Size Equation

Nano-Thermodynamics

Nano-size

	Bulk Material	Nano Material
Size (L)	~ 1 m	< 100 nm = 10^{-7} m
Property (A)	A ≠ A(L)	A = A(L)

- Characteristic lengths λ_C ~ 1- 100 nm
- Nano-physics: $L < \lambda_C$
- E.g.:
  - λ_e = electronic mean free path (10-100 nm)
  - λ_{exc} = excitonic Bohr radius (1-10 nm)
  - λ_M = magnetic domain (30-50 nm)

control L = control A(L)

Size Equation:

- Evolution of the chemical-physical properties vs. the nanostructures size
- Top-down approach

$$A(N) = A(\infty)\left(1 + \frac{C_N}{N^{\alpha}}\right)$$

$$A(R) = A(\infty)\left(1 + \frac{C_R}{R^{\alpha}}\right)$$

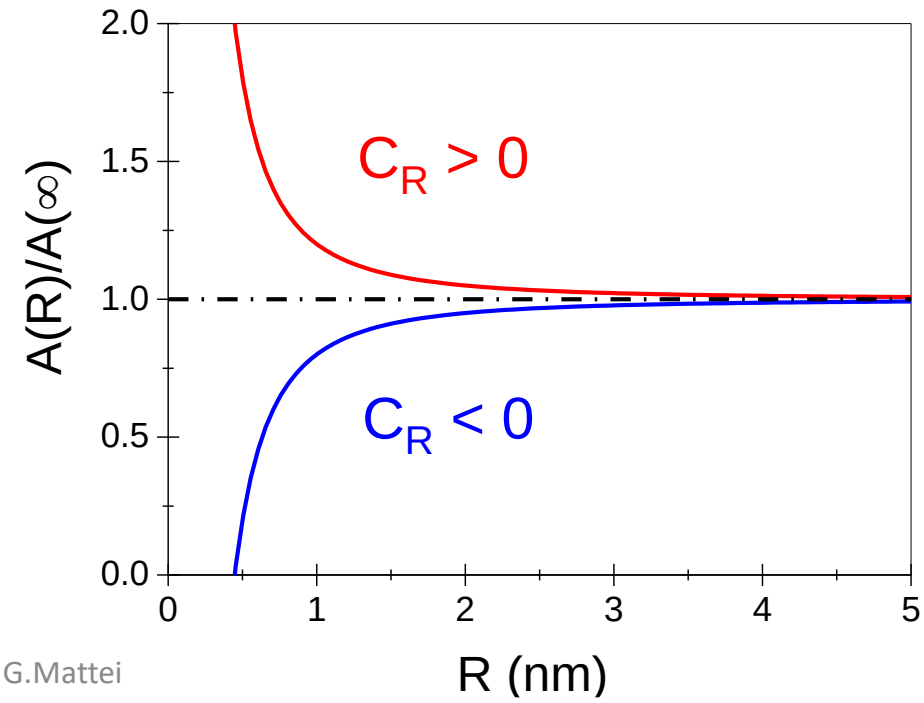
A = property

A(∞) = bulk limit of A

N = number of atoms

R = NP radius

C, α costants



Effective radius and atomic fraction at the surface

$$V = \frac{4\pi}{3} R_0^3 N = \frac{4\pi}{3} R_{eff}^3$$

$$R_{eff} = \left(\frac{V}{4\pi/3}\right)^{1/3} = R_0 N^{1/3}$$

$$S = 4\pi R_{eff}^2 = 4\pi R_0^2 N^{2/3}$$

$$N_{\sup} = \frac{S}{S_{at}} = \frac{4\pi R_0^2 N^{2/3}}{\pi R_0^2} = 4N^{2/3}$$

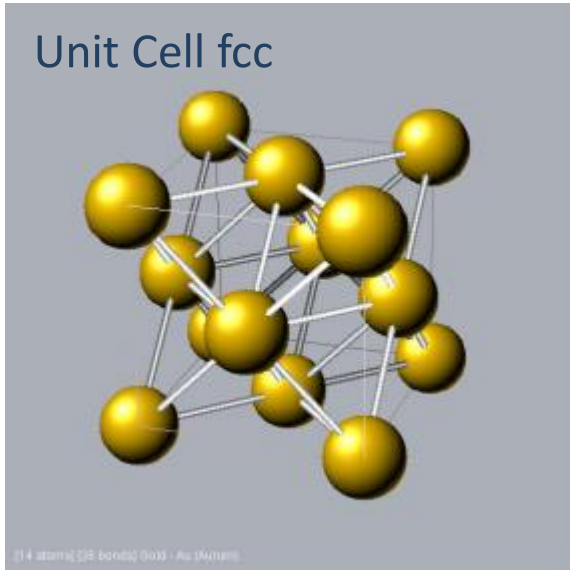
$$F = \frac{N_{\sup}}{N} = \frac{4}{N^{1/3}} = \frac{4R_0}{R_{eff}}$$

$\boldsymbol{V}$ = cluster volume

$\boldsymbol{S}$ = cluster surface

$\boldsymbol{R_0}$ = atomic radius

$$R_{0,fcc} = \frac{a}{4}\sqrt{2}$$

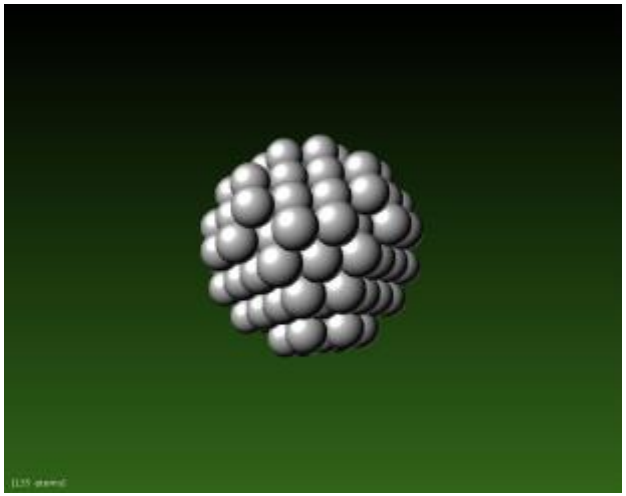


$\boldsymbol{F}$ = fraction of surface atoms

N	F
10^2	0.86
10^3	0.40
10^6	0.04

Surface effect

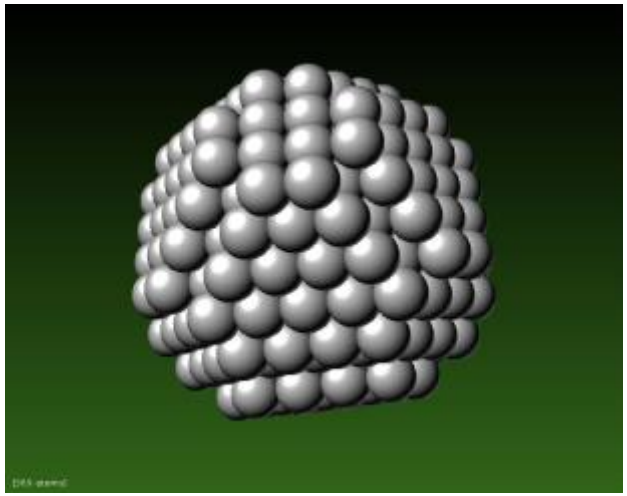
Co f.c.c. a = 0.35447 nm, $R_0 = a\,2^{1/2}/4 = 0.1253$ nm



n = 139 atoms

R_{eff} = 0.65 nm

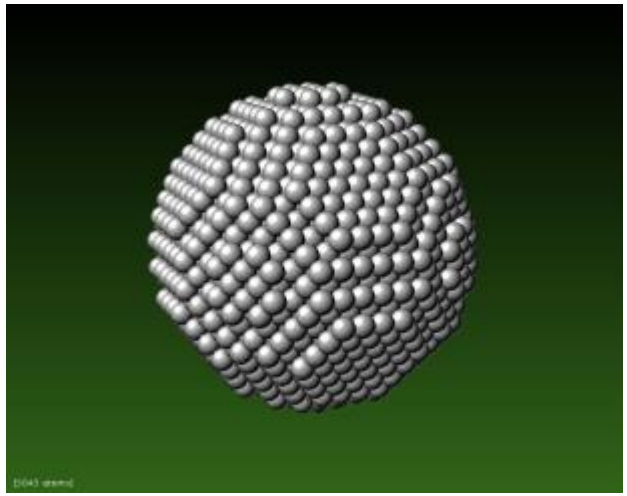
F = 77 %



n = 369 atoms

R_{eff} = 0.90 nm

F = 56 %



n = 3043 atoms

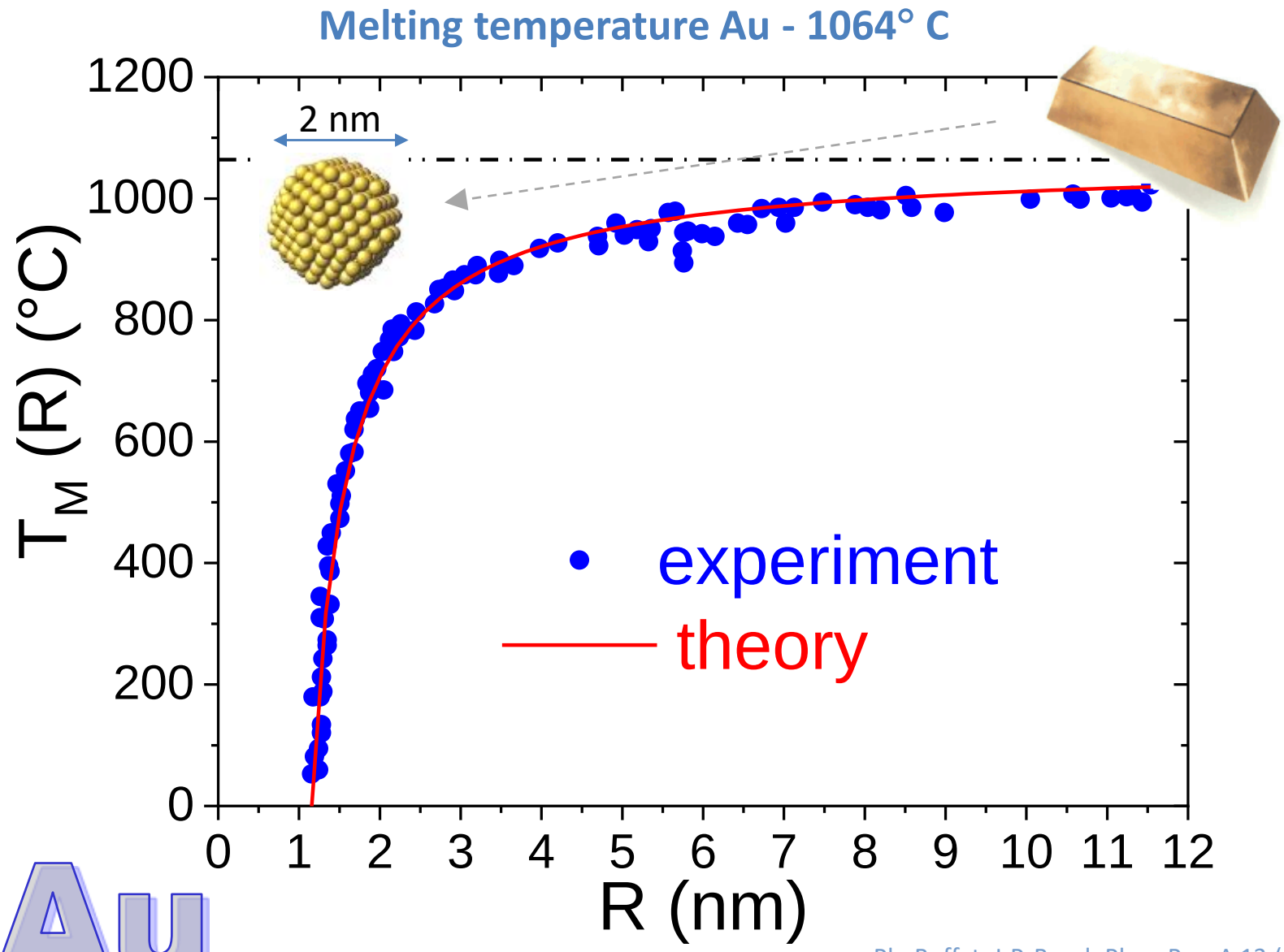
R_{eff} = 1.82 nm

F = 28 %

Thermodynamic Size Effect

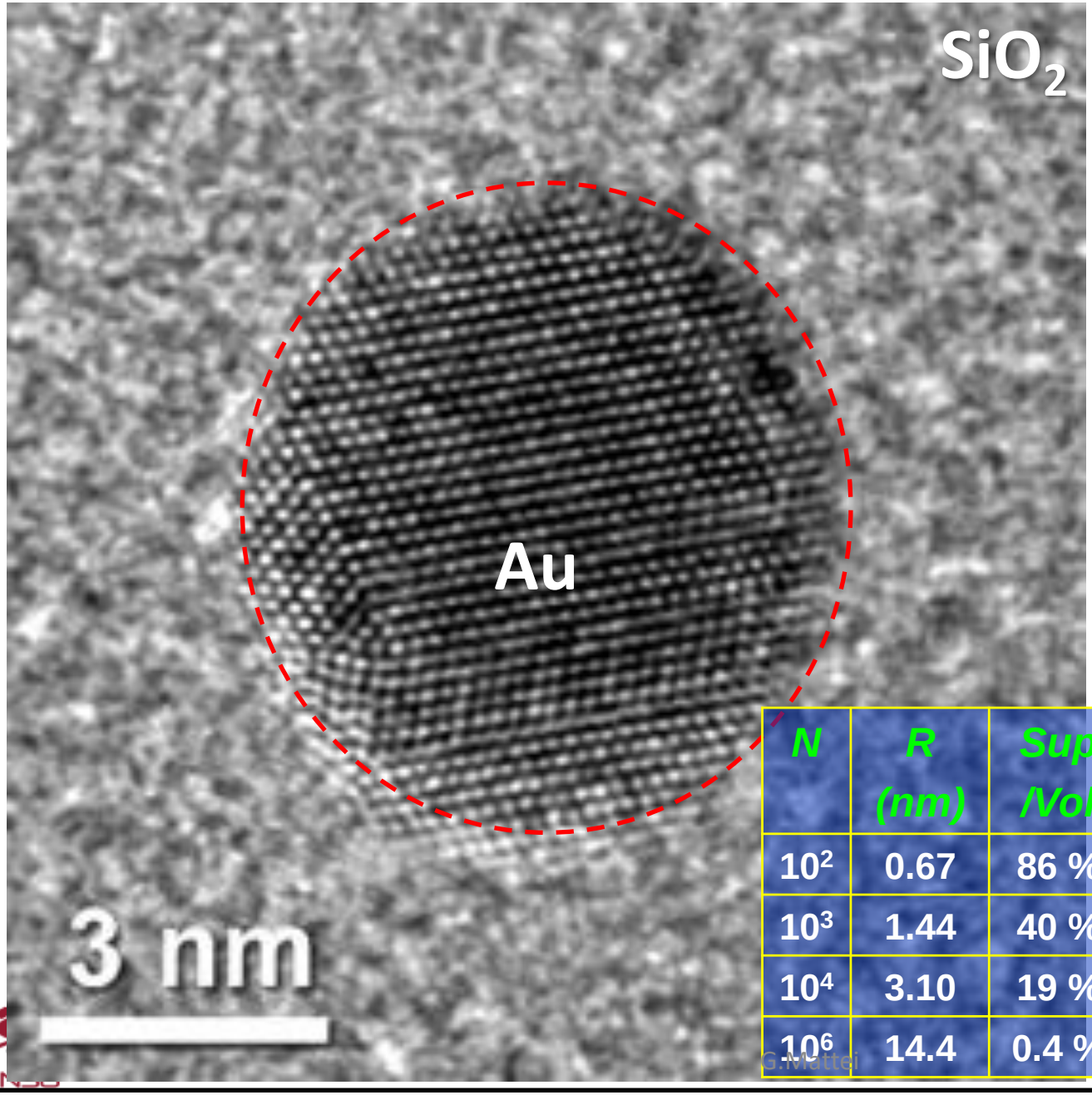
(TSE)

Example of A = A(L)

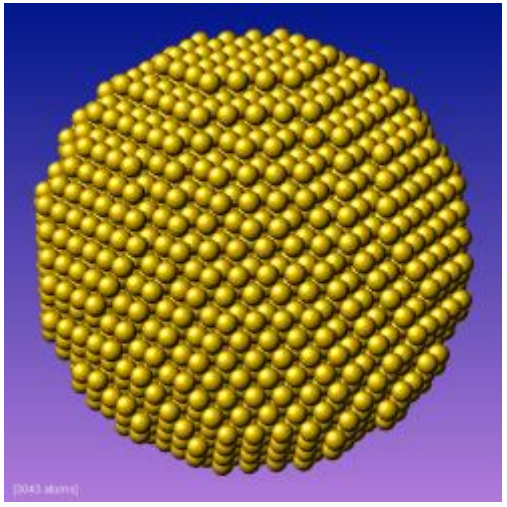


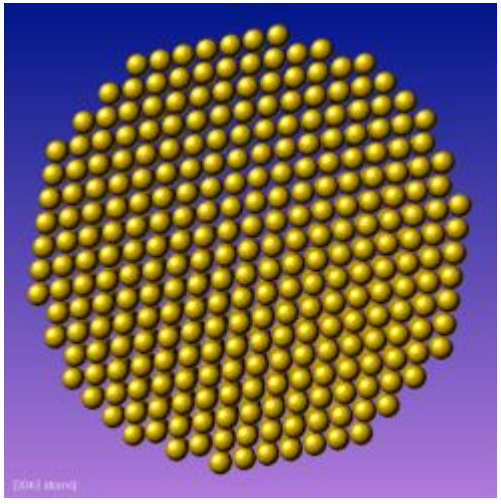
Ph. Buffat, J-P. Borel, Phys. Rev. A 13 (1976) 2287

Au NCs obtained by ion implantation in SiO_2



N	R (nm)	Sup /Vol
10^2	0.67	86 %
10^3	1.44	40 %
10^4	3.10	19 %
10^6	14.4	0.4 %





Au NC visto lungo la direzione <110>

Thermodynamic Size Effect

Given a spherical cluster with N atoms:

$$T_M(R) \quad \leftrightarrow \quad T_M(\infty)$$

At equilibrium between solid (S) and liquid (L) phases:

$$\mu_L(T,P) = \mu_S(T,P)$$

$$\mu \equiv \left.\frac{\partial G}{\partial N}\right|_{T,P} = \left.\frac{\partial U}{\partial N}\right|_{S,V}$$

First-order expansion of the chemical potential close to the bulk thermodynamic equilibrium (T_0,P_0) gives:

$$\mu(T,P) = \mu(T_0,P_0) + \frac{\partial \mu}{\partial T}(T - T_0) + \frac{\partial \mu}{\partial P}(P - P_0) + \ldots$$

Considering $U = U(S,V,N)$ and requiring that $U(\lambda S, \lambda V, \lambda N) = \lambda\, U(S,V,N)$ it results:

$$U \equiv TS - PV + \mu N$$

Thermodynamic Size Effect

Using the Gibbs-Duhem relation for $U(S,V,N)$

$$SdT - VdP + Nd\mu = 0$$

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP$$

$$d\mu = -sdT + \frac{1}{\rho}dP$$

$$\begin{cases} s \equiv \frac{S}{N} = -\left(\frac{\partial \mu}{\partial T}\right)_P \\ \frac{1}{\rho} \equiv \frac{V}{N} = \left(\frac{\partial \mu}{\partial P}\right)_T \end{cases}$$

therefore:

$$0 = \mu_L(T_0,P_0) + \frac{\partial \mu_L}{\partial T}(T - T_0) + \frac{\partial \mu_L}{\partial P}(P_L - P_0) - \mu_S(T_0,P_0) - \frac{\partial \mu_S}{\partial T}(T - T_0) - \frac{\partial \mu_S}{\partial P}(P_S - P_0) + \dots$$

Thermodynamic Size Effect

If T_0 and P_0 are at the triple point of the bulk phase:

$$\mu_L(T_0, P_0) = \mu_S(T_0, P_0)$$

$$0 = s_L(T - T_0) - \frac{1}{\rho_L}(P_L - P_0) - s_S(T - T_0) + \frac{1}{\rho_S}(P_S - P_0)$$

$$(s_L - s_S)(T - T_0) - \frac{1}{\rho_L}(P_L - P_0) + \frac{1}{\rho_S}(P_S - P_0) = 0$$

From Laplace law:

$$P_L = P_{ext} + 2\frac{\gamma_L}{R_L} \approx 2\frac{\gamma_L}{R_L}$$

$$P_S = P_{ext} + 2\frac{\gamma_S}{R_S} \approx 2\frac{\gamma_S}{R_S}$$

$$R_S = \left(\frac{\rho_L}{\rho_S}\right)^{1/3} R_L$$

when R ⇨ 0

$P_{ext} << P_L, P_S$

Thermodynamic Size Effect

Considering the Latent heat of fusion per atom L $\quad L = (s_L - s_S)T_0$

$$(s_L - s_S)T_0\left(\frac{T}{T_0} - 1\right) + 2\left(\frac{\gamma_S}{R_S\rho_S} - \frac{\gamma_L}{R_L\rho_L}\right) + P_0\left(\frac{1}{\rho_L} - \frac{1}{\rho_S}\right) = 0$$

$$\frac{\Delta T}{T_0} \equiv \frac{T - T_0}{T_0} = -\frac{2}{LR_S\rho_S}\left(\gamma_S - \gamma_L\left(\frac{\rho_S}{\rho_L}\right)^{2/3}\right) = -\frac{A}{R} < 0$$

Hypoteses:

1. First-order expansion of the chemical potential
2. Spherical Cluster
3. $\rho_L \sim \rho_S$

Thermodynamic Size Effect

Size equation

$$T_M(R) = T_M(\infty)\left(1 - \frac{C}{R}\right)$$

$$C \equiv \frac{2}{L\rho_S}\left(\gamma_S - \gamma_L\left(\frac{\rho_S}{\rho_L}\right)^{2/3}\right)$$

For Au:

L = 62700 J/kg (*latent heat of fusion*)

T_0 = 1336 K (*bulk melting temperature*)

ρ_L = 17280 kg/m^3 (*density of the liquid phase*)

ρ_S = 18400 kg/m^3 (*density of the solid phase*)

γ_L = 1.135 J/m^2 (*surface tension liquid phase*)

γ_S = 1.380 J/m^2 (*surface tension solid phase*)

C(Au) = 0.34 nm