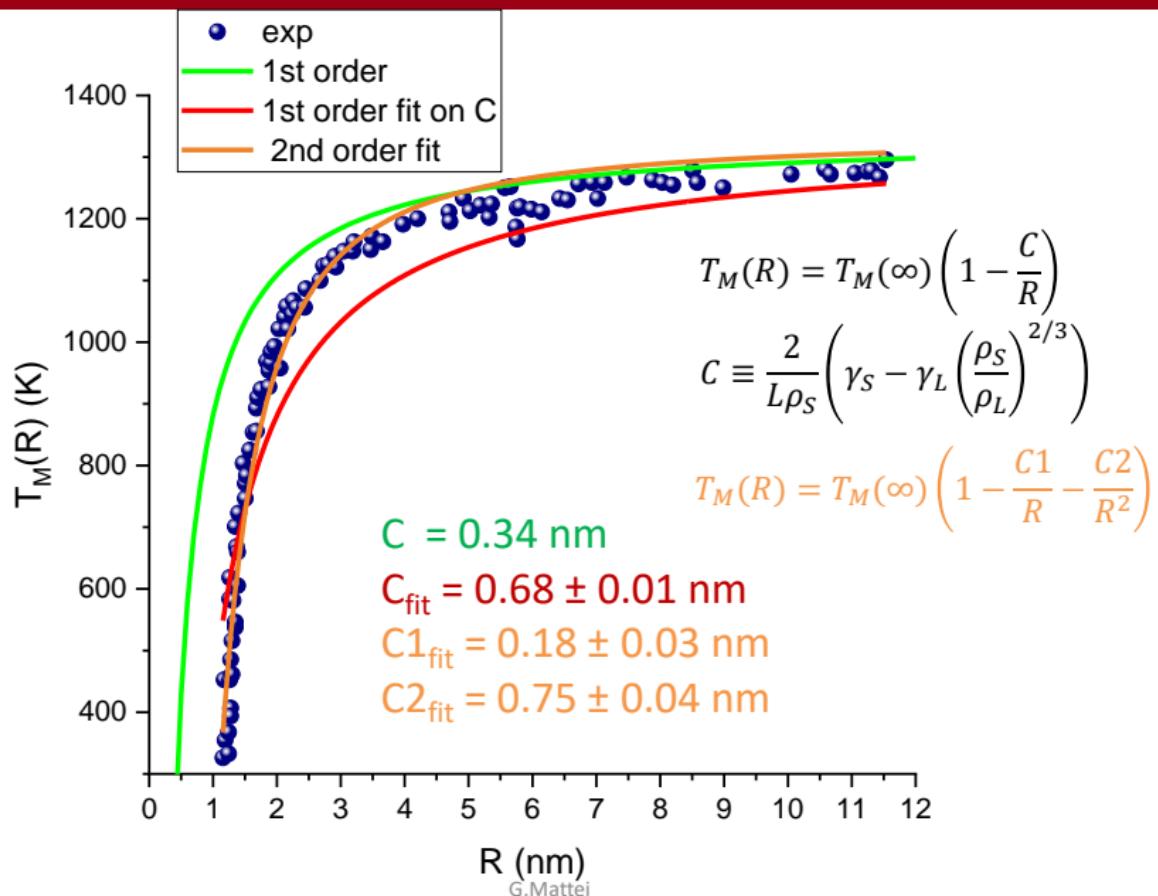


Thermodynamic Size Effect



Expanding to 1st order:

$$\begin{aligned} L(\Theta - 1) + 2 \left(\frac{\gamma_S}{R_S \rho_S} - \frac{\gamma_L}{R_L \rho_L} \right) &= 0 \\ L(1 - \Theta) - \frac{2}{R_S \rho_S} \Delta\gamma &= 0 \end{aligned} \quad \left\{ \begin{array}{l} \frac{T}{T_0} \equiv \Theta \\ \gamma_S - \gamma_L \left(\frac{\rho_S}{\rho_L} \right)^{2/3} \equiv \Delta\gamma \end{array} \right.$$

Expanding to 2nd order:

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

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

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

Thermodynamic Size Effect

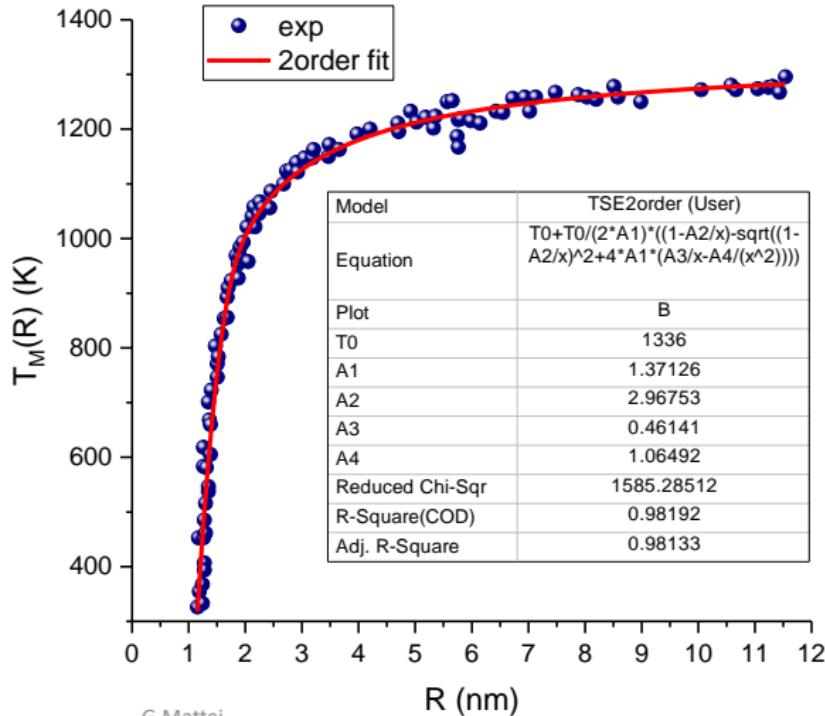
$$A_1(1 - \Theta)^2 + \left(1 - \frac{A_2}{R_S}\right)(1 - \Theta) - \frac{A_3}{R_S} + \frac{A_4}{R_S^2} = 0$$

$$X \equiv 1 - \Theta$$

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

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

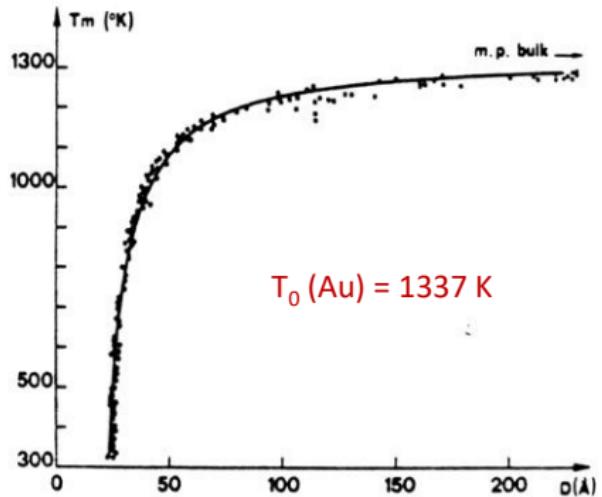
$$\begin{cases} A = A_1 \\ B = \left(1 - \frac{A_2}{R_S}\right) \\ C = -\frac{A_3}{R_S} + \frac{A_4}{R_S^2} \end{cases}$$



Thermodynamic Size Effect

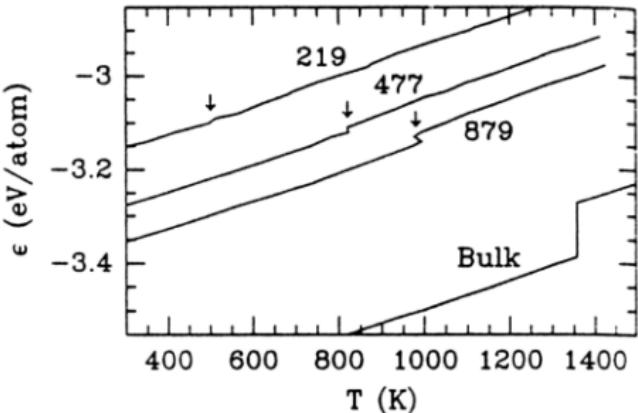
Experiment

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



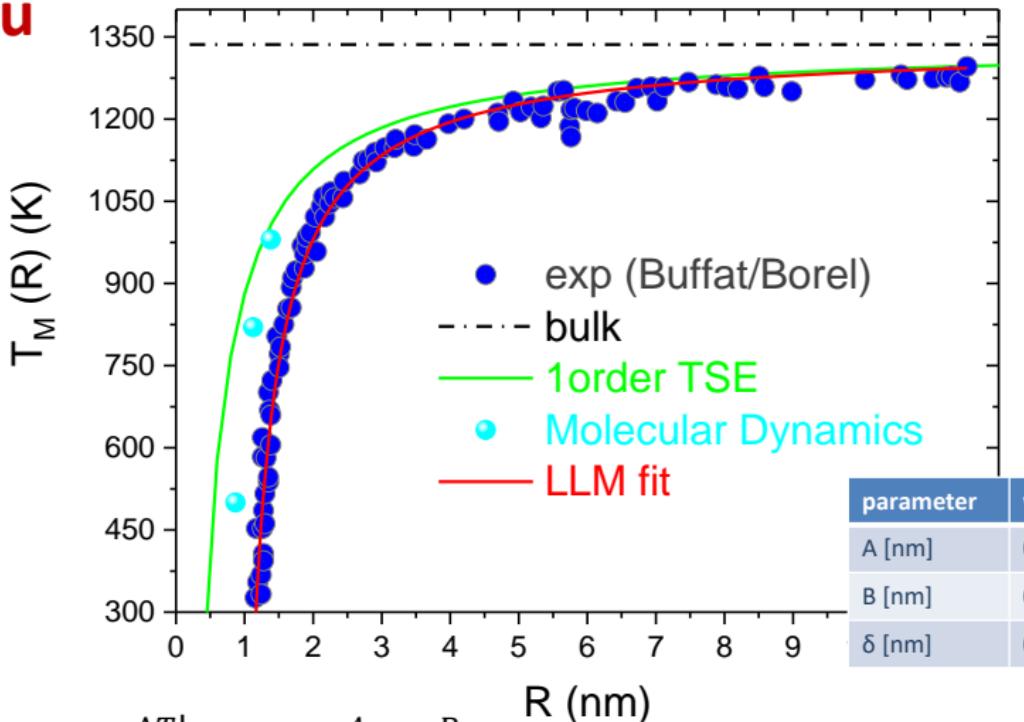
Numerical simulation

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

Thermodynamic Size Effect

Au


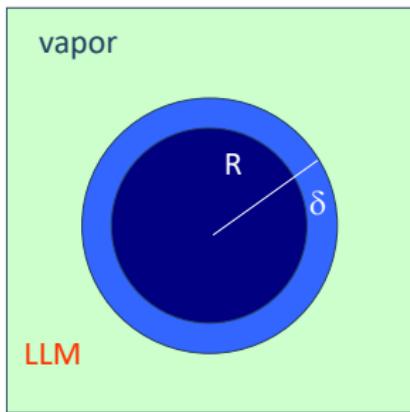
$$\left. \frac{\Delta T}{T_0} \right|_{LLM} = -\frac{A}{R - \delta} - \frac{B}{R}$$

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

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:

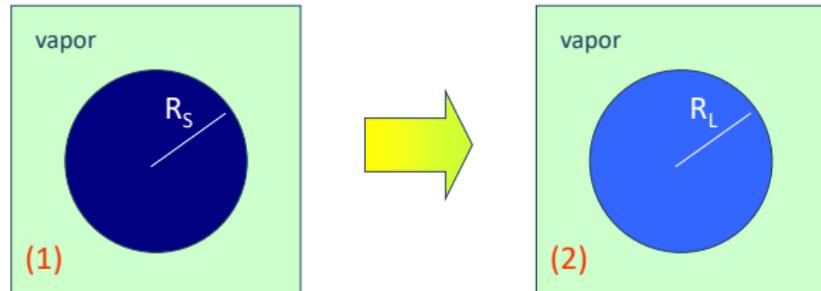
$$\gamma_{SL} = 1.135 \text{ J/m}^2 \text{ (solid-liquid surface tension)}$$

Thermodynamic Size Effect

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



$$G_2 = N\mu_L + 4\pi R_L^2 \gamma_{LV}$$

$$\Delta G_{2,1} \equiv G_2 - G_1$$

$$= N(\mu_L - \mu_S) + 4\pi R^2 \left[\gamma_{LV} \left(\frac{\rho_S}{\rho_L} \right)^{2/3} - \gamma_{SV} \right]$$

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

$$(\mu_L - \mu_S) = \frac{\Delta G_{vol}}{N} = \Delta g_{vol}$$

$$\Delta g_{vol} = \Delta h - T\Delta s$$

$$= L - T \frac{L}{T_0}$$

$$\frac{\partial \Delta G_{2,1}}{\partial R} = 0$$

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

Thermodynamic Size Effect

LLM

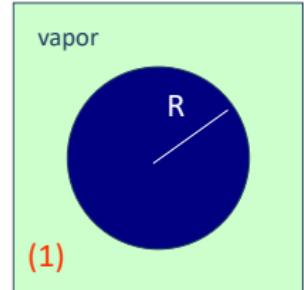
Compare the two configurations:

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

N: atoms solid phase

N': atoms liquid phase

γ : interfacial energy



N': atoms liquid phase

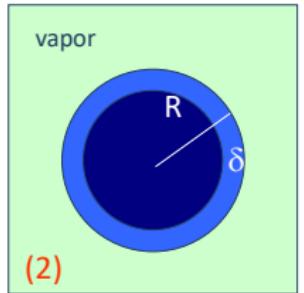
L: Latent heat of fusion

V_L: Volume liquid phase

δ : liquid layer thickness

Approx: $\rho_s \cong \rho_L \cong \rho$

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



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

Thermodynamic Size Effect

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

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

Smooth Interfaces Interaction (SII)

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

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

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

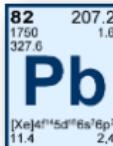
$$\Delta G_S$$

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

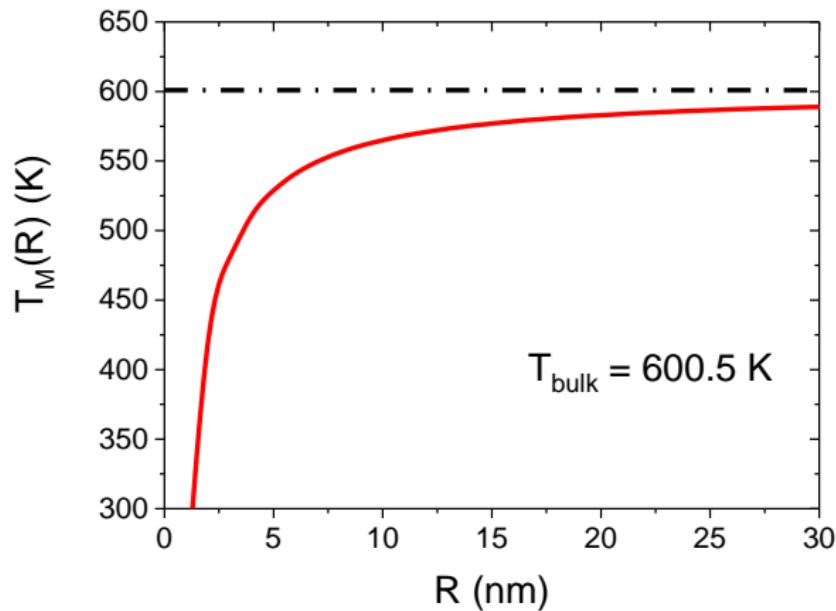
$$\Gamma \equiv \gamma_{SV} - \left[\gamma_{LV} + \gamma_{SL} \left(1 - \frac{\delta}{R} \right)^2 \right]$$

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

$$\left. \frac{\Delta T}{T_0} \right|_{SII} \xrightarrow[\xi \rightarrow 0]{} \left. \frac{\Delta T}{T_0} \right|_{LLM}$$

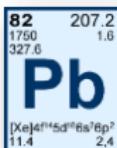


TSE on Pb nanoclusters



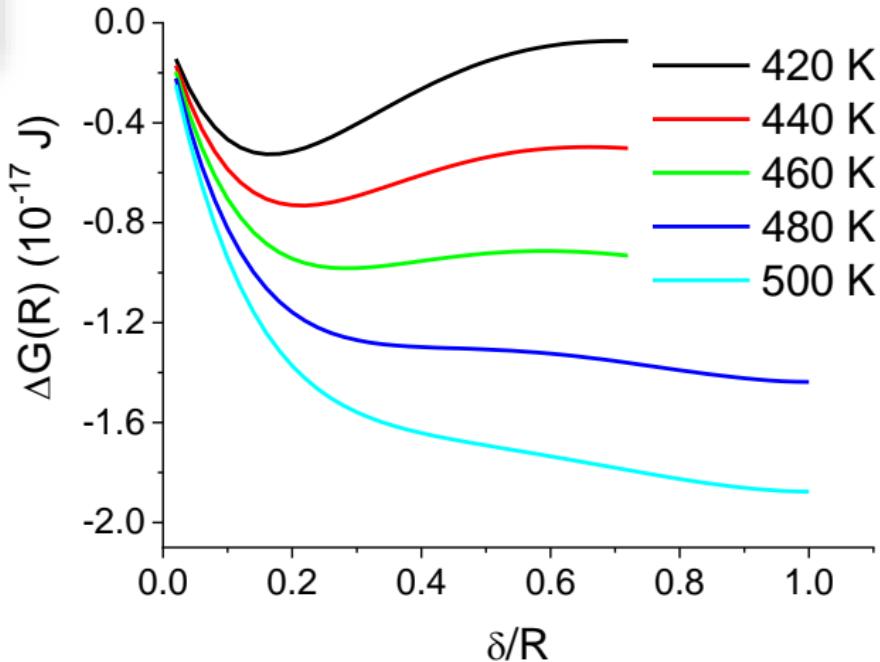
G. Mattei et al., *Transmission electron microscopy and optical characterization of nano-particles*, in Fundamental properties of nanostructured materials, World Scientific (Singapore) 1994, p.111-123

Thermodynamic Size Effect



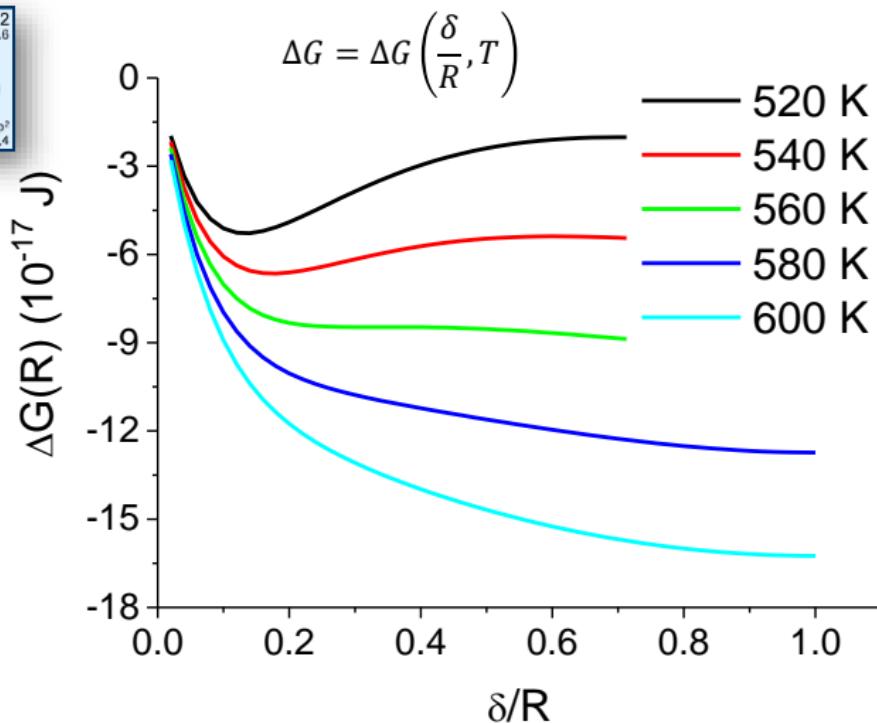
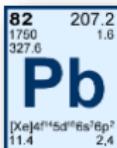
Pb
R = 5 nm

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



for $R = 5 \text{ nm}$ at $T \sim 480 \text{ K}$ no minimum in $\Delta G(R, \delta, T)$

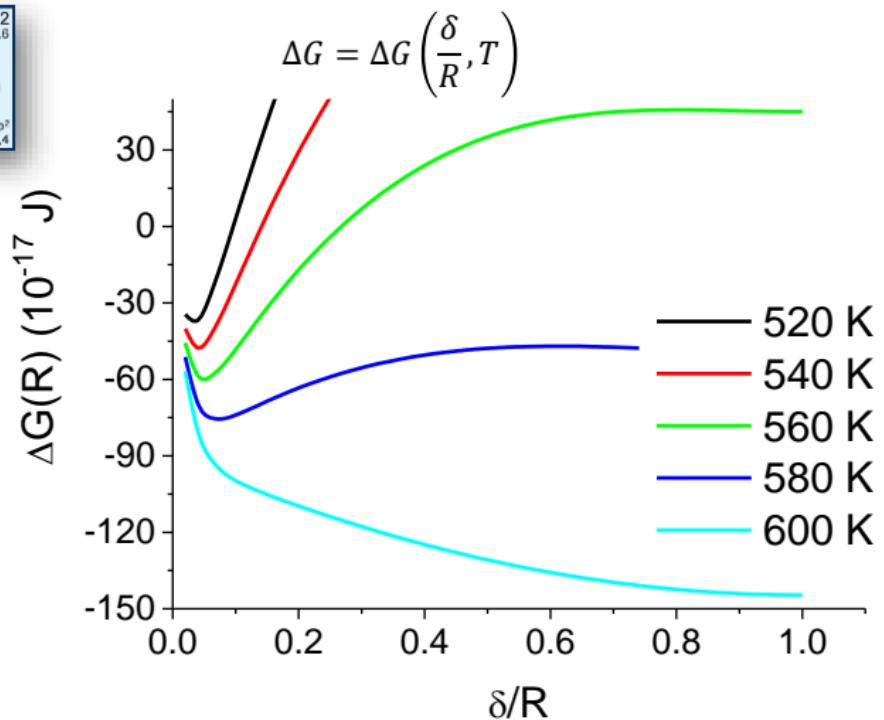
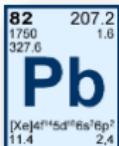
Thermodynamic Size Effect



Pb
R = 10 nm

for $R = 10 \text{ nm}$ at $T \sim 560 \text{ K}$ no minimum in $\Delta G(R, \delta, T)$

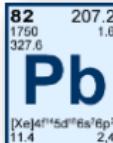
Thermodynamic Size Effect



Pb
R = 30 nm

for R = 30 nm at T ~ 590 K no minimum in $\Delta G(R, \delta, T)$

Thermodynamic Size Effect



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

Pb
R = 30 nm

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

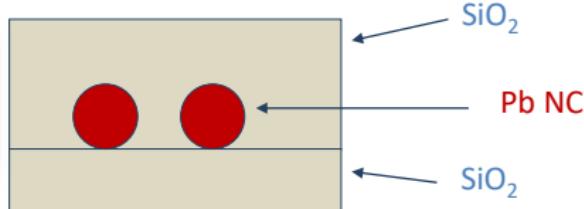
$$F = \frac{n_{\text{sup}}}{n} = \frac{4}{n^{1/3}} = 4 \frac{R_0}{R}$$

$$R_0 (\text{Pb, fcc}) = 0.175 \text{ nm}$$

$$F(\text{Pb, 30nm}) = 0.023 = 2.3\%$$

Thermodynamic Size Effect

82	207.2
1750	1.0
327.6	
Pb	
[Xe]4f ¹⁴ 5d ⁰ 6s ² 6p ²	
11.4	2.4

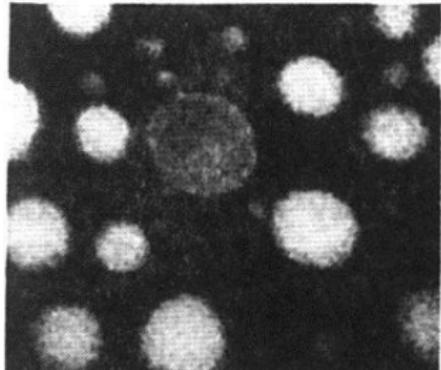


Gas Phase synthesis of Pb NCs
(Pb evaporation/condensation on
a SiO_2 substrate)

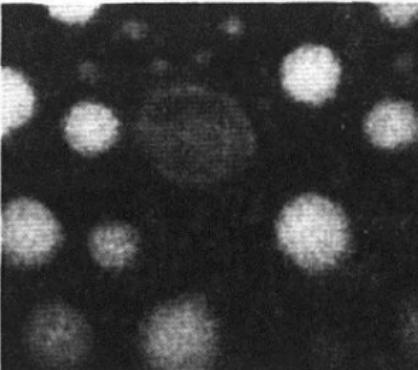
$$T_M(\text{bulk}) = 600 \text{ K}$$

Dark-field TEM Image of Pb NCs in SiO_2

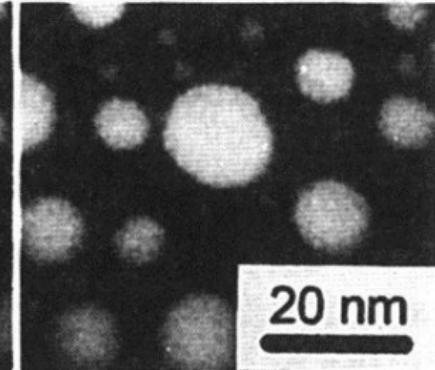
$T = 535 \text{ K}$



$T = 545 \text{ K}$



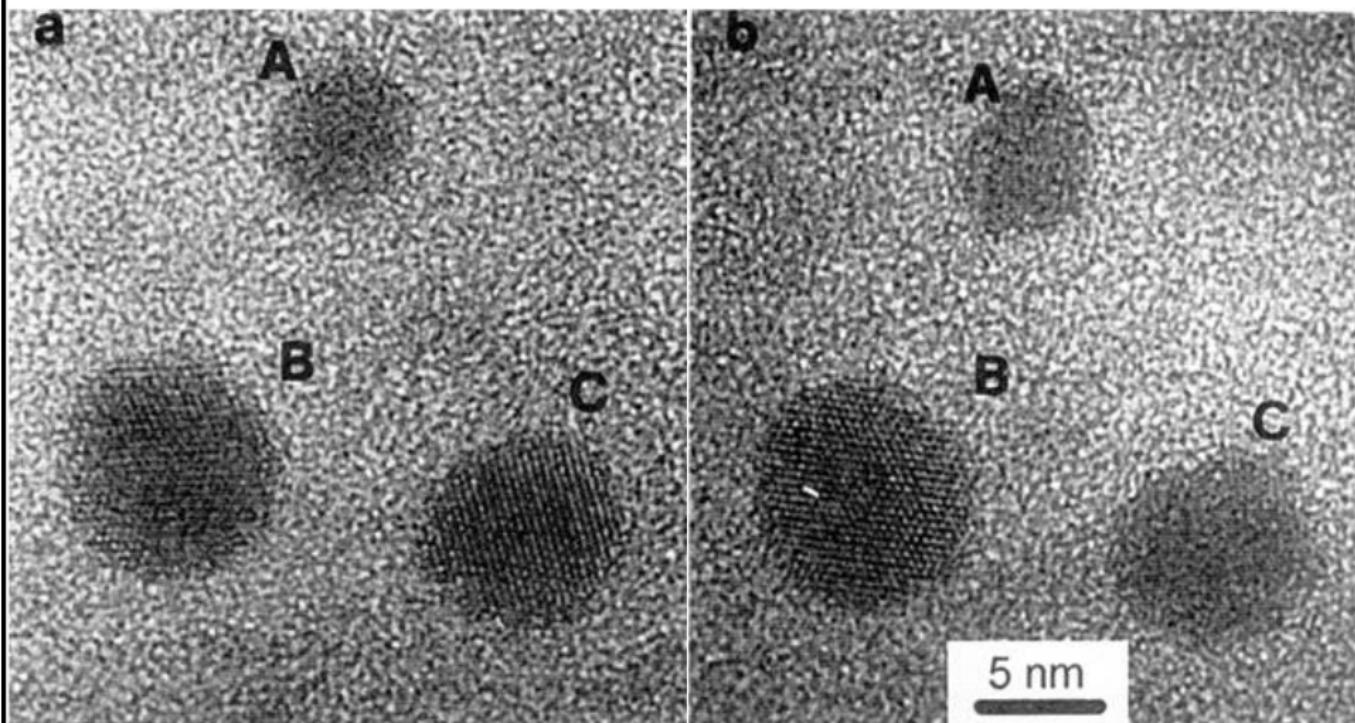
$T = 545 \text{ K}$



20 nm

Thermodynamic Size Effect

High-resolution TEM Image of Pb NCs in SiO₂



Thermodynamic Size Effect

Phase fluctuation in Pb NCs

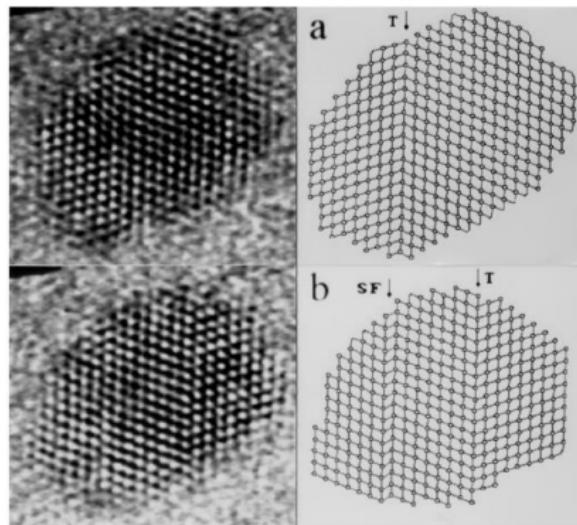


FIG. 3. Configuration transition, involving vanishing of a twin (T) on the left side, leaving a stalking fault (SF), and appearance of twin on the right side. (The first configuration was stable for 1.5 sec, the second configuration was stable for 6.5 sec, the transition time is less than 0.04 sec.)

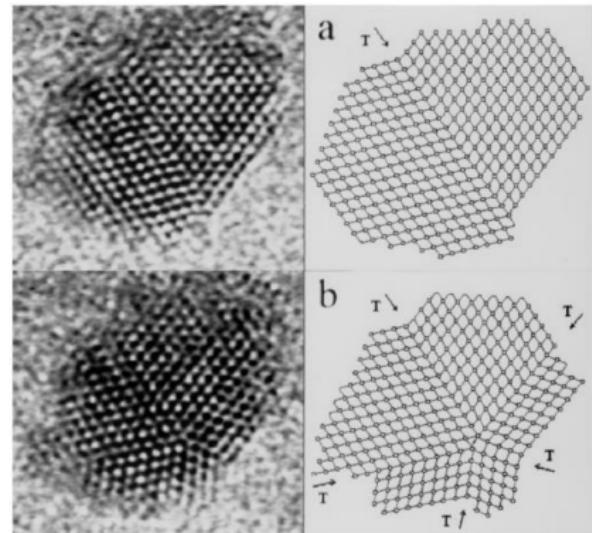


FIG. 4. Configuration transition, between single twin structure and a five-fold structure, by introducing four additional twins (marked with arrows). (The first configuration was stable for 7 sec; the second configuration was stable for 0.5 sec; the transition time is less than 0.04 sec.)