



Comparison of different model equations for size- and shape dependent molar Gibbs energies of nanophases to screen out the incorrect ones

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MISKOLCI
E G Y E T E M

Nano-materials are materials that contain at least one nano-phase.

A nano-phase is a phase with at least one of its dimensions below 100 nm, but with all its dimensions above 1 nm (to call it a phase and to avoid quantum effects).

All properties of nano-phases and nano-materials are size dependent: they depend on the nano-sizes of its nano-phases (in contrary the properties of macro-phases are size-independent).

Nano-phases do not have their own intrinsic properties, as their properties depend also on the surrounding phases. (in contrary to macro-phases that have their own intrinsic properties)

Molar Gibbs energy of a nano-phase



The generally accepted size-dependence:

$$G_{m,\Phi} = G_{m,b-\Phi} + z_{\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/\text{sur}}$$

Kelvin (1869): the nano-effect is caused by **large curvature**:

$$z_{\Phi} \equiv \kappa_{\Phi}$$

At least 2 out of these 3 equations are wrong, but which one?

Kaptay (2012): the nano-effect is caused by **large specific surface area**:

$$z_{\Phi} \equiv A_{sp,\Phi} \equiv \frac{A_{\Phi}}{V_{\Phi}}$$

Searcy (1970), later Lee+Kim (2014), later Wong+Wong (2025): the nano-effect is caused by the **derivative of surface area per volume**:

$$z_{\Phi} \equiv \frac{dA_{\Phi}}{dV_{\Phi}}$$



This talk is devoted to my friend Joonho Lee
(remembering his presentation in 2025-Calphad)



Re-derivation of the Kelvin equation



The integrated form of the molar Gibbs energy of a bulk phase:

$$G_{m,b-\Phi} = U_{m,b-\Phi} + p \cdot V_{m,b-\Phi} - T \cdot S_{m,b-\Phi}$$

The Laplace pressure-increase: $\Delta p_L = \kappa_\Phi \cdot \sigma_{\Phi/\text{sur}}$

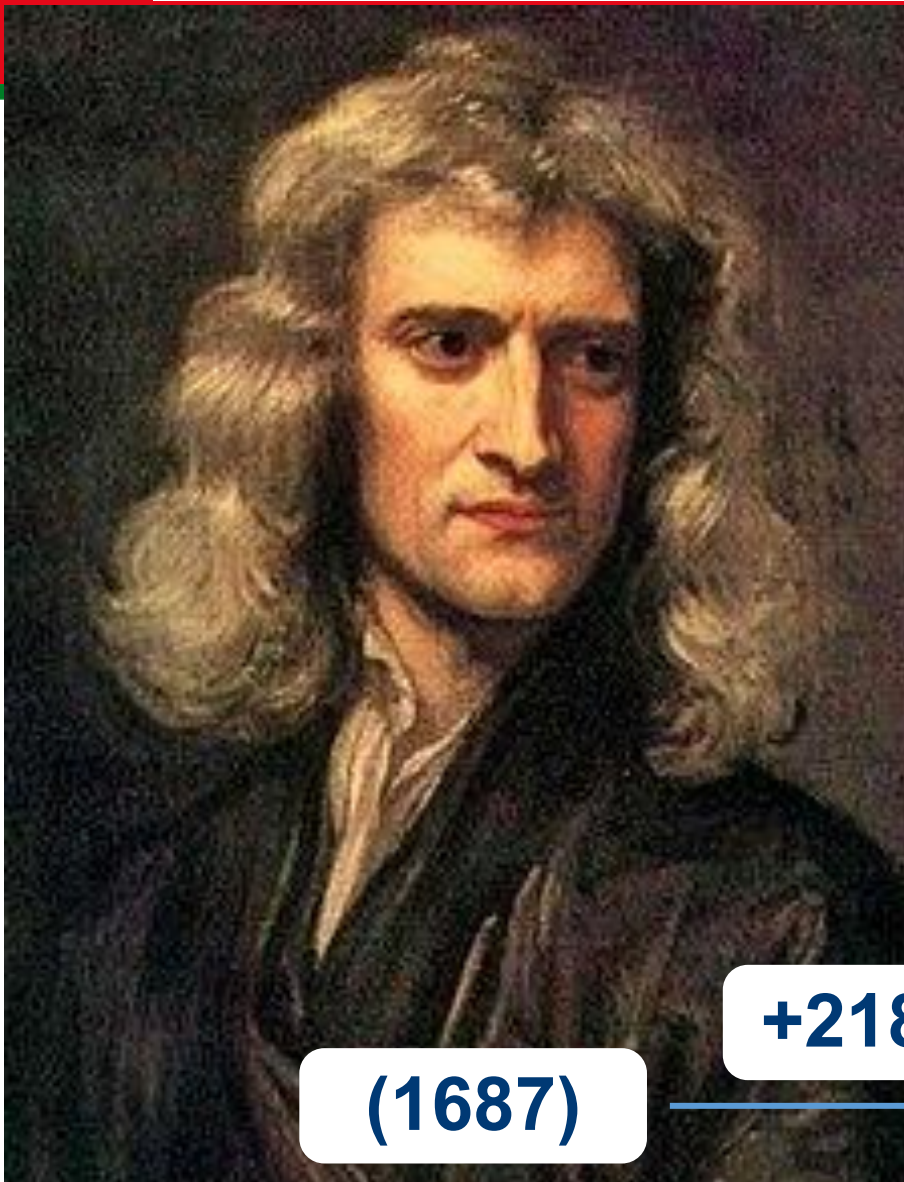
Kelvin (wrongly) supposed that the size-dependent term of the molar Gibbs energy is due to the (otherwise correct) Laplace pressure:

$$G_{m,\Phi} = U_{m,b-\Phi} + (p + \kappa_\Phi \cdot \sigma_{\Phi/\text{sur}}) \cdot V_{m,b-\Phi} - T \cdot S_{m,b-\Phi}$$

$$G_{m,\Phi} = G_{m,b-\Phi} + \kappa_\Phi \cdot V_{m,\Phi} \cdot \sigma_{\Phi/\text{sur}}$$

It is mathematically correct, but physically not: i). the Laplace pressure-increase has no influence outside the phase, so it has no influence on phase equilibria; ii). the surface term of Gibbs is „forgotten”, etc... (see below).

The normal way of scientific development



(1687)

Isaac Newton (1642 – 1727)

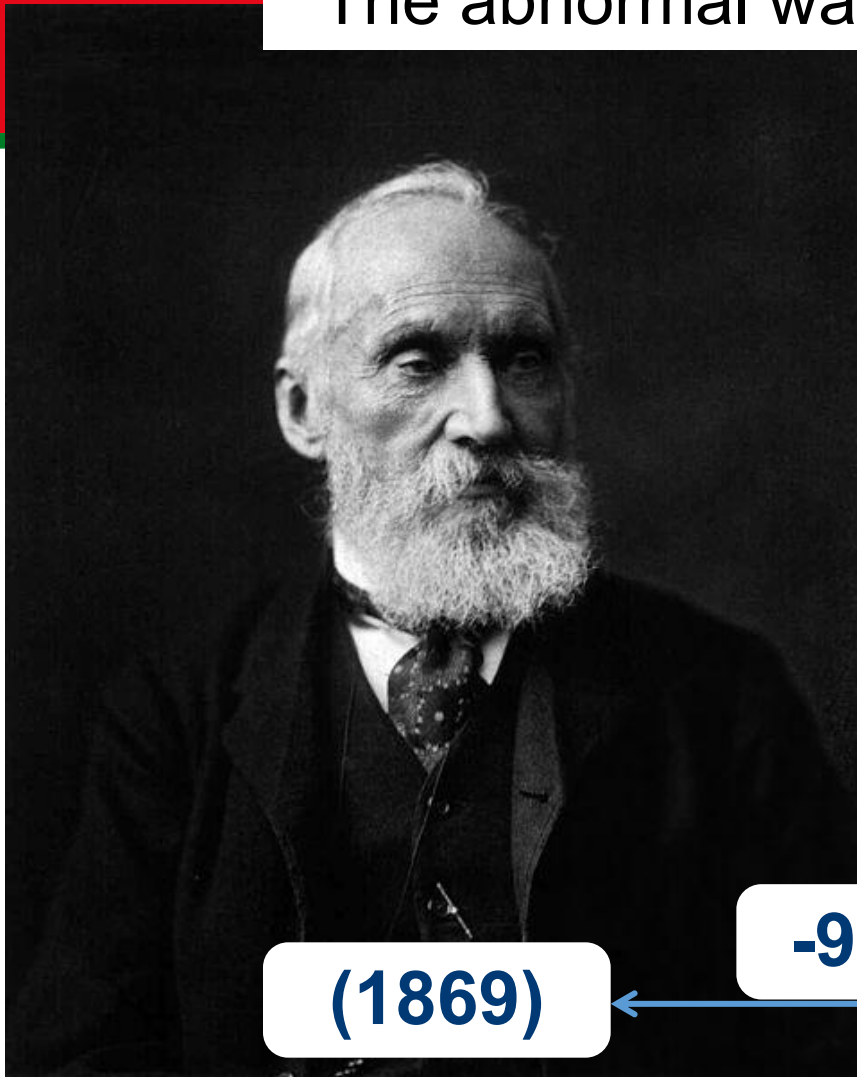
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(1905)

Albert Einstein (1879 – 1955)

The abnormal way of scientific development



(1869)

-9 ys !!



(1878)

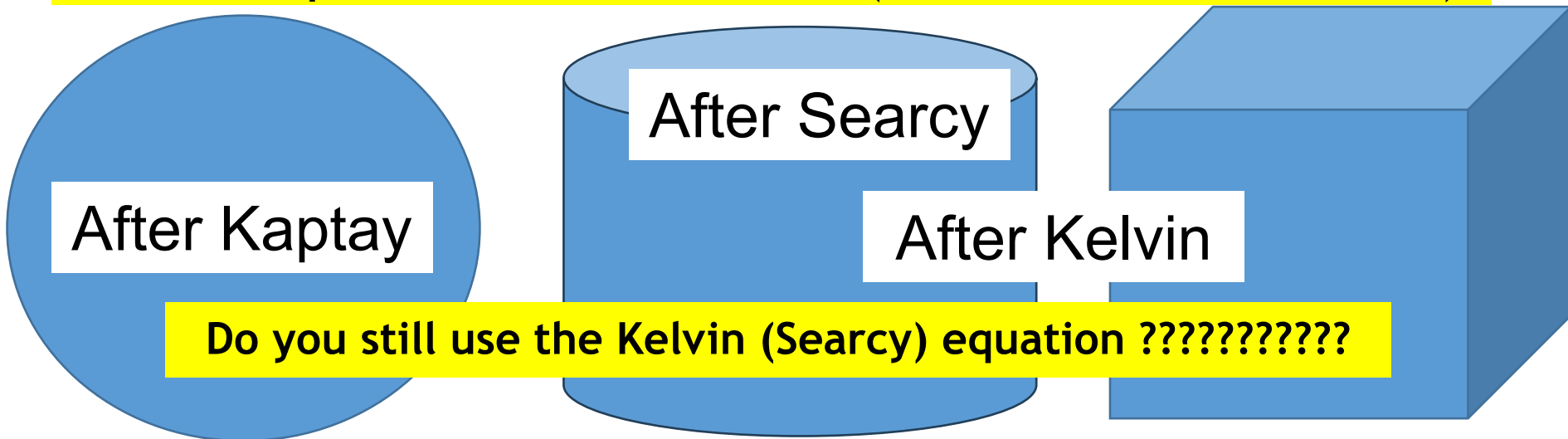
**William Thomson
(Lord Kelvin)
1824 - 1907**

**Josiah Willard Gibbs
1839 - 1903**

What is the shape of independent droplets?

„Why Kaptay is asking stupid questions **again?**” (from a reviewer)

He is actually asking a question with an obvious answer to check, if different equations are correct or not (like the ancient Greeks did).



$$G_{m,L,sphere} = G_{m,L,b} + \frac{2}{r} \cdot V_{m,L} \cdot \sigma_{L/G} > \begin{cases} G_{m,L,cube} = G_{m,L,b} \\ G_{m,L,cyli} = G_{m,L,b} + \frac{1}{r} \cdot V_{m,L} \cdot \sigma_{L/G} \end{cases}$$

$$G_{m,\alpha} = G_{m,\alpha,b} + A_{sp,\alpha/G} \cdot V_{m,\alpha} \cdot \sigma_{\alpha/G}$$

Sphere has the smallest specific surface area among 3D bodies, therefore the equilibrium shape of droplets is a sphere, after my equation

Re-derivation of the Searcy-equation



The fundamental equation of Gibbs (p-T = constant, 1-component phase)

$$dG_{\Phi} = G_{m,b-\Phi} \cdot dn_{\Phi} + \sigma_{\Phi/\text{sur}} \cdot dA_{\Phi}$$

$$\sigma_{\Phi/\text{sur}} \equiv \left(\frac{\partial G_{\Phi}}{\partial A_{\Phi}} \right)_{p,T,n}$$

Suppose the increase of surface area is proportional to the increase of the amount of matter (and so also to the increase of the volume):

$$n_{\Phi} = \frac{V_{\Phi}}{V_{m,\Phi}}$$

$$dn_{\Phi} = \frac{dV_{\Phi}}{V_{m,\Phi}}$$

$$dG_{\Phi} = G_{m,\Phi} \cdot dn_{\Phi}$$

$$dG_{\Phi} = \left(G_{m,b-\Phi} + \sigma_{\Phi/\text{sur}} \cdot \frac{dA_{\Phi}}{dn_{\Phi}} \right) \cdot dn_{\Phi}$$

$$dG_{\Phi} = \left(G_{m,b-\Phi} + \sigma_{\Phi/\text{sur}} \cdot V_{m,\Phi} \cdot \frac{dA_{\Phi}}{dV_{\Phi}} \right) \cdot dn_{\Phi}$$

$$G_{m,\Phi} = G_{m,b-\Phi} + \sigma_{\Phi/\text{sur}} \cdot V_{m,\Phi} \cdot \frac{dA_{\Phi}}{dV_{\Phi}}$$

OK, but if surface area is not independent on amount of matter, then how surface energy is defined?



Re-derivation of the Kaptay-equation (1)

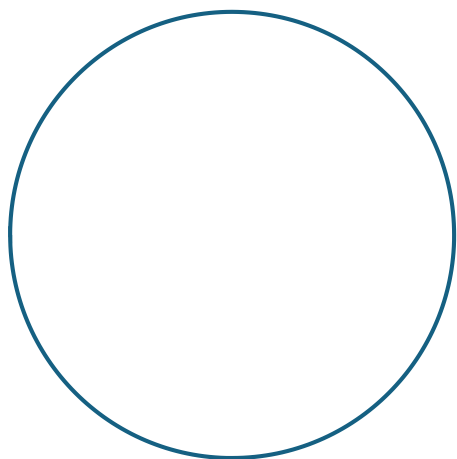


Same fundamental equation of Gibbs (p-T-n = constant, 1-component):

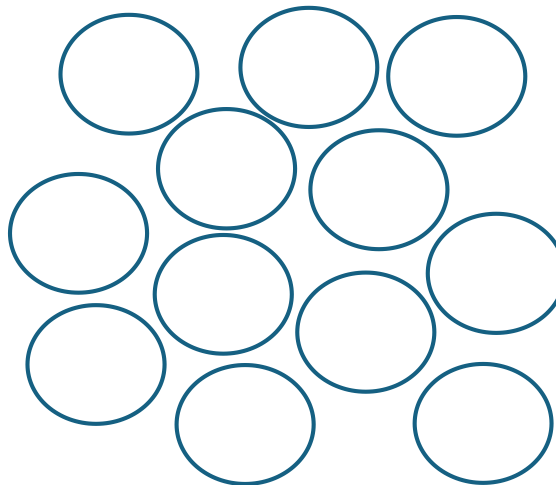
$$dG_{\Phi} = G_{m,b-\Phi} \cdot dn_{\Phi} + \sigma_{\Phi/\text{sur}} \cdot dA_{\Phi}$$

$$dG_{\Phi} = \sigma_{\Phi/\text{sur}} \cdot dA_{\Phi}$$

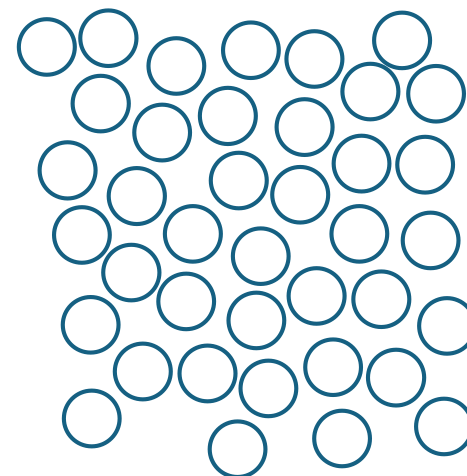
$$\sigma_{\Phi/\text{sur}} \equiv \left(\frac{\partial G_{\Phi}}{\partial A_{\Phi}} \right)_{p,T,n}$$



Case A



Case B



Case C

p_A	=	p_B	=	p_C
T_A	=	T_B	=	T_C
n_A	=	n_B	=	n_C
A_A	<	A_B	<	A_C



Re-derivation of the Kaptay-equation (2)



Same fundamental equation of Gibbs (p - T - n = constant, 1-component):

$$dG_{\Phi} = \sigma_{\Phi/\text{sur}} \cdot dA_{\Phi}$$

Take the integral with i). $A_{\Phi} = 0$: $G_{\Phi} = G_{b,\Phi}$, ii). $A_{\Phi} = A_{\Phi}$: $G_{\Phi} = G_{\Phi}$:

$$G_{\Phi} = G_{b,\Phi} + \sigma_{\Phi/\text{sur}} \cdot A_{\Phi}$$

Divide by the amount of matter in the phase:

$$n_{\Phi} = \frac{V_{\Phi}}{V_{m,\Phi}}$$

$$G_{m,\Phi} = G_{m,b,\Phi} + \sigma_{\Phi/\text{sur}} \cdot V_{m,\Phi} \cdot \frac{A_{\Phi}}{V_{\Phi}}$$

$$A_{sp,\Phi} \equiv \frac{A_{\Phi}}{V_{\Phi}}$$

$$G_{m,\Phi} = G_{m,b-\Phi} + \sigma_{\Phi/\text{sur}} \cdot V_{m,\Phi} \cdot A_{sp,\Phi}$$

What took so long? Integrating? Dividing? No, these were easy.

What was really difficult it was to claim that Kelvin was wrong.



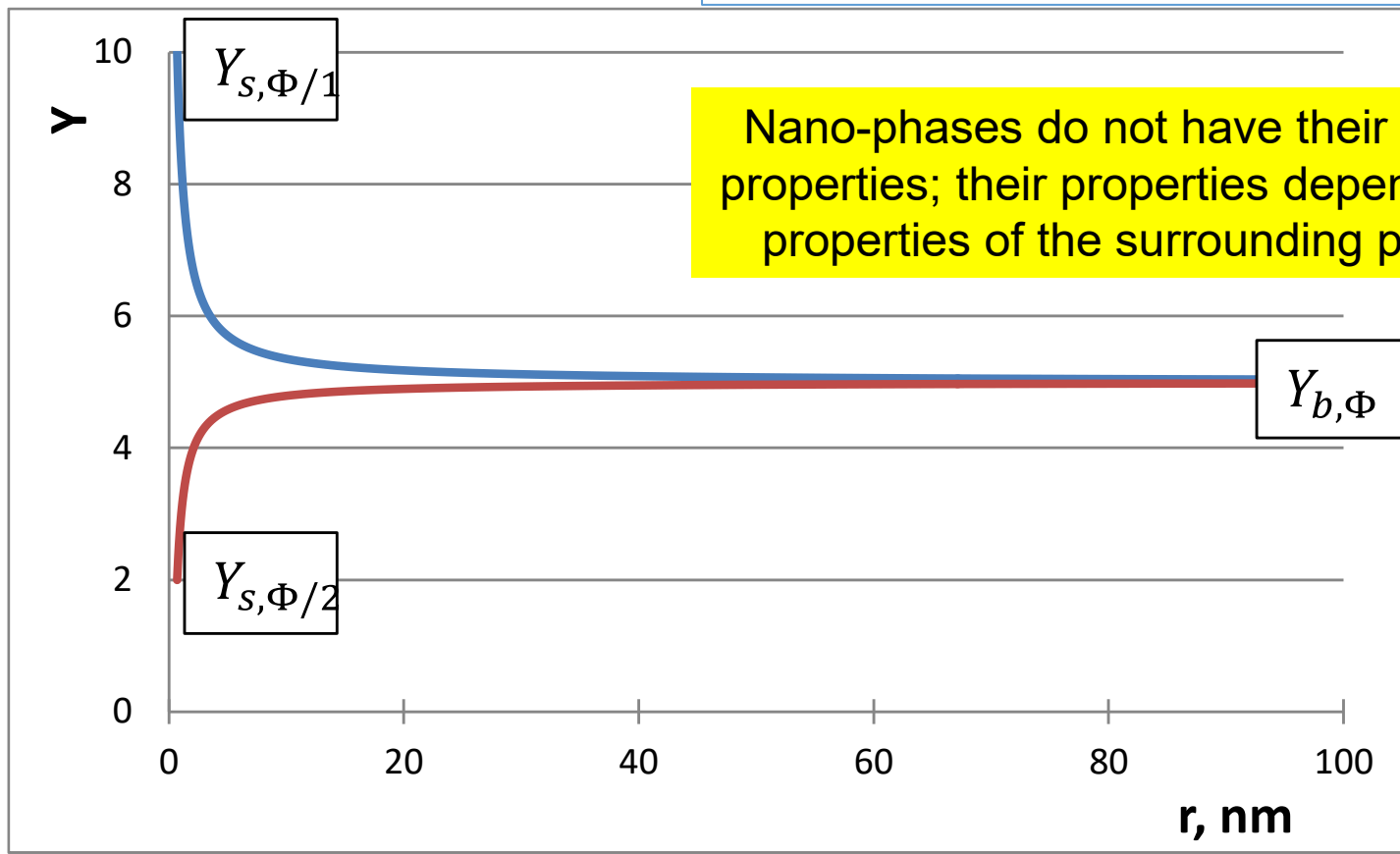
Size dependence of properties of nano-phases



Consider any property Y of phase Φ : Y_Φ . Its bulk value = $Y_{b,\Phi}$. Its surface value = $Y_{s,\Phi/\Psi}$. They are generally different ($Y_{s,\Phi/\Psi} \neq Y_{b,\Phi}$). The average property of the phase is proportional to the ratio of the surface atoms:

$$Y_\Phi \cong (1 - x_{s,\Phi}) \cdot Y_{b,\Phi} + x_{s,\Phi} \cdot Y_{s,\Phi/\Psi}$$
$$x_{s,\Phi} = A_{sp,\Phi} \cdot \frac{V_{m,\Phi}}{\omega_\Phi}$$

$$Y_\Phi \cong Y_{b,\Phi} + A_{sp,\Phi} \cdot \frac{V_{m,\Phi}}{\omega_\Phi} \cdot (Y_{s,\Phi/\Psi} - Y_{b,\Phi})$$



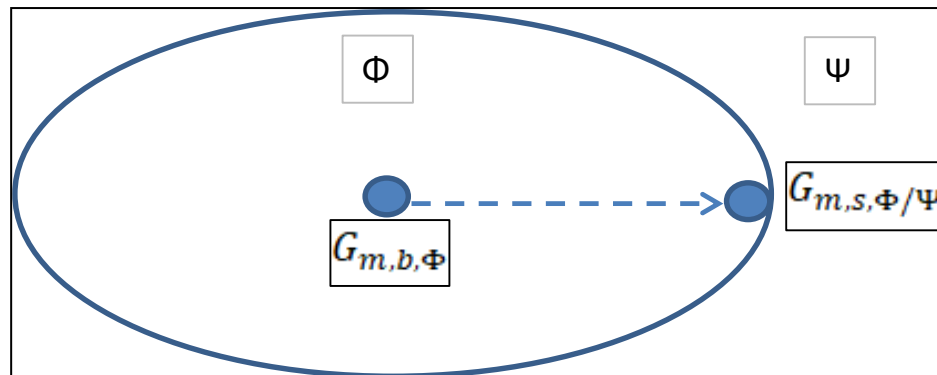
Size-dependence of the molar Gibbs energy + partials + Butler

$$Y_{\Phi} \cong Y_{b,\Phi} + A_{sp,\Phi} \cdot \frac{V_{m,\Phi}}{\omega_{\Phi}} \cdot (Y_{s,\Phi/\Psi} - Y_{b,\Phi})$$

4 new equations / page (((-:

$$Y \equiv G_m$$

$$G_{m,\Phi} \cong G_{m-b,\Phi} + A_{sp,\Phi} \cdot \frac{V_{m,\Phi}}{\omega_{\Phi}} \cdot (G_{m-s,\Phi/\Psi} - G_{m-b,\Phi})$$



$$\sigma_{\Phi/\Psi} = \frac{(G_{m-s,\Phi/\Psi} - G_{m-b,\Phi})}{\omega_{\Phi}}$$

This is a model equation of interfacial energy (J/m²).

$$G_{m,\Phi} = G_{m-b,\Phi} + A_{sp,\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi/\Psi}$$

$$G_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot G_{m,i(\Phi)} \quad G_{m-b,\Phi} = \sum_i x_{i(\Phi)} \cdot G_{m-b,i(\Phi)} \quad V_{m,\Phi} = \sum_i x_{i(\Phi)} \cdot V_{m,i(\Phi)}$$

$$G_{m,i(\Phi)} = G_{m-b,i(\Phi)} + A_{sp,\Phi} \cdot V_{m,i(\Phi)} \cdot \sigma_{i(\Phi)/\Psi}$$

This is true only if the Butler equation is valid:

$$\sigma_{\Phi/\Psi} = \sigma_{i(\Phi)/\Psi}$$



The performance of the models

$$G_{m,\Phi} = G_{m,b-\Phi} + z_{\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi}/\text{sur}$$

	$z_{\Phi} \equiv$	κ_{Φ}	$\frac{dA_{\Phi}}{dV_{\Phi}}$	$A_{sp,\Phi} \equiv \frac{A_{\Phi}}{V_{\Phi}}$
Nano-phase		Kelvin	Searcy	Kaptay
sphere of radius r_{Φ}		$2/r_{\Phi}$	$2/r_{\Phi}$	$3/r_{\Phi}$
cube of side a_{Φ}		0	$4/a_{\Phi}$	$6/a_{\Phi}$
thin film (increase A)		0	$1/d_{\Phi}$	$2/d_{\Phi}$
thin film (increase d_{Φ})		0	0	$2/d_{\Phi}$
cylinder (increase r)		$1/r_{\Phi}$	$1/r_{\Phi} + 2/L_{\Phi}$	$2/r_{\Phi}$
cylinder (increase L)		$1/r_{\Phi}$	$2/r_{\Phi}$	$2/r_{\Phi}$

Experiments: inversely proportional to the characteristic size, so both the Kelvin equation and the Searcy equation should be excluded.

Kinetics has no effect on thermodynamics (Searcy is excluded)

Homogeneous nucleation after Gibbs

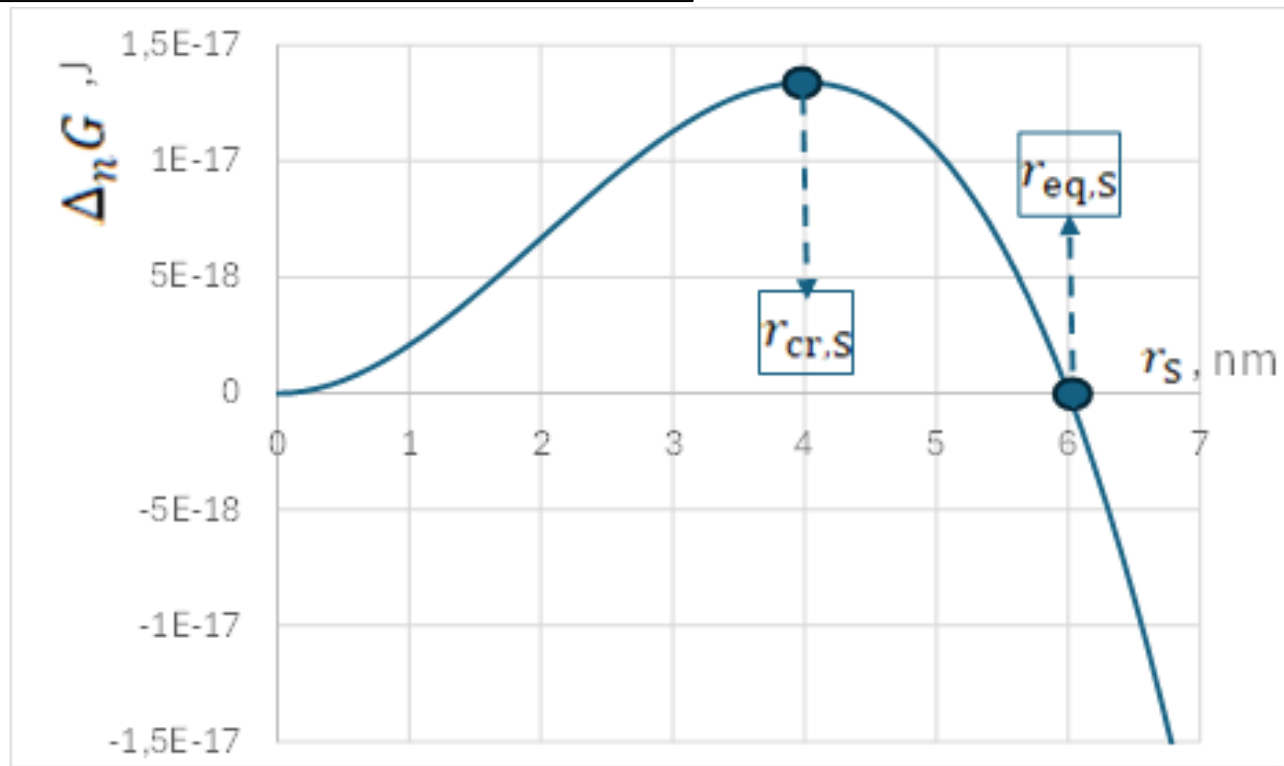


$$\Delta_n G = \frac{4}{3} \cdot \pi \cdot r_S^3 \cdot \frac{G_{m,b-S} - G_{m,b-L}}{V_{m,S}} + 4 \cdot \pi \cdot r_S^2 \cdot \sigma_{S/L}$$

$$r_{cr,S} = \frac{2 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

$$r_{eq,S} = \frac{3 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

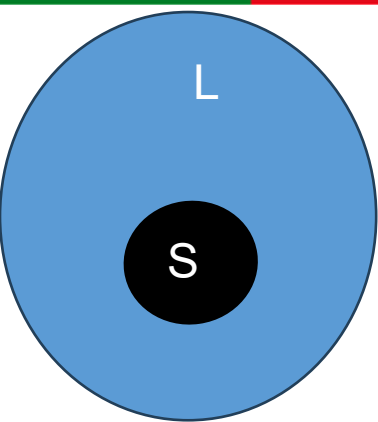
nucleation



$$G_{m,b-S} - G_{m,b-L} = -1,000 \text{ J/mol}, V_{m,S} = 10^{-5} \text{ m}^3/\text{mol}, \sigma_{S/L} = 0.2 \text{ J/m}^2$$



Equilibrium size of a solid nano-sphere in a large liquid (1)



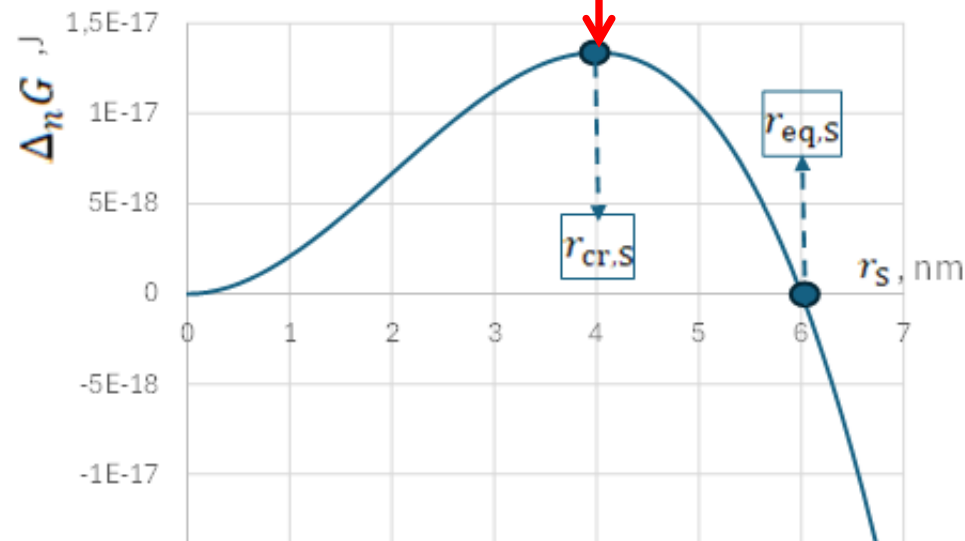
Equilibrium after the Kelvin and Searcy equations

$$G_{m,b-L} = G_{m,b-S} + \frac{2}{r_{eq,S}} \cdot V_{m,S} \cdot \sigma_{S/L}$$

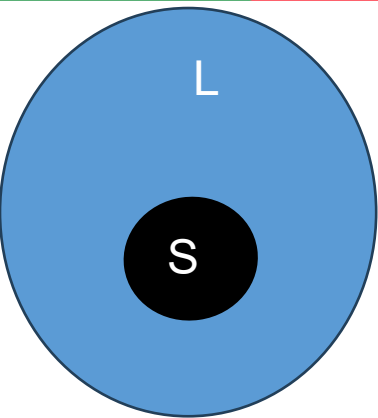
$$r_{eq,S} = \frac{2 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

$$r_{cr,S,Gibbs} = \frac{2 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

Equilibrium size after Kelvin and Searcy coincides with the critical radius of nucleation after Gibbs, corresponding to the maximum of a Gibbs energy change. This is a clear contradiction, meaning that both the Kelvin and the Searcy equations are wrong.



Equilibrium size of a solid nano-sphere in a large liquid (2)



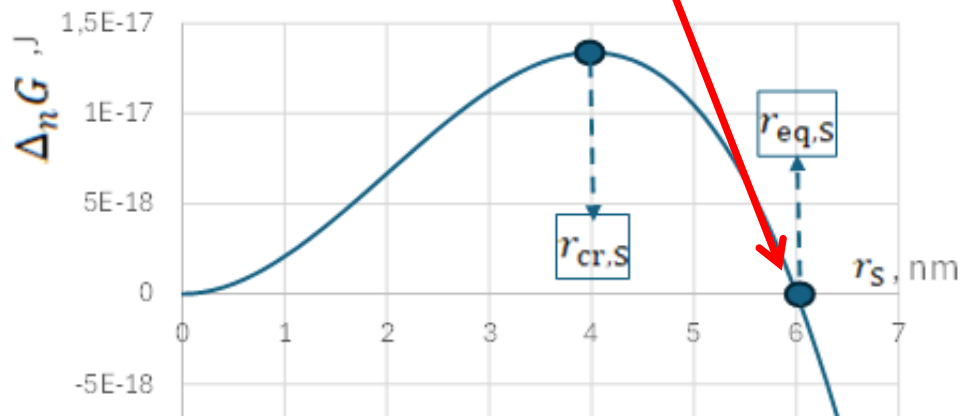
Equilibrium after the Kaptay equation

$$G_{m,b-L} = G_{m,b-S} + \frac{3}{r_{eq,S}} \cdot V_{m,S} \cdot \sigma_{S/L}$$

$$r_{eq,S} = \frac{3 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

$$r_{eq,S,Gibbs} = \frac{3 \cdot V_{m,S} \cdot \sigma_{S/L}}{G_{m,b-L} - G_{m,b-S}}$$

Equilibrium size after the Kaptay equation coincides with the equilibrium size of nucleation after Gibbs, corresponding to zero Gibbs energy change. This is an additional confirmation of the Kaptay equation.



Conclusions regarding the Kelvin equation



$$G_{m,\Phi} = G_{m,b-\Phi} + \kappa_{\Phi} \cdot V_{m,\Phi} \cdot \sigma_{\Phi}/\text{sur}$$

Contradictions:

1. Derivation is wrong (the Laplace pressure has no influence outside of the phase so it has no influence on phase equilibria + the surface term of Gibbs is „forgotten”),
2. non-curved phases have no nano-effect? Wrong conclusion on cubic shape of nano-droplets
3. Is really a cylinder of same radius more stable than a sphere? NO.
4. Equilibrium size coincides with critical size of nucleation after Gibbs. NO.

Please, do not use the Kelvin equation for nano-Calphad calculations.

Please, also forget the Gibbs-Thompson equation and the Freundlich-Ostwald equation, which are consequences of the Kelvin equation.



Conclusions regarding the Searcy equation



$$G_{m,\Phi} = G_{m,b-\Phi} + \sigma_{\Phi/\text{sur}} \cdot V_{m,\Phi} \cdot \frac{dA_{\Phi}}{dV_{\Phi}}$$

Contradictions:

1. Derivation is wrong (surface area is independent on amount of matter),
2. Thin films grown perpendicular to substrate have no nano-effect? Wrong conclusion.
3. Depending on the kinetic path different thermodynamic results follow. NO.
4. Equilibrium size coincides with critical size of nucleation after Gibbs. NO.

Please, do not use the Searcy (Lee-Kim, or Wong-Wong) equation for nano-Calphad calculations.

Please, do not call this equation as „Gibbsian thermodynamics” (Wong-Wong).



Conclusions regarding the Kaptay equation



$$G_{m,\Phi} = G_{m,b-\Phi} + \sigma_{\Phi/sur} \cdot V_{m,\Phi} \cdot A_{sp,\Phi}$$

Contradictions: none.

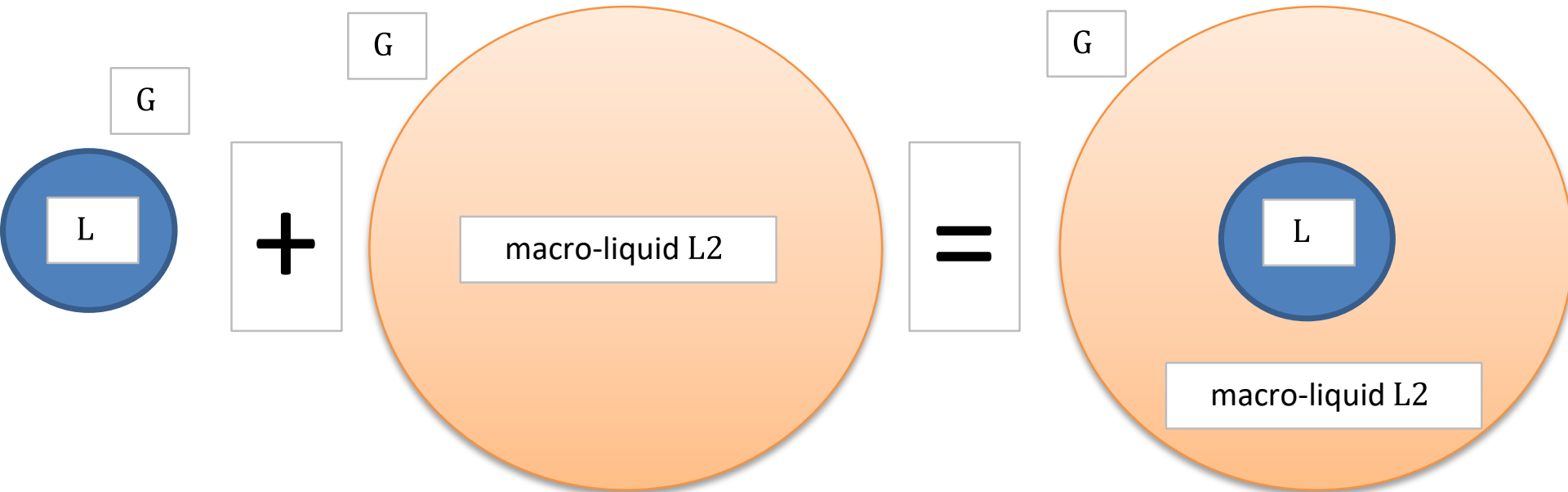
1. Derivation is easy without any contradiction,
2. All nano-phases have a nano-effect (as they should).
3. Equilibrium size coincides with equilibrium size of nucleation after Gibbs.

Please, do use this equation for nano-Calphad calculations.

Please, put into a museum the Kelvin equation, the Gibbs-Thompson equation, the Freundlich-Ostwald equation, and the Searcy (Lee-Kim and Wong-Wong) equation.



Extension to multi-phase situations (1)



$$G_{m,\alpha,cont} = G_{m,\alpha,ind} + \frac{V_{m,\alpha}}{V_{\alpha}} \cdot \Delta(A \cdot \sigma)_{cont}$$

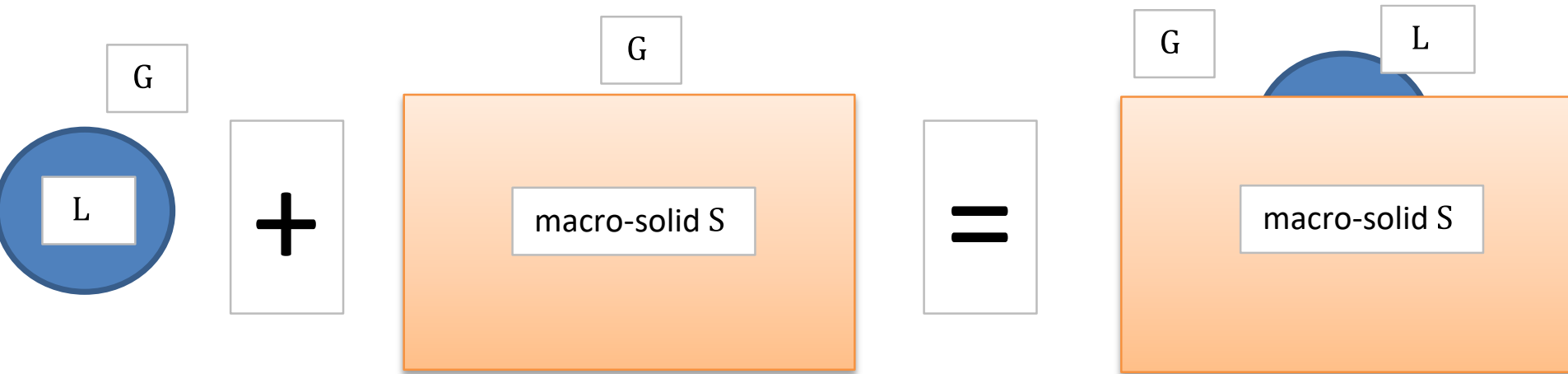
$$\Delta(A \cdot \sigma)_{inc} = 4 \cdot \pi \cdot r^2 \cdot (\sigma_{L2/L} - \sigma_{L/G})$$

$$G_{m,L,inc} = G_{m,L,b} + \frac{3}{r} \cdot V_{m,L} \cdot \sigma_{L2/L}$$

It is an obvious result, proving the validity of the general method



Extension to multi-phase situations (2)

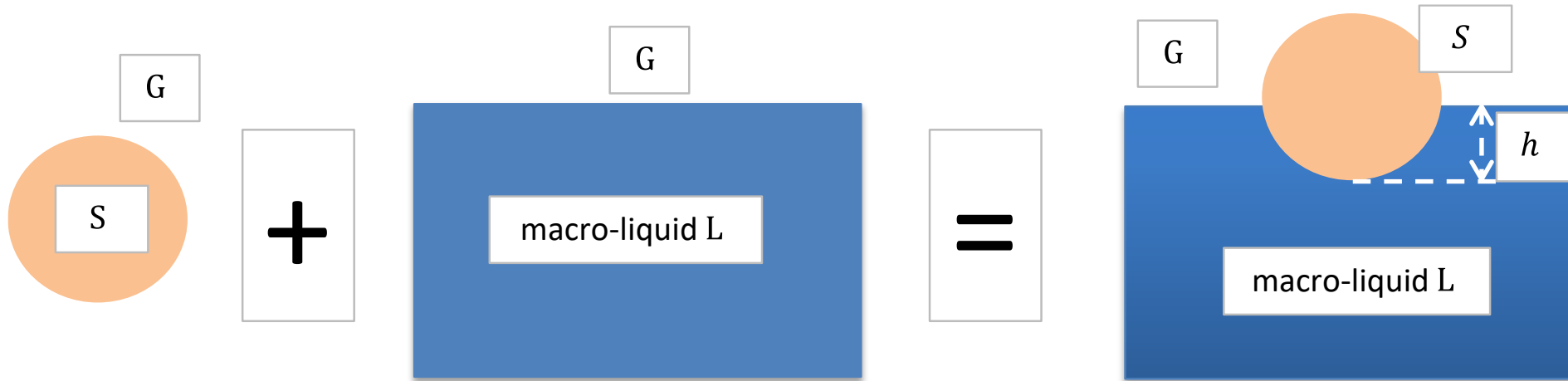


$$G_{m,\alpha,cont} = G_{m,\alpha,ind} + \frac{V_{m,\alpha}}{V_{\alpha}} \cdot \Delta(A \cdot \sigma)_{cont}$$

$$\Delta(A \cdot \sigma)_{sess} = A_{L/G} \cdot \sigma_{L/G} + A_{S/L} \cdot (\sigma_{S/L} - \sigma_{S/G}) - 4 \cdot \pi \cdot r^2 \cdot \sigma_{L/G}$$

$$G_{m,L,sess} = G_{m,L,b} + \frac{3}{r} \cdot V_{m,L} \cdot \sigma_{L/G} \cdot \left(\frac{2 - 3 \cdot \cos\Theta + \cos^3\Theta}{4} \right)^{1/3}$$

Extension to multi-phase situations (3)



$$G_{m,\alpha,cont} = G_{m,\alpha,ind} + \frac{V_{m,\alpha}}{V_{\alpha}} \cdot \Delta(A \cdot \sigma)_{cont}$$

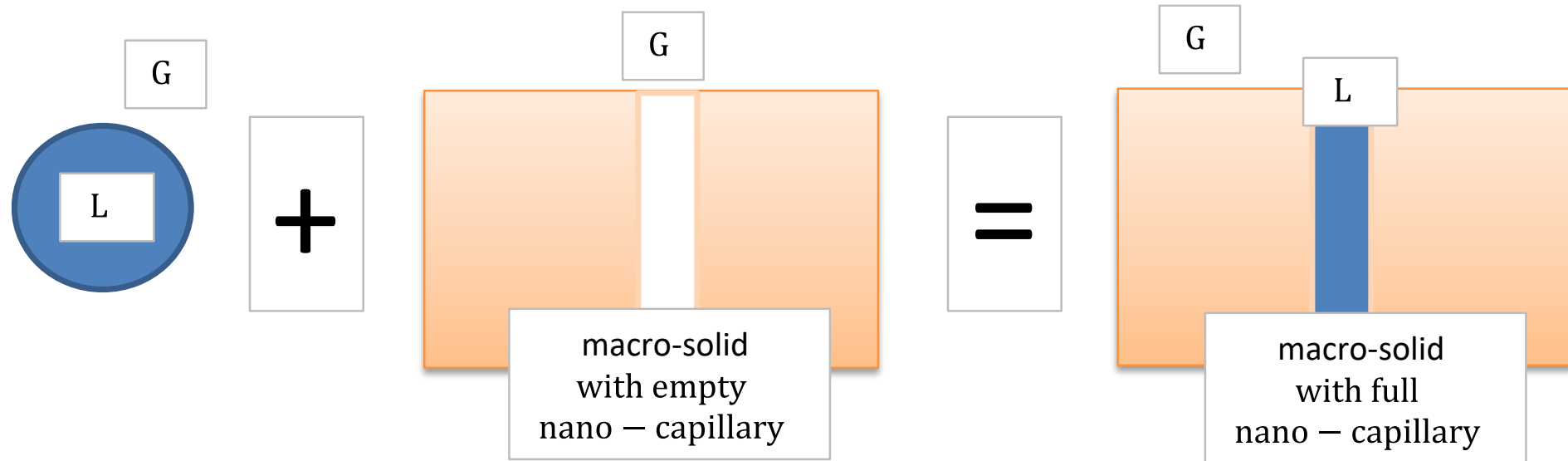
$$\Delta(A \cdot \sigma)_{float}$$

$$= A_{S/L} \cdot \sigma_{S/L} + A_{S/G} \cdot \sigma_{S/G} - \Delta A_{L/G} \cdot \sigma_{L/G} - 4 \cdot \pi \cdot r^2 \cdot \sigma_{S/G}$$

$$G_{m,S,float} = G_{m,S,b} + \frac{3}{r} \cdot V_{m,S} \cdot \sigma_{S/G} \cdot \left[1 - \frac{\sigma_{L/G}}{\sigma_{S/G}} \cdot \left(\frac{1 + \cos\Theta}{2} \right)^2 \right]$$



Extension to multi-phase situations (4)

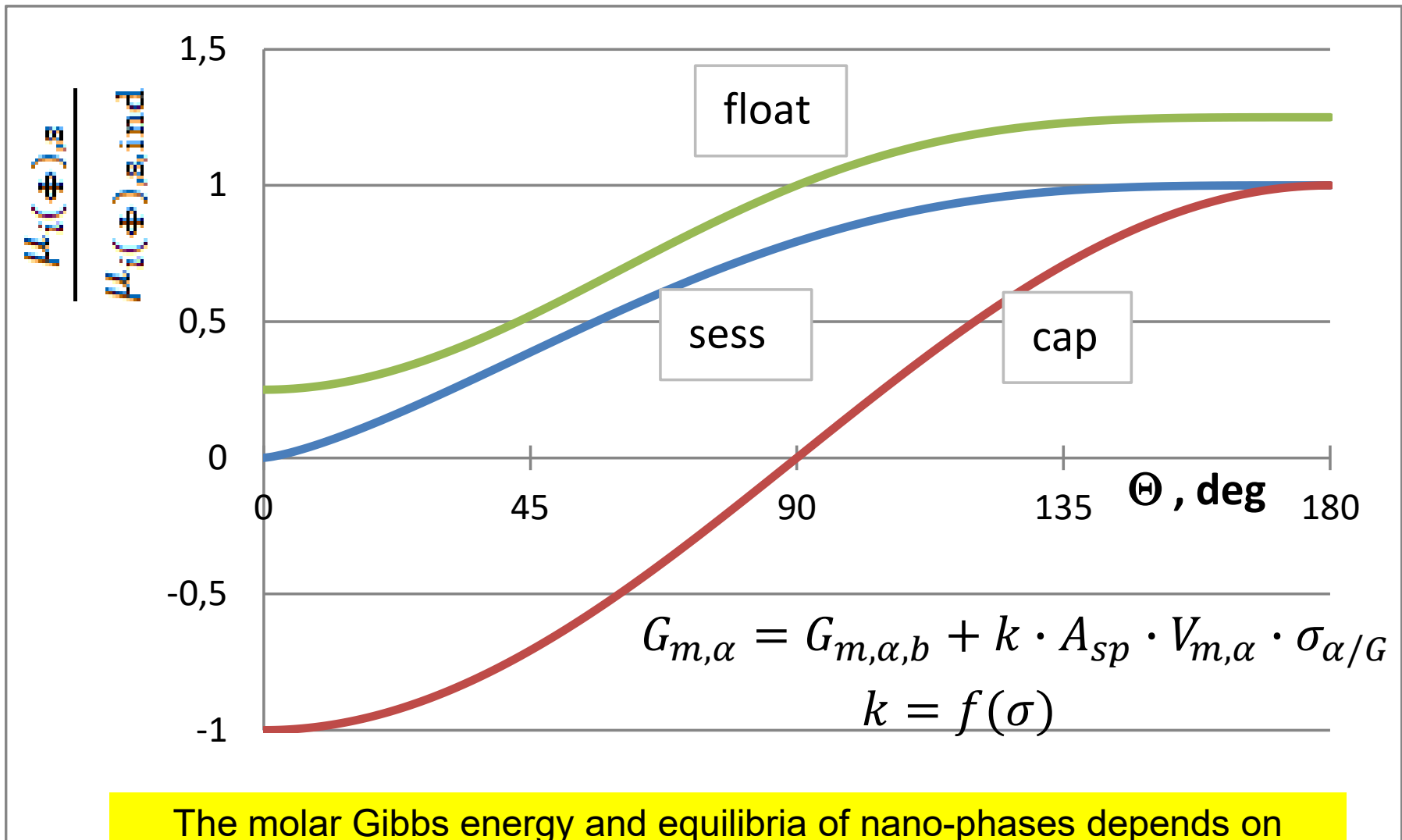


$$G_{m,\alpha,cont} = G_{m,\alpha,ind} + \frac{V_{m,\alpha}}{V_{\alpha}} \cdot \Delta(A \cdot \sigma)_{cont}$$

$$\Delta(A \cdot \sigma)_{cap} = A_{S/L} \cdot (\sigma_{S/L} - \sigma_{S/G}) - 4 \cdot \pi \cdot r^2 \cdot \sigma_{L/G}$$

$$G_{m,L,cap} = G_{m,L,b} - \frac{2}{r_c} \cdot V_{m,L} \cdot \sigma_{L/G} \cdot \cos\Theta$$

Extension to multi-phase situations (sum)



The molar Gibbs energy and equilibria of nano-phases depends on surrounding phases (not true for macro-phases)

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B. Wong, E.A. Wong. Reply to comment by George Kaptay. J Mater Sci 61 (2026) 4379-4383.