How Stable and Active Materials would be under 100 nm

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nano.ipm.ac.ir/CV_Yaghmaee.pdf

Scheme of lecture

Transparences: 2-4
- why small scale materials …(where)???
- why cohesion
  * classical macro view
  * under 50-100 nm ?

Transparences: 5-8
- first approach (only bulk "inside" size dependency)
- theory and refinement
- computational example

Transparences: 9-12
- second approach: concerning the surface cohesion energy
- hypothesis
- theory and new equations

Transparences: 13-15
- computation
  * comparing with bulk version
  * comparing different metals
  * comparing with experimental observation

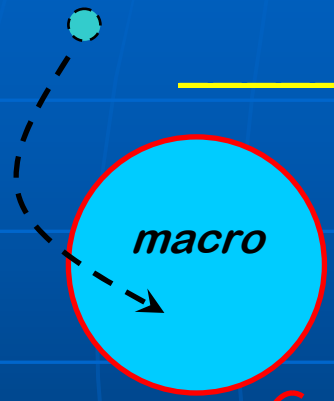
Transparences:
- activity
- computational analysis

Transparences: 17
- conclusions and overview

Why Cohesion

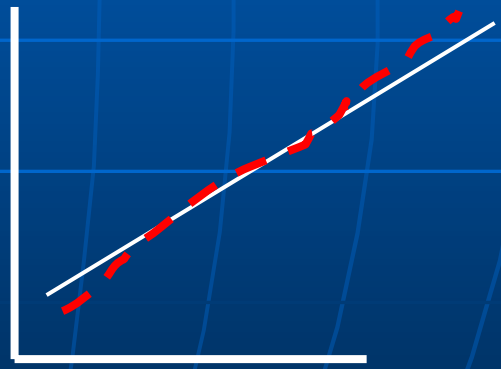
effects physico - chemical properties

- *first order phase transition, or even higher*
- *solubility, oxidation, …*
- *activity (indirectly biological effect)*
- *…*



- *Classical: bulk value (above 50-100 nm materials)*
  - *(-) sublimation almost [1-2]*
  - *metals scaling [1-2]*
  - *we know its effect on physico-chemical properties*

$$\Delta U_{coh} \approx \Delta_f H_s - \Delta_f H_g = \Delta_C H = -\Delta_S H$$



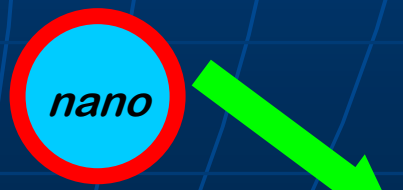
- *Under 50-100 nm*

$$E_b$$

$$(I) \quad E_p \propto E_b$$

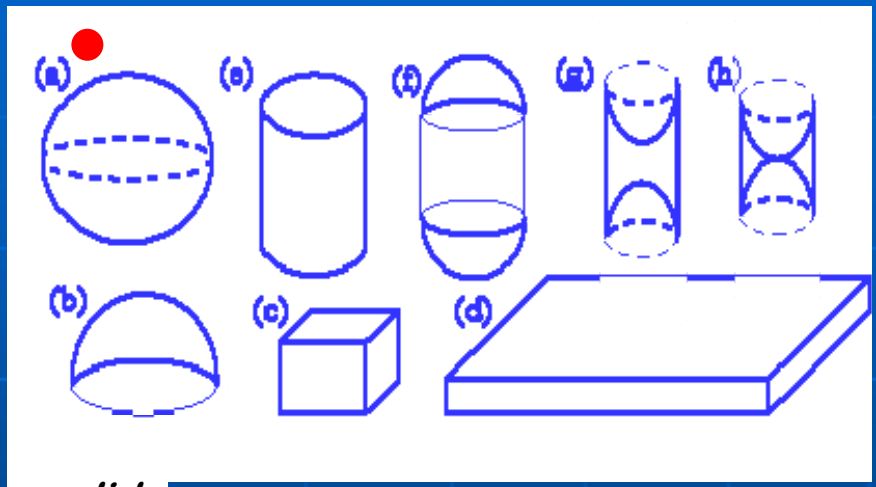
$$(II) \quad E_p \propto E_i \quad E_S$$

- *bulk (inside) cohesion*
- *surface cohesion*

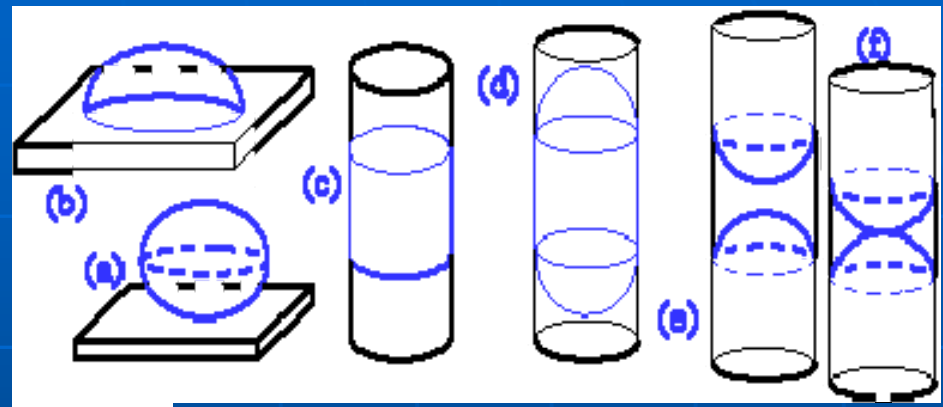


Under 50-100 nm

$\Delta_m H$



solid



liquid

Schematics of basic free standing solid state shapes in nano-scale world.

Approaches:

nano

$(I) \quad E_p \propto E_b \quad ???$

- **First Approach:** bulk cohesion energy
- **Second Approach:** surface cohesion energy and its effect on total cohesion energy

First Approach: bulk cohesion energy

2002 , W.H.Qi, et al, [3]

size dependency of cohesion energy.

$$E_p = E_b\left(1 - d_a \cdot \frac{1}{D_p}\right)$$ [J/atom of bulk] or [J/mol] (1)

The fundamental hypothesis behind Eq(1) are;

i. when a spherical particle is separated into its atoms/molecules by applying the cohesion energy, if the volume remains constant, then we may write:

$$n = d_a^3 / D_p^3$$

ii. by defining the surface area change during applying the given energy for separation of a particle into n atoms which apparently equals to surface energy of solid materials multiplying by the total surface area, then we may write:

$$E_n = \Delta A \cdot \delta^o$$

iii. cohesion energy per atoms from the previous two points will be:

$$E = \pi \cdot \delta^o \cdot d_a^2 \cdot (1 - d_a / D_p)$$

iv. these two energies (ii. and iii.) phenomenologically are equal, then we can write:

$$E_n = E$$

Packing factor correction

in [3], regarding the steps i.

condition of constant volume

real materials volume packing factor

$$f_v \cdot V_p = n \cdot V_a$$

$$E_p = E_b \cdot \left(1 + \frac{1}{f_v} \cdot d_a \cdot \frac{1}{D_p}\right)$$

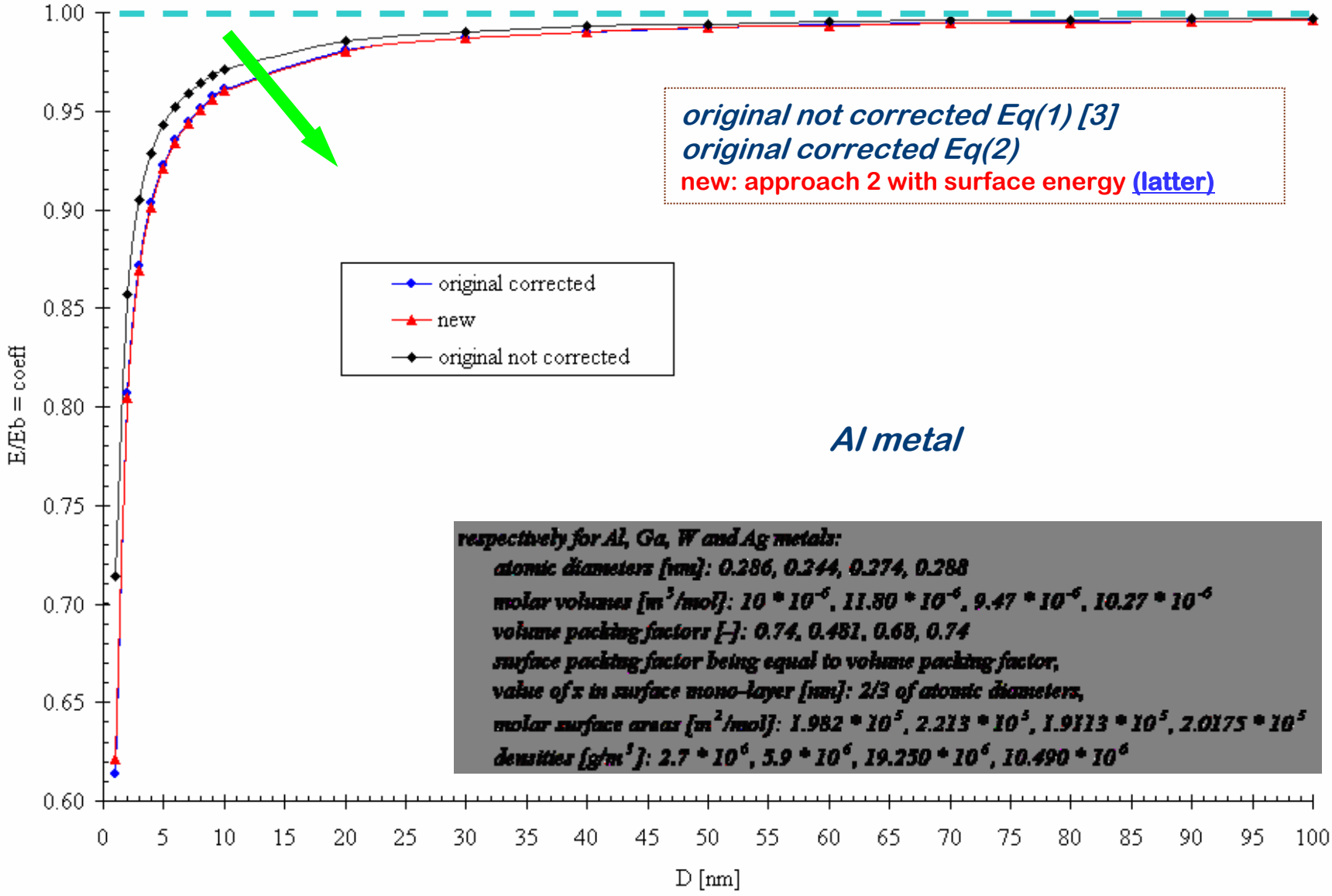
[J/atom of bulk] or [J/mol] (2)

Comparing Eq(1) and Eq(2),

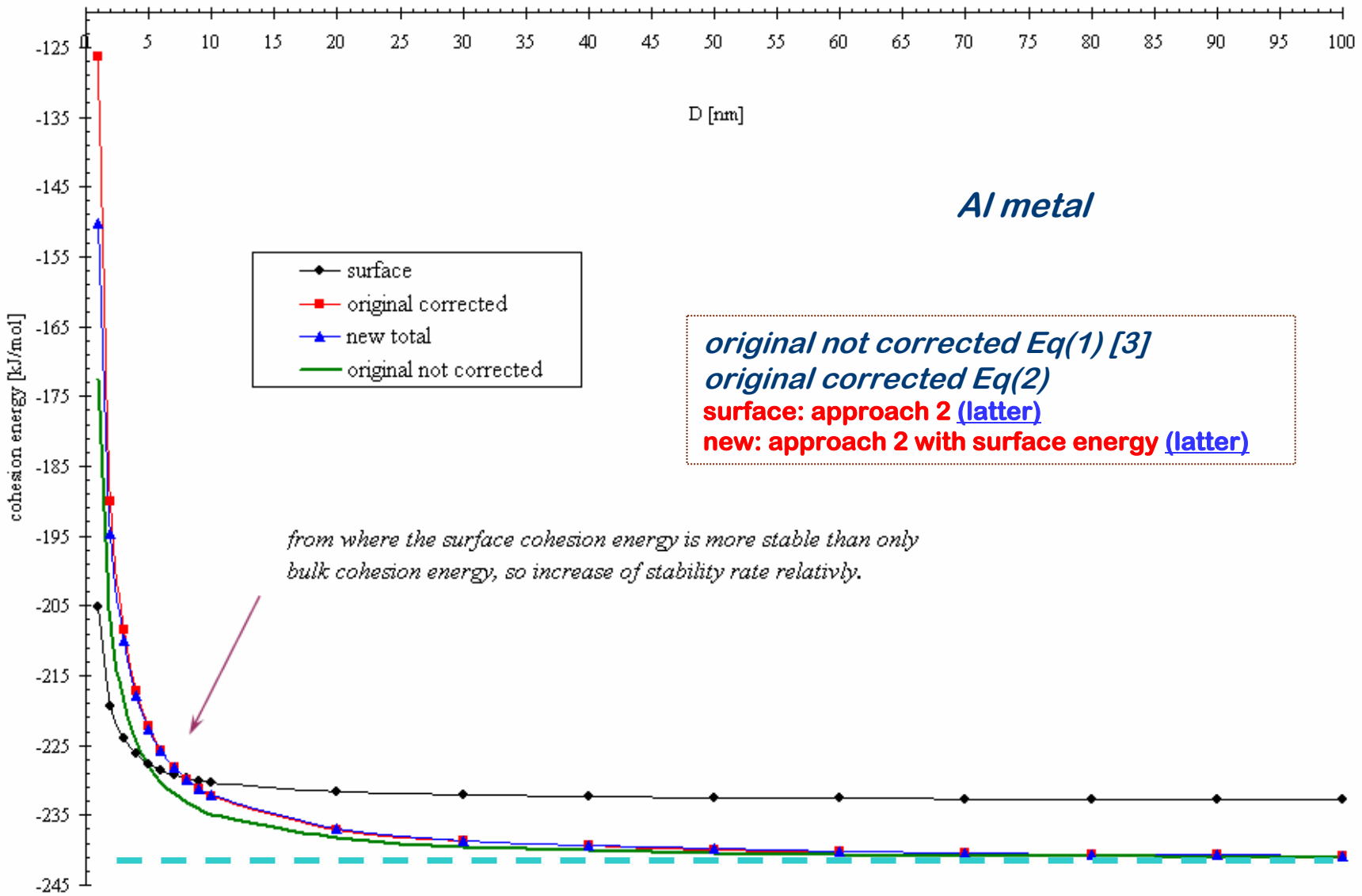
usual metallic crystal structure with fcc

packing factor of 0.74

we expect 35% faster size variation effect respectively



Comparison of coefficient of bulk cohesion energy for Al metal.



Comparison of different cohesion energies for Al metal.

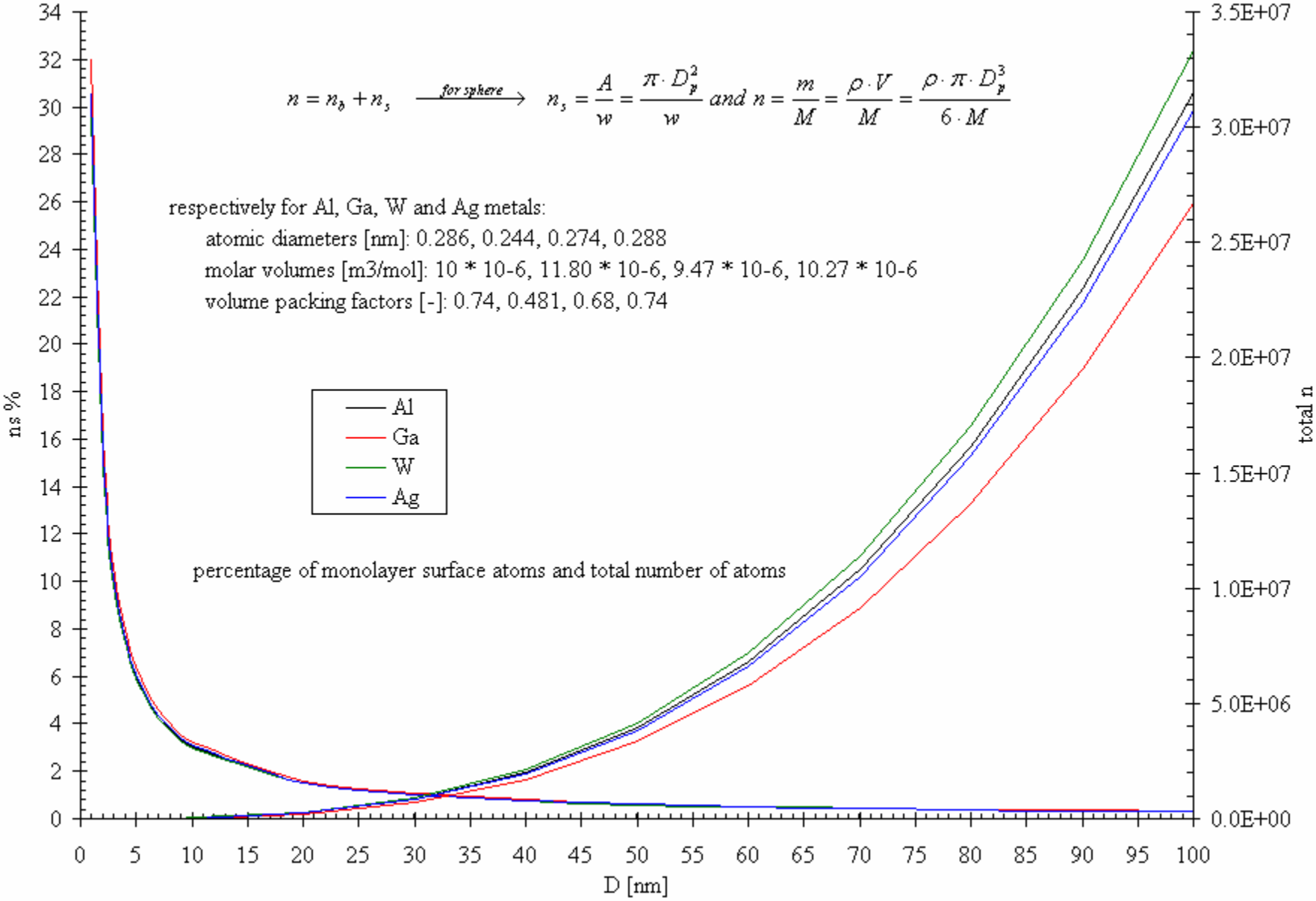
$$n = n_b + n_s \xrightarrow{\text{for sphere}} n_s = \frac{A}{w} = \frac{\pi \cdot D_p^2}{w} \text{ and } n = \frac{m}{M} = \frac{\rho \cdot V}{M} = \frac{\rho \cdot \pi \cdot D_p^3}{6 \cdot M}$$

respectively for Al, Ga, W and Ag metals:

atomic diameters [nm]: 0.286, 0.244, 0.274, 0.288

molar volumes [m3/mol]: 10 * 10-6, 11.80 * 10-6, 9.47 * 10-6, 10.27 * 10-6

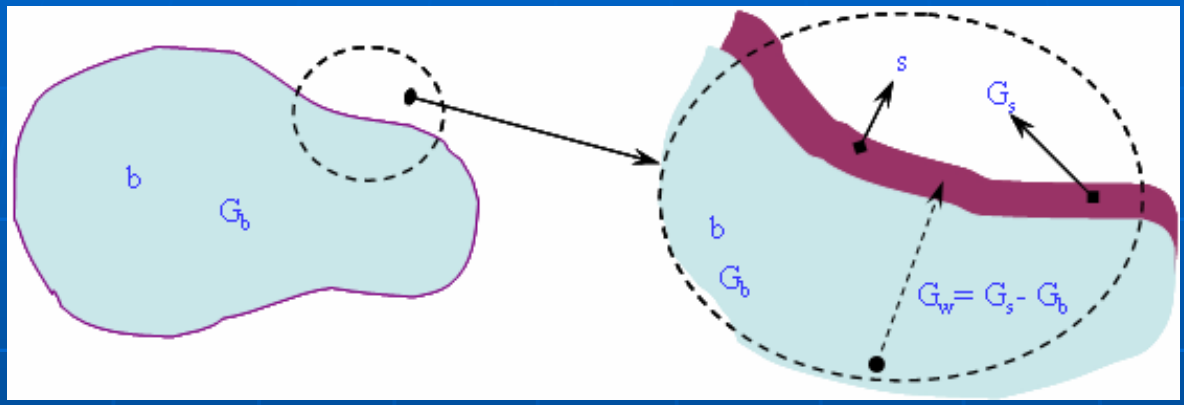
volume packing factors [-]: 0.74, 0.481, 0.68, 0.74



pre 9

Xie, Qi: 2004 [4] from embedded NP in matrix got the wholly free standing coefficient as 3/4 in Eq(1) and said it is the surface effect

Second Approach: considering the surface cohesion energy



Schematics of surface and Gibbs free energy related things.

total Gibbs free energy of a system

$$G^{\Sigma} = n \cdot G_b + \delta \cdot A \qquad [J] \qquad (3)$$

By considering the amount of materials gathered in surface as well as bulk

$$n = n_b + n_s \xrightarrow{\text{for sphere}} n_s = \frac{A}{w} = \frac{\pi \cdot D_p^2}{w} \text{ and } n = \frac{m}{M} = \frac{\rho \cdot V}{M} = \frac{\rho \cdot \pi \cdot D_p^3}{6 \cdot M} \qquad (4)$$

Consequently through Eq(3), we can write similar algorithms for any physico-chemical quantity of materials like cohesion energy

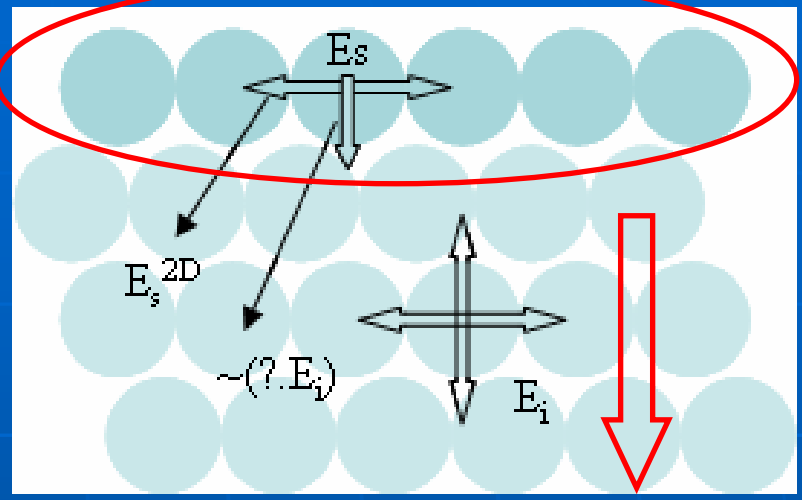
$$E = n_b \cdot E_b + n_s \cdot E_s \xrightarrow{\text{then}} E_p = n_i \cdot E_i + n_s \cdot E_s \qquad [J] \qquad (5)$$

modeling the surface cohesion energy

$$E_p = n_i \cdot E_i + n_s \cdot E_s \qquad [J] \quad (5)$$

from Eq(2)

?



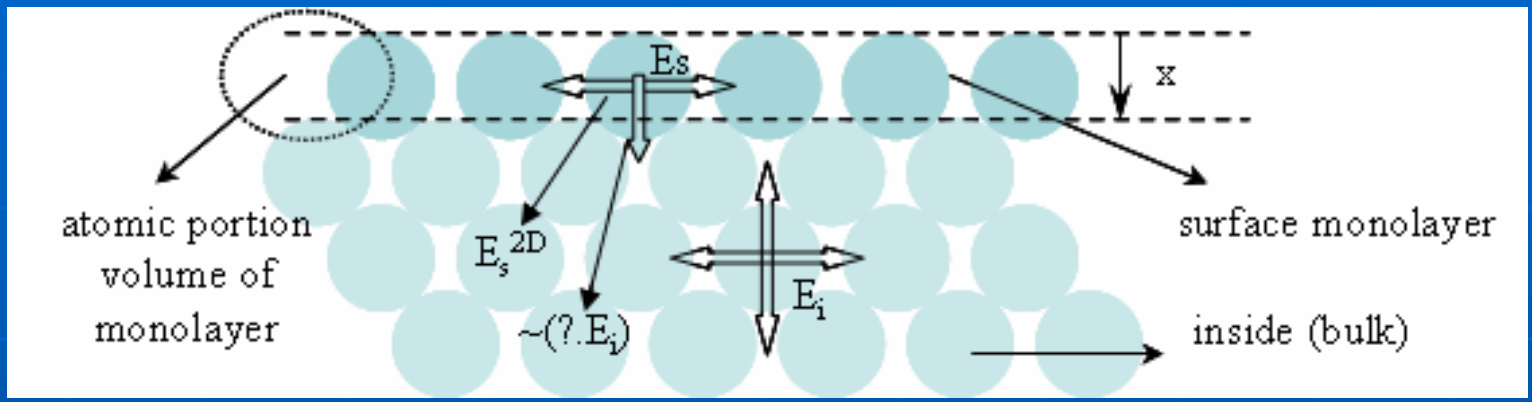
Schematics of surface energies at outer layers

As here we assume mono atomic/molecular surface layer. then we can summarize such estimation, as:

$$E_s = \frac{1}{6} \cdot E_i + E_s^{2D} \xrightarrow{\text{then in Eq(2)}} E_p = n_i \cdot E_i + n_s \cdot \left(\frac{1}{6} \cdot E_i + E_s^{2D} \right) \qquad [J/mol] \quad (6)$$

?

2D term of surface cohesion energy E_s^{2D}



Schematics of cohesion energies and surface monolayer

- *suppose there is a virtual 2D monolayer surface*
- *an amount of energy equal to* E_s^{2D} *in order to separate it into atoms/molecules*

use the algorithm similar bulk (inside)

- *the energy required to separate the atoms from the first layer (the one needed for compensating the 2D stability) proportional to making the surface area changed from initial state to areas of total separated atoms/molecules building the monolayer surface*
- *the proportionality factor is the surface energy of solid material, thus:*

$$E_s^{2D} = \delta \cdot \Delta A_s^{2D} = \delta \cdot (A_s^{final} - A_s^{initial}) \qquad (7)$$

During the separation: assumption of constant volume rule

$$n_s \cdot \frac{4}{3} \cdot \pi \left(\frac{d_a}{2} \right)^3 \equiv f_s \cdot V_s^{2D} \quad (8)$$

$$f_s \leq f_V$$

Regarding the Fig.1. and x *from volume constant condition we get:*

$$n_s = \frac{f_s \cdot (10 \cdot x \cdot D_p^2 - 12 \cdot x^2 \cdot D_p + 8 \cdot x^3)}{d_a^3} \quad (9)$$

Then Eq(7) changes to:

$$E_s^{2D} = \delta \cdot \left(n_s \cdot \pi \cdot {d_a}^2 - \pi \cdot {D_p}^2 \right) \quad [J] \quad (10)$$

By combining the hypothesis of Eqs(1-2) above, we may write further:

$$E_s^{2D} = E_b \cdot \left(1 - \frac{1}{f_s} \cdot d_a \cdot \frac{{D_p}^2}{(10 \cdot x \cdot D_p^2 - 12 \cdot x^2 \cdot D_p + 8 \cdot x^3)} \right) \quad [J/atom\ surface] \quad (11)$$

Combining the Eq(11) and Eq(6) regarding Eq(5), the total surface cohesion energy for complete sphere will be in [J/atom surface]

$$E_s = E_b \cdot \left(\frac{7}{6} - \frac{1}{f_v} \cdot d_a \cdot \frac{1}{D_p} \cdot \left(1 - \frac{f_v}{f_s} \cdot \frac{{D_p}^3}{(10 \cdot x \cdot D_p^2 - 12 \cdot x^2 \cdot D_p + 8 \cdot x^3)} \right) \right) \quad (12)$$

Computation Analysis

What we have till now:

$$E_p = E_b \cdot \left(1 - d_a \cdot \frac{1}{D_p}\right)$$

original not corrected

[J/atom of bulk] or [J/mol] [3] (1)

$$E_p = E_b \cdot \left(1 - \frac{1}{f_v} \cdot d_a \cdot \frac{1}{D_p}\right)$$

[J/atom of bulk] or [J/mol] (2)

original corrected

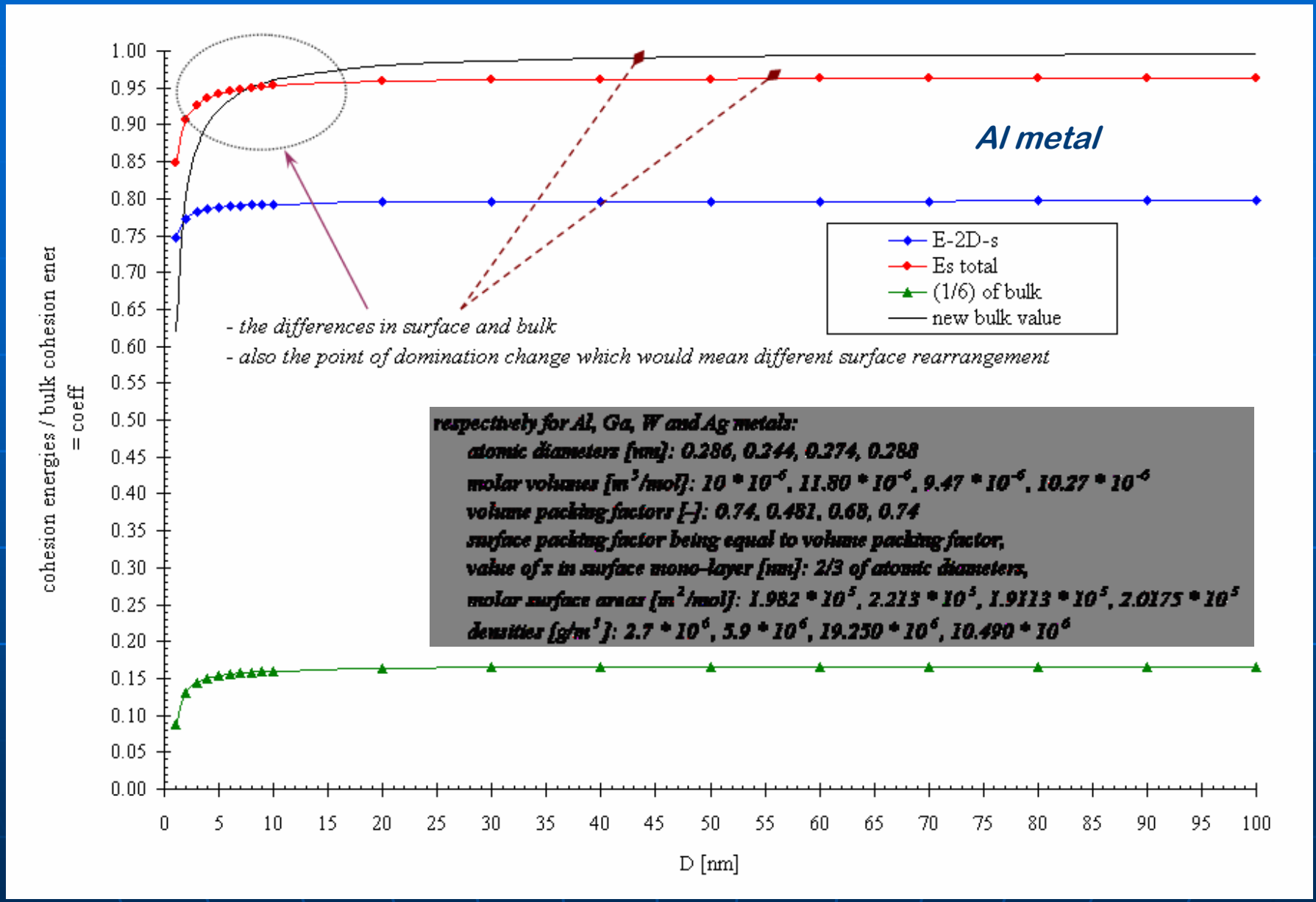
$E_p = n_i \cdot E_i + n_s \cdot E_s$ *[J] (5)* new

[J/atom surface] (12)

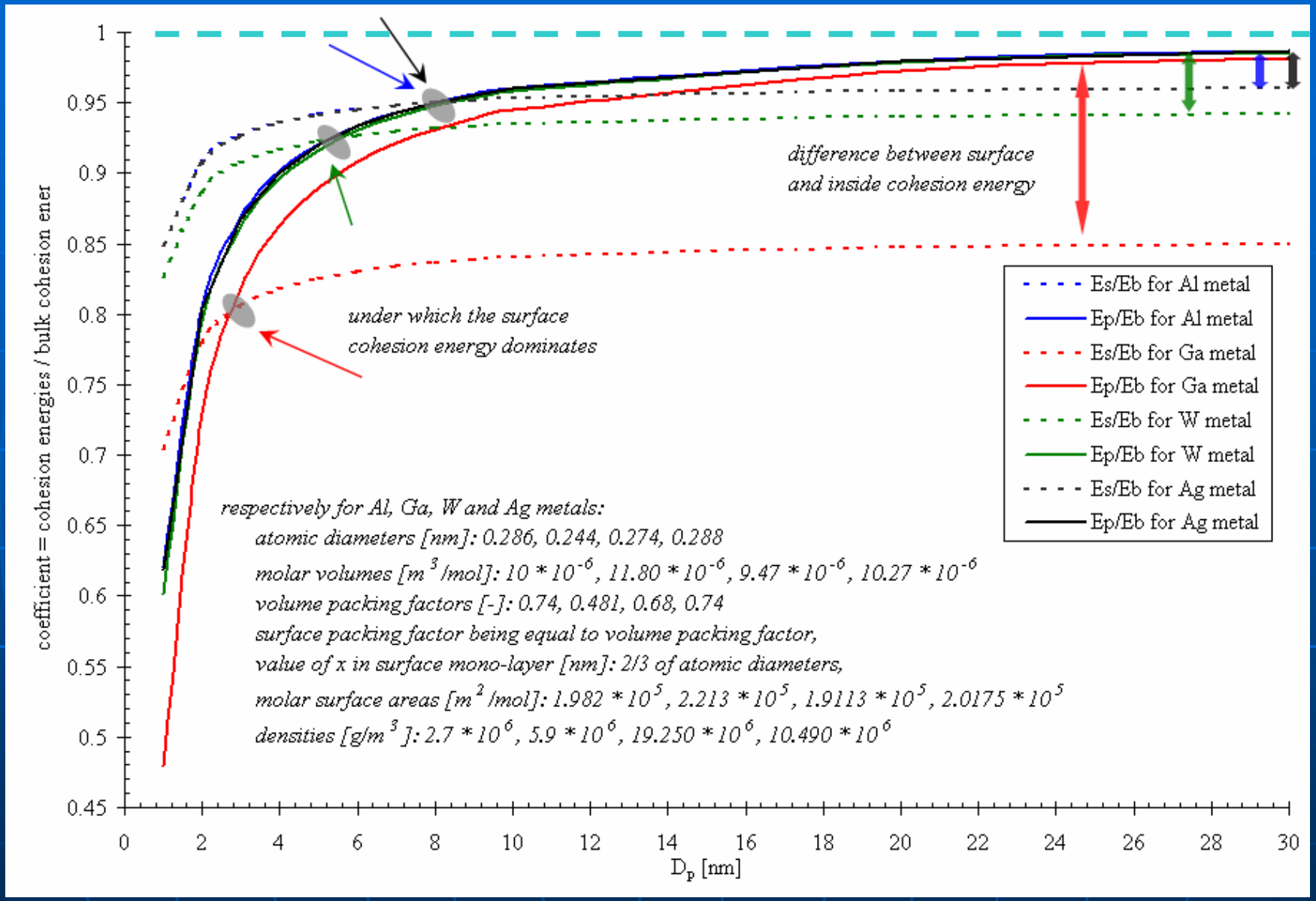
$$E_s = E_b \cdot \left(\frac{7}{6} - \frac{1}{f_v} \cdot d_a \cdot \frac{1}{D_p} \cdot \left(1 - \frac{f_v}{f_s} \cdot \frac{D_p^{\,3}}{(10 \cdot x \cdot D_p^2 - 12 \cdot x^2 \cdot D_p + 8 \cdot x^3)}\right)\right)$$

Xie, Qi: 2004 [4] from embedded NP in matrix got the wholly free standing coefficient as 3/4 in Eq(1) and said it is the surface effect

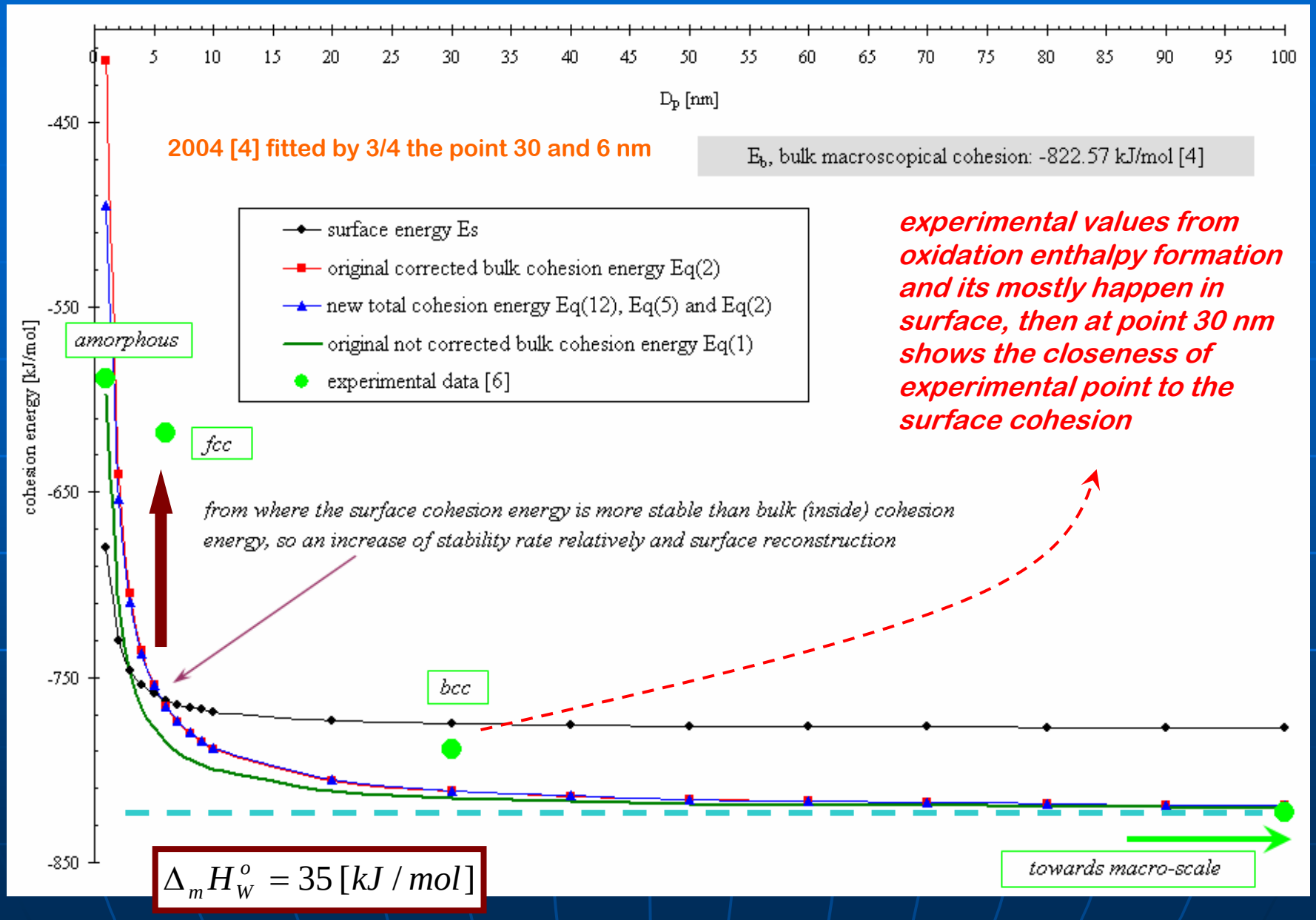
for Al, Ag, Ga and W



Comparison of coefficient of different cohesion energies for Al metal



Comparing the coefficient of cohesion energies for different metals



Comparing the calculated and experimental observation of cohesion energies for W metal

Conclusions and Overview

- new scale of properties of nano-materials (via Cohesion scale)

i. introduction of bulk (inside) cohesion energy of nano-materials
ii. development of a thermodynamical model for surface cohesion energy of nano-materials,
iii. series of computational analysis for comparing the materials like: Al, Ga, W and Ag metals,
iv. discussion the critical size and its relation to surface cohesion energy domination,
v. comparison the experimental values of W metal with computational simulation,

- activity of nano-particles … (under construction)

Further Steps

-shape effect on cohesion phenomena
-globalizing the activity of particles and experimental comparison (if any)
-size and shape effect of first order phase transitions
-size and shape effect on higher order phase transitions ?
…
-mixing or solving the particles together or in a bigger system
-phase diagram (state equation) of mono-particle
-state equation of multi- particles
…

Nomenclature

E, G : respectively cohesion and Gibbs free energy [kJ/mol] or [kJ],
f : packing factor,
d_a, D_p : respectively diameter of atom and diameter of particle [nm],
n : number of mole [mol],
A : area of material [m^2],
δ^o : surface energy per unit area at 0 K [J/m^2],
Δ : symbol showing the difference between two states of a quantity,
$b, i, p, s, \sum, v$: in subscribe and superscript respectively: bulk, inside, particle, surface, total and volume,
w, ρ, V, M, m, x : respectively molar surface area [m^2/mol], density [g/m^3], volume [m^3], molar mass [g/mol], mass [g] and actual atomic height of mono surface layer [nm]

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