# The Gibbs Equation versus the Kelvin and the Gibbs-Thomson Equations to Describe Nucleation and Equilibrium of Nano-Materials

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The Kelvin equation, the Gibbs equation and the Gibbs-Thomson equation are compared. It is shown that the Kelvin equation (on equilibrium vapor pressure above nano-droplets) can be derived if the inner pressure due to the curvature (from the Laplace equation) is substituted incorrectly into the external pressure term of the Gibbs equation. Thus, the Kelvin equation is excluded in its present form. The Gibbs-Thomson equation (on so-called equilibrium melting point of a nano-crystal) is an analog of the Kelvin equation, and thus it is also excluded in its present form. The contradiction between the critical nucleus size (from the Gibbs equation) and the so-called equilibrium melting point of nano-crystals (from the Gibbs-Thomson equation) is explained. The contradiction is resolved if the Gibbs equation is applied to study both nucleation and equilibrium of nano-crystals. Thus, the difference in the behavior of nano-systems compared to macro-systems is due to their high specific surface area (Gibbs) and not to the high curvature of their interface (Kelvin). Modified versions of the Kelvin equation and the Gibbs-Thomson equation are derived from the Gibbs equation for phases with a general shape and for a spherical phase.

**Keywords:** Kelvin, Gibbs, Gibbs-Thomson, Nucleation, Nano Thermodynamics.

## 1. INTRODUCTION

This paper deals with contradictions between equations published more than a century ago by Thomson (later Sir Kelvin)[1] and Gibbs.[2] This story might seem to be suitable for a history of science. Nevertheless, it is published in this journal, as these equations are more vital today than ever (see Fig. 1). Moreover, they co-exist in the literature and so the hidden contradiction in understanding equilibrium and nucleation in nano-materials is still with us. On the other hand, nanoscience and nanotechnology is becoming more and more accurate as more and more precise measurements become available. This process will inevitably lead to the experimental realization of the contradiction in question. Thus, it is time to make a clear distinction between the reliabilities of the Kelvin equation, of the Gibbs equation, and of the Gibbs-Thomson equation (with Thomson = Kelvin to make the picture even more complex).

First, it was Thomson who derived an equation for the equilibrium vapor pressure above nano-droplets.[1] This equation is known today as the Kelvin equation and is one of the fundamental equations of surface chemistry, including physical chemistry, chemical

engineering, colloid chemistry, catalysis, surfactants[3–13] and even microelectronics.[14] This equation was derived using the Laplace equation,[15] describing the pressure increase within a phase due to the curvature of its outer interface. Thus, the Kelvin equation is due to the curvature effect. At a later date, the Kelvin equation was transformed (nor by Thomson, neither by Gibbs) into the so-called Gibbs-Thomson equation, by coupling the Kelvin equation[1] with the Gibbs equation on heterogeneous equilibrium[2] to describe the equilibrium melting point of a small solid crystal in its own liquid. The Gibbs-Thomson equation is one of the fundamental equations of materials science and engineering, including physical metallurgy, solidification, electrochemistry, capillarity and nanoscience.[16–22] The Kelvin and the Gibbs-Thomson equations are analogous equations. The Kelvin equation describes the size dependence of vapor pressure at a fixed temperature, while the Gibbs-Thomson equation describes the size dependence of the (melting) temperature at a fixed pressure.

Gibbs published his 2-part paper on the foundation of chemical (materials) equilibrium thermodynamics[2] after the paper of Thomson.[1] Although he made a reference to Thomson and shortly described his results, he did not say
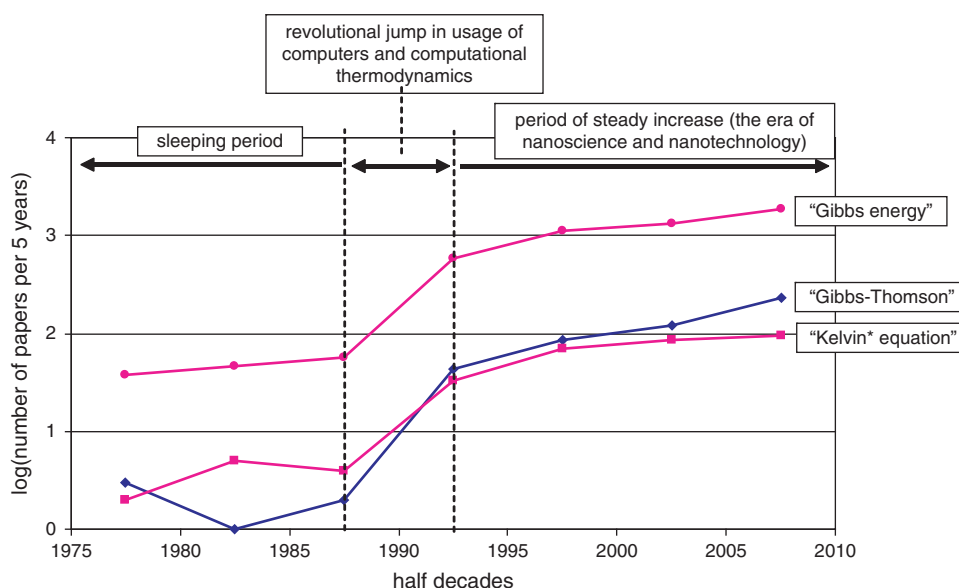
**Fig. 1.** A semi-logarithmic time evolution of the number of papers per half decades with key-words "Kelvin* equation", "Gibbs-Thomson" and "Gibbs energy" [Web of Science]. The time period when personal computers became a wide-spread tool for the solution of the Gibbs and related equations is clearly visible. In the current steady increase the increasing role of nanoscience and nanotechnology is also involved.

anything particular about the Kelvin equation. The present author presumes that it was due to the polite personality of Gibbs. Gibbs walked along his own path and added to his so-called Gibbs energy a new surface term, without using the Laplace equation (he used the Laplace equation to derive the size dependence of the surface tension).[2] From the Gibbs equation enhanced by the surface term, anyone can easily derive an alternative of the Kelvin equation and that of the Gibbs-Thomson equation (see below). However, this solution seemed to Gibbs so obvious that he presumably did not see any need in a direct conflict with an elder British colleague. Instead, Gibbs showed something else for the first time: the thermodynamics of nucleation.[2, 4, 8–10, 17, 20–22]

To make the situation even more confused, the original Kelvin equation (and its later analogue, the Gibbs-Thomson equation) formally can be derived if the internal Laplace pressure is substituted (in a theoretically incorrect way) into the external pressure term of the Gibbs equation. Although this result is different, for a spherical particle it is quite similar to the surface term introduced by Gibbs. Probably this is the reason, why the 3 equations (the Kelvin equation and the Gibbs-Thomson equation from the one hand and the Gibbs equation from the other hand) coexist in the literature even today.

The situation varies from field to field and from subject to subject. The situation in the field of nucleation is clear: all authors in chemistry, physics and materials use the same Gibbs equation.[2, 4, 8–10, 17, 20–22] On the other hand, the situation with the equilibrium of nano-materials is complex and contradictory. Chemists, and especially colloid chemists (for whom the original Kelvin equation was mostly valuable) keep with the Kelvin equation.[3–13, 23]

Biology, medicine[24–27] and materials science[16–22, 28–30] took a lot from chemistry, including the Kelvin equation, often in the revised form of the Gibbs-Thomson equation. Computational materials science (including Calphad) is born from materials science and chemistry, and that is why it uses the same type of Kelvin (Gibbs-Thomson) equation.[31–38] In contrary, the physics community usually applies the Gibbs equation to describe phase equilibria in nano materials.[39–46] There are also some papers suggesting the combination of the Kelvin and Gibbs effects.[47–48]

The co-existence of the contradictory equations is most obvious in monographs, where the contradicting equations appear side by side and it should have been bothering for many authors.[4, 8–10, 17, 20–22] Some of them are indeed "surprised" to face such a situation, but to the best knowledge of the present author the contradiction described here is clearly presented for the first time. This paper is written to show the contradiction in the literature and to explain the reasons behind them. The present author suggests to "forget" the Kelvin equation and the Gibbs-Thomson equation in their present forms, and use them in modified forms, being in accordance with the Gibbs equation.

## 2. COMPARISON OF THE EXISTING EQUATIONS

At the first sight, the Kelvin equation, the Gibbs equation and the Gibbs-Thomson equation do not seem to be related, at all. Therefore, they should be brought into the same ground to have a chance to compare them. For this purpose let us divide the molar Gibbs energy of a

condensed phase $\Phi$ ($G_\Phi$, J/mol) to the following two terms:

$$G_\Phi = G_\Phi^b + G_\Phi^s \qquad (1)$$

where superscripts $b$ and $s$ denote the bulk and surface terms of the Gibbs energy of a condensed phase $\Phi$. The bulk term includes all possible terms routinely used by chemical (materials) thermodynamics, including the Calphad community (standard, configurational, excess, magnetic, etc.,). It will not be detailed here, as it can be found in many papers and also in monographs.[49–51] The surface term, being responsible for the presence of the surface (interface) is the subject of this paper. The Kelvin, the Gibbs-Thomson and the Gibbs equations will be brought to the common ground of the surface term of Eq. (1).

## 2.1. On the Kelvin Equation

The Kelvin equation for the vapor pressure of a spherical liquid droplet of radius $r$ is written as follows[a]:[1]

$$p = p^\circ \cdot \exp\left(\frac{2 \cdot \sigma_{lg} \cdot V_{l,m}}{r \cdot R \cdot T}\right) \qquad (2)$$

where $R$ is the gas constant (J/molK), $T$ is absolute temperature (K), $p$ and $p^\circ$ (bar) are equilibrium vapor pressures above curved and flat surfaces, respectively, $\sigma_{lg}$ (J/m$^2$) surface tension of the liquid/gas (l/g) interface, $V_{l,m}$ (m$^3$/mol) molar volume of the liquid. Eq. (2) has a more general form, when a sphere is replaced by a figure with two principal radii to the given point of its curved surface $r_1$ and $r_2$ (m), and the Laplace equation is applied, as:[15]

$$\frac{2}{r} = \frac{1}{r_1} + \frac{1}{r_2} \qquad (2.a)$$

Eq. (2) is valid for a droplet in a large vapor phase. For a bubble in a large liquid phase a similar equation is valid with a negative sign under "exp".[3–14] When a droplet (bubble) is situated within a narrow place (capillary, for example), the surface tension term is multiplied by the cosine of the contact angle.[3–14] All these variations of the Kelvin equation will not be discussed in details here, as all are consequences of the basic Eq. (2).

To obtain the surface term of the Gibbs equation from Eq. (2), one should remember the general condition of equilibrium between a one-component liquid and its vapor:[2]

$$G_l = G_g \qquad (3)$$

Treating the vapor (gas phase) as perfect gas, and taking into account Eq. (1), Eq. (3) can be re-written as:

$$G_l^\circ + G_l^s = G_g^\circ + R \cdot T \cdot \ln\left(\frac{p}{p^*}\right) \qquad (4)$$

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[a]It should be noted for historical correctness that in the original paper of Thomson[1] Eq. (2) is written in a simplified linear form. However, the "Kelvin equation" today is known in the form of Eq. (2).[3–13]

where the $G_\Phi^\circ$ terms are standard Gibbs energies of the phases ($\Phi = l$ (liquid) or $\Phi = g$ (gas)), $p^* = 1$ bar, the standard pressure. For a large liquid phase with a negligible surface term, the equilibrium vapor pressure is called the standard vapor pressure (denoted as $p^\circ$) and can be expressed from Eq. (4) as follows:

$$p^\circ = p^* \cdot \exp\left[\frac{G_l^\circ - G_g^\circ}{R \cdot T}\right] \qquad (5)$$

This equation is widely known and accepted in thermodynamics of materials and physical chemistry.[9] Expressing from both Eqs. (4–5) the expression $\left(G_l^\circ - G_g^\circ\right)$ and making these two equations equal, the vapor pressure above the curved surface ($p$) can be expressed as:

$$p = p^\circ \cdot \exp\left[\frac{G_l^s}{R \cdot T}\right] \qquad (6)$$

Comparing Eqs. (2, 6) the surface term of the Gibbs energy due to Kelvin follows:

$$G_l^s = \frac{2 \cdot \sigma_{lg} \cdot V_{l,m}}{r} \qquad (7)$$

Eq. (7) will be taken as the surface term of the Gibbs energy, in accordance with the Kelvin equation. As the Kelvin equation was derived from the Laplace equation, Eq. (7) is also due to the curvature of the surface, and the extra pressure caused by this curvature.

It is interesting to see how Eq. (7) can be derived if the Gibbs treatment is developed further, without knowing anything about the results of Kelvin. The bulk Gibbs energy terms for a liquid are written as:[2]

$$G_l = U_l + p \cdot V_{l,m} - T \cdot S_l \qquad (8)$$

where the new letters denote bulk inner molar energy ($U_l$, J/mol) and bulk molar entropy ($S_l$, J/molK) of the liquid. The pressure within a spherical phase of radius $r$ is the sum of the outside pressure p$^\circ$ and the inner Laplace pressure:[15]

$$p = p^\circ + \frac{2 \cdot \sigma_{lg}}{r} \qquad (9)$$

Substituting Eq. (9) into Eq. (8) and taking into account that the bulk term by definition is the sum of all terms except those, including surface properties ($G_l^b = U_l + p^\circ \cdot V_{l,m} - T \cdot S_l$), the following equation is obtained:

$$G_l = G_l^b + \frac{2 \cdot \sigma_{lg} \cdot V_{l,m}}{r} \qquad (10)$$

From the comparison of Eqs. (1, 10) one can obtain the surface term of the Gibbs energy in accordance with the Kelvin equation, i.e., Eq. (7). Thus, Eq. (7) is reproduced. Although all written above seems to be quite transparent, there are three problems with Eq. (7):

(i) as follows from Eq. (7), nano-phases with plane surfaces (such as thin films or crystals surrounded by flat crystal planes) are expected to have no surface term of their Gibbs energy, as they have no curvature. Thus, nano-crystals and thin films are expected to have the same thermodynamic properties as the bulk phase. This consequence contradicts experimental observations,[52–56] etc.[b]

(ii) Eq. (9) should not be substituted into the Gibbs equation (8), and that is why Eqs. (10, 7) are incorrect from the thermodynamic point of view. The reason is that Eq. (8) is written with external variables $p$ and $T$, to be dictated by us (scientists, engineers). Internal pressure, such as the Laplace pressure (the second term of Eq. (8)) should not be substituted into the expression for the external pressure.

(iii) the Laplace equation itself (together with all other interfacial forces) can be derived from the Gibbs equation (see Appendix). This is an additional reason why the substitution of the Laplace equation back into the same Gibbs equation is meaningless.

## 2.2. On the Gibbs-Thomson Equation

The Gibbs-Thomson equation is an analogue of the Kelvin equation, i.e., it can be derived from Eq. (7). Let us consider a pure, spherical solid phase of radius $r$, situated in a large liquid phase of the same component. Then, in analogy with Eq. (3), the condition of its equilibrium is written as:

$$G_l = G_s \qquad (11)$$

As the liquid phase is large, the Laplace pressure has an insignificant effect on the pressure within the liquid, and so its Gibbs energy is equal to its standard Gibbs energy. On the other hand, the solid is a small phase with increased pressure within, and so its Gibbs energy should be modified with the surface term of Eq. (7). Thus, Eq. (11) can be re-written as:

$$H_l^\circ - T \cdot S_l^\circ = H_s^\circ - T \cdot S_s^\circ + \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{r} \qquad (12)$$

where $\sigma_{sl}$ (J/m$^2$) is the solid/liquid interfacial energy, and the standard Gibbs energy is re-written by Eq. (8), after making its first two terms equal the molar standard enthalpy ($H$) of the phase (J/mol). The molar enthalpy and entropy changes of melting are defined as: $\Delta_m H^\circ \equiv H_l^\circ - H_s^\circ$ and $\Delta_m S^\circ \equiv S_l^\circ - S_s^\circ$. Substituting these definitions into Eq. (12):

$$\Delta_m H^\circ = T \cdot \Delta_m S^\circ + \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{r} \qquad (12.a)$$

For a large value of $r$ the surface term of Eq. (12.a) is negligible, and at the equilibrium melting point of a flat

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[b]There is a secondary effect on the dependence of the Gibbs energy on the thickness of a thin film, which makes the properties of a thin film thickness-dependent. Here this effect is not discussed in details.

phase ($T = T_m^\circ$) the following can be written: $\Delta_m H^\circ = T_m^\circ \cdot \Delta_m S^\circ$. This equation is commonly accepted in the thermodynamics of bulk materials. Substituting it back into Eq. (12.a), the equilibrium temperature can be expressed, what is denoted as $T_m$:

$$T_m = T_m^\circ - \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{r \cdot \Delta_m S^\circ} \qquad (13.a)$$

Eq. (13.a) is the Gibbs-Thomson equation. As follows from the above, it is an analogue of the Kelvin Eq. (2), although they look quite different. According to literature, Eq. (13.a) describes the equilibrium melting point, at which a solid spherical crystal of radius $r$ has the same Gibbs energy as that of the large liquid phase of the same 1-component material around it.[4, 8–9, 17, 20–22] Although it is often called "the equilibrium melting point of a nano-crystal", in fact there is no global equilibrium in the system: the crystal of this size at this temperature will spontaneously transform the whole large liquid phase into a large crystal, at least, if its initial radius $r$ is larger than the critical radius of nucleation (see below). This is because $T_m$ is lower than $T_m^\circ$ and thus a macroscopic solid is more stable compared to the macroscopic liquid. Thus, the temperature calculated by Eq. (13.a) will be called here "the so-called equilibrium melting point of a nano-crystal" and not "the equilibrium melting point of a nano-crystal". It will be called like this even after the Gibbs-Thomson equation (13.a) will be corrected (see below).

Eq. (13.a) can be also written in the following analogous form, expressing "the so-called equilibrium size of the nano-crystal", $r_{eq}$ (m) as function of temperature, $T$:

$$r_{eq} = \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{(T_m^\circ - T) \cdot \Delta_m S^\circ} \qquad (13.b)$$

Eq. (13.b) has the same limitation as Eq. (13.a). It expresses the condition when the small crystal of equilibrium size has the same Gibbs energy as that of the macroscopic liquid phase at a given temperature below the melting point. Due to this latter condition, Eq. (13.b) does not correspond to the global equilibrium of the system (what would be a macroscopic solid crystal instead of a macroscopic liquid phase with a nano-crystal).

## 2.3. On the Gibbs Equation

Gibbs[2] used a simple $A_\Phi \cdot \sigma_{\Phi s}$ term as a surface term for his general energy Eq. (1) ($A_\Phi$ is the surface area of phase $\Phi$, m$^2$, while $\sigma_{\Phi s}$ is the surface energy of phase $\Phi$ with its surroundings, J/m$^2$). However, the unit of the $A_\Phi \cdot \sigma_{\Phi s}$ term is J. To convert it to J/mol as requested by Eq. (1), it should be divided by the number of moles within the phase, $n_\Phi$. One of the ways to express $n_\Phi$ is through the ratio of the volume and the molar volume of the phase: $n_\Phi = V_\Phi / V_{\Phi,m}$. Then, the following surface term is obtained in the unit of

J/mol: $A_\Phi \cdot \sigma_{\Phi s} \cdot V_{\Phi,m}/V_\Phi$. Let us introduce the specific surface are of the phase: $A_{S,\Phi} \equiv A_\Phi/V_\Phi$ (m²/m³ =1/m). Then, the requested surface term of the molar Gibbs energy in accordance with the original ideas of Gibbs is found as:

$$G_\Phi^s = A_{S,\Phi} \cdot \sigma_{\Phi s} \cdot V_{\Phi,m} \qquad (14)$$

For a liquid spherical droplet of radius r the specific surface area equals: $A_{S,l} = 3/r$. Substituting this equation into Eq. (14):

$$G_l^s = \frac{3 \cdot \sigma_{lg} \cdot V_{l,m}}{r} \qquad (15)$$

For the case of solid phases surrounded by flat crystal planes, Eq. (14) can be written as:

$$G_\Phi^s = V_{\Phi,m} \cdot \sum_{hkl} A_{S,\Phi,hkl} \cdot \sigma_{\Phi s, hkl} \qquad (16)$$

where the summation is performed along all *hkl* crystal plane indexes, with the *hkl*-dependent surface energy, and the specific surface area of each plane is defined as: $A_{S,\Phi,hkl} \equiv A_{\Phi,hkl}/V_\Phi$. Substituting this equation into Eq. (16) the following final equation is obtained:

$$G_\Phi^s = \frac{V_{\Phi,m}}{V_\Phi} \cdot \sum_{hkl} A_{\Phi,hkl} \cdot \sigma_{\Phi s, hkl} \qquad (17)$$

where the first term is the inverse of the number of moles in the given phase ($n_\Phi = V_\Phi/V_{\Phi,m}$).

As a particular case of Eq. (17), let us consider the thin liquid film (*l*) covering the large flat solid surface of surface area $A_l$ with the thickness of $\delta$. The liquid film has two sides: the solid/liquid and the liquid/gas sides, with identical surface areas of $A_l$, but different interfacial energies $\sigma_{sl}$ and $\sigma_{lg}$). The volume of the thin film is: $V_l = A_l \cdot \delta$. Substituting all these values into general Eq. (17), for thin liquid films the following equation is obtained:

$$G_l^s = \frac{\sigma_{sl} + \sigma_{lg}}{\delta} \cdot V_{l,m} \qquad (18)$$

Thus, the Gibbs energy provides a surface Gibbs energy term to thin films, being inversely proportional to the thickness of the film. As a consequence, the melting point of thin films will be also inversely proportional to the film thickness, in accordance with experimental observations.[53–54] As was mentioned above, thin films are wrongly expected to have zero surface Gibbs energy term and thickness-independent melting point in accordance with the Kelvin and Gibbs-Thomson equations.

From the comparison of Eqs. (7, 15) one can see that although the two equations (the Kelvin equation and the Gibbs equation) are similar, they are not identical. Thus, both cannot be valid. The difference between Eqs. (2a, 7) and Eqs. (14, 15) for some simple geometries are shown in Table I. One can see that for a sphere and for a cylinder the resulting equations are similar, but different. For a thin film and a crystal the results are qualitatively different. The difference between the Gibbs and Kelvin equations are principal: the Kelvin equation is due to the curvature, while the Gibbs equation is due to the specific surface area.

**Table I.** The expressions for the surface term of the Gibbs equation for some liquid and solid geometries, calculated by Eqs. (2a, 7) and by Eqs. (14, 15).

| Geometry | Kelvin, Eqs. (7, 2a) | Gibbs, Eqs. (14, 15) |
|---|---|---|
| Sphere of radius $r$ | $\dfrac{2 \cdot \sigma_{lg} \cdot V_{l,m}}{r}$ | $\dfrac{3 \cdot \sigma_{lg} \cdot V_{l,m}}{r}$ |
| Long cylinder of radius $r$ | $\dfrac{\sigma_{lg} \cdot V_{l,m}}{r}$ | $\dfrac{2 \cdot \sigma_{lg} \cdot V_{l,m}}{r}$ |
| Large thin film of thickness $\delta$ | $0$ | $\dfrac{\sigma_{sl} + \sigma_{lg}}{\delta} \cdot V_{l,m}$ |
| Crystal with planar planes | $0$ | $\dfrac{V_\Phi}{V} \cdot \sum_{hkl} A_{hkl} \cdot \sigma_{\Phi s, hkl}$ |

### 2.4. The Contradiction Around the Nucleation Theory

Now, let us briefly show the treatment of Gibbs for homogeneous nucleation.[2, 4, 8–10, 17, 20–22] For this, let us substitute Eq. (14) into Eq. (1) for the spherical solid phase of radius $r$ within a large liquid phase:

$$G_s = G_s^b + \frac{3 \cdot \sigma_{sl} \cdot V_{s,m}}{r} \qquad (19.a)$$

First, let us derive the equation for the homogeneous nucleation of the solid nucleus from the supercooled liquid of the same pure phase. For this, let us suppose that before the solid nucleus appeared, its space was occupied by the liquid phase, without any phase boundary with the outer liquid phase, and so:

$$G_l = G_l^b \qquad (19.b)$$

Let us denote the Gibbs energy change upon nucleation the difference between Eqs. (19a–b) multiplied by the amount of moles within the solid nucleus (and thus having a unit of J): $\Delta_n G = n_s \cdot (G_s - G_l)$. Substituting here Eqs. (19a–b) and equations $n_s = V_s/V_{s,m}$, $V_s = (4/3) \cdot \pi \cdot r^3$, the following equation is obtained:

$$\Delta_n G = \frac{4 \cdot \pi \cdot r^3}{3} \cdot \frac{G_s^b - G_l^b}{V_{s,m}} + 4 \cdot \pi \cdot r^2 \cdot \sigma_{sl} \qquad (20)$$

If the difference in heat capacities between the solid and liquid phases is negligible, the following approximation can be used: $G_s^b - G_l^b \cong (T - T_m^\circ) \cdot \Delta_m S^\circ$. Substituting this equation into Eq. (20):

$$\Delta_n G = \frac{4 \cdot \pi \cdot r^3}{3} \cdot \frac{(T - T_m^\circ) \cdot \Delta_m S^\circ}{V_{s,m}} + 4 \cdot \pi \cdot r^2 \cdot \sigma_{sl} \qquad (20.a)$$

Equation (20.a) is shown graphically in Figure 2. The second term of Eq. (20.a) is always positive. Thus, nucleation can be a favorable process only, if $T < T_m^\circ$, i.e., in the super-cooled state. In this case Eq. (20.a) predicts that $\Delta_n G$ starts at a zero value at $r = 0$ and goes through a maximum point at a certain critical size $r_{cr}$. At $r > r_{cr}$
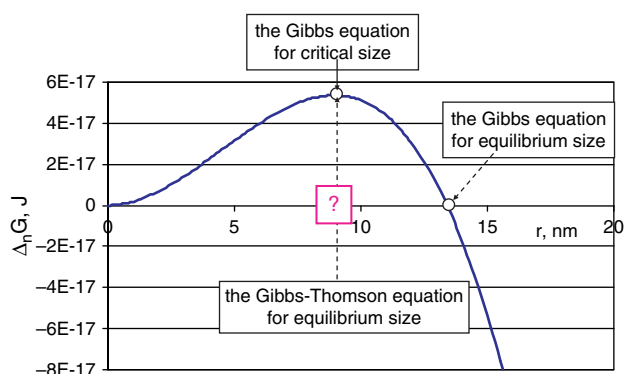
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**Fig. 2.** The nucleation curve, calculated by Eq. (20.a) (parameters for Al: $T_m^\circ = 933$ K, $\Delta_m S^\circ = 11.5$ J/molK, $V_{s,m} = 10.6$ cm$^3$/mol, $\sigma_{sl} = 0.16$ J/m$^2$, $T = 900$ K). The critical size is shown at $r_{cr} = 8.94$ nm, as calculated by Eq. (21). The "so called equilibrium size" is shown at the same size of $r_{eq} = 8.94$ nm, as calculated by the Gibbs-Thomson Eq. (13.b) and is also shown at $r_{eq} = 13.4$ nm, as calculated by the Gibbs Eq. (21.a), or by the corrected Gibbs-Thomson Eq. (25.b).

nucleation becomes a favorable process, as from this size on $\Delta_n G$ gradually decreases with size. The critical size (see Fig. 2) is found from substituting Eq. (20.a) into the condition of the maximum point: $d\Delta_n G/dr = 0$:

$$r_{cr} = \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{(T_m^\circ - T) \cdot \Delta_m S^\circ} \qquad (21)$$

Eq. (21) is widely accepted in the literature. As one can see, Eq. (21) is identical with Eq. (13.b), the Gibbs-Thomson equation for the "so-called equilibrium size of a nano-crystal" (see above and Fig. 2). Thus, two quantities, which must not be equal, appear to be equal. These quantities should not be equal, as the so-called equilibrium radius should appear at $\Delta_n G = 0$, while the critical radius should appear at the maximum of the $\Delta_n G$ curve, which is not at $\Delta_n G = 0$ (see Fig. 2). That is why this coincidence is called a "surprising fact".[10] For us this coincidence is an obvious contradiction and it proves that something is wrong around the Gibbs-Thomson (Kelvin) and the Gibbs equations, i.e., at least one of them is wrong. Above it was shown that the Gibbs-Thomson equation is the analogue of the Kelvin equation, what is obtained by a theoretically inadequate substitution of the Laplace equation into the Gibbs equation. On the other hand, the present author cannot find anything wrong with the surface term of Gibbs. This is the basis to declare in this paper that both the Kelvin and the Gibbs-Thomson equations are wrong in their present forms and the Gibbs equation is right. Now, let us express "the so-called equilibrium size of the nano-crystal", substituting the condition $\Delta_n G = 0$ into Eq. (20.a):

$$r_{eq} = \frac{3 \cdot \sigma_{sl} \cdot V_{s,m}}{(T_m^\circ - T) \cdot \Delta_m S^\circ} \qquad (21.a)$$

Eq. (21.a) is in accordance with the Gibbs equation and Figure 2, and does not contradict Eq. (21). Thus, the above

contradiction (the surprising equality of Eqs. (21, 13b)) is resolved.

Above, a particular case of nucleation of a solid crystal from the supercooled, 1-component liquid was considered. A similar derivation leads to the critical nucleus radius, if nucleation takes place from an over-saturated vapor:

$$r_{cr} = \frac{2 \cdot \sigma_{sl} \cdot V_{s,m}}{R \cdot T \cdot \ln (p/p^\circ)} \qquad (21.b)$$

One can see again the surprising co-incidence between critical and equilibrium radii, i.e., Eqs. (2, 21.b), in analogy with Eqs. (21, 13.b) discussed above.

## 3. DERIVATION OF THE MODIFIED EQUATIONS

As Eqs. (1, 14–15) were found to be correct, let us apply them to find the corrected forms for the Kelvin equation and for the Gibbs-Thomson equation.

### 3.1. The Modified Kelvin Equation

If Eqs. (14–15) are used to describe the surface term of the Gibbs energy of a liquid instead of Eq. (7), then instead of Eqs. (2–2.a) the following equations are obtained for the equilibrium vapor pressure above a liquid phase:

The general equation:

$$p = p^\circ \cdot \exp\left(\frac{A_S \cdot \sigma_{lg} \cdot V_{l,m}}{R \cdot T}\right) \qquad (22.a)$$

For the case of a spherical droplet of radius r:

$$p = p^\circ \cdot \exp\left(\frac{3 \cdot \sigma_{lg} \cdot V_{l,m}}{r \cdot R \cdot T}\right) \qquad (22.b)$$

One can see that the only difference between Eqs. (2, 22.b) is that coefficient 2 is replaced by coefficient 3, i.e., the effect of curvature (more precisely: the effect of specific surface area) has become more pronounced. There has been a number of measurements which have proven an approximate validity of the Kelvin equation (2).[57–58] Based on this, one can claim that Eq. (2) is proven to be correct. However, one should remember the size dependence of surface tension. It is known since Gibbs that the surface tension of droplets in a vapor phase decreases when its size decreases.[2, 59–62] Thus, it is quite possible that the size effect of surface tension partly compensates for the 3/2 increase between Eqs. (2, 22.b) and this explains why the difference between Eqs. (2, 22.b) has not been noted (let us also remind the uncertainty of measurements at nano-scale).

### 3.2. The Modified Gibbs-Thomson Equation

If Eqs. (14–15) are used to describe the surface term of the Gibbs energy of a solid crystal instead of Eq. (7), then instead of Eq. (13) the following equations are obtained for the so called equilibrium melting point of a nano-crystal:

The general equation:

$$T_m = T_m^\circ - \frac{A_S \cdot \sigma_{sl} \cdot V_{s,m}}{\Delta_m S^\circ} \tag{25.a}$$

For the case of a spherical crystal of radius $r$:

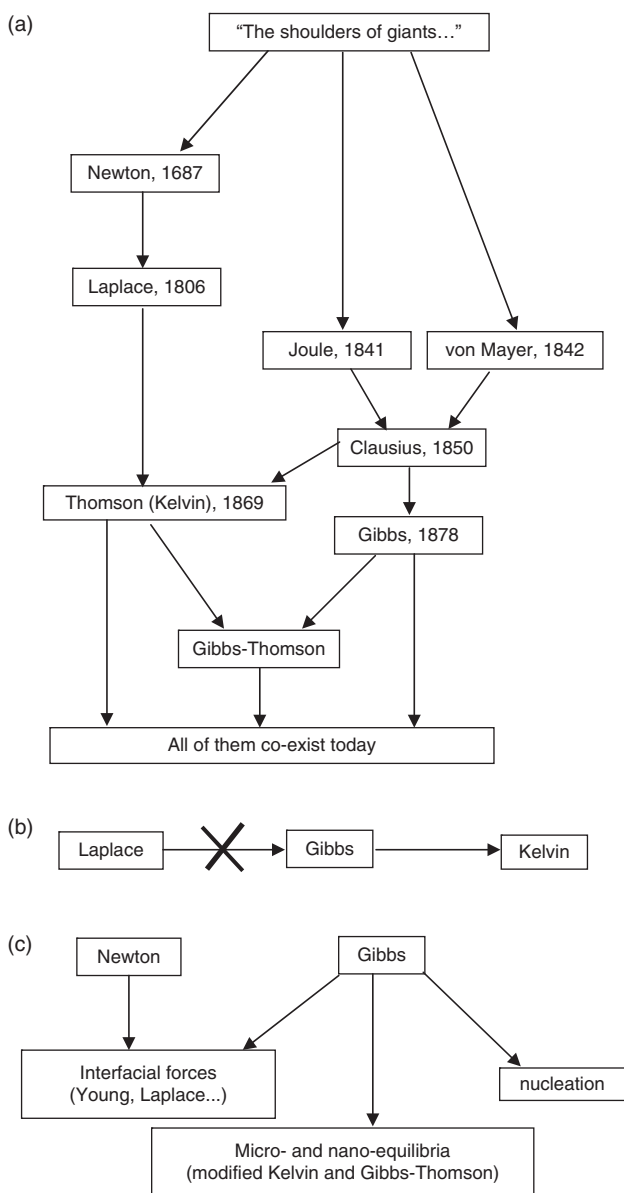$$T_m = T_m^\circ - \frac{3 \cdot \sigma_{sl} \cdot V_{s,m}}{r \cdot \Delta_m S^\circ} \tag{25.b}$$



**Fig. 3.** The historical (Fig. 3(a)), the illogical (Fig. 3(b)) and the logical (Fig. 3(c)) hierarchies of scientific achievements in the field of this paper.

One can see that the only difference between Eqs. (13, 25.b) is that coefficient 2 is replaced by coefficient 3, i.e., the effect of curvature (more precisely: the effect of specific surface area) has become more pronounced. It is also obvious that Eqs. (21.a, 25.a) are identical equations. This was expected, as both are derived from the same Gibbs equation.

## 4. ON THE HISTORICAL AND LOGICAL HIERARCHIES OF EQUATIONS

The history of science is not always a logical array of events.[63–66] The historical and logical sequences of events in the field of this paper are shown in Figure 3. As follows from Figures 1, 3a, the three equations (those of Kelvin, of Gibbs, and of Gibbs-Thomson) co-exist even today. Figure 3b shows an illogical sequence (wide-spread in today's literature), with the Laplace equation being substituted into the Gibbs equation (see above and Appendix). On the other hand, in Figure 3c we show that all the three sub-branches of science i. interfacial forces, ii. micro- and nano-equilibrium and iii. nucleation all follow from the same Gibbs equation.

## 5. CONCLUSIONS

The Gibbs energy of a phase is divided into bulk and surface terms. Two alternative equations are shown for the surface term, originating from the works of Kelvin and Gibbs. It is shown that the Kelvin (Gibbs-Thomson) equation can be obtained if the Laplace equation is introduced into the Gibbs equation in a theoretically wrong way (confusing external and inner pressures). Thus, the Gibbs equation should be used not only for nucleation (as it is commonly done), but also to calculate nano-phase equilibria. As a consequence, the often used phrase/explanation "phenomena due to high curvature" should be replaced by the phrase/explanation "phenomena due to high specific surface area".

The modified versions of the Kelvin and Gibbs-Thomson equations are presented in this work, being in accordance with the Gibbs equation. In this way the "surprising" contradiction between the nucleation theory of Gibbs and between the equilibrium Gibbs-Thomson equation is resolved. Once again it is shown that the historical sequence of events does not correspond to the logical sequence to present scientific knowledge.

## 6. Appendix. The Derivation of the Laplace Equation from the Gibbs Equation

As was shown above, the surface term of the Gibbs energy is written as (in J):[2]

$$G^s = A \cdot \sigma \tag{A1}$$

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Using the Newton's principle connecting force and energy, the general equation of interfacial forces is written as:[67]

$$F^s = -\frac{dG^s}{dx} \qquad (A2)$$

where $x$ is path of the movement of a phase or interface, the minus sign indicates that only processes accompanied by the negative change of the Gibbs energy take place spontaneously in nature.

Let us consider a spherical phase with a constant surface energy $\sigma$ and with a gradually increasing radius $x$. Then, its surface area is: $A = 4 \cdot \pi \cdot x^2$. Substituting this equation into Eq. (A1) and substituting it into Eq. (A2), one can obtain:

$$F^s = -8 \cdot \pi \cdot x \cdot \sigma \qquad (A3)$$

The interfacial force described by Eq. (A3) acts at each point perpendicular to the surface of the sphere. That is why, the interfacial pressure can be defined as: $p^s = F^s/A$. Substituting the equation $A = 4 \cdot \pi \cdot x^2$ and Eq. (A3) into this equation $p^s = F^s/A$, the following expression is obtained for the interfacial pressure:

$$p^s = -\frac{2 \cdot \sigma}{x} \qquad (A4)$$

The minus sign in Eq. (A4) shows that the vector of the interfacial pressure is pointed against the vector of the growing radius, i.e., from outwards to inwards of the sphere. Eq. (A4) is the simplest form of the Laplace equation. Thus, it is proven that the Laplace equation follows from the surface term of the Gibbs energy introduced by Gibbs. As shown in,[67] all other interfacial forces follow from the same Gibbs equation, as well (see also Fig. 3(c)).

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