



Application of the nano-Calphad method to select stable binary nano-crystalline alloys

George Kaptay

Professor, corresponding member
of the Hungarian Academy of Sciences

MISKOLCI
EGYETEM

Calphad

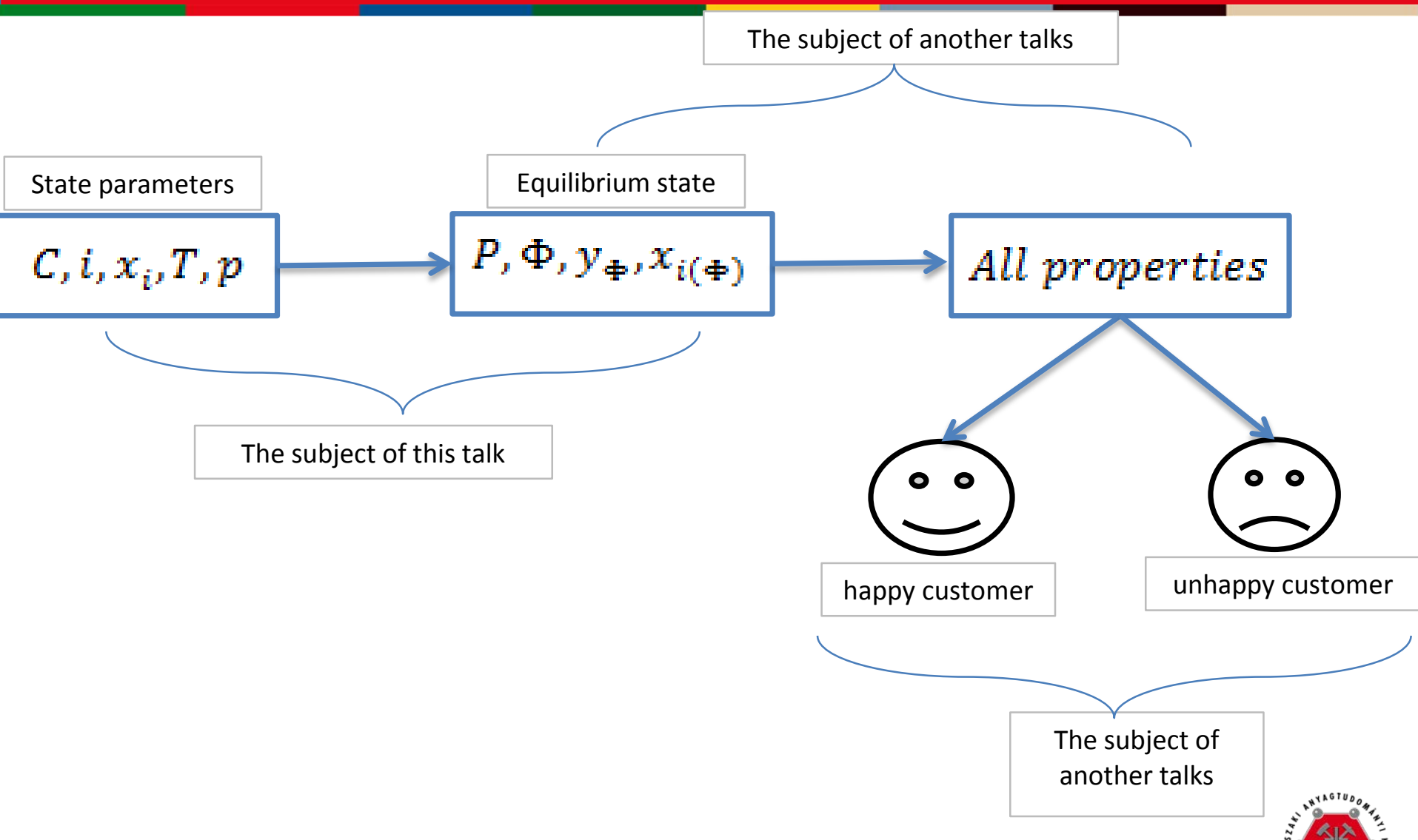


Nano-Calphad



Stabilization of nano-grains in polycrystals

Part 1. The essence of Calphad



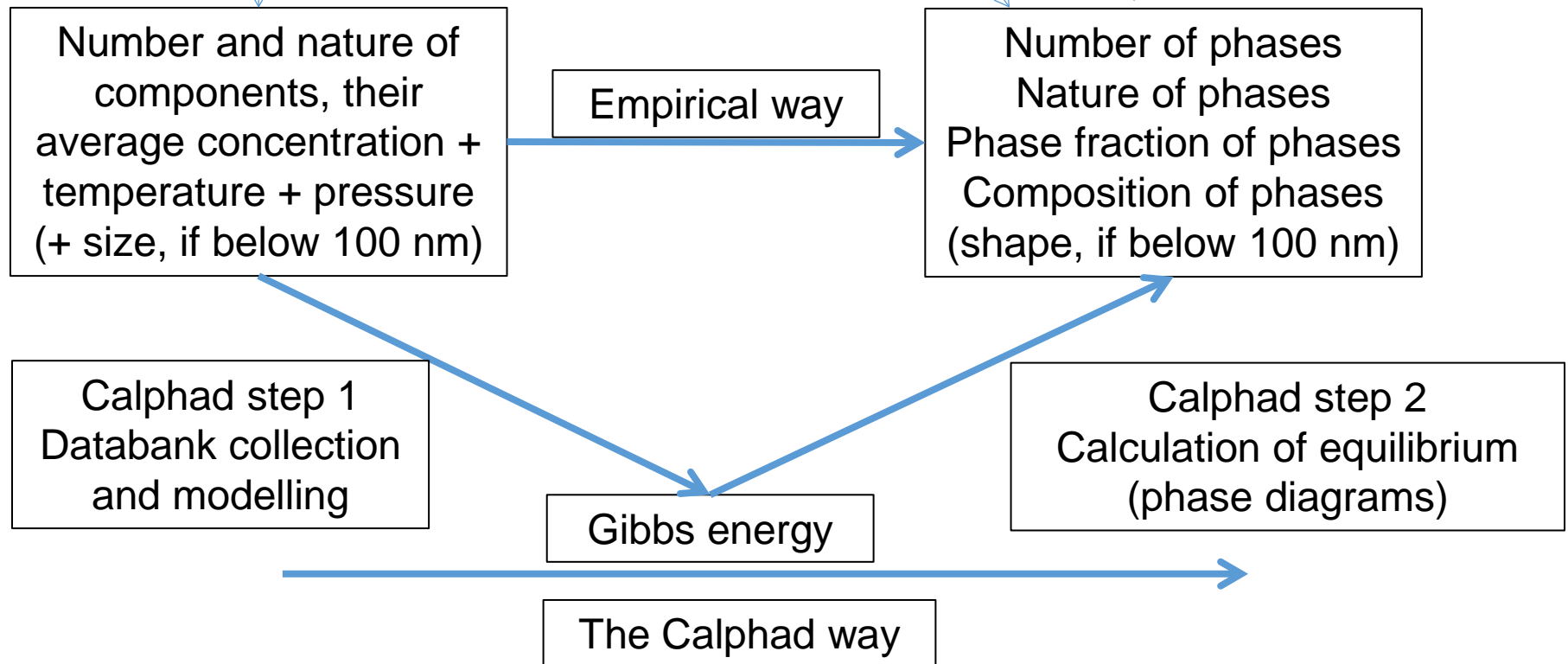
CALPHAD = **CA**lculat**ion** of **PHA**se **D**iagrams / equilibrium



Calphad



What we define and what Nature (God) defines



Number of experiments needed for 84 stable elements:

$$100^{85} = 10^{170}$$

Years needed if each hs performs 1 experiment per day:

$$10^{158}$$

Mission Impossible



Materials balance



System: your selection of a 3-D part of a Universe, including some matter n (mole), containing C ($= 1, 2, \dots$) components, each denoted as $i = A, B$, etc... (component = element)

$$n = n_A + n_B \qquad x_B \equiv \frac{n_B}{n} \qquad x_A = 1 - x_B$$

Phase: a homogenous 3-D part of the system, formed spontaneously (not by us): $\Phi = \alpha, \beta \dots$ (their number: $P = 1, 2, \dots$)

$$n = \sum_{\Phi} n_{\Phi} \qquad y_{\Phi} \equiv \frac{n_{\Phi}}{n} \qquad y_{\alpha} = 1 - y_{\beta}$$

Each phase is composed of the same components as the system:

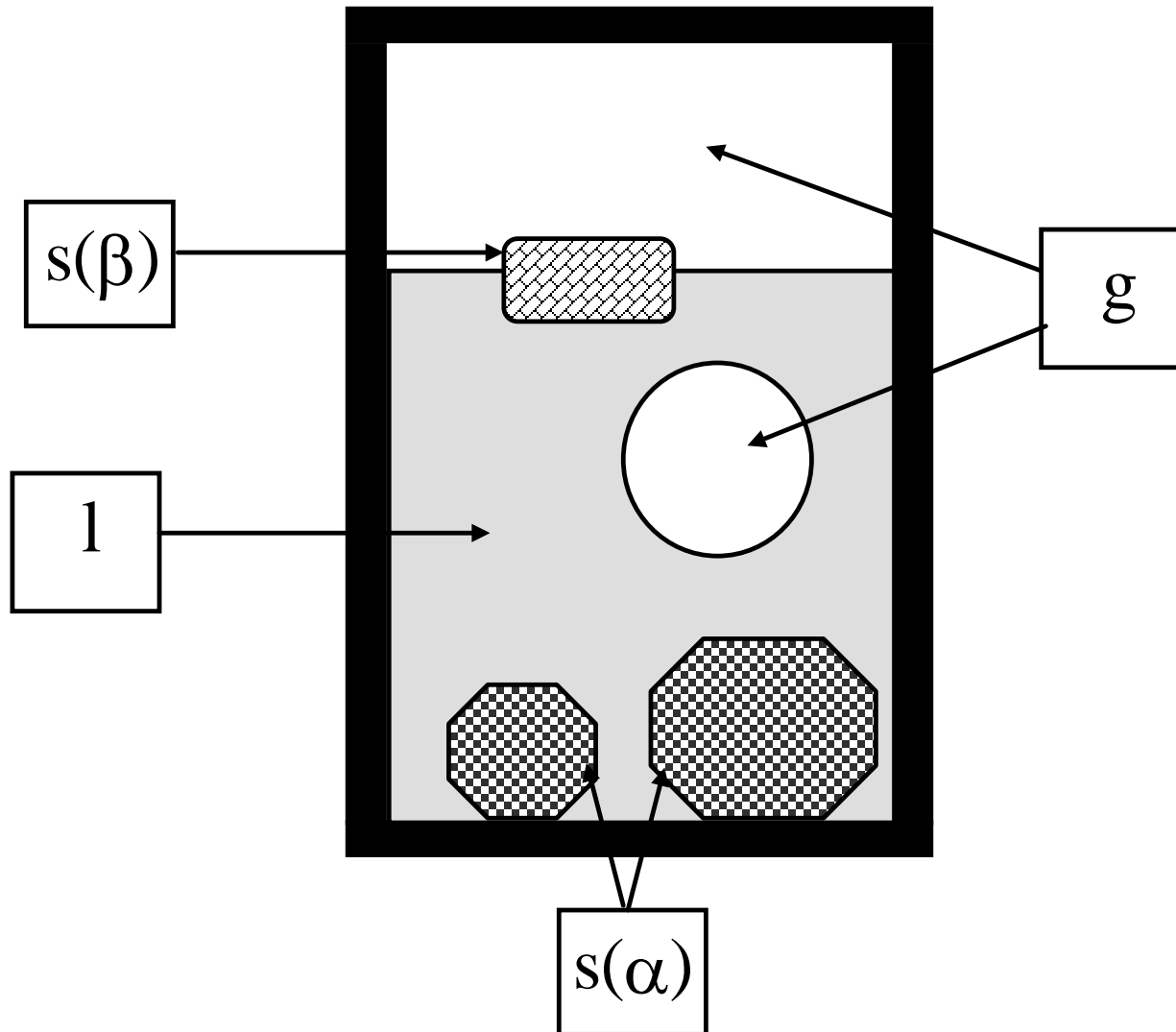
$$n_{\Phi} = n_{A(\Phi)} + n_{B(\Phi)} \qquad x_{B(\Phi)} \equiv \frac{n_{B(\Phi)}}{n_{\Phi}} \qquad x_{A(\Phi)} = 1 - x_{B(\Phi)}$$

Materials balance equation:

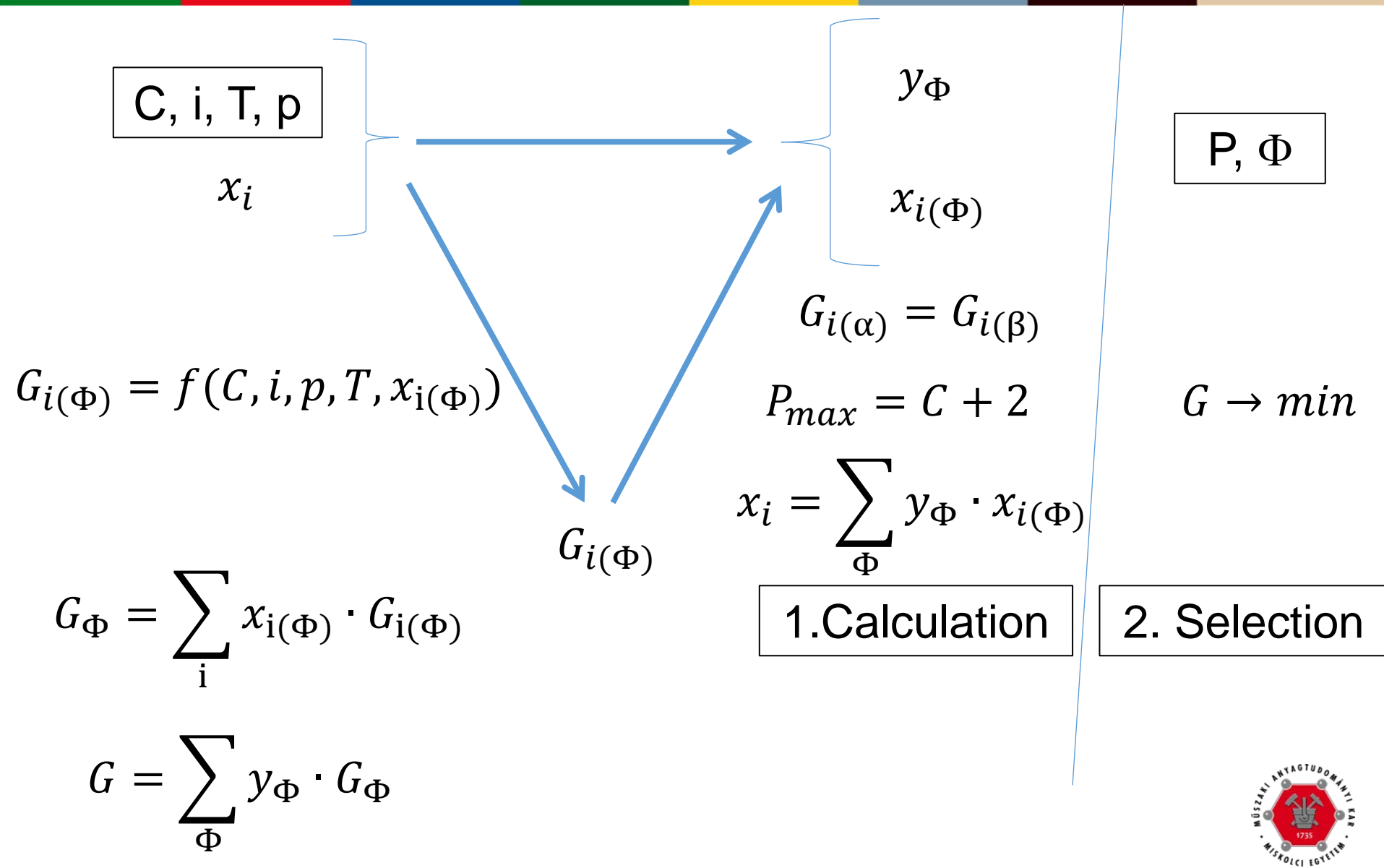
$$x_B = \sum_{\Phi} y_{\Phi} \cdot x_{B(\Phi)}$$



An example of a 4-phase system



Calphad



Does the solution exist?



Un-knowns for equilibrium state: y_{Φ} and $x_{i(\Phi)}$

Their number: $(P-1) + P(C-1) = PC - 1$

Equations: $G_{i(\alpha)} = G_{i(\beta)}$ and $x_i = \sum_{\Phi} y_{\Phi} \cdot x_{i(\Phi)}$

Their number: $C(P-1) + C-1 = PC - 1$

As the number of un-knowns equals the number of equations,

the solution always exists

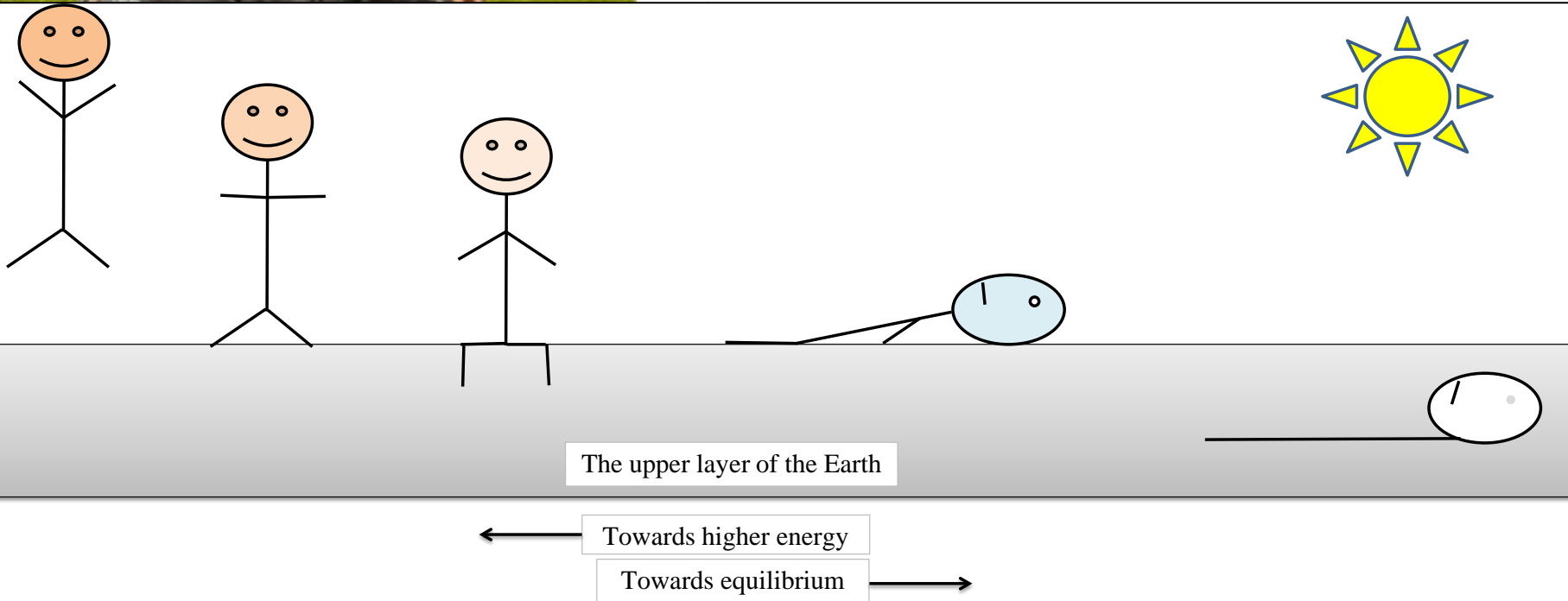




$$G \rightarrow \min$$

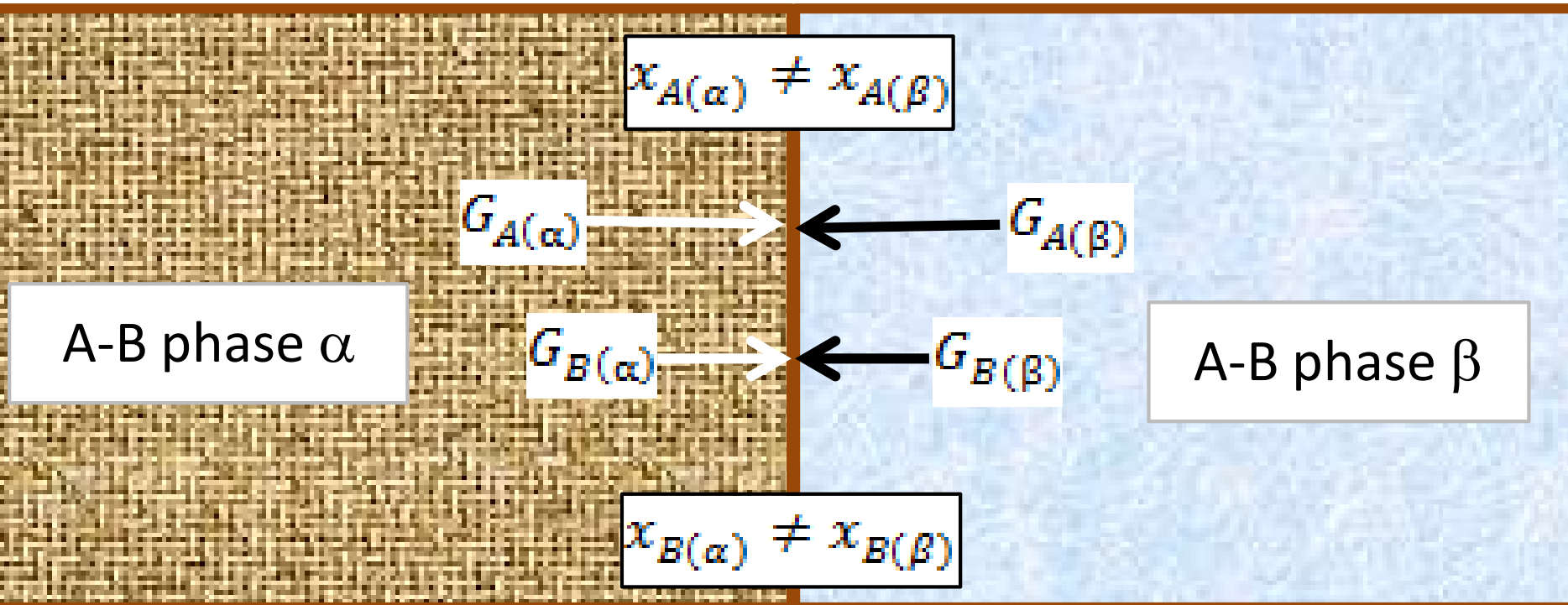
Why??

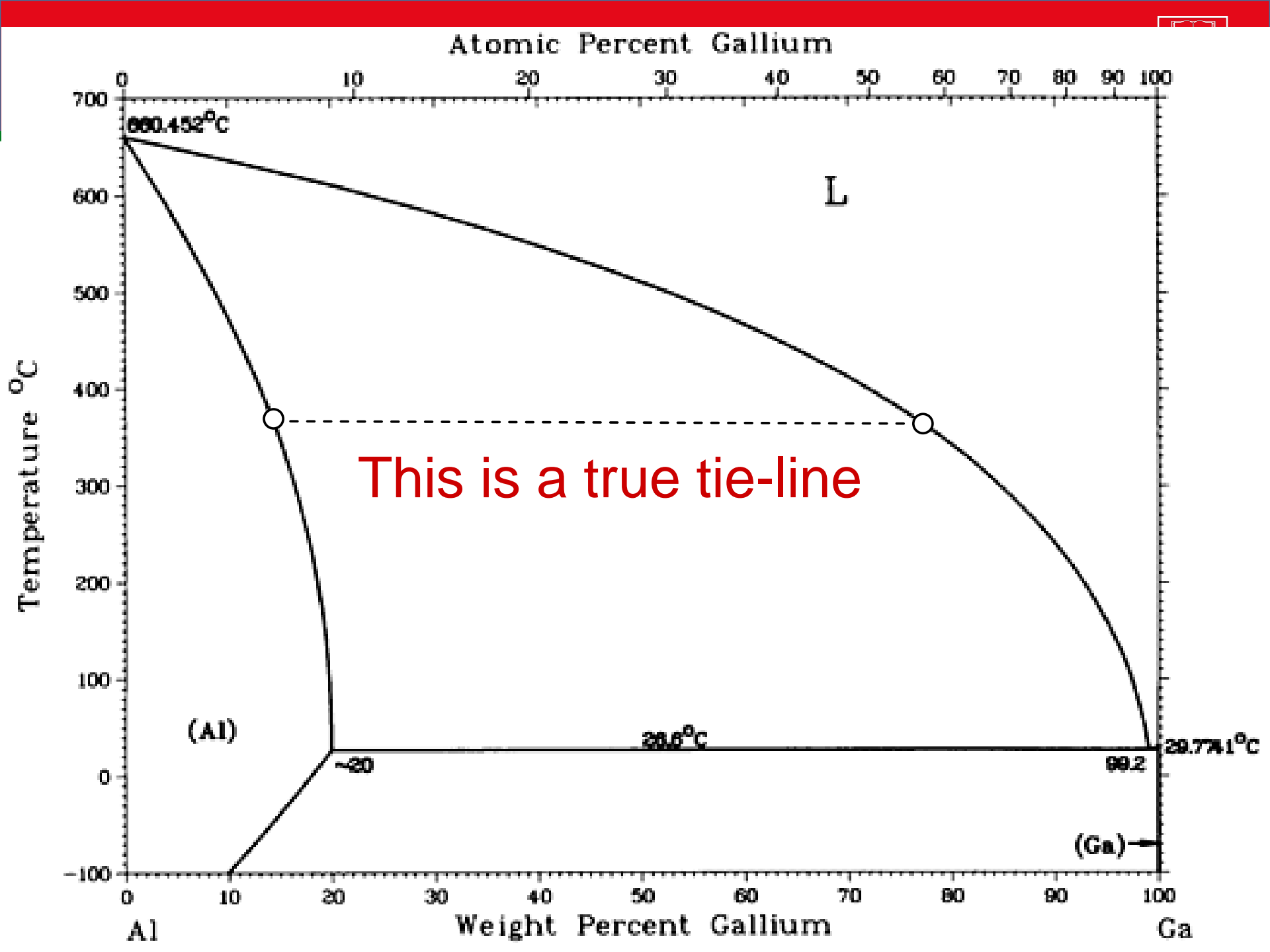
There are at least two explanations....



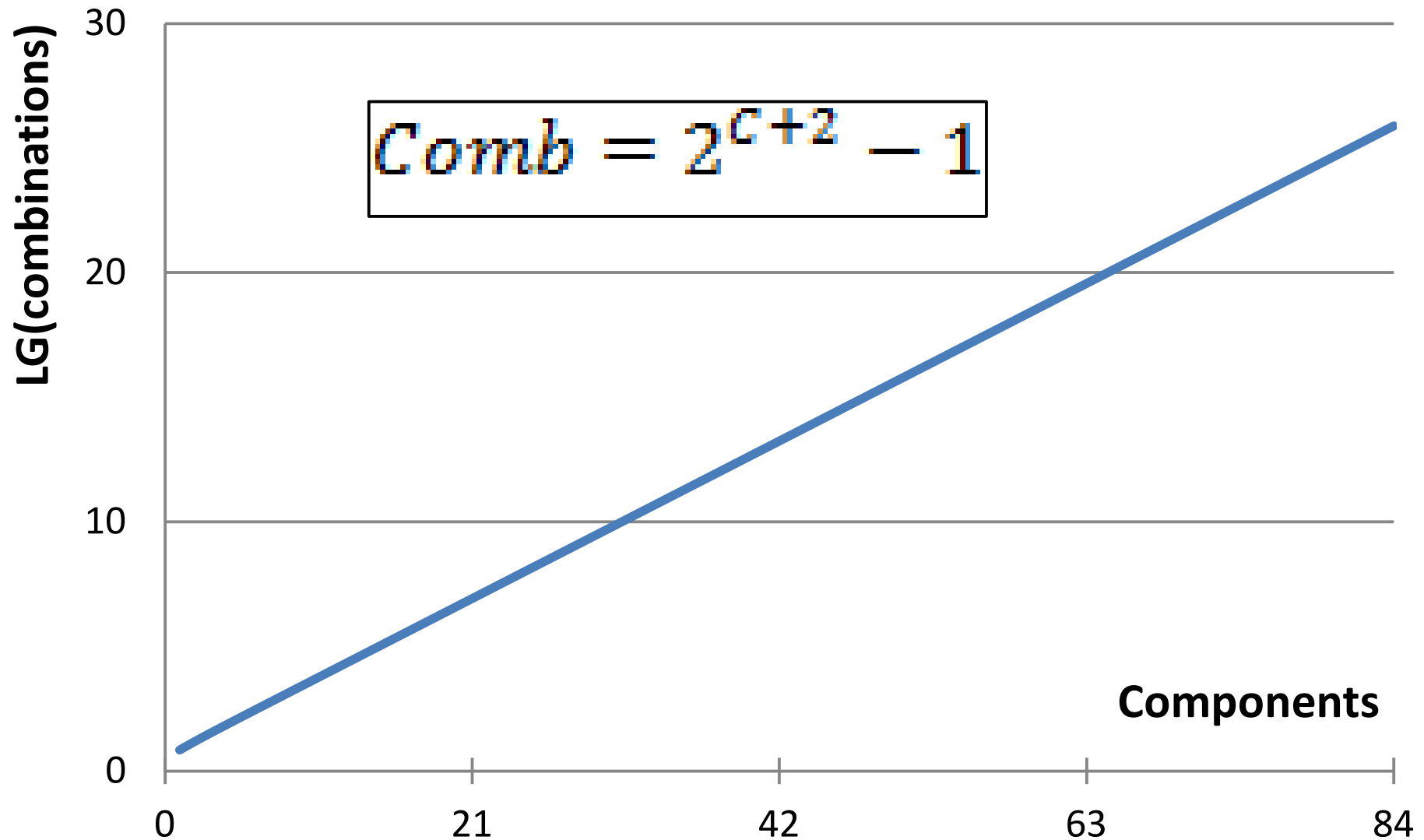
Why?

$$G_{i(\alpha)} = G_{i(\beta)}$$





Calphad needs supercomputers



Part 2. The essence of nano-Calphad

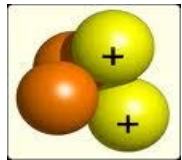


Nano-Calphad \equiv Calphad applied to nano-materials

Nano-materials \equiv materials with at least 1 phase with at least one of its dimensions below 100 nm

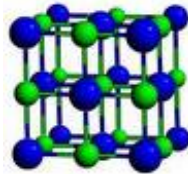


Nano came last



fm

pm



nm



μm



mm



m



km

f-T

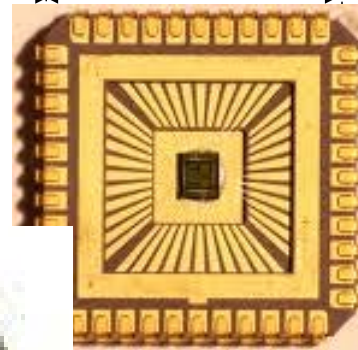
p-T

n-T

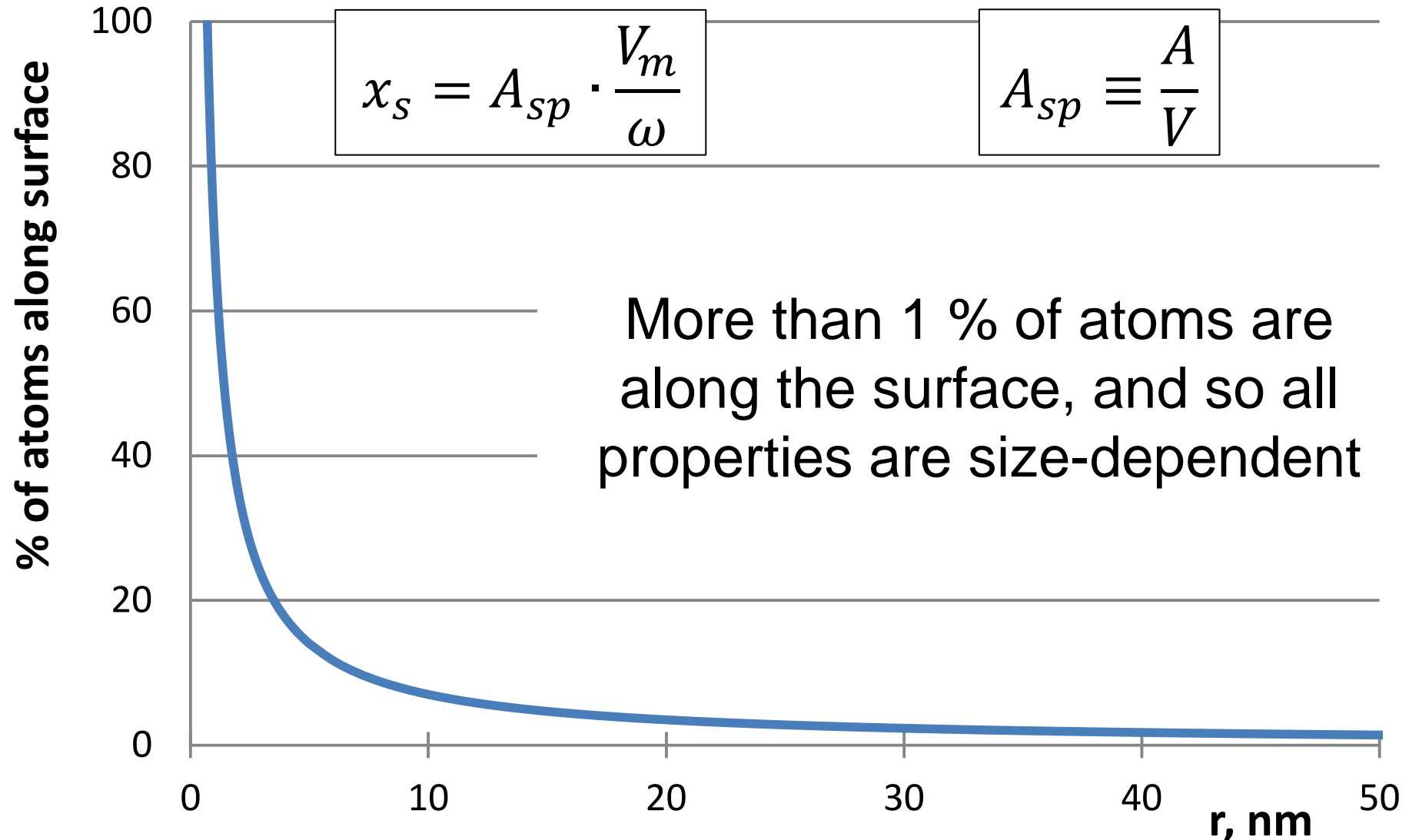
$\mu\text{-T}$

T

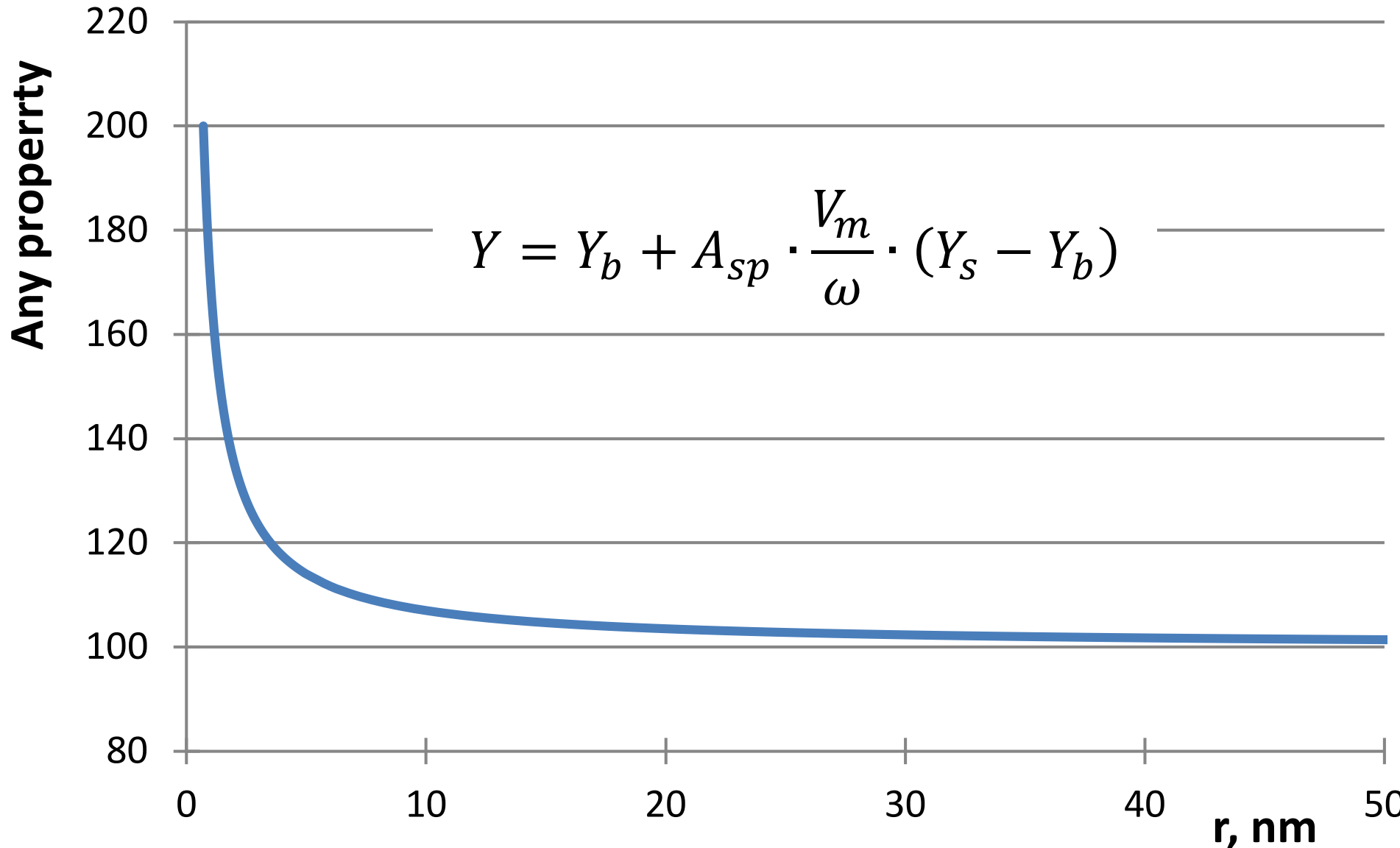
logL



Why nano-materials are so special?



Size dependence of properties



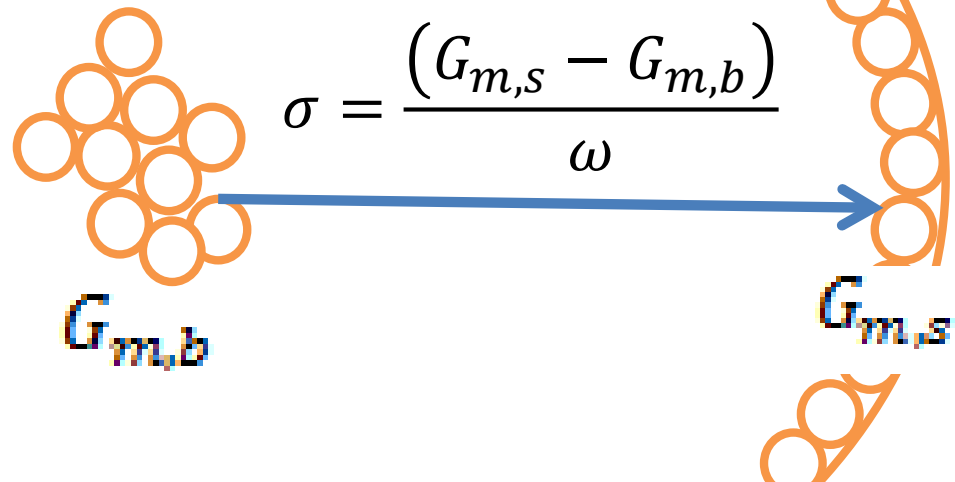
Size dependence of molar Gibbs energy 1



$$Y = Y_b + A_{sp} \cdot \frac{V_m}{\omega} \cdot (Y_s - Y_b)$$

$$Y \equiv G_m \quad G_m = G_{m,b} + A_{sp} \cdot \frac{V_m}{\omega} \cdot (G_{m,s} - G_{m,b})$$

$$G_m = G_{m,b} + A_{sp} \cdot V_m \cdot \sigma$$



Size dependence of molar Gibbs energy 2



Gibbs, 1878:

$$G = G_m + A \cdot \sigma$$

Divide by n: $G_m = G_{m,b} + A_{sp} \cdot V_m \cdot \sigma$

$$n = \frac{V}{V_m}$$

$$A_{sp} \equiv \frac{A}{V}$$

$$G_m \equiv \frac{G}{n}$$

$$G_{m,b} \equiv \frac{G_b}{n}$$

Size dependence of chemical potential



$$G_m = G_{m,b} + A_{sp} \cdot V_m \cdot \sigma$$

$$G_m = \sum_i x_i \cdot \mu_i \quad G_{m,b} = \sum_i x_i \cdot \mu_{i,b} \quad V_m = \sum_i x_i \cdot V_{m,i}$$

$$G_m = \sum_i x_i \cdot \mu_i = \sum_i x_i \cdot (\mu_{i,b} + A_{sp} \cdot V_{m,i} \cdot \sigma)$$

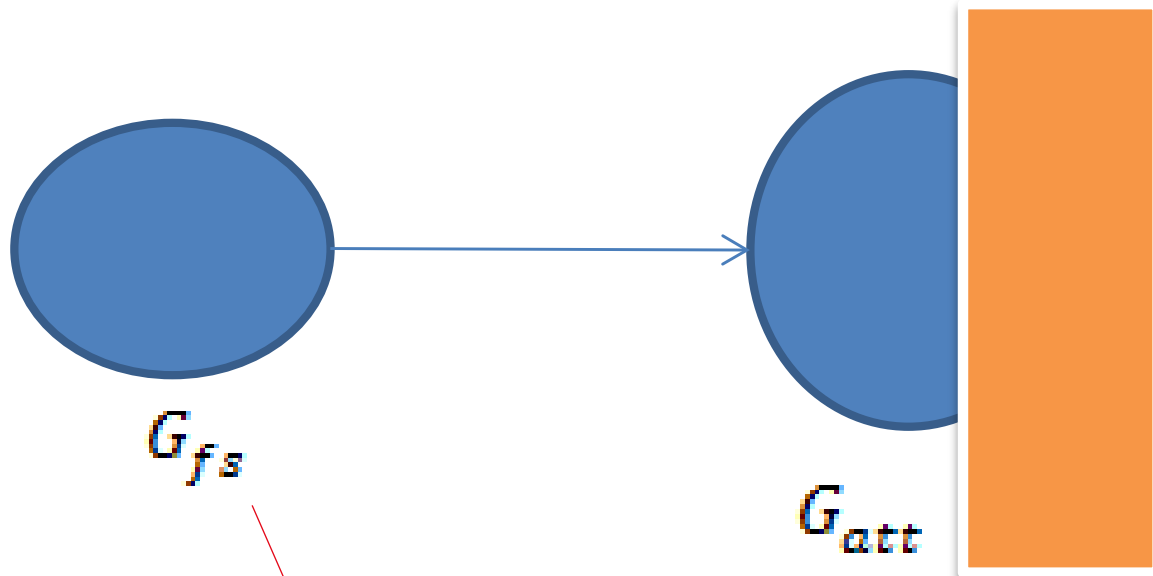
$$\sigma = \sigma_i$$

$$\mu_i = \mu_{i,b} + A_{sp} \cdot V_{m,i} \cdot \sigma_i$$



Chemical potential in multi-phase situations

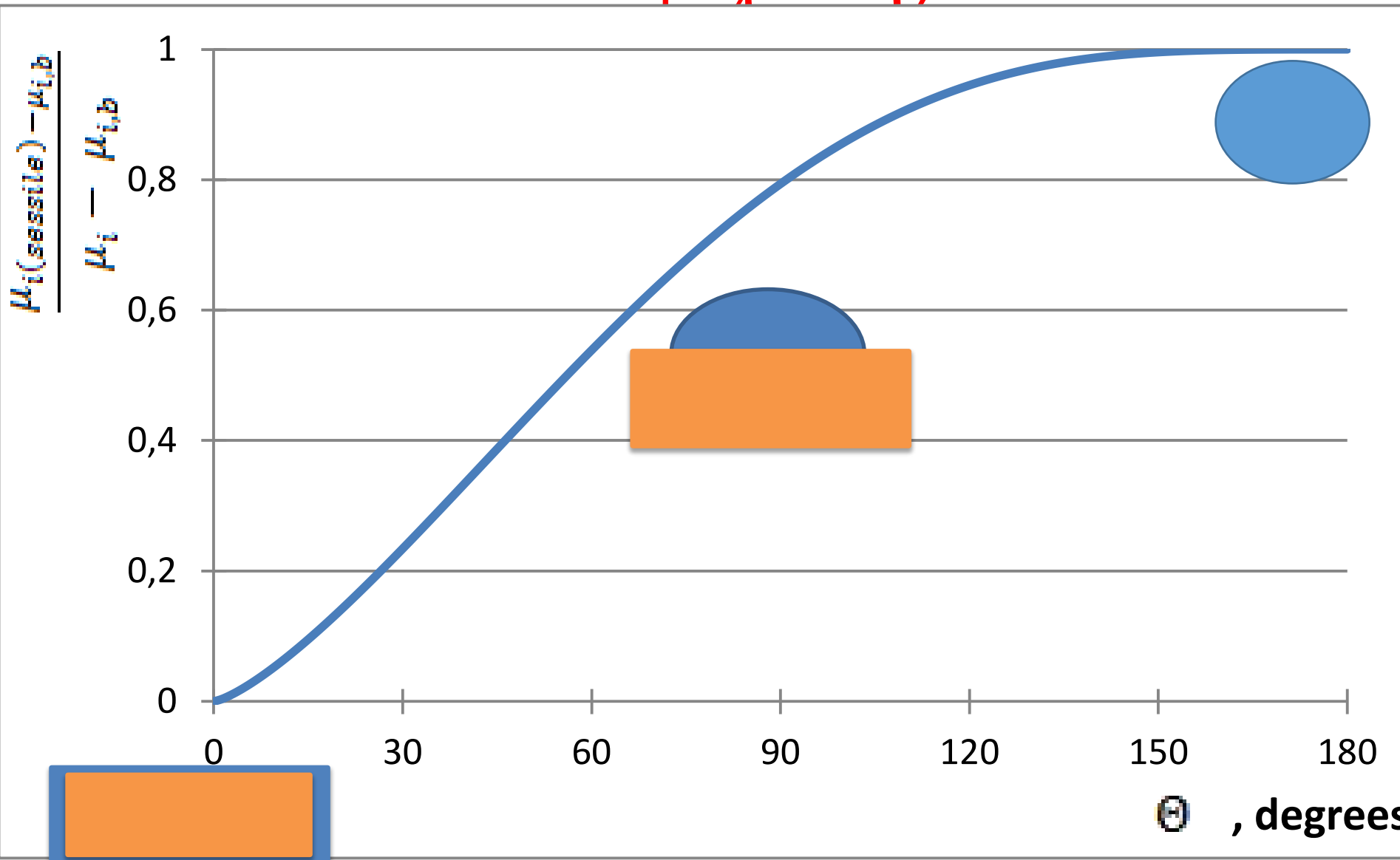




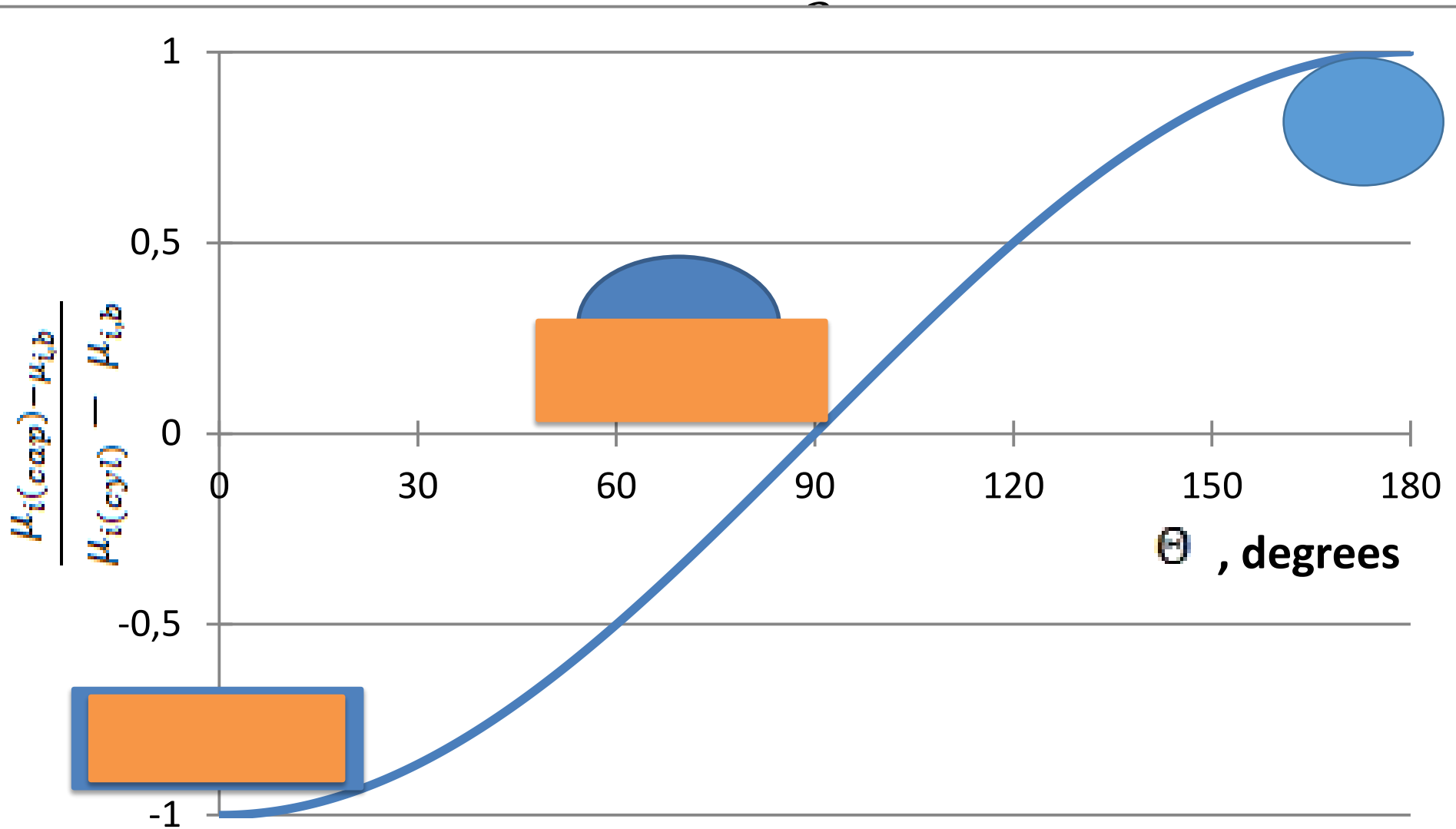
The diagram illustrates a process where a small blue oval nucleus on the left transitions to a larger blue oval nucleus on the right, which is partially covered by an orange rectangular block. A blue arrow points from the small nucleus to the larger one. Below the small nucleus is the label G_{fs} , and below the larger nucleus is the label G_{att} . A red arrow points from G_{fs} to the first term of the equation below, and a black arrow points from G_{att} to the numerator of the fraction in the equation.

$$\mu_i = \mu_{i,b} + A_{sp} \cdot V_{m,i} \cdot \sigma + V_{m,i} \cdot \frac{G_{att} - G_{fs}}{V}$$

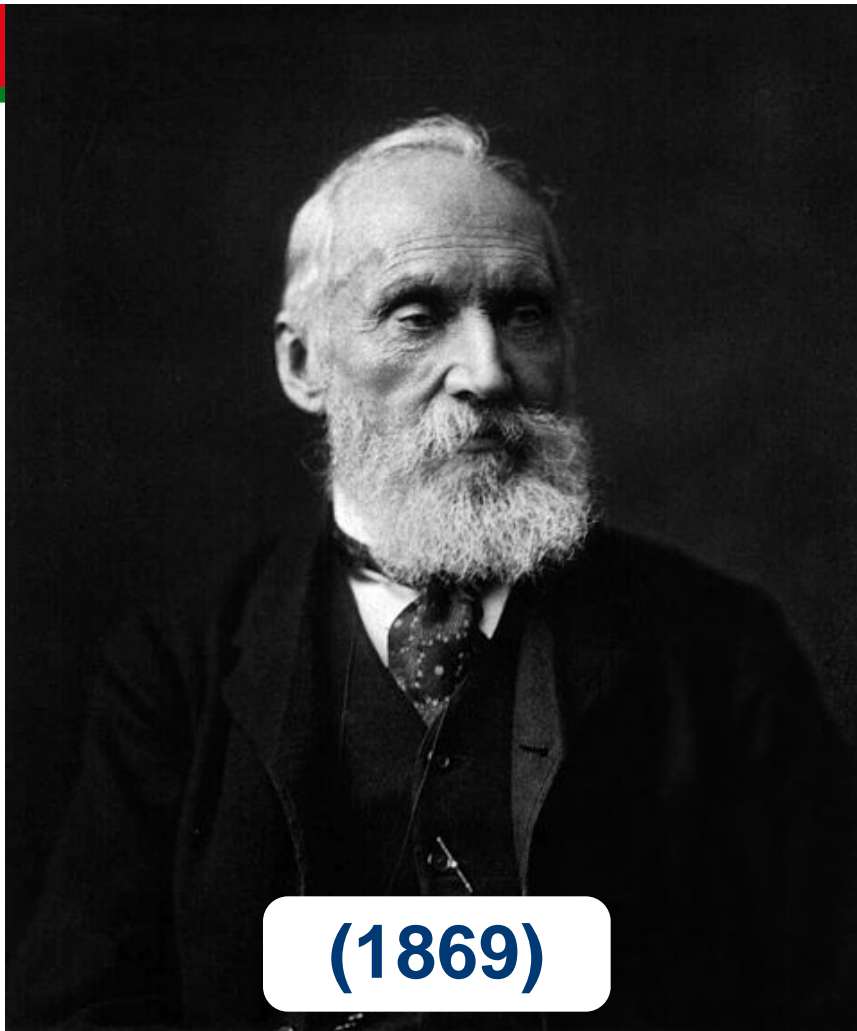
Case 1: sessile drop



Case 2: Liquid confined in capillaries



The historical accident: nano-Calphad came before Calphad



(1869)

**William Thomson
(Lord Kelvin)
1824 - 1907**



(1878)

**Josiah Willard Gibbs
1839 - 1903**



The Kelvin equation and the reasons of its incorrectness



$$G_m = U_m + p \cdot V_m - T \cdot S_m \quad p_{in} = p_{out} + \sigma \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

$$\cancel{G_m = G_{m,b} + \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cdot V_m \cdot \sigma}$$

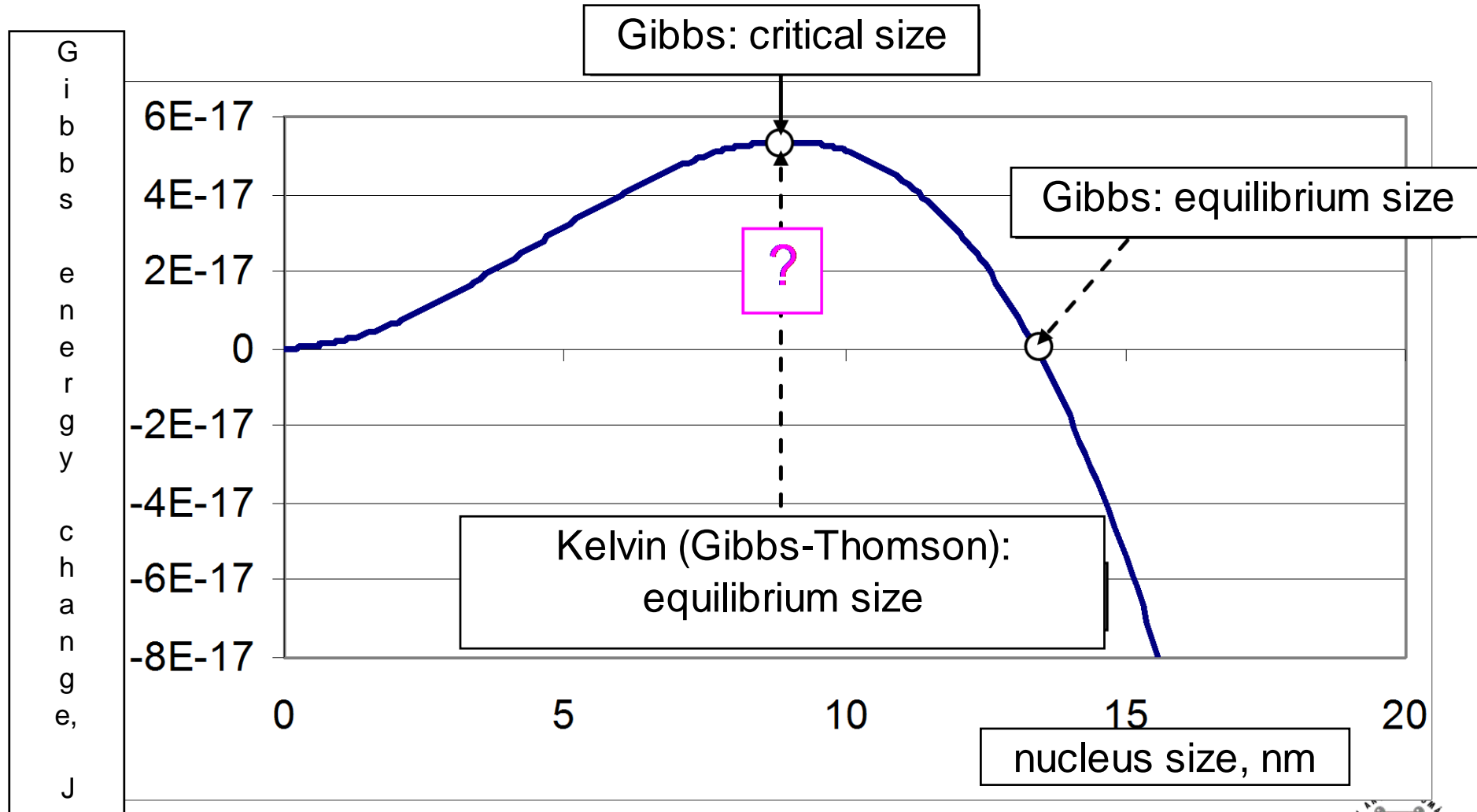
Reasons of incorrectness:

- p is a state parameter, not an inside pressure $p(in)$
- No nano-effect for not-curved phases ? (cubic nano-L)
- The surface term of Gibbs is forgotten,
- The Laplace pressure is obtained from $G....$
- Contradiction with nucleation theory

$$G_m = G_{m,b} + A_{sp} \cdot V_m \cdot \sigma$$



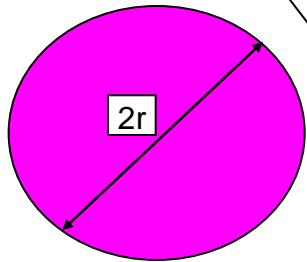
The nucleation contradiction



Kelvin (Gibbs-Thomson) or Gibbs?

Kelvin (**curvature**)

$$G_{\Phi} - G_{\Phi}^b = \sigma_{\Phi g} \cdot V_{m,\Phi} \cdot \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$



$$\frac{2 \cdot \sigma \cdot V_m}{r}$$



0

Gibbs (**specific surface area**)

$$G_{\Phi} - G_{\Phi}^b = A_{S,\Phi} \cdot \sigma_{\Phi s} \cdot V_{\Phi,m}$$

$$\frac{3 \cdot \sigma \cdot V_m}{r}$$

$$\frac{(\sigma_{in} + \sigma_{out}) \cdot V_m}{\delta}$$

CALORIMETRIC INVESTIGATION OF THE LIQUID Sn-3.8Ag-0.7Cu ALLOY WITH MINOR Co ADDITIONS

. J. Phys. Chem. C, 120 (2016) 1881-1890

Andriy Yakymovych

University of Vienna, Austria

George Kaptay

University of Miskolc, Hungary

Ali Roshanghias, Hans Flandorfer, Herbert Ipser

University of Vienna, Austria

High-Temperature Calorimeter



- SETARAM ©
- High temperature calorimeter (twin calorimeter)
- ambient to 1000° C

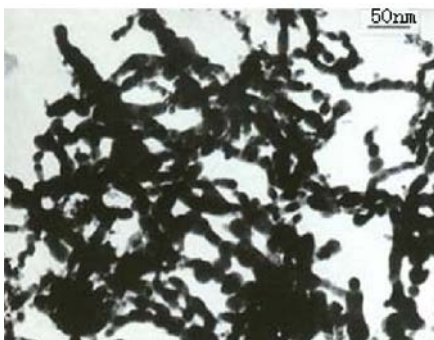


Equipped with an automatic dropping device

Materials

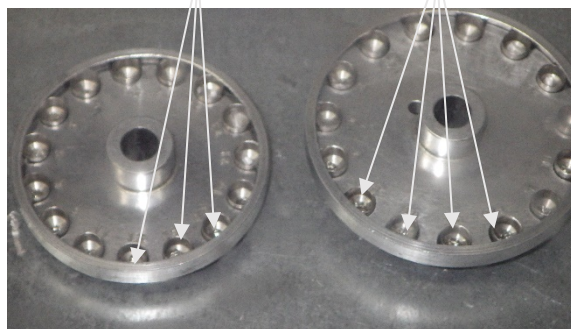


High purity metals in bulk form Alfa Aesar (99.99%)

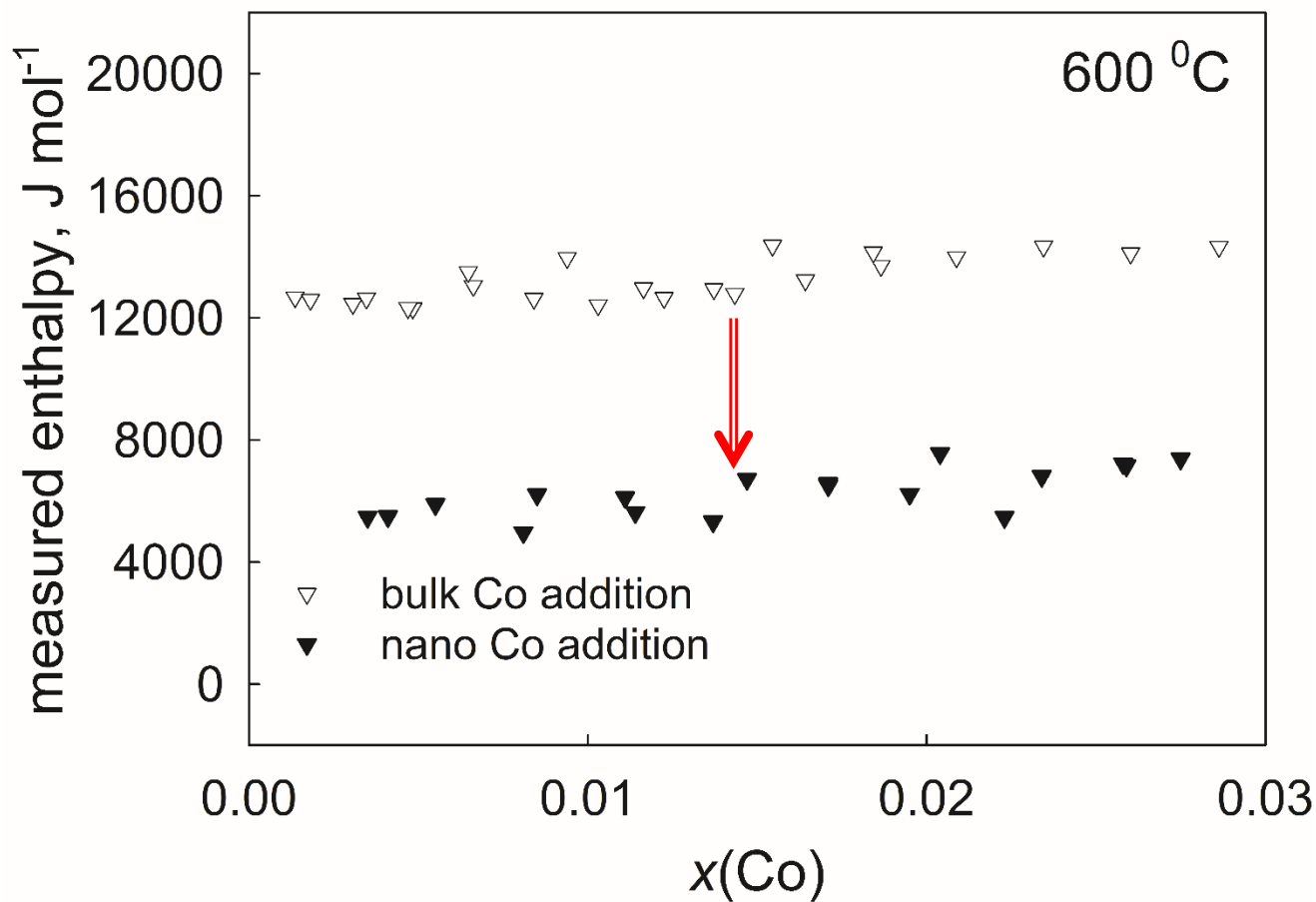


Empirical Formula	Co
CAS No.	7440-48-4
Molecular weight	58.93 amu
Purity	99.9 % (metal basis)
Average particle size	28 nm (TEM)
Particle size range	0-60 nm (TEM)
Specific Surface Area	40 to 60 m ² /g (BET)
Colour	Black
Morphology	spherical
Bulk Density	0.10-0.25 g/cm ³

Sn-3.8Ag-0.7Cu foil



Results



$$\Delta H_{nano} = (-7.5 \pm 1.5) \text{ kJ/mol}$$



Theoretical Consideration



$$\begin{array}{ccccc} H_{mix,nano} & = & H_{mix-bulk} & + & \Delta H_{nano} \\ \text{nano-liquid} & & \text{bulk-liquid} & & \text{nano-bulk} \end{array}$$

$$G_m = G_{m,b} + A_{sp} \cdot V_m \cdot \sigma \longrightarrow \Delta H_{nano} = (0 - A_{sp}) \cdot V_m \cdot \sigma_{sg,H}$$

$$A_{sp} \cdot V_m = A_{BET} \cdot M$$

$$\Delta H_{nano} = -A_{BET} \cdot M \cdot \sigma_{sg,H}$$

$$A_{BET} = (50 \pm 10) \cdot 10^3 \text{ m}^2 \cdot \text{kg}^{-1}$$

$$M = 58.933 \cdot 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$$

$$\sigma_{sg,H,T_D} \cong (2.80 \pm 0.15) \text{ J} \cdot \text{m}^{-2}$$

$$\Delta H_{n,th} = (-8.2 \pm 2.1) \text{ kJ/mol}$$

$$\Delta H_{n,exp} = (-7.5 \pm 1.5) \text{ kJ/mol}$$

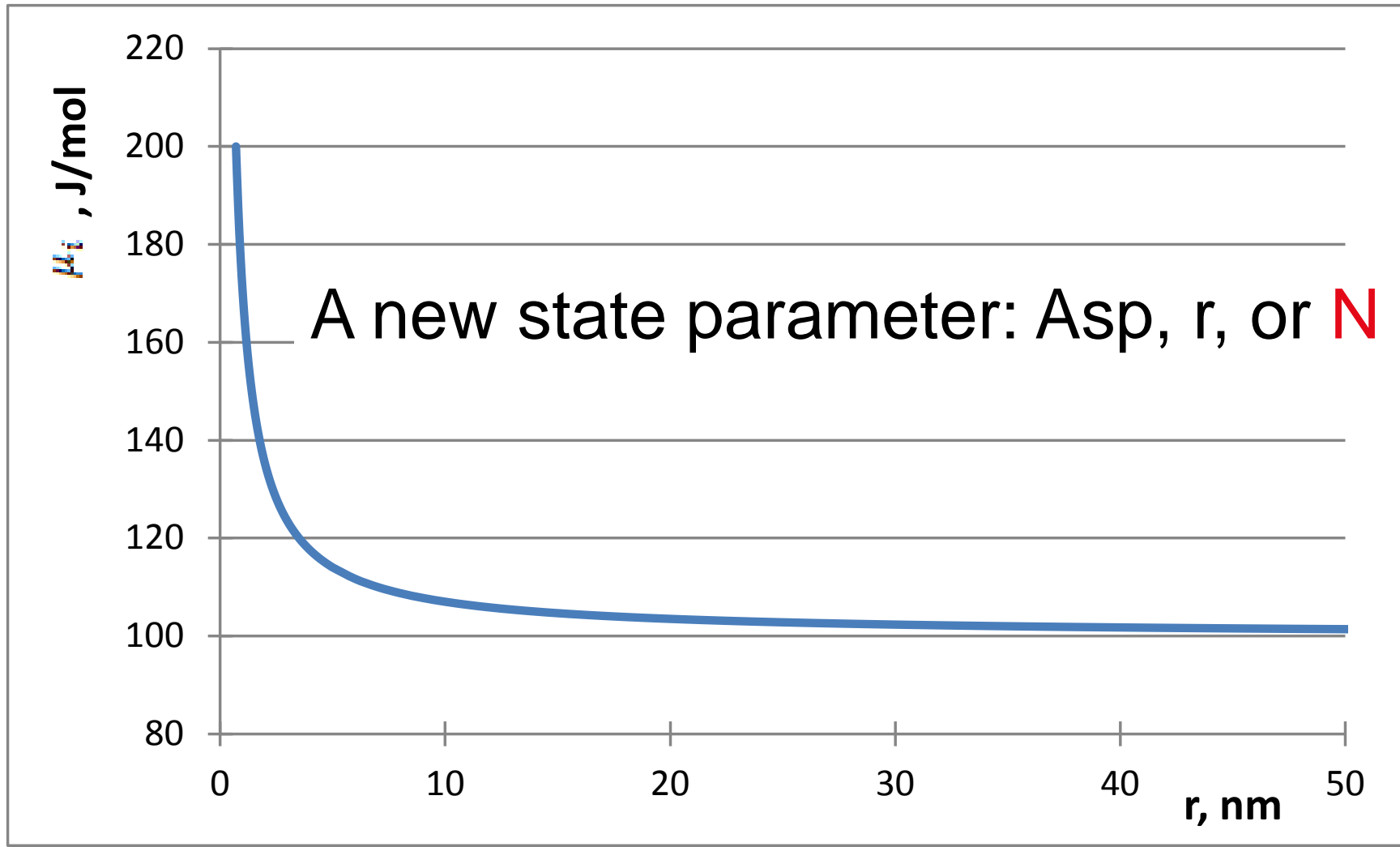


A new state parameter



$$\mu_{i(\alpha)} = \mu_{i(\beta)}$$

$$\mu_i = \mu_{i,b} + A_{sp} \cdot V_{m,i} \cdot \sigma_i$$



The extended phase rule of Gibbs

P = number of phases, C = number of components, F = freedom

Gibbs, 1875:

$$P_{\max} = 2 + C$$

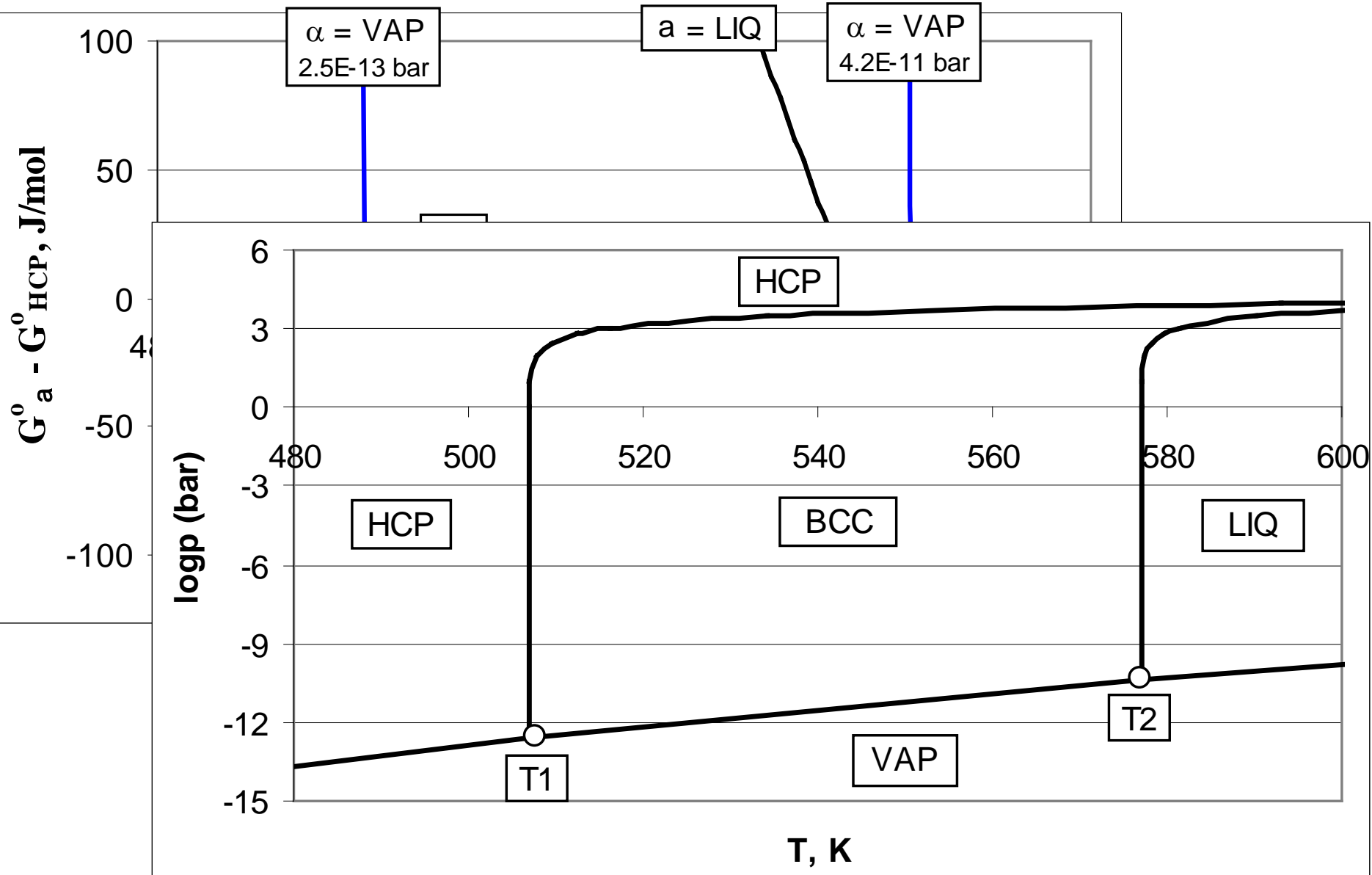
$$F = C + 2 - P$$

Due to a new, independent variable:

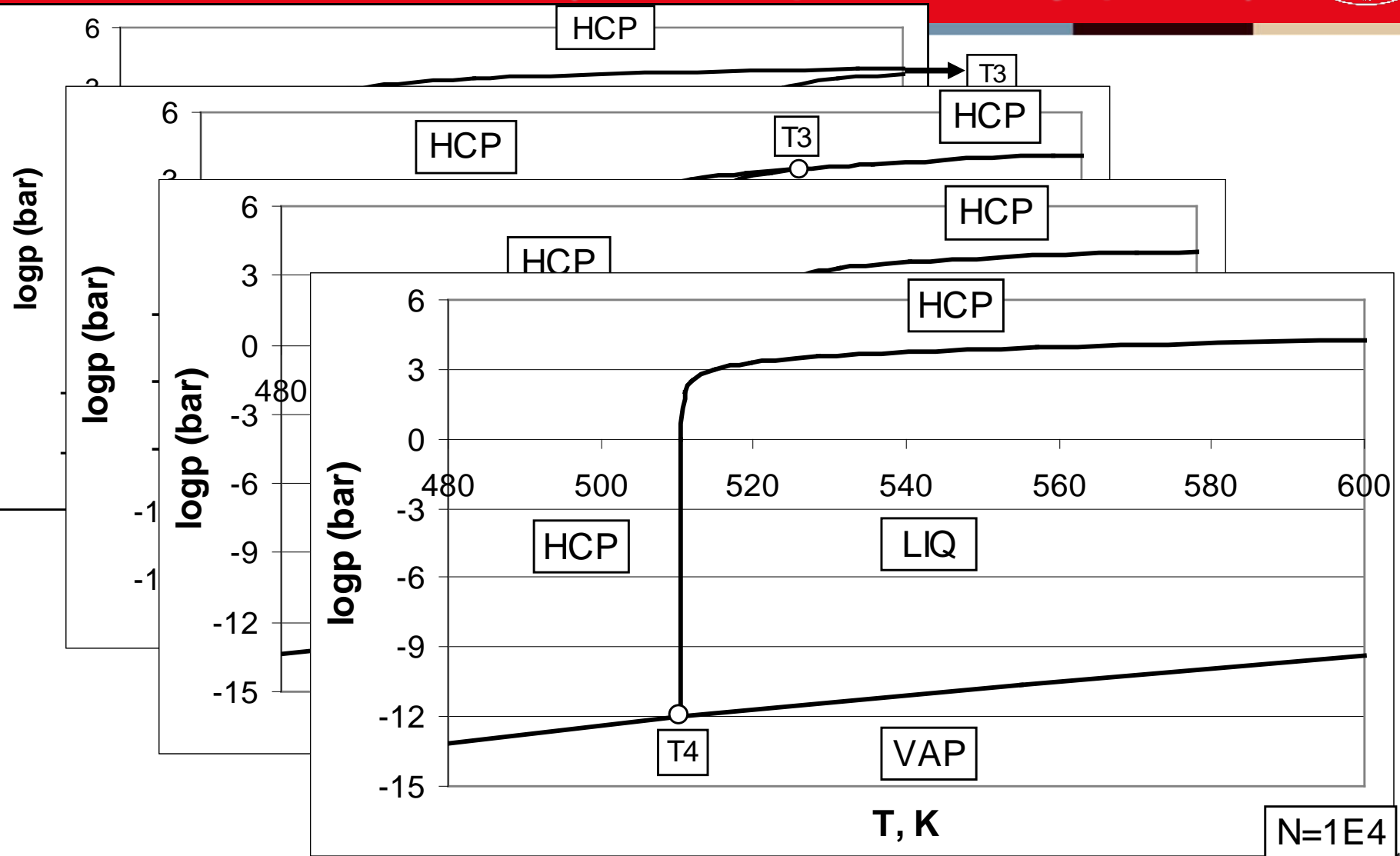
$$P_{\max} = 3 + C$$

$$F = C + 3 - P$$

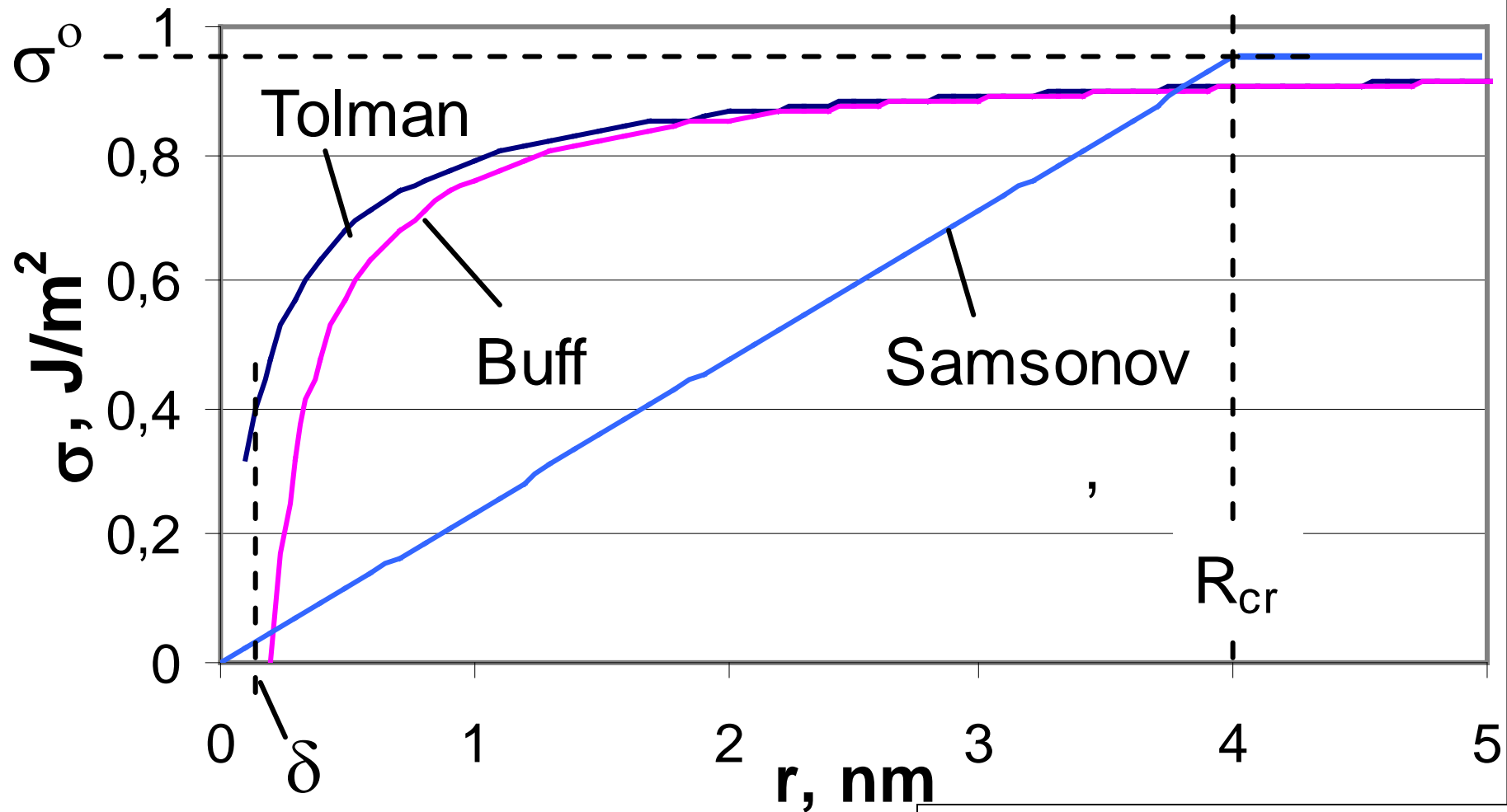
Macro-thallium



Nano-thallium (with a quaternary point)



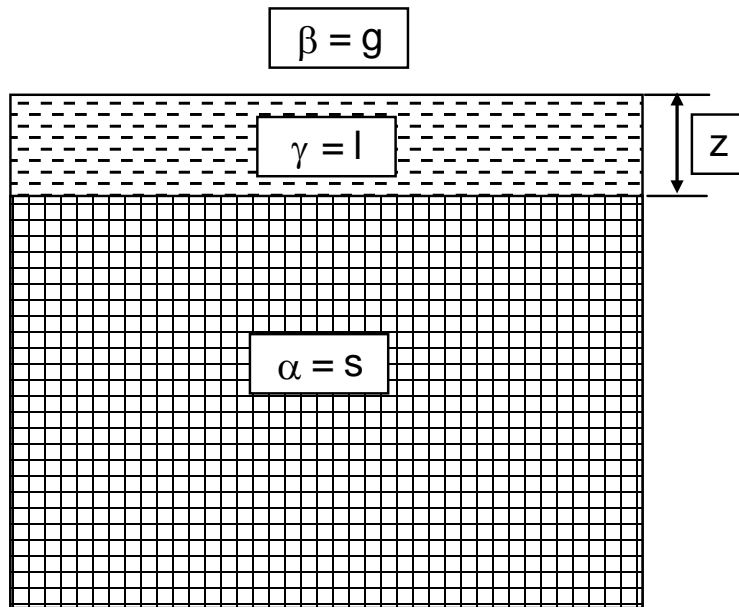
The size dependence of interfacial energies



Buff, 1951:

$$\sigma = \sigma^0 \cdot \left(1 - \frac{2 \cdot \delta}{r} + \frac{3 \cdot \sigma_{sl} \cdot V_s}{(r + 2 \cdot \delta) \cdot \Delta_m S} \right) T_m = T_m^0 - \frac{3 \cdot \sigma_{sl} \cdot V_s}{(r + 2 \cdot \delta) \cdot \Delta_m S}$$

The separation dependence of interfacial energies



metals:

$$f(z) = \exp\left(\frac{-z}{\xi}\right)$$

non-metals:

$$f(z) = \left(\frac{\xi}{\xi + z}\right)^2$$

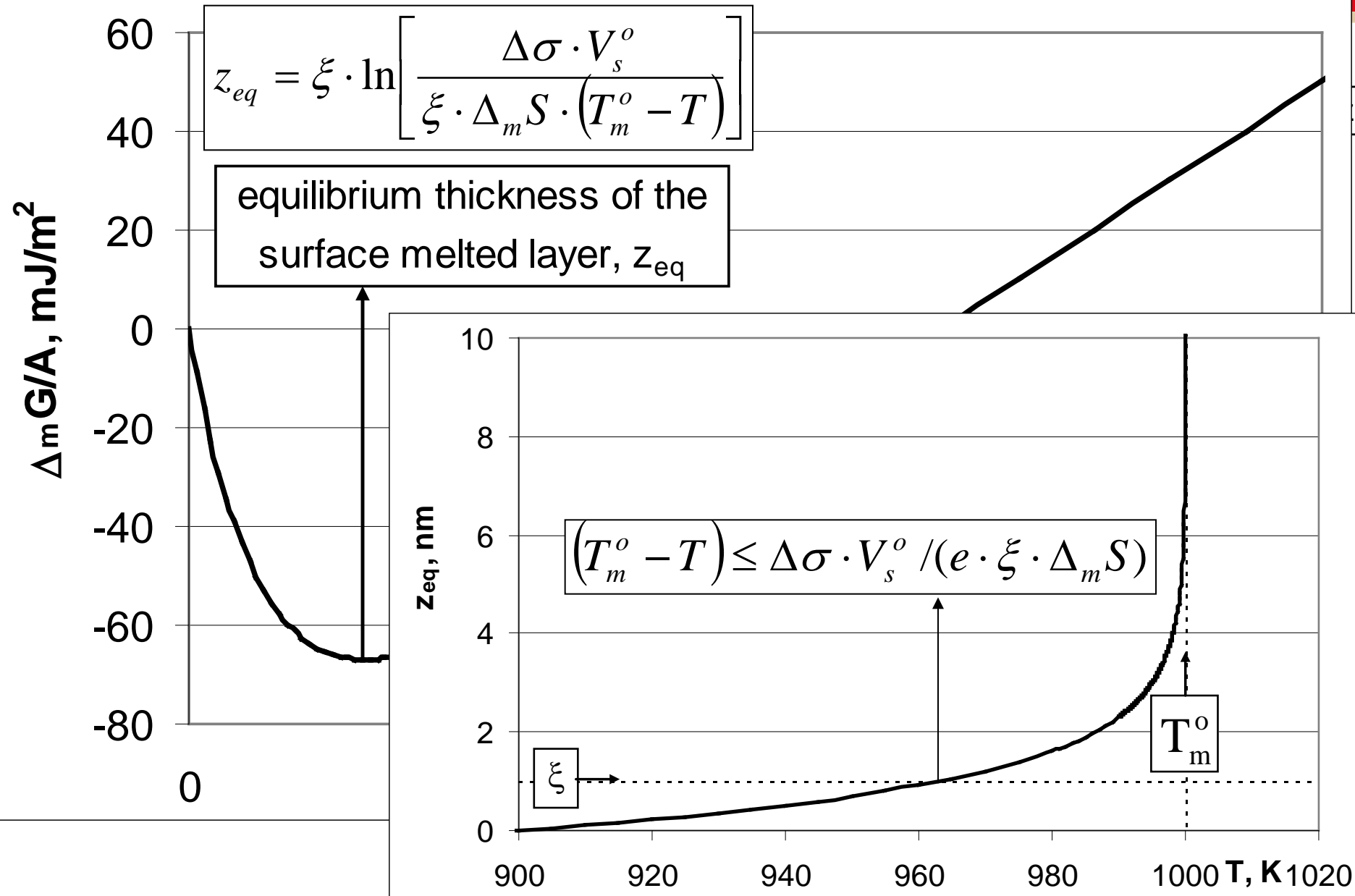
$$\sigma_{\alpha/\gamma}(z) = \sigma_{\alpha/\gamma} + (0.5 \cdot \sigma_{\alpha/\beta} - \sigma_{\alpha/\gamma}) \cdot f(z)$$

$$\sigma_{\beta/\gamma}(z) = \sigma_{\beta/\gamma} + [0.5 \cdot \sigma_{\alpha/\beta} - \sigma_{\beta/\gamma}] \cdot f(z)$$

$$\sigma(z) = \sigma_{s/l} + \sigma_{l/g} + \Delta\sigma \cdot \exp\left(\frac{-z}{\xi}\right)$$

$$\Delta\sigma \equiv \sigma_{s/g} - \sigma_{s/l} - \sigma_{l/g}$$

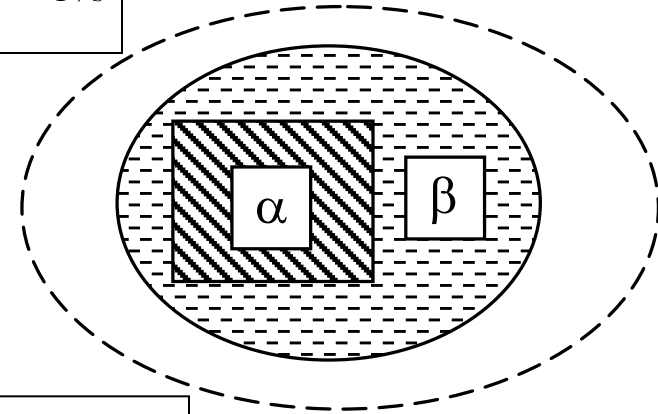
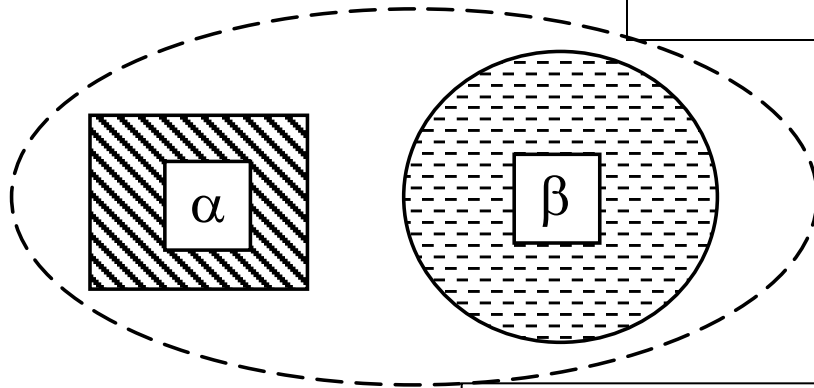
Surface melting



The role of the relative arrangement of phases

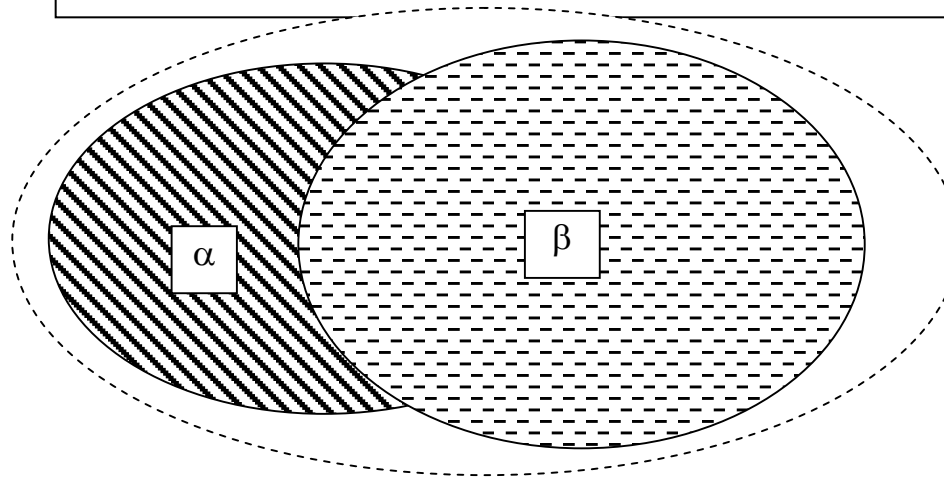
Equilibrium arrangement corresponds to minimum Gibbs energy

$$\Delta G_{\Phi}^{\text{surf}} = V_{\Phi} \cdot \sum_s A_{\Phi/s, \text{spec}} \cdot \sigma_{\Phi/s}$$

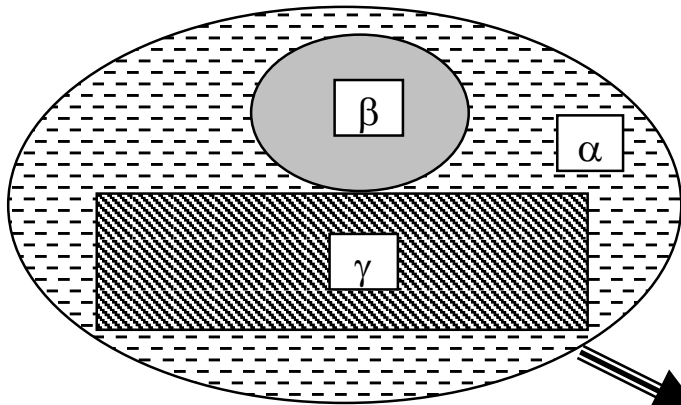


Same results for $N > 10^{12}$

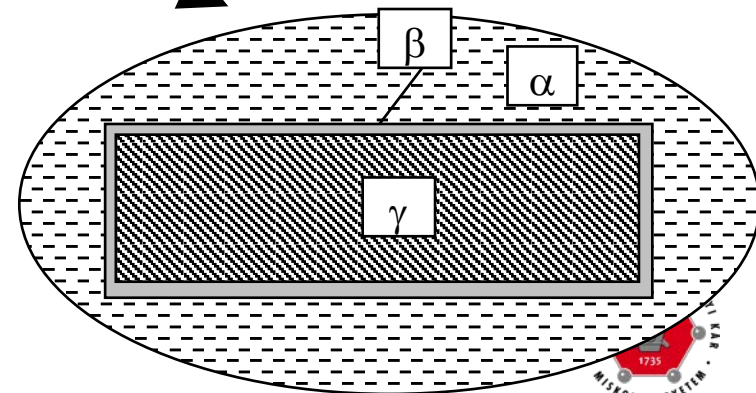
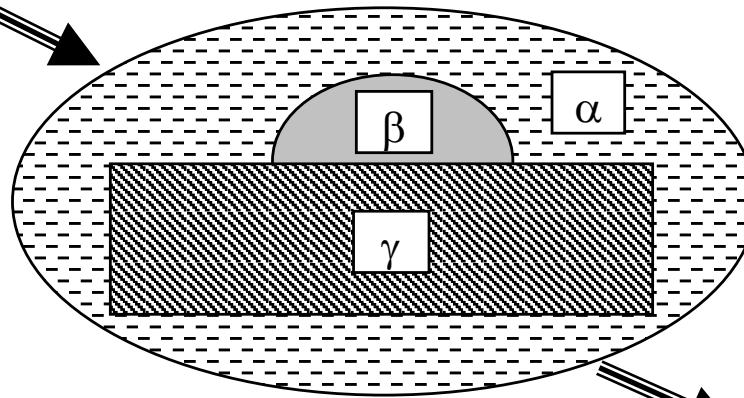
Different results for $N < 10^{12}$



6. Dependence on the substrate material



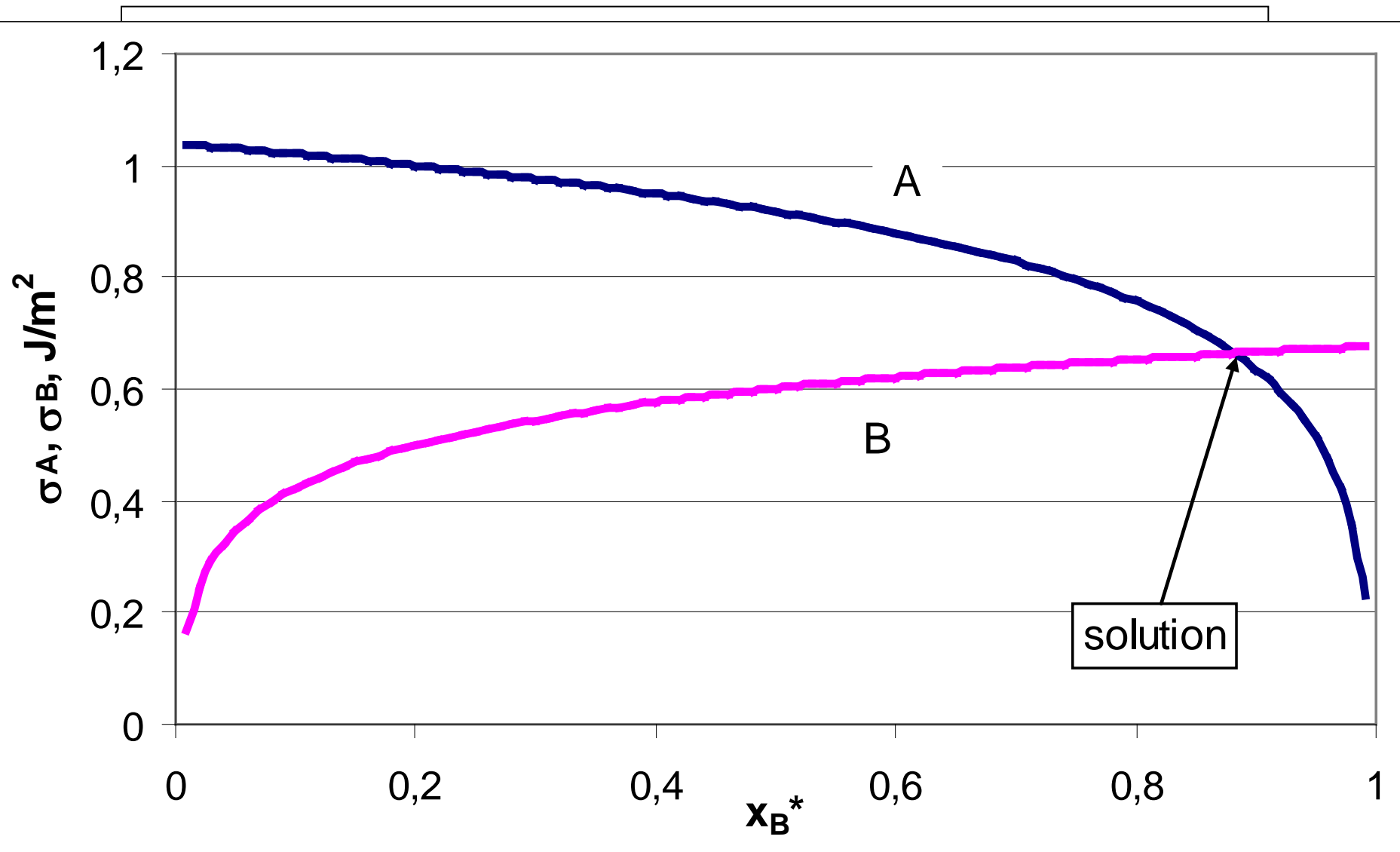
$$\Delta G_{\Phi}^{\text{surf}} = V_{\Phi} \cdot \sum_s A_{\Phi/s, \text{spec}} \cdot \sigma_{\Phi/s}$$

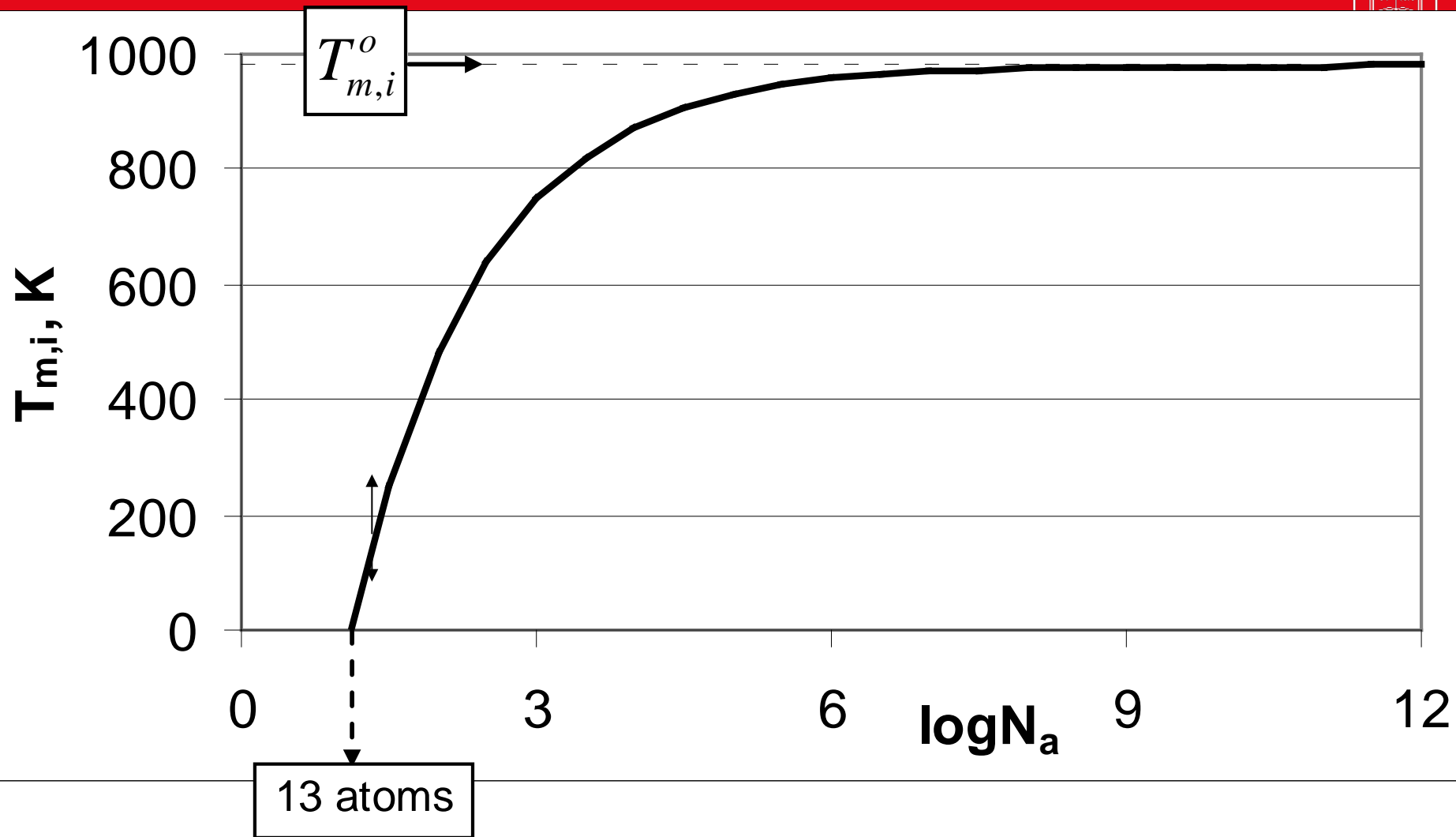


Wettable substrates stabilize
nano-droplets



Dependence on segregation (Butler)



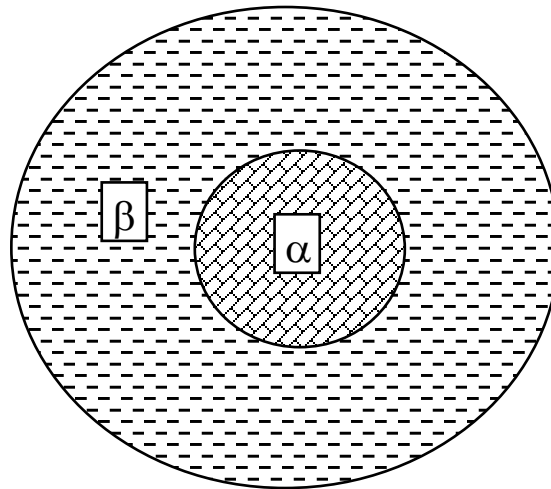


What is the critical N below which thermodynamic is not valid is a „religious” question (at $N = 13$: $T_m \approx 0$ K, what is OK): only the fluctuation increases with smaller N

Algorithm for 2-phase, 2-component nano-phase-equilibria (1)



1. Fix values for p , T , x_A , N
2. Suppose a certain phase-arrangement, e.g.



3. Suppose a value for y_α ($0 < y_\alpha < 1$), then:

$$N_\alpha = y_\alpha \cdot N$$

$$N_\beta = (1 - y_\alpha) \cdot N$$



Algorithm for nano phase equilibria (2)



4. Suppose a value for $x_{A,\alpha}$ ($0 < x_{A,\alpha} < 1$), then: $x_{B,\alpha} = 1 - x_{A,\alpha}$

$$x_{A,\beta} = \frac{x_A - y_\alpha \cdot x_{A,\alpha}}{1 - y_\alpha} \quad x_{B,\beta} = 1 - x_{A,\beta}$$

5. Find σ_α and σ_β from the Butler equation (modify $x_{A\alpha}$).

6. Check, if the equations for G-s with σ -s are satisfied

$$G_{A,\alpha} = G_{A,\beta}$$

$$G_{B,\alpha} = G_{B,\beta}$$

7. If not, select new values for $(x_{A,\alpha}, y_\alpha)$ and go back to Step 3

8. If yes, check solution for other phase arrangements / shapes and select equilibrium arrangement / shape configuration for the phases by minimizing Gibbs energy

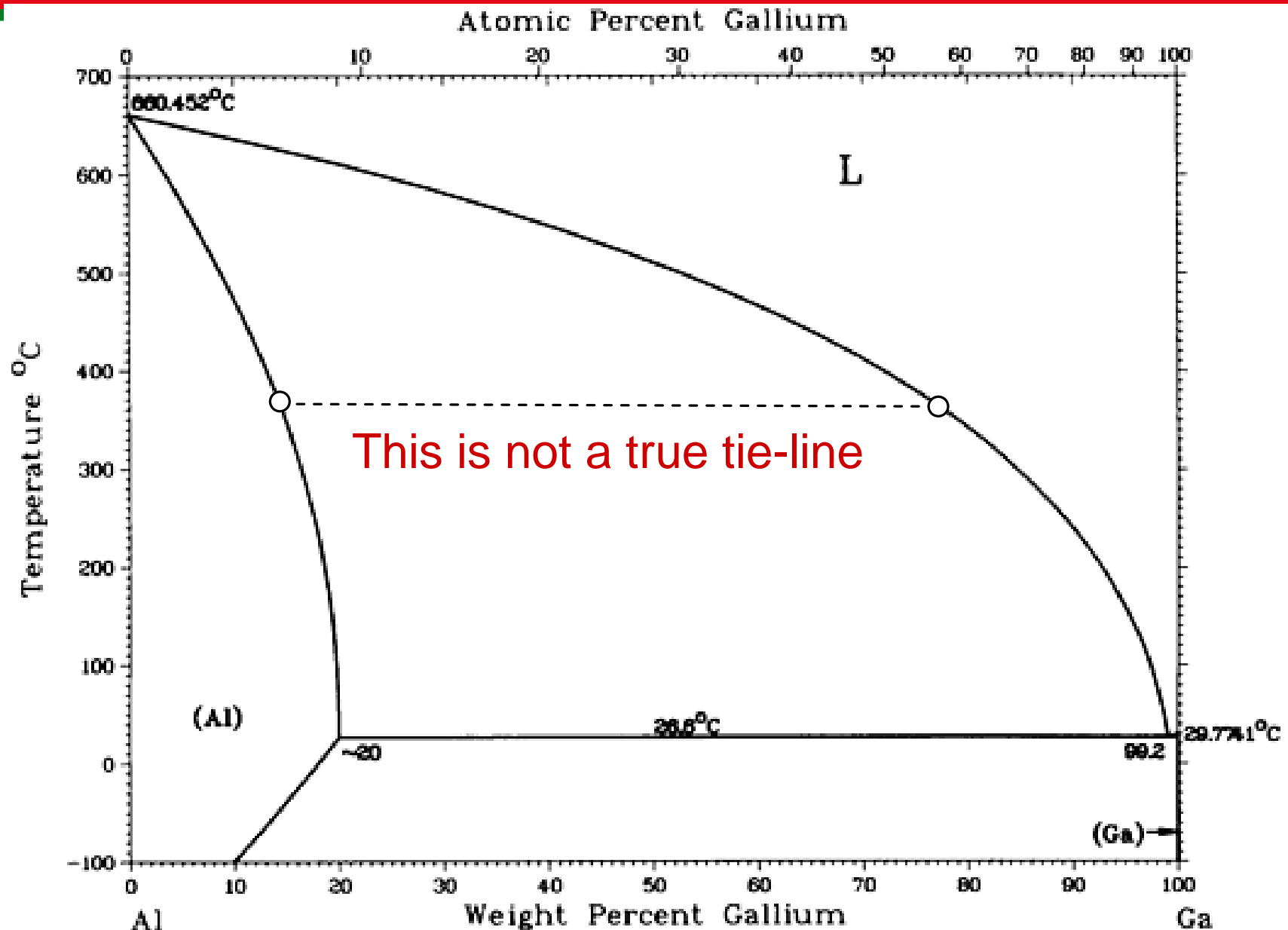


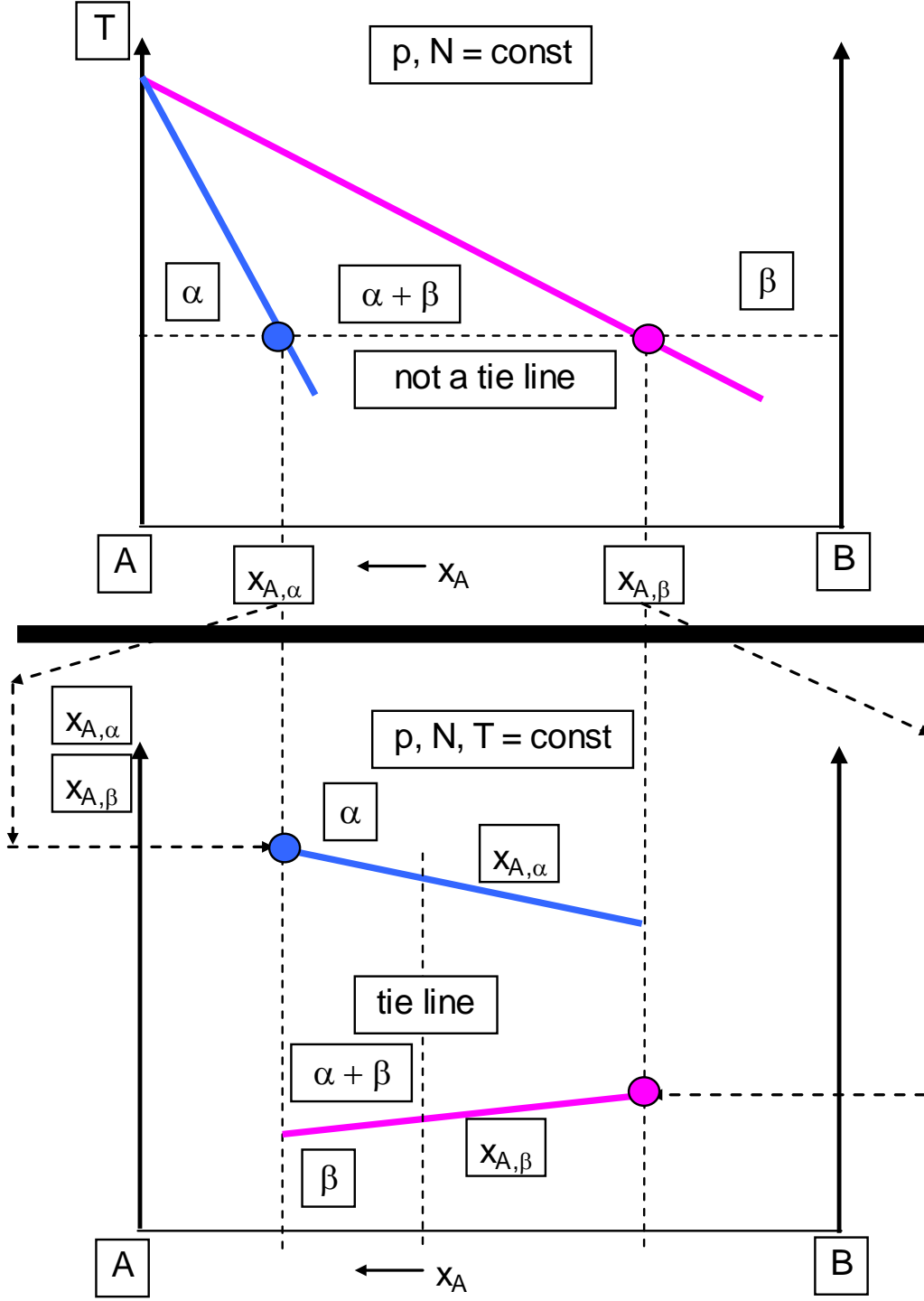
Algorithm for nano phase equilibria (3)



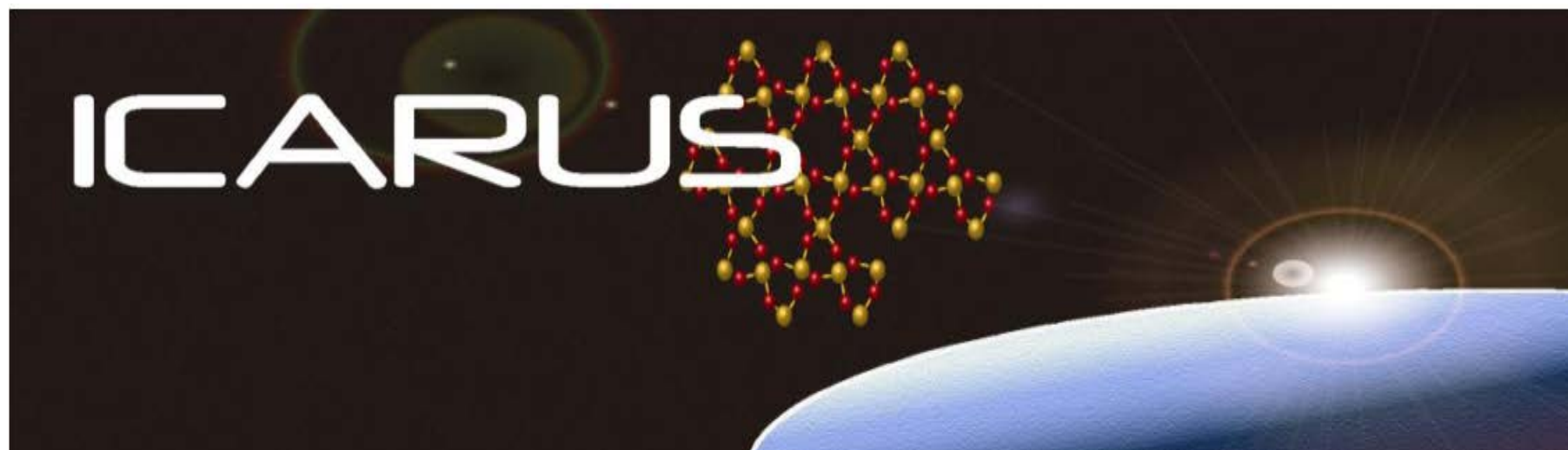
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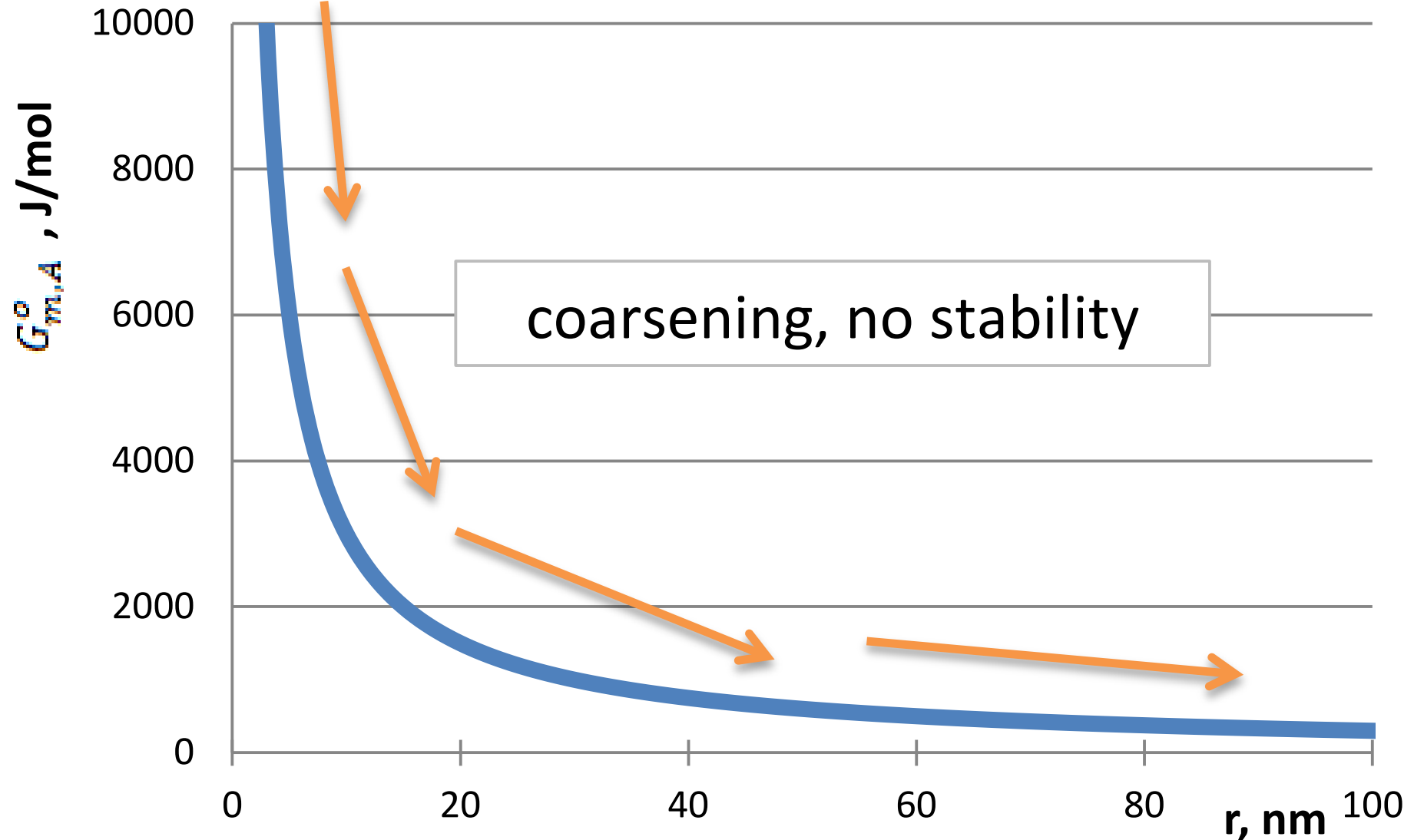




Part 3. Thermodynamic stabilization of nano-alloys vs grain coarsening and precipitation



The case of pure metals



2-component alloys (GB = grain boundary)



A = bulk component, B = segregated component, x_B = average mole fraction

$$r_{min} \cong \frac{r^*}{x_B} - 3 \cdot r_a$$

$$x = \frac{x_B - y}{1 - y}$$

$$y = \frac{r^*}{r + 3 \cdot r_a}$$

$$r^* \equiv \frac{4}{3} \cdot k \cdot \frac{f_{gb}}{f_b} \cdot r_a$$

y = GB-ratio, r_a = atomic radius, f_b, f_{gb} = bulk and GB filling ratios, x = B mole fraction in bulk, r_{min} = minimum possible grain size, ω_B^o, σ_B^o = molar surface area and GB energy of component B, Ω = bulk interaction energy, V_m = molar volume, G_m molar Gibbs energy.

$$r_a = \left(\frac{3 \cdot f_b \cdot V_m}{4 \cdot \pi \cdot N_{Av}} \right)^{1/3}$$

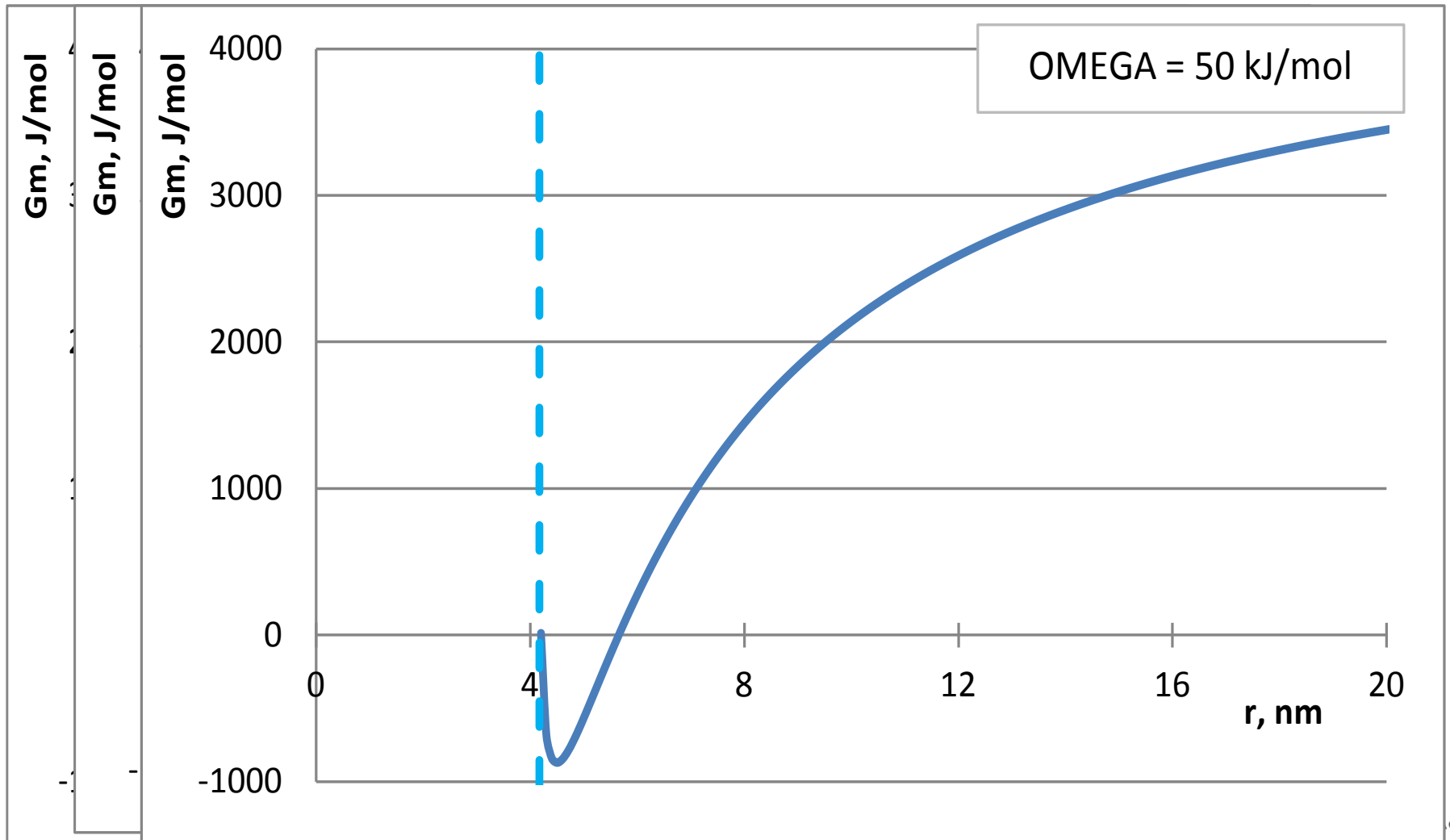
$$\omega_B^o = \pi \cdot r_a^2 \cdot \frac{N_{Av}}{f_{gb}}$$

$$G_m = R \cdot T \cdot [x \cdot \ln x + (1 - x) \cdot \ln(1 - x)] + \Omega \cdot x \cdot (1 - x) +$$

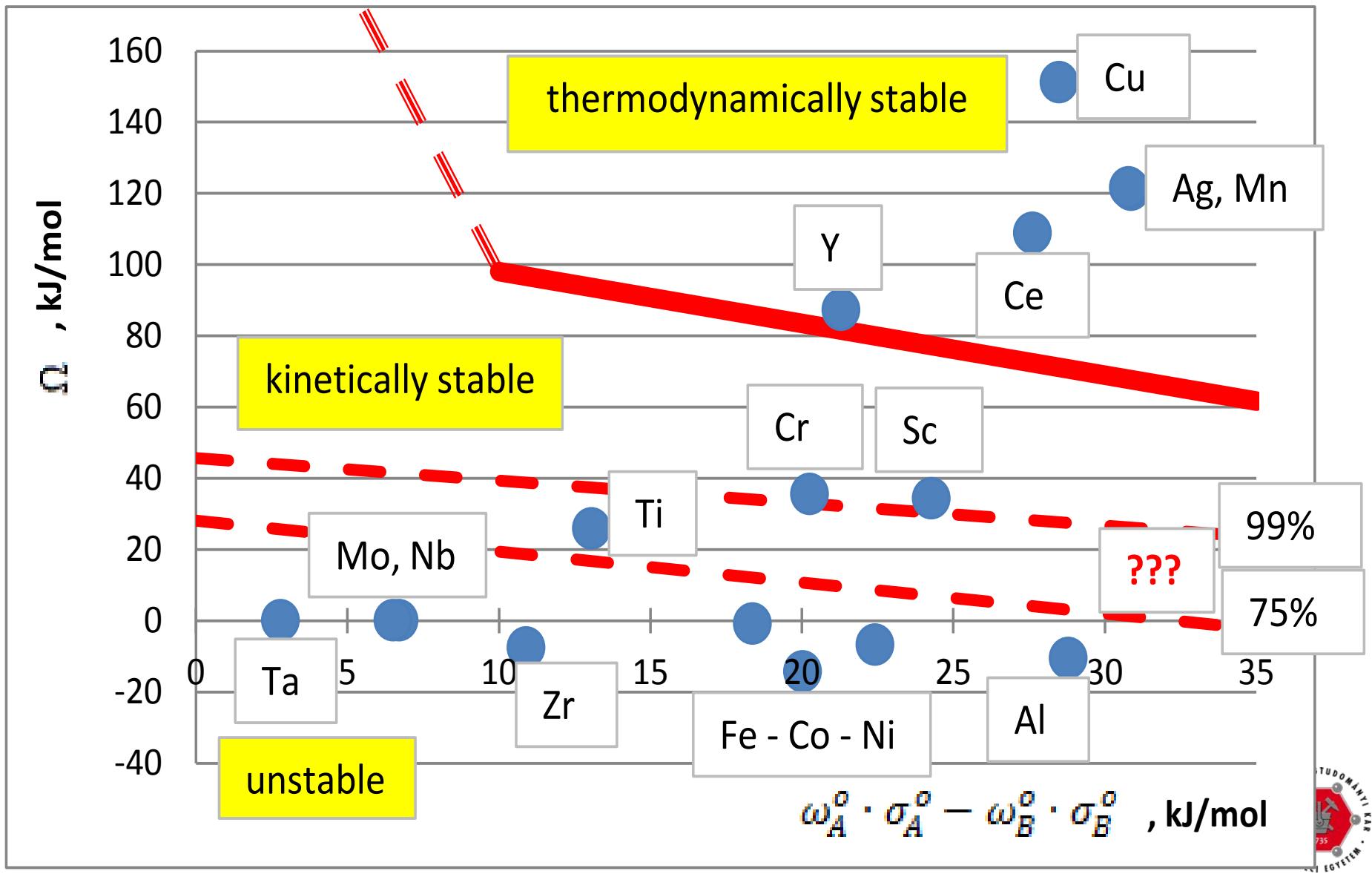
$$+ \frac{k}{r + 3 \cdot r_a} \cdot \frac{V_m}{\omega_B^o} \cdot \left[\omega_B^o \cdot \sigma_B^o \cdot \left(1 + \frac{3 \cdot r_a}{r} \right) - R \cdot T \cdot \ln x - \Omega \cdot (1 - x)^2 \right]$$



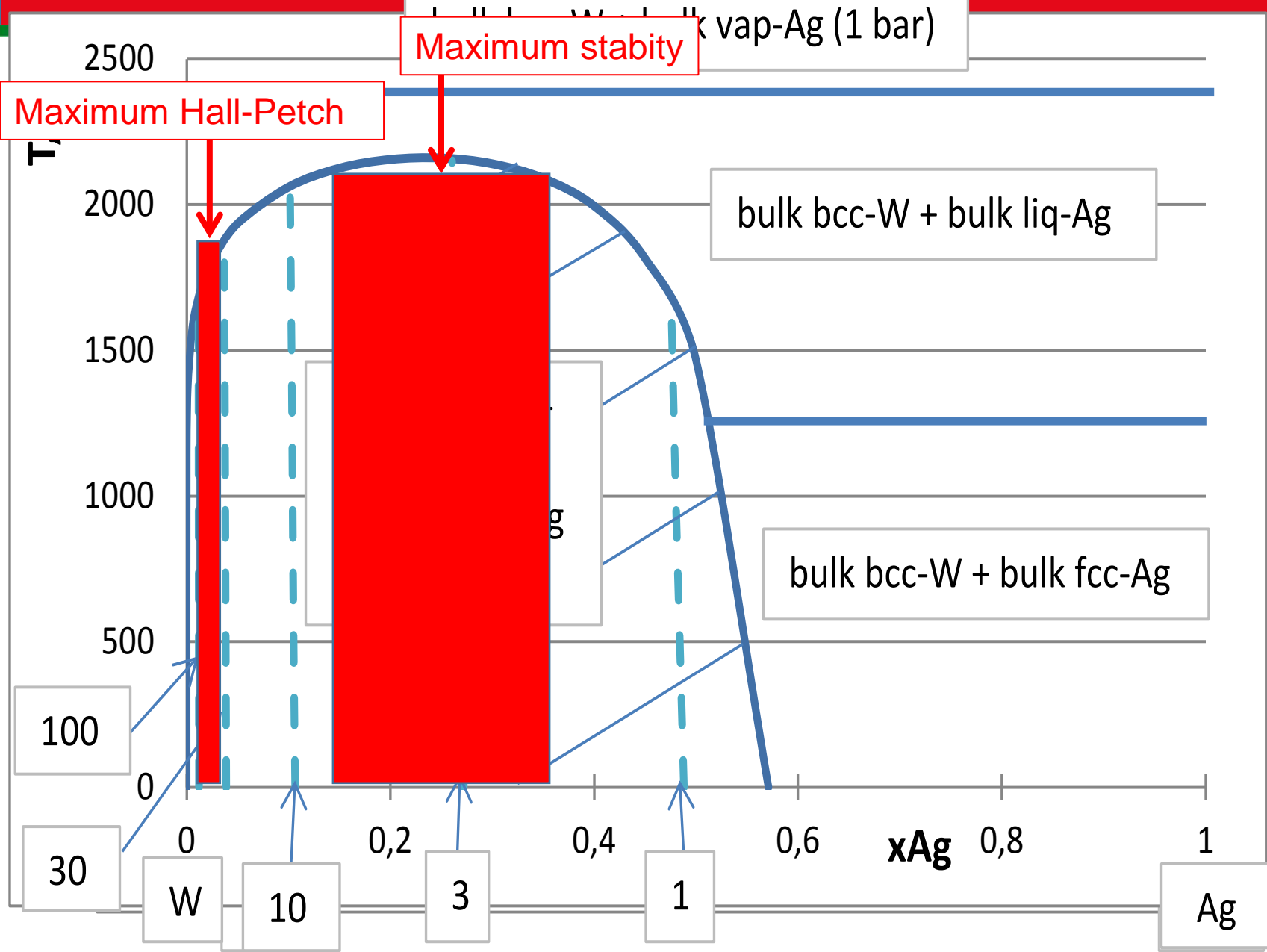
W-"Ag" alloys, 500 K, 15 mol% Ag



Stability diagram for W-based alloys



W-Ag phase diagram



Theoretically selected stable nc alloys



W-based alloys: **Ag**, Au, Ba, Bi, Cd, Ce, **Cr**, Cs, **Cu**, Eu, Gd, Hg, Ho, In, K, **La**, Li, Mg, Na, Nd, Pb, Pu, Rb, Sb, Sc, Sm, Sn, Tb, Th, Tl, Tm, U, Y, Yb, Zn.

Mo-based alloys: **Ag**, Ba, Bi, Ca, Cd, Ce, Cs, **Cu**, Er, Eu, Hg, Ho, In, K, **La**, Li, Mg, Na, Nd, Pb, Rb, Sm, Sr, Tl, Yb.

Nb-based alloys: **Ag**, Ba, Bi, Ca, Cd, Ce, Cs, **Cu**, Er, Eu, Gd, Hg, K, **La**, Li, Mg, Na, Rb, Sc, Sm, Tl, Y, Yb.

Ti-based alloys: Ba, Ca, Ce, Cs, Eu, Gd, K, La, Li, **Mg**, Na, Nd, Rb, Sr, Yb.

Al-based alloys: **Bi**, Cd, Cs, In, K, Na, Pb, Rb, Tl.

Mg-based alloys: Cs, K, Na, Rb.



Key papers



Calphad, 56 (2017) 169-184.

J. Phys. Chem. C, 120 (2016) 1881-1890.

J. Mater. Sci., 51 (2016) 1738-1755.

Langmuir 31 (2015) 5796-5804.

Acta Mater, 60 (2012) 6804-6813.

J Mater Sci, 47 (2012) 8320-8335.

Int. J. Pharmaceutics, 430 (2012) 253-257.

J Nanosci Nanotechnol, 12 (2012) 2625-2633

J. Nanosci. Nanotechnol., 10 (2010) 8164–8170

kaptay@hotmail.com

