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A new paradigm on the chemical potentials of components in multi-component nano-phases within multi-phase systems†

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The chemical potentials of components in nano-phases determine the equilibrium of nano-materials. In this paper the difference between the equilibrium of a nano-phase and the equilibrium of an analogous macro-phase under the same constraints is called a "nano-effect". Historically the first paper to describe the nano-effect was published by Kelvin (1871), claiming that it is due to the increased curvature of the nano-phase. This approach forms the basis of the Kelvin paradigm, still widely used in chemistry, biology and materials science (but not in physics). The Kelvin paradigm is the basis of the Kelvin equation, the Gibbs–Thomson equation and the Ostwald–Freundlich equation for the vapor pressure, melting point and solubility of nano-phases, respectively. The Kelvin paradigm is also successful in the interpretation of more complex phenomena, such as capillary condensation. However, the Kelvin paradigm predicts no nano-effect for not curved nano-phases, such as crystals and thin films, contradicting experimental facts. Moreover, it wrongly predicts that a cubic (or any other crystal-shaped) nano-droplet is more stable than a spherical nano-droplet of the same volume (this contradiction is shown here for the first time). In addition to its positive features, these and other shortcomings of the Kelvin paradigm call for a paradigm shift. A new paradigm is presented in this paper, claiming that the nano-effect is due to the increased specific surface area of the nano-phase. Chemical potentials of components in multi-component phases are derived in this paper within this new paradigm. These equations are extended for nano-phases in multi-phase situations, such as liquids confined within nano-capillaries, or nano-sized sessile drops attached to flat solid substrates. The new paradigm leads to similar results compared to the Kelvin paradigm for the case of capillary condensation into capillaries (this is because the specific surface area of a cylindrical wall is the same as the curvature of the spherical phase: $2/r$). However, the new paradigm is able to provide meaningful solutions also for problems, not tractable by the Kelvin equation, such as the case of crystals and thin films having no curvature.

1. Introduction

The steady development of nano-technologies[1–17] requires a solid theoretical basis and clear techniques to calculate the equilibrium of nano-systems. Nano-systems contain at least one phase with at least one of its dimensions below 100 nm. Phase equilibria, and thus all properties of such systems are functions of the nano-dimensions. Similarly to macro-systems, the equilibrium in nano-systems is also calculable through the chemical potentials of the components.[18–32] Therefore, the knowledge of accurate equations describing the chemical potential of components in nano-phases is of primary importance. Unfortunately, this subject is far from being clear today, despite its 146 years history. The goal of this paper is to review the subject and to offer a new solution to this old problem.

For brevity, the expression "nano-effect" will be used in this paper, meaning the difference between the equilibrium of a nano-phase and the equilibrium of an analogous macro-phase under the same constraints. Examples of nano-effect include the increased vapor pressure around a liquid nano-droplet, a solid nano-crystal or a solid thin film, an increased solubility of a nano-crystal, a nano-droplet or a thin film in a solution, a decreased (or sometimes increased) melting point of a nano-crystal and a thin solid film inside or outside capillaries, a decreased vapor pressure above the liquid confined in well wetted capillaries and in nano-bubbles, *etc.* A successful paradigm should be able to explain all these phenomena not only in qualitative, but also in a quantitative way.

Historically the first equation on nano-equilibria was due to Kelvin (W. Thomson, 1871), who claimed that the increased vapor pressure around a liquid nano-droplet is due to its

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increased curvature.[33] This very first attempt to describe equilibrium in nano-systems is still in use today. Adamson[34] even calls the Kelvin equation one of the three fundamental equations of surface science (the other two being the Laplace equation[35] and the Gibbs adsorption equation[36]). The Kelvin equation is a basis to form a current paradigm (called here the "Kelvin paradigm") for equilibrium of nano-materials. This paradigm is followed in chemistry,[34,37–45] biology,[46–49] materials science[50–67] and even in microelectronics.[68] The Kelvin equation was extended later to describe the size dependence of the melting point and the solubility of the nano-particles. The size dependence of the melting point is described by the so-called Gibbs–Thomson equation, derived not by Gibbs, rather by J. J. Thomson,[69] while the size dependence of solubility was described by the so-called Freundlich–Ostwald equation, originally derived by Ostwald[70] and corrected later by Freundlich[71] to bring it to agreement with the Kelvin paradigm. The success of the Kelvin paradigm is due to the fact that it describes well the equilibrium of curved fluid nano-systems, including nano-droplets and liquids confined in nano-capillaries.[34,72–76]

Although the Kelvin equation does not predict any nano-effect for not curved phases such as crystals and thin films, this situation was partly "resolved" by treating crystals as spheres of inscribed radius within cubes.[34] The limit of such a "flexible" interpretation of a curvature was reached when the behavior of thin films was studied, as it is really hard to inscribe a sphere within a thin film. This is the main reason why the Kelvin paradigm and its analogues are not used in physics (another reason is that physics developed independently of chemistry).

In addition to the problem describing equilibrium of non-curved nano-phases, the Kelvin paradigm has further hidden flaws, discussed in the present paper. All this is an indication that the general validity of the Kelvin paradigm can be questioned. This is not surprising, as the science on equilibrium of nano-materials should have been created as an extension of the science on equilibrium of macro-materials. However, the Kelvin equation was published in 1871,[33] before Gibbs published in 1875–1878 his monumental work on the equilibrium of heterogeneous (macroscopic) substances.[36] In his work, Gibbs added a surface term to his bulk Gibbs energy term, as we call it today. Later in this paper it will be shown that the new paradigm is based on this part of Gibbs' work. Looking at the publication dates above, one can ask why Gibbs did not correct the Kelvin equation similarly as it is offered here? At this point let us mention that Gibbs actually referred to the Kelvin equation in his work, but did not comment on it. One possible explanation is that Gibbs did not want to enter into an open conflict with an elder and well (much better than himself at the time) established fellow-scientist. A second explanation is that Gibbs might have supposed that what is written by him is obvious, anyway. If any, it was Gibbs' most important mistake: supposing that whatever was written by him was so obvious to all of his readers.

Recently an alternative approach was partly developed on the equilibrium of nano-systems. This new paradigm claims that the nano-effect is due to the increased specific surface area of a nano-phase.[77–79] This new approach treats successfully the problems of one-component not curved nano-phases, such as nano-crystals and thin films, without any need to draw artificial inscribed spheres into them. It should be mentioned that the same approach was first used by Ostwald[70] (who not only translated Gibbs into the German language, but also "interpreted" his writings and got a Nobel prize in chemistry in 1909). Unfortunately, the Ostwald equation was soon "corrected" by Freundlich[71] from the Gibbs-type equation to the Kelvin-type equation, and thus the original Ostwald approach is lost/forgotten. Now it is time to correct it back.

It is also important to realize that the new paradigm has been developed only partly; today it can tackle only the simplest one-component and two-phase problems. The goal of this paper is to fill this knowledge gap and to extend the ability of the new paradigm to describe the equilibrium of nano-materials in multi-component and multi-phase nano-systems. The subject will be put into a wider historical perspective in this paper: the general framework of equilibrium of nano-materials and the Kelvin paradigm will be also discussed in details.

2. The general framework for the equilibrium of nano-systems

Before we start let us state that the surface term to the chemical potential will have a significant effect only if at least one of the sizes of the phase is below 100 nm. On the other hand, if the size of the phase is below 1 nm or so, the meaning of the phase becomes questionable. Therefore, all the equations which follow will be valid only for those phases, which have at least one of their dimensions below 100 nm, but have all of their dimensions above 1 nm.

2.1. The chemical potential

The condition of equilibrium of heterogeneous substances including nano-phases is formally the same as given by Gibbs for macro-phases:[36]

$$\mu_{i(\alpha)} = \mu_{i(\beta)} \tag{1}$$

where $\mu_{i(\alpha)}$ (J mol^{-1}) is the chemical potential of component i in phase α, $\mu_{i(\beta)}$ (J mol^{-1}) is the same for phase β. For component i in a nano-phase α the chemical potential is written in all papers as:

$$\mu_{i(\alpha)} = \mu^{\mathrm{b}}_{i(\alpha)} + z\cdot V_{\mathrm{m},i(\alpha)}\cdot\sigma_{\alpha/\beta} \tag{2}$$

where $\mu^{\mathrm{b}}_{i(\alpha)}$ (J mol^{-1}) is the bulk chemical potential of component i in phase α, while the second term is responsible for the surface effect, with $V_{\mathrm{m},i(\alpha)}$ (m^3 mol^{-1}) the partial molar volume of component i in phase α, $\sigma_{\alpha/\beta}$ (J m^{-2}) the surface tension (interfacial energy) between nano-phase α and the surrounding phase β, z ($1/m$) is a size- and shape dependent constant of a positive value, being different for each model discussed in this paper. In the historical Kelvin paradigm $z = 2/r$ for a sphere of radius r. Simple examples of how to apply eqn (1) and (2) are shown in ESI A.†

As follows from the unit of parameter z, it is inversely proportional to the characteristic size of the phase (radius for a sphere or a cylinder, side length of a cube, thickness of a thin film, *etc.*). For free standing phases (such as a spherical liquid droplet levitating in a vapor phase) parameter z is only size- and shape-dependent. However, for more difficult situations, such as a nano-sized liquid sessile droplet attached to a solid slab, parameter z will also depend on the contact angle of the liquid on the solid slab. Different approaches existing in the literature differ in how this parameter z is interpreted, defined and calculated. The goal of this paper is to derive proper expressions for parameter z for free standing nano-phases and also for nano-phases attached to other phases.

2.2. The integral molar Gibbs energy of a nano-phase

Now, let us derive the integral molar Gibbs energy of a nano-phase α using the following generally valid equation:

$$G_{\mathrm{m},\alpha} = \sum_i x_{i(\alpha)} \cdot \mu_{i(\alpha)} \tag{3a}$$

where $G_{\mathrm{m},\alpha}$ (J mol^{-1}) is the integral molar total Gibbs energy of phase α, $x_{i(\alpha)}$ (dimensionless) is the molar ratio of component i in phase α. Now, let us substitute eqn (2) into eqn (3a):

$$G_{\mathrm{m},\alpha} = G^{\mathrm{b}}_{\mathrm{m},\alpha} + z \cdot V_{\mathrm{m},\alpha} \cdot \sigma_{\alpha/\beta} \tag{3b}$$

where $G^{\mathrm{b}}_{\mathrm{m},\alpha}$ (J mol^{-1}) is the integral molar bulk Gibbs energy of phase α, written as:

$$G^{\mathrm{b}}_{\mathrm{m},\alpha} = \sum_i x_{i(\alpha)} \cdot \mu^{\mathrm{b}}_{i(\alpha)} \tag{3c}$$

and $V_{\mathrm{m},\alpha}$ (m^3 mol^{-1}) is the integral molar volume of phase α, written as:

$$V_{\mathrm{m},\alpha} = \sum_i x_{i(\alpha)} \cdot V_{\mathrm{m},i(\alpha)} \tag{3d}$$

The integral molar Gibbs energy of phase α written by (eqn (3b)) takes into account the surface effect, similarly to the original equation of Gibbs, written for the absolute Gibbs energy of phase α as:[36]

$$G_{\alpha} = G^{\mathrm{b}}_{\alpha} + A_{\alpha} \cdot \sigma_{\alpha/\beta} \tag{4}$$

where G_{α} (J) is the integral absolute (not molar) total Gibbs energy of phase α, G^{b}_{α} (J) is the integral absolute (not molar) bulk Gibbs energy of phase α, A_{α} (m^2) is the surface area of phase α. When the original equation of Gibbs (4) is converted into the molar Gibbs energy of eqn (3b), the surface area term (m^2) of eqn (4) is replaced by the molar volume term (m^3 mol^{-1}) multiplied by the geometric parameter z ($1/m$).

2.3. The chemical potential of a one-component nano-phase

As a first simplest approach let us apply eqn (4) of Gibbs for a one-component phase:

$$G^{\mathrm{o}}_{i(\alpha)} = G^{\mathrm{o,b}}_{i(\alpha)} + A_{\alpha} \cdot \sigma^{\mathrm{o}}_{i(\alpha)/\beta} \tag{4a}$$

where G^{o}_{α} (J) is the standard integral absolute (not molar) total Gibbs energy of pure component i in phase α, $G^{\mathrm{o,b}}_{i(\alpha)}$ (J) is the standard integral absolute (not molar) bulk Gibbs energy of pure component i in phase α, $\sigma^{\mathrm{o}}_{i(\alpha)/\beta}$ (J m^{-2}) the surface tension (interfacial energy) between nano-phase α made of pure component i and the surrounding phase β. The standard chemical potential of a pure component in a one-component phase is simply obtained by dividing the standard integral absolute Gibbs energy of the phase by the amount of matter within this phase, the same being true also for the bulk quantity:

$$\mu^{\mathrm{o}}_{i(\alpha)} = \frac{G^{\mathrm{o}}_{i(\alpha)}}{n_{i(\alpha)}} \tag{4b}$$

$$\mu^{\mathrm{o,b}}_{i(\alpha)} = \frac{G^{\mathrm{o,b}}_{i(\alpha)}}{n_{i(\alpha)}} \tag{4c}$$

Thus, dividing eqn (4a) by the amount of matter within this phase, the following is obtained:

$$\mu^{\mathrm{o}}_{i(\alpha)} = \mu^{\mathrm{o,b}}_{i(\alpha)} + \frac{A_{\alpha}}{n_{i(\alpha)}} \cdot \sigma^{\mathrm{o}}_{i(\alpha)/\beta} \tag{4d}$$

The amount of matter can be written as the ratio of the volume (V_{α}, m^3) and the molar volume ($V^{\mathrm{o}}_{\mathrm{m},i(\alpha)}$, m^3 mol^{-1}) of the phase:

$$n_{i(\alpha)} = \frac{V_{\alpha}}{V^{\mathrm{o}}_{\mathrm{m},i(\alpha)}} \tag{4e}$$

Now, let us define the specific surface area of the phase ($A_{\mathrm{sp},\alpha}$, m^{-1}) as the ratio of its surface area to its volume:

$$A_{\mathrm{sp},\alpha} \equiv \frac{A_{\alpha}}{V_{\alpha}} \tag{4f}$$

Substituting eqn (4e) into eqn (4d) and taking into account eqn (4f), the following final equation is obtained for the standard chemical potential of a one-component nano-phase:

$$\mu^{\mathrm{o}}_{i(\alpha)} = \mu^{\mathrm{o,b}}_{i(\alpha)} + A_{\mathrm{sp},\alpha} \cdot V^{\mathrm{o}}_{\mathrm{m},i(\alpha)} \cdot \sigma^{\mathrm{o}}_{i(\alpha)/\beta} \tag{4g}$$

According to eqn (4g), the standard chemical potential of a one-component nano-phase is proportional to the specific surface area of the phase. Comparing eqn (2) and (4g), parameter z for the free standing one-component nano-phase is identical to the specific surface area of the phase:

$$z = A_{\mathrm{sp},\alpha} \tag{4h}$$

The same result of eqn (4g) was achieved by the author before[77–79] for 1-component and 2-phase situations. This paper is devoted to the extension of eqn (4h) to multi-component and multi-phase situations.

2.4. A validity test for models on equilibrium of nano-materials

The molar Gibbs energy of the system, containing a nano-phase is generally written as:

$$G_{\mathrm{m}} = \sum_{\alpha} y_{\alpha} \cdot G_{\mathrm{m},\alpha} \tag{5}$$

where y_α (dimensionless) is the phase ratio of phase α. For a one-phase system: $G_{\mathrm{m}} = G_{\mathrm{m},\alpha}$. According to the most basic principle of chemical thermodynamics, the system will gain equilibrium in such of its possible states, which provides a minimum value for G_{m}, or for $G_{\mathrm{m},\alpha}$ for a one-phase system.[36] As follows from eqn (3b), for a given phase α of given composition, pressure, temperature, size and given surrounding phase β, all properties ($G^{\mathrm{b}}_{\mathrm{m},\alpha}$, $V_{\mathrm{m},\alpha}$, $\sigma_{\alpha/\beta}$) are fixed except parameter z, which is also shape dependent. Thus, the equilibrium shape of a phase will be the one with a minimum z value for given volume. According to the well-known experimental evidence, a nano-droplet (in the absence of gravity and other phases except the equilibrium vapor phase) prefers a spherical shape. This particular test will be performed for all models to check whether a given model predicts an equilibrium spherical shape for a nano-droplet, or not. Surprisingly, it will turn out that the Kelvin paradigm does not pass this elementary test.

3. The approach based on the curvature of the nano-phase (the Kelvin paradigm)

3.1. The derivation of the key equations for the Kelvin paradigm

The chemical potential is usually written using the following three terms:

$$\mu_{i(\alpha)} = U^{\mathrm{b}}_{i(\alpha)} + p \cdot V_{\mathrm{m},i(\alpha)} - T \cdot S^{\mathrm{b}}_{i(\alpha)} \tag{6a}$$

where $U^{\mathrm{b}}_{i(\alpha)}$ (J mol^{-1}) is the partial molar inner energy of component i in bulk phase α, p (Pa) is the outside pressure (=one of the state parameters), T (K) is the absolute temperature (=the second state parameters), $S^{\mathrm{b}}_{i(\alpha)}$ (J mol^{-1} K^{-1}) is the partial molar entropy of component i in bulk phase α. If the surrounding of phase α is under the standard pressure of p^{o} and if phase α is curved from outside (such as a small sphere), then the pressure inside this phase is written by the Laplace equation:[35]

$$p_{\mathrm{in}} = p^{\mathrm{o}} + \sigma_{\alpha/\beta} \cdot \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{6b}$$

where r_1 (m) and r_2 (m) are the two principal radii of curvature of phase α. Now, let us substitute the inner pressure of eqn (6b) into eqn (6a) to replace the state parameter p:

$$\mu_{i(\alpha)} = \mu^{\mathrm{b}}_{i(\alpha)} + \left(\frac{1}{r_1} + \frac{1}{r_2}\right) \cdot V_{\mathrm{m},i(\alpha)} \cdot \sigma_{\alpha/\beta} \tag{6c}$$

where the chemical potential of the bulk is written as:

$$\mu^{\mathrm{b}}_{i(\alpha)} = U^{\mathrm{b}}_{i(\alpha)} + p^{\mathrm{o}} \cdot V_{\mathrm{m},i(\alpha)} - T \cdot S^{\mathrm{b}}_{i(\alpha)} \tag{6d}$$

Comparing eqn (2) and (6c) the requested equation for parameter z:

$$z = \frac{1}{r_1} + \frac{1}{r_2} \tag{6e}$$

Eqn (2) and (6e) form the basis of the Kelvin paradigm. Using these equations, the classical Kelvin, Ostwald–Freundlich and Gibbs–Thomson equations are derived for spherical nano-phases (see ESI A†). When phase α is a sphere of radius r, then $r_1 = r_2 = r$ and thus parameter z of the general eqn (2) equals: $z = 2/r$. When phase α is a cylinder of radius r then $r_1 = r$, $r_2 = \infty$ and thus parameter z of the general eqn (2) equals: $z = 1/r$. The curvature can also have a negative sign, for example for a liquid meniscus within a well wetted solid capillary, or within a bubble. The curvature of the spherical cap at the end of the liquid cylinder within a cylindrical solid capillary is written as:

$$z = -\frac{2 \cdot \cos \Theta}{r}, \tag{6f}$$

where r (m) is the radius of a cylinder, Θ (degree) is the contact angle of the liquid on the inner wall of the cylindrical capillary. To add to confusion let us mention that in some works coefficient 2 in eqn (6f) is replaced by coefficient 1,[39,43] referring to the fact that the curvature of the cylinder is not $2/r$, rather $1/r$.

Whichever is the right numerical coefficient in eqn (6f), it indeed provides a negative curvature for well wetting liquids ($\Theta < 90°$). This makes the Kelvin paradigm very versatile as it can predict accurately both the increase and the decrease of the chemical potential within curved nano-phases. Eqn (6f) is also the basis to interpret capillary condensation.

3.2. The list of reasons why the Kelvin paradigm is not acceptable

Although the derivation of eqn (6e) is perfect mathematically, this equation and the following Kelvin paradigm are connected with the following contradictions:

i. Eqn (6e) was derived by substituting the inner pressure to replace the state parameter (=the outside pressure), which is theoretically incorrect,

ii. when eqn (6e) is derived, it is done from the understanding that the inner pressure within the nano-phase is higher than the outer pressure around this phase, and so it seems to lead to higher activity (escaping tendency, after Lewis) of the components of this nano-phase. However, this increased activity is compensated by the same Laplace pressure by which it was created, as the vector of the Laplace pressure points perpendicular to the curved surface from outside towards inside of the nano-phase (this is how the inner phase of higher pressure is in mechanical equilibrium with an outer phase of lower pressure). Thus, the extra activity inside the nano-phase is also compensated by the Laplace pressure, thus it has no influence outside the nano-phase, *i.e.* it cannot lead to increased vapor pressure, or to increased solubility in any outer phase.

iii. Eqn (6e) predicts that any nano-phase surrounded by flat (not curved) planes (such as crystals, or thin films) has no nano-effect; however, this prediction contradicts the experimental observations. Particularly, it follows that for a nano-phase of given volume, a cube (or any other not curved phase such as a thin film) has a lower integral Gibbs energy compared to a sphere, so a liquid droplet would prefer a crystal shape, such as a cube or thin film: this is certainly non-sense and contradicts experimental observations. This contradiction proves further that eqn (6e) is wrong. At this point let me mention that one can consider the atoms/molecules along the edges or the corners of the cube to provide the missing curvature for the cube. However, it is not the curvature of the cubic phase, it is rather the curvature of the atoms/molecules. Furthermore, if the curvature of the atoms/molecules is taken into account to calculate the nano-effect, then this effect would be size-independent, as small and large cubes have equally small atoms/molecules. This conclusion on the size-independent nano-effect also contradicts experimental facts.

iv. The curvature effect is actually used in another aspect of chemical thermodynamics: already Gibbs,[36] and later Tolman[80] showed that the surface tension of small curved phases is curvature dependent. Using the same effect twice is not reasonable.

v. The curvature induced interfacial (Laplace) pressure can be derived from the interfacial term of the Gibbs energy,[81,82] so it is not reasonable to substitute this effect back into the same Gibbs energy (chemical potential) again, while forgetting at the same time about the surface term of the Gibbs energy (see eqn (4)), as was done when eqn (6e) was derived,

vi. the equilibrium size of the nano-particle as follows from eqn (6e) for a spherical nano-nucleus coincides with the critical size of the nucleus; however, the later corresponds to the maximum of the Gibbs energy and not to its minimum (as we expect for an equilibrium size). Thus, eqn (6e) contradicts the nucleation theory of Gibbs (for details see ref. 79).

vii. Eqn (6e) is principally different from eqn (4h) obtained for a one-component case. This principal difference between a one-component and multi-component phases shows that something must be wrong. As nothing is wrong (to our opinion) with eqn (4h) then (6e) must be wrong.

Based on the above seven reasons, the validity of the Kelvin paradigm is under question. Thus, it is subject to the paradigm shift, supposing that a new and better paradigm is developed.

4. A possible approach, based on the definition of the chemical potential

The chemical potential of component i in a macroscopic phase α is defined as:[36]

$$\mu_{i(\alpha)} \equiv \left(\frac{\mathrm{d}G_\alpha}{\mathrm{d}n_{i(\alpha)}}\right)_{p,T,n_{j(\alpha)}} \tag{7a}$$

where G_α (J) is the absolute (not molar) total Gibbs energy of phase α, including also component i, $n_{i(\alpha)}$ (mol) is the amount of component i in phase α, $n_{j(\alpha)}$ (mol) is the amount of any other component j in phase α. As follows from eqn (7a), the derivative should be taken at constant values of all state parameters except the amount of matter of the component in question, *i.e.* at constant outside pressure, at constant temperature and at constant amount of matter of other components. The consequences of eqn (7a) under these constraints are described elsewhere.[83–85] However, as follows from eqn (4), the Gibbs energy of a nano-phase is also dependent on the surface area of the phase, *i.e.* the surface area is also a state parameter for a nano-phase. Therefore, the chemical potential of a component in a nano-phase should be defined as:

$$\mu_{i(\alpha)} \equiv \left(\frac{\mathrm{d}G_\alpha}{\mathrm{d}n_{i(\alpha)}}\right)_{p,T,n_{j(\alpha)},A_\alpha} \tag{7b}$$

If eqn (4) is substituted into eqn (7b), the following equation is obtained:

$$\mu_{i(\alpha)} = \mu^{\mathrm{b}}_{i(\alpha)} + A_\alpha \cdot \left(\frac{\mathrm{d}\sigma_{\alpha/\beta}}{\mathrm{d}n_{i(\alpha)}}\right)_{p,T,n_{j(\alpha)},A_\alpha} \tag{7c}$$

From comparison of eqn (2) and (7c) one can obtain the expression for parameter z:

$$z = \frac{A_\alpha}{V_{\mathrm{m},i(\alpha)} \cdot \sigma_{\alpha/\beta}} \cdot \left(\frac{\mathrm{d}\sigma_{\alpha/\beta}}{\mathrm{d}n_{i(\alpha)}}\right)_{p,T,n_{j(\alpha)},A_\alpha} \tag{7d}$$

Let us note that $n_{i(\alpha)} = n_\alpha \cdot x_{i(\alpha)}$ (where $x_{i(\alpha)}$ is the mole fraction of component i in phase α) and so: $\mathrm{d}n_{i(\alpha)} = n_\alpha \cdot \mathrm{d}x_{i(\alpha)}$. Also remember that (see eqn (4e)): $n_\alpha = V_\alpha / V_{\mathrm{m},\alpha}$. Substituting these equations into eqn (7d) and taking into account eqn (4f), the following equation is found:

$$z = A_{\mathrm{sp},\alpha} \cdot \frac{V_{\mathrm{m},\alpha}}{V_{\mathrm{m},i(\alpha)}} \cdot \left(\frac{\mathrm{d}\ln\sigma_{\alpha/\beta}}{\mathrm{d}x_{i(\alpha)}}\right)_{p,T,n_{j(\alpha)},A_\alpha} \tag{7e}$$

As follows from eqn (7e), parameter z is proportional to the specific surface area of the phase, which is in agreement with eqn (4h), obtained above for one-component phases. The value of $V_{\mathrm{m},\alpha}/V_{\mathrm{m},i(\alpha)}$ of eqn (7e) is around unity. However, different components of the solution can have different values and even different signs of $(\mathrm{d}\ln\sigma_{\alpha/\beta}/\mathrm{d}x_{i(\alpha)})_{p,T,n_{j(\alpha)},A_\alpha}$ of eqn (7e) leading to different signs of parameter z. On the other hand, parameter z is expected to have only positive values. The possible negative value of parameter z proves that eqn (7b) is not a proper basis to derive the chemical potential for nano-phases and so this approach is not considered here further.

5. The approach based on the specific surface area of nano-phases (the new paradigm)

5.1. Derivation of the key equation for the new paradigm

Let us re-write the classical eqn (4) of Gibbs for a multi-component nano-phase in a somewhat different form:

$$G_\alpha = \sum_i n_{i(\alpha)} \cdot \mu^{\mathrm{b}}_{i(\alpha)} + A_\alpha \cdot \sigma_{\alpha/\beta} \tag{8a}$$

Now, let us express A_α from eqn (4f) and let us substitute this equation into eqn (8a):

$$G_\alpha = \sum_i n_{i(\alpha)} \cdot \mu^{\mathrm{b}}_{i(\alpha)} + A_{\mathrm{sp},\alpha} \cdot V_\alpha \cdot \sigma_{\alpha/\beta} \tag{8b}$$

The absolute volume of the nano-phase can be written as:

$$V_\alpha = \sum_i n_{i(\alpha)} \cdot V_{\mathrm{m},i(\alpha)} \tag{8c}$$

Now, let us substitute eqn (8c) into eqn (8b) and note that the number of moles is a common multiplicator of both terms in the right hand side:

$$G_\alpha = \sum_i n_{i(\alpha)} \cdot \left[\mu^{\mathrm{b}}_{i(\alpha)} + A_{\mathrm{sp},\alpha} \cdot V_{\mathrm{m},i(\alpha)} \cdot \sigma_{\alpha/\beta}\right] \tag{8d}$$

On the other hand, the following equation is also valid, by definition:[36]

$$G_\alpha = \sum_i n_{i(\alpha)} \cdot \mu_{i(\alpha)} \tag{8e}$$

Comparing eqn (8d) and (e), the following equation is obtained for the chemical potential of component i in a free standing nano-phase α:

$$\mu_{i(\alpha)} = \mu^{\mathrm{b}}_{i(\alpha)} + A_{\mathrm{sp},\alpha} \cdot V_{\mathrm{m},i(\alpha)} \cdot \sigma_{\alpha/\beta} \tag{8f}$$

From the comparison of eqn (2) and (8f), the final equation is obtained for parameter z for free standing nano-phases:

$$z = A_{\mathrm{sp},\alpha} \tag{8g}$$

One can see that eqn (4h) and (8g) are identical, so our result for parameter z is identical for one-component and multi-component phases. Thus, although eqn (8f) is obtained using an independent derivation, it is a natural and logical extension of eqn (4g) from a one-component system to multi-component systems. In other words, eqn (4g) is a boundary case of a more general eqn (8f). Eqn (8f) is practically more useful compared to the equations of the Kelvin paradigm, because it provides some nano-effect not only for nano-phases surrounded by curved surfaces, but also for nano-phases surrounded by flat (not curved) surfaces, such as crystals and thin films. This approach is also free from the failure of the Kelvin approach, as it predicts that liquid droplets will gain spherical shapes (and not cubic shapes, as predicted by the Kelvin approach – see above). This is because a sphere provides a minimum specific surface area among all 3-dimensional bodies of the same volume (see also Table 1).

Eqn (8f) is also in agreement with a wide-spread interpretation of why nano-phases have size-dependent properties: it is because the ratio of their surface atoms/molecules among all atoms/molecules within the nano-phase is significant and varies with the size of the nano-phase. As this surface ratio of atoms/molecules is proportional to the specific surface area of the phase (see ESI B† and eqn (9)), it is reasonable that the surface term of the chemical potential is also proportional to the same physical quantity.

$$x_{\mathrm{s}} = A_{\mathrm{sp},\alpha} \cdot \frac{V_{\mathrm{m},\alpha}}{\omega_\alpha}, \tag{9}$$

where x_{s} (dimensionless) is the molar ratio of the surface atoms/molecules among its all atoms/molecules, ω_α ($\mathrm{m^2\ mol^{-1}}$) is the molar surface area of phase α.

Table 1 The number of sides, the equations for specific surface areas of nano-phases of different simple shapes and the ratio of it to that of a sphere of equal volume

Description of the nano-phase α	Number of sides	$A_{\mathrm{sp},\alpha}$	$A_{\mathrm{sp},\alpha}/A_{\mathrm{sp,sphere}}$
Sphere of radius r	∞	$3/r$	1.000
Tetrahedron of side length a	4	$14.70/a$	1.490
Cube of side length a	6	$6/a$	1.241
Octahedron of side length a	8	$7.348/a$	1.183
Dodecahedron of side length a	12	$2.694/a$	1.098
Icosahedron of side length a	20	$3.970/a$	1.065
Nano-sheet of thickness t	2	$2/t$	Undefined ($\gg 1$)
A long wire/cylinder with radius r_{cap}	1	$2/r_{\mathrm{cap}}$	Undefined[a]
A long nano-tube with inner and outer radii r_i and r_{o}	2	$2/r_i + 2/r_{\mathrm{o}}$	Undefined ($\gg 1$)

[a] When the end walls of the cylinder are neglected, a cylinder seems to provide smaller specific surface area compared to the sphere of the same volume, but for a 3-dimensional cylinder (with its end walls) this is never the case.

5.2. Application of the new paradigm to free standing nano-phases

For free standing nano-phases eqn (8f) can be coupled with the equations of ESI A† to obtain expressions for phase equilibria.

In Table 1, equations for the specific surface areas of different simple shapes of free standing nano-phases are summarized ("free standing" means here that a given phase is fully surrounded only by one macroscopic phase, usually a vapor phase, or a macroscopic liquid or solid phase). In the last column of Table 1 the ratio of the specific surface area of the given phase to that of a sphere of the same volume is shown. As follows from this comparison, the specific surface area of all polyhedra are larger than that of a sphere, but these values gradually approach the specific surface area of a sphere of the same volume as the number of sides of the polyhedron increases. This is because a sphere can be considered as a polyhedron with infinite number of sides.

In Table 2 equations for vapor pressure, solubility and melting point of different free standing nano-phases are collected. For this purpose, equations of Table 1 are substituted into eqn (8g), and the result is substituted into eqn (A1b), (A2c), (A3c) of ESI A.† These equations are similar (although not identical) to the equations of the Kelvin paradigm for the curved phases. These equations are also similar (although not

Table 2 Equations for vapor pressure, solubility and melting point of free standing nano-phases of different shapes (derived using eqn (A1b), (A2c), (A3c), (8g) and Table 1)

Shape of the phase[a]	$\ln\left(\frac{p_i}{p_i^{\infty}}\right) =$	$\ln\left(\frac{x_{i(\mathrm{l})}}{x_{i(\mathrm{l})}^{\infty}}\right) =$	$T_{\mathrm{m},i} - T_{\mathrm{m},i}^{\infty} =$
Sphere	$\frac{3\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{r\cdot R\cdot T}$	$\frac{3\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{r\cdot R\cdot T}$	$\frac{-3\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{r\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Tetrahedron	$\frac{14.70\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{a\cdot R\cdot T}$	$\frac{14.70\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot R\cdot T}$	$\frac{-14.70\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Cube	$\frac{6\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{a\cdot R\cdot T}$	$\frac{6\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot R\cdot T}$	$\frac{-6\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Octahedron	$\frac{7.348\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{a\cdot R\cdot T}$	$\frac{7.348\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot R\cdot T}$	$\frac{-7.348\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Dodecahedron	$\frac{2.694\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{a\cdot R\cdot T}$	$\frac{2.694\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot R\cdot T}$	$\frac{-2.694\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Icosahedron	$\frac{3.970\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{a\cdot R\cdot T}$	$\frac{3.970\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot R\cdot T}$	$\frac{-3.970\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{a\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Nano-sheet[b]	$\frac{2\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{t\cdot R\cdot T}$	$\frac{2\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{t\cdot R\cdot T}$	$\frac{2\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{t\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Long wire/cylinder	$\frac{2\cdot V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{r_{\mathrm{cap}}\cdot R\cdot T}$	$\frac{2\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{r_{\mathrm{cap}}\cdot R\cdot T}$	$\frac{-2\cdot V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{r_{\mathrm{cap}}\cdot \Delta_{\mathrm{m}}S_i^{\mathrm{o}}}$
Long nano-tube[b]	$\frac{V_{\mathrm{m},i(\mathrm{l})}\cdot\sigma_{\mathrm{l/v}}}{R\cdot T}\left(\frac{2}{r_i}+\frac{2}{r_{\mathrm{o}}}\right)$	$\frac{V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{R\cdot T}\left(\frac{2}{r_i}+\frac{2}{r_{\mathrm{o}}}\right)$	$\frac{-V_{\mathrm{m},i(\mathrm{s})}\cdot\sigma_{\mathrm{s/l}}}{\Delta_{\mathrm{m}}S_i^{\mathrm{o}}}\left(\frac{2}{r_i}+\frac{2}{r_{\mathrm{o}}}\right)$

[a] The sphere is characterized by its radius r, the thin film by its thickness t, the long cylinder by its radius r_{cap}, the long tube with its inner and outer radii r_i and r_{o}, other bodies by their side lengths a. [b] For simplicity the same phase is supposed on both sides of the nano-sheet and inside/outside of the nano-tube.

identical) to the equations of the Kelvin paradigm, if the crystals are replaced by inscribed spheres. The equations provided in Table 2 for thin solid films are missing from the subjects covered by the Kelvin paradigm due to the difficulty to replace a thin solid film by an inscribed sphere.

It should be noted that in a given nano-system usually a large amount of similar, but not identical nano-phases are present. This dispersity of nano-phases can be handled, if the minimum, average and maximum sizes of the nano-phase are known and correspondingly the maximum, average and minimum chemical potentials are calculated through their specific surface areas. This feature will definitely lead to uncertainty in nano-thermodynamics, but this uncertainty is an inherent property of the nano-system and is not a consequence of the present model.

5.3. Extension of the new paradigm to multi-phase situations

So far, the new paradigm was worked out only for free standing nano-phases, *i.e.* for 2-phase systems. However, the Kelvin paradigm is also able to explain more complex phenomena, such as capillary condensation, involving more than two phases. Herewith the new paradigm is extended to treat these more complex problems.

To calculate phase equilibria for nano-phases attached to other phases, eqn (8f) should be modified. For this purpose, a third term should be added to eqn (8f) as:

$$\mu_{i(\alpha)} = \mu_{i(\alpha)}^{\mathrm{b}} + A_{\mathrm{sp},\alpha}\cdot V_{\mathrm{m},i(\alpha)}\cdot\sigma_{\alpha/\beta} + V_{\mathrm{m},i(\alpha)}\cdot\frac{G_{\mathrm{att}}-G_{\mathrm{fs}}}{V_{\alpha}} \quad (10)$$

where G_{att} (J) is the absolute (not molar) Gibbs energy of phase, attached to some other phases (*i.e.* being in a multi-phase situation), while G_{fs} (J) is the absolute (not molar) Gibbs energy of free-standing phase, not attached to any other phase except the fully surrounding vapor (or other) phase (*i.e.* being in a 2-phase situation). As follows from eqn (10), the chemical potentials of components will be different within the same nano-phase, if this nano-phase is surrounded by different phases, *i.e.* if it is involved in different multi-phase situations.

5.3.1. The case of nano-sized liquid sessile drops. First, let us derive an equation for the chemical potential of a component within a nano-sized liquid sessile drop. The starting state is a free standing spherical liquid nano-drop of radius r, with a specific surface area of $3/r$. Let this nano-drop touch a flat surface of a macroscopic solid phase, and form a sessile nano-drop. This nano-sized sessile droplet will form a spherical cap of radius r_{c} and contact angle of Θ on the solid slab. The volumes of the free standing spherical nano-drop and that of the sessile nano-drop should be equal:

$$\frac{4}{3}\cdot\pi\cdot r^3 = \frac{1}{3}\cdot\pi\cdot {r_{\mathrm{c}}}^3\cdot\left(2-3\cdot\cos\Theta+\cos^3\Theta\right) \quad (11a)$$

The total interfacial energy (G_{fs}, J) of the system containing a free standing spherical nano-droplet and a free standing solid slab is written as:

$$G_{\text{fs}} = 4\cdot\pi\cdot r^2\cdot\sigma_{\text{lv}} + A^{\text{o}}_{\text{sv}}\cdot\sigma_{\text{sv}} \tag{11b}$$

where A^{o}_{sv} (m^2) is the surface area of the free standing solid slab, σ_{sv} (J m^{-2}) is the surface energy of the solid slab. The total interfacial energy (G_{att}, J) of the system containing a nano-droplet attached to a flat surface of the same solid slab as above, is written as:

$$G_{\text{att}} = A_{\text{lv}}\cdot\sigma_{\text{lv}} + (A^{\text{o}}_{\text{sv}} - A_{\text{sl}})\cdot\sigma_{\text{sv}} + A_{\text{sl}}\cdot\sigma_{\text{sl}} \tag{11c}$$

where A_{lv} (m^2) is the liquid/vapor surface area of the sessile nano-droplet, attached to the solid slab, A_{sl} (m^2) is the common solid–liquid interfacial area of the sessile nano-droplet and the solid slab, σ_{sl} (J m^{-2}) is the solid/liquid interfacial energy. The interfacial areas of the sessile nano-drop can be expressed from the geometry of the spherical cap of radius r_{c}:

$$A_{\text{lv}} = 2\cdot{r_{\text{c}}}^2\cdot\pi\cdot(1 - \cos\Theta) \tag{11d}$$

$$A_{\text{sl}} = {r_{\text{c}}}^2\cdot\pi\cdot(1 - \cos^2\Theta) \tag{11e}$$

Now, let us express r_{c} from eqn (11a), substitute this expression into eqn (11d) and (e), and substitute the resulting expressions together with eqn (11c) into eqn (10), taking into account the left-hand side of eqn (11a) for V_α and also the Young equation ($\sigma_{\text{lv}}\cdot\cos\Theta = \sigma_{\text{sv}} - \sigma_{\text{sl}}$). The final equation for the chemical potential of a component within a sessile nano-drop follows as:

$$\mu_{i(\text{l,sessile})} = \mu^{\text{b}}_{i(\text{l})} + \frac{3}{r}\cdot V_{\text{m},i(\text{l})}\cdot\sigma_{\text{lv}}\cdot\left(\frac{2 - 3\cdot\cos\Theta + \cos^3\Theta}{4}\right)^{1/3} \tag{11f}$$

where r is the radius of the free standing nano-drop, with the volume of the sessile nano-drop being equal to the volume of this free standing spherical nano-drop, while $3/r$ is the specific surface area of the latter: $A_{\text{sp},\alpha} = 3/r$ (see Table 1). For comparison, the chemical potential of a component in a free standing spherical droplet can be found by substituting this latter expression into eqn (8f):

$$\mu_{i(\text{l})} = \mu^{\text{b}}_{i(\text{l})} + \frac{3}{r}\cdot V_{\text{m},i(\text{l})}\cdot\sigma_{\text{lv}} \tag{11g}$$

Comparing eqn (11f) and (g) one can see that the expression of the chemical potential within a sessile drop is very similar to that within a free standing droplet, the only difference being the correcting parenthesis at the end of eqn (11f). Naturally, eqn (11f) simplifies back to eqn (11g) at $\Theta = 180°$, which is a reasonable boundary condition for eqn (11f). Another boundary condition of eqn (11f) is that at $\Theta = 0°$ the expression in parenthesis of eqn (11f) becomes nil, and so the chemical potential of components in a perfectly wetting nano-droplet becomes identical to the bulk chemical potential of the same component ($\mu_{i(\text{l,sessile})} = \mu^{\text{b}}_{i(\text{l})}$). It means that the solid slab perfectly wetted by the nano-droplet perfectly stabilizes the nano-droplet (as much as if it was a macro-phase).

Comparing eqn (2) and (11f), the following expression is obtained for parameter z for the nano-sized sessile droplet:

$$z_{\text{sessile-drop}} = \frac{3}{r}\cdot\left(\frac{2 - 3\cdot\cos\Theta + \cos^3\Theta}{4}\right)^{1/3} \tag{11h}$$

It is important to underline that even in this complex 3-phase situation the chemical potential is proportional to the specific surface area of the nano-droplet, although corrected by a complex expression containing the contact angle.

Now, let us substitute eqn (11h) into eqn (A1b)† to get the equilibrium vapor pressure of component i above a nano-sized sessile droplet:

$$p_{i(\text{sessile})} = p_i^\infty\cdot\exp\left[\frac{3\cdot V_{\text{m},i(\text{l})}\cdot\sigma_{\text{l/v}}}{r\cdot R\cdot T}\cdot\left(\frac{2 - 3\cdot\cos\Theta + \cos^3\Theta}{4}\right)^{1/3}\right] \tag{11i}$$

The dimensionless ratio $\frac{p_{i(\text{sessile})}}{p_i^\infty}$ is shown in Fig. 1 as function of the contact angle of the sessile drop on the solid slab. It shows a steady increase of the vapor pressure above a nano-sized sessile droplet with increasing its contact angle, which is a reasonable result. For the sessile drop perfectly wetting the slab: $p_{i(\text{sessile})} = p_i^\infty$.

5.3.2. The case of liquids confined in long cylindrical nano-capillaries. Let us consider a porous body with N empty cylindrical nano-capillaries of length h and inner radii r_{cap}. Let us also consider the same amount and shape and size of free-standing liquid nano-cylinders. Their surface area and volume are written as:

$$A = A_{\text{sv}} = A_{\text{lv}} = N\cdot 2\cdot\pi\cdot r_{\text{cap}}\cdot h \tag{12a}$$

$$V_{\text{l}} = V_{\text{pore}} = N\cdot\pi\cdot{r_{\text{cap}}}^2\cdot h \tag{12b}$$

For long cylinders the specific surface area:

$$A_{\text{sp,lv}} = \frac{2}{r_{\text{cap}}} \tag{12c}$$

The total surface Gibbs energy of the free standing liquid nano-cylinders and that of the porous body with the empty nano-cylinders is written as:

$$G_{\text{fs}} = A\cdot(\sigma_{\text{lv}} + \sigma_{\text{sv}}) \tag{12d}$$

The total surface Gibbs energy of the system with the liquid fully filling the nano-capillaries in the porous body is written as:

$$G_{\text{att}} = A\cdot\sigma_{\text{sl}} \tag{12e}$$

Let us substitute eqn (12a) into eqn (12d) and (e). Further, let us substitute the resulting equations, together with eqn (12b) and (c) into eqn (10), taking into account the Young equation ($\sigma_{\text{lv}}\cdot\cos\Theta = \sigma_{\text{sv}} - \sigma_{\text{sl}}$). Finally, the chemical potential of a component in a liquid, confined within long nano-capillaries of radius r_{cap} follows as:

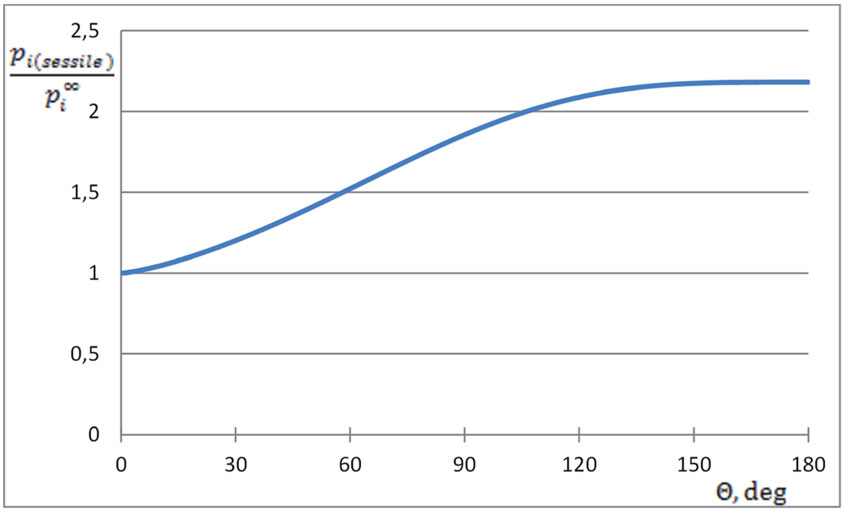

Fig. 1 The dimensionless ratio of the equilibrium vapor pressure above the nano-sized liquid sessile droplet to the equilibrium vapor pressure above a large droplet as function of its contact angle on a large solid slab (the value at $\Theta = 180°$ corresponds also to the free standing droplet; parameters: $V_{m,i(l)} = 18$ cm^3 mol^{-1}, $\sigma_{l/v} = 72$ mN m^{-1}, $r = 2$ nm, $T = 300$ K).

$$\mu_{i(\text{l-capillary})} \cong \mu_{i(\text{l})}^{\text{b}} - \frac{2}{r_{\text{cap}}} \cdot V_{\text{m},i(\text{l})} \cdot \sigma_{\text{lv}} \cdot \cos\Theta \quad (12f)$$

From the comparison of eqn (2) and (12f) the expression for parameter z is obtained as:

$$z_{\text{l-capillary}} \cong -\frac{2 \cdot \cos\Theta}{r_{\text{cap}}} \quad (12g)$$

Let us mention that the expression $2/r_{\text{cap}}$ in eqn (12g) is the specific surface area of the nano-capillary (see eqn (12c)). Thus, even in this complex 3-phase situation the chemical potential is proportional to the specific surface area of the cylindrical capillaries, although corrected by a complex expression containing the contact angle. Let us also mention that eqn (12g) is the same as eqn (6f), which followed from the Kelvin equation. Thus, the Kelvin paradigm and the new paradigm provide identical results for some of the problems. It is good news for a new paradigm, as in this particular case the validity of the Kelvin equation was experimentally validated.[72–76] This coincidence is due to the fact that the curvature of the sphere and the specific surface area of the cylindrical wall is described by the same expression $2/r$ (if r denotes both the radius of the sphere and the radius of the cylinder).

Now, let us substitute eqn (12g) into eqn (A1b)† to get the equilibrium vapor pressure of component i above a liquid, confined within long nano-capillaries:

$$p_{i(\text{capillary})} \cong p_i^\infty \cdot \exp\left(-\frac{2 \cdot V_{\text{m},i(\text{l})} \cdot \sigma_{\text{l/v}}}{r_{\text{cap}} \cdot R \cdot T} \cdot \cos\Theta\right) \quad (12h)$$

The dimensionless ratio $\frac{p_{i(\text{capillary})}}{p_i^\infty}$ is shown in Fig. 2 as function of the contact angle. It shows the stabilization of the liquid within well wetted capillaries ($\Theta < 90°$) and destabilization of the liquid within poorly wetted capillaries ($\Theta > 90°$). The behavior of the liquid within neutrally wetted capillaries ($\Theta = 90°$) is the same as that of the macro-liquid. Fig. 2 is in agreement with the well-known experimental fact that capillary condensation takes place only at $\Theta < 90°$. Eqn (12h) and Fig. 2 are identical to the results obtainable using the Kelvin paradigm, at least, if coefficient 2 of eqn (12h) is not corrected to coefficient 1, as explained in ref. 39 and 43. This coincidence is due again to the fact that the curvature of the sphere and the specific surface area of the cylindrical wall is described by the same expression $2/r$ (if r denotes both the radius of the sphere and the radius of the cylinder).

5.3.3. The case of a liquid in vicinity of a nano-bubble. Now, let us consider two, identical cylindrical capillaries in a vapor phase. Suppose that a perfectly wetting ($\Theta = 0°$) liquid condensates into these capillaries and the menisci of the condensed liquid reach the ends of the capillaries. If these two capillaries are turned towards each other, a spherical nano-bubble is formed between the two liquid nano-cylinders. The radius r_{bub} of this nano-bubble will be the same as that of the inner radius of the capillary. The equilibrium vapor pressure within this spherical nano-bubble can be written by eqn (12h) if $\Theta = 0°$ and if $r_{\text{cap}} = r_{\text{bub}}$ are substituted into it:

$$p_{i(\text{capillary})} \cong p_i^\infty \cdot \exp\left(-\frac{2 \cdot V_{\text{m},i(\text{l})} \cdot \sigma_{\text{l/v}}}{r_{\text{bub}} \cdot R \cdot T}\right) \quad (13a)$$

If eqn (13a) is coupled with eqn (A1b),† parameter z can be obtained for the liquid phase in the vicinity of the nano-bubble as:

$$z_{\text{l-bubble}} = -\frac{2}{r_{\text{bub}}} \quad (13b)$$

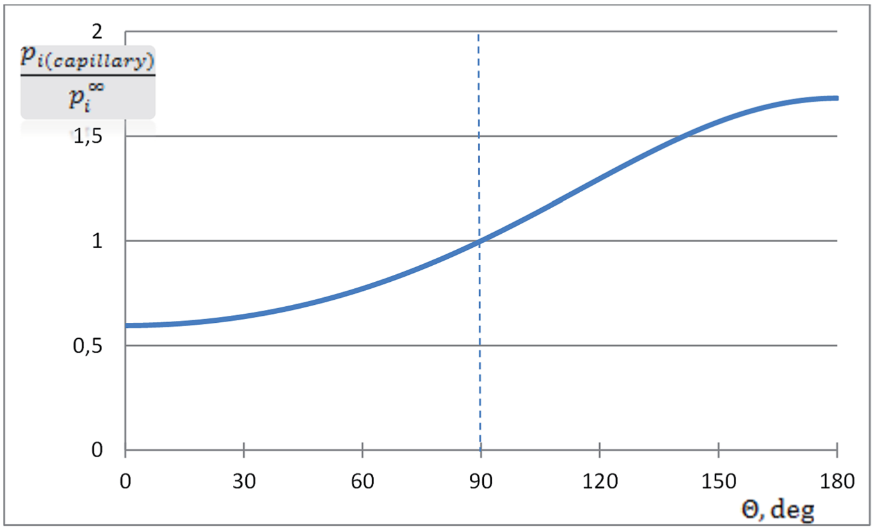

Fig. 2 The dimensionless ratio of the equilibrium vapor pressure above the liquid confined in long, cylindrical capillaries to the equilibrium vapor pressure above a large droplet as function of its contact angle on inner walls of the capillaries (the value at $\Theta = 0°$ corresponds also to the nano-bubble of the same radius as the capillary; parameters: $V_{m,i(l)} = 18$ cm^3 mol^{-1}, $\sigma_{l/v} = 72$ mN m^{-1}, $r_{cap} = 2$ nm, $T = 300$ K).

Although this result is derived from the new paradigm, it is in full agreement with the Kelvin paradigm.[34,43] Again, this coincidence is due to the fact that the curvature of the sphere and the specific surface area of the cylindrical wall is described by the same expression $2/r$ (if r denotes both the radius of the sphere and the radius of the cylinder).

6. Discussion

The most important result of this paper is that the new paradigm (=the nano-effect is due to the increased specific surface area of the nano-phase) is extended to multi-component nano-solutions and also to multi-phase situations including nano-phases. The new paradigm is found applicable and successful in all cases, where the Kelvin paradigm (=the nano-effect is due to the increased curvature of the nano-phase) was applicable and successful. However, the new paradigm is successful also in areas, where the Kelvin paradigm provided a practical failure (or when it was pushed to draw artificial inscribed spheres): this is the equilibrium of nano-crystals and thin films. Moreover, the new paradigm is free of those contradictions (see above), which lead to the criticism of the Kelvin paradigm.

Summarizing the above, the present author thinks that the new paradigm is ready to replace the Kelvin paradigm. This paradigm shift, however, will not happen by the publication of this paper. Many further discussions are ahead before the community can accept or reject this new paradigm.[86]

7. Conclusions

1. The chemical potential of component i in a nano-phase α is generally written as:

$$\mu_{i(\alpha)} = \mu^{b}_{i(\alpha)} + z\cdot V_{m,i(\alpha)}\cdot\sigma_{\alpha/\beta} \tag{2}$$

2. The molar Gibbs energy of a nano-phase α is generally written as:

$$G_{m,\alpha} = G^{b}_{m,\alpha} + z\cdot V_{m,\alpha}\cdot\sigma_{\alpha/\beta} \tag{3b}$$

3. Following Kelvin, parameter z of eqn (2) and (3b) is derived as the curvature of the nano-phase, using the Laplace pressure. This result is found wrong for many different reasons (see above). Thus, the Kelvin paradigm should be replaced by a new paradigm.

4. The application of the formal definition of chemical potential under proper constraints does not lead to a meaningful result in this case, as the constancy of the surface area (as a new state parameter for nano-phases) should be guaranteed when the derivative of the Gibbs energy is taken as function of the amount of matter of the component in question.

5. Parameter z of eqn (2) and (3b) is derived here as the specific surface area for free standing one-component and multi-component nano-phases:

$$z = A_{sp,\alpha} \tag{8g}$$

6. A general method is developed here to derive equations for parameter z for nano-phases in multi-phase situations. The following expression is obtained for a nano-sized sessile drop, attached to a solid slab with a contact angle of Θ:

$$z_{\text{sessile-drop}} = \frac{3}{r}\cdot\left(\frac{2 - 3\cdot\cos\Theta + \cos^3\Theta}{4}\right)^{1/3} \tag{11i}$$

where r is the radius of the free standing spherical nano-drop, with the volume of the sessile nano-drop being equal to its volume, $3/r$ is the specific surface area of the free-standing nano-droplet. As a second example, the following expression is obtained for a liquid phase, confined within long cylindrical capillaries, wetted by the liquid with a contact angle of Θ:

$$z_{\text{l-capillary}} \cong -\frac{2 \cdot \cos \Theta}{r_{\text{cap}}} \tag{12g}$$

where r_{cap} is the radius of the cylindrical nano-capillary, $2/r_{\text{cap}}$ being its specific surface area. As a third example, the following expression is obtained for a liquid phase in the vicinity of the nano-bubble of radius r_{bub}:

$$z_{\text{l-bubble}} = -\frac{2}{r_{\text{bub}}} \tag{13b}$$

As a result, the chemical potentials of components will be different within the same nano-phase, if this nano-phase is surrounded by different phases, *i.e.* if it is involved in different multi-phase situations. This is demonstrated here by the differences in eqn (11i), (12g) and (13b). Eqn (12g) and (13b) are the same in the framework of the Kelvin paradigm and in the framework of this new paradigm. This is because te curvature of a sphere coincides with the specific surface area of a cylinder wall.

7. Summarizing: the new paradigm states that nano-effects are due to the increased specific surface areas of the nano-phases. The new paradigm offers a theoretically coherent method to describe multi-component and multi-phase equilibria of nano-materials in all areas covered and by the Kelvin paradigm and beyond. Thus, the new paradigm is ready to replace the Kelvin paradigm.

8. It should be noted that the present model does not take into account the size-dependence of various physico-chemical properties of nano-phases, such as the size dependence of surface tension, *etc.* These effects should be added to the major effect connected with specific interfacial area, considered here in details.

Conflicts of interest

The author declares no conflict of interest.

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